



Institute of Chemistry

***Ab initio*-based Magnetic Properties and Phase Stabilities of Rare-Earth-Free Hard Magnets**

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*"If you think you understand quantum mechanics,
you don't understand quantum mechanics."*

—Richard Feynman

Abstract

Magnets are crucial materials for many modern technologies such as renewable energy generation (wind turbines). New, cost-effective rare-earth (RE) free magnets are required to reduce the environmental impact of rare-earth mining and to lessen the influence of monopoly positions on the world market, as well as to bridge the performance gap between ferrites and Nd-Fe-B magnets. One potential gap magnet is the Fe_2P compound, which exhibits high magnetic properties and is well known in magnetocaloric materials. In this thesis, the effects of Si for P and Co for Fe substitution on the magnetic properties, the Curie temperature and the phase stabilities of Fe_2P -based compounds are explored in the framework of density functional theory to reveal potential new hard magnetic materials.

First the effect of pure Si and Co substitution on the lattice parameters of $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ and $\text{Fe}_{2-y}\text{Co}_y\text{P}$ was investigated. The magnetic moments and the derived magnetization and maximum energy product of each compound were analyzed. An analysis of the exchange interaction energies and the Curie temperatures was performed using the AkaiKKR code. The anisotropy of the compounds was examined using non-collinear DFT calculations. Whenever possible, the theoretical results were compared to available experimental data.

After clearing the influence of pure Si and Co substitution, the combined effect of both elements on the mentioned properties was investigated. For quaternary compounds the same trends as for single element substitution were found in case of lattice parameters and magnetic moments. For the T_C s, three different trends depending on Si concentration were found. The anisotropy was calculated to decrease with both elements, but Si providing a higher resilience against the loss of uniaxial anisotropy. The general suitability regarding the magnetic properties was then evaluated by calculation of the hardness factor.

Ab initio-based Gibbs energies have been computed using the phonopy package to construct finite temperature phase stability diagrams. For ternary $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ and $\text{Fe}_{2-y}\text{Co}_y\text{P}$ only low element substitutions are found to be stable with rising temperature. Following this, a combined phase stability evaluation for Si and Co in quaternary $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ compounds was conducted. Contrary to ternary findings, compounds with high Si and Co concentrations were found to stabilize first, shifting to lower Si concentrations with increasing temperatures.

A final assessment of magnetic properties, Curie temperature and phase stabilities was provided to identify suitable magnetic materials. One noteworthy composition is $\text{Fe}_{1.84}\text{Co}_{0.16}\text{P}_{0.84}\text{Si}_{0.16}$, showing a hardness factor of 1.4, a theoretical Curie temperature of 558 K and the highest stability of all considered compounds.

Zusammenfassung

Magneten sind wichtige Materialien für moderne Technologien wie die Erzeugung erneuerbarer Energien (Windkraftanlagen). Neue, kosteneffiziente Magnete ohne seltene Erden sind erforderlich, um die Umweltauswirkungen des Abbaus dieser Elemente, sowie den Einfluss von Monopolen auf dem Weltmarkt zu verringern. Zusätzlich kann so die bestehende Leistungslücke zwischen Ferrit- und Nd-Fe-B Magneten überbrückt werden. Ein potenzieller Magnet für diese Lücke ist das Material Fe_2P , welches hohe magnetische Eigenschaften ausweist und bereits als magnetokalorisches Material bekannt ist. In dieser Arbeit wurde der Effekt von Si und Co Substitution auf die magnetischen Eigenschaften, die Curie Temperatur T_C und die Phasenstabilität von Fe_2P -basierten Materialien im Rahmen von DFT untersucht, um neue hartmagnetische Verbindungen zu identifizieren.

Zunächst wurde der einzelne Einfluss von Si und Co Substitution auf die Strukturparameter und magnetischen Eigenschaften von $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ und $\text{Fe}_{2-y}\text{Co}_y\text{P}$ Verbindungen untersucht. Eine Analyse der Austauschwechselwirkungsenergien und der Curie Temperatur wurde unter Verwendung des AkaiKKR-Codes durchgeführt. Die Anisotropie der Verbindungen wurde mittels nicht-kollinearer DFT-Rechnungen ermittelt. Soweit möglich wurden die Ergebnisse mit experimentellen Daten verglichen.

Nach den einzelnen Effekten von Si und Co wurde der kombinierte Einfluss von beiden Elementen fokussiert. Für quaternäre Verbindungen wurden bei den magnetischen Momenten und Strukturparametern die gleichen Trends wie für die einzelnen Elemente gefunden. Für die Curie Temperatur wurden drei Effekte in Abhängigkeit von der Si Konzentration entdeckt. Die Anisotropie verringert sich mit der Substitution beider Elemente, aber ein höherer Si Anteil wirkt einem Verlust der uniaxialen Anisotropy entgegen. Die magnetischen Eigenschaften der Materialien wurden durch den Härtefaktor bewertet.

Ab initio basierte Gibbs Energien wurden mit dem Phonopy-Programmpaket berechnet um Phasendiagramme bei erhöhten Temperaturen zu erstellen. Für $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ und $\text{Fe}_{2-y}\text{Co}_y\text{P}$ Verbindungen wurde nur ein geringer Substitutionsgrad bei erhöhten Temperaturen als stabil identifiziert. Der kombinierte Einfluss von Si und Co in $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ Verbindungen wurde ebenfalls untersucht. Entgegen den bisherigen Funden, zeigen hohe Si und Co Konzentrationen eine schnelle Stabilisierung. Erst bei höheren Temperaturen verschiebt sich die Stabilitätsgrenze zu niedrigeren Si Gehalten.

Eine Einschätzung der magnetischen Eigenschaften, Curie Temperaturen und Phasenstabilitäten wurde durchgeführt. Ein nennenswertes Material stellt $\text{Fe}_{1.84}\text{Co}_{0.16}\text{P}_{0.84}\text{Si}_{0.16}$ dar, welches einen Härtefaktor von 1.4, eine Curie Temperatur von 558 K und eine hohe Stabilität aufzeigt.

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Chapter 1

Introduction

Magnetic materials play a vital role in the development of modern technologies, such as renewable energy generation and sustainable transportation. They are essential components in generators and actuators, and are therefore the subject of increasing scientific interest [1, 2]. A large portion of the world market is dominated by high-performance magnets consisting of rare-earth (RE) and transition metal (TM) elements, with low-performance ferrite magnets owning the second largest share. This results in a significant performance gap, as either high-performance $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnets or low-performance ferrites are used, depending on application needs. However, since many of the rare-earth elements are considered critical for future applications [3], the interest in RE-free magnetic materials has risen in the past decade and much research is devoted to the reduction of RE elements in magnets [4, 5].

This first chapter provides information on the fundamentals of magnetism and a brief description of the historical development of magnetic materials to improve readability for the reader. The current world market situation for permanent magnets and the known problems associated with the mining and processing of rare-earth elements will then be explained, to underline the importance of reducing the RE content in magnets. Finally, this chapter will conclude with a description of the Fe_2P compound and the aims and motivation of this work. The second chapter will provide an overview of the theoretical details and methods used to calculate the results. Chapter 3 will entail a more detailed description about the program packages and the input parameters. The subsequent chapter will present the main results of this thesis, beginning with the magnetic properties and followed by the associated phase stabilities. Lastly, a final conclusion and an outlook will be given.

1.1 Magnetic Properties

1.1.1 Forms of Magnetism

The property of attracting ferrous materials originates from the magnetic moments of the atoms in a compound. In the classical Bohr definition the magnetic moments are a result

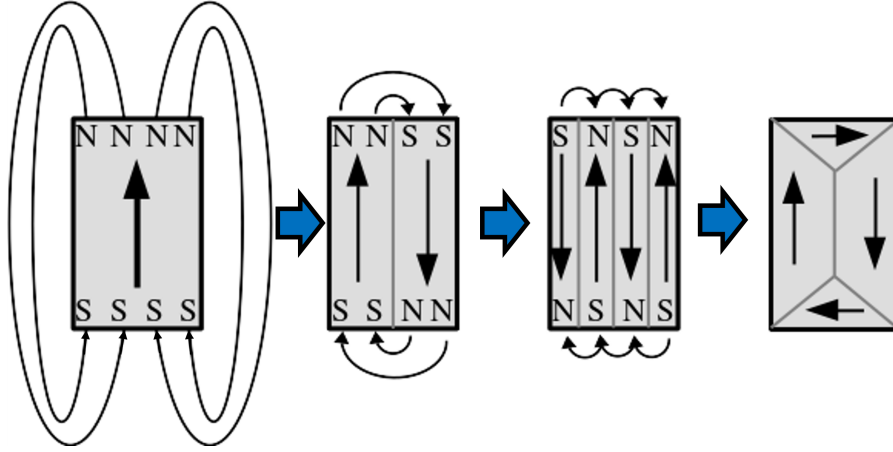


Figure 1.1: Formation of small magnetic domains to reduce the outer magnetic field and the magnetostatic energy. Image is based on [6].

of the motion of electrical charges, *i.e.* electrons, and the magnetic field generated by this orbital motion. This creates an orbital magnetic moment and a spin magnetic moment, which are both measured in Bohr magnetons μ_B . Since electrons possess an intrinsic spin angular momentum of $s = \frac{1}{2}$, the total magnetic moment is composed of a spin (S) and an orbital (L) magnetic moment. These contributions can be combined in two ways in the form of LS and JJ couplings with $J = L + S$. With a completely filled electron shell the electrons pair themselves with other electrons that have an opposing intrinsic magnetic moment, which results in a total magnetic moment of zero.

The magnetic moments are located in small regions of the material called magnetic domains. These domains play a crucial part in defining the type of magnetism that a material shows. The magnetic domains are formed to reduce the internal energy, more specifically the magnetostatic energy. Smaller domains generate smaller magnetic fields rather than one large field for one domain, consequently requiring less energy (see Fig. 1.1 [7, 8]). There are several types of magnetism and not all of them exhibit the well known property of attracting ferrous materials. They are defined by the response of the local magnetic domains of a material to an applied external magnetic field. These types of magnetism are namely paramagnetism, diamagnetism, ferromagnetism, antiferromagnetism and ferrimagnetism. The last one is considered as a subclass of ferromagnetism. In 2024 a new type of magnetism, the altermagnetism, was proven to exist in MnTe and RuO₂ [9, 10] and is a topic of high scientific interest.

Ferromagnetism

Ferromagnetism is the best-known type of magnetism, as it is the main form of magnetism that exhibits the pivotal property of attracting ferrous materials. In a ferromagnetic

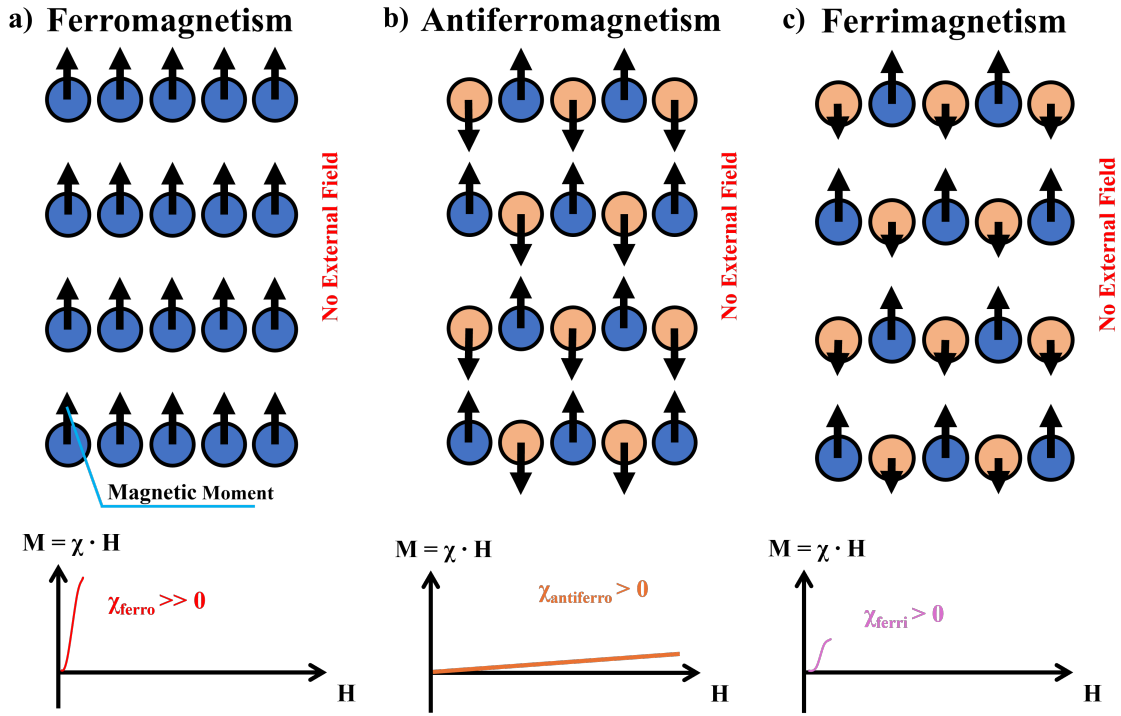


Figure 1.2: Schematic depiction of the magnetic moments in a a) ferro-, b) antiferro- and c) ferrimagnetic material without an external field applied. Below each magnet type the magnetic susceptibility for the materials is depicted by the plot of the magnetization against the magnetic field.

material, the local magnetic moments are all linked and aligned parallel to each other as can be seen in Fig. 1.2 a). When an external magnetic field is applied to these materials, all the magnetic domains realign themselves parallel to the external fields direction. Even after the external field has been removed, the magnetic moments of the domains stay in the induced direction, thus causing the macroscopic effect of magnetism. As the name already suggests the most known material for this type of magnetism is iron. This behavior results in a high magnetic susceptibility χ , which describes the ratio of magnetization to the applied magnetic field ($\chi = \frac{M}{H}$) for ferromagnetic materials and is a dimensionless property. Ferromagnetic materials are common materials in modern industry, being used in hard-drives, motors, generators or even in smartphones. They have an enormous impact on society with their wide range of usability [11, 12, 13].

Antiferromagnetism

Antiferromagnetism is considered a subclass of ferromagnetism, where two alternating sublattices with linked magnetic moments exist (see Fig. 1.2 b)). The defining feature of antiferromagnetism is that all magnetic moments are of the same order, but those of each sublattice are directed in opposing directions [14, 15, 16]. This causes the magnetic

moments to cancel each other, which results in a net magnetic moment of zero for the whole material. A prominent example for antiferromagnetism is the element manganese, which shows antiferromagnetic ordering below 100 K, and manganese oxide. So far, antiferromagnetic materials have a rather limited use in industry. However, with the emergence of spintronic applications, antiferromagnetic materials are expected to find many uses in this field [17].

Ferrimagnetism

Another important subclass of ferromagnetism is ferrimagnetism. Ferrimagnetic materials are similar to antiferromagnetic materials as they have two alternating magnetic sublattices with linked magnetic moments in opposing directions, as is visible in Fig. 1.2 c). Unlike antiferromagnetism, the magnetic moments of each sublattice are of different size and therefore do not cancel each other completely. This results in a remaining magnetic moment, that is considerably weaker compared to ferromagnets but not zero [18, 15]. This type of magnetism is mostly seen in materials with atoms of different elements occupying different sublattices. Good examples for ferrimagnetic materials are ferrite magnets like Fe_2O_3 . These magnets have a wide range of uses in the industry due to their low costs and easy manufacturing. They are used in the cores of coils for microwave systems and in electrical circuits as ferromagnetic insulators [19].

Paramagnetism

Para and Diamagnetism are the most common types of magnetism and one of them is almost always present even in "non-magnetic" materials. In case of paramagnetism the material has independent and finite local magnetic moments, which are aligned in random directions. This causes a net magnetic moment of zero for the material. The reason for this type of magnetism are unpaired electrons in the material. Due to the net magnetic moment of zero, paramagnetic materials are macroscopically observed as non-magnetic, as they do not attract ferrous materials. However, if an external magnetic field is applied to a paramagnetic material the randomly oriented magnetic moments all align parallel to the applied field, this behavior is depicted in Fig. 1.3 a). Paramagnetic materials therefore show a very small positive susceptibility between 10^{-5} and 10^{-3} [20, 21].

Diamagnetism

The other most common type of magnetism is diamagnetism which is, similarly to paramagnetism, only a very weak form of magnetism and only noticeable when an external magnetic field is present. It can be found in most materials and without an external field

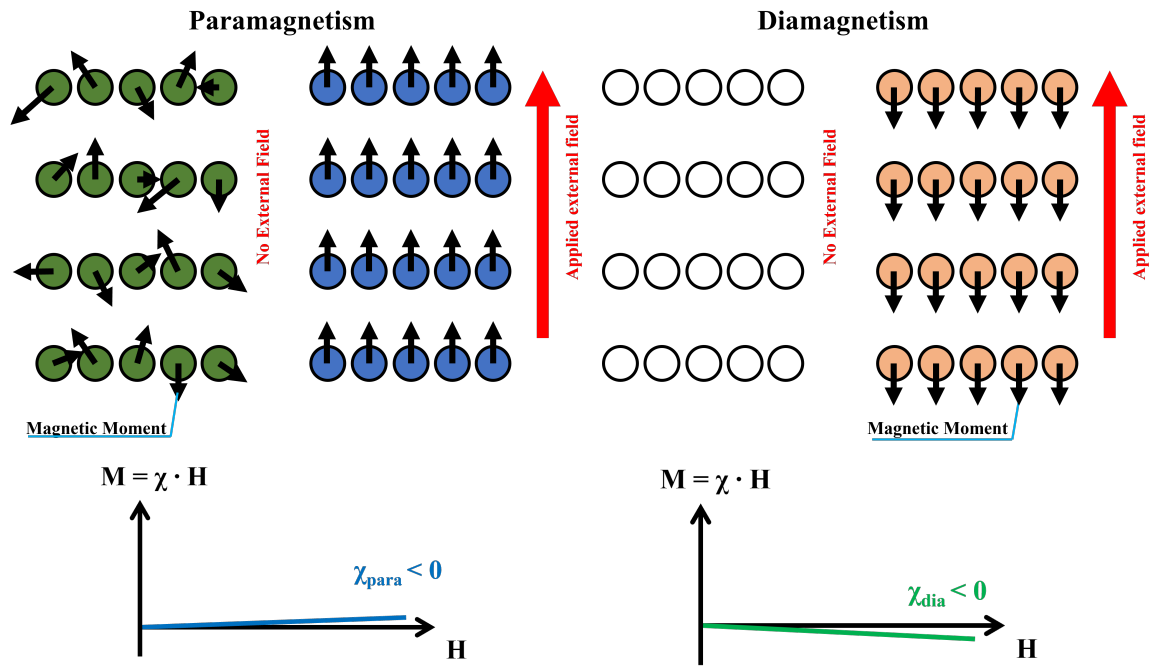


Figure 1.3: Schematic depiction of the magnetic ordering in a paramagnetic and diamagnetic material with and without an external field applied. Below each magnet type the magnetic susceptibility for the materials is depicted by the plot of the magnetization against the magnetic field.

applied, no magnetic moments are observable, as depicted in Fig. 1.3 b). Diamagnetism is generally attributed to materials which have all electrons paired and therefore a total magnetic moment of zero. Because of this total magnetic moment of zero, it is also considered macroscopically as "non-magnetic". When an external magnetic field is applied, magnetic moments are induced. These induced magnetic moments then align themselves in the opposite direction of the field, thus weakening it. As diamagnetism is only a very weak form of magnetism it shows only small negative susceptibility values between 10^{-5} and 10^{-6} [20, 21].

Altermagnetism

Altermagnetism is the newest form of magnetism and was proven to exist in 2024 by Krempasky *et al.* [9] and Fedchenko *et al.* [10]. It is a very rare and special form of magnetism, where the collinear ordered magnetic moments of the sublattices cancel each other like in antiferromagnetism. However, altermagnetism has a crucial difference to antiferromagnetism. The magnetic moments in an altermagnetic material are additionally to different spin states of the magnetic moments also in different electronic states. This means that the magnetic moments are also dependent on the orientation of the atom, as demonstrated in Fig. 1.4. In general they show similarities both to antiferromagnetic

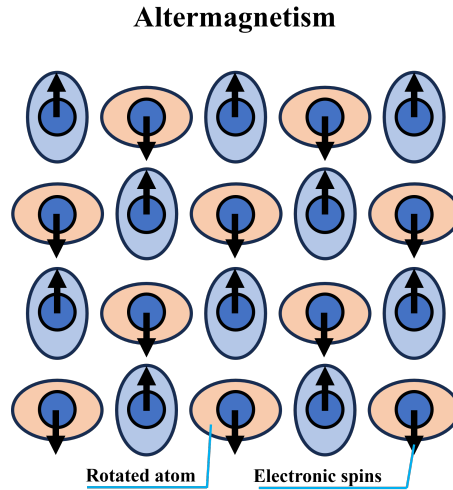


Figure 1.4: Schematic representation of the altermagnetic configuration in a material. The electronic spins are independent from the orientation of the atom.

as well as ferromagnetic materials and are expected to be found in more materials in the future. The hope with these materials is to develop new technologies in the field of spintronics.

1.1.2 Hysteresis Loop

One of the most common ways to demonstrate the various magnetic properties and the distinction between soft and hard magnetic materials is through the magnetic hysteresis loop (Fig. 1.5). In this loop, the magnetization M , which describes the quantity of the magnetic moments per unit volume, is plotted against the magnetic field strength H [16, 22, 23]. At the starting point 1, the magnetization is zero due to the magnetic moments of the magnetic domains being aligned in different directions. As the magnetic field strength H increases, the magnetization also rises until it reaches a maximum at point 2. At this point, all magnetic moments are aligned in the same direction, parallel to each other. This point therefore represents the saturation magnetization M_S , which is the highest possible magnetization for a material. When the applied field is then lowered to zero, the magnetization decreases slightly due to partial domain wall motion and domain realignment. The remaining magnetization at point 3 is called the remanent magnetization M_r . For hard magnetic materials, this property needs to be as large as possible, as it describes how much a magnet stays magnetized without an applied external field. Further decreases of the magnetic field in the opposite direction lead to a drop of the magnetization until the material is fully demagnetized. At this point, the magnetic domains align in two opposing directions, canceling each other out. This point also defines the coercivity field strength H_C , which describes the needed external field strength to

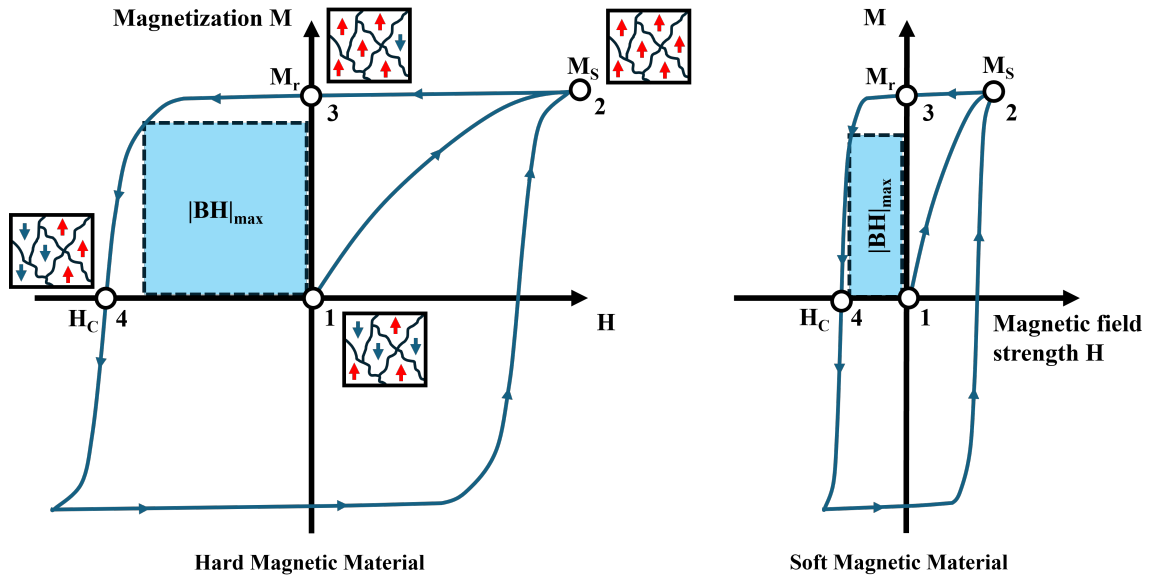


Figure 1.5: Hysteresis loop of a hard and a soft magnetic material with the magnetic orientation at different points as insets to show how the magnetic ordering changes with the magnetization.

completely demagnetize a material. This property also needs to be as high as possible in hard magnetic materials to prevent a permanent magnet from being easily demagnetized. Further lowering of the magnetic field strength results in a magnetization in the opposite direction. A following increase of the field back to zero then results in a mirrored version of the first two quadrants of the hysteresis loop. Furthermore, the second quadrant of the loop describes the important magnetic property of the maximum energy product $|BH|_{max}$. It is a figure of merit for the performance of a magnet and can be derived from the largest possible square area enclosed by the hysteresis loop and the origin. The maximum energy product is also a magnetic property of a magnet that should be maximized in a hard magnetic material.

1.1.3 Magnetization and Maximum Energy Product $|BH|_{max}$

The magnetization of a material describes the magnetic moments per volume element [24]:

$$M = \frac{1}{V} \sum_i (m_i) \quad (1.1)$$

with M as magnetization, V as volume and m_i as the magnetic moments at site i with the unit of Bohr magneton (μ_B). As the magnetization is the result of the alignment of a finite number of magnetic moments within a volume element, a maximum magnetization occurs when all magnetic moments are aligned parallel to each other. This state is the

saturation magnetization, which is indicated by point 2 in the hysteresis loop. The SI unit for the magnetization is amperes per meter (A/m), but it is also often expressed in electromagnetic units per cubic centimeter (emu/cm³). A more convenient way to express the magnetization is via the magnetization polarization J , which describes the response of matter to an applied magnetic field due to the alignment of magnetic moments [23]. It is connected to the magnetization by the factor of μ_0 ($\mu_0 = 4 \pi \cdot 10^{-7}$ H/m), known as the magnetic field constant, and can be calculated using the following connection:

$$J = \mu_0 \cdot M. \quad (1.2)$$

The polarization is given in the SI unit of tesla and is used in the calculation of other magnetic properties. In this work, it is referred to as $\mu_0 M_S$ and is calculated using the theoretical maximum magnetization and will also simply be referred to as the magnetization saturation.

The property of the maximum energy product $|BH|_{max}$, is derived from the magnetization. It is a figure of merit to define the highest possible magnetic strength of a material and can be derived graphically from the largest possible area of a rectangle in the second quadrant of the magnetic hysteresis loop [25]. It is given in kJ/m³ and for an ideal rectangular hysteresis loop the $|BH|_{max}$ can be approximated as:

$$|BH|_{max} = \frac{1}{4} \mu_0 M_S^2. \quad (1.3)$$

It is defined as the maximum value of the product of the negative magnetic flux density $-B$ and the magnetic field H . The value of $|BH|_{max}$ is also important because it can be used to determine the minimum volume of a material required to achieve a target flux density.

1.1.4 Curie Temperature

The Curie temperature is another crucial property that defines the suitability of a magnetic material for industrial applications. It is defined as the temperature at which the long-range ferromagnetic order vanishes, resulting in a transition from ferromagnetic to paramagnetic behavior [26, 21, 20]. Above the Curie temperature, the material exhibits no spontaneous magnetization, but can still be magnetized in the presence of an external magnetic field. Therefore, the Curie temperature reflects the influence of temperature on the magnetic ordering of a material. At low temperatures the magnetic moments of a ferromagnetic material are all ordered parallel to each other in the same direction. As this is a temperature-driven thermodynamic phase transition, an increase in temperature leads to disruptions of this parallel alignment. At the Curie temperature, the added en-

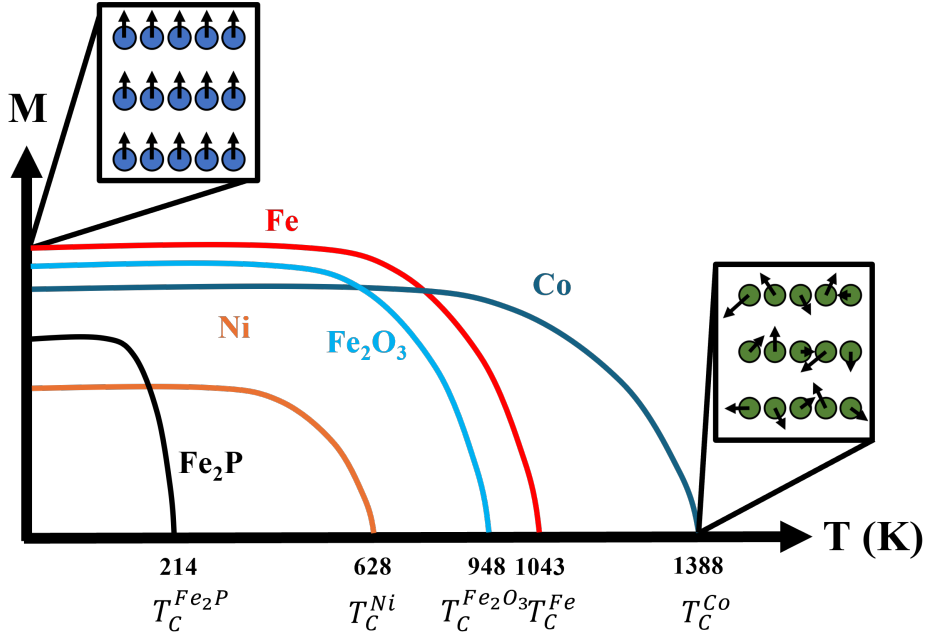


Figure 1.6: Schematic change of the magnetization with increasing temperature up to the Curie temperature T_C for different elements and compounds. The magnetic ordering at 0 K and at the T_C are shown in insets. The indicated T_C s of the materials are from experimental findings [6, 11, 27, 28, 29].

ergy causes all the magnetic moments to diverge from the parallel ordering, resulting in a spontaneous magnetization of zero. As no spontaneous magnetization remains above the T_C , materials with a low T_C are unsuitable for most technologies operating at elevated temperatures. Fig 1.6 shows the schematic development of the magnetization of some elements and compounds (Fe, Co, Ni, Fe_2O_3 , Fe_2P) in dependence of temperature, alongside their respective T_C s (1041, 1388, 628, 948 and 216 K [6, 11, 27, 28, 29]).

In this work, the total value of the Curie temperature is based on the calculation of the exchange interaction energies J_{ij} in the mean-field approximation. This approximation is prone to systematically overestimate the T_C up to 40 %. Consequently the calculated absolute values have to be interpreted with caution, while the resulting trends of the T_C s are meaningful. The T_C is calculated using the following equation:

$$k_B T_C = \frac{3}{2} J_0, \quad (1.4)$$

with k_B as the Boltzmann constant ($k_B = 1.3806 \cdot 10^{-23}$ J/K) and J_0 as the sum of the J_{ij} energies of a given lattice site to all remaining sites. The exchange interactions describe the strength of the spin coupling and therefore define how much energy is needed to disrupt the parallel alignment of the spins. Positive values of J_{ij} favor a ferromagnetic alignment, while a negative values favor an antiferromagnetic ordering. The exchange

interaction energies are influenced by the atomic distances, the crystal structure and the type of orbitals of the contributing atoms [6, 21].

Analogous to the Curie temperature for ferromagnetic materials, a similar transition point exists for antiferromagnetic materials. This temperature marks the transition from antiferromagnetic to paramagnetic and is called the Néel temperature [20].

The Curie temperature also has an influence on the specific heat capacity of a ferromagnetic material. At the T_C , the heat capacity often exhibits a magnetic phase transition, which may be of first or second-order depending on the material. This often results in a significant peak around the T_C , enabling the measurement of the T_C by investigation of the heat capacity and the accompanied transition.

1.1.5 Magnetocrystalline Anisotropy

The coercivity of a magnetic material plays an important role as it denotes the strength required to demagnetize a material. One key factor influencing the coercivity is the magnetocrystalline anisotropy (MAE), which describes the materials energy dependence on the direction of the magnetization. The main cause of this lies within the spin-orbit coupling. Due to this connection and the non-spherical distribution of $3d$ or $4f$ electrons, the rotation of the orbital angular momentum is energetically coupled to the electron spin and the overlap of the wavefunction of neighboring atoms. This overlap of the wavefunctions contributes to the exchange interactions and the Coulomb energy, leading to different energies depending on the direction. This phenomenon is presented schematically in Fig. 1.7. Consequently, this also causes a preferred crystallographic direction for the orbital angular momentum and the spin moment of the compound, leading to directions that are easier or harder to magnetize [21].

As magnetism originates from the motion of electrons, the energy for a given magnetization direction $M(r)$ is identical to the energy for the opposing direction on the same axis ($M(r) = -M(r)$). This correlation implies that the highest energy typically reaches a maximum near $\theta = 90^\circ$ in uniaxial systems, that are dominated by the first-order anisotropy constant. This is illustrated in Fig. 1.8.

As the anisotropy is closely related to the crystal structure of a compound, it can result in a varying number of easy magnetization axes. If there is only one easy axis, as in case of the hexagonal crystal structure, the anisotropy is called uniaxial. Another case is the cubic anisotropy [31], which will not be addressed in this work as Fe_2P predominantly adopts a hexagonal symmetry.

The uniaxial anisotropy can be described by the energy difference ΔE_{MAE} , that can be expressed using the anisotropy constants K_u , and the angle between the magnetization and the easy axis θ , in the following relation [23, 25]:

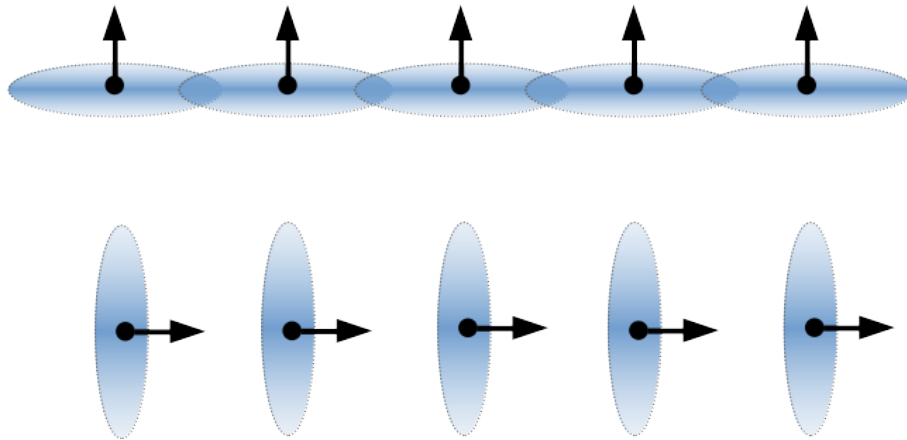


Figure 1.7: The connection of the orbital angular momentum and the spin moment via spin-orbit-coupling leads in combination with a non spherical distribution of $3d$ and $4f$ electrons to a different overlap of the wavefunctions of atoms and therefore a preferred orientation. Image is adapted from [21].

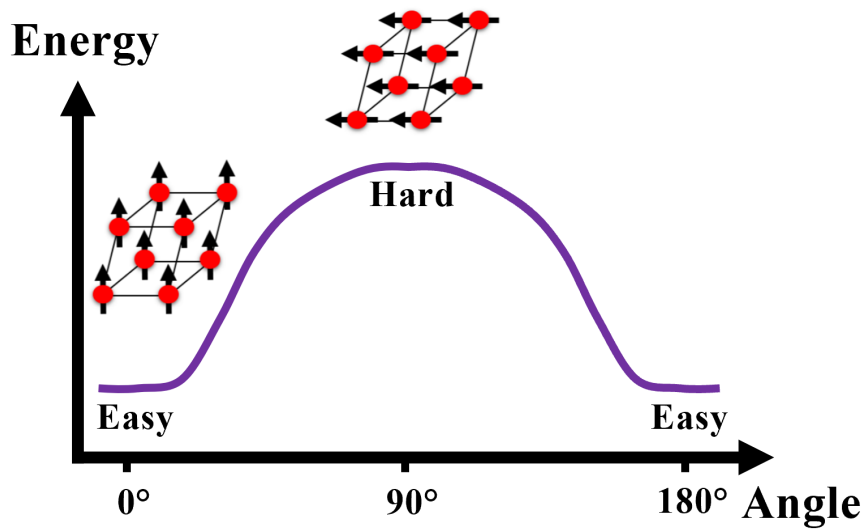


Figure 1.8: Change of the magnetocrystalline anisotropy energy in dependence of the magnetization angle. The magnetization direction of the representative unit cell is shown. Image is based on [30].

$$\Delta E_{MAE} = K_1 \sin^2 \theta + K_2 \sin^4 \theta + \dots \quad (1.5)$$

In this equation, the energy difference is calculated utilizing the anisotropy constants of increasing orders, such as K_1 , K_2 , and so on. However, in most cases, the first-order anisotropy constant K_1 provides a sufficient description of the uniaxial anisotropy, as the second-order constant K_2 is often much smaller K_1 [23, 25]. This simplifies equation 1.5 accordingly:

$$\Delta E_{MAE} = K_1 \sin^2 \theta \quad (1.6)$$

This assumption can be used as long as K_1 provides a positive value. If $K_1 < 0$, the higher-order anisotropy terms must be considered in order to determine the easy direction in the basal plane of the crystal [32]. For magnetocrystalline anisotropy calculations in this work, only K_1 was considered. The values of E_{MAE} and K_1 are measured in J/m³ and are most commonly expressed in MJ/m³ [16]. Based on the anisotropy constant and the magnetization, the theoretical anisotropy field H_a can be calculated via equation 1.7.

$$H_a = \frac{2K_1}{\mu_0 M_S} \quad (1.7)$$

The upper limit of the anisotropy field is defined by the coercivity field H_c ($H_a \leq H_c$), which is shown in the hysteresis loop in Fig. 1.5.

As the magnetocrystalline anisotropy energies are based on spin-orbit coupling, the exchange-correlation functional used in a calculation plays an important role. For some materials, the LSDA and GGA functionals can either yield results that are close to the experimental findings. Typically, the LSDA functional produces more reliable magnetocrystalline anisotropy results than the GGA functional. This phenomenon will be further explained in the theoretical details section addressing the exchange-correlation functionals.

Furthermore, with the connection of the spin and the crystal structure by spin-orbit coupling, the MAE is also influenced by the band filling. A reduction or addition of electrons shifts the Fermi energy, causing a change in the occupied and unoccupied states contributing to the MAE. In general, large energy differences between the occupied and unoccupied states result in low, while small differences achieve large MAE values [33].

1.1.6 Magnetic Hardness Factor

Depending on their anisotropy and magnetization, magnetic materials can be classified as soft, semi-hard or hard magnets. One property that can be used to quantify this

Table 1.1: Magnetic properties, such as the Curie temperature, the polarization magnetization, anisotropy constant and hardness factor of some magnetic materials. Data from [34].

Magnet	T_C (K)	$\mu_0 M_S$ (T)	K_1 (MJ/m ³)	κ
Nd ₂ Fe ₁₄ B	588	1.61	4.9	1.54
Sm ₂ Co ₁₇	1190	1.21	4.2	1.89
SmCo ₂	1020	1.05	17.0	4.40
Alnico 5	1210	1.40	0.32	0.45

classification is the hardness factor κ , which is determined by the following equation [34, 16]:

$$\kappa = \sqrt{\frac{K_1}{\mu_0 M_S^2}}, \quad (1.8)$$

with K_1 as the first order anisotropy constant and $\mu_0 M_S^2$ as the magnetization. As a rule of thumb, a hardness factor below 0.1 defines a soft magnet, while values between 0.1 and 1 classify a magnet as semi-hard. With $\kappa > 1$ a material qualifies as a hard magnet. However, it should be noted that exceptionally high hardness factors can also be achieved by materials with low magnetization and high anisotropy values compared to the magnetization. One example of such a case is the material Hematite (α -Fe₂O₃) which has a magnetization of only 3 mT and an anisotropy constant K_1 of 9 kJ/m³. These values result in a hardness factor κ of ~ 32 . Therefore, it is important to consider the magnetization value of the compound when evaluating the hardness factor. Nevertheless, the magnetic hardness is still regarded as a rule of thumb for assessing the suitability of a material as a magnet and generally provides a useful first estimate. The magnetic properties and hardness factors of some well known magnetic materials, such as the Nd₂Fe₁₄B magnet, are listed in Tab. 1.1 for comparison.

The high hardness factors of the RE-TM magnets in this table are the result of the combination of rare-earth and transition metal elements. The high anisotropy of these magnets can be attributed to the 4*f* electrons of the rare-earth elements, while the high magnetization mostly belongs to transition metals, such as Fe and Co. As can be seen in the Table, the RE-free Alnico 5 magnet exhibits a considerable amount of magnetization from the TM elements but lacks the anisotropy to achieve a high hardness factor.



Figure 1.9: Lodestone, south pointer and floating compass. Images are from [35, 36, 37].

1.2 Historical Development of Magnetic Materials

Magnetic materials have been known to mankind since ~ 600 BC. The first recorded discovery of a magnetic material was the Lodestone ($\text{Fe}^{2+}\text{Fe}_2^{3+}\text{O}_4$) in Greece by Thales of Miletus (see Fig. 1.9). Noteworthy inventions involving magnets include the south pointer in ancient China and the floating compass, that was first reported by Shen Kua in 1088 and by Alexander Neckham in Europe between 1157 - 1217 [16, 22, 38]. The south pointer was used to arrange streets in grid-like patterns, while the floating compass enabled seafarers to explore much further due to its reliable navigation capabilities. The latter also led to the discovery of America by Christopher Columbus in 1492 and the voyage around the world by Ferdinand Magellan from 1519 to 1522.

However, the theory and the underlying physics of (electro)magnetism were only established in 1864 by James Clerk Maxwell with the Maxwell equations [39]:

$$\begin{aligned} \nabla \cdot E &= \frac{\rho}{\varepsilon_0} & \nabla \cdot B &= 0 \\ \nabla \times E &= -\frac{\partial B}{\partial t} & \nabla \times B &= \mu_0 \left(J + \varepsilon_0 \frac{\partial E}{\partial t} \right) \end{aligned}$$

with E - the electric field, B the magnetic field, ρ - electric charge density, J - current density, ε - vacuum permittivity, μ_0 vacuum permeability.

Nonetheless, only minor improvements on hard magnetic materials were made due to an insurmountable self-demagnetization problem ($H_d = -NM$, with N as a shape-dependent demagnetization factor and M as magnetization) and considerable shape restrictions. Additionally to these reasons, electromagnets were simply deemed as more effective at that time. The demagnetization is caused by the two relations $\nabla \cdot B = 0$ and $B = \mu_0(M + H)$. The first describes the requirement for the number of magnetic lines leaving a volume element to be equivalent to the number of entering lines. The magnetic lines are therefore infinite or forming a loop. To meet the second equations requirement as well, the magnetization direction in a material must be opposite to the internal magnetic

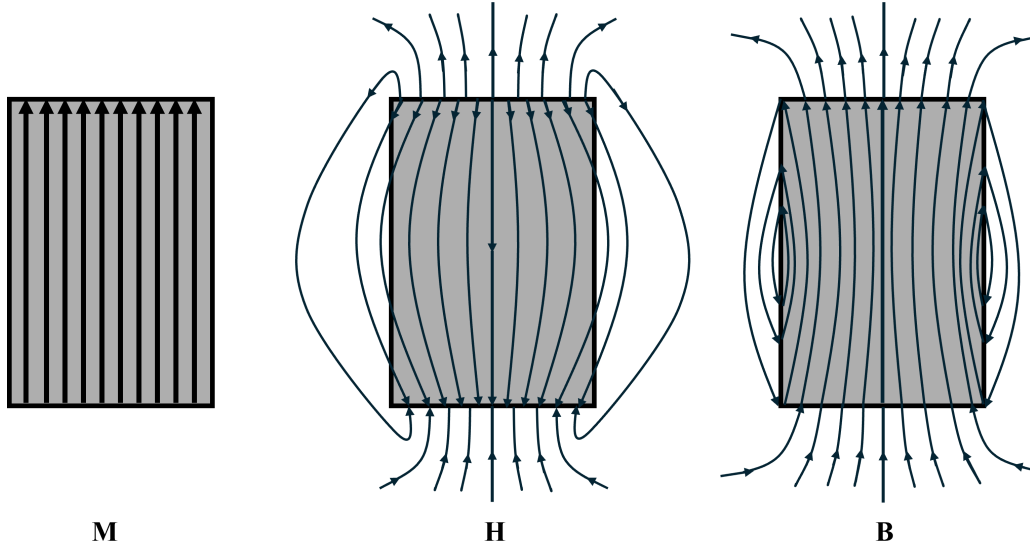


Figure 1.10: **Left:** Depiction of the direction of the Magnetization M in a magnet. **Middle:** Depiction of the magnetic field H opposing the magnetization. **Right:** Resulting flux density B of the magnet. Image is based on from Vandenbossche *et al.* [40].

field. This phenomenon is shown in Fig. 1.10.

This stagnation ended in the 20th century, when new magnetic materials were developed in quick succession, as shown in Fig. 1.11. The first of these material emerged around 1917 in the form of steel magnets (KS steel) [47] with a maximum energy product $|BH|_{max}$ of 8 kJ/m³. Although, this $|BH|_{max}$ is relatively small, it is still higher than that of conventional steel. To improve these steel magnets further, they were alloyed with a mixture of tungsten (W), chromium (Cr) and iron-carbon (Fe-C) alloys to suppress the domain wall movement during heat treatment.

The first ferrite magnets were developed around 1930 based on α -Fe₂O₃. They were easy to manufacture, corrosion-resistant and made from inexpensive materials, resulting in low production costs. However, these magnets have several drawbacks: their relatively low $|BH|_{max}$ of ~ 25 kJ/m³, their brittleness, which makes it difficult to form them into certain shapes, and their low mechanical strength. Ferrites are still the second most widely produced type of magnet on the market today due to their low cost and high availability [2].

Approximately 10 years later, the next compound family consisting of aluminum (Al), nickel (Ni) and cobalt (Co) was developed [48]. These Alnico compounds exhibited much better magnetic properties (~ 25 kJ/m³) than magnetic steels and ferrites, combined with a high Curie temperature T_C and a high resistivity to corrosion. Due to their high magnetic properties, a much lower volume of the material was needed to achieve a certain magnetic strength. Nevertheless, alnico magnets did receive as much attention as the ferrite magnets, primarily due to their low coercivity [49] and their high production cost.

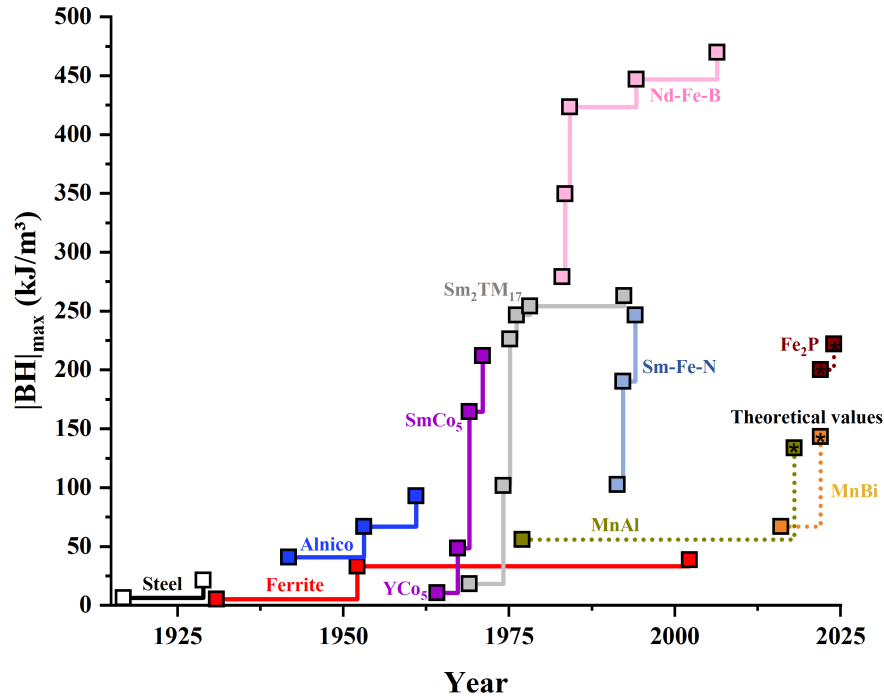


Figure 1.11: Historical development of the maximum energy products of magnetic materials from 1910 to 2025. Data is adapted from [41] and Data was added from [42, 43, 44, 45, 46].

They were expensive to manufacture and easy to demagnetize, making them less attractive than the much cheaper ferrites.

The full potential of ferrite magnets was recognized in 1951 with the development of the first hexagonal ferrite [50]. This resulted in a much better understanding of the coercivity, enabling greater progress in developing new magnets. It overcame the shape restrictions and enabled scientists to achieve coercivities H_c higher than the spontaneous magnetization of a material. This dramatically improved the usability of magnetic materials.

Around 1965, the next major breakthrough occurred, leading to the suppression of RE-free magnet research. The YCo₅ compound, and therefore the first RE-TM based magnet, was invented [51]. It showed a promising T_C and high magnetic moments, due to the used transition metal. This was combined with a high coercivity, contributed by the rare-earth element. This proved to be an important development, as RE-TM magnets are still considered as the strongest available magnets today. Shortly after the YCo₅ magnet, the SmCo₅ magnet was developed, featuring a phenomenal $|BH|_{\max}$ of ~ 200 kJ/m³. This was a significant advance because, at that time, the highest $|BH|_{\max}$ was attributed to the RE-free alnico 5 magnet with 60 kJ/m³. It also further reduced the needed material volume for a defined magnetic strength.

Soon after the discovery of SmCo_5 , the first magnet in the 2:17 phase was identified. $\text{Sm}_2\text{Co}_{17}$ magnets are still used today as high-performance magnets when high T_C values combined with high magnetic moments are required. They have $|BH|_{\max}$ of 294 kJ/m^3 , which is only bested by few other materials. One such material was independently developed by Sagawa *et al.* [52] and Croat *et al.* [53] in 1982 and 1984. They both discovered the high performance $\text{Nd}_2\text{Fe}_{14}\text{B}$ material, which had an initial $|BH|_{\max}$ of 286 kJ/m^3 . This material was favoured over Sm-Co based magnets due to the cheaper materials involved. Since then, $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnets have been significantly improved, achieving a maximum energy product of $\sim 500 \text{ kJ/m}^3$, and are considered as the strongest magnet type currently available. Nevertheless, $\text{Nd}_2\text{Fe}_{14}\text{B}$ has a comparably low Curie temperature of 585 K , making it unsuitable for high temperature applications without further modifications. To compensate the low T_C , the $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnet must be enhanced with expensive and critical elements like Dy or Tb. This improves the T_C but also increases the costs for these magnets.

Starting around 2010, the focus of research has shifted towards the reduction of RE elements and RE-free magnetic materials. In 2011, the Chinese government introduced drastic export limitations on RE elements, which further pushed these efforts and led to the rediscovery of many promising materials such as MnAl , MnBi or Fe_{16}N_2 alloys [54, 55, 1, 56, 57, 58, 59]. These materials all provide relatively good magnetic properties and are free of the expensive and critical rare-earth elements. The Mn-based materials are of particular interest as they exhibit relatively high anisotropy values despite not containing any RE elements [60]. Notably, MnBi even shows an increase of the anisotropy at higher temperatures [61]. Theoretical investigations report that MnBi reaches $|BH|_{\max}$ values of up to 143 kJ/m^3 [44, 45], while MnAl achieves 134 kJ/m^3 [45]. However, current experimental findings are lower at 67 and 56 kJ/m^3 , respectively [46]. These materials are intensively studied by the working of Oliver Gutfleisch at the university of Darmstadt in Germany. Another material class are Fe-Ni alloys, which have high magnetization and T_C values [62]. These materials are focus of several working groups in Japan and have been found to be very promising [63].

The Fe_2P compound is another material of interest, that was characterized in 1930 by Sterling *et al.* [64]. Since then, its magnetic properties, especially its unique first-order magnetic transition and an associated big latent heat, have been thoroughly investigated. Until a few years ago, the magnetocaloric effect of Fe_2P -type compounds, was the main focus of research for these materials, with much attention being directed towards $(\text{Fe,Mn})_2(\text{P,Si})$ for magnetic refrigeration and environment friendly cooling [65, 66]. Nowadays, the Fe_2P compound is subject to extensive research due to its high modifiability through the substitution of Fe and P with other elements. One research group

focusing on this material is Francois Guillous group at the University of Caen, who have successfully synthesized some quaternary $(\text{Fe,Co})_2(\text{P,Si})$ compounds and enhanced the Curie temperature and other magnetic properties [67, 68, 69].

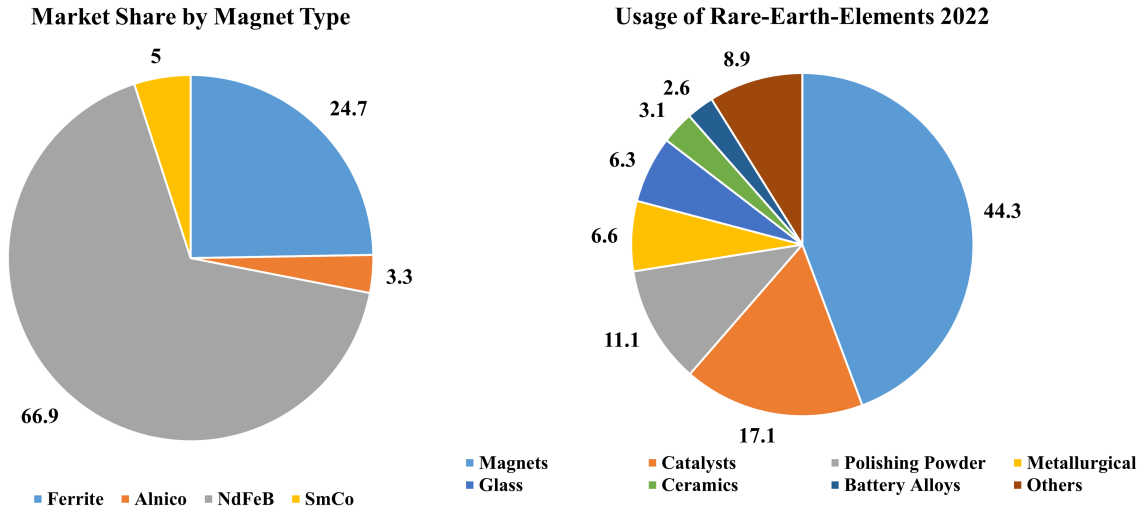


Figure 1.12: Market share by magnet type and usage of RE-elements in the year 2022. Data for the market shares is taken from [2], and for the demand of REEs from [70].

1.3 Current World Market Situation

To further understand the importance of reducing the use of the RE elements in magnets and the increasing need for sustainable materials, it is necessary to consider the global market for RE elements, as well as their mining and the processing. This will be examined in this section of the work.

The current world market is dominated by two families of magnetic materials. Nd-Fe-B magnets hold the largest market share of 67 %, followed by Ferrite magnets with 24.7 % [2]. SmCo and Alnico magnets have comparably small market shares of 5 and 3.3 %, respectively. This distribution is visible in Fig. 1.12. The demand for magnetic materials is expected to rise further in the coming years due to advancements in green technologies such as electric vehicle motors. However, this increasing demand leads to the crucial problem of the supply of rare-earth elements. In 2024, around 390000 metric tons of rare earth oxides were mined, with approximately 70 % of this amount originating from China. Additionally, China has by far the largest reserves of rare-earth elements with 44 million tons, followed by Brazil with around half as much with 21 million tons. Furthermore, in 2023, the processing of these mined rare-earth minerals was predominantly happening in China with ~ 90 % of the world's production [71, 72]. These factors demonstrate China's monopoly in this economic sector and its significant influence over these materials. The Chinese government has utilized this influence several times in the past. For example, in 2011, export tariffs were imposed, resulting in a significant spike in RE prices. More recently, in 2019 and 2025, the Chinese government threatened to stop exporting rare-earth elements to the US in response to the trade conflict with the govern-

Table 1.2: Mining of RE-oxides of different countries from 2020 to 2024 and the estimated reserves of each country in tonnes. Data is taken from [73, 74, 75, 76, 77]

Country	Mine Production (t)					Reserves in 2024 (t)
	2020	2021	2022	2023	2024	
China	140000	168000	210000	255000	270000	44000000
United States	39000	42000	42000	41600	45000	1900000
Myanmar	31000	35000	12000	43000	31000	NA
Australia	21000	24000	18000	16000	13000	5700000
Thailand	3600	8200	7100	3600	13000	4500
India	2900	2900	2900	2900	2900	6900000
Russia	2700	2600	2600	2500	2500	3800000
Madagascar	2800	6800	960	2100	2000	NA
Vietnam	700	400	1200	300	300	3500000
Brazil	600	500	80	140	20	21000000
Other Countries	400	760	80	8950	14230	4080000
Total	240000	290000	300000	376000	390000	>90000000

NA - Not available

ment of Donald Trump. In April 2025, the Chinese government also limited the amount of RE elements exported to other countries. This poses major challenges for all western countries as these elements are important for many modern technologies. Fig. 1.12 shows the demand for rare-earth elements in 2022 for the different areas of application. The manufacturing of magnets, the usage as catalysts and the production of polishing powders are the most important applications, accounting to 44.3, 17.1 and 11.1 %, respectively. Especially the magnetic materials sector is particularly dependent on RE elements. Reducing the amount of RE elements in magnets would therefore reduce the dependence on China as a supplier of resources for important magnetic materials.

1.4 Mining and Processing of Rare-Earth elements

Due to the high demand for RE elements for modern technologies, large quantities of these elements must be mined, separated and processed to match the needs of the different industry branches. However, the mining and processing of RE elements has a drastic environmental impact [78, 79, 80], which is considered one of the biggest associated problem. In nature, rare-earth elements can only be found mixed together in low concentrations and in combination with radioactive elements such as uranium or thorium [81]. This makes them difficult to extract and separate, as this process requires different chemicals such as acids and solvents. Consequently, this also leads to large quantities of waste that need to be disposed of properly [82, 79]. The mined minerals are first concentrated in a flotation



Figure 1.13: Environmental change in Myanmar from November 2013 (**left**) to December 2022 (**right**) caused by mining operations for rare-earth elements. All brown lines are new streets and sites destroyed by the mining and in-situ leaching for RE-oxides. Images are taken from Google Earth at the coordinates $25^{\circ}38'00''\text{N } 98^{\circ}20'28''\text{E}$ [85].

process, where the RE elements are combined with flotation reagents that cause them to separate and float to the surface. An alternative to this flotation process is to extract the RE elements directly from the ground using a method called in-situ leaching. In this method, PVC pipes are drilled into the ground and chemicals such as ammonium nitrate are injected to extract the RE elements. However, both processes result in tailings (up to 40 t per ton of REO), which include heavy and radioactive elements, as well as inorganic phosphorus compounds. These tailings are often discharged into open tailing ponds. This often causes these hazardous compounds to seep into the soil and groundwater. A prime example of these environmental dangers posed by these tailing ponds is the giant tailing pond of the Bayan Obo Mining district in China, which is estimated to cover an area of $\sim 10 \text{ km}^2$ [83, 79]. It is assumed that this pond contains 70000 tons of radioactive thorium. Furthermore, this wastewater is slowly seeping into the ground and is likely to contaminate the groundwater and the near Yellow river, which provides fresh water for the entire region.

Another major exporter of RE elements is Myanmar, which mined approximately 31000 tons of rare-earth oxides in 2024 (see Tab. 1.2). However, most of these oxides are extracted by Chinese companies and exported back to China for processing [80]. In 2022, most mining operations in Myanmar were done illegally in the Kachin State, with no consideration for the environment or local people, thus destroying vast regions in the process [84, 80]. The extent of this destruction can be estimated from Fig. 1.13.

As the demand for rare-earth elements is steadily increases [86], great efforts are being made to establish new mines and production facilities in countries like Brasil, Australia, Sweden or Norway [78]. Additionally, the Mountain Pass mine in California has been reopened and is expected to be operational by 2025 to mine and process RE elements.

This was done to meet the demand of the US industry and counteract the monopoly position of China [87, 88]. Nevertheless, these efforts are still in their beginning phases and will only start to affect the position of China in a few years.

Overall, reducing the amount of RE elements in magnetic materials would be a significant step towards a greater independence from China as a supplier, as well as reducing the environmental impact of mining and processing of RE-oxides.

1.5 Motivation of this work

The development of new magnetic materials that contain fewer or no rare-earth elements is nowadays a crucial research topic, driven by both the significant environmental impact of rare-earth mining and processing and the strong market dominance of a small number of suppliers. The rising demand for magnetic materials, driven by their role in generators and wind turbines is a major factor in the growing interest in new RE-free magnets, as well [89, 90, 91, 92, 93, 94, 43, 95].

Consequently, reducing of these elements would greatly benefit the environment by lowering their impact on it. Additionally, it could promote the development of new green technologies that do not use RE elements, which would also decrease the dependency on critical materials. Another problem arising from the dominance of RE-based magnets and ferrites is a significant performance gap between both material families. Currently, there exists no widely adopted and commercially attractive magnet between the expensive, high performance Nd-Fe-B magnets (nowadays: $|BH|_{max}$ of > 500 kJ/m³) and the cheap ferrite magnets (nowadays: $|BH|_{max}$ up to 40 kJ/m³) with lower magnetic properties [2]. Although Alnico magnets fall within this gap, they remain economically unattractive for many large-scale applications. This necessitates the search for a suitable magnet to fill this gap for cases where higher magnetic properties than those given by ferrites are needed.

The monopoly of China on the supply of these critical elements is another reason for the growing importance of reducing RE elements in magnetic materials. The Chinese government has imposed export restrictions on other countries on multiple occasions in the past, using their monopoly as political leverage in negotiations. This is one of the reasons why the light and heavy rare earths have been labeled as critical raw materials by the European Union. This means, that these elements are important for future technologies, but their supply is considered as insecure, non sustainable or very vulnerable to interruptions. Therefore, a reduction of RE elements in magnets would significantly decrease the dependency on China as a supplier and make the European union more independent on a global scale. To this end, the European Union has initiated several projects that include the promotion of magnet recycling (REEPRODUCE [96]), the development of new RE-free magnetic materials (CoCoMag [97]) and the establishment of a reliable supply chain (REEsilience [98]). In addition to these projects, the European Raw Materials Alliance [99] was founded to address further problems associated with these critical materials.

One potential gap magnet to tackle the mentioned issues is the Fe₂P compound, as illustrated in Fig. 1.14. It exhibits promising magnetic properties, such as a high magnetization and a high uniaxial anisotropy. These properties are combined with low costs due to its main component being the inexpensive and readily available element iron (Fe). The

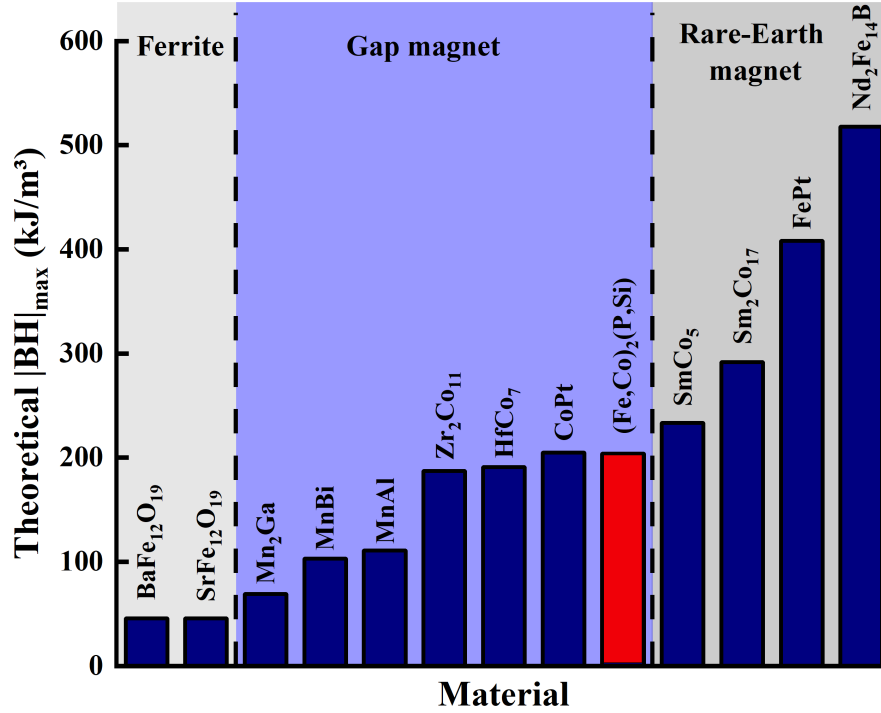


Figure 1.14: Theoretical maximum energy products of ferrites, gap magnets and RE-magnets with the Fe₂P material marked in red. Image is based on data from [42].

low cost in particular makes this compound more desirable than comparable materials such as CoPt, HfCo₇ or Zr₂Co₁₁, which incorporate highly expensive and critical elements like platinum, zirconium, hafnium or cobalt. Although cobalt is also used in this study as a potential substitute, the amounts used are generally much lower than in these compounds and it can therefore still be considered as a suitable iron replacement. In Fig.1.15 are the prices for the corresponding oxides of Fe and the RE elements neodymium (Nd), dysprosium (Dy) and terbium (Tb) on the world market since 2008 shown, highlighting the significant price difference between these elements.

Interestingly, Fe₂P is not recently discovered material. It well known and received much attention in the 20th century due to its high uniaxial anisotropy and high magnetocaloric effect in the (Fe,Mn)₂(P,A) compound with A = As, Ge or Si [103, 104, 105, 106]. This attention was driven by a unique first-order magnetic transition from ferromagnetic to paramagnetic, associated with a massive latent heat. This enables these compounds to be used as materials for effective magnetic cooling at ambient temperature. They are comparable in effectiveness to the giant magnetocaloric effect material Gd₅Ge₂Si₂, but without the associated criticality and scarcity of Gd or Ge [65, 66]. Another favorable property of Fe₂P is its stability regarding the substitution of Fe and P with other substitutes. This makes it highly tunable to meet specific requirements. In recent years, the Fe₂P-type materials have been reinvestigated as purely magnetic materials, due to

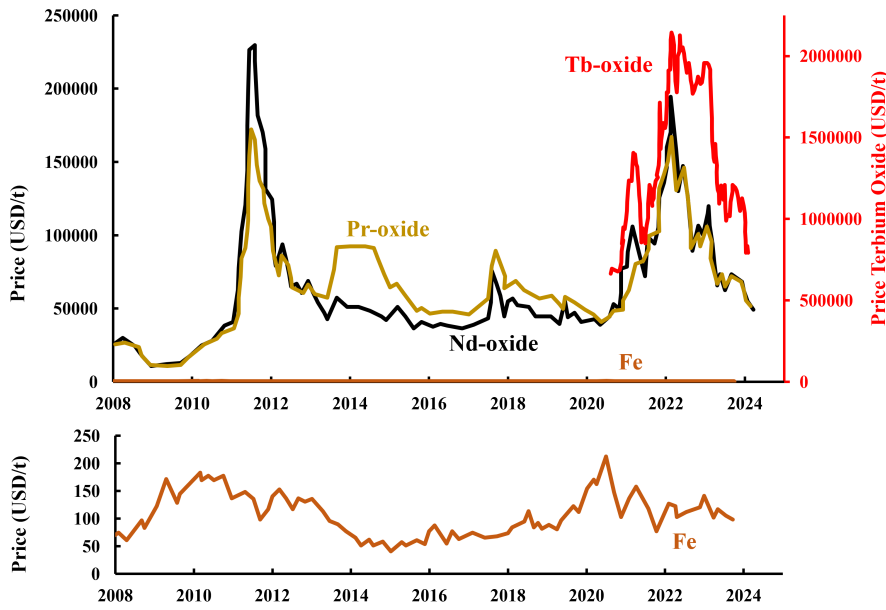


Figure 1.15: Development of the prices of the three rare-earth-oxides Pr- (yellow), Nd- (black) and Tb-oxide (red) [100, 101] and the element Fe (orange) in USD/t from 2008 to 2024 [102].

their mentioned high magnetocrystalline anisotropy and magnetization. This was further promoted by global developments that have led to an increased demand for the reduction of RE elements in magnets. Since then, the focus of Fe and P substitution with other elements has shifted from the magnetocaloric effect to improving the magnetic properties and making this material more suitable as a hard magnet [67, 69, 42, 68]. The effects of these compositional substitutions on the magnetic properties have not yet been explored in great detail and further investigations are needed.

The most significant drawback of Fe_2P is the comparatively low Curie temperature of 214 K [29, 28, 107, 27], which hinders its suitability for most commercial applications. However, the Curie temperature of Fe_2P can be readily modified by the mentioned substitution of Fe and P with elements such as Mn [103, 108, 109, 104], Co [106, 43, 110, 111, 112], Ni [113, 114, 115, 116], B [117, 118, 119, 120], Si [121, 119, 120, 122, 43, 114, 123, 112], Ge [124, 103] or As [105, 119, 108]. It has been reported, that these substitutions can greatly enhance the Curie temperature of the compound, and in some cases, the other magnetic properties as well. The present study investigates the influence of Si and Co substitution on the phase stability and the magnetic properties, such as the magnetic moments, Curie temperature and magnetocrystalline anisotropy in order to provide insights into the effects of these elements in this compound family.

The selection of these elements as the primary focus is based on promising results in the literature for these elements. Furthermore, preliminary screenings for various element

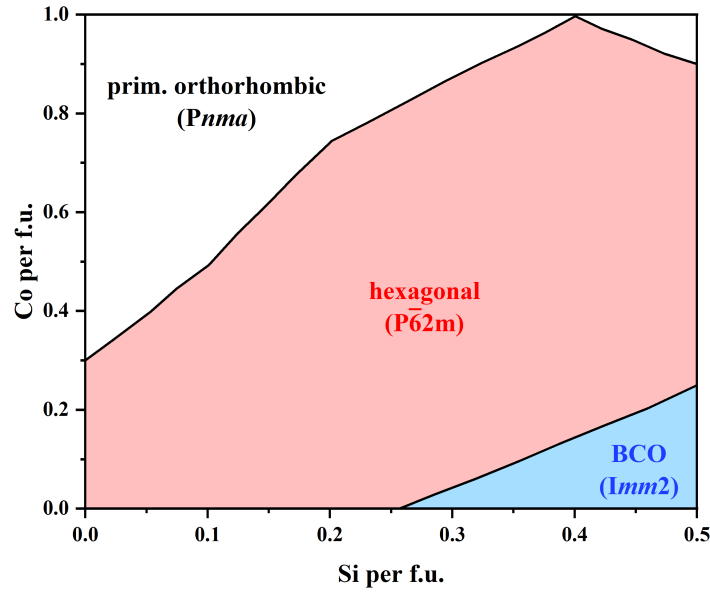


Figure 1.16: Experimentally found stable compounds at room temperature in dependence of Si and Co contents for Fe_2P -based compound. Image derived from [68].

substitutions for P and Fe have demonstrated that Si and Co each provide a substantial improvement of formation energy, magnetic moment and Curie temperature.

However, the incorporation of these elements also introduces a challenge to the stability of the hexagonal crystal structure of Fe_2P . As the amounts of Si and Co increase, transitions to other, less favorable crystal structures, such as the body-centered-orthorhombic (BCO) or the Co_2P phase, start to appear. These phases are less desirable than the hexagonal crystal structure because they exhibit inferior magnetic properties, including lower magnetic moments and especially less coercivity. Note, that even though the BCO phase has lower magnetic properties than the hexagonal one, it is still considerably good. This was demonstrated in recent investigations by Surilemu *et al.* [125], who investigated BCO structured Fe_2P -based compounds. In the case of Si for P substitution, a phase transition to the BCO phase is reported to occur at $\sim 20\text{-}25\%$ Si per f.u. at room temperature by Bao *et al.* [68]. In 1995, Severin *et al.* [123] reported on the temperature dependence of the phase transition from hexagonal to BCO-structured Fe_2P . They found that, as temperatures increase, a greater amount of Si could be substituted without a phase transition occurring. Additionally, Bao *et al.* [68] found that simultaneous Co substitution significantly enlarges the stability range of the hexagonal crystal structure. This result is shown in Fig. 1.16. To avoid the phase transition to the BCO phase, this work primarily focuses on low Si and Co substitutions to ensure the compound retains the hexagonal crystal structure. To gain a comprehensive understanding, the impact of both Si and Co substitution was examined up to $x = 0.5$ Si and $y = 1.0$ Co per f.u. For

simultaneous Si and Co substitutions, only two low Si cases (0.08 Si and 0.16 Si) and one high Si (0.41 Si) case were considered in greater detail. The possible transition to a primitive orthorhombic structure at high Co substitution levels has not been investigated in this work.

Motivated by these considerations, this work aims to identify suitable Fe_2P -based compounds for magnetic materials by employing theoretical density functional theory investigations (DFT). The advantage of DFT against experimental works is that it is a fast, robust and reliable method for predicting the properties of a compound and finding suitable materials, without the need of lengthy experiments. It also has the advantage of low cost, as no physical materials are needed to perform these investigations. First, the magnetic properties of the considered Fe_2P -based alloys are explored, followed by phase stability calculations. Finally, both parts are combined to provide an assessment of promising Fe_2P -based materials.

Chapter 2

Theoretical Background

To investigate the intrinsic magnetic properties of each considered compound, *ab initio* density functional theory (DFT) calculations were performed. These calculations aim to provide an atomistic understanding of the properties and to reveal the influence of the substitute elements. Each computed property was then compared with available theoretical and experimental data.

The purpose of this second chapter is to offer insights into the theoretical methods used to calculate the magnetic properties. At the beginning of the chapter, the fundamentals of the thesis’s primary method, the density functional theory, are elaborated. Building on this foundation, the essential concepts of quantum mechanics are explained to provide a solid understanding of the theory behind the calculations. This work focuses particularly on the quantum mechanical origin of magnetism and the calculation of phase stabilities at finite temperatures within the CALPHAD framework [126, 127].

2.1 Density Functional Theory

Since the beginning of computational chemistry and physics, DFT has emerged as one of the most widely used quantum mechanical methods for describing the electronic structure of different systems. The first attempt to use the electron density instead of a wave function to describe the properties of a compound was reported in the form of the Thomas-Fermi model in 1927 [128]. The modern DFT method was first introduced in 1964 with the Hohenberg-Kohn theorems by Pierre Hohenberg and Walter Kohn [129], and was shortly thereafter improved by Walter Kohn and Lu Jeu Sham with the Kohn-Sham equations [130]. Similar to Hartree-Fock (HF) and post-Hartree-Fock (post-HF) methods, such as Configuration Interaction (CI) and Coupled-Cluster (CC), DFT provides an accurate description of the electron interactions within a compound by solving the fundamental Schrödinger equation. As these calculations do not require additional experimental data, they are referred to as *ab-initio* or first-principle methods [131, 132].

However, unlike to HF-based methods, DFT does not incorporate a Slater determinant, which is composed of single-electron wave functions, to tackle the description of the many electron wave function. Instead, the DFT method proposed by Hohenberg and Kohn

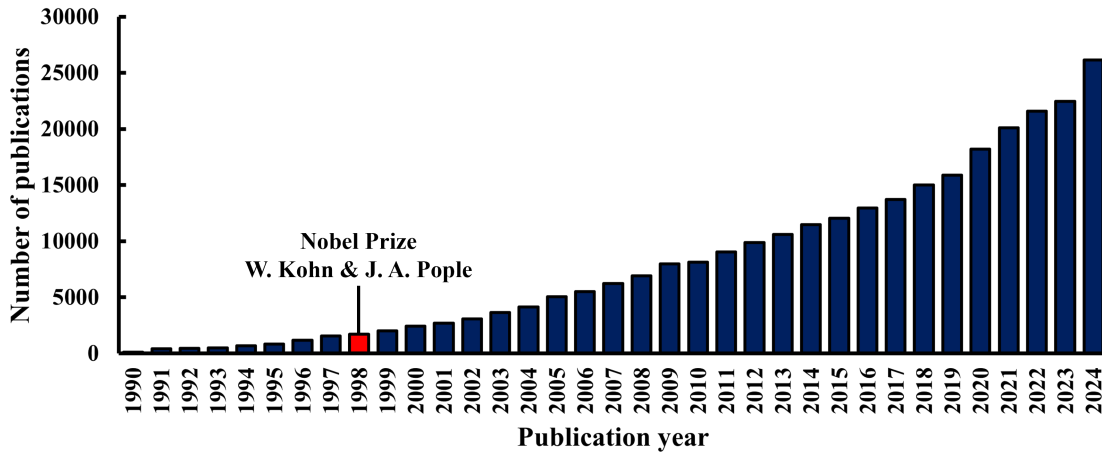


Figure 2.1: Number of publications with the search tag DFT in the web of science from 1990 to 2024. The nobel prize in chemistry for Walter Kohn and John A. Pople (1998) [134] has been marked in the diagram. The data was taken directly from web of science [135].

uses the electron density of the system to calculate the ground-state properties of the compound. This approach is very convenient, as it reduces the number of variables from $4N$ (three spatial variables and one spin variable for each electron) in the case of the many-body wave function, to just three variables for the electron density (three spatial coordinates). This advantage was somewhat less pronounced after the reintroduction of orbitals with the Kohn-Sham equations, where the number of variables increased to $3N$. Nevertheless, this is still a significant improvement in terms of calculation time. The description was partially reimplemented via a wave function, and the many-body problem was mapped using non-interacting quasi-particles. This simplified the multi-electron problem to that of non-interacting electrons in an effective potential [89, 133]. This forms the basis for modern DFT approaches, and the number of publications utilizing DFT has steadily increased since then, as can be seen in Fig. 2.1. Most improvements to DFT nowadays can be seen in better functionals, and the importance of DFT was recognized in 1998 when Walter Kohn and John A. Pople were awarded the Nobel prize in chemistry [134].

2.1.1 Schrödinger Equation

The Schrödinger equation is the fundamental basis of quantum mechanics and was proposed in 1926 by Erwin Schrödinger. It provides a way to calculate the wave function of any system. With the solution of the Schrödinger equation all properties of a system can be determined, and it is the starting point of many *ab initio* methods. In its time independent, non-relativistic state, the equation is defined as follows [136, 137, 20, 132, 138]:

$$\hat{H}\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) = E\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N). \quad (2.1)$$

In this equation, $\hat{H}$ denotes the molecular Hamiltonian for a system that is independent from a magnetic and an electric field with K nuclei and N electrons. The Hamiltonian is crucial in describing the wave function, as it is composed of the kinetic energy of the electrons ($\hat{T}_N$) and nuclei ($\hat{T}_K$) and the Coulomb interactions (attraction and repulsion) between the electrons and nuclei ($\hat{V}_{N,N}$, $\hat{V}_{K,K}$ and $\hat{V}_{N,K}$) (see Eq. 2.2).

$$\hat{H} = \hat{T}_K + \hat{T}_N + \hat{V}_{N,N} + \hat{V}_{K,K} + \hat{V}_{N,K} \quad (2.2)$$

Expressing each of these contributions in atomic units ($e = m_e = \hbar = \frac{1}{4\pi\epsilon_0} = 1$ [138]) leads to Eq. 2.3. In this equation K describes the total number of nuclei, N the total number of electrons, Z the atomic number of the denoted nuclei, and R and r the distances between nuclei and electrons, respectively. The letters i and j serve the purpose to identify the N electrons, while the letters A and B are used to mark the K nuclei. The remaining variables are the mass of the nucleus A (M_A) and ∇_q^2 as the sum of the differential operators for the three spatial coordinates (see Eq. 2.4).

$$\hat{H} = -\sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{A=1}^K \frac{1}{2M_A} \nabla_A^2 - \sum_{i=1}^N \sum_{A=1}^K \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} + \sum_{A=1}^K \sum_{B>A}^K \frac{Z_A Z_B}{R_{AB}} \quad (2.3)$$

$$\nabla_q^2 = \frac{\partial^2}{\partial x_q^2} + \frac{\partial^2}{\partial y_q^2} + \frac{\partial^2}{\partial z_q^2} \quad (2.4)$$

As the Schrödinger equation is an eigenvalue equation, the Hamilton operator and the energy eigenvalue E are closely connected. Therefore, a defined Hamiltonian results in an explicit energy eigenvalue, making H an important key to solving the Schrödinger equation.

2.1.2 Born-Oppenheimer Approximation

Nevertheless, the Schrödinger equation is very difficult to solve because it takes all the electrons and nuclei of a compound into account. In fact, it is so complex, that an exact solution is impossible for most systems. To circumvent this complexity, some assumptions and approximations can be made. One of the best-known approximations Born-Oppenheimer Approximation, postulated in 1927 by Max Born and Robert J. Oppenheimer [139]. Based on the exceptionally greater mass of the atom nuclei compared to the electrons (the H nucleus weighs ~ 1800 times more than its electron), and the

consequently greater velocity of the electrons, the atomic nuclei can be considered as stationary, with the electrons moving within their resulting field. This leads to a separation of the electronic and nuclear degrees of freedom. Treating the nuclei as fixed causes the potential energy of repulsion between the cores to be constant ($V_{K,K} = \text{constant}$) and the kinetic energy of the nuclei to be zero ($T_K = 0$). Since adding a constant to an operator only affects the eigenvalue of an operator and not its eigenfunctions, the constant term can be neglected initially and simply be added to the calculated energy eigenvalue (*i.e.* E_{elec}) later [136]. This simplifies the molecular Hamiltonian to the electronic Hamiltonian (H_{elec}) [136, 132, 137]:

$$\hat{H}_{elec} = \hat{T}_N + \hat{V}_{N,K} + \hat{V}_{N,N} = - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^K \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} \quad (2.5)$$

Using the electronic Hamiltonian in the Schrödinger equation yields the electronic wave function ϕ_{elec} and the electronic energy E_{elec} [136, 137, 132].

$$\hat{H}_{elec}(r; R) \phi_{elec}(r; R) = E_{elec}(R) \phi(r; R) \quad (2.6)$$

The electronic wave function depends explicitly only on the electron coordinates r , while the nuclear coordinates R are entered parametrically and do not appear explicitly. To obtain the total energy of a system (E_{tot}) the previously neglected constant term of core repulsion $V_{K,K}$, must be added to the electronic energy as mentioned before [136].

$$E_{tot} = E_{elec} + \sum_{A=1}^K \sum_{B>A}^K \frac{Z_A Z_B}{R_{AB}} \quad (2.7)$$

Although Hartree-Fock methods and DFT both use the simplified electronic Hamiltonian as a basis, the two methods diverge in their subsequent calculations. HF-methods use an approach that involves approximating the wavefunction with a Slater determinant and applying the variational principle to determine the lowest possible ground-state energy ($E_{exact} \leq E_{HF} = \frac{\langle \phi_{HF} | \hat{H} | \phi_{HF} \rangle}{\langle \phi_{HF} | \phi_{HF} \rangle}$). In contrast, density functional theory incorporates the electron density ρ to describe the energy of the system.

2.1.3 Hohenberg-Kohn Theorem

As previously mentioned, the Born-Oppenheimer approximation significantly simplifies the Hamiltonian. In 1964, Hohenberg and Kohn proposed the Hohenberg-Kohn theorems [140] and attempted to solve the Hamiltonian by reducing the many-body wave function to the electron density $\rho(r)$. Although this concept had already been described in the Thomas-Fermi model in 1927 [128], the Hohenberg-Kohn theorems are considered

the foundation of modern DFT because they provide a solid theoretical basis and verify the connection between a system's energy and its electron density in the first theorem. The second theorem showed that the variational principle also applies to the electron density, just as in the MO theory [141].

The first Hohenberg-Kohn theorem is considered an existence theorem showing the direct connection between the electron density and the energy of a system. It was argued that, since the electron density ρ defines the number of electrons in a system, the ground-state wave function Ψ and all associated electronic properties are also defined by $\rho(r)$ [131]. To prove this assumption, they only used the minimum energy principle for the ground-state. They considered the electron density $\rho(r)$ for the non-degenerate ground-state of some N-electron systems, defining N by simple quadrature. The external potential $v(r)$, which is the potential generated by the electrons' and nucleus's Coulomb potential ($\hat{V}_{N,K}$), is also defined by the electron density.

Assuming that two potentials v and v' , which differ by more than a constant, result in the same ground-state density ρ , would consequently mean that there are two Hamiltonians, H and H' , with the same ground-state density but different normalized wave functions, Ψ and Ψ' [131]. To address this occurring $\hat{H}$ problem, Hohenberg and Kohn then took Ψ' as a trial wave function, resulting in the following equation:

$$E_0 < \langle \Psi' | \hat{H} | \Psi' \rangle = \langle \Psi' | \hat{H}' | \Psi' \rangle + \langle \Psi' | \hat{H} - \hat{H}' | \Psi' \rangle = E'_0 + \int \rho(r)[v(r) - v'(r)]dr, \quad (2.8)$$

with E_0 and E'_0 as the ground-state energies for each Hamiltonian $\hat{H}$ and $\hat{H}'$. Similarly, using Ψ as the trial wave function for $\hat{H}'$, results in the slightly different equation:

$$E'_0 < \langle \Psi | \hat{H}' | \Psi \rangle = \langle \Psi | \hat{H} | \Psi \rangle + \langle \Psi | \hat{H}' - \hat{H} | \Psi \rangle = E_0 - \int \rho(r)[v(r) - v'(r)]dr. \quad (2.9)$$

Combining both, Eq. 2.8 and Eq. 2.9 yields a contradiction ($E_0 + E'_0 < E'_0 + E_0$), which proves that two different potentials v with the same ground-state density ρ cannot exist. This contradiction also means that ρ defines the number of electrons N, the potential v , the kinetic energy $T_N(\rho)$, the potential energy $V_{N,N}(\rho)$ and even the total energy $E(\rho)$.

$$E_v(\rho) = T_N(\rho) + V_{N,K}(\rho) + V_{N,N}(\rho) = \int \rho(r)v(r)dr + F_{HK}(\rho) \quad (2.10)$$

with

$$F_{HK}(\rho) = T_N(\rho) + V_{N,N}(\rho) \quad (2.11)$$

Furthermore, the potential energy of the electron repulsion $V_{N,N}(\rho)$ can be divided into a classical repulsion term $J(\rho)$ and a non-classical term, which is a major part of the exchange-correlation energy.

$$V_{N,N}(\rho) = J(\rho) + \text{non-classical} \quad (2.12)$$

The second Hohenberg-Kohn theorem demonstrates the viability of the variational principle for the energy using the electron density. The following was stated for a trial density $\tilde{\rho}(r)$ with $\tilde{\rho}(r) \geq 0$ and $\int \tilde{\rho}(r)dr = N$:

$$E_0 \leq E_v(\tilde{\rho}) \quad (2.13)$$

with $E_v(\tilde{\rho})$ as the energy functional. To prove this assumption, Hohenberg and Kohn used the first theorem as a basis, with $\tilde{\rho}$ defining its own potential $\tilde{v}$, its Hamiltonian $\hat{H}$ and wave function $\tilde{\Psi}$. This was then used as a trial function for the external potential of v .

$$\langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle = \int \tilde{\rho}(r)v(r)dr + F_{HK}(\tilde{\rho}) = E_v(\tilde{\rho}) \geq E_v(\rho) \quad (2.14)$$

This equation exactly illustrates what Hohenberg and Kohn wanted to show: it describes the variational principle for the electron density. However, with an assumed differentiability of $E_v(\rho)$, it is required for the ground-state density to satisfy the stationary principle to fulfill the variational principle.

$$\delta\{E_v(\rho) - \mu[\int \rho(r)dr - N]\} = 0, \quad (2.15)$$

resulting in the Euler-Lagrange equation with μ as the chemical potential:

$$\mu = \frac{\delta E_v(\rho)}{\delta \rho(r)} = v(r) + \frac{\delta F_{HK}(\rho)}{\delta \rho(r)} \quad (2.16)$$

This shows that, with the exact term of F_{HK} , which is defined independently of the external potential $v(r)$, equation 2.15 results in an exact solution for the ground-state electron density. This concludes that F_{HK} is a universal functional for $\rho(r)$ that can be used for any system. Defining F_{HK} , which includes the exchange-correlation energy, is therefore a crucial step in achieving an almost exact solution for the ground-state energy.

2.1.4 Kohn-Sham Equations

Although the Hohenberg-Kohn theorems showed great promise in calculating the ground-state energy using only the electron density ρ , the results were inaccurate due to the

drastic approximations that had to be made. The most problematic term was found to be the determination of the kinetic energy. To address this issue, Walter Kohn and Lu Jeu Sham proposed a method to approximate the kinetic energy in 1965 [130]. They reintroduced orbitals in such a way that the computation of the kinetic energy could be performed with good accuracy and only requiring a small additional correction [131]. Starting from the ground-state kinetic energy T , the natural spin orbitals ψ_i and their occupation numbers n_i are incorporated into the equation

$$T = \sum_i^N n_i \langle \psi_i | -\frac{1}{2} \nabla^2 | \psi_i \rangle. \quad (2.17)$$

Using the requirements of the Pauli principle ($0 \leq n_i \leq 1$) and the Hohenberg-Kohn theorems, we can derive that T is a functional of the electron density in the following way:

$$\rho(r) = \sum_i^N n_i \sum_s |\psi_i(r, s)|^2. \quad (2.18)$$

This means that, for interacting systems, there are an infinite number of terms, so the formulations had to be simplified. Kohn and Sham proposed the following simplifications for both equations [131, 132].

$$T_s(\rho) = \sum_i^N \langle \psi_i | -\frac{1}{2} \nabla^2 | \psi_i \rangle \quad (2.19)$$

and

$$\rho(r) = \sum_i^N \sum_s |\psi_i(r, s)|^2. \quad (2.20)$$

These two equations assume $n_i = 1$ for N orbitals and $n_i = 0$ for all other cases, which is viable for wave functions that describe N non-interacting electrons. In simple terms, Kohn and Sham mapped the system using a non-interacting reference system. This results in the Hamiltonian $\hat{H}_s$, which includes no Coulomb energy from electron-electron repulsion and defines the ground-state electron density exactly as ρ .

$$\hat{H}_s = \sum_i^N \left(-\frac{1}{2} \nabla_i^2 \right) + \sum_i^N v_s(r_i) \quad (2.21)$$

Consequently, this Hamiltonian H_s leads to the wave function Ψ_s with

$$\Psi_s = \frac{1}{\sqrt{N!}} \det(\psi_1 \psi_2 \dots \psi_N), \quad (2.22)$$

where ψ_i are the N lowest eigenstates (orbitals) of the one-electron Hamiltonian $\hat{h}_s$, that are defined as follows:

$$\hat{h}_s \psi_i = \left[-\frac{1}{2} \nabla^2 + v_s(r) \right] \psi_i = \epsilon_i \psi_i \quad (2.23)$$

The kinetic energy can then be calculated as

$$T_s(\rho) = \langle \Psi_s | \sum_i^N \left(-\frac{1}{2} \nabla_i^2 \right) | \Psi_s \rangle = \sum_{i=1}^N \langle \psi_i | -\frac{1}{2} \nabla^2 | \psi_i \rangle. \quad (2.24)$$

However, the form of this kinetic energy $T_s(\rho)$ is restricted in that it must be non-interacting and v -representable. This means that there must be a non-interacting ground-state with $\rho(r)$. This problem was solved through a further separation of F_{HK} , which was defined in equation 2.11:

$$F(\rho) = T_s(\rho) + J(\rho) + E_{xc}(\rho) \quad (2.25)$$

with

$$E_{xc} \equiv T(\rho) - T_s(\rho) + V_{NN}(\rho) - J(\rho). \quad (2.26)$$

E_{xc} is called the exchange-correlation energy and describes the resulting energy difference between the exact kinetic energy T and the kinetic energy of the non-interacting system T_s and the before mentioned non-classical part of V_{NN} .

This changes the Euler equation from Eq. 2.16 accordingly to

$$\mu = v_{eff}(r) + \frac{\delta T_s(\rho)}{\delta \rho(r)}. \quad (2.27)$$

The used effective potential v_{eff} can be expressed as

$$v_{eff}(r) = v(r) + \frac{\delta J(\rho)}{\delta \rho(r)} + \frac{\delta E_{xc}(\rho)}{\delta \rho(r)} = v(r) + \int \frac{\rho(r')}{|r - r'|} dr' + v_{xc}(r). \quad (2.28)$$

The property of v_{xc} is the exchange-correlation potential that is defined as

$$v_{xc}(r) = \frac{\delta E_{xc}(\rho)}{\delta \rho(r)} \quad (2.29)$$

In summary, the Kohn-Sham approach reintroduces orbitals to improve the description of the kinetic energy and mapped the problem onto a reference system of non-interacting particles that generates the same density as a system of interacting particles. They then separated the kinetic energy further into the energy from the non-interacting system (T_s), the classical repulsion term J and the exchange-correlation energy that includes the energy difference between the exact kinetic energy T and T_s , as well as the non-classical part of

V_{NN} . It can then be started with a guessed density $\rho(r)$, followed by the construction of the effective potential v_{eff} by using Eq. 2.28 and Eq. 2.29. A new density $\rho(r)$ can then be determined via Eq. 2.23 in combination with Eq. 2.20. Finally, the energy can be calculated using the found density and the expanded energy functional with the following relation:

$$E(\rho) = \int \rho(r)v(r)dr + T_s(\rho) + J(\rho) + E_{xc}(\rho) \quad (2.30)$$

Now the only unknown contribution is the exchange-correlation energy E_{xc} that can be further approximated with specific exchange-correlation functionals such as the local-density approximation or the generalized gradient approximation.

2.2 Exchange Correlation Potentials

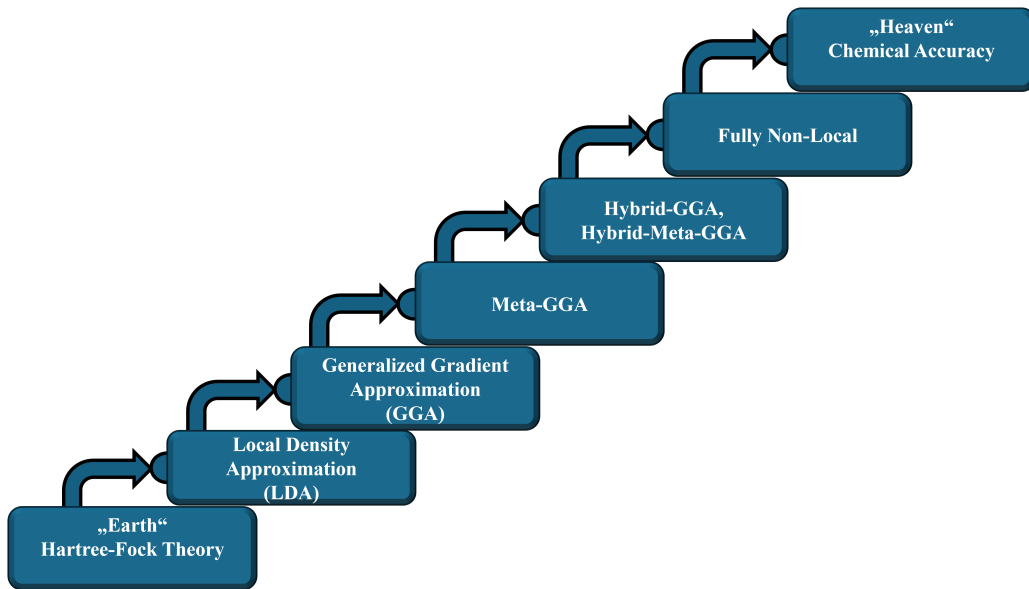


Figure 2.2: Ordering of the most general exchange correlation functionals regarding the quality of the calculations. The lowest quality is attributed to Hartree-Fock, while the highest quality is expected for an assumed chemical accuracy.

As the Kohn-Sham approach handles most of the kinetic energy, the only unknown term in density functional theory is the exchange-correlation energy, denoted as E_{xc} . To account for this missing energy, various approximations have been developed and implemented to enable accurate calculations. Depending on the complexity of the approximation, the calculations differ in terms of computational cost and quality. The different classes of these exchange-correlation functionals are shown in Fig. 2.2, where they are arranged in ascending order based on complexity and quality. This arrangement is known as

the Jacobs ladder. The most basic and simple approximations are located at the "ground" of the ladder, while the top represents precise, but very complex and time-consuming, methods of covering the exchange-correlation. This work focuses on the local (spin) density approximation (L(S)DA) and the generalized gradient approximation (GGA), which are common exchange-correlation functionals used in materials science to describe solid-state materials, such as the compounds examined in this study [131, 132, 142].

2.2.1 Local Density Approximation

The local density approximation (LDA) is one of the lower steps on the Jacobs ladder, ranking only above the "earth" level of Hartree-Fock. It is considered a fundamental approximation with a low accuracy and low computational effort. This approximation is based on a uniform electron gas, where the electrons move within a positive background charge distribution to create a charge-neutral system. While the overall number of electrons N and the volume of the gas V are considered as infinite, the electron density $\frac{N}{V}$ is seen as finite and constant at each point in the system. This model can be used for an idealized metal and yields relatively good results for metals such as sodium. However, for any other system with varying electron densities, this model is inaccurate. In the following equation, ϵ_{xc} is defined as the exchange-correlation energy per particle of the uniform electron gas with the density $\rho(r)$. This energy is additionally weighted by the probability of $\rho(r)$ to account for the fact that an electron is present at this position in space.

$$E_{xc}^{LDA}(\rho) = \int \rho(r) \epsilon_{xc}(\rho) dr \quad (2.31)$$

The exchange correlation energy $\epsilon_{xc}(\rho)$ can further be divided into the explicit exchange and correlation energies $\epsilon_x(\rho)$ and $\epsilon_c(\rho)$.

$$\epsilon_{xc}(\rho) = \epsilon_x(\rho) + \epsilon_c(\rho) \quad (2.32)$$

ϵ_x represents the exchange energy of an electron in the uniform electron gas and was already described by Bloch and Dirac and used by Slater in the approximation for the HF exchange.

$$\epsilon_x = -\frac{3}{4} \sqrt[3]{\frac{3\rho(r)}{\pi}} \quad (2.33)$$

Using this exchange-term retrieves the $\rho^{4/3}$ dependence of the exchange energy and is often called the Slater-exchange S . Although the direct expression of the correlation term is not known, accurate Monte-Carlo simulations of the correlation energy are available

from Ceperley and Alder from 1980 [143]. Other analytical expressions of ϵ_c have been proposed by Vosko, Wilk and Nusair (VWN) in 1980 [144] and by Perdew and Wang in 1992 [145].

The unrestricted local spin density approximation (LSDA) is an extension of the local density approximation, in which the electron density is replaced by two spin densities $\rho_\alpha(r)$ and $\rho_\beta(r)$. These two spin densities are summed to give the electron density: $\rho_\alpha(r) + \rho_\beta(r) = \rho(r)$. This splitting of the electron density while maintaining the dependence on it provides more accurate results for most systems. Especially systems with differing numbers of electrons for α and β benefit from the higher flexibility of having two variables instead of one. LSDA also provides higher accuracy for systems with an even number of electrons because it allows for a breaking of the symmetry. This unrestricted version of LDA is defined as follows:

$$E_{XC}^{LSDA}[\rho_\alpha, \rho_\beta] = \int \rho(r) \epsilon_{XC}(\rho_\alpha(r), \rho_\beta(r)) dr \quad (2.34)$$

There are expressions for the exchange and correlation energies for both the simple case with equal spin densities for $\rho_\alpha(r)$ and $\rho_\beta(r)$ ($\rho_\alpha(r) = \rho_\beta(r) = \frac{1}{2}\rho(r)$), as well as for spin-polarized cases ($\rho_\alpha(r) \neq \rho_\beta(r)$). The degree of spin-polarization is described by a spin-polarization parameter ζ , which can attain values between 0 and 1 and is described by the following equation:

$$\zeta = \frac{\rho_\alpha(r) - \rho_\beta(r)}{\rho(r)} \quad (2.35)$$

The biggest drawback of L(S)DA is its drastic approximation of the dependency of the exchange-correlation potential on the local densities for $\rho_\alpha(r)$ and $\rho_\beta(r)$. This clearly does not reflect the behavior in real systems. Nevertheless, L(S)DA is used successfully in the calculation of properties such as equilibrium structures, harmonic frequencies and charge moments, but it fails for calculations of binding energies, overestimating by a relatively large degree. Even so, it is usually still more precise than the Hartree-Fock method. The local (spin) density approximation is the only DFT functional that has been extensively explored and is well understood. This is also why LDA forms the basis of most other exchange-correlation functionals, being incorporated into most of them in one way or another.

2.2.2 Generalized Gradient Approximation

The local (spin) density approximation is considered insufficient for most problems in chemistry due to high degree of deviation. This means that it is not well suited to be used in computational chemistry. It was only with the development of the first extensions

to LDA, that DFT became accurate enough for chemical problems. One such extension, which greatly improved the accuracy of the exchange-correlation functional greatly, was to include the inhomogeneity of the electron density by considering the gradient of the electron density $\nabla\rho(r)$:

$$E_{xc}^{GGA}(\rho) = \int \rho(r) \epsilon_{xc}(\rho(r), \nabla\rho) dr. \quad (2.36)$$

This improves the local density approximation, as it now considers a non-uniform electron gas. However, although it sounds simple, the implementation is slightly more complicated. Including the first-order corrections for the exchange term improves the exchange energy, but incorporating the first-order correlation correction often produces positive results, which makes it worse than LSDA. This is caused by the gradient terms, as these disrupt the important requirement for the Fermi hole to integrate to -1 and the Coulomb hole to 0. This initial attempt is known as the gradient expansion approximation [132, 142]. To solve this problem, the Fermi hole and the Coulomb hole were simply forced to sum to -1 and 0 respectively, and exchange holes that violated the rule of being always negative were set to zero. Functionals that implement these requirements in this way are known as generalized gradient approximations (GGA) and are among the most widely used functionals today. Many different GGA approaches have been proposed in the past. The most prominent of these are the PW91 exchange functional by Perdew and Wang from 1992 [145, 146], and the PBE functional by Perdew, Burke and Ernzerhof [147] from 1996, which was used in this work.

A common misconception is that GGA functionals are frequently designated as non-local. However, it should be noted that this term is somewhat deceptive, as the relevant quantities are dependent on the density (and its derivatives) at a given point, rather than the spatial volume. In the PBE functional, the exchange part is expressed as an additional factor multiplied onto the LSDA functional, with a dimensionless gradient variable x . This variable is defined as:

$$x = \frac{|\nabla\rho|}{\rho^{4/3}} \quad (2.37)$$

This combines into the following relations for the PBE functional:

$$\epsilon_x^{PBE} = \epsilon_x^{LDA} F(x), \quad (2.38)$$

$$F(x) = 1 + a - \frac{a}{1 + bx^2}, \quad (2.39)$$

with ϵ_x^{PBE} and ϵ_x^{LDA} as the exchange functionals for GGA and LSDA, $F(x)$ as the enhancement factor, x as the dimensionless gradient variable and a and b as non-empirical

parameters, that are obtained from fitting to experimental data. The corresponding correlation part for PBE is defined in a similar way by a factor that is added to the LDA part. The used t variable is derived from x by a spin-polarization function.

$$\epsilon_c^{PBE} = \epsilon_c^{LDA} + H(t) \quad (2.40)$$

$$H(t) = cf_3^3 \ln \left[1 + dt^2 \left(\frac{1 + At^2}{1 + At^2 + A^2t^4} \right) \right] \quad (2.41)$$

$$A = d \left[\exp \left(-\frac{\epsilon_c^{LDA}}{cf_3^3} \right) - 1 \right]^{-1} \quad (2.42)$$

$$f_3(\zeta) = \frac{1}{2} [(1 + \zeta)^{2/3} + (1 - \zeta)^{2/3}] \quad (2.43)$$

$$t = [2(3\pi^3)^{1/3} f_3]^{-1} x \quad (2.44)$$

The magnetocrystalline anisotropy, which is predicated on the spin-orbit-couplings, necessitates the cautious selection the choice of the exchange-correlation functional for the purpose of calculation. While GGA is frequently more robust and yields superior results for structural parameters, LSDA is often a reliable choice for the calculation of magnetic properties. This observation is also applicable to the MAE, wherein the LSDA functional regularly displays values that are more approximate to the experimental results. The underlying reasons for this behavior are a stronger suppression of the small orbital magnetic moments in GGA, which translates directly to smaller anisotropy values. Another key point is the higher self-interaction error in GGA which arises from the incorporation of the gradient. This can lead to a more pronounced delocalization of the electronic structure and the emergence of instabilities and noise, which can subsequently influence the small energy differences. Furthermore, LSDA actually profits from an accidental cancellation of errors in $3d$ elements. It has been demonstrated that, in instances where binding energies are overestimated, the influence of underestimated lattice constants is compensated [148, 149, 150].

2.3 Ultra-soft Pseudopotentials and the Projector Augmented Wave method

Another important aspect in DFT, next to the choice of the exchange-correlation functional, is the treatment of the nuclei-electron interaction. There are two well-known methods for addressing the interactions: the projector augmented wave method (PAW) by Blöchl [151, 152] and the ultrasoft pseudopotentials (USPP) method by Vanderbilt [153].

The functionality of both methods is based on the replacement of the effects of the motion of the electrons near the atom core by an effective potential. The effective reduction in computational effort is particularly pronounced high for larger elements lower down the periodic table, owing to the heightened significance of relativistic effects [154]. Pseudopotentials are generally defined by a core radius r_c that can vary according to the angular momentum of the valence orbitals. Up to this core radius the applied pseudopotential is an analytical function. Examples of such functions include polynomial and spherical Bessel functions. This method effectively smooths the wave function near the core region and significantly reduces the computational costs. However, beyond the core radius, the pseudopotential and its first and second derivatives are required to match the reference wave function and its derivatives exactly. This requirement is illustrated in Fig. 2.3, where the pseudo potential (V_{PS}) differs from the all-electron potential ($-Z/r$) below the core radius r_c . This results in a pseudo wave function that is much easier to calculate than the all-electron wave-function, shows oscillating behavior. After the core radius, both the pseudopotential and the pseudo wave function are identical to their respective counterparts [154].

This consequently leads to certain conditions that the plane waves need to fulfill in order to recreate the wave function properly. For hard pseudopotentials, *i.e.* a small r_c , more plane wave basis functions are required for the accurate reconstruct the wavefunction beyond r_c . Conversely, soft pseudopotentials (large r_c) demand fewer plane wave basis functions to project the wave function. However, a value of r_c that is too large can also negatively impact the quality of the results and reduce the transferability of the potential to other problems. In addition to the matching the potential and wave function at r_c , a norm-conserving condition can be imposed on the distance $< r_c$. This condition requires the integrals of the square of the reference and the pseudo wavefunction between 0 and r_c to be equal. In the ultrasoft pseudopotential method by Vanderbilt [153], this norm-conserving requirement is additionally relaxed, which lowers the number of plane waves required. However, a disadvantage of these pseudopotentials is that properties connected to core electrons, such as NMR activity, cannot be estimated, as these electrons are not well described by the pseudopotential [154].

In the projector augmented wave method (PAW), the core electrons are formally retained. The valence electrons are expanded using a plane wave basis, to which a contribution from the core region is added. This contribution is based on the core radius of each nucleus and is evaluated on a grid. This is then complemented by the difference between two sets of densities: one from the all-electron atomic orbitals, and the other from a set of nodeless pseudo-atomic orbitals. This extension allows the wave function in the core region to adapt to different environments and become more flexible. Assuming fully opti-

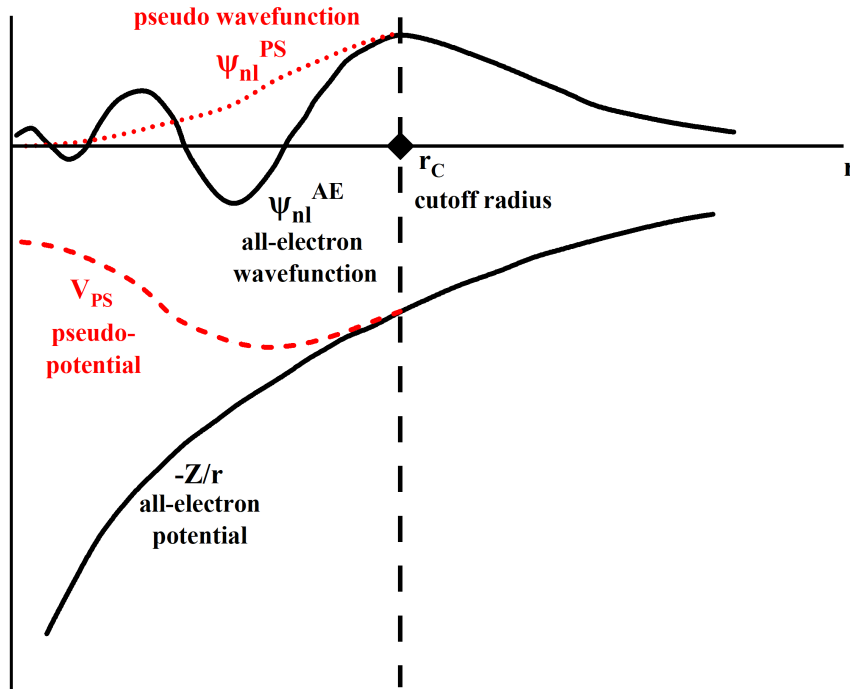


Figure 2.3: Schematic representation of the radial dependence of typical pseudopotentials in comparison with the all-electron potential. In the lower part are the pseudopotentials shown, while in the upper part the wavefunctions are compared. Above the point r , both potentials and wavefunctions have identical values. The image is adapted from [155].

mized atomic orbitals, the PAW method would be equivalent to all-electron mixed basis set methods.

One noteworthy approximation is the frozen-core approximation. In this approximation the core electrons are included in the treatment of the valence electrons, but the orbitals are kept fixed at their atomic values and are described by a fixed expansion in a suitable basis set. This approach has the advantage of retaining the full electron-electron interactions while excluding changes to the core orbitals caused by the molecular environment. Thus, the computational cost for elements with higher ordering numbers can be significantly reduced, and a variational collapse when using relativistic wave functions in calculations is prevented [154].

Finally, it is important to note that pseudopotentials depend on the exchange-correlation functional used. This means that the potential for LSDA is different from the potential for GGA. However, these differences are generally very small, and the pseudopotentials can often be used for different functionals without prior optimization [154].

2.4 Magnetism in Density Functional Theory

The magnetic moment consists of two parts: a spin contribution and an orbital contribution. The spin magnetic moment, which arises from the spin orientation of electrons orbiting the atomic nucleus, is the main contributor to the magnetic moment. The orbital magnetic moment results from the electrons moving around the atom core itself. However, the orbital magnetic moment is often much smaller than the spin magnetic moment. In the case of Fe atoms, which make up most of the investigated Fe_2P compound, the orbital contribution to the magnetic moment accounts to only $0.09 \mu_B$ per atom and is therefore negligible. In this study, only the spin magnetic moment is investigated, which is a sufficiently precise approximation.

For the description of the magnetism, the formalism as proposed by Barth and Hedin [156] for spin-polarized cases was used with the generalization of replacing the scalar density with a Hermitian 2×2 matrix.

$$n_{\alpha\beta}(r) = \sum_{i=1}^N \psi_i^{*\alpha}(r) \psi_i^\beta(r), \quad (2.45)$$

with α and β as (+) and (-). Considering the Pauli matrices σ , the matrix can be broken down into a scalar and a vectorial part, connected to the charge and magnetization densities, in the following way [156, 89]:

$$n(r) = \frac{1}{2}(n(r)I + \sigma \cdot m(r)) = \frac{1}{2} \begin{pmatrix} n(r) + m_z(r) & m_x(r) - im_y(r) \\ m_x(r) + im_y(r) & n(r) - m_z(r) \end{pmatrix}. \quad (2.46)$$

With this in mind, the Schrödinger equation can be reformulated into the following relation:

$$\left[\left(-\frac{\hbar^2}{2m} \nabla^2 + \sum_{\alpha} \int \frac{n_{\alpha\alpha}(r')}{|r-r'|} dr' \right) I + v(r) + \frac{\delta E_{xc}}{\delta n(r)} \right] \begin{pmatrix} \psi_i^{(+)}(r) \\ \psi_i^{(-)}(r) \end{pmatrix} = \epsilon_i \begin{pmatrix} \psi_i^{(+)}(r) \\ \psi_i^{(-)}(r) \end{pmatrix}. \quad (2.47)$$

In this equation I , which is the identity matrix, and the exchange correlation function are expressed as two 2×2 matrices. Furthermore, the potential matrices can be described by a scalar potential together with the magnetic field $B(r)$, resulting in the following connection:

$$v(r) = v(r)I + \mu_B \sigma \cdot B(r), \quad (2.48)$$

$$v_{xc}(r) = v_{xc}(r)I + \mu_B \sigma \cdot B_{xc}(r), \quad (2.49)$$

with $\mu_B = \frac{e\hbar}{2mc}$. Assuming collinear magnetic structures, the magnetic and exchange fields in the potential matrices are in the z direction and lead to a decoupling of the

Schrödinger equation into two equations that incorporate the Coulomb potential $v_{Coulomb}$ and the exchange-correlation potential $v_{xc}^{+,-}$ with respect to the spin-up (+) or spin-down (−) part of the diagonal density matrix [156, 89]:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + v_{Coulomb}(r) + v(r) + B_z(r) + v_{xc}^{(+)}(r)\right)\psi_i^{(+)}(r) = \epsilon_i^{(+)}\psi_i^{(+)}(r), \quad (2.50)$$

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + v_{Coulomb}(r) + v(r) + B_z(r) + v_{xc}^{(-)}(r)\right)\psi_i^{(-)}(r) = \epsilon_i^{(-)}\psi_i^{(-)}(r). \quad (2.51)$$

Both Eq. 2.50 and 2.51 need to be solved independently, doubling the effort compared to non-magnetic calculations. These two equations can be used to calculate all magnetic structures. Additionally, the spin density of can be expressed in the following way:

$$m(r) = -\mu_B \sum_{\alpha,\beta} \psi_{\alpha}^{(+)}(r) \sigma_{\alpha\beta} \psi_{\beta}(r) \quad (2.52)$$

Integrating over the spin density results in the important property of the spin magnetic moment.

$$M_{spin} = \int m(r) dr = \int (n^{(+)}(r) - n^{(-)}(r)) dr. \quad (2.53)$$

Since the accuracy of the magnetic properties depends on the exchange-correlation functional, considerable thought must be given to the choice of the functional. Previous investigations showed that the GGA functional produced results that were closer to experimental data, while the LSDA functional yielded results that differed more. The GGA functional was therefore chosen for calculations in this work.

2.5 Computational Thermodynamics

One of the main focuses of this work lies within the calculation of the phase stabilities for the investigated compounds. To make these predictions, the compounds' free energies are needed in high quality in order to properly describe their thermodynamic properties and the resulting phase stabilities. To address these properties, it is necessary to go beyond 0 K DFT and use finite temperature DFT [157, 158, 159].

The Helmholtz free energies were calculated as a function of temperature within the adiabatic approximation [160]. In this approximation, the basis for the decoupling are the much faster non-configurational degrees of freedom (*i.e.* the electronic, vibrational and magnetic degrees of freedom) compared to the configurational (*i.e.* diffusion controlled) degrees. This time-scale separation allows a solid-state phase to be described as fully equilibrated at a given temperature when only the fast non-configurational degrees of

freedom are considered. Consequently, the non-configurational part of the free energy can be treated as a single-value function of temperature at every point, considering atomic configurations.

This results in the description of the Helmholtz free energy as the sum of the three non-configurational contributions (electronic, vibrational and magnetic) and the decoupling of the degrees of freedom as a function of temperature and volume in the following way

$$F(T, V) = E_0(V) + F^{el}(T, V) + F^{vib}(T, V) + F^{mag}(T, V), \quad (2.54)$$

with the zero-temperature total energy E_0 , electronic F^{el} , vibrational F^{vib} and magnetic F^{mag} contributions of the free energy. Each contribution is explained in more detail in the following sections. In this work, the phonon-magnon and phonon-electron couplings have been neglected, as their contribution is expected to be small compared to the dominant free energy terms and would require substantially higher computational effort [161, 162]. These contributions will be covered in future investigations.

2.5.1 Electronic Free Energy

In order to calculate the electronic contribution to the free energy ($F^{el}(T, V)$) the proposed scheme by Gillan *et al.* [158] was employed. In their finite temperature scheme, $F^{el}(T, V)$ is given as

$$F^{el}(T, V) = E_0(T) - TS^{el}, \quad (2.55)$$

with E_0 as the total calculated energy of the crystal structure at 0 K and S^{el} as the electronic entropy. For the determination of E_0 available structural and magnetic data in literature have been considered to find the ground-state of all relevant phases. Different magnetic and structural cases for all compounds have been investigated as well. For the optimal description of the ground-state energy, a least-square fit to the Murnaghan equation of state has been incorporated [163, 164].

$$E(V) = E(V_{eq}) + \frac{BV}{B'^2 - B'} \left[B' \left(1 - \frac{V_{eq}}{V} \right) + \left(\frac{V_{eq}}{V} \right)^{B'} - 1 \right], \quad (2.56)$$

with V_{eq} as the ground-state volume at the equilibrium lattice constant, the bulk modulus denoted as $B = -V(\partial P/\partial V)_T$ and the connection of the energy to the pressure defined as $P = -(\partial E/\partial V)_T$. The variable B' is the derivative of B with respect to pressure. The variables V_{eq} , B_{eq} and B'_{eq} correspond to zero pressure ($P = 0$ Pa) in the equation. The electronic entropy S^{el} from eq. 2.55 is calculated with the following equation:

$$S^{el} = 2k_B \sum_i (f_i \ln f_i + (1 - f_i) \ln(1 - f_i)). \quad (2.57)$$

In Eq. 2.57, the prefactor 2 takes the spin degeneracy of the quasi-particles into account and k_B is the Boltzmann constant ($k_B = 1.380649 \cdot 10^{-23} \text{ J/K}$). The variable f_i describes the occupation numbers at thermal equilibrium, which are obtained using the Fermi function:

$$f_i = \frac{1}{\exp(\frac{\epsilon_i - \epsilon_F}{k_B T}) + 1}. \quad (2.58)$$

In Eq. 2.58, ϵ_i represents the one particle energies and ϵ_F the Fermi energy. Due to the appearance of the absolute temperature T in the equation, the occupation numbers f_i are temperature dependent. This results in an entropy of zero for $T \rightarrow 0$, and therefore a return to the conventional 0 K calculation scheme.

2.5.2 Vibrational Free Energy

The vibrational contribution is calculated using the direct force constant method [165], in which the unperturbed and perturbed ground-states are calculated. This method is based on the Hellmann-Feynman forces [166] of the perturbed structures, where small atomic displacements of $0.02 \text{ \AA}$ cause symmetrically inequivalent directions. These forces are then Fourier transformed after being summarized in a dynamical matrix. Diagonalization then yields the desired phonon frequencies for each q-point in reciprocal space [167]. The phonon frequencies ω_i , are the eigenvalues of the dynamical matrix D :

$$D(q)v_i(q) = \omega_i(q)v_i(q), \quad (2.59)$$

where v_i are the eigenvectors at the wave vector q . Expressing the dynamical matrix in reciprocal space makes it easier to apply to periodic systems. A 3×3 matrix can then be used to represent a crystal with a single atom in the following way:

$$D_{\mu,\nu}(q) = \frac{1}{\sqrt{M}} \sum_I^N \phi_{I\mu,\nu} \exp[iq \cdot R_I]. \quad (2.60)$$

In this equation, M represents the mass of the species, R_I are the atom positions in the supercell relative to a reference atom, μ and ν are the three spatial dimensions x , y and z and ϕ denotes the force constant matrix. The elements of the matrix can be evaluated with the following equation:

$$\phi_{I\mu,\nu} = \frac{\partial^2 F^{el}}{\partial u_{I\mu} \partial u_{I\nu}} = \frac{\partial \tilde{F}_{I\mu}^{HF}}{\partial u_{I\nu}}. \quad (2.61)$$

In Eq. 2.61, $u_{I\mu}$ describes the displacement of atom I toward direction μ and the displacement $u_{I\nu}$ toward direction ν . The variable $\partial \tilde{F}_{I\mu}^{HF}$ is the Hellmann-Feynman force acting

on atom I .

With a fixed volume this approach is known as the *harmonic approximation*. The vibrational contribution per elementary unit cell is then [160]:

$$F^{vib} = \frac{1}{N} \sum_i^{3N} \left\{ \frac{\hbar\omega_i}{2} + k_B T \ln[1 - \exp(-\frac{\hbar\omega_i}{k_B T})] \right\}, \quad (2.62)$$

with the reduced Planck constant $\hbar$, the temperature T and the Boltzmann constant k_B . This equation sums all $3N$ phonon states, with N is the total number of atoms. Although the equation for the force constant matrix ϕ (Eq. 2.61), contains the electronic energy F^{el} , which is dependent on the electronic temperature, the expected impact of this temperature on the force constants is small. Based on this assumption, F^{el} can be replaced by E^{el} at $T = 0$, which will remove the explicit temperature dependence of the phonon frequencies ($\omega_i(V, T) \rightarrow \omega_i(V)$). To achieve a volume dependency in the vibrational contribution, the method is repeated for different unit cell volumes and the energy is then minimized. This translates the harmonic approximation into the *quasi-harmonic approximation* [168], where the phonon frequencies depend implicitly on the temperature by the influence of temperature on the volume. This method can be used to investigate the vibration modes and the contributions to the free energy in order to identify the mechanisms behind the thermal expansions and the crystal stability in relation to temperature.

2.5.3 Magnetic Free Energy

The magnetic contribution to the free energy is an important factor for metals and alloys with magnetic properties. In 1976, Inden *et al.* [169] proposed an approach for thermodynamic modeling, which paved the way for the CALPHAD [126] method. This method investigates the magnetic Gibbs energy and magnetic transitions of compounds. The CALPHAD method can be used to approximate the magnetic contribution of experimental heat capacities for magnetic materials. However, the physical background of the model leaves much to be desired.

The Inden model includes the Curie temperature T_C , the magnetic moment (β) and the magnetic enthalpy ratio. The magnetic enthalpy ratio is further divided into a short-range order (SRO) and a long-range order (LRO). All of these parameters can be obtained from experiments or calculations.

In the model, the heat capacity is separated into a short-range order part for paramagnetic ordering above T_C and a long-range order part for ferromagnetic ordering below the T_C . The expressions for the two magnetic contributions are given below, with the T_C

considered in form of the reduced temperature ($\tau = T/T_C$):

$$C_P^{LRO} = K^{LRO} R \ln \frac{1 + \tau^3}{1 - \tau^3} \quad \tau < 1, \quad (2.63)$$

$$C_P^{SRO} = K^{SRO} R \ln \frac{1 + \tau^{-5}}{1 - \tau^{-5}} \quad \tau > 1. \quad (2.64)$$

In both equations C_P^{LRO} and C_P^{SRO} are the magnetic contributions to the heat capacity in the ferromagnetic and paramagnetic ordered states, respectively. K^{LRO} and K^{SRO} are both constants for long- and short-range orderings and R is the universal gas constant ($R = 8.314462 \text{ J mol}^{-1} \text{ K}^{-1}$). Hillert and Jarl [170] modified this model by using truncated Taylor expansions to sufficiently described both contributions.

$$C_P^{LRO} = 2K^{LRO} R \left(\tau^3 + \frac{1}{3}\tau^9 + \frac{1}{5}\tau^{15} \right) \quad \tau < 1 \quad (2.65)$$

$$C_P^{SRO} = 2K^{SRO} R \left(\tau^{-5} + \frac{1}{3}\tau^{-15} + \frac{1}{5}\tau^{-25} \right) \quad \tau > 1 \quad (2.66)$$

The magnetic entropy of the considered element was taken into account by Inden with the mean magnetic moment $\bar{\beta}$ of the elements via the following connection:

$$S^{mag} = R \ln(\bar{\beta} + 1) \quad (2.67)$$

With all parts of the magnetic free energy considered, the complete expression for the magnetic Gibbs free energy contribution is then defined as follows:

$$G^{mag} = RT \ln(\bar{\beta} + 1) g(\tau) \quad (2.68)$$

$$g(\tau) = \begin{cases} 1 - \frac{1}{A} \left[\frac{79\tau^{-1}}{140f} + \frac{474}{497} \left(\frac{1}{f} - 1 \right) \left(\frac{\tau^3}{6} + \frac{\tau^9}{135} + \frac{\tau^{15}}{600} \right) \right] & \tau < 1, \\ -\frac{1}{A} \left(\frac{\tau^{-5}}{10} + \frac{\tau^{-15}}{315} + \frac{\tau^{-25}}{1500} \right) & \tau \geq 1, \end{cases} \quad (2.69)$$

$$A = \frac{518}{1125} + \frac{11692}{15975} \left(\frac{1}{f} - 1 \right). \quad (2.70)$$

In this set of equations, f is the magnetic enthalpy ratio, which is a structural factor that accounts to $f = 0.4$ for bcc and $f = 0.28$ for fcc structures.

In Eq. 2.68 the value of $\bar{\beta}$ influences the shape of the peak in the heat capacity. In 2012, Xiong et al. [171] proposed to consider the sublattice magnetic moments in an alloy

to maximize the magnetic entropy.

$$S_{max}^{mag} = R \ln(\beta^* + 1) = R \sum_i x_i \ln(\beta_i + 1), \quad \text{with } \beta^* = \prod_i (\beta_i + 1)^{x_i} - 1. \quad (2.71)$$

β^* denotes the effective magnetic moment and x_i is the atomic components concentration. The mentioned approach by Xiong *et al.* [171] uses an effective magnetic moment rather than an averaged moment in order to maximize magnetic entropy and avoid conceptual errors. In this study, the magnetic moments were calculated using *ab initio* methods.

In their work, Xiong *et al.* [171] also incorporated proposed modifications by Chen and Sundman [172] into the calculation of the Gibbs energy. They expanded Eq. 2.72 and 2.73 for the heat capacity by adding an additional term to the Taylor expansion to align the results more precisely to experimental enthalpy values.

$$C_P^{LRO} = 2K^{LRO}R \left(\tau^3 + \frac{1}{3}\tau^9 + \frac{1}{5}\tau^{15} + \frac{\tau^{21}}{7} \right) \quad \tau < 1 \quad (2.72)$$

$$C_P^{SRO} = 2K^{SRO}R \left(\tau^{-7} + \frac{1}{3}\tau^{-21} + \frac{1}{5}\tau^{-35} + \frac{\tau^{-49}}{7} \right) \quad \tau > 1 \quad (2.73)$$

They also modified the f -factor to $f = 0.37$ for bcc and $f = 0.25$ for non-bcc structures and they changed $g(\tau)$ to the following expressions for the different τ values

$$g(\tau) = \begin{cases} 0 & \tau \leq 0 \\ 1 - \frac{1}{D} \left[0.38438376 \frac{\tau^{-1}}{f} + 0.63570895 \left(\frac{1}{f} - 1 \right) \left(\frac{\tau^3}{6} + \frac{\tau^9}{135} + \frac{\tau^{15}}{600} + \frac{\tau^{21}}{1617} \right) \right] & 0 < \tau \leq 1, \\ -\frac{1}{D} \left(\frac{\tau^{-7}}{21} + \frac{\tau^{-21}}{630} + \frac{\tau^{-35}}{2975} + \frac{\tau^{-49}}{8232} \right) & \tau > 1, \end{cases} \quad (2.74)$$

$$D = 0.33471979 + 0.49649686 \left(\frac{1}{p} - 1 \right). \quad (2.75)$$

In this approach, the completely disordered magnetic state is used as the reference state. It is reported by Xiong *et al.* [171] that the magnetic entropy at 0 K reaches the maximum magnetic entropy value ($-R \ln(\beta^* + 1)$), which is inconsistent with the third law of thermodynamics. It is therefore necessary to adjust the non-magnetic entropy by $R \ln(\beta^* + 1)$ in order to accurately describe the magnetic entropy at 0 K.

The approach by Inden *et al.* [169, 173] can be modified in many ways, as some changes have been proposed in the literature [127]. Nevertheless, the general approach of the Inden model is still extensively used in the CALPHAD community to describe the thermodynamic properties of various alloys.

2.5.4 Derived Properties

Various thermodynamic properties can be derived from the sum of the calculated Helmholtz free energy $F(T, V)$, such as the temperature dependence of the equilibrium volume at a given pressure P , the thermal expansion ϵ and the coefficient α , the constant volume heat capacity C_V , the constant pressure heat capacity C_P and the Grüneisen parameter γ .

$$P = - \left(\frac{\partial F(T, V)}{\partial V} \right)_{V=V_{eq}}, \quad (2.76)$$

$$\epsilon(T) = \frac{a(T) - a(T_{ref})}{a(T_{ref})}, \quad (2.77)$$

$$\alpha(T) = \frac{1}{a(T)} \frac{\partial a(T)}{\partial T}, \quad (2.78)$$

$$C_V = -T \left(\frac{\partial^2 F(T, V)}{\partial T^2} \right)_{V,V}, \quad (2.79)$$

$$C_P = -T \left(\frac{\partial^2 F(T, V)}{\partial T^2} \right)_{V,P}. \quad (2.80)$$

The thermal expansion is calculated using the lattice constants $a(T)$ and $a(T_{ref})$, which are the lattice constants at a specific (T) and a reference temperature (T_{ref}).

Furthermore, by executing the calculation procedures of each contribution for different volumes and fitting the resulting energies by a Burch-Murnaghan equation of states[163], the energy can be minimized. Combining this with an assumed constant pressure, the Helmholtz free energy gets converted to the Gibbs free energy G . The Gibbs free energies are later used for the investigations of the phase stabilities of the compounds. This approach translates the *harmonic approximation* to the mentioned *quasi-harmonic approximation* [168]. One advantage of this calculation method is a wide validity of the results for many bulk materials below their melting points. The *quasi-harmonic approximation* delivers reasonable values for the mentioned properties and in the past Grabowski *et al.* [174] have proven the validity of this method for many fcc structured metals.

Chapter 3

Computational Details

3.1 Structural Relaxation Calculations

First-principles calculations were performed within the framework of spin-polarized density functional theory (DFT) using the Vienna *ab initio* Simulation Package (VASP, version 6.5.1) [152, 175, 176]. The projector-augmented wave method (PAW) was employed as implemented in VASP. Exchange-correlation effects were treated within the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) [147]. For structural relaxation of supercells containing 36 atoms, the Brillouin zone was sampled using a Γ -centered $10 \times 10 \times 10$ k -point mesh. For supercells with 72 atoms the k -point mesh was reduced to $6 \times 6 \times 6$. The supercells were constructed by enlarging the primitive unit cell of Fe_2P by 2×2 (36 atoms) or by $2 \times 2 \times 2$ (72 atoms) and a step-wise substitution of Fe and P atoms with Co and Si. For each substitution, all possible Wyckoff positions were considered and the atom positions and volumes were optimized self-consistently in the calculations. The energetically most favorable substitution site was chosen for each following substitution. The cutoff energy for the plane-wave basis was taken as 500 eV, and the width of the smearing parameter (Methfessel-Paxton broadening) was set to 0.01 eV. The convergence criteria within the self-consistent field scheme were set to be 10^{-5} eV for all considered alloys. All of these input parameters provided an energy convergence with an error equal to or smaller than 1 meV/atom.

3.2 Screening Calculations

To identify suitable substitution elements that enhance the magnetic properties of Fe_2P without compromising structural stability, systematic screening calculations were performed. In these element screening computations the primitive hexagonal unit cell of Fe_2P , consisting of six Fe atoms and three P atoms, was considered. The Fe atoms were equally distributed in two sublattices, namely $3f$ and $3g$. The P atoms were distributed in a ratio of 2:1 into the $2c$ and $1b$ position. A schematic picture of the hexagonal unit cell is presented in Fig 3.1.

In the case of Fe substitution, one Fe atom was replaced by one of the substitute

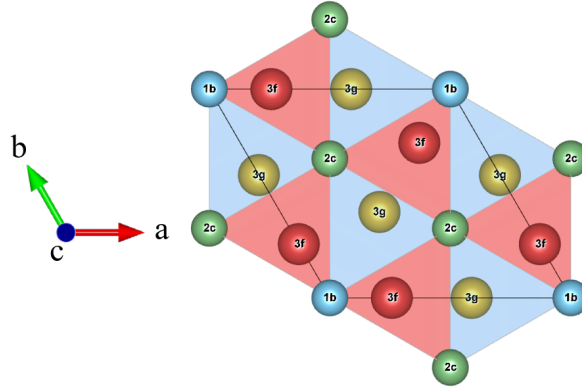


Figure 3.1: Schematic representation of the hexagonal crystal structure of Fe_2P along the crystallographic c -direction. The $3f$ (red) and $3g$ (yellow) Wyckoff sites are occupied by Fe atoms, while the $2c$ (green) and $1b$ (blue) positions are filled by P atoms.

elements and each position in both sublattices ($3f$ and $3g$) were evaluated separately and the configuration with the lowest total DFT energy was selected. These substitution levels were chosen as a compromise between sufficient chemical perturbation and computational feasibility, while remaining within experimentally relevant concentration ranges. For P, the substitution with other elements was investigated in the $2c$ and $1b$ sublattices, following the same procedure as with Fe, considering all atom positions in each sublattice.

3.3 Magnetocrystalline Anisotropy (MAE)

Magnetocrystalline anisotropy calculations were performed using the generalized gradient approximation (GGA) and the local spin density approximation (LSDA), as it is well established that LSDA can yield improved magnetocrystalline anisotropy values for systems dominated by $3d$ electrons due to favorable error cancellation [150, 148, 149]. The optimized geometries from collinear self-consistent GGA calculations were used as input for non-collinear calculations to account for the changes in cell volumes and c/a ratios. This approach ensures consistent structural parameters while avoiding artificial MAE contributions arising from geometry relaxations with spin-orbit coupling. Both, the volume and the c/a ratio have a significant influence on MAE and Curie temperature, as they influence the distances between the atoms. In the non-collinear calculations, the spin-orbit coupling was taken into consideration. Due to the small energy scale of the MAE (typically $\mu\text{eV} - \text{meV}$), significantly stricter k -point sampling and energy convergence criteria were applied. The k -point mesh density was increased to $12 \times 12 \times 12$ for supercells with 36 atoms and $8 \times 8 \times 8$ for supercells consisting of 72 atoms. The convergence criteria was set to 10^{-7} eV. The energy was calculated for the change from

the easiest to the hardest direction to magnetize. To determine the change from the easy to the hard magnetization direction, the crystallographic directions [100], [010] and [001] were calculated and compared. For hexagonally structured compounds, this translates to [001] as the easy and [100] as the hardest direction for magnetization. For the BCO and primitive orthorhombic structures a directional change from [010] to [100] was additionally investigated. The magnetocrystalline anisotropy energy was obtained from total-energy differences between different magnetization directions according to Eq. 1.5.

3.4 Electronic, vibrational and magnetic contributions to Helmholtz Free Energy

All finite-temperature calculations were performed for the Helmholtz free energy, which was subsequently converted to Gibbs free energy for phase-stability analysis. The calculation of phase stabilities requires the thermodynamic contributions of the electronic, magnetic and vibrational energies. The overall workflow of the finite temperature free energy calculation is summarized in Fig. 3.2.

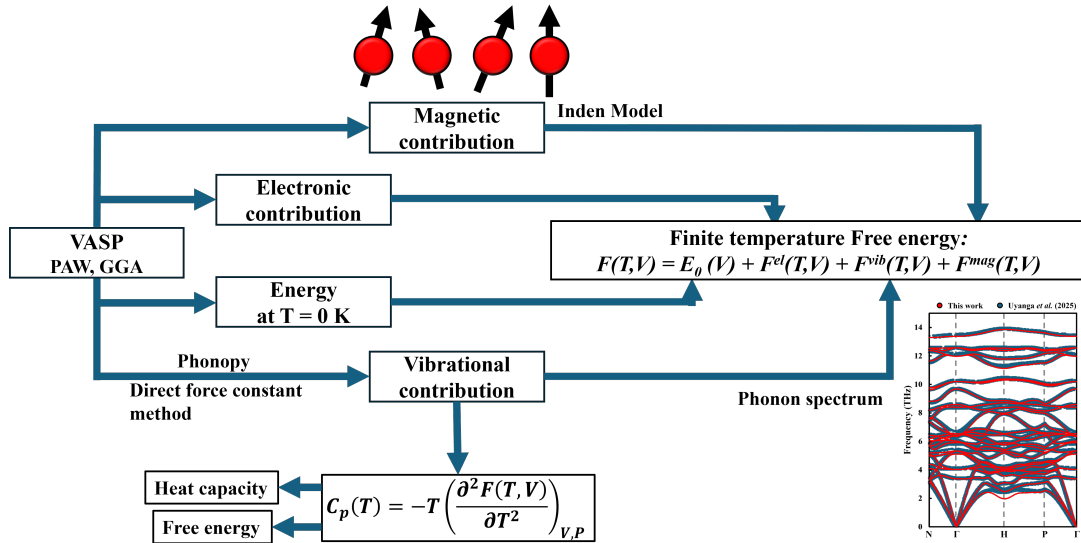


Figure 3.2: Schematic representation of the required steps for the calculation of finite temperature free energy values. The literature data for the phonon spectra used for comparison is from Uyanga *et al.* [177].

The electronic contribution was calculated via the finite temperature DFT scheme as proposed by Mermin *et al.* [157] with a dense k -point mesh of $10 \times 10 \times 10$ for supercells containing 32 atoms, resulting in a k -point density of $32 \cdot 10^3$ kp-atoms. The cutoff-energy was chosen as 500 eV and the convergence criteria to terminate the electronic loop was set to 10^{-7} eV to provide a convergence of ≤ 1 meV/atom. For these calculations it is

important to use Fermi-Dirac broadening (ISMEAR = -1), to have the SIGMA value correspond to the electronic temperature of the system. The SIGMA value was used in the range from 0.01 to 0.15. The resulting energy differences were then evaluated using the CALPHAD scheme by fitting a polynomial function to the results, to achieve the electronic energy [126, 127].

The vibrational energy contribution was calculated by considering the direct force constant method, which employs small displacements of 0.02 Å to calculate the Hellmann-Feynman forces [165, 166]. The number of displacements for this method is connected to the symmetry of the crystal structure, namely the translational and rotational symmetry, and the occupation of the sublattices. The displaced input geometries have been generated using the phonopy package [178, 179] and the forces have been calculated using VASP. The Methfessel-Paxton broadening scheme was utilized with a broadening parameter set to 0.1 eV. The k -point density was set to $6 \times 6 \times 6$ for supercells with 72 atoms. In combination with a convergence criteria of 10^{-7} eV this led to a reasonable accuracy of the forces with a convergence of ~ 1 meV/atom.

For the calculation of the magnetic free energy, the Inden model as proposed by Xiong *et al.* [171] was utilized. The required sublattice magnetic moments were calculated using VASP and used as an input parameter for the model. The Curie temperatures T_C were taken from theoretical calculations using the AkaiKKR code. The structural parameter f was determined according to the proposed value for each crystal structure. If no value was proposed, the structural parameter was set to $f = 0.3$ to provide a reasonable structural factor.

3.5 AkaiKKR Exchange Interaction Energies J_{ij} and Curie Temperature T_C

In order to estimate the Curie temperature T_C , the exchange interaction energies J_{ij} for the converged ferromagnetic (FM) states of the hexagonal structure have been calculated via the Liechtenstein method [180]. In the Liechtenstein formalism, exchange parameters are derived from infinitesimal rotations of magnetic moments around the collinear ground state using the magnetic force theorem. In this method an effective spin Heisenberg model is used and solved in a mean-field approximation (MFA). In this Heisenberg model, the Hamiltonian for the spin-spin interaction is written as $\mathcal{H} = -\sum_{i \neq j} J_{ij} \vec{S}_i \vec{S}_j$, with $\vec{S}_i$ and $\vec{S}_j$ as the spin of the i and j site and J_{ij} as the exchange coupling constant between both sites. In the magnetic force theorem approach the exchange energies are determined by calculations of total energy variations for small deviations of some magnetic moments from the ground state magnetic configuration. The magnetic coupling constants were calculated

using density functional theory, following the Korringa-Kohn-Rostoker (KKR) [181, 129] Greens's function method, implemented in the AkaiKKR [182] code - also known as MACHIKANNEYAMA. Within the atomic sphere approximation (ASA) and the coherent potential approximation (CPA), local lattice distortions and short-range order effects are neglected, which represents an inherent approximation of the method [183, 184]. The atomic sphere radii were based on the Wigner-Seitz radii of each atom. Continuous concentration changes for both the Fe and P sublattices are considered based on KKR-CPA. All KKR calculations are based on the local density approximation (LDA) [140, 130], taking the exchange-correlation function as parametrized by Moruzzi, Janak und Williams (MJW) [185]. In this work, the scattering is considered up to d -scattering ($l_{max} = 2$) in the systems. For the Brillouin zone quality 448 k-points in the irreducible Brillouin zone were chosen together with an edelt (an imaginary energy attached to the Fermi energy) value of 0.001 Ry to achieve a convergence of the Curie temperatures up to a variation of only 5 K. As an input structure for each KKR calculation, the theoretically relaxed (VASP, GGA-PBE) values are considered.

Chapter 4

Results

4.1 Substitution-free Fe₂P

4.1.1 Hexagonal Fe₂P - ($P\bar{6}2m$)

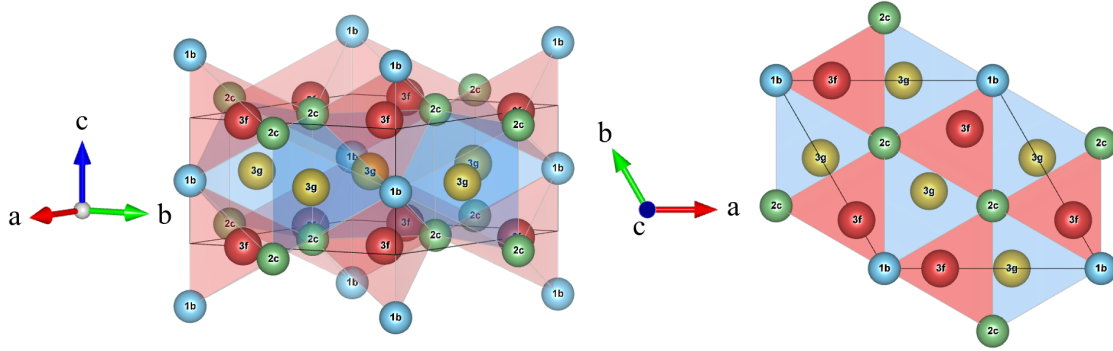


Figure 4.1: Hexagonal primitive unit cell with three functional units in the unit cell boundaries. The different Wyckoff positions ($3f$ - red, $3g$ - yellow, $1b$ - blue and $2c$ - green) are shown for each atom and the tetrahedral and square based pyramidal environments are marked with red and blue filling. The tetrahedral environment surrounds the $3f$ Fe atoms and the square based pyramidal environment is visible around the $3g$ Fe atoms.

The magnetic material Fe₂P features a stable hexagonal crystal structure ($P\bar{6}2m$) with two distinct Wyckoff positions for each the Fe and P atoms. The primitive unit cell consists of six Fe atoms, that are distributed equally between the weakly magnetic $3f$ ($0.83 \mu_B/\text{functional unit (f.u.)}$) and the stronger magnetic $3g$ ($2.24 \mu_B/\text{f.u.}$) site. The three P atoms are separated in the $2c$ and $1b$ positions with a ratio of 2:1. The Fe atoms in the $3f$ position located in a tetrahedral environment, that is formed by two metalloids in the $2c$ and two metalloids in the $1b$ positions. The Fe atoms in the $3g$ site are surrounded by four metalloids in the $2c$ sites and one metalloid in the $1b$ position, creating a square based pyramid. Both, the $3f$ and $3g$ positions, are occurring in alternating layers in the c direction of the crystal. The hexagonal crystal structure and the developed tetrahedral and square based pyramidal environments are visualized in Fig. 4.1.

The calculated physical properties, such as the lattice constants a and c , volume and bulk modulus, are shown in Tab. 4.1. It is visible, that the lattice constants a ($5.808 \text{ \AA}$)

4.1. Substitution-free Fe₂P

Table 4.1: Physical and magnetic properties of the hexagonally structured (P $\bar{6}2m$) Fe₂P compound. The physical properties include the lattice constants a and c , the unit cell volume and the bulk modulus B . The magnetic properties are described by the properties of the magnetic moment (Total, $3f$ and $3g$ specific) per functional unit, the magnetization saturation $\mu_0 M_S$ in T, the maximum energy product $|BH|_{max}$, the Curie temperature T_C , the anisotropy constant K_1 (GGA and LSDA) and the theoretical hardness factor κ .

Compound	Lattice constant (Å)		Volume (Å ³)	Mag. Moment (μ_B /f.u.)			$\mu_0 M_S$ (T)	$ BH _{max}$ (kJ/m ³)	T_C (K)	K_1 (MJ/m ³)	B (GPa)	κ
	a	c		Total	$3f$	$3g$						
Fe ₂ P (P $\bar{6}2m$)												
This work	5.808	3.425	100.09	3.01	0.83	2.24	1.06	222	340	3.26 ¹ (1.33) ²	214	1.92
Theory	5.809 ³	3.425 ³	100.07 ³	3.01 ³	0.83 ³	2.23 ³	1.04 ³			3.0 ³	219 ⁴	
Experiment	5.872 ⁴	3.460 ⁴		2.87 ⁴	0.63 ⁴	2.12 ⁴	1.03 ⁶		216	2.68 ^{6,7} 2.32 ^{5,8}	223 ⁹	

¹ Calculated with GGA exchange functional. ² Calculated with LSDA exchange functional. ³ Data from Khongorzul *et al.* [186]. ⁴ Data from Tobola *et al.* [187]. ⁵ Data from Fujii *et al.* [107]. ⁶ Data from He *et al.* [42]. ⁷ Data from Measured at 2.0 K. ⁸ Measured at 4.2 K. ⁹ Data from Dera *et al.* [188], Combined data from Jain *et al.* [190], Horton *et al.* [191] and de Jong *et al.* [189] in the Materials Project [189, 190, 191].

and c (3.425 Å) and the volume V (100.1 Å³) are almost identical with other theoretical literature from Khongorzul *et al.* [186] and show a good agreement with experimental data by Tobola *et al.* [187]. The calculated bulk modulus B (214 GPa) of the Fe₂P compound shows a similar trend of a slight underestimation compared to the experimental value (223 GPa) by Dera *et al.* [188] and corroborates with the theoretical data from de Jong *et al.* [189]. It was calculated using the Birch-Murnaghan equation of states.

The Fe₂P material has been identified as a promising candidate for use as a gap magnet, as it combines a relatively high magnetization and uniaxial anisotropy with the absence of rare-earth elements, positioning it between ferrite and Nd-Fe-B magnets. It features a high total magnetic moment of 3.01 μ_B /f.u. and a high theoretical polarization magnetization of 1.06 T. This compares well to an experimental value of 1.03 T [188]. The computed maximum energy product $|BH|_{max}$ is estimated as 222 kJ/m³, which is one of the highest values reported for rare-earth free magnetic materials [42]. Another auspicious property of the Fe₂P material is a high uniaxial magnetocrystalline anisotropy due to its hexagonal crystal structure. For the GGA functional the first order anisotropy constant K_1 is calculated as 3.26 MJ/m³ and the anisotropy field H_a as 6.17 T. However, as the GGA functional occasionally yields underestimating values [148, 149, 150], the LSDA functional is also considered for the hexagonally structured compounds, providing a benchmark for the compounds of interest. Using the LSDA functional, K_1 is estimated as 1.33 MJ/m³ and the anisotropy field as 2.52 T. Comparing these results to experimental data by Fujii *et al.* [107] and He *et al.* [42], it is clear that the MAE results are clearly underestimated when LSDA is employed. Although LSDA can yield improved MAE

values for certain $3d$ systems, for hexagonal Fe₂P the GGA results show closer agreement with the available experimental data for K_1 of 2.68 and 2.32 MJ/m³ and an anisotropy field H_a of 6.5 T.

Note, that the GGA functional does not always yield more reliable magnetocrystalline anisotropy result. Depending on the material, it was shown in literature that the LSDA functional sometimes describes the MAE better than GGA [192, 193]. The underlying reasons for the often better performance are a beneficial cancellation of errors for $3d$ elements in LSDA, a lower orbital magnetic moment in GGA that translates to smaller MAE values, a stronger delocalization of the electronic structure and emerging noise and instabilities connected to the incorporation of the gradient terms in GGA [148, 149, 150].

The theoretical Curie temperature of this study is estimated to be 340 K, which is a clear overestimation to the experimental value of 214 K [29, 28, 107, 27]. However, this higher value is to be expected as the T_C is calculated using a mean-field approximation, which is prone to an overestimation of up to 40 - 50 %. Additionally, the main point of the calculated T_C s is to reproduce and show the occurring trends of the T_C s with the substitution of elements in the material. The overall magnetic hardness factor (see Eq. 1.8) of 1.92 indicates that Fe₂P fulfills key intrinsic criteria of a permanent magnet, although its low Curie temperature limits practical applicability. Therefore, the Curie temperature of 214 K, which is not addressed at all in the calculation of the hardness factor, needs to be enhanced.

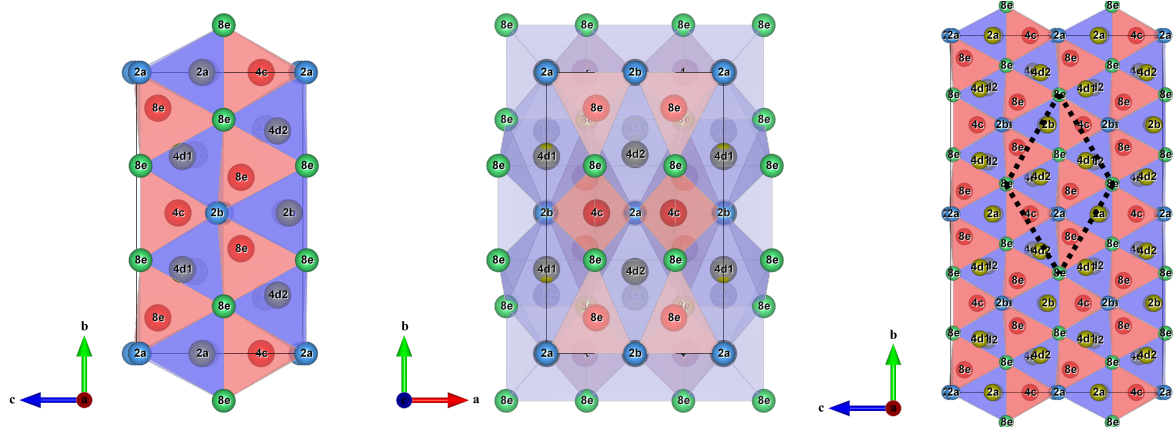
4.1.2 Body-centered-orthorhombic Fe_2P - ($Imm2$)

Figure 4.2: Body-centered-orthorhombic conventional unit cell ($Imm2$) with 12 functional units in the cell boundaries. The unit cell is shown along the a (**left**) and c (**middle**) crystallographic directions. The different Wyckoff positions (Fe: $8e$, $4c$ - blue, $4d_1$, $4d_2$, $2b$, $2a$ - red, P: $8e$ - green and $2b$, $2a$ - yellow) are shown for each atom. The tetrahedral ($8e$ and $4c$ Fe atoms) and square based pyramidal environments ($4d_1$, $4d_2$, $2b$ and $2a$ Fe atoms) are marked with red and blue filling, respectively. **Right:** Enlarged BCO crystal structure with the respective unit cell boundary for the hexagonal crystal structure to emphasize the only small distortion from it.

Although the body-centered-orthorhombic (BCO) crystal symmetry ($Imm2$) of Fe_2P is not stable at ambient conditions, it plays a key role as a competing phase during Si substitution and must therefore be considered to understand phase transitions and stability limits. During Si for P substitution, the BCO structure appears as a secondary phase ~ 0.20 - 0.25 Si per f.u. The crystal symmetry of the BCO phase is depicted in Fig. 4.2.

In the BCO structure, the Fe atoms are distributed across six Wyckoff positions, while the P atoms are positioned in three different Wyckoff sites. The primitive unit cell consists of 12 Fe and 6 P atoms, thus corresponding to two hexagonal primitive cells. The Fe sites can be denoted as $8e$, $4c$, $4d_1$, $4d_2$, $2b$ and $2a$, while the P sites are named as $8e$, $2b$ and $2a$. Additionally, the body-centered-orthorhombic unit cell is closely related to the hexagonal crystal structure, and is achieved by slight deformations of the hexagonal cell. This connection is also depicted in Fig. 4.2 (right). The Wyckoff positions of the hexagonal cell therefore translate to the BCO positions as described in Tab. 4.2 and create similar tetrahedral ($8e$, $4c$) and square-based pyramidal ($4d_1$, $4d_2$, $2b$, $2a$) environments around the Fe atoms in the unit cell.

The calculated lattice parameters, the bulk modulus the magnetic properties of the substitution-free BCO Fe_2P compound, including the total magnetic moment per f.u., $\mu_0 M_S$, $|BH|_{max}$, T_C and MAE, are described in Tab. 4.3.

4.1. Substitution-free Fe₂P

Table 4.2: Corresponding Wyckoff positions in the hexagonal and BCO crystal structures.

Hex. ($P\bar{6}2m$)	BCO ($Imm2$)
$3f$	$8e, 4c$
$3g$	$4d_1, 4d_2, 2b, 2a$
$2c$	$8e$
$1b$	$2a, 2b$

Table 4.3: Physical and magnetic properties of the BCO structured ($Imm2$) Fe₂P compound. The physical properties include the lattice parameters a , b and c , the unit cell volume and the bulk modulus B . The magnetic properties are described by the properties of the total magnetic moment per functional unit, the magnetization saturation $\mu_0 M_S$ in T, the maximum energy product $|BH|_{max}$, the theoretical Curie temperature T_C (calculated in MFA), the anisotropy constant K_1 and the theoretical hardness factor κ .

Compound	Lattice constant (Å)			Volume (Å ³)	Total Mag. Moment (μ_B /f.u.)	$\mu_0 M_S$ (T)	$ BH _{max}$ (kJ/m ³)	T_C (K)	K_1 (MJ/m ³)	B (GPa)	κ
Fe ₂ P ($Imm2$)	a	b	c								
This work	6.487	10.111	6.062	397.60	3.07	1.08	231	690	0.596	209	0.80

In the BCO structure, the lattice parameters differ significantly from those of the hexagonal structure. The angles α , β and γ are all 90°, and the constants a (6.487 Å), b (10.111 Å) and c (6.062 Å) are all different, with b surpassing the other two at 10.111 Å. This results in a rectangular prism with a rectangular base forming the unit cell (see Fig. 4.2) with a volume of 397.6 Å³. The bulk modulus is calculated as 209 GPa, which is slightly lower than the value of 214 GPa for the hexagonal symmetry. The magnetic moment per f.u. is slightly higher than that of the hexagonal structure, with a value of 3.06 μ_B /f.u. Based on these results the important values of the saturation magnetization $\mu_0 M_S$ and the $|BH|_{max}$ can be calculated as 1.08 T and 231 kJ/m³.

However, formation and competition energy calculations show that the BCO structure is 0.9 meV/f.u. less stable than the hexagonal structure at 0 K. This energy difference is very small and in the typical accuracy of DFT. However, finite temperature contributions significantly favor the hexagonal phase making it the dominant phase. Consequently, there is no available experimental data concerning the T_C and MAE of the substitution-free BCO Fe₂P compound. The theoretical calculations of this work revealed another possible drawback of the BCO crystal symmetry, with a notably lower MAE of only 0.596 MJ/m³. Furthermore, the T_C calculations estimate a value of 690 K, which is an enormous overestimation compared to the theoretical T_C of the hexagonal crystal of 340 K. This value is nevertheless considered for the estimation of trends in the T_C s occurring by substitution of P with Si later in this work. The overall hardness factor for BCO Fe₂P

can be calculated from these properties as 0.80. The low value can be attributed to the low MAE of the BCO compound.

4.1.3 Primitive Orthorhombic Fe₂P - (*Pnma*)

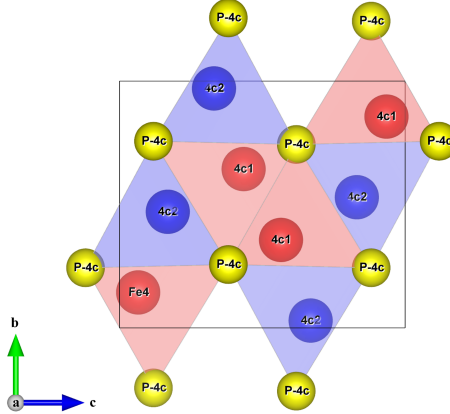


Figure 4.3: Representation of the primitive orthorhombic unit cell (*Pnma*) with 4 functional units in the unit cell boundaries. The different Wyckoff positions (Fe: $4c_1$ - red, $4c_2$ - blue, P: $4c$ - yellow) are shown for each atom. The tetrahedral ($4c_1$ Fe atoms) and square based pyramidal environments ($4c_2$ Fe atoms) are marked with red and blue filling, respectively.

The recently synthesized primitive orthorhombic (*Pnma*) phase of Fe₂P provides an important low-temperature structural variant that enables assessment of competing stability and magnetic behavior beyond the hexagonal phase. This symmetry was first observed in meteorites, but was successfully synthesized for the first time in 2024 by Kong *et al.* [194]. This crystal structure consists of 8 Fe atoms and 4 P atoms. The Fe atoms are evenly distributed in two $4c$ Wyckoff positions, while the P atoms are in one separate $4c$ Wyckoff site. Similar to the hexagonal structure, the Fe atoms in one $4c$ position are in a tetrahedral environment (red), build by the surrounding 4 metalloid atoms. The Fe atoms in the second $4c$ lattice are enclosed by a square based pyramidal environment (blue) formed by five metalloid atoms. This indicates, that the primitive orthorhombic symmetry can be interpreted as a distorted derivative of the hexagonal structure. For a better distinction between both Fe crystal sites, the Fe atom in the tetrahedral environment is labeled as $4c_1$ and the Fe atom surrounded by the square-based pyramid as $4c_2$. The resulting unit cell for the primitive orthorhombic *Pnma* compound can be seen in Fig. 4.3. The calculated structural and magnetic properties for the primitive orthorhombic crystal have been summarized in Tab. 4.4, and are compared to available experimental data.

Table 4.4: Physical and magnetic properties of the primitive orthorhombic structured (*Pnma*) Fe₂P compound. The physical properties include the lattice parameters a , b and c , the unit cell volume and the bulk modulus B . The magnetic properties are described by the properties of the total magnetic moment per functional unit, the magnetization saturation $\mu_0 M_S$ in T, the maximum energy product $|BH|_{max}$, the Curie temperature T_C , the anisotropy constant K_1 and the theoretical hardness factor κ .

Compound	Lattice constant (Å)			Volume (Å ³)	Mag. Moment (μ_B /f.u.) Total	$\mu_0 M_S$ (T)	$ BH _{max}$ (kJ/m ³)	T_C (K)	K_1 (MJ/m ³)	B (GPa)	κ
Fe ₂ P (<i>Pnma</i>)	a	b	c								
This work	3.571	5.606	6.512	130.3	1.73	0.62	76	308	1.352	171	2.11
Experiment	3.573 ¹	5.781 ¹	6.649 ¹	137.31 ¹	1.46 ¹			248 ¹			

¹ Data from Kong *et al.* [194] measured at 2 K.

As can be seen, the calculated lattice constants a , b and c of this study are in relatively good agreement with the experimental values. While the constant a seems to be almost identical, the theoretical constants b (5.606 Å) and c (6.512 Å) are slightly smaller than the experimental values of 5.781 and 6.649 Å, respectively. This slight underestimation of the lattice constants is consequently also visible in the volume which is ~ 7 Å³ smaller than the value obtained from experiment. The structural parameter of the bulk modulus accounts to a significantly lower value of 171 GPa, compared to the hexagonal (214 GPa) and BCO (209 GPa) structures. The lower bulk modulus reflects the reduced packing efficiency and symmetry of the *Pnma* structure. The theoretical total magnetic moment of the compound is slightly overestimated at 1.73 μ_B /f.u. against an experimental value of 1.46 μ_B /f.u. However, this overestimation of DFT was also observed in calculations by Kong *et al.* [194] with a theoretical result of 1.84 μ_B /f.u.

Based on the magnetic moments estimated in this study, the saturation magnetization and $|BH|_{max}$ yield values of 0.62 T and 76 kJ/m³. These values are much lower than those of the hexagonal compound, which has a magnetic moment of 3.01 μ_B /f.u., a $\mu_0 M_S$ of 1.06 T and a $|BH|_{max}$ of 222 kJ/m³. However, the primitive orthorhombic crystal has a small advantage over the other two crystals, as it exhibits a slightly improved Curie temperature of 248 K. In the mean-field approximation the Curie temperature is calculated as 308 K, which falls within the expected range of the known overestimation. Lastly, the MAE of the primitive orthorhombic structure is determined as 1.35 MJ/m³ and therefore between the hexagonal and BCO compounds. These properties accumulate in an overall hardness factor of 2.11, mostly due to the MAE. However, the much lower magnetic moment renders the compound considerably less attractive than the hexagonal structure. Calculations at 0 K for the formation energy revealed that the primitive orthorhombic structure is favored at low temperatures by ~ 30 meV/f.u., matching with an experimental value of 20.8 meV/f.u. At higher temperatures, the hexagonal phase is considered as the preferred phase, consistent with the observations from Kong *et al.* [194] and the

observed stability of the hexagonal phase up to Co concentrations ~ 0.3 Co per f.u. [106]. Nevertheless, the primitive orthorhombic structure will be considered in this work for the ternary $\text{Fe}_{2-y}\text{Co}_y\text{P}$ compounds, as these compounds transition to this symmetry when Fe is substituted with Co.

4.2 Screening of Elements for Substitution

Several metalloids (non-metals) and metals have been suggested in the literature for tuning the magnetic properties of the hexagonal Fe_2P compound by substitution of Fe or P. Especially the low T_C can easily be enhanced by these substitutions [106, 43, 110, 111, 112, 121, 119, 120, 122, 114, 123].

In this first part, the *p*-block elements B, C, N, Al, Si, Ga, Ge and As were screened as substitutes for P. In these calculations, one P atom in either the *2c* and *1b* site of the primitive hexagonal unit cell (6 Fe, 3 P atoms) was replaced by one atom of the substitute elements. This equates to a 33 % substitution of P, resulting in compositions of $\text{Fe}_2\text{P}_{0.67}\text{A}_{0.33}$, where A represents the aforementioned substitute elements. These substitution levels were chosen to introduce a pronounced chemical perturbation while remaining within experimentally relevant concentration regimes.

In the second part, possible *3d*-metal substitutes ranging from Sc to Cu for Fe substitution were examined. Fe substitution was additionally considered to P substitution as it also known to significantly influence the magnetic properties of Fe_2P [103, 108, 109, 104, 106, 43, 110, 111, 112, 113, 114]. The substitution of these elements with one Fe atom in either the *3f* or *3g* position amounts to a concentration of ~ 0.16 of the respective element M. This concentration was again chosen to achieve a distinct chemical influence, while staying within a reasonable concentration range. This results in compositions of $\text{Fe}_{1.84}\text{M}_{0.16}\text{P}$.

For a systematic understanding, the calculated structural parameters, such as the lattice constants and volume, for all considered substitute elements are listed in Tab. 4.5. A generally good agreement with experimental data was achieved.

For all of these compounds, the formation energy E_{Form} , the magnetic moments and the Curie temperature were calculated and compared to substitution-free Fe_2P to determine the influence of the elements.

The results of the screening calculations are presented in Fig. 4.4. As illustrated in the upper image, the formation energy of all considered *p*-block elements is observed to increase compared to substitution-free Fe_2P . This indicates that all elements yield a decrease of the stability. The lowest increase of E_{Form} is attributable to Si in the *2c* position, with a difference of 0.14 eV/f.u. It is noteworthy, that the substitution into the

4.2. Screening of Elements for Substitution

Table 4.5: Calculated lattice parameters of the considered non-magnetic (NM), antiferromagnetic (AFM) and ferromagnetic (FM) substitute elements for P (left side) and for Fe (right side) substitution. The calculated data is compared with available experimental data.

P Substitute	Lattice Constant (Å)			Volume (Å ³)	Fe Substitute	Lattice Constant (Å)			Volume (Å ³)
	<i>a</i>	<i>b</i>	<i>c</i>			<i>a</i>	<i>b</i>	<i>c</i>	
trigonal NM B	4.898 (4.908) ¹	4.898 (4.908) ¹	12.524 (12.567) ¹	260.25 (262.16) ¹	hexagonal NM Sc	3.295 (3.309) ²	3.295 (3.309) ²	5.157 (5.273) ²	48.49 () ²
trigonal NM C	2.467 (2.47) ³	2.467 (2.47) ³	7.803 (6.79) ³	41.14 (35.9) ³	hexagonal NM Ti	2.924 (2.906) ⁴	2.924 (2.906) ⁴	4.623 (4.667) ⁴	34.24 (34.14) ⁴
simple cubic NM N	5.815 (5.649) ⁵	5.815 (5.649) ⁵	5.815 (5.649) ⁵	196.64 (180.27) ⁵	bcc NM V	2.978 (3.027) ⁶	2.978 (3.027) ⁶	2.978 (3.027) ⁶	26.42 (27.74) ⁶
fcc NM Al	4.039 (4.037) ⁷	4.039 (4.037) ⁷	4.039 (4.037) ⁷	65.89 (65.79) ⁷	bcc NM Cr	2.839 (2.884) ⁸	2.839 (2.884) ⁸	2.839 (2.884) ⁸	22.87 (24.0) ⁸
fcc NM Si	5.468 (5.381) ⁹	5.468 (5.381) ⁹	5.468 (5.381) ⁹	163.5 (155.81) ⁹	bcc AFM Mn	8.540 (8.913) ¹⁰	8.540 (8.913) ¹⁰	8.540 (8.913) ¹⁰	622.84 (707.94) ¹⁰
NM base-centered orthorhombic Ga	4.432 (4.523) ¹¹	7.598 (7.661) ¹¹	4.556 (4.524) ¹¹	153.40 (156.76) ¹¹	fcc FM Co	3.517 (3.42) ¹²	3.517 (3.42) ¹²	3.517 (3.42) ¹²	43.50 (40.02) ¹²
fcc NM Ge	5.675 (5.658) ¹³	5.675 (5.658) ¹³	5.675 (5.658) ¹³	182.75 (181.09) ¹³	fcc FM Ni	3.518 (3.45) ¹²	3.518 (3.45) ¹²	3.518 (3.45) ¹²	43.54 (41.06) ¹²
NM base-centered orthorhombic As	3.755 (3.760) ¹⁴	3.755 (3.760) ¹⁴	11.113 (10.548) ¹⁴	135.69 (129.13) ¹⁴	fcc NM Cu	3.777 (3.615) ⁸	3.777 (3.615) ⁸	3.777 (3.615) ⁸	53.88 (47.2) ⁸

¹ Data by Decker *et al.* [195]

³ Data by Hassel *et al.* [197]

⁵ Data by Schuch *et al.* [199]

⁷ Data by Fortes *et al.* [201]

⁹ Data by Kitano *et al.* [203]

¹¹ Data by Sharma *et al.* [205]

¹³ Data by Cooper *et al.* [207]

² Data by Spedding *et al.* [196]

⁴ Data by Novoselova *et al.* [198]

⁶ Data by Colligan *et al.* [200]

⁸ Data by Swanson *et al.* [202]

¹⁰ Data by Gazzara *et al.* [204]

¹² Data by Häglund *et al.* [206]

¹⁴ Data by Schiferl *et al.* [208]

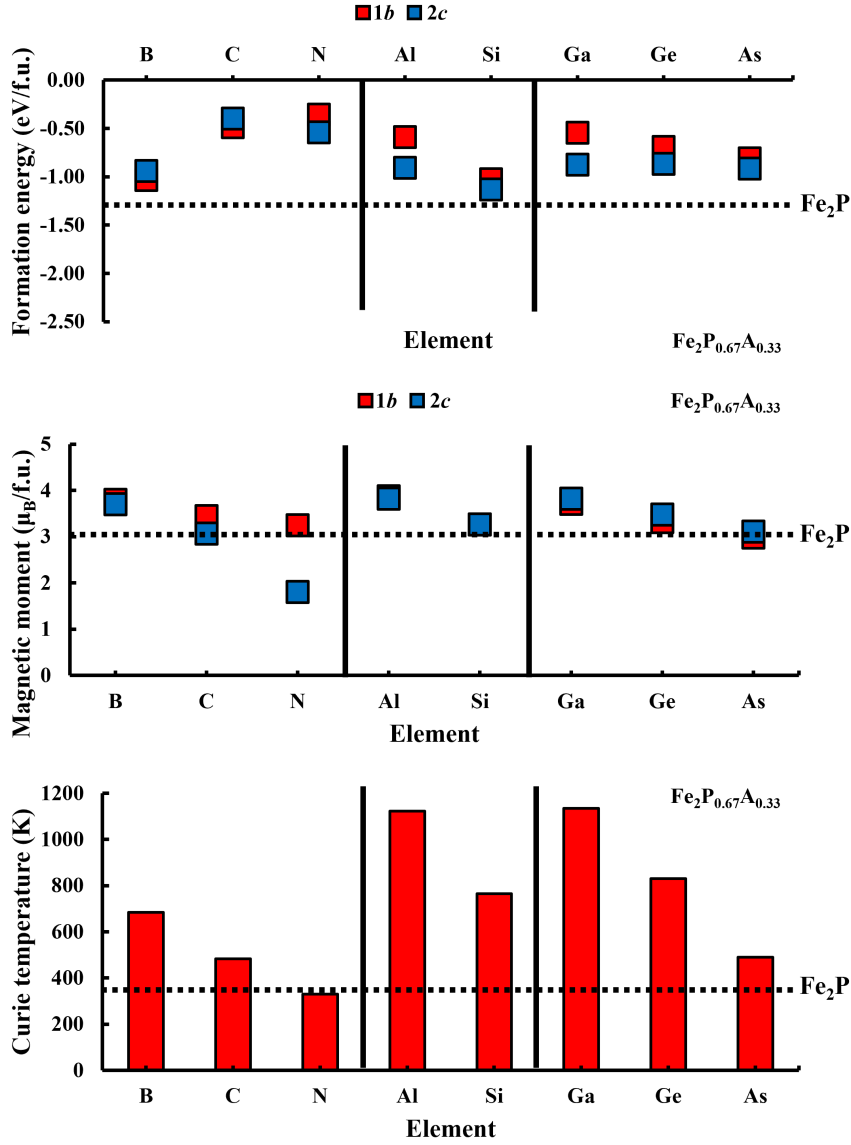


Figure 4.4: Calculated formation energy (eV/f.u.) (**upper image**), magnetic moments (μ_B /f.u.) (**mid image**) and Curie temperature (K) (**lower image**) for the screened metalloids for P substitution in $\text{Fe}_2\text{P}_{0.67}\text{A}_{0.33}$. A describes the metalloid exchanged with P. The calculated values of the substitution-free Fe_2P compound of this work are given as a dashed line for each property. The vertical black lines denote the change to a higher period in the elemental table.

1b site appears to be favored by B and C, while all other elements are calculated to prefer the 2c position. The formation energy has been calculated using the following equation:

$$E_{Form} = \frac{(E(Fe_{2-y}M_yP_{1-x}A_x) - (2-y) \cdot E(Fe) - y \cdot E(M) - (1-x) \cdot E(P) - x \cdot E(Si))}{N}, \quad (4.1)$$

with M as the theoretical 0 K energy of the substitute metal for Fe and A as the 0 K energy of the substitute metalloid for P. For the ground-states of the metalloids A, the 0 K energies of trigonal non-magnetic B, trigonal non-magnetic C, simple cubic non-magnetic N, face-centered cubic (fcc) non-magnetic Al, fcc non-magnetic Si, orthorhombic non-magnetic Ga, fcc non-magnetic Ge and orthorhombic non-magnetic As were chosen.

Another interesting result can be seen in the influence of these substitutions on the magnetic moment (middle image) and the Curie temperature (bottom image). It can be seen that the magnetic moments decrease from B to N, from Al to Si, and from Ga to As, suggesting a dominant magnetovolume contribution associated with the atomic size. In case of the Curie temperature, this effect is even more visible. Within the same period of the periodic table, the T_C decreases. Moving to the next period, however, the T_C increases again as visible from ~ 330 K for N to above 1000 K for Al. Aluminum also has a significantly higher T_C than B, which is directly above it in the periodic table. Therefore, the size of the atoms plays a significant role in defining the magnetic moment and the Curie temperature.

Taking the formation energy, magnetic moments and Curie temperature into account, Si provides the most favorable balance between a low formation energy, enhanced magnetic moment, and increased Curie temperature. This is followed by B, As and Ge substitution. Despite the significant improvement in T_C with Al, the substantial rise in formation energy renders this substitution thermodynamically unfavorable. Therefore, Si was chosen as the most promising candidate for P substitution for this work.

For Fe substitution, all 3d elements from Sc to Cu have been investigated. The results for these elements are shown in Fig. 4.5. Although early 3d elements (Sc to Cr) improve formation energies, their severe suppression of magnetic moments and Curie temperature excludes them from permanent-magnet applications. Elements with a higher atomic number than Fe (Co to Cu) display slightly lower formation energies than substitution-free Fe_2P , with differences of -0.11 and -0.07 eV/f.u. for Co and Ni in the 3f site, respectively. Cu seems to cause a general increase of the formation energy, as both investigated substitution sites yield higher values. The most noteworthy element is Mn, which sees a significant increase of the 0 K stability by -0.57 and -0.75 eV/f.u. for 3f and 3g, respectively. This is not surprising, given that Mn substitution is already well known in

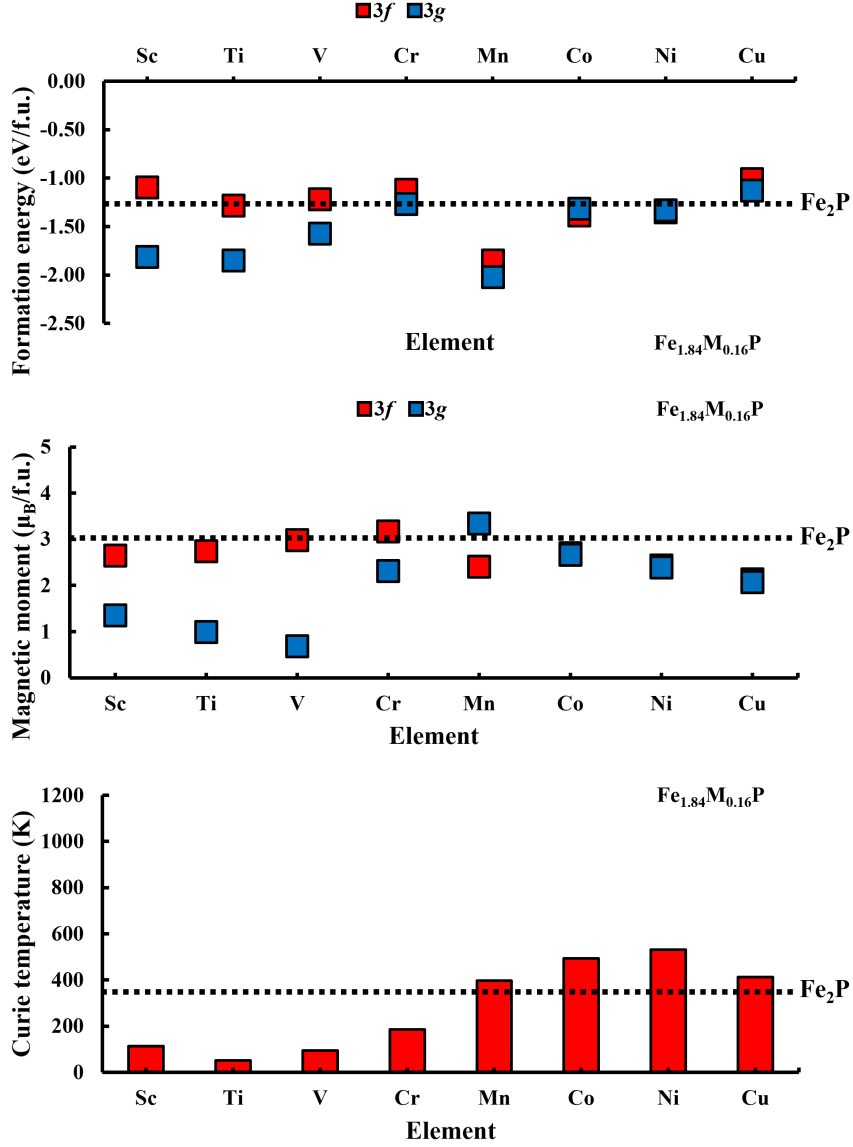


Figure 4.5: Calculated formation energy (eV/f.u.) (**upper image**), magnetic moments (μ_B /f.u.) (**mid image**) and Curie temperature (K) (**lower image**) for the screened metals for Fe substitution in $\text{Fe}_{0.84}\text{M}_{0.16}\text{P}$. M denotes the investigated metal substitutes. The calculated values of the substitution-free Fe_2P compound of this work are given as a dashed line for each property. The vertical black lines denote the change to a higher period in the elemental table.

magnetocaloric Fe_2P -based compounds [103, 108, 109, 104].

Another visible trend, is the change of the preferred substitution site. For elements with less electrons than Fe (Sc to Mn), the $3g$ position is the preferred substitution site, while elements with more electrons (Co to Ni) are preferred in the $3f$ site. This finding is consistent with previous literature describing a dependency of the preferred substitution site on the number of electrons [209]. However, although Sc to V look promising in terms of the formation energy, they all exhibit a drastic reduction of the magnetic moment at the preferred substitution site, as well as lower Curie temperatures than the substitution-free Fe_2P compound. The magnetic moment is lowered from $\sim 3 \mu_B/\text{f.u.}$ to values between 0.8 to $1.4 \mu_B/\text{f.u.}$, and the Curie temperature is estimated to be between 50 and 100 K. This excludes the elements from being suitable substitutes for Fe.

Of the remaining elements, Co demonstrates the optimal combination of formation energy, magnetic moments and Curie temperature, followed by Ni and Mn. While the magnetic moment decreases with Co to a value of $2.7 \mu_B/\text{f.u.}$, the T_C is greatly enhanced to 500 K. Additionally, E_{Form} decreases slightly, indicating a higher stability. For Ni and Mn, the magnetic moments amount to 2.4 and $3.2 \mu_B/\text{f.u.}$, and the T_C s to 520 and 400 K, respectively. Note, that the high magnetic moment caused by Mn, is already well-known in magnetocaloric $(\text{Mn,Fe})_2\text{P}$ compounds [210, 211, 118, 212, 65]. Although Mn shows promising magnetic moments and stability, the Curie temperature is less affected. Bearing this in mind, and given that the T_C is the main drawback of Fe_2P , Co is considered as a better substitution option due to its slightly lower formation energy compared to Fe, its significant influence on the T_C , and its only moderate negative effect on the magnetic moment. Based on these considerations, Co was selected as the most suitable Fe-site substitution element for further investigation.

4.3 Unary and Binary Reference Materials

Unary and binary reference materials were selected to provide consistent chemical reference states for formation and competition energy calculations, ensuring a thermodynamically meaningful stability analysis. These materials include the pure elements Fe, P, Si and Co, as well as the binary and ternary FeP , FeSi , FeCo and FeCoP compounds. Furthermore, a comparison of the computed properties of these compounds with experimental data can be used to benchmark the computational approach against available experimental data. The calculated structural and magnetic properties of the pure elements Fe (bcc), P (black P structured), Si (fcc) and Co (fcc), including the lattice parameters, volume and bulk modulus, as well as the magnetic moments, are listed in Tab. 4.6. The selection of the crystal structures of these elements was based on their thermodynamic stability

4.3. Unary and Binary Reference Materials

Table 4.6: Calculated structural (lattice parameters, volume and bulk modulus) and magnetic properties (magnetic moments) of unary elements chosen for reference materials in phase stability calculations. Literature data is given in parenthesis for comparison.

Compound	Lattice constant (Å)			Unit cell volume (Å ³)	Bulk modulus (GPa)	Mag. moment (μ_B /f.u.)
	<i>a</i>	<i>b</i>	<i>c</i>			
bcc Fe	2.838	2.838	2.838	22.86	177	2.2
	(2.868) ¹	(2.868) ¹	(2.868) ¹	(23.59) ¹	(168) ¹	(2.22) ¹
	(2.86) ²	(2.86) ²	(2.86) ²	(23.47) ²	(208) ²	(2.64) ²
black P	3.311	10.997	4.572	166.47	32	0.0
	(3.316) ³	(10.484) ³	(4.379) ³	(152.24) ³	(35) ⁴	-
	(3.30) ²	(10.93) ²	(4.54) ²	(163.66) ²	(33) ²	(0.0) ²
fcc Si	5.468	5.468	5.468	163.5	87	0.0
	(5.381) ⁵	(5.381) ⁵	(5.381) ⁵	(155.81) ⁵	(95) ⁵	-
	(5.44) ²	(5.44) ²	(5.44) ²	(161.32) ²	(89) ²	(0.0) ²
fcc Co	3.517	3.517	3.517	43.50	206	1.66
	(3.42) ⁶	(3.42) ⁶	(3.42) ⁶	(40.02) ⁶	(182) ⁷	(1.75) ⁸
	(3.51) ²	(3.51) ²	(3.51) ²	(43.37) ²	(201) ²	(1.84) ²

¹ Data by Kittel *et al.* [6].

² Combined data from Jain *et al.* [190], Horton *et al.* [191] and de Jong *et al.* [189] in the Materials Project.

³ Data by Lange *et al.* [214].

⁴ Data from Clark *et al.* [215].

⁵ Data by Kitano *et al.* [203].

⁶ Data by Haglund *et al.* [206].

⁷ Data from Gump *et al.* [216].

⁸ Data from Mohapatra *et al.* [59].

at ambient temperature. Especially P had to be chosen carefully due to the existence of many different allotropes [213].

A general comparison of the theoretical data with the experiment shows a good agreement, considering the known limitations and typical accuracy of DFT for structural and magnetic properties. Furthermore, the binary compounds FeP, FeSi and FeCo, and the ternary compound FeCoP, were considered, as these are required for the calculation of competition energy values for ternary and quaternary Fe₂P compounds. The selection of these compounds was made on the basis of their suitability as decomposition products in proximity to the substitution-free Fe₂P compound itself. The computed structural and magnetic parameters for primitive orthorhombic FeP, simple cubic FeSi, body centered cubic FeCo and primitive orthorhombic FeCoP have been listed in Tab. 4.7 together with available experimental and theoretical data for a further verification of results.

4.4. Ternary $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ compounds

Table 4.7: Calculated structural (lattice constants, volume and bulk modulus) and magnetic properties (magnetic moments) of binary and ternary compounds that are considered as reference materials for phase stability calculations. Literature data is given in parenthesis for comparison.

Compound	Lattice Constant (Å)			Volume (Å ³)	Bulk modulus (GPa)	Mag. moment (μ_B /f.u.)
	<i>a</i>	<i>b</i>	<i>c</i>			
FeP	3.054 (3.098) ¹	5.152 (5.183) ¹	5.758 (5.784) ¹	90.58 (92.85) ¹	202.71 (205) ¹	0.42
FeSi	4.448 (4.469) ²	4.448 (4.469) ²	4.448 (4.469) ²	88.02 (89.75) ²	197.93 (209) ³	0.0 -
FeCo	2.842 (2.85) ⁴	2.842 (2.85) ⁴	2.842 (2.85) ⁴	22.96 (23.15) ⁴	190 (190) ⁵	4.55 (4.84) ⁵
FeCoP	3.514 (3.397) ⁶	5.697 (5.751) ⁶	6.520 (5.872) ⁶	130.51 (114.72) ⁶	211.96 -	2.10 (1.86) ⁶
	(3.53) ⁵	(5.71) ⁵	(6.53) ⁵	(131.45) ⁵	-	(2.02) ⁵

¹ Data by Gu *et al.* [217]. ² Data by Cheng *et al.* [218] measured at 117.2 K. ³ Data by Knittle *et al.* [219]. ⁴ Data by Elias *et al.* [220]. ⁵ Combined data from Jain *et al.* [190], Horton *et al.* [191] and de Jong *et al.* [189] in the Materials Project. ⁶ Data by Fruchart *et al.* [106].

Similar to the outcomes observed for the unary elements, the theoretical data aligns with the experimental values. This demonstrates that the calculations are of sufficient precision for the magnetic and structural investigations of the compounds. Note, that a noticeable deviation of the theoretical data can be seen to the experimental data from Fruchart *et al.* [106]. Nevertheless, the structural parameters and the magnetic properties still match well enough to consider the precision as reliable. The calculated 0 K formation energies for these compounds are provided in the appendix A for further information.

4.4 Ternary $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ compounds

4.4.1 Hexagonal $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$

The hexagonally structured Fe_2P compound shows promising magnetic properties but suffers from a relatively low Curie temperature of 214 K [107, 27, 28, 29]. The substitution of Fe and P with other elements like Co [111, 106, 43, 110], Mn [103, 108, 109], Si [121, 120, 119, 43, 114] or Ge [124, 103] is reported to effectively enhance the magnetic properties and the Curie temperature. This section investigates the effect of Si substitution on the structural stability, magnetic properties, and Curie temperature of Fe_2P , with particular emphasis on the competition between the hexagonal and BCO phases.

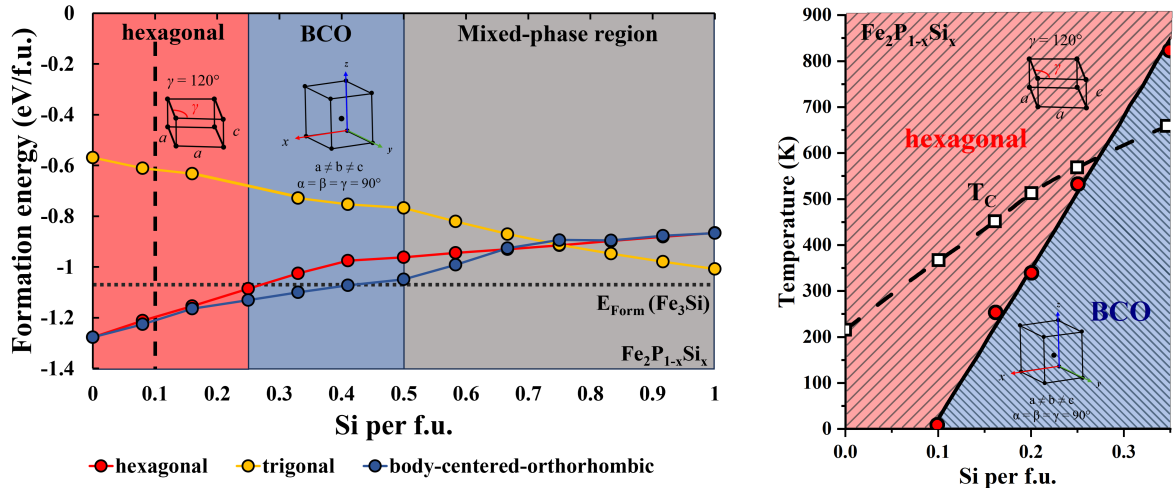


Figure 4.6: **Left:** Calculated phase formation energies at 0 K for the hexagonal, body-centered-orthorhombic (BCO) and trigonal structured $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ compounds in the range $0 \leq x \leq 1$ Si per f.u. The colored backgrounds indicate experimentally observed room temperature phase transitions found by Bao *et al.* [68]. The crystal symmetries are schematically shown in each section. The vertical dashed line describes the phase transition at 0 K proposed by Severin *et al.* [123]. The horizontal dotted line represents the calculated formation energy of Fe_3Si . **Right:** Experimental temperature dependence of the phase transition from hexagonal to BCO (solid line) and Curie temperatures of the $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ compounds (dashed line). The background color represents the related crystal symmetry, which is schematically shown. The image is based on data by Severin *et al.* [123].

Secondary phases and Formation Energies of hexagonal $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ Compounds

It is well documented in the literature that the substitution of P for Si significantly improves the magnetic properties of Fe_2P . However, it is also reported that Si induces a phase transition to a body-centered-orthorhombic structure. This transition is expected to occur $\sim 0.2 - 0.25$ Si per f.u. [67, 68], depending on the performed experiment. Furthermore, Severin *et al.* [123] established a correlation between the structural alteration of the crystal symmetry with Si substitution and temperature. In their work, they described that increasing temperatures enable a higher Si concentration in the hexagonal phase before a phase transition is induced. This dependence of the phase transition on the temperature and Si concentration is illustrated in Fig. 4.6.

For the theoretical investigation of the formation energy, one P atom in the unit cell is replaced by Si. To determine the preferential substitution position, the substitution of each P atom with Si was calculated, and the energetically most favorable structure was used as a starting point for the next substitution step. To calculate the formation energy, the energies of ferromagnetic bcc-structured Fe, non-magnetic orthorhombic black P, and non-magnetic fcc-structured Si were considered, based on them being the ground state of the compounds. The formation energy was then calculated using the following equation:

$$E_{Form} = (E(\text{Fe}_2\text{P}_{1-x}\text{Si}_x) - 2 \cdot E(\text{Fe}) - (1-x) \cdot E(\text{P}) - x \cdot E(\text{Si})) \cdot \frac{1}{N}, \quad (4.2)$$

with E_{Form} as the formation energy, $E(\text{Fe}_2\text{P}_{1-x}\text{Si}_x)$ as the calculated energy of the Si substituted compound, $E(\text{Fe})$, $E(\text{P})$ and $E(\text{Si})$ as the energies of the unary elements Fe, P and Si and N as the number of functional units in the unit cell.

To investigate the phase stability at 0 K, the formation energies of the $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ compounds were calculated in the hexagonal and body-centered-orthorhombic crystal structure for the full substitution up to 1.0 Si per f.u. The results are depicted in Fig. 4.6. For the sake of completeness, these calculations also included the formation energy of the trigonal structure of the metastable Fe_2Si compound. Note, that the Fe_2Si compound is only known to exist in meteorites, not under normal conditions.

In Fig. 4.6 (left), it can be seen that the BCO structure is favored over the hexagonal one with small amounts (0.08 Si per f.u.) of substituted Si. This result aligns with experimental data by Severin *et al.* [123], who estimated that the phase transition from hexagonal to BCO at 0 K is bound to happen at ~ 0.1 Si per f.u. This is indicated in the figure by a dashed vertical line at 0.08 Si per f.u. Additionally, the reported room temperature phase transitions to the BCO and a mixed-phase region by Bao *et al.* [68] are highlighted by a change to a blue and grey background. In the mixed-phase region the Fe_3Si compound starts to appear next to the hexagonal and BCO crystal structure, which also aligns with the calculated formation energy of ~ -1.08 eV/f.u. However, both the hexagonal and the BCO structure show increasing formation energy values with higher Si concentrations, which indicates a lower stability. These formation energies were investigated in more detail to understand the influence of Si on the phase stability. While formation energies assess the intrinsic stability relative to elemental reference states, competition energies (E_{Comp}) evaluate the stability against decomposition into competing binary (FeP and FeSi) and ternary phases. For 0 K investigations only the competition energies calculated with FeP, FeSi and Fe were considered, to show the direct influence of the element substitution in combination with the substitution free compound. This translates into the following equation:

$$E_{Comp} = (E(\text{Fe}_2\text{P}_{1-x}\text{Si}_x) - E(\text{Fe}) - (1-x) \cdot E(\text{FeP}) - x \cdot E(\text{FeSi})) \cdot \frac{1}{N}, \quad (4.3)$$

with $E(\text{FeP})$ and $E(\text{FeSi})$ as the energies of FeP and FeSi. For a good comparison the formation and the competition energies are depicted next to each other in Fig. 4.7. Additionally, the most stable P for Si substitution for both possible substitution sites,

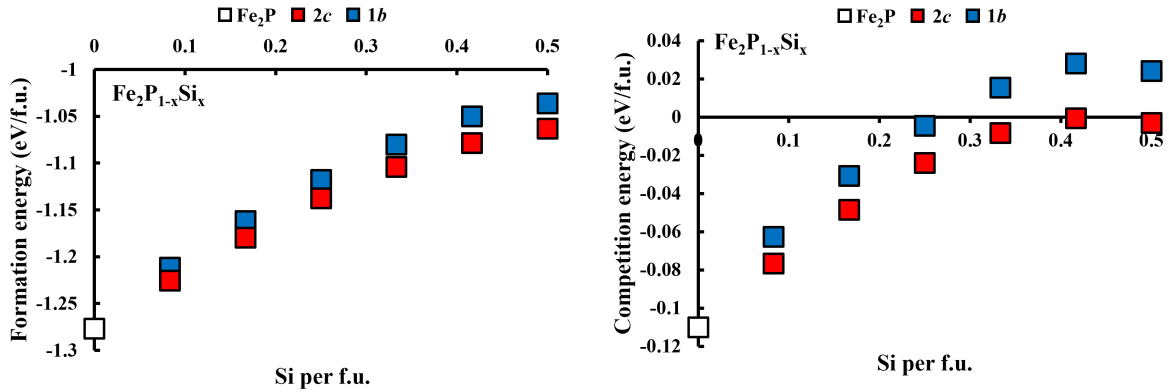


Figure 4.7: **Left:** Formation and **right:** competition energy for $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ compounds in the range $0 \leq x \leq 0.5$ Si per f.u. The substitution into the 2c and 1b site was considered for both cases and the most stable structure was taken as input for the next substitution.

namely 2c and 1b, are included in the Figure. It is noteworthy, that for all substitutions the 2c site is preferred. This result could not be reproduced in experiments, where a random distribution was found at low Si concentrations [121]. This deviation is assumed to be due to the very minor energy difference of ~ 10 meV between both substitution sites, which can already be overcome by small differences in temperature [221].

Both the formation and the competition energy are seen to increase with Si concentration. With each rise of the Si content, the energy difference between both the 2c and 1b site grows bigger, indicating a higher stability for the 2c position. With a high amount of substituted Si, a preferential substitution site for Si was experimentally determined to be in the 2c site, which can be explained by this increasing energy difference [209, 222, 223, 211]. Consequently, the energy difference is sufficiently large at elevated Si concentrations to prevent to be overcome by small temperature fluctuations. The formation energy amounts for the substitution-free Fe_2P compound to -1.27 eV/f.u., which increases with Si up to values of -1.07 eV/f.u. at 0.5 Si per f.u. The same trend is visible for the competition energy, that increases from -0.11 eV/f.u. to ~ 0 eV/f.u. at 0.41 Si in the 2c position. For the 1b site, positive and therefore unstable competition energies were calculated, starting from Si concentrations > 0.25 Si per f.u. This correlates to a solubility limit for Si of ~ 10 -13 at.% at 0 K.

Lattice Constants and Volume of hexagonal $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ Compounds

The substitution of P with Si has a significant influence on the lattice constants of the unit cell. With rising Si concentrations the lattice constant a and the volume increase, while the lattice constant c decreases. This consequently leads to a decline of the c/a ratio, which exerts an influence on the Curie temperature. The development of the lattice constants and the volume are shown in Fig. 4.8.

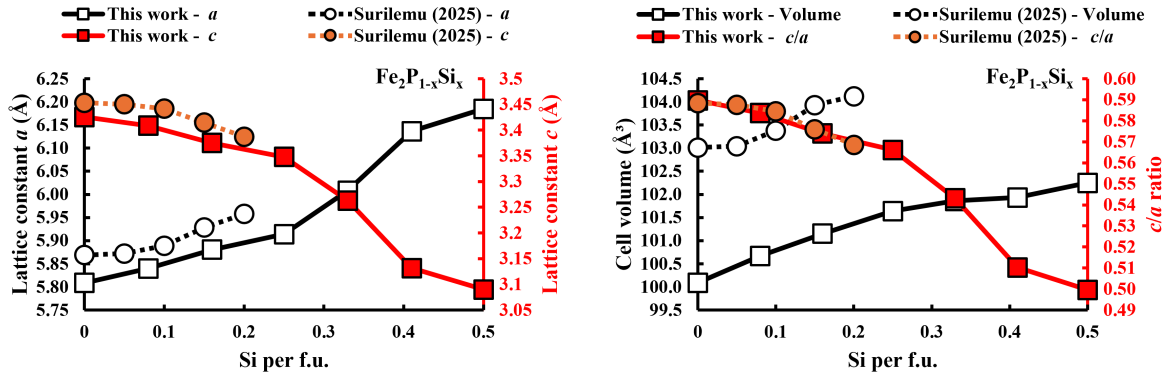


Figure 4.8: **Left:** Theoretical lattice constants a and c in dependence of Si substitution and **Right:** cell volume and c/a ratio in dependence of the Si concentration in $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ compounds between $0 \leq x \leq 0.5$. Experimental data from Surilemu *et al.* [125] (circles) is shown for comparison.

The Lattice constant a starts at 5.808 Å and increases to a value of 6.185 Å at 0.5 Si. Simultaneously, lattice constant c decreases from 3.425 to 3.090 Å. For the volume, this results in an overall increase of 2.2 % from 100.09 to 102.25 Å³. These changes are in agreement with experimental data found by Surilemu *et al.* [125] and Bao *et al.* [68] and are also reported in a publication [43]. Surilemu *et al.* [125] described an enlargement of the volume by 1.1 % with 0.25 Si per f.u., which matches an increase of 1.5 % in this work at equal Si concentrations. The underlying reason for the overall increase of the volume can be attributed to the larger atom size of Si atoms (1.10 Å) compared to P atoms (1.00 Å). This makes additional space for the atoms necessary [224, 225]. It is important to note, that the volume expansion plays a crucial role for the following magnetic properties. It is reported by He *et al.* [42], that Si influences the exchange interaction energies of the Fe atoms by modifying the lattice constants and therefore the distances between the atoms. They stated that the expansion is mostly affecting the low magnetic interactions of the $3f$ magnetic site. In general, the conducted calculations found that a reduction of c , diminishes the the distance between the interlayer $3f$ and $3g$ atoms. This influence on the exchange interaction energies was also further investigated later on in this work.

Magnetic Moments, Magnetization Saturation and Maximum Energy Product of hexagonal $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ Compounds

The reported expansion of the unit cell influences the magnetic moments of the Fe atoms in Fe_2P , as shown in Fig. 4.9. The total magnetic moments increase from $3.02 \mu_B/\text{f.u.}$ at $x = 0$ Si to $3.64 \mu_B/\text{f.u.}$ at $x = 0.5$ Si, which accounts to an improvement of ~ 20 %. At low Si concentrations the total magnetic moment is only slightly above the value of the substitution-free Fe_2P compound. This change of the total magnetic moment can be

connected to an increase of the magnetic moments of the Fe atoms in the $3f$ Wyckoff position. The $3f$ site of Fe_2P starts at a low magnetic moment $\sim 0.83 \mu_B/\text{f.u.}$, which increases with rising Si concentrations to values of 1.02 at 0.16 Si, and even up to $1.50 \mu_B/\text{f.u.}$ at 0.5 Si per f.u. This rise of the $3f$ magnetic moment is connected to the expansion of the unit cell and the accompanied strengthening of the exchange interaction energies for the $3f$ - $3f$ and $3f$ - $3g$ interactions, which agrees with findings by He *et al.*[42]. The $3g$ site on the other hand, is not significantly influenced by Si at all. The magnetic moment in the $3g$ position remains between 2.18 and $2.24 \mu_B/\text{f.u.}$ for the complete substitution range. These effects on the magnetic moments are in good agreement with other theoretical and experimental findings [68, 125, 123].

For a detailed analysis of the volume and atomic influence, additional calculations were performed. In these calculations the enlarged volumes of the compounds were taken as input, with the Si atoms replaced by P atoms. This ensures that the pure effect of the volume and the influence of Si on the magnetic moments is investigated. For $\text{Fe}_2\text{P}_{0.75}\text{Si}_{0.25}$, these calculations yield a magnetic moment of $3.07 \mu_B/\text{f.u.}$ when no Si is included in the unit cell. This result is slightly lower than the mentioned total magnetic moment with substituted Si of $3.30 \mu_B/\text{f.u.}$ The $\text{Fe}_2\text{P}_{0.5}\text{Si}_{0.5}$ compound yields without Si a magnetic moment of $3.30 \mu_B/\text{f.u.}$ compared to the magnetic moment of $3.64 \mu_B/\text{f.u.}$ with Si. These results are shown in Fig. 4.10.

The chemical influence reveals that the magnetic moment is mostly affected by the Si atoms, as the Si-free calculation for $x = 0.25$ Si only accounts to an increase of $0.05 \mu_B/\text{f.u.}$ compared to the substitution-free Fe_2P material. Nevertheless, the volume effect seems to increase with higher Si concentrations, as the magnetic moments increase from $3.07 \mu_B/\text{f.u.}$ at $x = 0.25$ Si to $3.30 \mu_B/\text{f.u.}$ at 0.5 Si per f.u. even when no Si incorporated in the compounds and only the lattice expansion is present. It can therefore be assumed, that a combined effect of both, volume and Si, causes the increase of the magnetic moments.

The magnetization saturation $\mu_0 M_S$ and the maximum energy product $|BH|_{\max}$ are important magnetic properties that are calculated from the magnetic moment, the composition of the compound and the volume, as shown in Eq. 1.2 and Eq. 1.3. According to these two relations, it is no surprise that the magnetization saturation and $|BH|_{\max}$ change parallel to the magnetic moments. The calculated values for $\mu_0 M_S$ and $|BH|_{\max}$ are shown in Tab. 4.8. The $\mu_0 M_S$ shows as an increase by $\sim 0.02 - 0.05$ T for each substitution, resulting in values from 1.06 T at $x = 0.0$ Si up to 1.24 T at $x = 0.5$ Si per f.u. This is in agreement with experimental data by He *et al.* [42], who reported $\mu_0 M_S$ values in the range of 1.03 - 1.15 T for Si substitution up to 0.25 Si per f.u. in $\text{Fe}_{1.82}\text{Co}_{0.18}\text{P}_{1-x}\text{Si}_x$ compounds. Parallel to the $\mu_0 M_S$, the $|BH|_{\max}$ increases similarly. The $|BH|_{\max}$ was

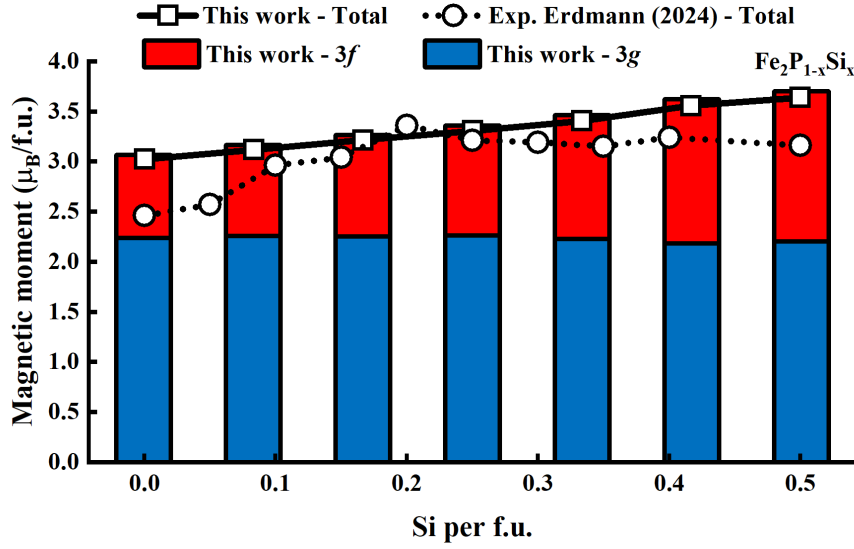


Figure 4.9: Theoretical (squares) and experimental (circles) magnetic moments for hexagonal $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ compounds between $0 \leq x \leq 0.5$ Si. The experimental total magnetic moments are from Erdmann *et al.* [43] and shown for comparison. The total magnetic moments are shown in black, while the partial magnetic moments of the $3f$ and $3g$ Wyck-off positions are depicted in red and blue, respectively.

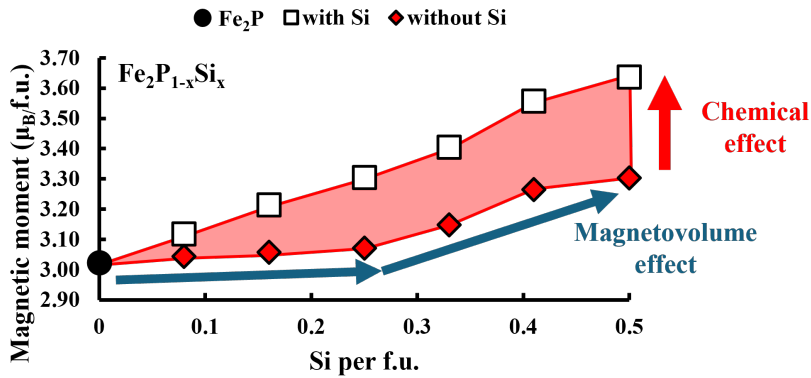


Figure 4.10: Chemical and volume influence of Si on the magnetic moments of the $\text{Fe}_2\text{P}_{0.75}\text{Si}_{0.25}$ and $\text{Fe}_2\text{P}_{0.5}\text{Si}_{0.5}$ compounds. The black squares denote the compounds with Si incorporated into the unit cell, while the red diamonds show the magnetic moment with Si turned back to P in the same unit cell. The magnetovolume effect is shown by a blue arrow, while the chemical effect is depicted in red.

4.4. Ternary $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ compounds

Table 4.8: Theoretical magnetization saturation $\mu_0 M_S$ and maximum energy product $|BH|_{max}$ derived from the calculated magnetic moments depicted in Fig. 4.9 for $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ compounds with $0 \leq x \leq 0.5$ Si. In the lower part of the table, available experimental data is depicted.

Compound	$\mu_0 M_S$ (T)	$ BH _{max}$ (kJ/m ³)
Fe_2P	1.06	222.3
$\text{Fe}_2\text{P}_{0.92}\text{Si}_{0.08}$	1.08	231.8
$\text{Fe}_2\text{P}_{0.84}\text{Si}_{0.16}$	1.11	245.7
$\text{Fe}_2\text{P}_{0.75}\text{Si}_{0.25}$	1.14	258.0
$\text{Fe}_2\text{P}_{0.67}\text{Si}_{0.33}$	1.17	273.9
$\text{Fe}_2\text{P}_{0.59}\text{Si}_{0.41}$	1.22	295.5
$\text{Fe}_2\text{P}_{0.5}\text{Si}_{0.5}$	1.24	307.8
Fe_2P	1.03*	211*
$\text{Fe}_{1.82}\text{Co}_{0.18}\text{P}_{0.89}\text{Si}_{0.11}$	1.09*	141*
$\text{Fe}_{1.82}\text{Co}_{0.18}\text{P}_{0.86}\text{Si}_{0.14}$	1.11*	162*
$\text{Fe}_{1.82}\text{Co}_{0.18}\text{P}_{0.81}\text{Si}_{0.19}$	1.09*	170*
$\text{Fe}_{1.84}\text{Co}_{0.16}\text{P}_{0.78}\text{Si}_{0.22}$	1.10*	183*
$\text{Fe}_{1.82}\text{Co}_{0.18}\text{P}_{0.74}\text{Si}_{0.26}$	1.15*	204*

* Data from He *et al.* [42] measured at 2 K.

calculated as 222.3 kJ/m³ for Fe_2P and rises to 307.8 kJ/m³ at $x = 0.5$ Si per f.u., which depicts a change by ~ 38 %. Since both properties are based on the magnetic moments, the trend of an increase is not surprising and is to be expected with rising magnetic moments.

Curie Temperature and Exchange Interaction Energies of hexagonal $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ Compounds

In this section, the evolution of the Curie temperature T_C and the underlying exchange interaction energies J_{ij} of hexagonal $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ compounds is analyzed in order to identify the microscopic mechanisms responsible for the enhancement of T_C upon Si substitution. The greatest drawback of the Fe_2P compound is a relatively low Curie temperature of 214 K [29, 28, 107, 27]. The substitution of P for Si was reported in the literature to be an effective way of modifying this property, enabling the compound to operate at elevated temperatures [106, 43, 110, 111, 121, 119, 120, 122, 43, 114, 123]. In this work, the mean-field approximation, as implemented in the AkaiKKR code was used to calculate the Curie temperatures T_C of the investigated compounds. The results of the substitution of P for Si are depicted in Fig. 4.11 (left side).

As reported in Sec. 4.1.1, the substitution-free Fe_2P compound exhibits a theoretical T_C of 340 K. Considering an overestimation up to 40 % this value seems to be in agreement

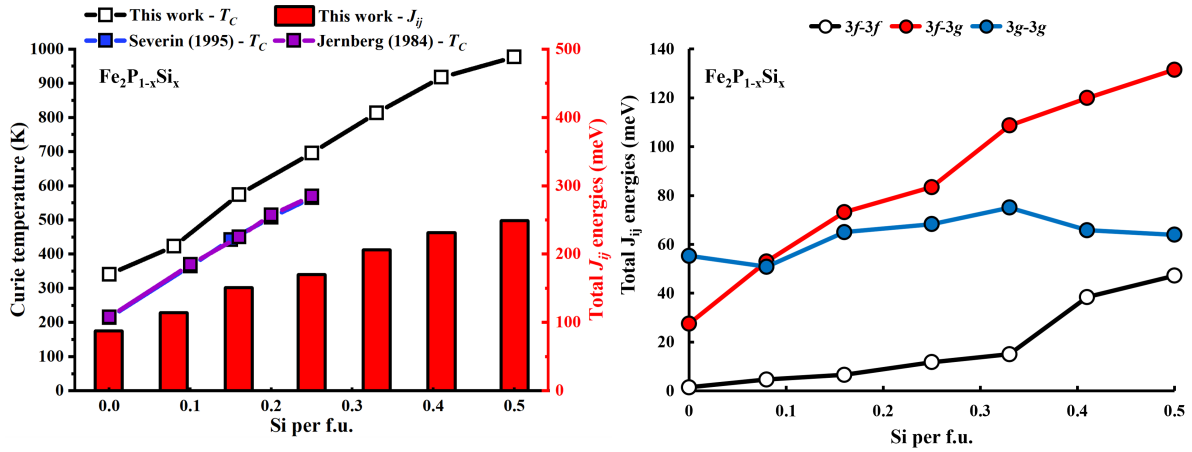


Figure 4.11: **Left:** Curie temperature T_C (black line) and J_{ij} exchange interaction energies (red columns) for Si substitution in hexagonally structured $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ compounds with $0 \leq x \leq 0.5$. Experimental data from Severin *et al.* [123] and Jernberg *et al.* [121] are shown for comparison. **Right:** Site specific partial exchange interaction energies for the 3f-f (black), 3f-3g (red) and 3g-3g (blue) exchange interactions in dependence of the Si concentration.

with the experimental value of 214 K [29, 28, 107, 27]. With increasing Si substitution, the T_C gets increased drastically. Small amounts of Si, like 0.08 and 0.16 Si per f.u., already result in theoretical T_C s of 423 and 574 K, which corroborates with experimental data by Severin *et al.* [123] and Jernberg *et al.* [121]. Both reported improved values of 370 and 450 K at $x = 0.1$ and 0.16 Si per f.u. The theoretical results depict an increase with Si up to a value of ~ 950 K.

To explain this increase, the exchange interaction energies J_{ij} need to be considered, as these are the basis for the calculation of the T_C . As shown in Fig. 4.11, the calculated Curie temperature increases monotonically with increasing Si concentration, following the same trend as the total exchange interaction energy, which confirms the direct correlation between T_C and J_{ij} in these compounds. For Fe_2P the total J_{ij} energies amount to 87 meV, which increases with Si up to ~ 250 meV at $x = 0.5$ Si per f.u. This improvement of the J_{ij} energies can be connected to the modification of the lattice parameters and the change of the atomic distances. Looking at the exchange interactions in more detail in Fig. 4.11 (right side), it is visible, that the 3f-3f and 3f-3g interactions are affected the most by Si, while the 3g-3g interactions remain stable $\sim 60 - 70$ meV. These findings are in good agreement with findings by He *et al.*[42].

In contrast, the 3f-3f interactions increase for Si concentrations > 0.33 Si per f.u. significantly up to a value of 47 meV. However, the greatest influence can be attributed to the 3f-3g interactions, that steadily increase with Si and reach 131 meV at $x = 0.5$ Si per f.u. At this point, the 3f-3g interactions contribute to more than half of the total J_{ij} en-

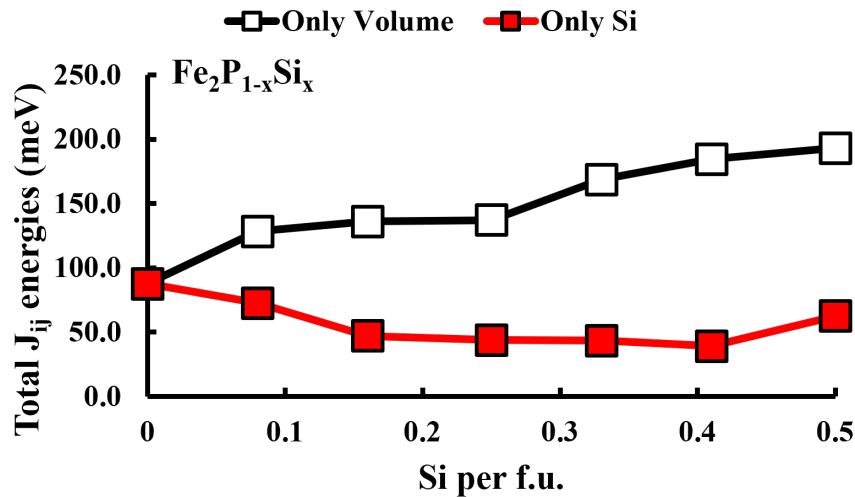


Figure 4.12: Theoretical exchange interaction energies J_{ij} showing the pure volume and atomic effect of Si with P substitution in hexagonally structured $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ compounds with $0 \leq x \leq 0.5$.

ergies of 250 meV and have a significant impact on the T_C . This strengthening of the $3f$ - $3g$ interactions can be connected to the changing c/a ratio, that decreases with rising Si concentrations. A decrease of the c/a ratio, consequently changes the distances between the $3f$ and $3g$ atoms. This reduces the distance and leads to an improvement of the exchange interactions.

Zhuravlev *et al.* [111] also investigated the band filling and its influence on the exchange interaction energies and described a similar influence for Si. They postulated that reducing the number of electrons has a negative effect on the material. However, as described above, the distortion of the unit cell has a positive effect in reducing the distance between the $3f$ and $3g$ atoms. They concluded that the positive effect completely overcomes the negative effect of the electron reduction. To verify this conclusion, additional calculations for the exchange interaction energies were performed. For the determination of the electron reduction effect, the unit cell of the substitution-free Fe_2P compound was taken as input with increasing concentrations of Si. This way the lattice parameters and the volume were kept constant and only the influence of Si was investigated. In another set of calculations the lattice parameters of the Si substituted compounds were used, but the Si concentration was set to be at a constant value of zero. These calculations ensure that the sole influence of the lattice distortion on the exchange interaction energies J_{ij} is examined. Both series of results are shown in Fig. 4.12.

It can be seen, that the change of the volume (black) yields a positive effect that improves the total J_{ij} s from 87 meV up to 193 meV at 0.5 Si per f.u. For the pure chemical effect of Si substitution without a volume change (red), a negative effect was

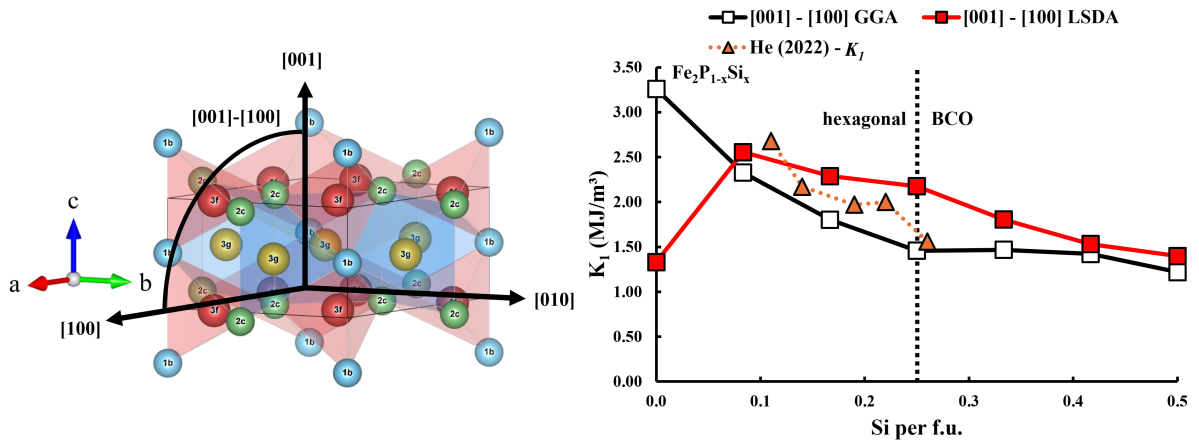


Figure 4.13: **Left:** Schematic illustration of the directional change from [001] to [100] (black) in the hexagonal crystal structure. **Right:** Calculated anisotropy constants K_1 for hexagonal $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ compounds with $0 \leq x \leq 0.5$ with the GGA (black) and LSDA (red) exchange functionals considered. The values are calculated for the directional change from [001] to [100]. Experimental values by He *et al.* [42] are added for comparison. The vertical dashed line marks the experimentally found phase transition from hexagonal to BCO structured compounds [68].

observed. Up to 0.41 Si, the J_{ij} s decrease from 87 meV to 39 meV. The last change yields a small increase of 24 meV to a final value of 63 meV, which still is lower than for substitution free Fe_2P . These results support the conclusion by Zhuravlev *et al.* [111], that the positive effect of the lattice distortion overcomes the negative effect of the electron reduction, leading to an increase of the J_{ij} energies and the T_C s with Si substitution.

Anisotropy Constant and Anisotropy Field of hexagonal $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ Compounds

In this section, the evolution of the first-order magnetocrystalline anisotropy constant K_1 and the corresponding anisotropy field H_a of hexagonal $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ compounds is analyzed in order to assess the impact of Si substitution on the uniaxial anisotropy and its implications for hard-magnetic behaviour. The Fe_2P compound exhibits a particularly high uniaxial anisotropy, which is influenced by the substitution of P with Si. The results of the non-collinear calculations of the anisotropy constant K_1 and the anisotropy field H_a can be seen in Fig. 4.13 and Tab. 4.9 for both the GGA and LSDA exchange functionals. The anisotropy constants K_1 are calculated using Eq. 1.5, while the anisotropy field H_a is calculated with Eq. 1.7.

Using the GGA functional, the initially high K_1 of 3.26 MJ/m³ gets reduced by Si substitution to a value of 1.46 MJ/m³ at $x = 0.25$ Si per f.u. At even higher Si concentrations K_1 seems to be less influenced and stagnates up to 0.41 Si. At $x = 0.5$ Si per f.u.,

Table 4.9: Calculated anisotropy constant K_1 (see Eq. 1.5) and anisotropy field H_a (see Eq. 1.7) for ternary $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ compounds with $0 \leq x \leq 0.5$. The first values are calculated using the GGA functional and in parenthesis are the results considering the LSDA functional given.

Compound	K_1 (MJ/m ³)	H_a (T)
Fe_2P	3.26 (1.33)	6.17 (2.52)
$\text{Fe}_2\text{P}_{0.92}\text{Si}_{0.08}$	2.33 (2.55)	4.30 (4.72)
$\text{Fe}_2\text{P}_{0.84}\text{Si}_{0.16}$	1.80 (2.29)	3.25 (4.12)
$\text{Fe}_2\text{P}_{0.75}\text{Si}_{0.25}$	1.46 (2.18)	2.57 (3.83)
$\text{Fe}_2\text{P}_{0.67}\text{Si}_{0.33}$	1.47 (1.80)	2.51 (3.09)
$\text{Fe}_2\text{P}_{0.59}\text{Si}_{0.41}$	1.42 (1.53)	2.33 (2.51)
$\text{Fe}_2\text{P}_{0.5}\text{Si}_{0.5}$	1.22 (1.40)	1.96 (2.25)

the anisotropy constant decreases slightly compared to the value at 0.41 Si to 1.22 MJ/m³. Employing the LSDA functional, a slightly different trend can be observed. The substitution-free Fe_2P compound starts with LSDA at a much lower value of 1.33 MJ/m³, which increases to 2.55 MJ/m³ with small amounts of Si. This indicates, that the description of Si substituted compounds yields a much better description via LSDA as for substitution-free Fe_2P . It can therefore deduced that only the substitution-free compound is poorly described by the LSDA functional. Extrapolating the LSDA results of the anisotropy constant of the ternary $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ compounds to the substitution-free Fe_2P compound, a value of ~ 2.7 MJ/m³ can be assumed. After the first increase, K_1 steadily decreases with added Si and ends at a comparable value to GGA with 1.4 MJ/m³. Comparing the achieved results with experimental data by He *et al.*, who investigated the MAE of $\text{Fe}_{1.84}\text{Co}_{0.16}\text{P}_{1-x}\text{Si}_x$ compounds in the range of $0 \leq x \leq 0.25$ Si, the same trend of a decrease with Si can be seen. However, with the experimental values being exactly between the results of both exchange functionals, an estimation of which functional provides a better description of the compound is difficult. To address this issue both functionals were considered for all following hexagonally structured compounds.

Since the calculation of the anisotropy field is based on the anisotropy constant, the same trends for K_1 apply to H_a . This results in significant decreases from 6.17 to 1.96 T for GGA and 4.72 T at $x = 0.08$ Si to 2.25 T for LSDA. Again, the low LSDA value of 2.52 T for the substitution free Fe_2P compound increases to 4.72 T with low Si concentrations of $x = 0.08$ Si per f.u. The trend aligns then again parallel to the GGA values

with an overall decrease of H_a . The decrease of K_1 matches with former literature by Zhuravlev *et al.* [111], who connected the anisotropy with the band filling of the Fe_2P compounds. This matches, as the substitution with Si reduces the number of electrons in the bands and therefore also the MAE as expected. The resulting impact of the reduced number of electrons enables either more or less states to be filled as the Fermi energy is shifted. This change of the involved states results in a decrease of the MAE, due to spin-orbit-coupling. Consequently, small changes of the Fermi energy can influence the MAE drastically [148].

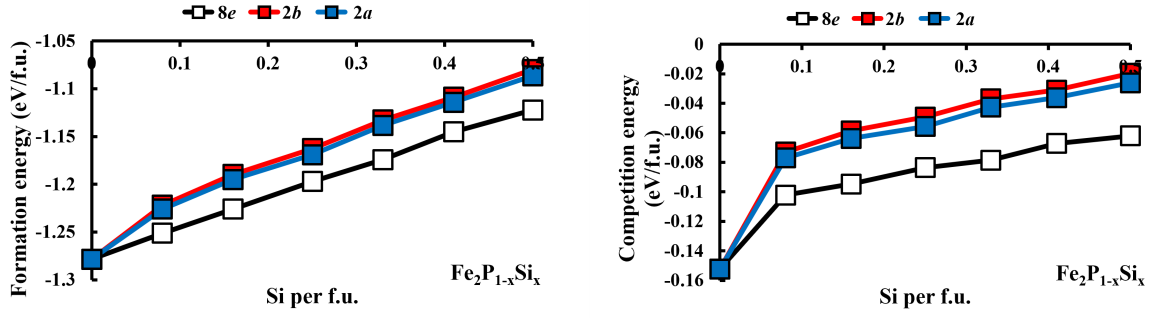


Figure 4.14: **Left:** Calculated site specific formation energy of the ternary $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ compounds in the BCO crystal symmetry for Si substitution into the 8e (black), 2b (red) and 2a (blue) P sites. The elements Fe, P and Si have been used as reference materials. **Right:** Calculated site specific competition energy of the ternary $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ compounds in the BCO crystal symmetry for Si substitution into the 8e (black), 2b (red) and 2a (blue) P sites. The compounds FeP, FeSi and Fe have been taken as reference states for the calculation.

4.4.2 Body-centered Orthorhombic $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$

Formation and Competition Energy of BCO $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ Compounds

In order to assess the thermodynamic relevance of the body-centered orthorhombic (BCO) phase upon Si substitution, the formation and competition energies of BCO structured $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ compounds were systematically evaluated. The BCO structure stabilizes with rising Si concentrations and even overcomes the hexagonal structure at $x = 0.25$ Si per f.u. The calculated formation energies, using the unary elements as reference, for the BCO structured ternary $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ compounds are depicted in Sec. 4.14. These calculations consider and investigate the substitution into the different P sites to identify the preferred substitution position for Si. It can clearly be seen, that the 8e site provides the lowest energy for Si substitution in all cases up to a concentration of $x = 0.5$ Si per f.u. This trend aligns with the found preferential substitution in the hexagonal structure in the 2c position. As already mentioned, the 2c site translates with the transition from hexagonal to BCO to the 8e position for the P atoms (see Tab. 4.2) [123]. The 2a and 2b sites are less stable than the 8e position by ~ 0.03 to 0.05 eV/f.u. The formation energy rises from -1.28 eV/f.u. to a value of -1.12 eV/f.u. at $x = 0$ and 0.5 Si, respectively. However, similarly to the hexagonal compound, increasing concentrations of Si lead to higher formation energies for the compounds, thus indicating a drop of the stability.

Using the binary compounds FeP, FeSi and the element Fe to calculate the competition energy, analogous to the calculations for the hexagonal phase, the same trend as for the formation energy can be seen. At $x = 0$ Si per f.u., the competition energy starts at -0.152 eV/f.u. and increases with Si to -0.084 and -0.062 eV/f.u. at $x = 0.25$ and

0.5 Si per f.u., respectively. Differently to the competition energy of the hexagonal phase, the values do not draw near to 0 eV/f.u., even in the $2b$ and $2a$ positions, that correspond to the hexagonal $1b$ site. These lower values indicate a higher stability of the BCO compounds at 0 K when the binary compounds FeP and FeSi are considered.

Comparing the results of the formation energies directly with the corresponding formation energies of the hexagonally structured compounds, a higher stability of the BCO phase for compounds at 0 K can be deduced (see Fig. 4.6).

Small amounts of Si (0.08 Si) already cause a higher stabilization of the BCO structure by ~ 0.025 eV/f.u., compared to the hexagonal phase. This difference further enlarges with Si and makes the energy difference more pronounced. At $x = 0.25$ Si the difference accounts to ~ 0.06 eV/f.u. Given the higher stability of the BCO structure at low Si concentrations, the question arises as to how the hexagonal structure remains stable up to Si contents of $x = 0.25$ Si per f.u. The answer to this question lies within the influence of temperature, that is not considered in these 0 K calculations. The phase stabilities at finite temperatures will be covered later in this work. Nevertheless, the higher stability of BCO at low temperatures corroborates with literature by Severin *et al.* [123], who showed that the Si induced transition from the hexagonal to the BCO structured Fe_2P compound is dependent on temperature. This leads to the hexagonal compound being stable at room temperature up to Si concentrations of $x = 0.25$ Si per f.u. However, at 0 K, the BCO structure is preferred against the hexagonal symmetry, when Si is incorporated into the unit cell of Fe_2P .

Lattice Constants and Volume of BCO $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ Compounds

Similar to the hexagonal compound, Si substitution into the BCO phase influences the lattice parameters and the volume of the compound. Without Si, the lattice constants a , b and c are calculated as 6.484, 10.106 and 6.058 Å and the resulting volume is determined as 397.0 Å³. Incorporating Si into the unit cell results in a general decrease of a and an increase of b , c , c/a and the volume, as visible in Fig. 4.15. While a diminishes from 6.484 Å to 6.322 Å for $x = 0.5$ Si per f.u., the lattice constants b and c rise from 10.106 and 6.058 Å to 10.379 and 6.192 Å at 0.5 Si, respectively. This correlates to an overall increase of the c/a ratio and volume by 5.4 and 2.4 %. These effects on the lattice parameters and the volume are comparable to the effects on the hexagonal crystal structure, where the volume increases by 2.2 %. This agrees with experimental results by Surilemu *et al.* [125], who found decreasing values for a (6.560 Å at 0.25 Si to 6.466 Å at 0.5 Si) and increasing values for b (10.347 Å at 0.25 Si to 10.424 Å at 0.5 Si) and c (6.120 Å at 0.25 Si to 6.184 Å at 0.5 Si). A good agreement with experiment was therefore achieved. The experimental results, are additionally shown in Fig. 4.15 to emphasize the agreement of the theoretical

4.4. Ternary $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ compounds

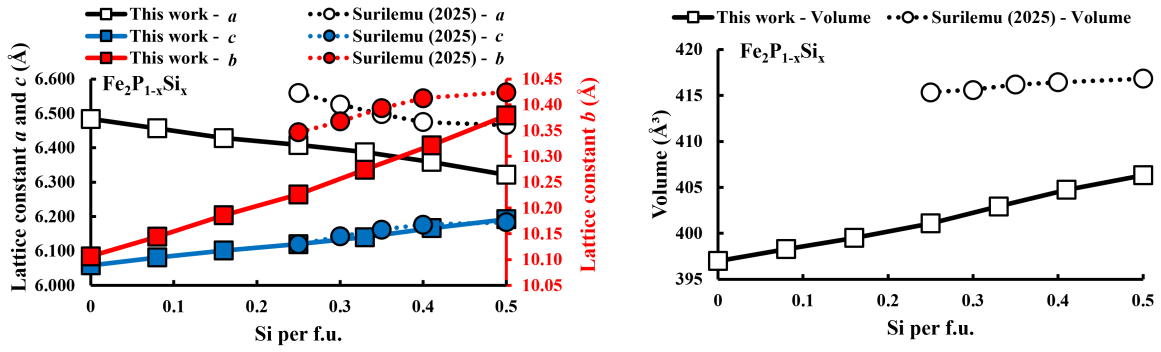


Figure 4.15: **Left:** Theoretical lattice parameters a (black), b (red) and c (blue) and **Right:** the unit cell volume (black) in dependence of the Si concentration for the BCO structured $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ compounds in the range of $0 \leq x \leq 0.5$ Si per f.u. Experimental data by Surilemu *et al.* [125] is shown for comparison.

trends with the experiment.

Magnetic Moments, Magnetization Saturation and Maximum Energy Product of BCO $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ Compounds

The incorporation of Si into the compound causes a moderate change of total magnetic moments. The substitution-free Fe_2P compound exhibits a total magnetic moment of $3.06 \mu_B/\text{f.u.}$ in the BCO structure. Si substitution increases the magnetic moment by a similar degree as in the hexagonal structure. This improvement is depicted in Tab. 4.10. The magnetic moment rises from $3.06 \mu_B/\text{f.u.}$ to $3.21 \mu_B/\text{f.u.}$ at $x = 0.25$ Si per f.u. and is further increased to $3.46 \mu_B/\text{f.u.}$ at 0.5 Si. The complete substitution up to 0.5 Si yields an improvement of 13.1 %. A detailed analysis of the site specific magnetic moments revealed that the $4d_2$, $2b$ and $2a$ sites remain constant at their respective moments of 0.77 , 0.42 and $0.19 \mu_B/\text{f.u.}$, respectively. Only minor fluctuations of $\sim 0.01 \mu_B/\text{f.u.}$ are observed. In contrast, the Fe $8e$, $4c$ and $4d_1$ sites exhibit a pronounced increase dependent on the Si concentration from 0.85 , 0.31 and $0.6 \mu_B/\text{f.u.}$ to values of 1.03 , 0.41 and $0.68 \mu_B/\text{f.u.}$, respectively. The largest contribution to the increase in total magnetic moment therefore originates from the Fe $8e$ site. Each site specific magnetic moment, as well as the total magnetic moment are illustrated in Fig. 4.16.

This rise of the magnetic moments simultaneously yields an increase of the magnetization saturation $\mu_0 M_S$ and maximum energy product $|BH|_{\max}$ for the compounds, which are listed in Tab. 4.10. In the case of the BCO structure, $\mu_0 M_S$ increases by an overall 10.2 % from 1.08 to 1.12 and 1.19 T at 0 Si, 0.25 Si and 0.5 Si per f.u. The $|BH|_{\max}$ rises at the same time from 230 kJ/m^3 by ~ 2.1 to 4.6 % between each investigated compound, to an overall value of 281 kJ/m^3 at $x = 0.5$ Si. This results in an increase of 51 kJ/m^3 (~ 22.1 %). Si substitution therefore improves the magnetic properties of the

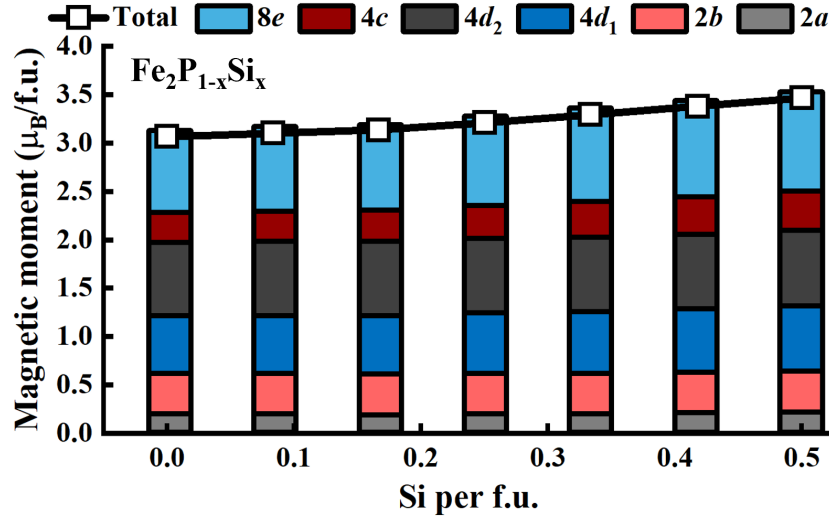


Figure 4.16: Calculated total (black line) and site specific magnetic moments for each Wyckoff position in the BCO structured unit cell for $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ compounds in the range of $0 \leq x \leq 0.5$ Si per f.u.

Table 4.10: Theoretical total magnetic moments ($\mu_B/\text{f.u.}$), magnetization saturation $\mu_0 M_S$ (T) and $|BH|_{\max}$ (kJ/m^3) of BCO structured ternary $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ compounds with Si concentrations up to $x = 0.5$ Si per f.u.

Compound	Mag Moment ($\mu_B/\text{f.u.}$)	$\mu_0 M_S$ (T)	$ BH _{\max}$ (kJ/m^3)
Fe_2P	3.06	1.08	230
$\text{Fe}_2\text{P}_{0.92}\text{Si}_{0.08}$	3.10	1.09	235
$\text{Fe}_2\text{P}_{0.84}\text{Si}_{0.16}$	3.15	1.10	241
$\text{Fe}_2\text{P}_{0.75}\text{Si}_{0.25}$	3.21	1.12	249
$\text{Fe}_2\text{P}_{0.67}\text{Si}_{0.33}$	3.29	1.14	259
$\text{Fe}_2\text{P}_{0.59}\text{Si}_{0.41}$	3.37	1.16	269
$\text{Fe}_2\text{P}_{0.5}\text{Si}_{0.5}$	3.46	1.19	281

BCO structure in a similar way to the hexagonally structured compounds.

As the BCO structure only recently started to gain more attention, no experimental data is available for comparison of magnetic moments. However, a similar trend can reasonably be anticipated for the BCO structure, as the underlying lattice distortions are comparable to those observed in the hexagonal compounds.

Curie Temperature and Exchange Interaction Energies of BCO $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ Compounds

Since the BCO compound is observed to appear at high Si concentrations, the Curie temperature in the BCO symmetry is important to investigate, as well. As already mentioned in Sec. 4.1.2, the calculated T_C s in the mean-field approximation yield very high values starting at 690 K for substitution-free Fe_2P . This value increases even further a maximum of 958 K at $x = 0.5$ Si per f.u. The detailed T_C results are depicted in Fig. 4.17 (left side). It should be emphasized that the Curie temperatures were calculated within the mean-field approximation, which is known to systematically overestimate experimental values. Consequently, the absolute T_C values should be interpreted with caution, while the observed trends remain meaningful. The achieved trend shows, that the increase of Si yields an high improvement of the Curie temperature. One T_C for BCO structured $\text{Fe}_2\text{P}_{0.65}\text{Si}_{0.35}$ was reported by Jernberg *et al.* [121] exhibiting a T_C of 660 K. This leads to the assumption, that BCO structured compounds with higher Si concentrations would also yield high Curie temperatures, making them interesting for future investigations.

The improvement of the T_C s can again be attributed to the optimization of the exchange interaction energies J_{ij} in response to the higher cell volume following the enlargement of the lattice parameters b and c . Positive values of J_{ij} favor a ferromagnetic alignment, whereas negative values indicate antiferromagnetic coupling. The larger volume enables the distances between the Fe atoms to reach optimal lengths, which consequently improves the J_{ij} interaction energies. The total J_{ij} energies and the contribution of each Wyckoff site that includes Fe atoms are depicted in Fig. 4.17 (right side).

In Fig. 4.17, the total J_{ij} energies rise from 527 meV to a value of 759 meV at $x = 0.5$ Si. The greatest contribution results from the $8e$ - $4d$ interactions that increase by 80 meV from 181 to 261 meV at 0 and 0.5 Si, respectively. The second and third greatest increase can be attributed to $4c$ - $4d$ (53 meV) and $8e$ - $2b$ (22 meV), which start at 73 and 57 meV at $x = 0$ Si and end at 126 and 79 meV at $x = 0.5$ Si. This covers two thirds (155 meV) of the overall improvement of 232 meV and the remaining 77 meV are contributed by other, smaller site specific exchange interactions.

The enhancement of the Curie temperature with increasing Si concentration is directly linked to the strengthening of the dominant exchange interaction energies, which in the

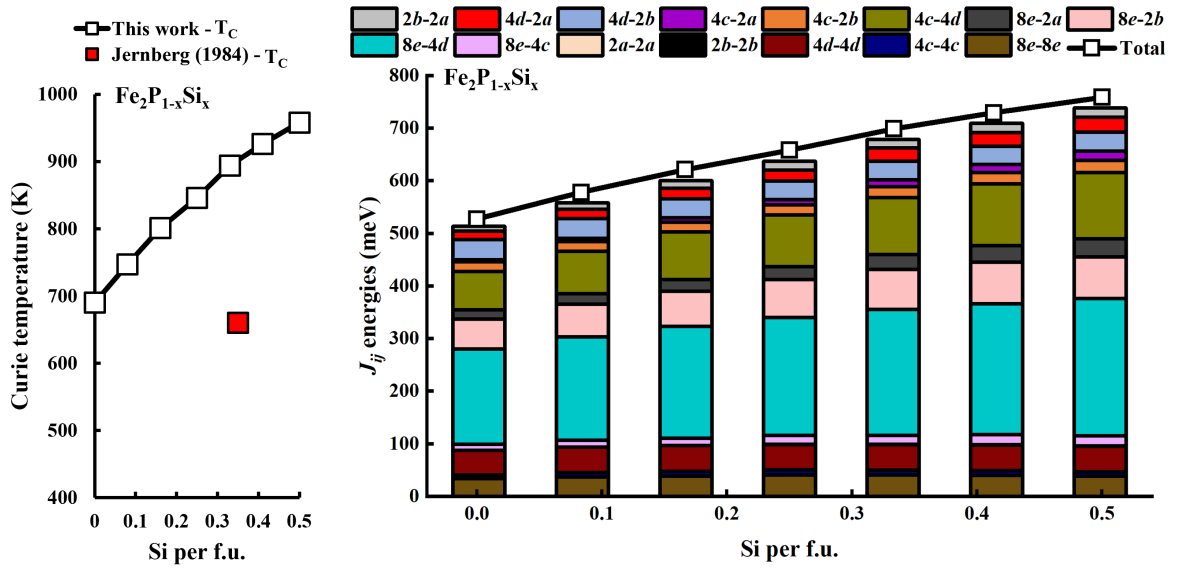


Figure 4.17: **Left:** Calculated Curie temperatures (black squares) for BCO structured ($Imm2$) $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ compounds in dependence of Si substitution in the range of $0 \leq x \leq 0.5$ Si. A known experimental value by Jernberg *et al.* [121] at $x = 0.35$ Si is shown for comparison. **Right:** Contributions of the different Wyckoff sites to the exchange interaction energies (meV) in BCO structured ($Imm2$) $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ compounds in dependence of Si substitution in the range of $0 \leq x \leq 0.5$ Si.

BCO structure are primarily driven by lattice distortions rather than by electronic band-filling effects. The decrease of the c/a ratio and the rise of the volume enable the atoms to optimize the distance between each other, yielding a strengthening of the interactions. The $8e$ and $4c$ sites in the BCO structure, corresponding to the $3f$ site in the hexagonal crystal, see the greatest changes, which emphasizes the close connection of both crystal symmetries to each other. It can therefore be hypothesized, that Si substitution into the BCO crystal achieves a similar positive volume effect with higher magnetic moments and higher J_{ij} energies.

Anisotropy Constant and Anisotropy Field of BCO $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ Compounds

The magnetocrystalline anisotropy of the BCO structured compounds are of particular interest, as this property is an important requirement for hard magnetic materials. The anisotropy constant of the substitution-free BCO structured Fe_2P compound is much lower than for the hexagonal phase. However, the incorporation of Si exhibits an opposite trend compared to the decrease in the hexagonal symmetry. In the case of the BCO compounds, the anisotropy constant is determined as 0.596 ([001]-[100]) and 0.568 MJ/m³ ([010]-[100]) and increases with Si up to 0.824 ([001]-[100]) and 1.174 MJ/m³ ([010]-[100]) at $x = 0.25$ Si per f.u. Note, that the easy direction in BCO equals the [100] direction,

4.4. Ternary $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ compounds

Table 4.11: Theoretical anisotropy constant K_1 and anisotropy field H_a values for the BCO structured $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ compounds for Si concentrations up to $x = 0.5$ Si per f.u. The values are calculated using the GGA exchange functional.

Compound	K_1	H_a	K_1	H_a
	[100]-[001] (MJ/m ³)	[100]-[001] (T)	[100]-[010] (MJ/m ³)	[100]-[010] (T)
Fe_2P	0.596	1.105	0.568	1.084
$\text{Fe}_2\text{P}_{0.92}\text{Si}_{0.08}$	0.674	1.237	0.807	1.364
$\text{Fe}_2\text{P}_{0.84}\text{Si}_{0.16}$	0.761	1.387	1.005	1.636
$\text{Fe}_2\text{P}_{0.75}\text{Si}_{0.25}$	0.824	1.472	1.174	1.865
$\text{Fe}_2\text{P}_{0.67}\text{Si}_{0.33}$	0.890	1.556	1.399	2.000
$\text{Fe}_2\text{P}_{0.59}\text{Si}_{0.41}$	0.936	1.602	1.544	2.058
$\text{Fe}_2\text{P}_{0.5}\text{Si}_{0.5}$	0.931	1.560	1.700	2.109

the compounds. With Si providing an electron less than P, the literature expects a loss of the anisotropy, as seen for the hexagonal crystal structure. This was clearly not achieved in case of the BCO compounds and could indicate that other mechanisms are more relevant for this crystal symmetry. Based on this result, the reduction of electrons in the band filling shifts the Fermi energy and changes the number of accessible states for the determination of the magnetocrystalline anisotropy in a positive way. Since the spin-orbit-coupling depends on the crystal structure, the BCO structure seems to be favorable for this shift of the Fermi energy. This finding of a higher anisotropy marks a point of interest for future investigations to explore the anisotropy of the BCO crystal in more detail.

Assessment of the BCO Crystal Structure for $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ Compounds

With an good understanding of the effect of Si substitution on the structural and magnetic properties BCO structured Fe_2P compounds, the suitability of these compounds as magnetic materials can be assessed. The substitution of Si significantly improves the magnetic moments and the Curie temperature. The only downside of these compounds is a comparably lower magnetic anisotropy. However, the lower anisotropy rises contrary to the findings in the hexagonal cell, which could be interesting for future research on this material. Consequently, the BCO symmetry can be assumed as a suitable structure for magnetic materials, which supports the rising interest of research on this symmetry next to the hexagonal compounds. However, due to the appearance of this structure at Si concentrations ≥ 0.25 Si per f.u. in $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$, and a reported higher stability range of the hexagonal compounds with additional Co substitution [42, 68, 67], only the hexagonal crystal structure will be considered for quaternary Si and Co substitutions in this work.

4.5 Ternary $\text{Fe}_{2-y}\text{Co}_y\text{P}$ compounds

4.5.1 Hexagonal

The element Co was identified as a promising candidate for the substitution of Fe in Fe_2P . The screening calculations revealed a reasonable improvement of the T_C and only a slight effect on the magnetic moments. However, the complete effect of these substitutions remains to be uncovered.

In the literature, the substitution of Fe in Fe_2P with other elements is described to take place in both the $3f$ and the $3g$ Wyckoff positions, depending on the number of d -electrons of the metal substitute. Elements with less electrons than Fe are favored in the $3g$ position, while those with more electrons are preferred in the $3f$ position [209]. This substitution scheme is supported by findings from Dung *et al.* [211] and Bacmann *et al.* [223], who described a preference of Mn for the $3g$ position. Consequently, for Co substitution this corresponds to a preferred substitution into the tetrahedron $3f$ site, as it has an additional electron compared to Fe. This preference is also documented by neutron diffraction experiments by Jain *et al.* [226] and theoretical investigations by Zhuravlev *et al.* [111].

In this work, the preferential substitution site for the substitution of Fe with Co was examined analogous to the employed scheme used for Si substitution. Unary elements and binary compounds were used as reference states for the formation and competition energies, respectively. In the literature, a room temperature phase transition to the primitive orthorhombic $Pnma$ phase occurs at $y = 0.3$ Co per f.u. [68]. To account for this structural change, both the hexagonal and the primitive orthorhombic ($Pnma$) phase were investigated with focus on the magnetic moments, magnetization saturation $\mu_0 M_S$, Curie temperature T_C , exchange interaction energies J_{ij} , anisotropy constant K_1 and anisotropy field H_a .

Secondary phases and Formation Energies of hexagonal $\text{Fe}_{2-y}\text{Co}_y\text{P}$ Compounds

In Fig. 4.19 (left) is the formation energy in dependence of the substituted amount of Fe for Co depicted. The formation energies have been calculated using a similar equation as seen with Si substitution. The element Co was implemented instead of Si in the following way:

$$E_{Form} = (E(\text{Fe}_{2-y}\text{Co}_y\text{P}) - (2 - y) \cdot E(\text{Fe}) - y \cdot E(\text{Co}) - E(\text{P})) \cdot \frac{1}{N}, \quad (4.4)$$

with $E(\text{Fe}_{2-y}\text{Co}_y\text{P})$ as the energy of the Co substituted compound and $E(\text{Fe})$, $E(\text{Co})$ and $E(\text{P})$ as the calculated 0 K energies of the unary elements. Similar to Si, the substitution free Fe_2P compound starts at a formation energy of ~ -1.28 eV/f.u. However, contrary to Si, the substitution of Co reduces E_{Form} to values of ~ -1.6 eV/f.u. at $y = 1$ Co per f.u.

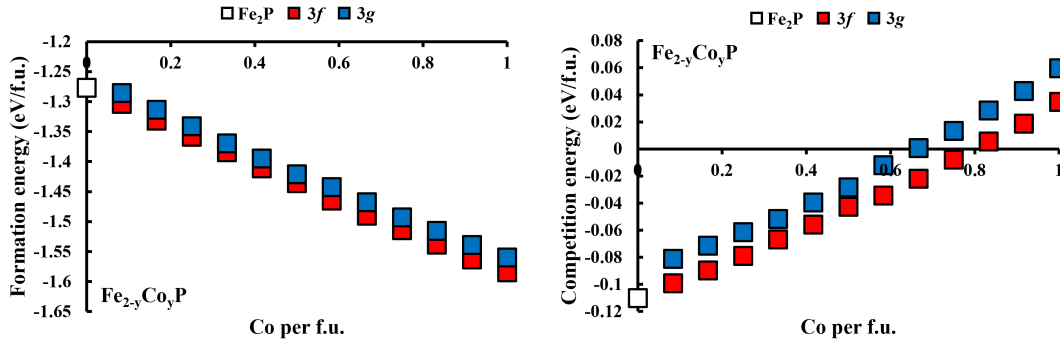


Figure 4.19: **Left:** Calculated formation energies of hexagonally structured $\text{Fe}_{2-y}\text{Co}_y\text{P}$ compounds between $0 \leq y \leq 1$ with the unary elements Fe, Co and P as reference elements. The substitution-free Fe_2P compound is given in black, while the investigated $3f$ and $3g$ sites are given in red and blue, respectively. Phase transitions to the primitive orthorhombic phase have not been considered. **Right:** Calculated competition energies of hexagonal $\text{Fe}_{2-y}\text{Co}_y\text{P}$ compounds between $0 \leq y \leq 1$ with FeP, FeCoP and Fe as reference materials. The substitution-free Fe_2P compound is given in black, while the investigated $3f$ and $3g$ sites are given in red and blue, respectively.

and achieves a stabilization of the alloys with increasing Co concentrations. The reason for this behavior could be a late transition to the known primitive orthorhombic structure or the ternary FeCoP compound. In the figure, it is visible that for all substitutions the $3f$ site is preferred for Co substitution. The energy difference between both substitution sites is calculated to be between 14 to 18 meV for up to $y = 0.5$ Co per f.u. At Co concentrations $y > 0.5$ Co per f.u., the energy difference enlarges slightly to 25 meV. These energy differences indicate a clear preference of the $3f$ site. This result aligns with already mentioned literature [209, 226, 211, 111, 223], that describes a preference of the $3f$ position with more electrons than Fe.

To provide an improved description of the phase stability, the competition energy of the $\text{Fe}_{2-y}\text{Co}_y\text{P}$ materials was calculated. With the consideration of other stable binary (FeP) and ternary materials (FeCoP) a more realistic assessment is achieved, as this energy describes the possibility of formation compared to these stable compounds. This leads to the following expression to calculate E_{Comp} :

$$E_{Comp} = (E(\text{Fe}_{2-y}\text{Co}_y\text{P}) - (1-y) \cdot E(\text{FeP}) - (1-y) \cdot E(\text{Fe}) - y \cdot E(\text{FeCoP})) \cdot \frac{1}{N}, \quad (4.5)$$

with $E(\text{FeP})$, $E(\text{FeCoP})$ and $E(\text{Fe})$ as the calculated energies of the respective materials. FeP and FeCoP were chosen as reference materials, due to their high stability and both being the most likely decomposition products of the ternary $\text{Fe}_{2-y}\text{Co}_y\text{P}$ compounds. The resulting competition energies are depicted in dependence of the Co concentration in

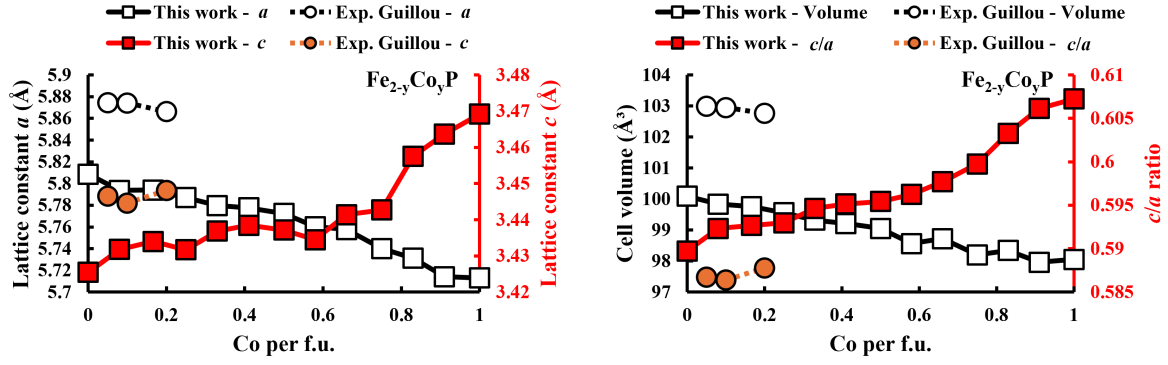


Figure 4.20: **Left:** Theoretical lattice constants a (black) and c (red) in dependence of the Co concentration in hexagonal $\text{Fe}_{2-y}\text{Co}_y\text{P}$ compounds between $0 \geq y \geq 1$. **Right:** Calculated Volume (black) and c/a ratio (red) in dependence of the Co concentration in hexagonal $\text{Fe}_{2-y}\text{Co}_y\text{P}$ compounds between $0 \geq y \geq 1$. Experimental data was provided by the working group of Prof. Guillou (circles).

Fig. 4.19 (right).

With rising Co concentrations, an increase of the competition energy is achieved. This trend contrasts the mentioned decreasing effect of Co on the formation energy. Starting at -0.11 eV/f.u., the competition energy steadily increases to a maximum value of 0.034 eV/f.u. at $y = 1$ Co per f.u. This opposing trend of rising energy values is connected to the high stability of the ternary FeCoP compound, that is used in the calculation of the competition energy. With increasing Co concentrations, a higher possibility of the formation of FeCoP can be assumed. This results in a increasing energies for the ternary $\text{Fe}_{2-y}\text{Co}_y\text{P}$ compounds. It can additionally be noted, that at $y \geq 0.83$ only positive result were calculated for both crystallographic sites, thus limiting the solubility to this Co concentration. This indicates that a substitution of Co into hexagonal Fe_2P is theoretically only possible up to a maximum of 0.83 Co per f.u., considering the mentioned reference phases. This site preference for the $3f$ site prevails for all considered ternary calculations and is in accordance with theoretical site preference results by Zhuravlev *et al.* [111] and experimental findings by Jain *et al.* [226] for concentrations up to 0.3 Co per f.u. For the complete substitution range up to 1 Co per f.u., the $3f$ site is always favored compared to the $3g$ position. The energy difference between both crystal positions remains in the same order as seen in the formation energies between 14 to 25 meV.

Lattice Constants and Volume of hexagonal $\text{Fe}_{2-y}\text{Co}_y\text{P}$ Compounds

Substitution Fe with Co significantly influences the lattice constants and the volume of the hexagonal unit cell, as illustrated in Fig. 4.20. As the Co concentration increases, the lattice constant a decreases from 5.808 Å to ~ 5.710 Å at $y = 1.0$ Co per f.u. In

parallel, the lattice constant c increases contrary to the trend of a . The length of c starts at 3.425 Å and enlarges a value of ~ 3.440 Å at $y = 0.75$ Co. Concentrations of Co > 0.75 Co affect the length of c much more and result in a greater enlargement, ending at 3.47 Å at $y = 1$ Co per f.u. Both changes of a and c directly influence the c/a ratio, which correlates to the Curie temperature by influencing the distances between the atoms. With a shrinking of lattice constant a and an enlargement of c , the c/a ratio increases from ~ 0.59 up to ~ 0.61 . The change of the lattice constants determines whether the unit cell and the volume expand or compress. However, contrary to the described trend for Si substitution in Sec. 4.4, the substitution of Co results in a compression of the unit cell by $\sim 2\%$ from 100 to 98 Å³. Cobalt therefore induces an opposing structural effect to Si substitution, which can negate the volume effect of Si for properties like the T_C . These findings corroborate with experimental data provided by the working group of Prof. Guillou, which is depicted in the figure (Fig. 4.20). The experimental data supports a slight decrease of lattice parameter a , a small increase of c and the corresponding compression of the volume. It also matches with the rise of the c/a ratio. As the reason for the shrinkage of the volume, the smaller atomic radius of Co (1.35 Å) compared to Fe (1.40 Å) [224, 225] can be assumed.

Magnetic Moments, Magnetization Saturation and Maximum Energy Product of hexagonal $\text{Fe}_{2-y}\text{Co}_y\text{P}$ Compounds

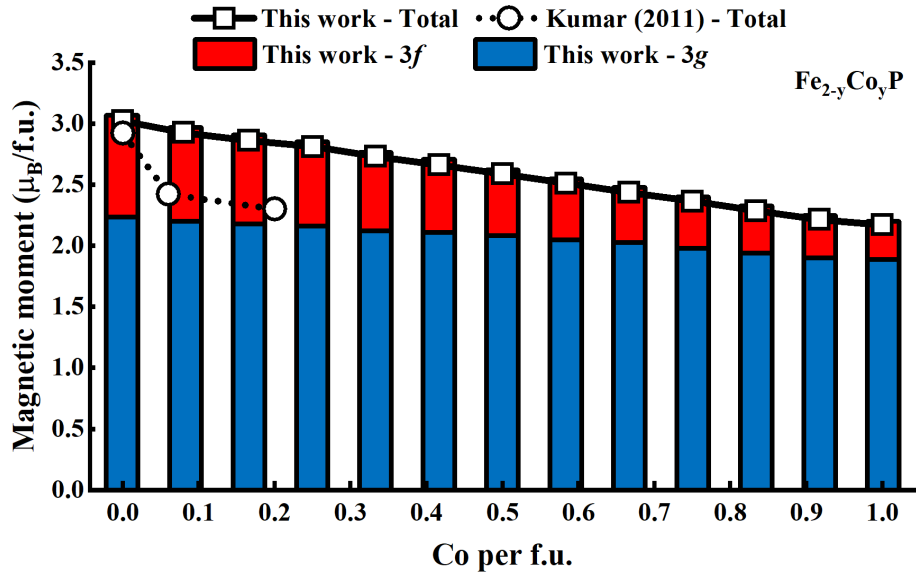


Figure 4.21: Calculated total (black line) and partial magnetic moments (columns) of the 3f (red) and 3g (blue) sites in dependence of the Co concentration in hexagonal $\text{Fe}_{2-y}\text{Co}_y\text{P}$ compounds between $0 \leq y \leq 1$. The experimental data (black dashed line) is taken from Kumar *et al.* [227].

As already experienced for the substitution of Si, the magnetic moment is a defining property that sees extensive changes in case of atomic replacements in the unit cell. When Fe is exchanged by Co, the total magnetic moment of $3.02 \mu_B/\text{f.u.}$ decreases systematically and ends at $2.17 \mu_B/\text{f.u.}$ at $y = 1$ Co per f.u. Investigating the site specific magnetic moments of the $3f$ and $3g$ site in detail, it is visible that mainly the $3f$ magnetic moment decreases. The results for the total and site specific magnetic moments are illustrated in Fig. 4.21. The $3f$ magnetic moment starts at $0.83 \mu_B/\text{f.u.}$ and decreases by 63 % to $0.31 \mu_B/\text{f.u.}$ at 1 Co per f.u. Differently to Si substitution, the $3g$ site is influenced as well, resulting in a decrease of the magnetic moment from $2.24 \mu_B/\text{f.u.}$ to $2.08 \mu_B/\text{f.u.}$ at $y = 0.5$ Co per f.u. This value further diminishes with more Co, leading to a remaining magnetic moment of $1.89 \mu_B/\text{f.u.}$ at $y = 1.0$ Co per f.u. The latter concentration, corresponds to a full substitution of the $3f$ position with Co atoms. Such a drop of the magnetic moment with Co substitution was also reported in literature by Kumar *et al.* [227], who reported a diminishing of the magnetic moment from $2.92 \mu_B/\text{f.u.}$ for substitution-free Fe_2P to $2.30 \mu_B/\text{f.u.}$ at $y = 0.2$ Co per f.u.

To gain a systematic understanding of the influence of Co on the magnetic moments, the magnetovolume and chemical effect of Co were investigated. The structural parameters of the Co substituted compounds were taken as input, with all Co atoms exchanged with Fe. Following this procedure, only the volume was changed and the sole effect of the volume was examined. The chemical effect was then deduced from the drop of the magnetic moment. These results are depicted in Fig. 4.22. The magnetic moments are influenced only by a small margin by a negative magnetovolume effect that yields only a decrease of $0.02 \mu_B/\text{f.u.}$ at $y = 0.5$ Co per f.u. Even the change of the volume corresponding to $y = 1$ Co per f.u. only results in a decrease by $0.13 \mu_B/\text{f.u.}$ However, the chemical effect of Co seems to be the dominant factor, as the sole effect of the Co atoms drastically reduces the magnetic moment by 0.42 and $0.73 \mu_B/\text{f.u.}$ at $y = 0.5$ and 1 Co per f.u., respectively. Additionally, the chemical effect can be seen to decrease the magnetic moments linearly by 0.12 to $0.16 \mu_B/\text{f.u.}$ with each increase of concentration. Consequently, the reduction of the magnetic moments can be attributed to the lower intrinsic magnetic moment of the Co atoms compared to Fe, as well as from changes in the site-resolved spin polarization.

The influence of Co on the total magnetic moment also translates to the magnetization saturation $\mu_0 M_S$ (Eq. 1.2) and maximum energy product $|BH|_{\max}$ (Eq. 1.3), as can be seen in Tab. 4.12. Consequently, this results in a decrease of both properties with increasing Co concentrations. The $\mu_0 M_S$ starts at 1.06 T for the substitution-free Fe_2P compound and gets reduced steadily with Co down to 0.78 T at $y = 1$ Co per f.u. As a consequence of the reduced saturation magnetization, the initial $|BH|_{\max}$ of $\sim 222 \text{ kJ/m}^3$ decreases by

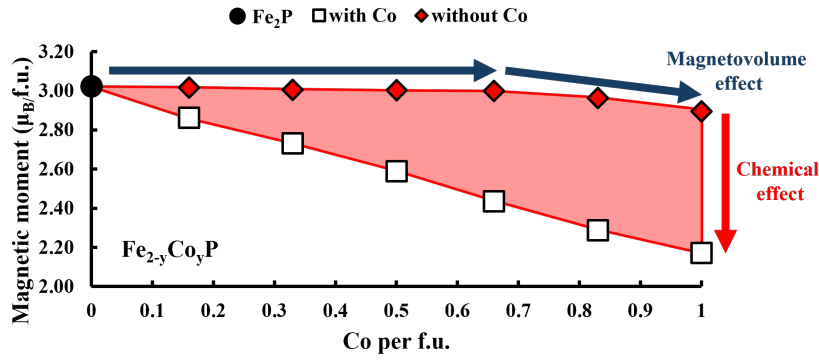


Figure 4.22: Chemical and volume effect of Co on the magnetic moments of hexagonal $\text{Fe}_{2-y}\text{Co}_y\text{P}$ compounds in the range $0 \leq y \leq 1$ Co per f.u. The black squares denote the compounds with Co incorporated into the unit cell, while the red diamonds show the magnetic moment with Co exchanged to Fe in the same unit cells. The magnetovolume effect is shown by a blue arrow, while the chemical effect is depicted in red.

102 kJ/m³ to 120 kJ/m³. This indicates, that a high degree of Co substitution causes such a significant amount of reduction, that the magnetic properties are not sufficient enough to provide a hardness factor above 1. The hardness factor will later be assessed to determine whether a compound is suitable as a hard, semi-hard or soft magnetic material. However, only the decrease of the magnetic properties are reason enough to keep the Co substitution to small amounts. Since the hexagonal Fe_2P compound is only stable up to $y = 0.3$ Co per f.u., only limited data for the hexagonal phase is available.

Using the magnetic moments and structural parameters from the work of Kumar *et al.* [227], theoretical magnetization and $|BH|_{max}$ values can be calculated. The magnetization accounts to 0.99, 0.82 and 0.75 T for Co concentrations of $y = 0, 0.06$ and 0.2 Co per f.u. The corresponding theoretical $|BH|_{max}$ results are determined as 195, 134 and 121 kJ/m³. Although the experimental results are much lower than the theoretical findings of this work, a good agreement of the resulting trends is visible. The seen difference between experiment and theory can be explained by the measurement of the experimental magnetic moments by Kumar *et al.* [227] being conducted at 85 K. This temperature difference can already achieve a significant decrease of the magnetic moments and cause such a deviation.

Curie Temperature and Exchange Interaction Energies of hexagonal $\text{Fe}_{2-y}\text{Co}_y\text{P}$ Compounds

The important property of the Curie temperature is significantly influenced by the substitution of elements into Fe_2P . Conducted screening calculations showed that the element Co has a high potential to increase the Curie temperature T_C . This can also be assumed

Table 4.12: Calculated magnetization saturation $\mu_0 M_S$ and maximum energy product $|BH|_{max}$ derived from the total magnetic moments of the calculated hexagonal $\text{Fe}_{2-y}\text{Co}_y\text{P}$ compounds in the range of $0 \leq y \leq 1$. Calculated results based on the experimental 85 K findings of Kumar *et al.* [227] are added for comparison.

Compound	$\mu_0 M_S$ (T)	$ BH _{max}$ (kJ/m ³)
Fe_2P	1.06	222
$\text{Fe}_{1.92}\text{Co}_{0.08}\text{P}$	1.02	209
$\text{Fe}_{1.84}\text{Co}_{0.16}\text{P}$	1.00	200
$\text{Fe}_{1.75}\text{Co}_{0.25}\text{P}$	0.99	194
$\text{Fe}_{1.67}\text{Co}_{0.33}\text{P}$	0.96	184
$\text{Fe}_{1.59}\text{Co}_{0.41}\text{P}$	0.94	175
$\text{Fe}_{1.5}\text{Co}_{0.5}\text{P}$	0.91	166
$\text{Fe}_{1.42}\text{Co}_{0.58}\text{P}$	0.89	158
$\text{Fe}_{1.33}\text{Co}_{0.67}\text{P}$	0.87	149
$\text{Fe}_{1.25}\text{Co}_{0.75}\text{P}$	0.84	141
$\text{Fe}_{1.16}\text{Co}_{0.84}\text{P}$	0.81	132
$\text{Fe}_{1.08}\text{Co}_{0.92}\text{P}$	0.79	124
FeCoP	0.78	120
Fe_2P^*	0.99	195
$\text{Fe}_{1.92}\text{Co}_{0.08}\text{P}^*$	0.82	134
$\text{Fe}_{1.84}\text{Co}_{0.16}\text{P}^*$	0.78	121

* Calculated from measured data by Kumar *et al* [227] at 85 K.

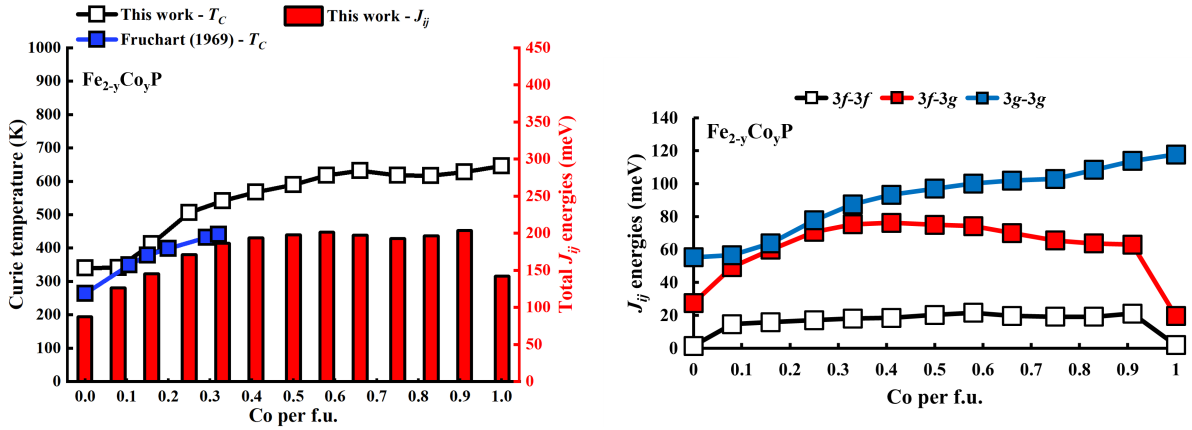


Figure 4.23: **Left:** Change of the calculated Curie temperature (black line) and total exchange interaction energies (red columns) for $\text{Fe}_{2-y}\text{Co}_y\text{P}$ compounds in the range $0 \leq y \leq 1$ Co per f.u. Experimental data from Fruchart *et al.* [106] is given for comparison. **Right:** Site specific exchange interaction energies for $3f-3f$ (black), $3f-3g$ (red) and $3g-3g$ (blue) in dependence of the Co substitution for $\text{Fe}_{2-y}\text{Co}_y\text{P}$ compounds in the range $0 \leq y \leq 1$.

based on the significantly higher T_C of Co (1388 K) compared to Fe (1041 K) [6, 11]. A detailed analysis of the substitution of Fe with Co corroborates with the screening result in Sec. 4.2 and is shown in Fig. 4.23. Furthermore, the increase of T_C matches well with experimental data by Fruchart *et al.* [106] and Kumar *et al.* [228], who both reported an improvement of the T_C connected to Co. Fruchart *et al.* described a rise of the T_C with Co substitution up to 430 K at 0.3 Co per f.u., while Kumar *et al.* measured a T_C of 415 K for 0.2 Co per f.u. in the hexagonal crystal structure.

The improvement of the T_C in this work, can be related to the increasing total exchange interaction energies with the addition of Co. While the J_{ij} energies rise up to $y = 0.8$ Co to a value of almost 200 meV, the T_C reaches a theoretical values above 600 K. A slight stagnation between $y = 0.66$ to 0.81 Co per f.u. is visible and results in stagnating total J_{ij} energies in this area. However, even with a decrease of the J_{ij} energies at $y = 1.0$ Co per f.u., due to the full substitution of the $3f$ site with Co, the Curie temperature still increases to a value of 646 K. This suggests that, in the fully substituted case, either the monotonically increasing $3g$ - $3g$ interaction energies play a more dominant role for the T_C , or additional effects beyond the total J_{ij} sum contribute to the magnetic ordering temperature.

A more thorough investigation on the volume and chemical effect, as done with Si and the magnetic moments, is depicted in Fig. 4.24. These results show that changes of the lattice parameters only exhibit a small negative effect on the exchange interaction energies, decreasing them from 87 meV (substitution-free Fe_2P) to 57 meV at $y = 1$ Co per f.u. On the other hand, the chemical influence of Co substitution reveals a positive effect and increases the J_{ij} s by ~ 110 meV to a value of 197 meV at $y = 0.5$ Co. Even higher Co concentrations have less influence on the exchange interaction energies and the increase only yields an improvement up to 212 meV at 0.92 Co. At 1 Co per f.u., a drop of the J_{ij} s to 142 meV is visible, which is to be expected due to the full occupation of the $3f$ site with Co and therefore a higher symmetry. This investigation shows us that the volume has an almost negligible effect on the exchange interaction energies in case of Co substitution, which matches with findings proposed by Zhuravlev *et al.* [111]. The main contribution to the J_{ij} s can therefore be attributed to the chemical influence of Co itself.

Anisotropy Constant and Anisotropy Field of hexagonal $\text{Fe}_{2-y}\text{Co}_y\text{P}$ Compounds

The key property of the magnetocrystalline anisotropy shows a significant influence of Co substitution. Similar to Si, the nature of this influence is negative and the anisotropy constant diminishes rapidly with increasing Co concentrations. The resulting trend for the calculated K_1 values is depicted in Fig. 4.25. Using the GGA functional, the initial

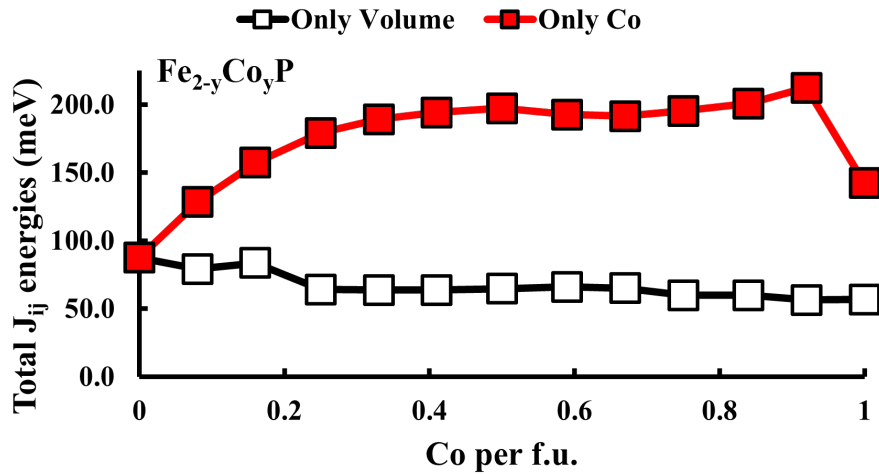


Figure 4.24: Theoretical total exchange interaction energies for the sole effect of volume and Co. The pure volume effect was investigated using the lattice parameters of the Co substituted materials, but with Co replaced by Fe. The chemical effect of Co was calculated by excluding the volume changes and only increasing the amount of Co in the unit cell.

value of 3.26 MJ/m^3 is roughly halved with each substitution step until reaching a value of 0.13 MJ/m^3 at $y = 0.67$ Co per f.u. Higher Co concentrations produce negative K_1 results, that account to -1.14 MJ/m^3 at $y = 1$ Co per f.u. Negative K_1 values indicate that the compound loses its uniaxial anisotropy. Consequently, the anisotropy must be calculated by including the higher-order anisotropy constants, such as K_2 and K_3 , to determine the easy basal plane for the anisotropy [32]. However, this thesis does not cover a more thorough investigation of the higher-order anisotropy terms, so this was not performed here. Employing the LSDA exchange functional, a similar trend can be observed with an even earlier negative value of -0.16 MJ/m^3 at $y = 0.67$ Co per f.u. The results for LSDA exhibit a value of -1.45 MJ/m^3 at $y = 1$ Co. A key difference from Si substitution for the LSDA functional is that the anisotropy constant does not increase with the initial substitution of Co, and K_1 sees a steady decrease. As the reason for this steady decrease a connection to the band filling of the compound can be assumed, resulting in a weakening of the spin-orbit-couplings by the addition of an electron into the band.

As the anisotropy field and the anisotropy constant are closely connected (see Eq. 1.7), H_a experiences the same development with Co as K_1 . This concludes to the same reduction of almost 50 % with each change of concentration. In the case of GGA, this accounts to a decrease from 6.17 T down to 0.3 T at $y = 0.67$ Co. Higher Co concentrations lead to a further decline of H_a to a negative value of -2.96 T at $y = 1$ Co per f.u. Using LSDA, the same trend is visible with even lower values compared to GGA. The lower

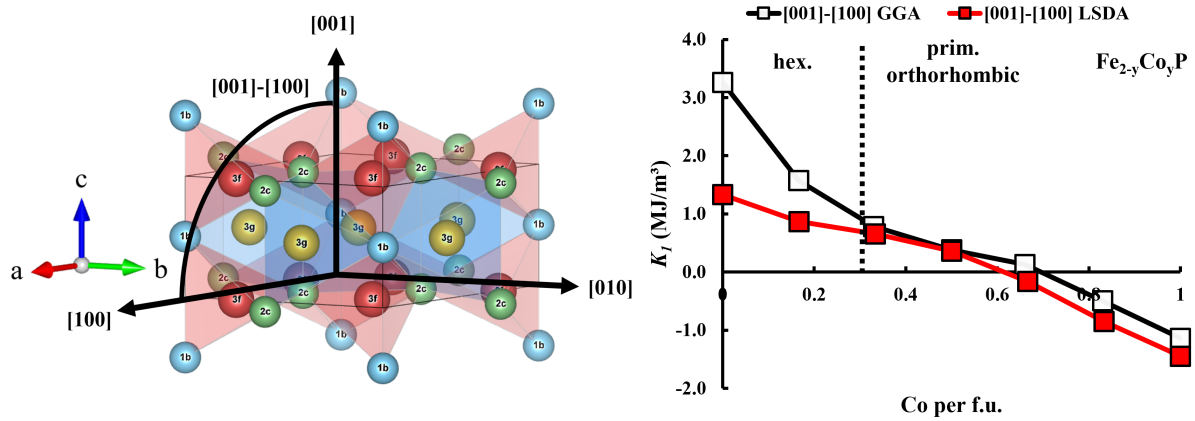


Figure 4.25: Theoretical anisotropy constants K_1 (MJ/m^3) of hexagonal $\text{Fe}_{2-y}\text{Co}_y\text{P}$ compounds in dependence on Co substitution for GGA and LSDA in the range of $0 \leq y \leq 1$. The energies are calculated for the change of the magnetization direction from $[001]$ to $[100]$. The dashed vertical line indicates the experimentally found phase transition from hexagonal to primitive orthorhombic.

result for substitution-free Fe_2P of 2.52 T is reduced to 0.79 T at 0.5 Co per f.u. This reduction continues on with negative values of -0.38, -2.10 and -3.75 T at $y = 0.67$, 0.83 and 1.0 Co per f.u., respectively. Since only limited data for the substitution of Co into Fe_2P is available, the results for the anisotropy can only be compared to literature by Fujii *et al.* [113] and Tujii *et al.* [229] for the substitution of Ni instead of Co. Both reported that Ni causes a decrease of K_1 . These findings are further supported by de Vos *et al.* [110], who identified a negative effect of Co on the anisotropy field up to Co concentrations of $y = 0.3$. The negative effect of Co substitution on the anisotropy can be expected to be a result of the addition of electrons and the connection to the band filling. With more electrons, the optimal amount of electrons is exceeded. The following shift of the Fermi energy leads to a change of the considered states contributing to the anisotropy of the material [148]. A higher energy difference between these occupied and unoccupied states, results in a lower contribution to the MAE. These results show us that Co has a significant negative influence on the anisotropy of the compound. The presented data has to be considered carefully, as the results are all calculated for the hexagonal crystal structure, which is known to transition to a primitive orthorhombic ($Pnma$) phase above $y = 0.3$ Co per f.u. It is therefore not the dominant crystal structure for the complete substitution range. However, the main focus of this investigation is to identify the trends of the substitution with Co in the hexagonal crystal symmetry.

Table 4.13: Calculated anisotropy constant K_1 (MJ/m³) and anisotropy field H_a (T) for ternary hexagonal $\text{Fe}_{2-y}\text{Co}_y\text{P}$ alloys in the range of $0 \leq y \leq 1$ Co per f.u.

Compound	K_1 (MJ/m ³)	H_a (T)
Fe_2P	3.26 (1.33)	6.17 (2.52)
$\text{Fe}_{1.84}\text{Co}_{0.16}\text{P}$	1.57 (0.87)	3.13 (1.72)
$\text{Fe}_{1.67}\text{Co}_{0.33}\text{P}$	0.78 (0.66)	1.64 (1.37)
$\text{Fe}_{1.5}\text{Co}_{0.5}\text{P}$	0.38 (0.36)	0.83 (0.79)
$\text{Fe}_{1.33}\text{Co}_{0.67}\text{P}$	0.13 (-0.16)	0.30 (-0.38)
$\text{Fe}_{1.17}\text{Co}_{0.83}\text{P}$	-0.50 (-0.85)	-1.22 (-2.10)
FeCoP	-1.14 (-1.45)	-2.96 (-3.75)

4.5.2 Primitive Orthorhombic ($Pnma$)

With increasing Co concentrations in the hexagonal crystal structure, a transition to the primitive orthorhombic ($Pnma$) arrangement of the unit cell is observed (see Sec. 4.1.3). This transition is reported at $y = 0.3$ Co per f.u. [106]. Consequently, it becomes necessary to also investigate the influence of Co substitution in compounds adopting the primitive orthorhombic structure in order to assess whether these materials exhibit potentially suitable magnetic properties.

Formation Energy and Competition Energy of primitive Orthorhombic $\text{Fe}_{2-y}\text{Co}_y\text{P}$ Compounds

To assess the suitability of these compounds as magnetic materials the formation and competition energies of the compounds are calculated. Both the formation and competition energy were calculated following the same approach as for the hexagonal phase (see Eq. 4.4 and 4.5). The resulting energy values are shown in Fig. 4.26.

It is noteworthy that, the formation energy of substitution-free Fe_2P in the primitive orthorhombic arrangement exhibits a lower formation energy with -1.3 eV/f.u. compared to the hexagonal structure with -1.28 eV/f.u. This matches with literature by Kong *et al.* [194], who reported a higher stability of the orthorhombic structure by 20 meV/f.u. They also reported that the primitive orthorhombic Fe_2P phase is supposed to be a low-temperature polymorph of the hexagonal phase, thus transforming to the hexagonal phase at ambient temperature. The formation energy depicts a similar trend to that of the hexagonal phase, with decreasing E_{Form} values as the Co concentration

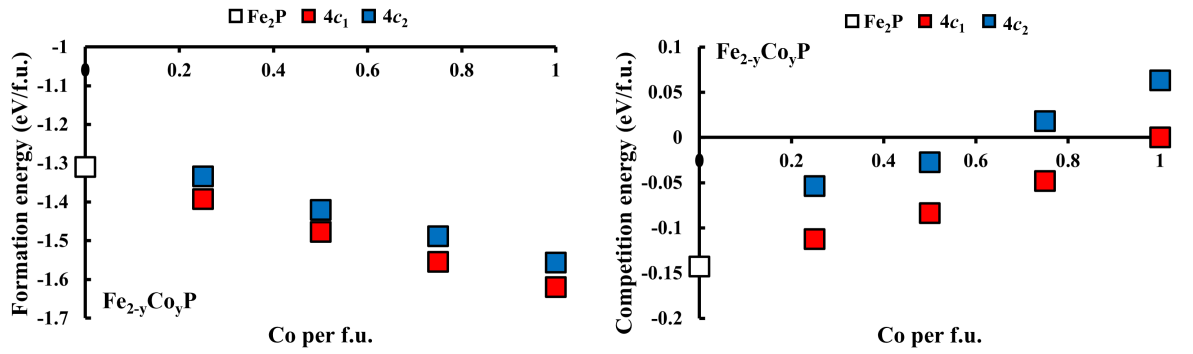


Figure 4.26: **Left:** Theoretical formation energies for ternary primitive orthorhombic $\text{Fe}_{2-y}\text{Co}_y\text{P}$ compounds up to 1 Co per f.u. using Fe, Co and P as reference elements. Substitution-free Fe_2P is given in black, while the $4c_1$ and $4c_2$ sites are given as red and blue squares. **Right:** Calculated competition energies for ternary primitive orthorhombic $\text{Fe}_{2-y}\text{Co}_y\text{P}$ compounds in the range $0 \leq y \leq 1$ Co per f.u. using FeP, FeCoP and Fe as reference phases. Substitution-free Fe_2P is given in black squares, while the $4c_1$ and $4c_2$ sites are given as red and blue squares.

risers. Without Co, the formation energy yields a value of -1.3 eV/f.u., which decreases with Co to -1.62 eV/f.u. at $y = 1$ Co per f.u. Another similarity to the hexagonal phase is the clear preference for one of the two Fe sites for substitution. The $4c_1$ site is favored over the $4c_2$ position in all investigated cases, as can be seen in Fig. 4.26. The difference between both substitution sites is calculated to range between 56 and 66 meV/f.u., with the largest difference of 66 meV/f.u. at $y = 0.75$ Co per f.u.

However, the competition energy calculations for the primitive orthorhombic crystal structure reveal a different trend than that seen in the formation energies. With a higher Co content, the energy increases for both substitution sites. The energy difference between the two sides remains unchanged, but the initial energy of -0.14 eV/f.u. at $y = 0$ Co increases to 0.2 and 63 meV/f.u. for the $4c_1$ and $4c_2$ position, respectively. This preference of $4c_1$ prevails for all considered compounds. The $4c_2$ site yields positive energies at Co concentrations of $y \geq 0.75$ Co and the $4c_1$ position only demonstrates a positive value at $y = 1$ Co per f.u. Since the competition energies are more reliable for making predictions as they describe the possibility of formation compared to the binary compounds, it can also be assumed that the primitive orthorhombic phase will become unstable at higher Co concentrations.

Lattice Constants and Volume of primitive Orthorhombic $\text{Fe}_{2-y}\text{Co}_y\text{P}$ Compounds

The substitution of Co into the primitive orthorhombic structure impacts the lattice constants and the volume of the unit cell. The already mentioned lattice constants for

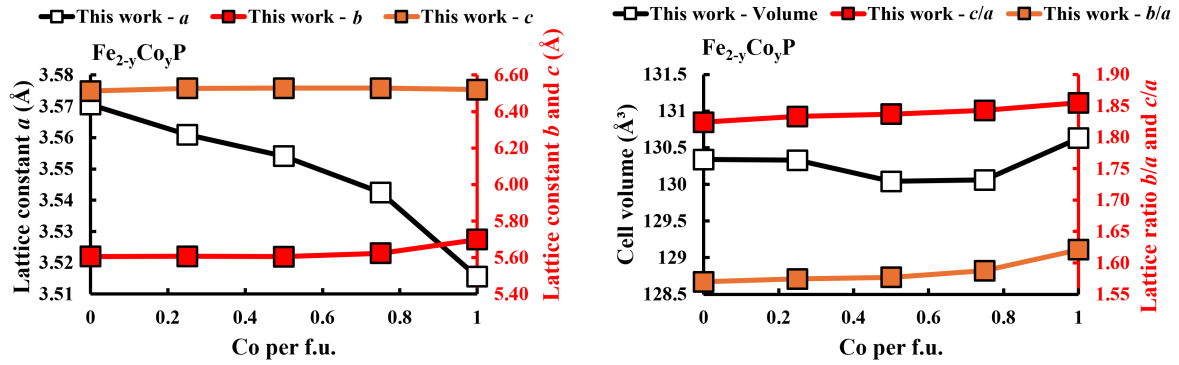


Figure 4.27: **Left:** Theoretical lattice constants a (black), b (red) and c (light red) for the primitive orthorhombic crystal structure in the range of $0 \leq y \leq 1$ Co per f.u. **Right:** Calculated volume (black) and lattice ratios c/a (red) and b/a (orange) for the primitive orthorhombic crystal structure in the range of $0 \leq y \leq 1$ Co per f.u.

substitution-free Fe_2P in the primitive orthorhombic structure are $a = 3.571$, $b = 5.606$ and $c = 6.512$ Å. The influence of Fe for Co substitution is comparable to the substitution into the hexagonal crystal structure, as illustrated in Fig. 4.27.

The lattice constant a experiences a similar decrease in dependence on Co substitution and reduces with $y = 1$ Co per f.u. to 3.516 Å. On the other hand, the other two constants b and c only see minor changes. Constant b remains constant up to $y = 0.5$ Co at ~ 5.606 Å. Above this concentration, it increases slightly to 5.624 and 5.699 Å at $y = 0.75$ and 1 Co per f.u., respectively. The lattice parameter c only sees a lengthening from 6.512 to 6.520 at $y = 1$ Co per f.u. This consequently effects the volume and the lattice ratios c/a and b/a . The unit cell volume decreases to a minimum of 130.04 Å³ at 0.5 Co. This is followed by an enlargement to 130.63 Å³. The rise of the volume can be attributed to the visible elongation of c at high amounts of Co. Both lattice ratios c/a and b/a see the same, but less pronounced, rise with Co as the hexagonal compounds. The c/a ratio is determined as 1.824 at $y = 0$ Co which increases to 1.855 at $y = 1$ Co per f.u. The other lattice ratio b/a also rises from 1.570 to 1.621 for the same Co concentrations. Comparing these results to the hexagonal crystal structure, the influence of Co on the lattice parameters seems to be much smaller and less impactful. This can be explained due to the lattice constants a and b being identical in the hexagonal symmetry. This enlarges the impact of a change of a much more in that structure. The size difference between Fe and Co (140 vs. 135 pm [224, 225]) can again be assumed as the reason for the change of the volume and lattice parameters.

Magnetic Moments, Magnetization Saturation and Maximum Energy Product of primitive Orthorhombic $\text{Fe}_{2-y}\text{Co}_y\text{P}$ Compounds

With the substitution of Co into the unit cell not only the lattice parameters are affected. The magnetic moments are influenced by both the volume effect of the lattice distortions and the chemical effect of Co. The magnetic moment of substitution-free Fe_2P in the primitive orthorhombic structure ($Pnma$) exhibits a mediocre total magnetic moment of $1.73 \mu_B/\text{f.u.}$ Co substitution of 0.25 Co per f.u. increases this initial value by 13 % to $1.95 \mu_B/\text{f.u.}$ Following this first improvement, the rise of the magnetic moments drastically flattens and further enhancements by Co result in increases between 1.3 and 3.9 %. This accounts to values of 1.98, 2.02 and $2.10 \mu_B/\text{f.u.}$ at $y = 0.5$, 0.75 and 1 Co per f.u., respectively.

For a systematic understanding, the site specific magnetic moments were investigated and the resulting values are depicted in Fig.4.28. The substitution-free Fe_2P compound exhibits a magnetic moment of $0.17 \mu_B/\text{f.u.}$ in the $4c_1$ position. The $4c_2$ site is determined as $1.59 \mu_B/\text{f.u.}$ These values both improve with Co substitution to 0.33 and $1.67 \mu_B/\text{f.u.}$ at $y = 0.25$ Co per f.u., respectively. This finding is in contrast to the observed behavior for the hexagonal symmetry. A higher concentration of Co only marginally influences both magnetic sites, which rise to 0.37 and $1.69 \mu_B/\text{f.u.}$ at 0.75 Co. A full substitution of the $4c_1$ site with Co yields a small decrease to $0.33 \mu_B/\text{f.u.}$, while the $4c_2$ position simultaneously improves to $1.8 \mu_B/\text{f.u.}$ This small overall increase of the total magnetic moment translates into a slight enhancement of the magnetization saturation $\mu_0 M_S$ and the maximum energy product $|BH|_{max}$. The resulting values for both properties are listed in Tab. 4.14. The magnetization rises from 0.62 T up to 0.75 T at $y = 1$ Co per f.u., while the corresponding $|BH|_{max}$ improves from 76 kJ/m^3 to 111 kJ/m^3 . Although these results are much lower than those for the hexagonal crystal structure, the substitution of Co raises the compounds to acceptable levels. The increase of the magnetic moments can be attributed to the comparably low magnetic moments of the compound and a magnetovolume effect. Even these small lattice distortions cause a change of the ratios and the atomic distances in the unit cell. This optimizes the distances, corresponding to a higher volume and a positive magnetovolume effect. It is conceivable that with further changes of the volume a higher magnetic moment can be achieved. This could be investigated in future works.

Curie Temperature and Exchange Interaction Energies of primitive Orthorhombic $\text{Fe}_{2-y}\text{Co}_y\text{P}$ Compounds

As the Curie temperature is readily influenced by the substitution with other elements, the impact of these atomic changes on the primitive orthorhombic structure are of special

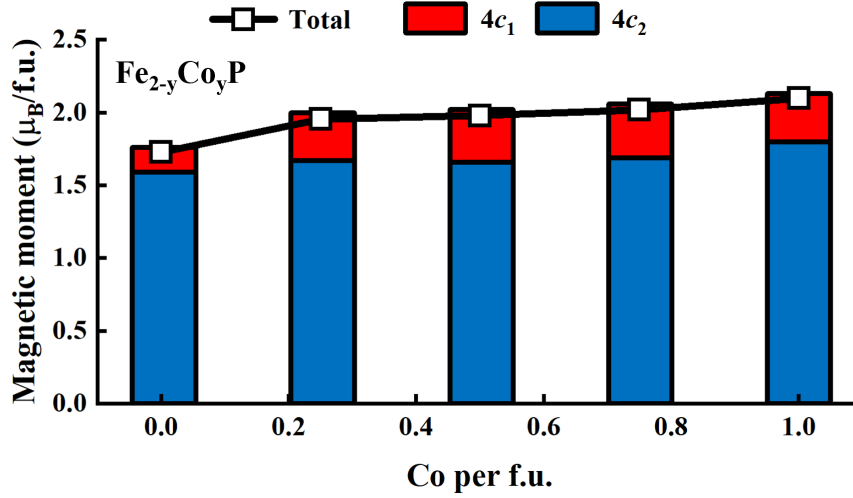


Figure 4.28: Calculated total (black line) and partial magnetic moments of the $4c_1$ (red column) and $4c_2$ (blue column) sites in dependence of the Co concentration in primitive orthorhombic $\text{Fe}_{2-y}\text{Co}_y\text{P}$ compounds in the range of $0 \leq y \leq 1$ Co per f.u.

Table 4.14: Theoretical magnetization saturation $\mu_0 M_S$ (T) and maximum energy product $|BH|_{max}$ (kJ/m³) of the ternary primitive orthorhombic ($Pnma$) structured $\text{Fe}_{2-y}\text{Co}_y\text{P}$ compounds with y up to 1 Co per f.u.

Compound	$\mu_0 M_S$ (T)	$ BH _{max}$ (kJ/m ³)
Fe_2P	0.62	76
$\text{Fe}_{1.92}\text{Co}_{0.25}\text{P}$	0.70	97
$\text{Fe}_{1.84}\text{Co}_{0.5}\text{P}$	0.71	100
$\text{Fe}_{1.75}\text{Co}_{0.75}\text{P}$	0.72	104
FeCoP	0.75	111

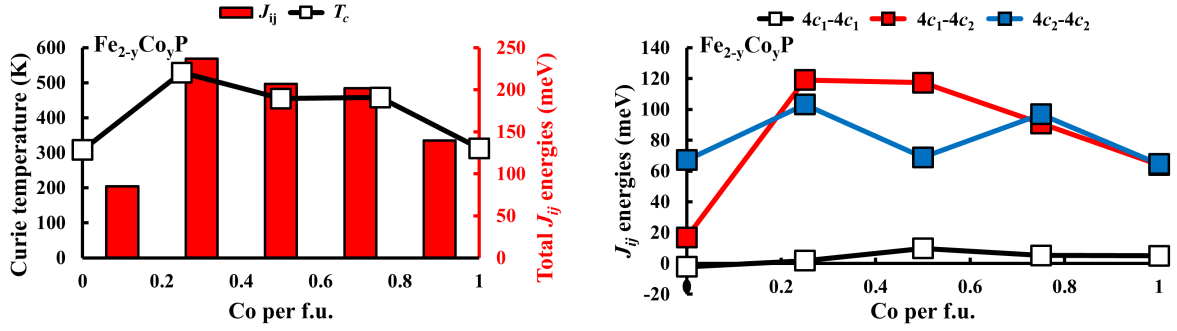


Figure 4.29: **Left:** Calculated Curie temperature (black line) for the ternary $\text{Fe}_{2-y}\text{Co}_y\text{P}$ compounds up to $y = 1$ Co per f.u. The exchange interaction energies of these compounds are shown by red columns. **Right:** Site specific exchange interaction energies for the $4c_1-4c_1$, $4c_1-4c_2$ and $4c_2-4c_2$ interactions of the Fe and Co atoms in ternary $\text{Fe}_{2-y}\text{Co}_y\text{P}$ alloys with $0 \leq y \leq 1$ Co per f.u.

interest. The substitution-free compound starts with a theoretical T_C of 308 K, which is below the calculated T_C of the hexagonal structure (340 K). The incorporation of Co results in an increase of the T_C to a value of 529 K at Co concentrations of $y = 0.25$ Co. However, higher amounts of Co lead to a reduction of the T_C to ~ 455 K at $y = 0.5$ Co and 313 K at $y = 1$ Co per f.u.

This effect can be explained by the investigation of the exchange interaction energies J_{ij} of the compounds. In Fig. 4.29 are both the calculated T_C s and the J_{ij} energies depicted. A parallel development of the J_{ij} energies and the T_C s is visible. Both the J_{ij} s and the T_C s exhibit an increase up to $y = 0.25$ Co, which is then followed by a decrease at Co concentrations $y \geq 0.25$ Co per f.u. In this trend, the J_{ij} energies increase from 85 to 237 meV, which explains the initial jump of the T_C . Thereafter, the exchange interaction energies decrease to 207, 202 and 140 meV at $y = 0.5$, 0.75 and 1 Co per f.u., respectively.

The site specific exchange interaction energies can be analyzed in more detail by investigating the $4c_1-4c_1$, $4c_1-4c_2$ and $4c_2-4c_2$ interaction energies. The site specific interactions will be handled according to their size. Therefore the $4c_1-4c_2$ interactions will be explained first, followed by $4c_2-4c_2$. The last contribution is the $4c_1-4c_1$ exchange interaction. Starting with the $4c_1-4c_2$ interactions, the initial value of 17 meV is tremendously improved to 119 meV with 0.25 Co per f.u. However, further Co substitution yields a steady decrease of the $4c_1-4c_2$ interactions, resulting in values of 117, 91 and 64 meV at 0.5, 0.75 and 1 Co per f.u., respectively. The reason for this decrease, can be deduced to be due to the chemical effect of Co and the slight decrease of the volume between 0.25 and 0.75 Co per f.u. The $4c_2-4c_2$ interaction energies are determined to yield an initial value of 67 meV at 0 Co per f.u. This value is then seen to oscillate between 60 and 103 meV in dependence of Co concentration. The smallest site specific contribution, can

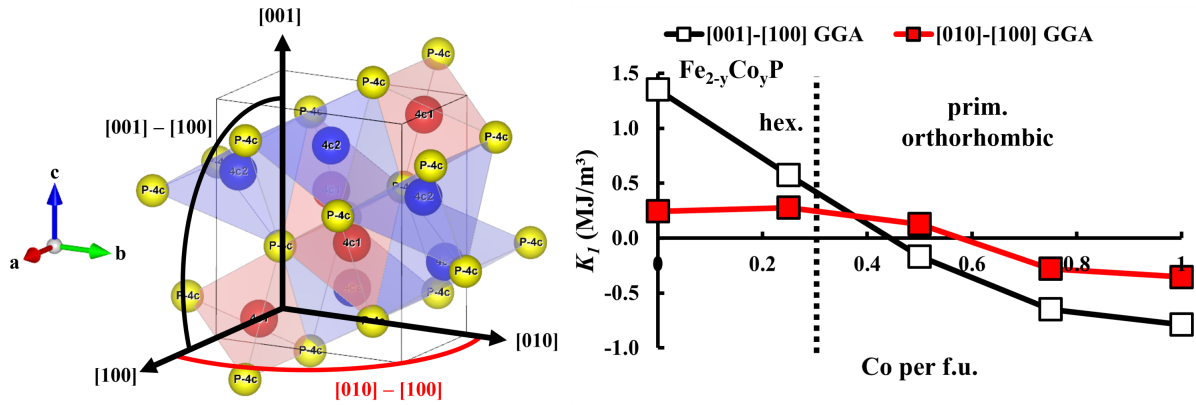


Figure 4.30: Theoretical anisotropy constants K_1 of ternary $\text{Fe}_{2-y}\text{Co}_y\text{P}$ compounds with $0 \leq y \leq 1$ Co per f.u. for the [001]-[100] (black) and the [010]-[100] (red) direction using the GGA exchange functional. The vertical dashed line marks the experimentally reported phase transition from hexagonal to prim. orthorhombic [194].

be attributed to the $4c_1$ - $4c_1$ interactions, which are negligibly small with a maximum of 10 meV at $y = 0.5$ Co per f.u. The greatest influence of Co can therefore be observed for the $4c_1$ - $4c_2$ interaction, yielding a substantial increase of 102 meV at low Co concentrations. The highest T_C can consequently be seen for the low Co case of $y = 0.25$, indicating that a low degree of Co substitution is optimal for the primitive orthorhombic crystal symmetry.

Anisotropy Constant and Anisotropy Field of primitive Orthorhombic $\text{Fe}_{2-y}\text{Co}_y\text{P}$ Compounds

With the primitive orthorhombic crystal structure appearing at medium to high concentrations of Co in the compound, the anisotropy of the primitive orthorhombic needs to be investigated as well. This helps to clarify the influence of Co on the secondary structure. The calculated first-order anisotropy constants K_1 (see Eq. 1.5) are depicted in Fig. 4.30 for the ternary $\text{Fe}_{2-y}\text{Co}_y\text{P}$ compounds with $0 \leq y \leq 1$ Co per f.u. in the primitive orthorhombic crystal structure.

It is visible, that an increase in the concentration of Co results in a loss of the anisotropy. The initial value at $y = 0$ Co is calculated as 1.35 MJ/m³ for directional change from [001] to [100]. This value undergoes a steady reduction connected to further Co substitution. At 0.5 Co, K_1 yields a negative value. Negative values of K_1 indicate the loss of uniaxial anisotropy, implying that higher-order anisotropy constants (K_2 , K_3 , ...) would be required to determine the easy plane of magnetization. The resulting value is further minimized to -0.79 MJ/m³ at $y = 1$ Co per f.u. An investigation of the directional change from [010] to [100] reveals a divergent trend from that observed in the first direc-

tional change. In this particular instance, the energy remains relatively constant ~ 0.25 to 0.28 MJ/m^3 until y reaches 0.5 Co per f.u. At this point, a positive anisotropy constant of 0.13 MJ/m^3 is achieved. This is in contrast to the value of the [001]-[100] directional change with -0.17 MJ/m^3 . Even higher concentrations of Co result in a similar loss of the uniaxial anisotropy, indicated by negative anisotropy constants of -0.28 and -0.35 MJ/m^3 at 0.75 and 1 Co per f.u., respectively. Note, that the change from the easy ([001]) to the hardest ([100]) direction is the important value as it depicts the highest theoretically possible energy difference between two directions. The directional change [010]-[100] is mainly shown for completeness.

The anisotropy field H_a sees the same trends as K_1 as they turn to negative values at 0.5 (> 0.5) Co per f.u. for the [001]-[100] ([010]-[100]) directional change. However, since the calculation of the anisotropy field also includes the magnetization saturation $\mu_0 M_S$, relatively high H_a values compared to other compounds can be achieved. This results in a H_a of 4.38 and 2.57 T at $y = 0$ Co for the [001]-[100] and [010]-[100] investigations, respectively. The anisotropy field H_a , derived from K_1 and $\mu_0 M_S$ (Eq. 1.7), represents a theoretical upper limit to the coercivity field and should not be directly compared with experimental coercivity values. With the complete substitution of the $4c_1$ site, this translates to negative H_a results of -2.10 and -1.53 T. This fast decrease of K_1 and H_a together with the loss of uniaxial anisotropy at medium Co concentrations, leads to the assumption that only small amounts of Co are suitable for the substitution into the primitive orthorhombic $\text{Fe}_{2-y}\text{Co}_y\text{P}$ compound. The reason for the rapid decrease is again connected to the band filling of the compound. The addition of electrons shifts the Fermi energy and increases the energy difference between the occupied and unoccupied states. This causes the anisotropy to reduce and causes even a loss of the uniaxial anisotropy. Note, that due to the primitive orthorhombic structure not being the main focus of this work, the anisotropy was only investigated using the GGA functional for this crystal structure.

Assessment of the primitive Orthorhombic Crystal Structure for $\text{Fe}_{2-y}\text{Co}_y\text{P}$ Compounds

The primitive orthorhombic crystal structure shows lower formation and competition energies than the hexagonal phase, which indicates a higher stability at 0 K [194]. However, it is experimentally known that the primitive orthorhombic phase transitions to the hexagonal one at ambient temperature. Even though the magnetic moments, and consequently $\mu_0 M_S$ and $|BH|_{\max}$, are slightly increased by Co substitution $y \geq 0.25$ Co, the T_C , the exchange interaction energies J_{ij} and the anisotropy constant K_1 are drastically decreasing. This excludes these $\text{Fe}_{2-y}\text{Co}_y\text{P}$ compounds at higher Co concentrations as suitable

hard magnetic materials. The investigation of the substitution of Co into the primitive orthorhombic structured Fe_2P compound leads to the general conclusion that even with the lower formation and competition energy, the hexagonal structure is to be preferred, because of its superior magnetic properties. With this conclusion in mind, only the hexagonally structured compounds are further examined for the simultaneous substitution of Si and Co in this thesis.

4.6 Quaternary $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ compounds

4.6.1 Simultaneous Si and Co Substitution

After elucidating the individual effects of Si and Co substitution on the structural stability and magnetic properties of Fe_2P -based compounds, their simultaneous substitution is investigated in order to assess whether a balanced combination of enhanced Curie temperature, magnetism and anisotropy can be achieved. Bao *et al.* [68] reported an increase of the stability range of the hexagonal Fe_2P crystal structure with simultaneous substitution of both elements. They reported a phase stability of the hexagonal structure up to $x = 0.5$ Si, when at least $y = 0.25$ Co per f.u. is present. They defined as the most promising compositional range Si concentrations between 0.1 and 0.25 Si per f.u., together with Co contents ranging from 0.25 to 0.75 Co per f.u. Based on these findings, the Si concentrations $x = 0.08, 0.16$ and 0.41 Si per f.u. were examined in detail to account for both the proposed low Si phases, as well as high Si containing compounds. For completeness, in all three cases the hexagonal structure was investigated for a range of $0 \leq y \leq 1$ Co per f.u. The investigation of the quaternary compounds focused entirely on hexagonally structured compounds, with neither the primitive orthorhombic nor the BCO phase being studied. The hexagonal crystal structure is mostly predominant in the set compositional ranges at room temperature (see Fig. 1.16). To quickly summarize the room temperature phase stabilities found by Bao *et al.* [68], the stable range at 0.08 Si accounts to Co concentrations up to ~ 0.4 Co per f.u., while the stable range increases at 0.16 Si to ~ 0.6 Co per f.u. A small exception present the 0.41 Si compounds, where the hexagonal phase starts to be stable at a Co concentration of 0.15 Co per f.u. However, the stability then reaches up to 1 Co per f.u. This range of the hexagonal crystal symmetry presents a variety of promising quaternary compounds that can be considered as potential hard magnets.

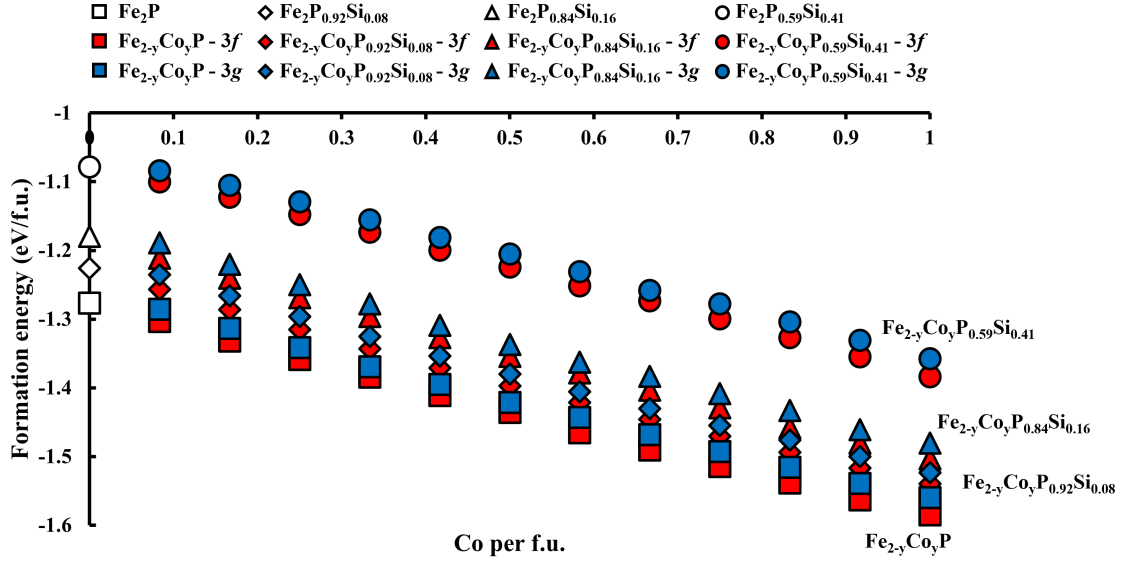


Figure 4.31: Theoretical formation energy at 0 K of hexagonal $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ alloys with $x = 0.0$ (squares), 0.08 (diamonds), 0.16 (triangles) and 0.41 Si (circles) and y in the range $0 \leq y \leq 1$ Co per f.u. The formation energies of the Co-free compounds are shown in black, while the $3f$ Wyckoff position is shown in red and the $3g$ site in blue for all Co substituted materials.

4.6.2 Formation energy and Competition Energy of hexagonal $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ Compounds

As already seen for ternary Si and Co substitutions, the formation and competition energies were calculated for each compound to achieve a fundamental understanding of the 0 K phase stability. The formation energy was calculated analogous to the ternary cases by using the calculated energy values of the pure elements as reference states. This culminates in a combination of both equations used in Sec. 4.4 and Sec. 4.5, that can be expressed as follows:

$$E_{Form} = (E(\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x) - (2-y) \cdot E(\text{Fe}) - y \cdot E(\text{Co}) - (1-x) \cdot E(\text{P}) - x \cdot E(\text{Si})) \cdot \frac{1}{N}, \quad (4.6)$$

with $E(\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x)$, $E(\text{Fe})$, $E(\text{Co})$, $E(\text{P})$ and $E(\text{Si})$ as the calculated energies at 0 K for each compound or element and N as the number of functional units in the unit cell of the $E(\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x)$ compound. The resulting formation energy values for all compounds with 0.08 , 0.16 and 0.41 Si per f.u. are cumulated in Fig. 4.31 in dependence of the substituted amount of Co. For completeness, the compounds describing the ternary Co substitution ($x = 0$ Si per f.u.) are also depicted in the image.

In these calculations, all Fe atoms in both Wyckoff sites ($3f$ and $3g$) were investigated for Co substitution. The energetically most favorable crystal composition was then taken

as input for further substitutions. This ensures a systematic approach for the substitution of the atoms into the crystal structure. The resulting formation energies for all compounds bridge the trends of ternary Si and Co substitution. In all considered materials the $3f$ position is clearly favored against the $3g$ site. The described preference of the $3f$ position for Co therefore applies for quaternary compounds independently from Si and Co concentration and matches with the ternary experimental Co findings [111, 226]. The favored $3f$ position is therefore taken as the main point of interest for the energy evaluation. It is notable, that the substitution of Si shifts the complete range of compounds upwards to higher energies. The Si-free compounds ($x = 0$) consequently show the lowest energy yields, starting at -1.28 eV/f.u. These initial values are steadily decreasing and at a full substitution ($y = 1$ Co per f.u.) of the $3f$ site an energy of -1.58 eV/f.u. is achieved. At 0.08, 0.16 and 0.41 Si, the formation energy starts at -1.23, -1.18 and -1.08 eV/f.u., respectively. These values then decreases in all three cases with rising Co contents until a complete filling of the $3f$ position with Co is realized. At this point the energy accounts to values of -1.54, -1.50 and -1.38 eV/f.u. for the respective Si concentrations.

The competition energy for the quaternary $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ materials was considered next to the formation energy to provide a more applicable stability assessment at 0 K. In this case, the competition energy was calculated using the computed energies of FeP, FeSi, FeCo, FeCoP, Fe and Co as reference phases. The binary materials were chosen based on their high stability and therefore high possibility to appear as decomposition products (see binary formation energies diagrams Fig. 5.1 in appendix A). The ternary FeCoP material was used, as it is the only explicitly known stable ternary compound consisting of Fe, Co and P. This concludes in the following equations, dependent on the concentration of Co:

$$\begin{aligned}
E_{Comp} = & (E(\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x) - ((1-x) - y) \cdot E(\text{FeP}) - x \cdot E(\text{FeSi}) \\
& - (x + ((1-x) - y)) \cdot E(\text{Fe}) - y \cdot E(\text{FeCoP})) \cdot \frac{1}{N}, \\
& \text{for } y \leq (1-x);
\end{aligned} \tag{4.7}$$

$$\begin{aligned}
E_{Comp} = & (E(\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x) - (1-x) \cdot E(\text{FeCoP}) - x \cdot E(\text{FeSi}) \\
& - (y - (1-x)) \cdot E(\text{FeCo}) - (((2-y) - (1-x) - x) \\
& - (y - (1-x))) \cdot E(\text{Fe})) \cdot \frac{1}{N}, \\
& \text{for } 0.66 \leq y \leq 0.75 \text{ and } x = 0.41;
\end{aligned} \tag{4.8}$$

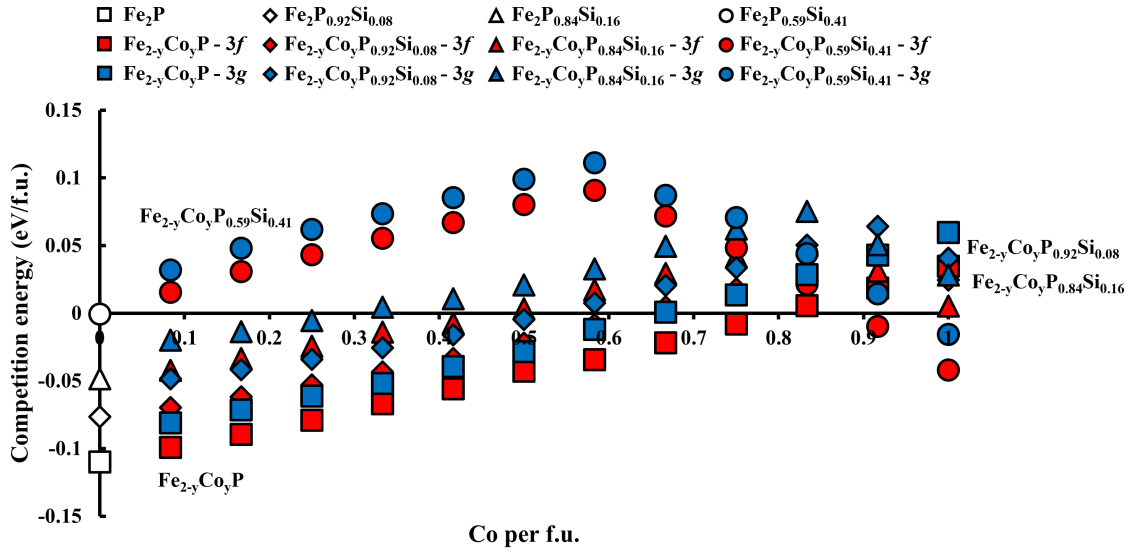


Figure 4.32: Theoretical competition energy at 0 K of hexagonal $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ alloys with $x = 0.0$ (squares), 0.08 (diamonds), 0.16 (triangles) and 0.41 Si (circles) and y in the range $0 \leq y \leq 1$ Co per f.u. The competition energies of the Co-free compounds are shown in black, while the $3f$ Wyckoff position is shown in red and the $3g$ site in blue for all Co substituted materials.

$$\begin{aligned}
 E_{Comp} = & (E(\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x) - (1-x) \cdot E(\text{FeCoP}) - x \cdot E(\text{FeSi}) \\
 & - ((2-y) - (1-x) - x) \cdot E(\text{FeCo}) - ((y - (1-x)) - \\
 & ((2-y) - (1-x) - x)) \cdot E(\text{Co})) \cdot \frac{1}{N}, \\
 & \text{for: } y = 0.92 \text{ and } x = 0.16; \\
 & \text{for: } 0.84 \leq y \leq 0.92 \text{ and } x = 0.41;
 \end{aligned} \tag{4.9}$$

$$\begin{aligned}
 E_{Comp} = & (E(\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x) - (1-x) \cdot E(\text{FeCoP}) - x \cdot E(\text{FeSi}) \\
 & - (y - (1-x)) \cdot E(\text{Co})) \cdot \frac{1}{N}, \\
 & \text{for } y = 1.
 \end{aligned} \tag{4.10}$$

The theoretical competition energy results for each compound using these equations are illustrated in Fig. 4.32 for 0 K investigations.

In contrast to the ternary competition energy calculations, the combined effects of Si and Co have to be taken into account. This leads to the interesting case of a higher Co concentration compared to P. As the amount of Co is dealt with by the reference phase of FeCoP, a higher amount of Co than P limits the consideration of this phase, due to the simultaneous rise of the P concentration. This issue is resolved by using the second

and third equation, including FeCo and either the unary element Fe and Co. The last equation is then used for all Si concentrations and $y = 1$ Co per f.u. For 0.08 Si, only the last compound is affected by this change of equations, whereas at 0.16 and 0.41 Si, all materials with $y > 0.84$ and 0.59 Co per f.u. experience this change. This alteration of the equations is visible as a shift from an upwards to a downwards trend in the competition energy. When only equation 4.7 is used, which fully accounts for the high stability of FeCoP, the competition energy values increase from -0.11, -0.077, -0.049 and -0.0007 eV/f.u. to 0.035, 0.047, 0.050 and 0.091 eV/f.u., respectively, at $x = 0, 0.08, 0.16$ and 0.41 Si. These values were achieved at Co concentrations of $y = 1, 0.91, 0.83$ and 0.58 Co per f.u. After these maxima, the energy decreases due to the inclusion of the less stable binary (FeCo) and unary (Fe and Co) reference materials. The quaternary compounds yield competition energies of 0.035, 0.025, 0.005 and -0.042 eV/f.u. for the full substitution of the $3f$ position at 0, 0.08, 0.16 and 0.41 Si per f.u.

For all Si compositions, the energy results are seen to turn positive after a certain Co concentration is reached. These Co concentrations are, respectively, 0.83, 0.66, 0.5 and 0.08 Co per f.u. for the Si compound range of 0, 0.08, 0.16 and 0.41 Si per f.u. These findings suggest that higher Si concentrations restrict the amount of Co that can be substituted into hexagonal $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ materials at 0 K. Especially at high Si concentration, no Co substitution should therefore be possible as all competition energies yield values > 0 eV/f.u. This would indicate, that quaternary compounds only stabilize below Si concentrations of 0.41 Si. Nevertheless, it is known that these high Si containing quaternary compounds exist, as Bao *et al.* [68] was able to synthesize some of them. However, these calculations only represent a temperature of 0 K. Finite temperature calculations are covered later in this work to investigate the effect of temperature on the stability of the compounds.

4.6.3 Lattice Constants and Volume of hexagonal $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ Compounds

With the simultaneous substitution of Si and Co into the Fe_2P compound the lattice constants are influenced by the combined effects of both elements. This can be seen in Tab. 4.15 and Fig. 4.33. The table and the figure also depict the c/a ratio, volume and the magnetic moment per functional unit of the compounds. The lattice parameters are important, as they give insights into possible reasons for changes of the T_C s and J_{ij} energies. Especially the c/a ratio and therefore the distances between the atoms, are reported to influence the exchange interaction energies in experimental results for quaternary compounds [43, 68]. In $(\text{Mn,Fe})_2(\text{P,Si})$ compounds, a general rise of c/a is expected to yield a decrease of the T_C [230].

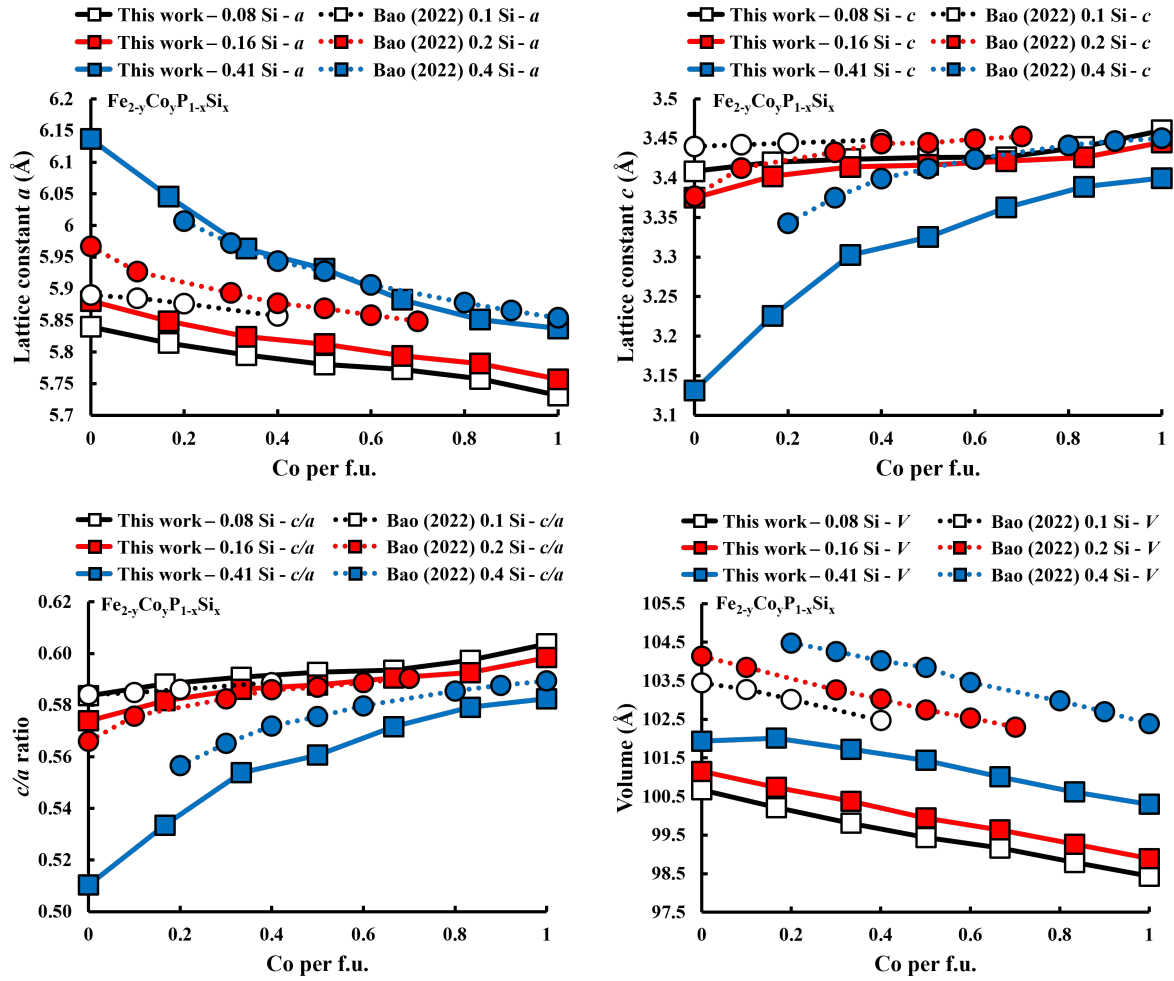


Figure 4.33: Calculated lattice parameters a and c as well as unit cell volume and c/a ratio for the hexagonally structured quaternary $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ compounds with $x = 0.08, 0.16$ and 0.41 Si per f.u. Available experimental data from Bao *et al.*[68] is added for comparison.

As already seen, the substitution of Si increases the lattice constant a and reduces c , while Co opposingly reduces a and increases c . These developments are attributed to the larger and smaller atom size of Si and Co compared to P and Fe [224, 225]. Both of these effects are translated to the quaternary $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ compounds in this work. The ternary $\text{Fe}_2\text{P}_{0.92}\text{Si}_{0.08}$ compound exhibits the initial lattice constants $a = 5.840$ Å and $c = 3.408$ Å. With increasing Co concentrations, the lattice constant a contracts to a final value of 5.731 Å at $y = 1$ Co per f.u. On the other hand, the lattice constant c increases slightly with Co, except for no change between $y = 0.5$ and 0.67 Co per f.u. After this plateau, c enlarges and ends with 3.460 Å at 1 Co per f.u. This consequently affects the c/a ratio of the compound and results in an increase from 0.5836 at $y = 0$ Co to 0.6037 at $y = 1$ Co per f.u. The unit cell of these compounds retracts with additional Co and the volume decreases from 100.67 to 98.44 Å.

At Si concentrations of $x = 0.16$ and 0.41 Si per f.u., the same changes for a and c are visible. At 0.16 Si, the lattice constants yield initial values of $a = 5.881$ Å and $c = 3.375$ Å. Co substitution reduces a and enlarges c to 5.757 and 3.445 Å at $y = 1$ Co per f.u. Following the change of the lattice constants, the c/a ratio increases similar to 0.08 Si. The ratio accounts to 0.5739 at 0 Co per f.u., which changes with Co to 0.5877 at $y = 0.5$ Co and ends at 0.5984 at $y = 1$ Co per f.u. The enlargement and retraction of the lattice constants result in a drop of the volume from 101.15 to 98.89 Å³.

At even higher Si concentrations of $x = 0.42$ Si per f.u., the lattice constants are determined as $a = 6.137$ and $c = 3.131$ Å. Increasing amounts of Co cause these values to change according to the influence of Co, namely a decrease of a to 5.837 Å and an increase of c to 3.400 Å at 1 Co per f.u. This translates to an improvement of the c/a ratio from 0.5102 to 0.5824 at 1 Co per f.u. However, it is noteworthy that in case of the high Si quaternaries, the lattice constants experience a significantly higher change with Co than at lower Si concentrations. This result is depicted in Fig. 4.33. Nevertheless, the changes of a and c , compensate each other and result in a similar unit cell contraction with Co compared to compounds with less Si incorporated. The volume decreases from 101.94 to 100.30 Å³.

Since only limited data is available for quaternary $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ compounds, the results can only scarcely be compared with experimental data. However, data by He *et al.* [42] and Bao *et al.* [68] show similar results for the evolution of the lattice constants. He *et al.* [42] investigated increasing Si concentrations in $\text{Fe}_{1.92}\text{Co}_{0.08}\text{P}_{1-x}\text{Si}_x$ alloys. On the other hand, Bao focused on the substitution of Co into $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ with Si concentrations of $x = 0.1, 0.2$ and 0.4 Si per f.u. The results of Bao *et al.* [68] are additionally shown in Fig. 4.33 to emphasize the agreement between the experiment and the data of this thesis. In the data of Bao *et al.* [68], Co substitution yields similar effects on the structural parameters with a decrease of a and the volume, as well as an increase of c and c/a . This shows that in the limits of DFT a good agreement with the available experimental data was achieved.

4.6.4 Magnetic Moments, Magnetization Saturation and Maximum Energy Product of hexagonal $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ Compounds

The sole addition of Si exhibits an increase of the magnetic moments and consequently the magnetization up to 1.22 T at $x = 0.41$. On the other hand, the pure substitution of Co decreased the magnetic moments and the magnetization, due to its inherently lower magnetic moment (see Sec. 4.5). Both of these effects combine in the quaternary

4.6. Quaternary $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ compounds

Table 4.15: Calculated lattice parameters and magnetic moments for the quaternary $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ alloys with $x = 0.08, 0.16$ and 0.41 Si per f.u. and $0 \leq y \leq 1$ Co per f.u.

Compound	Lattice Constant [Å]		c/a	Volume [Å ³]	Mag Mom [μ_B /f.u.]
	a	c			
<i>x = 0.08 Si</i>					
Fe ₂ P _{0.92} Si _{0.08}	5.840	3.408	0.5836	100.7	3.12
Fe _{1.92} Co _{0.08} P _{0.92} Si _{0.08}	5.823	3.414	0.5863	100.3	3.03
Fe _{1.84} Co _{0.16} P _{0.92} Si _{0.08}	5.817	3.417	0.5874	100.1	2.95
Fe _{1.75} Co _{0.25} P _{0.92} Si _{0.08}	5.805	3.420	0.5891	99.8	2.87
Fe _{1.67} Co _{0.33} P _{0.92} Si _{0.08}	5.794	3.425	0.5911	99.7	2.79
Fe _{1.58} Co _{0.42} P _{0.92} Si _{0.08}	5.788	3.430	0.5926	99.5	2.71
Fe _{1.5} Co _{0.5} P _{0.92} Si _{0.08}	5.783	3.430	0.5931	99.3	2.65
Fe _{1.42} Co _{0.59} P _{0.92} Si _{0.08}	5.776	3.430	0.5938	99.1	2.58
Fe _{1.33} Co _{0.67} P _{0.92} Si _{0.08}	5.771	3.429	0.5942	99.0	2.51
Fe _{1.25} Co _{0.75} P _{0.92} Si _{0.08}	5.764	3.432	0.5954	98.9	2.44
Fe _{1.16} Co _{0.84} P _{0.92} Si _{0.08}	5.755	3.440	0.5977	98.7	2.37
Fe _{1.08} Co _{0.92} P _{0.92} Si _{0.08}	5.738	3.452	0.6016	98.4	2.29
FeCoP _{0.92} Si _{0.08}	5.727	3.458	0.6038	98.3	2.22
<i>x = 0.16 Si</i>					
Fe ₂ P _{0.84} Si _{0.16}	5.881	3.375	0.5739	101.2	3.21
Fe _{1.92} Co _{0.08} P _{0.84} Si _{0.16}	5.857	3.394	0.5795	100.9	3.13
Fe _{1.84} Co _{0.16} P _{0.84} Si _{0.16}	5.849	3.402	0.5816	100.7	3.04
Fe _{1.75} Co _{0.25} P _{0.84} Si _{0.16}	5.836	3.407	0.5838	100.5	2.94
Fe _{1.67} Co _{0.33} P _{0.84} Si _{0.16}	5.824	3.414	0.5862	100.4	2.88
Fe _{1.58} Co _{0.42} P _{0.84} Si _{0.16}	5.817	3.419	0.5877	100.1	2.80
Fe _{1.5} Co _{0.5} P _{0.84} Si _{0.16}	5.812	3.416	0.5878	99.9	2.73
Fe _{1.42} Co _{0.59} P _{0.84} Si _{0.16}	5.804	3.420	0.5893	99.8	2.65
Fe _{1.33} Co _{0.67} P _{0.84} Si _{0.16}	5.794	3.421	0.5905	99.6	2.58
Fe _{1.25} Co _{0.75} P _{0.84} Si _{0.16}	5.785	3.422	0.5915	99.4	2.52
Fe _{1.16} Co _{0.84} P _{0.84} Si _{0.16}	5.782	3.426	0.5926	99.3	2.44
Fe _{1.08} Co _{0.92} P _{0.84} Si _{0.16}	5.768	3.424	0.5937	98.8	2.38
FeCoP _{0.84} Si _{0.16}	5.757	3.445	0.5984	98.9	2.29
<i>x = 0.41 Si</i>					
Fe ₂ P _{0.59} Si _{0.41}	6.137	3.131	0.5102	101.9	3.56
Fe _{1.92} Co _{0.08} P _{0.59} Si _{0.41}	6.088	3.183	0.5229	102.0	3.46
Fe _{1.84} Co _{0.16} P _{0.59} Si _{0.41}	6.046	3.226	0.5336	102.0	3.35
Fe _{1.75} Co _{0.25} P _{0.59} Si _{0.41}	5.993	3.279	0.5471	102.0	3.26
Fe _{1.67} Co _{0.33} P _{0.59} Si _{0.41}	5.964	3.303	0.5538	101.7	3.15
Fe _{1.58} Co _{0.42} P _{0.59} Si _{0.41}	5.938	3.329	0.5607	101.7	3.06
FFe _{1.5} Co _{0.5} P _{0.59} Si _{0.41}	5.932	3.325	0.5606	101.4	2.99
Fe _{1.42} Co _{0.59} P _{0.59} Si _{0.41}	5.911	3.350	0.5668	101.4	2.92
Fe _{1.33} Co _{0.67} P _{0.59} Si _{0.41}	5.883	3.363	0.5717	101.0	2.82
Fe _{1.25} Co _{0.75} P _{0.59} Si _{0.41}	5.870	3.370	0.5742	100.7	2.74
Fe _{1.16} Co _{0.84} P _{0.59} Si _{0.41}	5.851	3.389	0.5792	100.6	2.64
Fe _{1.08} Co _{0.92} P _{0.59} Si _{0.41}	5.844	3.381	0.5786	100.1	2.57
FeCoP _{0.59} Si _{0.41}	5.837	3.400	0.5824	100.3	2.49

compounds, where materials with more Si demonstrate higher magnetic moments (0.08 Si - $3.12 \mu_B/\text{f.u.}$, 0.16 Si - $3.21 \mu_B/\text{f.u.}$ and 0.41 Si - $3.56 \mu_B/\text{f.u.}$). These magnetic moments get reduced with the addition of Co. However, this reduction is only visible in the weaker magnetic $3f$ site and not in the $3g$ site and can consequently be connected to the lower magnetic moment of Co compared to Fe. The magnetic moments in the $3f$ site start at 0.84, 0.92 and $1.33 \mu_B/\text{f.u.}$ and diminish to 0.34, 0.36 and $0.41 \mu_B/\text{f.u.}$ at $y = 1$ Co per f.u. The magnetic moments in the $3g$ position remain constant between 2.0 to $2.2 \mu_B/\text{f.u.}$ The development of the magnetic moments is depicted in Fig. 4.34. This development of the magnetic moments can be explained by the volume and chemical effects of Si and Co. The positive volume and chemical effect are seen to increase the magnetic moments, while the negative chemical effect of Co reduces it (see Sec. 4.4.1 and 4.5.1).

This evolution of the magnetic moments causes a reduction of the magnetization to values of 0.79, 0.82 and 0.87 T at $y = 1$ Co per f.u. for $x = 0.08$, 0.16 and 0.41 Si, respectively. The steady decrease of the magnetic moments and magnetization also affects the $|BH|_{max}$, as stated before in the sections for the ternary Si and Co substitution. The initially high $|BH|_{max}$ values decrease alongside the magnetization and drop below 200 kJ/m^3 at Co concentrations of $y = 0.33$, 0.42 and 0.67 for the Si concentrations of $x = 0.08$, 0.16 and 0.41 Si per f.u., respectively. Both effects, the increase with Si and the decrease with Co have also been reported by Uyanga *et al.*[177], who investigated hexagonal quaternary compounds with up to 0.24 Si and 0.12 Co per f.u.

4.6.5 Curie Temperature and Exchange Interaction Energies of hexagonal $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ Compounds

The simultaneous substitution of Si and Co is a promising method to significantly improve the low Curie temperature of Fe_2P . Both elements already revealed a great potential in ternary substitutions. Now the combined effect is investigated to see whether the combination of both elements accumulates into a significant impact on the T_C . Three distinct trends of the Curie temperature are identified depending on the Si concentration: (i) a pronounced increase at low Si contents, (ii) a saturation or weak enhancement at intermediate levels, and (iii) a reduction or flattening of T_C at high Si in combination with Co substitution. It is reported in the literature [68, 67], that the c/a ratio has a great effect on the T_C of these quaternary compound. However, a clear trend of an increase or decrease of the T_C s connected to a lower (Si substitution) or higher (Co substitution) c/a ratio can not be determined from the data of Tab. 4.15 and Fig. 4.35.

In both substitution scenarios the T_C is seen to rise by a great margin. Taking a look at Si substitution first, the c/a ratio is reduced from 0.5897 at $x = 0$ Si to 0.5836, 0.5739 and 0.5102 at $x = 0.08$, 0.16 and 0.42 Si, respectively. At the same time the theoretical

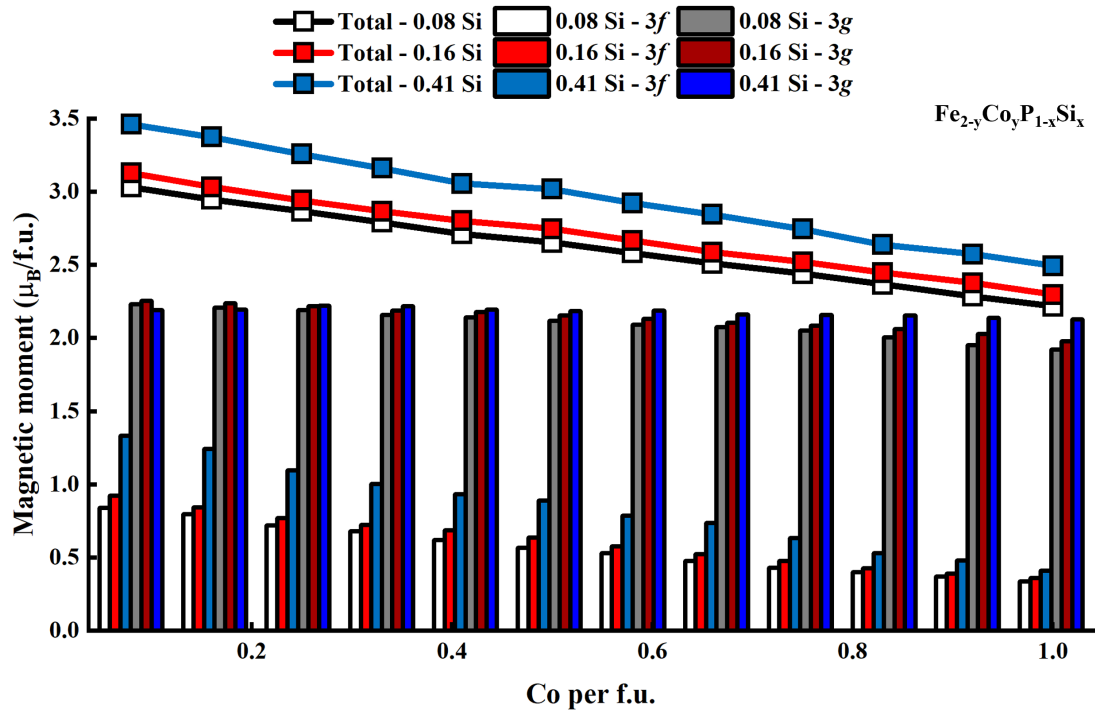


Figure 4.34: Total and site specific magnetic moments of the quaternary $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ materials with $x = 0.08$ (black), 0.16 (red) and 0.41 (blue) Si per f.u. in the range of $0.08 \leq y \leq 1$ Co per f.u. The lines denote the total magnetic moments per functional unit, while the columns show the site specific magnetic moment for each Wyckoff position.

Table 4.16: Theoretical magnetization saturation ($\mu_0 M_S$) and maximum energy product ($|BH|_{max}$) values for the hexagonally structured quaternary $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ compounds.

	x = 0.08		x = 0.16		x = 0.41	
	$\mu_0 M_S$ (T)	$ BH _{max}$ [kJ/m ³]	$\mu_0 M_S$ (T)	$ BH _{max}$ [kJ/m ³]	$\mu_0 M_S$ (T)	$ BH _{max}$ [kJ/m ³]
$\text{Fe}_2\text{P}_{1-x}\text{Si}_x$	1.08	232	1.11	246	1.22	296
$\text{Fe}_{1.92}\text{Co}_{0.08}\text{P}_{1-x}\text{Si}_x$	1.06	222	1.08	234	1.19	280
$\text{Fe}_{1.84}\text{Co}_{0.16}\text{P}_{1-x}\text{Si}_x$	1.03	211	1.05	221	1.16	266
$\text{Fe}_{1.75}\text{Co}_{0.25}\text{P}_{1-x}\text{Si}_x$	1.00	201	1.02	208	1.12	248
$\text{Fe}_{1.67}\text{Co}_{0.33}\text{P}_{1-x}\text{Si}_x$	0.98	191	1.00	199	1.09	234
$\text{Fe}_{1.58}\text{Co}_{0.42}\text{P}_{1-x}\text{Si}_x$	0.95	181	0.98	191	1.05	220
$\text{Fe}_{1.5}\text{Co}_{0.5}\text{P}_{1-x}\text{Si}_x$	0.93	174	0.96	185	1.04	216
$\text{Fe}_{1.42}\text{Co}_{0.59}\text{P}_{1-x}\text{Si}_x$	0.91	165	0.94	175	1.01	202
$\text{Fe}_{1.33}\text{Co}_{0.67}\text{P}_{1-x}\text{Si}_x$	0.89	156	0.91	165	0.99	194
$\text{Fe}_{1.25}\text{Co}_{0.75}\text{P}_{1-x}\text{Si}_x$	0.86	148	0.89	157	0.95	181
$\text{Fe}_{1.16}\text{Co}_{0.84}\text{P}_{1-x}\text{Si}_x$	0.84	140	0.86	149	0.92	167
$\text{Fe}_{1.08}\text{Co}_{0.92}\text{P}_{1-x}\text{Si}_x$	0.81	131	0.84	141	0.90	161
$\text{FeCoP}_{1-x}\text{Si}_x$	0.79	124	0.82	132	0.87	151

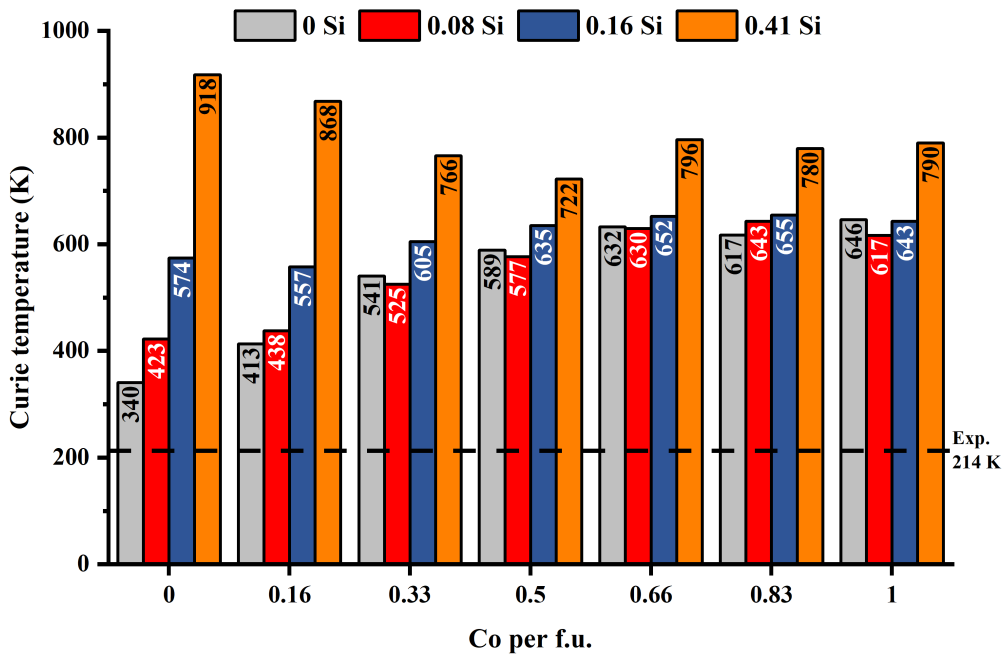


Figure 4.35: Theoretical Curie temperature calculated in the mean field approximation with the AkaiKKR code for quaternary $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ compounds with $x = 0, 0.08, 0.16$ and 0.41 Si per f.u. in the range of $0 \leq y \leq 1$ Co per f.u. The horizontal dashed line shows the experimental T_C of substitution free Fe_2P and is taken from Caron *et al.* [27].

Curie temperature of these compounds rises from 340 K to 423, 574 and 918 K for each of the mentioned concentrations. In contrast, Co substitution results in an increase of the c/a ratio, reaching values of 0.6038, 0.5984 and 0.5824 for compounds containing 0.08, 0.16 and 0.41 Si, respectively. The corresponding T_C s of the compounds increase to values above 600 K. The only exception for the trend of an increase can be seen for compounds with a Si concentration of $x = 0.41$ Si per f.u., where the Co-free compound starts at 918 K and the T_C reduces with additional Co to a final result of 790 K. This reduction is limited to Co concentrations up to $y = 0.33$ Co, beyond which the Curie temperature exhibits a plateau behavior in the range of approximately 720 to 790 K.

It is noteworthy that, increasing Si concentration leads to a reduction of the influence of Co on the T_C . Depending on the Si concentration, three distinct effects on the T_C can be identified. At low Si concentrations (0 and 0.08 Si), Co substitution causes a significant increase of the T_C s, while at medium (0.16 Si) concentrations the Curie temperature already starts at 574 K and only improves slightly to values ~ 650 K. At $x = 0.41$ Si, the T_C even decreases from 918 K to 722 K at $y = 0.5$ Co, before stabilizing ~ 790 K. These results were also published by Erdmann *et al.* [43] and matches with literature by Bao *et al.* [68], who discovered the same effects in dependence on Si. The available experimental T_C s for these compounds are additionally depicted in Fig. 4.36.

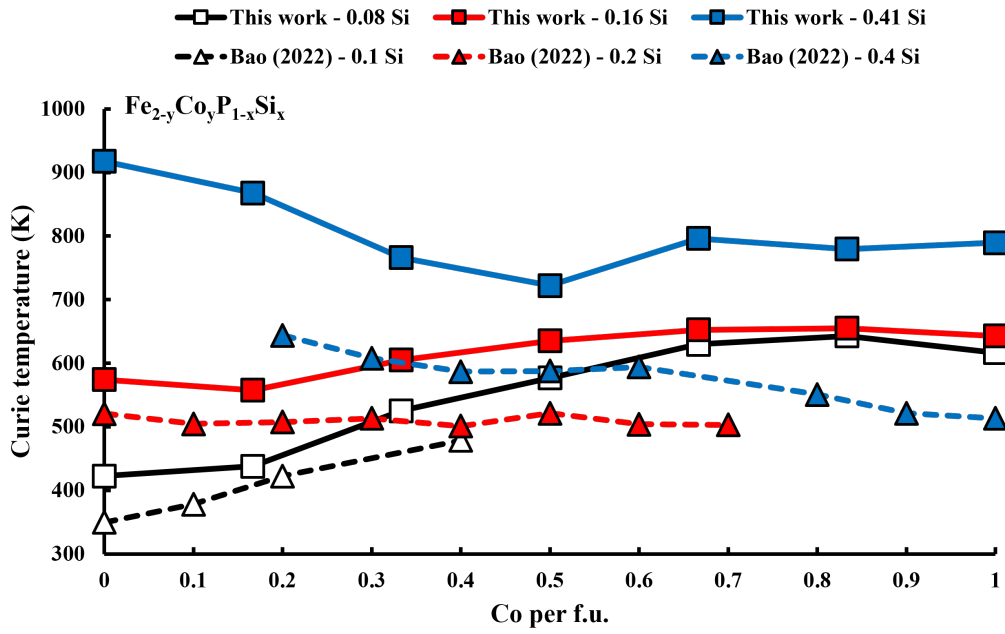


Figure 4.36: Comparison of calculated (squares and solid line) and experimental (triangles and dashed lines) Curie temperatures for hexagonal quaternary $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ compounds in the substitution range of $0 \leq y \leq 1$ Co per f.u. The theoretical data shows Si concentrations of $x = 0.08$ (black), 0.16 (red) and 0.41 (blue) Si, while the experimental data depicts Si concentrations of $x = 0.1$ (black), 0.2 (red) and 0.4 (blue) Si per f.u. The experimental data is adapted from Bao *et al.* [68].

A direct comparison of the computed and experimental T_C s shows a good agreement considering the known overestimation of the MFA. In both theoretical and experimental data, an increase of T_C with Co at low Si concentrations, a stagnation at intermediate Si levels and a decrease at high Si concentrations are observed. The effect at medium Si is less pronounced in the theoretical calculations, which can be attributed to the lower Si concentration of 0.16 instead of 0.2. However, the visible increase at this concentration is still less pronounced than for 0.08 Si and a further flattening with more Si can be assumed. The found trends suggest a maximum theoretical $T_C \sim 650$ K, which can be achieved by Co substitution. The three cases of $x = 0$, 0.08 and 0.16 Si all reach a maximum around this Curie temperature. Only with $x = 0.41$ Si, a higher $T_C \sim 780$ to 790 K was achieved. This indicates that the improvement of the T_C by adding Co is limited to a certain threshold and only the additional effect of lattice distortions by Si can enhance the Curie temperature above this point.

Summarizing the influence of Si and Co on the Curie temperature, both elements are found to induce a substantial enhancement of T_C within the present theoretical framework. The strongest enhancement is associated with Si substitution, resulting in a theoretical T_C of 918 K for the ternary $\text{Fe}_2\text{P}_{0.59}\text{Si}_{0.41}$ compound. However, phase stability considerations strongly suggest that this compound is unlikely to remain stable in the hexagonal crystal symmetry. High T_C s resulting from combined Si and Co substitutions are expected to reach a maximum around 600 to 650 K. Nevertheless, smaller combined substitutions of Si and Co already achieve significant improvements of the T_C at lower concentrations, which should also be taken into account. At $x = 0.16$ Si and $y = 0.16$ Co, a calculated T_C of 557 K was achieved. This matches with available T_C data [68], showing a Curie temperature of ~ 500 K for $\text{Fe}_{1.8}\text{Co}_{0.2}\text{P}_{0.8}\text{Si}_{0.2}$. This indicates that even moderate Si and Co substitutions may allow quaternary $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-y}\text{Si}_y$ compounds to reach Curie temperatures that are potentially relevant for selected industrial applications.

To fully understand these effects, the exchange interaction energies J_{ij} have to be considered, as these are the underlying values for the determination of the T_C (see Eq. 1.4). As already covered for the ternary Si and Co substitutions, Si exhibits a negative chemical effect on the J_{ij} s that is overcome by a positive volume effect (see Fig. 4.12). Contrary to this, Co substitution exhibits a positive chemical effect and the lattice parameters only having a small volume effect on the J_{ij} energies (see Fig. 4.24). In combination, these opposing chemical effects suggest a potentially enhanced net exchange interaction compared to single-element substitution.

Bearing this in mind, the total exchange interaction energies and the $3f$ - $3f$, $3f$ - $3g$ and $3g$ - $3g$ site interactions for the simultaneous Si and Co substitution have been investigated. The results for the J_{ij} s are shown in Fig. 4.37. It is visible by the significant upwards shift

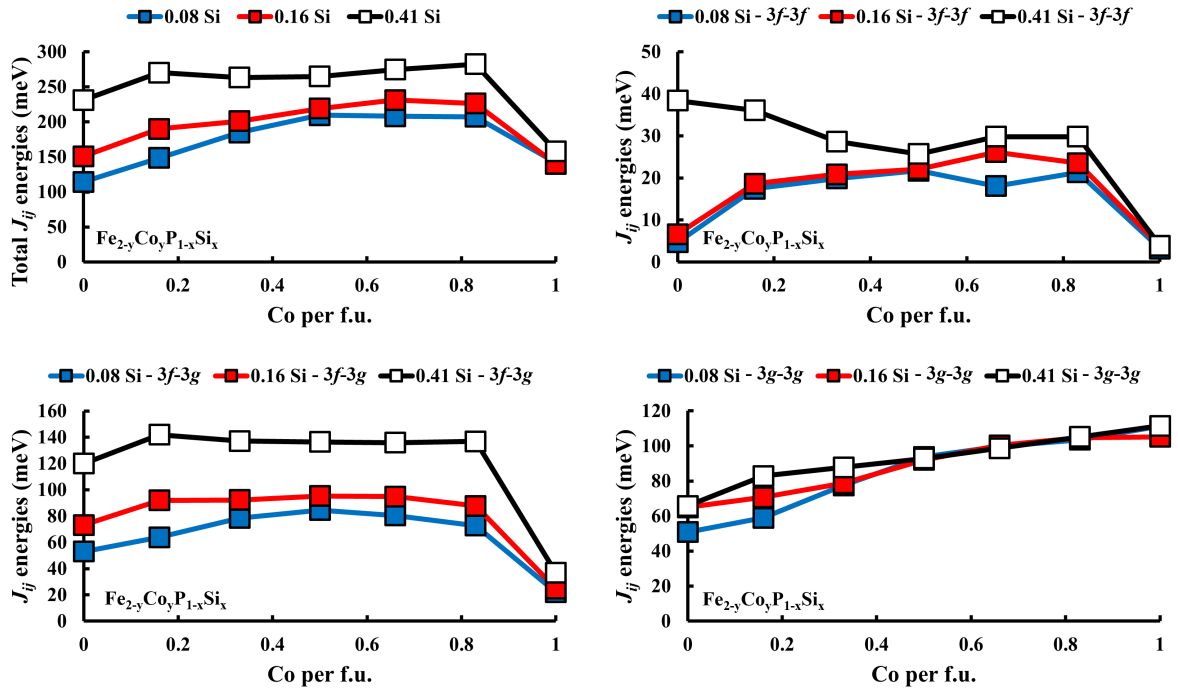


Figure 4.37: Calculated exchange interaction energies of the quaternary $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ compounds for $x = 0.08, 0.16$ and 0.41 Si per f.u. in the range of $0 \leq y \leq 1$. The total exchange interaction energies as well as the site specific energies for the contributions of $3f-3f$, $3f-3g$ and $3g-3g$ are shown

with Si, that the total J_{ij} s are mostly enhanced by Si substitution and its positive volume effect. Nevertheless, the substitution of Co further improves the total J_{ij} s over the course of the substitution range. This effect gets smaller with higher Si substitution, accounting to an overall increase of ~ 50 meV from $y = 0$ Co to 0.83 Co per f.u. This results in a final value of 282 meV. For $x = 0.08$ and 0.16 Si, the enhancement is a bit higher accounting to increases from 114 and 150 meV to 208 and 226 meV at $y = 0.83$ Co per f.u. Note, that the drop of the J_{ij} s at $y = 1$ Co per f.u. is the result of the complete substitution of the $3f$ site with Co.

Investigating the site specific J_{ij} energies, the single contributions of Si and Co can be seen in the diagrams. As the Si investigations have shown, mostly the $3f-3g$ and at higher Si concentrations the $3f-3f$ interactions are improved. This result applies for all quaternary compounds as well. The J_{ij} s for these contributions are following the same course of the results and are mostly shifted upwards with Si. The site specific exchange interactions will be discussed by starting with the $3f-3f$ exchange interaction energies due to their assumed greater influence on the T_C s. This is followed by the high $3f-3g$ and the $3g-3g$ interactions.

The greatest difference in the site specific interaction energies is noticeable for the

$3f$ - $3f$ interactions. At $x = 0.41$ Si the J_{ij} s yield an initial value ~ 40 meV which is then reduced to ~ 30 meV with Co substitution. This behavior indicates that variations in the $3f$ - $3f$ exchange interaction exerts a dominant influence on the Curie temperature. At this point, the $3f$ - $3f$ exchange interaction energies are the only contribution that diminishes similar to the calculated T_C s, that decrease from 918 to 722 K. All other exchange interactions increase with the addition of Co. With the previously mentioned findings, this could indicate that the volume effect of the lattice distortions caused by Si is much greater than the compensation with the chemical effect of Co. Therefore, the small opposite volume effect on the lattice parameters with Co substitution causes a loss in the $3f$ - $3f$ J_{ij} s that is not completely compensated. With $y \geq 0.5$ Co per f.u. the T_C s increase again, as after this point the chemical effect of Co shows a higher impact than the removal of the lattice changes of Si.

The $3f$ - $3g$ interaction energies show the highest values of all three site specific interactions. At low Si concentrations, the $3f$ - $3g$ energies are of similar size to the $3g$ - $3g$ interactions and are seen to only increase slightly with the substitution of Co. At $x = 0.08$ Si, the highest value is seen at $y = 0.5$ Co per f.u. with 85 meV. This value decreases to 73 meV at 0.83 Co, before the full substitution of the $3f$ site causes a drop to 22 meV at 1 Co per f.u. With increasing Si concentrations, the $3g$ - $3g$ exchange interactions are shifted to higher values. At 0.16 Si, the J_{ij} starts at 73 meV and improve to values ~ 95 meV at 0.5 Co per f.u. With the highest investigated Si concentration of 0.41 Si, the $3f$ - $3g$ interactions clearly surpass the $3g$ - $3g$, accounting to 120 to 140 meV.

Since Si is seen to mostly affect the $3f$ position, the $3g$ - $3g$ interactions are almost unchanged and no upwards shift is visible. They start relatively high ~ 50 to 65 meV and steadily increase with Co substitution. With the full substitution of the $3f$ site, the $3g$ - $3g$ interactions reach a final energy ~ 105 - 111 meV. Co substitution can therefore be assumed to greatly strengthen the $3g$ - $3g$ interactions.

The general increase of the exchange interactions underlines the increase of the T_C . However, the influence of Co substitution on the exchange interaction energies is observed to saturate at higher Co concentrations. This supports the assumption that Co can only improve the T_C to a certain point. With Si substitution shifting the J_{ij} energies upwards, higher T_C s can be realized as seen for 0.41 Si per f.u.

4.6.6 Anisotropy Constant and Anisotropy Field of hexagonal $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ Compounds

The anisotropy of the quaternary $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ compounds is another crucial magnetic property that needs to be considered for the determination of the suitability as a hard magnetic material. In Fig. 4.38 are the calculated anisotropy constants K_1 for

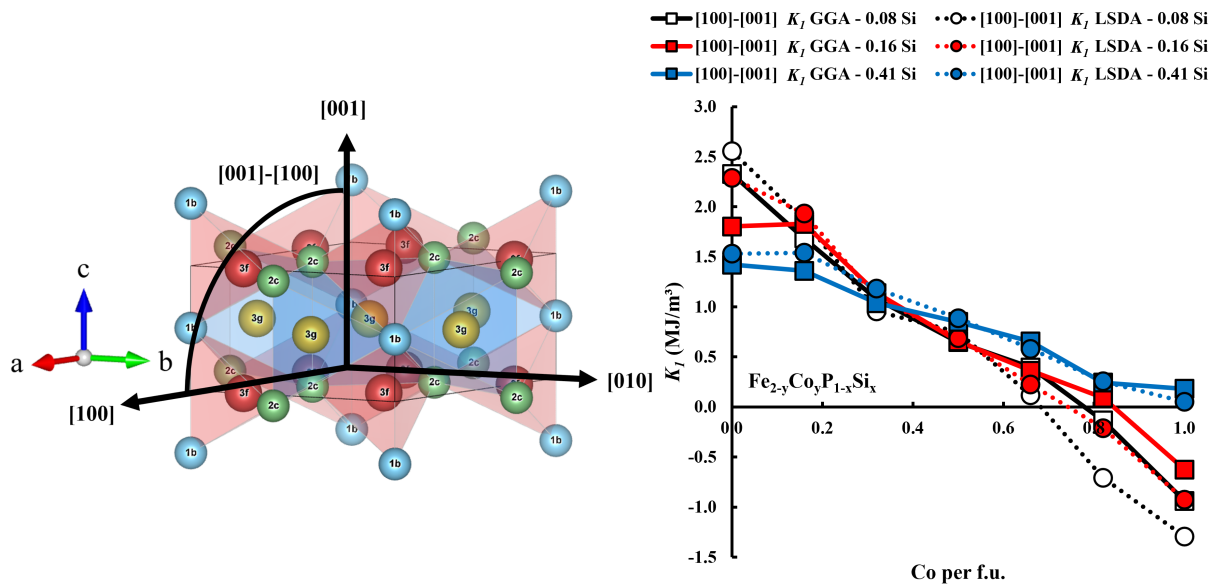


Figure 4.38: **Left:** Schematic depiction of the hexagonal unit cell with the directional change from [001] to [100] marked in black. **Right:** Calculated anisotropy constants K_1 for the substitution of Co in $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ compounds using the GGA (squares, solid lines) and LSDA (circles, dashed line) exchange correlation functionals. The anisotropy constants are calculated for $x = 0.08$ (black), 0.16 (red) and 0.41 (blue) Si per f.u. in the range of $0 \leq y \leq 1$ Co per f.u.

the 0.08, 0.16 and 0.41 Si compounds in dependence of the Co substitution depicted. A schematic hexagonal unit cell is additionally to provide a good understanding of the directional change of the magnetization. The anisotropy constants are calculated using the [001] direction as the easy axis and the [100] direction as the hard magnetic axis. Similar to the influence of Co substitution on K_1 (Fig. 4.25), a decreasing trend of the values with more Co can be seen. This matches with ternary Co substitution findings by de Vos *et al.* [110].

This negative trend is further reinforced by Si substitution, which is also seen to decreases the anisotropy. This translates to a decrease of the initial values in the order of 2.33 (2.56), 1.80 (2.29) and 1.42 (1.53) MJ/m³ for $x = 0.08$, 0.16 and 0.41 Si for the GGA (LSDA) functional. In general, both exchange functionals yield very similar results and only a very minor differences are calculated between them. This is in contrast to the results for the substitution-free Fe_2P compound and pure Si substitution, where the results for the functionals differ greatly. This leads to the conclusion, that in case of quaternary $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ compounds both functionals are reasonable to use. Similar to ternary Co substitution, Co causes a loss of the uniaxial anisotropy at higher Co concentrations in the quaternary compounds. This effect is observable by negative anisotropy constants at $y \geq 0.66$ and $y \geq 0.81$ Co per f.u. in case of $x = 0.08$ and 0.16 Si. At high

4.6. Quaternary $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ compounds

Table 4.17: Theoretical anisotropy constant K_1 (MJ/m³) and anisotropy field H_a (T) for hexagonal $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ materials for the Si concentrations 0.08, 0.16 and 0.41 Si per f.u. The values are calculated using the GGA exchange functional. Results from considering the LSDA functional are listed in parenthesis.

Compound	$x = 0.08$ Si		$x = 0.16$ Si		$x = 0.41$ Si	
	K_1 (MJ/m ³)	H_a (T)	K_1 (MJ/m ³)	H_a (T)	K_1 (MJ/m ³)	H_a (T)
$\text{Fe}_2\text{P}_{1-x}\text{Si}_x$	2.33 (2.56)	4.30 (4.72)	1.80 (2.29)	3.25 (4.12)	1.42 (1.53)	2.33 (2.51)
$\text{Fe}_{1.84}\text{Co}_{0.16}\text{P}_{1-x}\text{Si}_x$	1.69 (1.87)	3.27 (3.62)	1.83 (1.93)	3.47 (3.67)	1.36 (1.54)	2.37 (2.68)
$\text{Fe}_{1.67}\text{Co}_{0.33}\text{P}_{1-x}\text{Si}_x$	1.08 (0.96)	2.20 (1.95)	1.14 (1.10)	2.27 (2.19)	1.04 (1.18)	1.91 (2.18)
$\text{Fe}_{1.5}\text{Co}_{0.5}\text{P}_{1-x}\text{Si}_x$	0.65 (0.75)	1.39 (1.61)	0.66 (0.69)	1.37 (1.44)	0.85 (0.89)	1.65 (1.72)
$\text{Fe}_{1.33}\text{Co}_{0.67}\text{P}_{1-x}\text{Si}_x$	0.39 (0.12)	0.89 (0.26)	0.36 (0.23)	0.80 (0.50)	0.66 (0.58)	1.34 (1.19)
$\text{Fe}_{1.16}\text{Co}_{0.84}\text{P}_{1-x}\text{Si}_x$	-0.14 (-0.71)	-0.32 (-1.68)	0.09 (-0.21)	0.21 (-0.49)	0.24 (0.26)	0.53 (0.56)
$\text{FeCoP}_{1-x}\text{Si}_x$	-0.94 (-1.30)	-2.38 (-3.29)	-0.63 (-0.93)	-1.54 (-2.29)	0.18 (0.05)	0.42 (0.12)

Si concentrations ($x = 0.41$ Si), the uniaxial anisotropy prevails even up to high Co concentrations of $y = 1$ Co per f.u.

This finding indicates that the substitution of Si enhances the resilience of the compound against the loss of the uniaxial anisotropy by Co substitution. This makes the substitutional combination of both elements promising for adjusting the MAE of desirable compounds. Zhuravlev *et al.* [111] and Surilemu *et al.* [125] also proposed such a higher resilience to be connected to the band filling with electrons. The findings of this thesis support this conclusion, as with a higher reduction of the number of electron due to Si, a higher number of electrons can be compensated by Co before a surplus of electrons is added to the bands. Therefore an optimal number of electrons for the hexagonal $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ compounds can be expected.

As the calculation of anisotropy field H_a is based on the anisotropy constant K_1 , the anisotropy field sees the same changes. The corresponding values of the anisotropy field for the simultaneous Si and Co substitution can be seen in Tab. 4.17. In all three cases ($x = 0.08, 0.16$ and 0.41 Si), the substitution of Co into the $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ compounds results in a decrease of H_a . The already mentioned influence of Si can also be seen by the decrease of the initial values. The anisotropy field turns to negative values $y \geq 0.66$ and 0.84 Co per f.u. for compounds with $x = 0.08$ and 0.16 Si with the GGA

functional. Higher Co concentrations yield slightly lower values and a change to negative results for $x = 0.08$ and 0.16 Si at $y \geq 0.66$ Co per f.u. when the LSDA functional is used. For the $\text{Fe}_{2-y}\text{Co}_y\text{P}_{0.59}\text{Si}_{0.41}$ materials, both functionals yield positive values even up to $y = 1$ Co, which is a consequence of the higher resilience with more Si. The maximum positive H_a values for each Si concentration are listed in Tab. 4.17 as 0.89 (0.26) T for $x = 0.08$ Si, 0.21 (0.50) T at $x = 0.16$ Si, and 0.42 (0.12) T at $x = 0.41$ Si. Note, that the highest LSDA value for $x = 0.16$ Si (0.50 T) is derived from a Co concentration of $y = 0.67$ Co, whereas the GGA functional yields slightly higher values and remains positive up to higher Co concentrations. Since no experimental anisotropy data is available for quaternary $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ materials, no comparison can currently be made.

As the underlying reasons for the changes of the anisotropy the proposed band filling with electrons can be assumed. Consequently, the position of the Fermi energy of the compound is affected and therefore also the MAE. The shift of the Fermi energy alters the energy difference between the occupied and unoccupied states near the Fermi energy, leading to a change of the MAE. Nevertheless, to achieve an optimal MAE the substitution of Si and Co needs to be as small as possible to provide a high anisotropy. Especially the substitution of Co should be minimized as it was found to influence K_1 to a greater degree than Si. In this work, an optimal maximum for Co of $y = 0.33$ Co per f.u. is proposed to remain at anisotropy constants above 1.0 MJ/m^3 .

4.6.7 Magnetic Hardness Factor of hexagonal $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ Compounds

Following a comprehensive investigation into the magnetic properties, the suitability of the quaternary $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ compounds as magnetic materials can be estimated. A general rule of thumb is the magnetic hardness factor κ , that determines whether a compound can be classified as a soft ($\kappa \leq 0.1$), a semi-hard ($0.1 < \kappa \leq 1$) or a hard magnetic material ($\kappa > 1.0$) [34]. The magnetic hardness factor is calculated using the saturation magnetization $\mu_0 M_S$ and the anisotropy constant K_1 via the following relation:

$$\kappa = \sqrt{\frac{K_1}{\mu_0 M_S^2}}. \quad (4.11)$$

The 0 K magnetic property investigations in this work revealed that Si increases the magnetic moments of the compounds, but in parallel reduces the anisotropy. For Co substitution, an overall decrease of both properties was seen. These results were also translated onto the quaternary compounds. The combined influence of both elements is evidenced in section 4.6, cumulating in the conclusion that only minor amounts of Si and

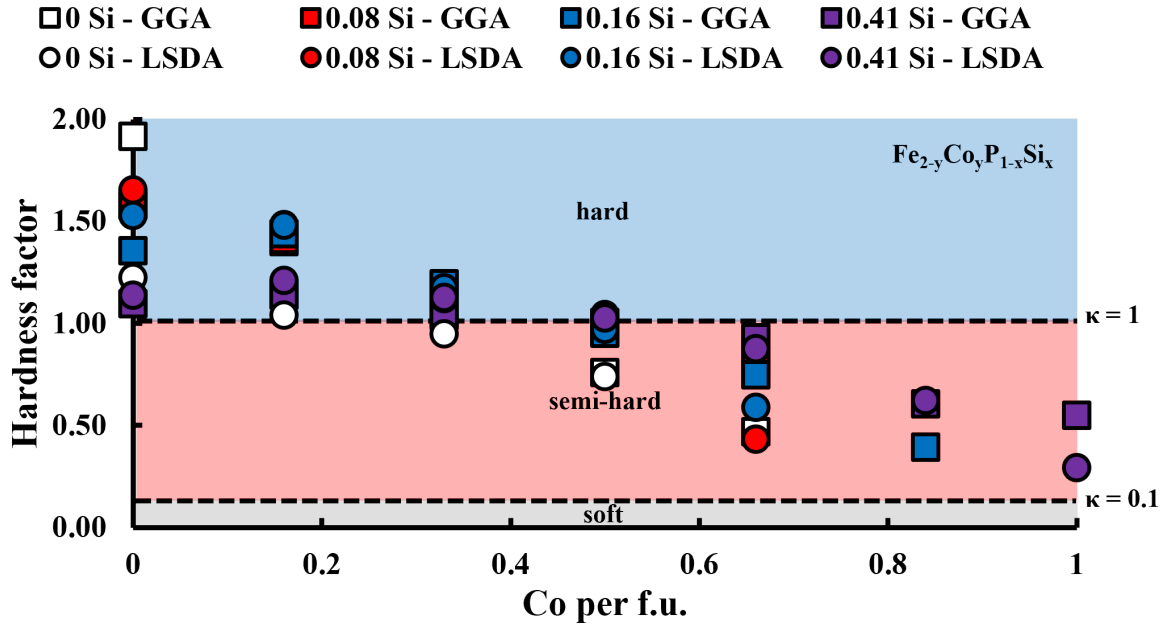


Figure 4.39: Schematic representation of the theoretical hardness factors for ternary and quaternary $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ compounds with $x = 0$ (black), 0.08 (red), 0.16 (blue) and 0.41 (violet) Si per f.u. Values considering the GGA functional are denoted by squares, while the results using the LSDA functional are given as circles. The area characteristic for soft ($\kappa \leq 0.1$), semi-hard ($0.1 < \kappa \leq 1$) and hard magnetic materials ($\kappa > 1$) are highlighted in gray, red and blue, respectively.

Co should be substituted into Fe_2P to optimize the magnetic properties. This assessment of minor amounts of substitution is further supported by the consideration of the hardness factor. The calculated hardness factors, as well as the considered $\mu_0 M_S$ and K_1 values are listed in Tab. 4.18. Furthermore, the development for each Si concentration with Co is depicted in Fig. 4.39 to provide a general overview of the substitution trends.

From first-principles calculations one clear trend for the 0 K magnetic hardness is visible. Both Si and Co substitution show a decrease of the hardness factor. The hardness factor for substitution-free Fe_2P starts at 1.92 using the GGA functional (squares). In the figure, the magnetic hardness drops with Si but remains above $\kappa = 1$ with 0.41 Si per f.u. This same trend is evident in Tab. 4.18, where the hardness of the ternary Si compounds is reduced from 1.92 to 1 (1.07) at $x = 0.5$ Si per f.u. for GGA (LSDA). The highest magnetic hardness, resulting from these 0 K investigations, is therefore achieved with low Si substitutions at 0.08 and 0.16 Si with 1.58 and 1.35. A minimal incorporation of Si is thus recommended. Co substitution demonstrates analogous trends and exerts an even more pronounced effect on the reduction of the hardness factor. It is observed that the magnetic hardness undergoes a decline from 1.92 to 0.47 at $y = 0.66$ Co. The LSDA functional yields similar results albeit being limited to $y = 0.5$ Co with a hardness of 0.74. Note, that with the negative K_1 values occurring at high Co substitutions, no hardness

4.7. Finite Temperature Phase Stabilities

Table 4.18: Calculated 0 K hardness factors, magnetization saturation $\mu_0 M_S$ and anisotropy constant K_1 for ternary and quaternary $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ materials with $x = 0.0, 0.08, 0.16$ and 0.41 Si per f.u. and y in the range $0 \leq y \leq 1$ Co per f.u. The values calculated using the LSDA functional are given in parenthesis, while the GGA value is given without brackets.

<i>Si subst.</i>	<i>Co-Free</i>			<i>Co subst.</i>	$x = 0.0$ Si			$x = 0.08$ Si			$x = 0.16$ Si			$x = 0.41$ Si		
	$\mu_0 M_S$ (T)	K_1 (MJ/m ³)	κ		$\mu_0 M_S$ (T)	K_1 (MJ/m ³)	κ	$\mu_0 M_S$ (T)	K_1 (MJ/m ³)	κ	$\mu_0 M_S$ (T)	K_1 (MJ/m ³)	κ	$\mu_0 M_S$ (T)	K_1 (MJ/m ³)	κ
Fe_2P	1.06	3.26	1.92	$\text{Fe}_2\text{P}_{1-x}\text{Si}_x$	1.06	3.26	1.92	1.08	2.33	1.58	1.11	1.803	1.35	1.22	1.422	1.10
		1.33	(1.22)			1.33	(1.22)		(2.55)	(1.65)		(2.29)	(1.53)		(1.53)	(1.14)
$\text{Fe}_2\text{P}_{0.92}\text{Si}_{0.08}$	1.08	2.33	1.58	$\text{Fe}_{1.84}\text{Co}_{0.16}\text{P}_{1-x}\text{Si}_x$	1.00	1.57	1.40	1.03	1.69	1.41	1.05	1.829	1.44	1.15	1.360	1.14
		2.55	(1.65)			0.87	(1.04)		(1.87)	(1.48)		(1.93)	(1.48)		(1.54)	(1.21)
$\text{Fe}_2\text{P}_{0.84}\text{Si}_{0.16}$	1.11	1.80	1.35	$\text{Fe}_{1.67}\text{Co}_{0.33}\text{P}_{1-x}\text{Si}_x$	0.96	0.78	1.04	0.98	1.08	1.19	1.00	1.138	1.19	1.08	1.036	1.05
		2.29	(1.53)			0.66	(0.95)		(0.96)	(1.12)		(1.10)	(1.17)		(1.18)	(1.13)
$\text{Fe}_2\text{P}_{0.75}\text{Si}_{0.25}$	1.14	1.46	1.19	$\text{Fe}_{1.5}\text{Co}_{0.5}\text{P}_{1-x}\text{Si}_x$	0.91	0.38	0.76	0.93	0.65	0.97	0.96	0.656	0.95	1.03	0.850	1.00
		2.18	(1.45)			0.36	(0.74)		(0.75)	(1.04)		(0.69)	(0.97)		(0.89)	(1.03)
$\text{Fe}_2\text{P}_{0.67}\text{Si}_{0.33}$	1.17	1.47	1.16	$\text{Fe}_{1.34}\text{Co}_{0.66}\text{P}_{1-x}\text{Si}_x$	0.87	0.13	0.47	0.89	0.39	0.80	0.90	0.363	0.75	0.98	0.655	0.93
		1.80	(1.29)			-0.16	(-)		(0.12)	(0.43)		(0.23)	(0.59)		(0.58)	(0.88)
$\text{Fe}_2\text{P}_{0.59}\text{Si}_{0.41}$	1.22	1.42	1.10	$\text{Fe}_{1.17}\text{Co}_{0.83}\text{P}_{1-x}\text{Si}_x$	0.81	-0.50	-	0.84	-0.14	-	0.86	0.091	0.39	0.92	0.243	0.60
		1.53	(1.14)			-0.85	(-)		(-0.71)	(-)		(-0.21)	(-)		(0.26)	(0.62)
$\text{Fe}_2\text{P}_{0.5}\text{Si}_{0.5}$	1.24	1.22	1.00	$\text{FeCoP}_{1-x}\text{Si}_x$	0.78	-1.14	-	0.79	-0.94	-	0.81	-0.625	-	0.87	0.181	0.55
		1.40	(1.07)			-1.45	(-)		(-1.29)	(-)		(-0.93)	(-)		(0.05)	(0.29)

* - Missing hardness factors are caused by negative K_1 values.

factor can be calculated. These hardness factors of these compounds are consequently absent in Fig. 4.39. In the case of quaternary compounds, both decreasing effects are taken into account, resulting in rapidly falling hardness factors. It is observed that both of the used exchange functionals yield similar results for the anisotropy, resulting in close hardness values. Nevertheless, for all three considered Si concentrations (0.08, 0.16 and 0.41 Si), a Co substitution of $y \geq 0.5$ Co per f.u. results in a hardness $\kappa \leq 1$. This restricts the range of potentially suitable hard magnetic compounds to a maximum Co substitutions of $y = 0.33$ Co per f.u. in this work. For an optimal magnetic material, Si and Co substitution should be minimized to achieve the best possible magnetization and anisotropy. Nevertheless, while these 0 K calculations show promising results regarding the magnetic properties, the phase stabilities at finite temperatures need to be investigated to determine a materials full suitability as a magnet. These finite temperature calculations will be performed in the upcoming section to provide these insights.

4.7 Finite Temperature Phase Stabilities

With the general magnetic properties of the investigated compounds covered, further research is required in order to reveal the finite temperature phase stabilities of these materials. It is imperative that a compound demonstrates an adequate phase stability at elevated temperatures in order to ensure manufacturability and to prevent the decomposition into other compounds. Another main focus of this thesis are these finite temperature phase stabilities of the investigated ternary and quaternary $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ compounds. So far, the only indicators for the stability of these compounds are the 0 K formation and competition energies, calculated from the energies of the elements and binary and

ternary compounds. To properly assess the stability of a material, finite temperature investigations are needed.

One method of predicting the stability is to construct phase formation diagrams, taking the Gibbs free energy of the compounds of interest into account. The Gibbs free energy is estimated by calculating the static, vibrational, electronic and magnetic contributions of the Helmholtz free energy at each temperature (Eq. 4.12).

$$F(T, V) = F_0(V) + F_{vib}(T, V) + F_{elec}(T, V) + F_{mag}(T, V), \quad (4.12)$$

with $F(T, V)$ as the Helmholtz free energy, $F_0(V)$ as the energy at 0 K, $F_{vib}(T, V)$ as the vibrational free energy contribution, $F_{elec}(T, V)$ as the electronic free energy contribution and $F_{mag}(T, V)$ as the magnetic free energy contribution. All contributions in the equation are shown in dependence of the volume and temperature. The calculation of each contribution is described in more detail in Sec. 2.5. The execution of these theoretical investigations at varying volumes for each compound incorporates the effect of the volume in a quasi-harmonic approximation. Assuming a constant pressure, the minimization of the Helmholtz free energy at each temperature, using the Birch-Murnaghan equation of states, converts the Helmholtz free energy to the Gibbs free energy values.

In this section, the performed calculations are first compared with available experimental heat capacities and phonon dispersion lines for the substitution-free Fe_2P material. Subsequently, the investigation shifts to the influence of Si and Co substitution on the Gibbs free energy of the ternary materials. For a systematic understanding, the energy development of the hexagonal and BCO $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ structures, as well as the development of the hexagonal and primitive orthorhombic $\text{Fe}_{2-y}\text{Co}_y\text{P}$ compounds, are compared to demonstrate the influence of temperature on these crystal structures. Following the ternary compounds, the stability of the hexagonally structured quaternary $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ alloys is investigated.

4.7.1 Phonon Dispersion Lines - Fe_2P

To provide an evaluation of the validity of the calculated phase stability data, the theoretical harmonic phonon dispersion lines of the substitution-free Fe_2P compound is analyzed together with phonon dispersion lines from literature. The phonon dispersion lines are calculated using the phonopy package for phonon calculations [178, 179]. The underlying principle for the phonon dispersion lines is the finite displacement method, where the energy differences for small distortions (0.02 Å) of the atomic positions in the supercell are calculated. Based on this principle to simulate the vibrations, the harmonic phonon dispersion lines are constructed using the following relation [179] in the harmonic

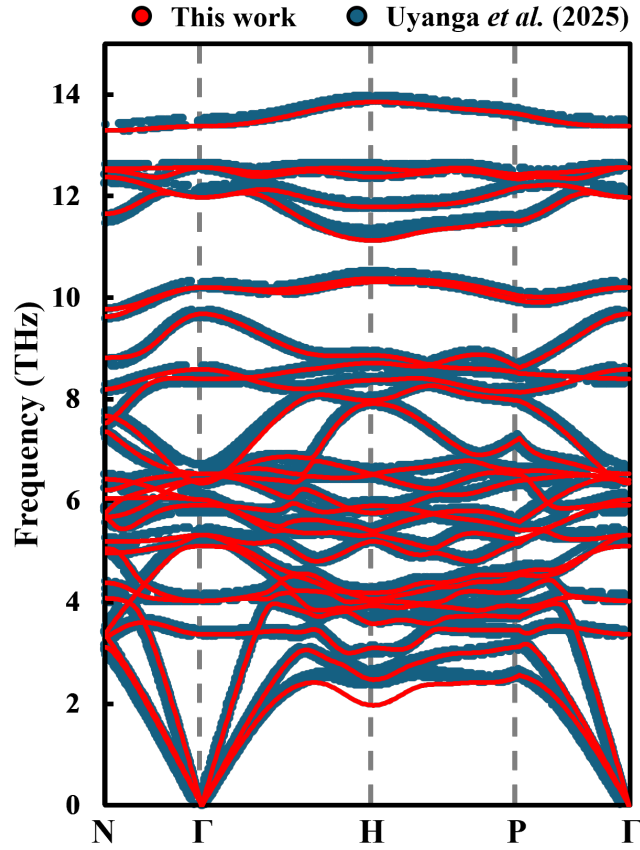


Figure 4.40: Theoretical harmonic phonon dispersion lines (red lines) calculated for the Fe_2P compound with the phonopy program package. Theoretical phonon lines from Uyanga *et al.* [177] (blue dots) are shown for comparison.

approximation:

$$E = \sum_{q\nu} \hbar\omega(q\nu) \left[\frac{1}{2} + \frac{1}{\exp(\hbar\omega(q\nu)/k_B T) - 1} \right], \quad (4.13)$$

with $q\nu$ as the phonon eigenmode, $\hbar$ as the reduced Planck constant, ω as the eigenvalues, k_B as the Boltzmann constant and T as the temperature. The resulting harmonic phonon dispersion lines for the substitution-free Fe_2P compound are depicted in Fig. 4.40 together with the theoretical phonon band structure from Uyanga *et al.* [177].

A comparison of the phonon dispersion spectra shows a good agreement with each other. The only visible difference between both spectra is a slightly lower frequency for the lowest line. The value for this line at the high symmetry point H is ~ 2 THz, while Uyanga *et al.* [177] reports a frequency of 2.3 THz at this point. Besides this, only minor shifts are visible. This demonstrates that the calculations are performed in good precision. For further verifications, additional phonon dispersion lines for other binary and unary elements were calculated and added to appendix B. As the phonon dispersion lines for

ternary and quaternary compounds are very complex due to the high number of lines, their spectra are excluded.

4.7.2 Heat Capacity

To provide an additional way to validate the calculated data of this work, the calculated heat capacities of compounds are compared to available experimental data. The heat capacity at constant pressure C_p , which is in general more viable for solid state materials, can be derived from the Helmholtz free energy by the following connection:

$$C_P = -T \left(\frac{\partial^2 F(T, V)}{\partial T^2} \right)_{V, P}. \quad (4.14)$$

with T as the temperature and $F(T, V)$ as the Helmholtz free energy. The calculated heat capacity for the substitution-free Fe_2P compound is depicted in Fig. 4.41. A generally good agreement of the theoretical data with experimentally available data by Beckman *et al.* [231] and Hudl *et al.* [232] is achieved. The shift of the theoretical maximum (~ 250 K) to a higher temperature can be explained by the calculated Curie temperature in the mean-field approximation. As it is known for this case that the T_C is overestimated, a correctional factor of 0.75 was implemented for the theoretical T_C s used in phase stability calculations. This factor reduces the theoretical T_C s to better account for the magnetic contribution and improve the modelling of the phase stabilities. The theoretical Curie temperatures were used instead of experimental T_C s to provide a consistent approach for the calculation of the phase stabilities. Additionally, experimental T_C s are not known for every investigated compound.

For further clarification, the calculated ternary Si heat capacity data is compared to provided experimental values of the working group of Prof. Francois Guillou. The $\text{Fe}_2\text{P}_{0.92}\text{Si}_{0.08}$ and $\text{Fe}_2\text{P}_{0.84}\text{Si}_{0.16}$ data is depicted with experimental data for hexagonally structured $\text{Fe}_{1.93}\text{P}_{1-x}\text{Si}_x$ materials with $x = 0.1$ and 0.15 Si per f.u. The development of the heat capacity for these compounds is shown in Fig. 4.42. In this figure the heat capacity including the magnetic contribution is illustrated as a dotted line, while the vibrational and electronic contribution to the heat capacity is demonstrated by a dashed line. The experimental data is included as red and black lines.

The comparison of the experimental and computational values show a good agreement at low temperatures up to 175 K. After this point the heat capacity with the magnetic contribution starts to overestimate, while the vibrational and electronic contribution further corroborate well up to 200 K. This deviation is to be expected, as the precise calculation of the heat capacity is difficult to achieve due to a high complexity of the method and the heat capacity being very sensitive to small energy fluctuations [233]. Additionally,

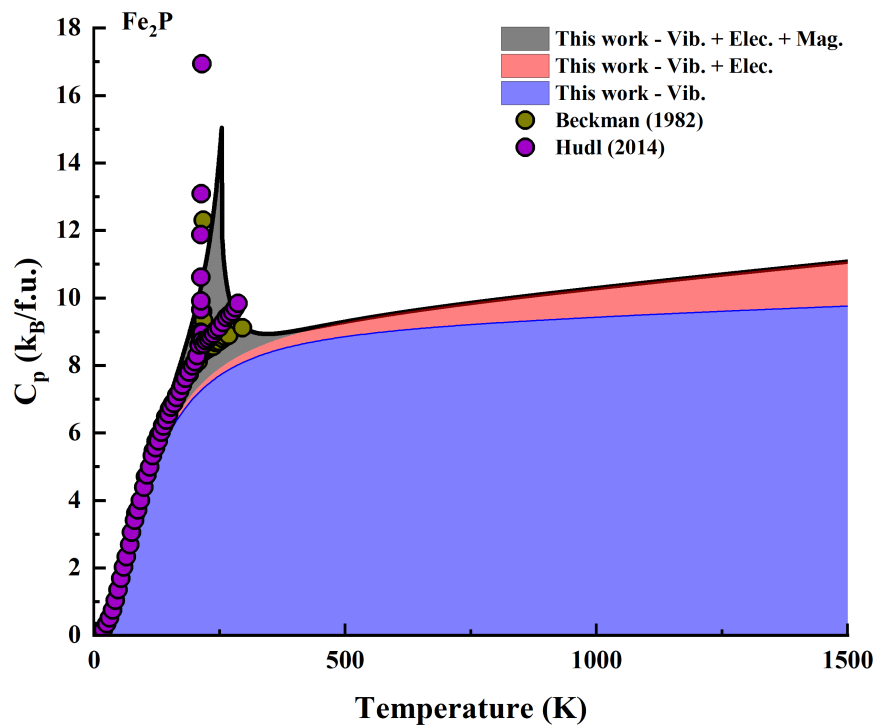


Figure 4.41: Calculated heat capacity at constant pressure C_p for the hexagonal Fe_2P compound. The influence of the vibration (blue area), the electronic (red area) and the magnetic contribution (black are) are shown. Experimental data for comparison by Beckman *et al.* [231] and Hudl *et al.* [232] are shown as circles.

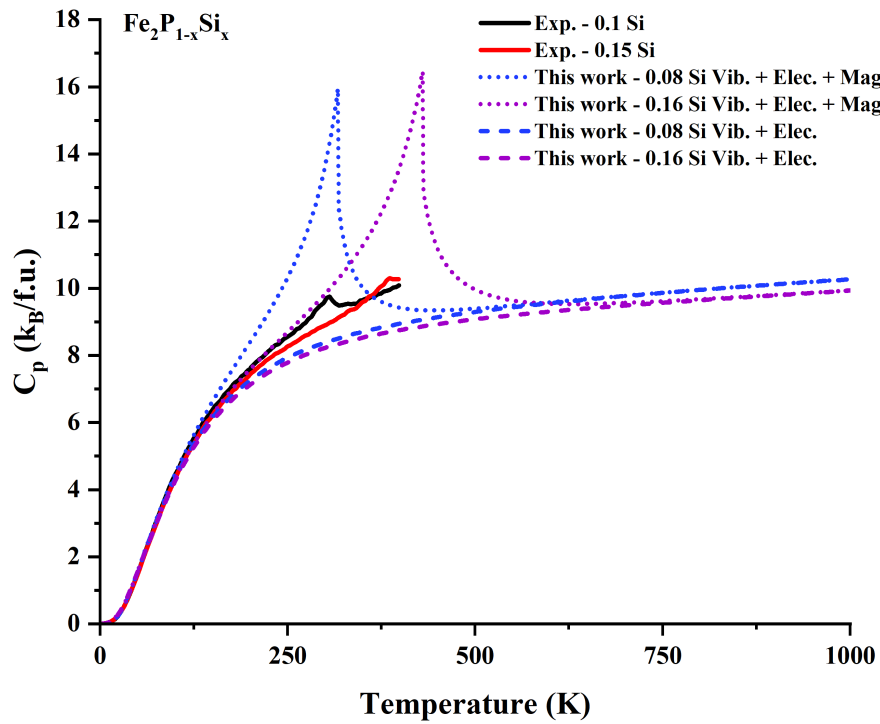


Figure 4.42: Calculated heat capacity at constant pressure C_p for the hexagonal ternary $\text{Fe}_2\text{P}_{0.92}\text{Si}_{0.08}$ and $\text{Fe}_2\text{P}_{0.84}\text{Si}_{0.16}$ compound. This data is compared to experimental data for $\text{Fe}_{1.93}\text{P}_{0.9}\text{Si}_{0.1}$ (black) and $\text{Fe}_{1.93}\text{P}_{0.85}\text{Si}_{0.15}$ (red). The experimental data was provided by the working group of Prof. Francois Guillou.

the magnetic moment plays an important factor in the calculation of the magnetic contribution and is only described by the mean magnetic moment at 0 K. The experimental values are also subject to uncertainties in the measurement. Nevertheless, the temperature at which the magnetic contribution peaks, is very similar for the experimental and calculated results. This shows, that the correction of the calculated Curie temperatures seems to be reasonable for this work. This comparison also provides a good validation for our calculated values as the magnetic contribution in experiments is usually much more pronounced than in this case.

4.7.3 Ternary Phase Stabilities - Si Substitution

The influence of Si substitution on the Gibbs energies and the stability of the compounds is investigated. The formation and competition energies are calculated similar to the calculations at 0 K with Eq. 4.2 and Eq. 4.3. However, in this case the computed Gibbs energies are used as the corresponding energy values for the compounds. Ternary Gibbs phase diagrams are constructed using the finite temperature Gibbs energies. In these diagrams, the reference states are taken as the corners of the triangle. As we only consider stoichiometric compounds, the isothermic ternary phase diagrams only contain the actual composition of the compounds. The formation and competition energies are represented via color coding. Except the highlighted compounds, all other points in these phase diagrams are results from linear interpolation.

In Fig. 4.43 are two ternary phase diagram with the unaries Fe, P and Si as reference states depicted. However, the area of interest can be limited to the high Fe content area in the upper third of the ternary phase diagram, as demonstrated in the right side of the figure. For all following Fe-P-Si ternary phase diagrams only the high Fe content area is shown. The isothermic ternary phase diagrams have been constructed in the range of 0 to 1500 K. As reference compounds for these phase diagrams three different setups have been used. The first arrangement handles the already mentioned unary elements as reference states for the formation energy. In the other two variants, the competition energies are calculated by considering Fe, FeP and FeSi in one case and Fe, Fe₂P and FeSi in the other variant. The zoomed in ternary phase diagrams for the formation energies at $T = 0, 300, 500, 750, 1000, 1250, 1500$ and 1750 K are illustrated in Fig. 4.44.

An increase of the temperature slightly decreases the formation energies for the investigated Fe₂P compounds. This drop in energies can mainly be attributed to compounds with low Si concentrations. At all temperatures the unary formation energy of the compounds are negative, indicating stable compounds when unary elements are used as reference states. However, the negative trend of Si on the stability persists at temperatures above 0 K. This effect lessens at high temperatures and the formation energy reaches

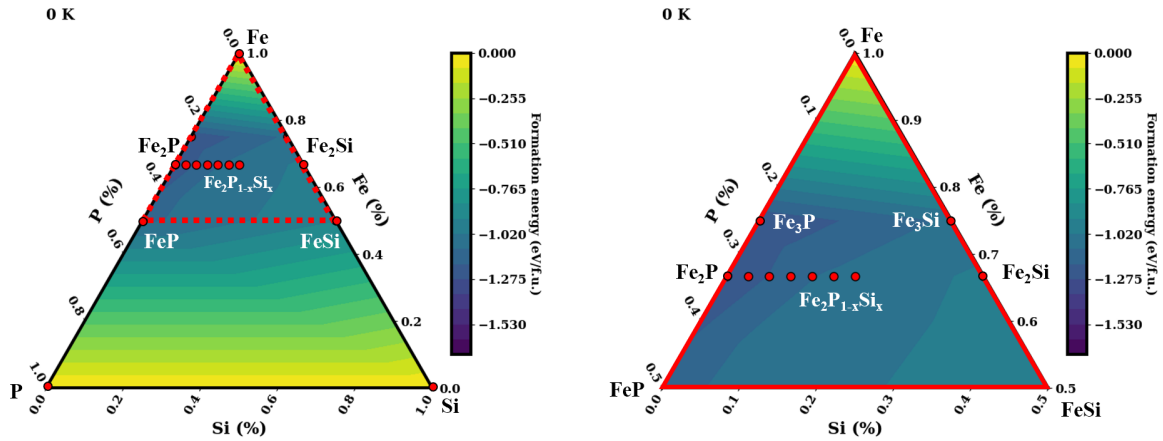


Figure 4.43: **Left:** Ternary phase diagram for the ternary Fe-P-Si compounds using the unary elements Fe, P and Si as reference materials. The Fe-rich area (≥ 0.66 % Fe) of interest is marked by a dashed red triangle. **Right:** Enlargement of the Fe-rich (≥ 0.66 % Fe) area for better visibility of the considered compounds.

values between -1.02 and -1.53 eV/f.u. at 1750 K for the ternary $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ compounds.

Similar to the formation energy, the competition energies for the temperatures 0, 500, 1000 and 1500 K are illustrated in isothermic ternary phase diagrams in Fig. 4.45. On the left side of the figure, the competition energies are calculated using the Gibbs free energy of the binary compounds FeP and FeSi, as well as the unary element Fe. This leads to the complete high Fe content area being interpolated. On the right side Fe₂P, FeSi and Fe are taken as the reference compounds, which leads to a slightly lower range of compositions. With Fe₂P as a reference compound, not considered compositions are kept as white and are not depicted in the phase diagram.

Using FeP, FeSi and Fe, the negative influence of Si on the stability prevails at 0 K, increasing the values of E_{Comp} with more Si. This is shown by a color gradient from greenish to more yellowish. This initial effect is still present at elevated temperatures but the competition energies show decreasing results. At 0 K the energies account to values between -0.075 and -0.15 eV/f.u. While the initial 0 K value of the compound with $x = 0.5$ Si lies within -0.025 and 0.05 eV/f.u., the competition energy for this compound decrease to -0.075 eV/f.u. at 500 K. At even higher temperatures, the energy further reduces to -0.150 eV/f.u. at 1000 K and -0.225 eV/f.u. at 1500 K. This temperature effect is visible for all compounds and demonstrates the increasing stability and therefore higher manufacturability of these compounds.

Nevertheless, using Fe₂P, FeSi and Fe as reference states produces results that are

4.7. Finite Temperature Phase Stabilities

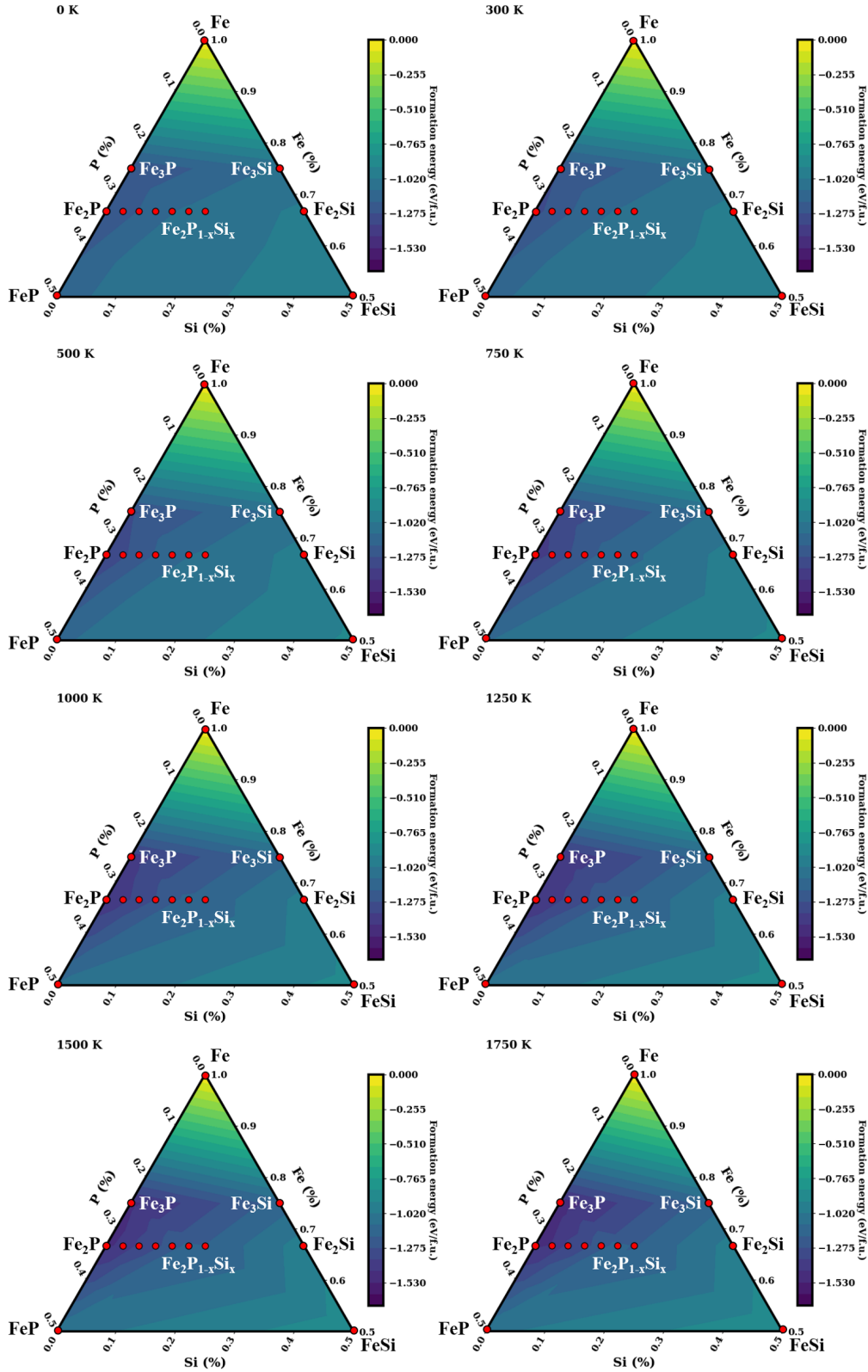


Figure 4.44: Calculated isothermic ternary phase diagrams in the Fe-rich area with investigated compounds marked by red dots. The unary elements Fe, P and Si are used as reference phases for the calculation of the formation energy. The diagrams are depicted for the temperatures 0, 300, 500, 750, 1000, 1250, 1500 and 1750 K. All points except the marked compounds are achieved by linear interpolation.

closer to realistic conditions for manufacturing of these compounds, as Fe_2P exhibits a high stability and is much more likely to form than ternary compounds. This makes the ternary compounds much harder to synthesize. In fact, if the ternary compounds are unstable, they are more likely to decompose back into substitution-free Fe_2P than into the FeP compound or the unary elements. However, for the 0 K preferential sites calculations, FeP was a suitable reference material as it was possible to compare the influence of the energy directly with Fe_2P itself.

Keeping this in mind, the right side of Fig. 4.45 can be considered. With Fe_2P as a reference state, the competition energy starts at positive E_{Comp} values (> 0 eV/f.u.) for the complete substitutional range of compounds. The highest energy is attributed to $\text{Fe}_2\text{P}_{0.67}\text{Si}_{0.33}$, with 0.0468 eV/f.u., which indicates an instability and decomposition to Fe_2P , FeSi and Fe . Increasing the temperature yields a significant difference of the energies to the calculation with FeP , FeSi and Fe as reference states. For Fe_2P , FeSi and Fe the rise of the temperature causes an initial destabilization of the compounds. This can be explained by the increasing stability of the substitution-free Fe_2P material at higher temperatures. The greatest contribution to these rising energies is attributable to the vibrational part of the Gibbs energy that consists of positive values before decreasing and turning negative. This results in energies > 0 eV/f.u. for all $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ compounds and a widening of the yellow area at 500 K. Even higher temperatures then cause the energy values to diminish and the competition energies to turn negative for compounds with low Si concentrations. These results are in agreement with the experimental data by Severin *et al.* [123] and Jernberg *et al.* [121] who also reported a lowering of the stability of hexagonal $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ compounds with Si. However, as the temperature plays an important part for the phase stability, it can be expected that higher temperatures above the investigated temperature range could lead to a stabilization of $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ compounds with higher Si contents. This assumption is supported by Jernberg *et al.* [121], who determined the transition temperature from hexagonal to BCO at 0.35 Si per f.u. to be ~ 800 K, while the transition at $x = 0.25$ is expected to occur at ~ 520 K. Another noticeable point in the ternary phase diagrams diagram marks the compound $\text{Fe}_2\text{P}_{0.5}\text{Si}_{0.5}$. Due to the increasing influence of the decomposition product FeSi , the competition energy at this point starts to decrease and shows lower energies than the Si range of $0.33 \geq x \geq 0.41$.

A detailed development of the calculated competition energies for the compounds with $x = 0.08, 0.16, 0.25$ and 0.33 Si per f.u. is shown in Fig. 4.46. In general, the same temperature effect of a small increase at lower to medium temperatures and a steady decrease thereafter can be seen, just like in the ternary isothermic phase diagrams. However, the isothermic phase diagrams are more suited to show the general trends for a broader range of materials in dependence of the compound composition. The temperature

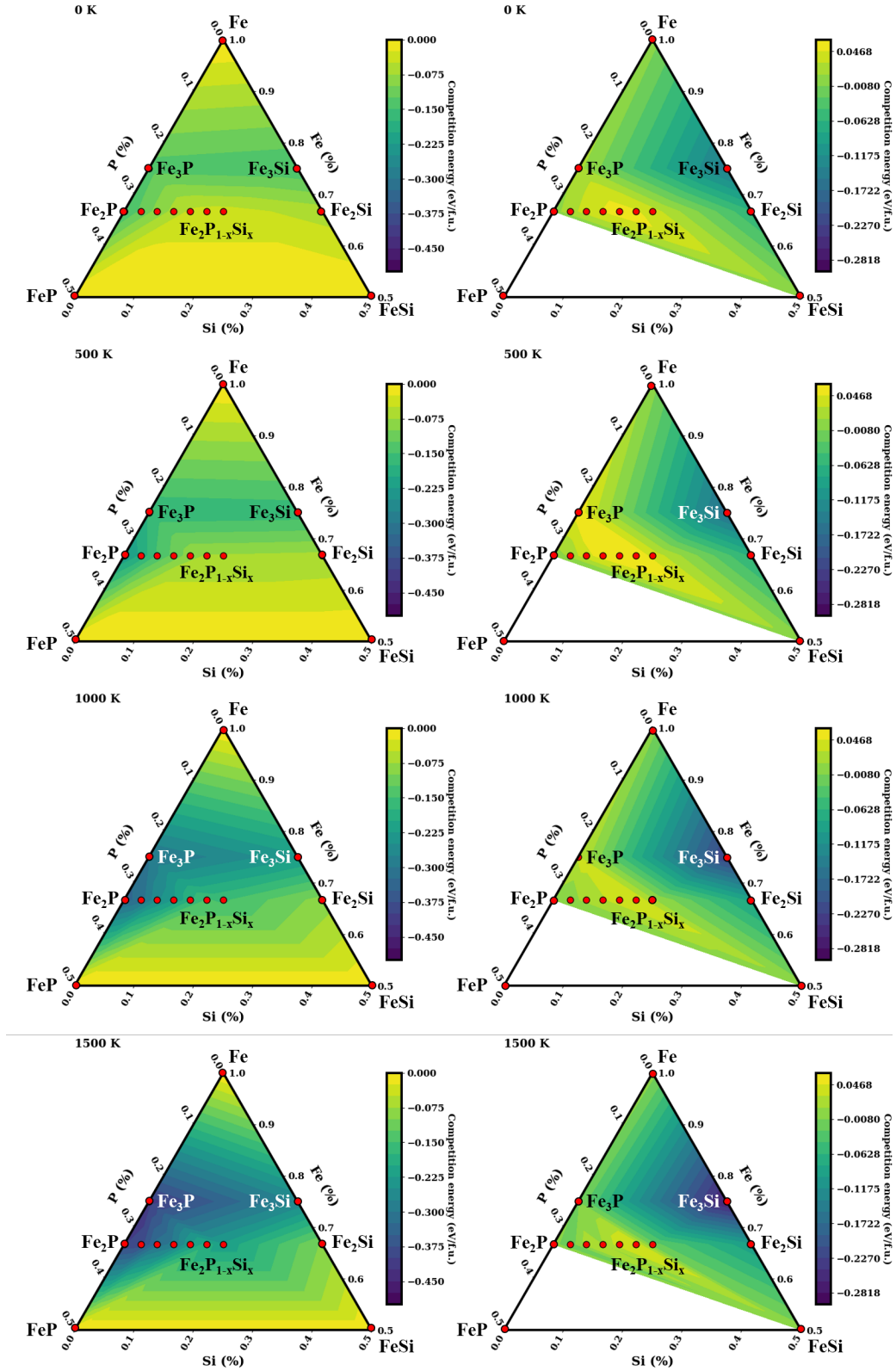


Figure 4.45: Calculated isothermic ternary phase diagrams in the Fe-rich area with investigated materials marked by red dots. **Left:** Calculated competition energies with the binary compounds FeP, FeSi and the element Fe as reference phases. **Right:** Calculated competition energies with the binary compounds Fe₂P, FeSi and the element Fe as reference phases. The diagrams are shown for temperatures of 0, 500, 1000 and 1500 K.

developments are more suited to pinpoint the specific temperature at which a compound stabilizes. The critical formation temperature of compounds incorporating low amounts of Si are seen to stabilize at much lower temperatures with $\text{Fe}_2\text{P}_{0.92}\text{Si}_{0.08}$ (black line) stabilizing at 800 K and $\text{Fe}_2\text{P}_{0.75}\text{Si}_{0.25}$ (blue line) slightly above 1800 K. Note, that at $x = 0.16$ and 0.33 Si (red and violet line), the development of the energy differs from the expected evolution seen at $x = 0.08$ and 0.25 Si. These deviations could be caused by the substitution of Si into a finite cell size under periodic conditions. Especially for the calculation of the phonon energies, these periodic boundary conditions can cause self-interaction errors of the small displacements from the employed finite displacement method [179, 234]. This makes a considerably enlarged unit cell necessary to minimize these effects. In this work, only an increase of the supercells by $2 \times 2 \times 2$ was considered. As it seems, the supercell might have been too small for 0.16 and 0.33 Si to negate these self-interaction problems and should be addressed in future works by a further enlargement of the unit cell.

In the energy curve for $x = 0.16$ Si, the competition energies stay positive at all temperatures, showing no stabilization of the compound. For a better description in this case, the mean value of the $x = 0.08$ and $x = 0.25$ Si is assumed. With this approximation, the competition energy achieves a critical temperature for formation at ~ 1250 K (red dashed line), which matches with a need for a higher temperature with more Si to manufacture the material. In following quaternary considerations the calculated non-mean values are used, but a comparison in relevant cases with the mean values of 0.08 and 0.25 Si will be made. Si concentrations above $x = 0.25$ Si do not reach zero and stay positive in the complete temperature range. This is shown by the energy development of the $\text{Fe}_2\text{P}_{0.67}\text{Si}_{0.33}$ compound that starts to plateau and increase at temperatures above 1300 K. Therefore ternary $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ compounds with $x > 0.25$ Si do not stabilize at elevated temperatures.

With the clarified temperature dependence of the hexagonal compounds, a comparison of the Si substituted compounds with the BCO structure can be made. The competition energy in dependence of the temperature for the hexagonal (full line) and the BCO (dashed lines) structured $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ compounds are shown in Fig. 4.47 for $x = 0.08, 0.16$ and 0.25 Si per f.u. In this comparison, the BCO materials all exhibit negative values, which indicates an increasing stability with Si for the BCO structures. This aligns well with the mentioned experimental findings [121, 123]. However, in case of the hexagonal 0.08 Si structure, the competition energy of the hexagonal compound crosses the competition energy of the BCO structure and shows that at $T > 1200$ K the hexagonal structure is favored. For the other Si concentrations, this effect can not be seen, even though in experiments the hexagonal structure is stable up to $0.2 - 0.25$ Si per f.u. An explanation for

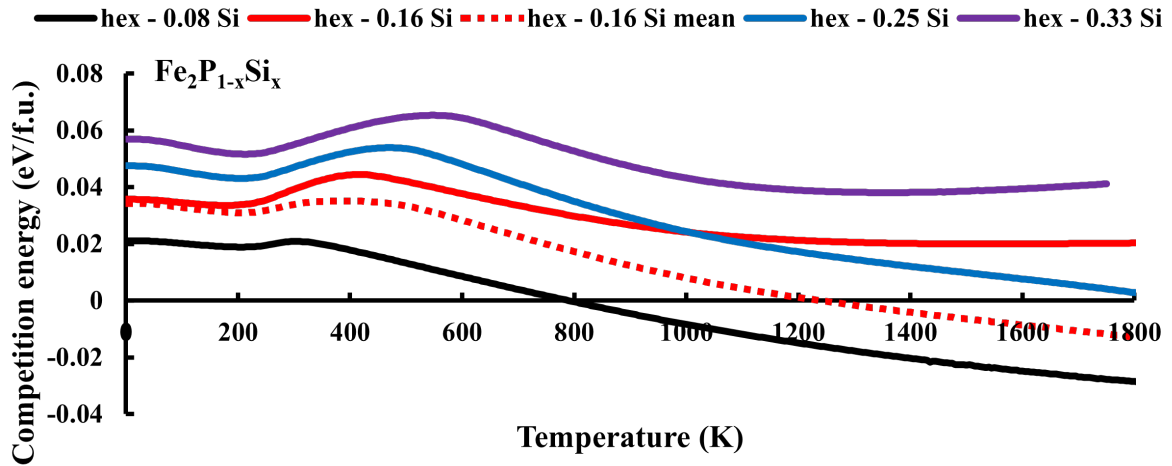


Figure 4.46: Theoretical competition energies (eV/f.u.) for ternary $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ materials with $x = 0.08$ (black), 0.16 (red), 0.25 (blue) and 0.33 (violet) Si per f.u. in dependence of temperature up to 1800 K. For $x = 0.16$ Si per f.u., the mean values (dashed line) between 0.08 and 0.25 Si are shown as an additional approximation. The reference phases for the calculation of E_{Comp} are Fe_2P , FeSi and Fe .

this deviation can be provided with the underlying Gibbs energy values being dependent on the calculated T_C s for the magnetic contribution. As these T_C s are overestimated in the mean-field approximation and corrected by 25 %, these values can still be too high for an assessment. Especially the T_C s of the BCO compounds are relatively poorly described (see Sec. 4.4.2). This indicates that the significantly higher T_C s of the BCO compounds shift the proper trends to temperatures above the investigated range in this work. Nevertheless, the trends of the hexagonal 0.08 Si compounds seem to be properly described as the hexagonal compound is the dominant compound at higher temperatures and the influence of Si matches with literature. This leads to the assumption that the calculations in this work are precise enough for the important hexagonal crystal structure. This lays a good foundation for the stability investigation of the quaternary compounds.

4.7.4 Ternary Phase Stabilities - Co Substitution

With the effect of Si on the phase stabilities uncovered, the effect of Co was investigated. For this case, the formation energies were calculated using the unary elements Fe, P and Co as reference states. The resulting ternary phase diagrams are shown in Fig. 4.48.

At low temperatures a decreasing effect on the formation energies can be seen with increasing Co concentrations in the compounds. This general trend diminishes at increasing temperatures and the compounds near the diagram axis with less Co are seen to increase faster in stability than compounds in the middle of the phase diagram. Since

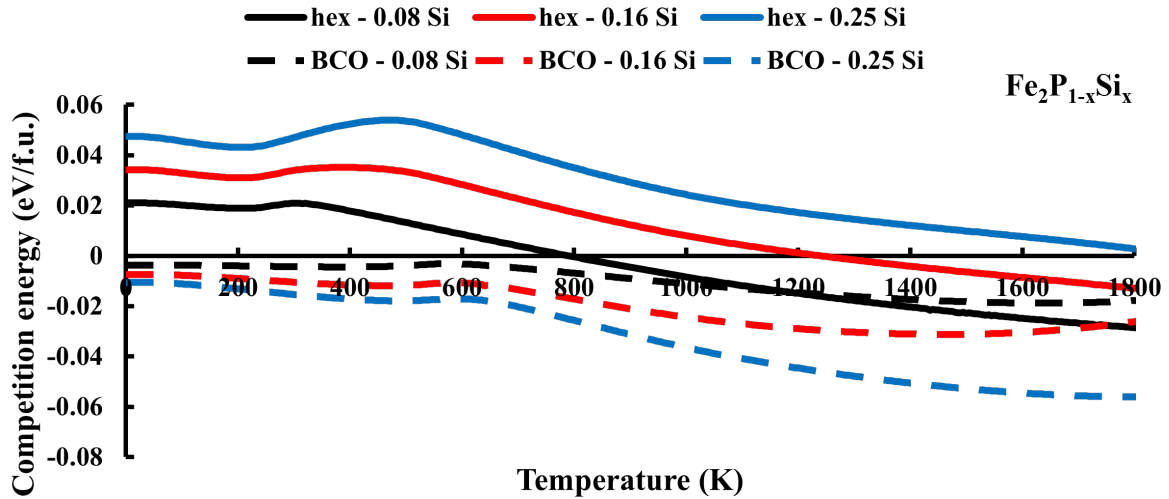


Figure 4.47: Comparison of the competition energies of hexagonally and BCO structured $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ materials with $x = 0.08$ (black), 0.16 (red) and 0.25 (blue) Si per f.u. for temperatures up to 1800 K.

the influence of Co is very small and hard to determine in the ternary phase diagrams, a detailed analysis of the formation energies of the $\text{Fe}_{2-y}\text{Co}_y\text{P}$ compounds was performed. In Fig. 4.49, the formation energies for these compounds are shown in dependence of the temperature together with the stable orthorhombic FeCoP material.

In this figure, the development of the formation energies clearly shows an increase of the energies with rising temperatures in dependence on the Co concentration. At low Co contents, the formation energies first decrease up to ~ 1000 K before starting to slowly increase. At a Co concentration of $y = 0.66$ the energies stagnate and then increase at $T \geq 1000$ K. The complete substitution of the $3f$ site with 1 Co per f.u., even further pushes this effect and leads directly to increasing formation energies in dependence of temperature. This negates the originally decreasing effect of Co and makes Co substituted $\text{Fe}_{2-y}\text{Co}_y\text{P}$ compounds at higher temperatures (> 1250 K for 0.33 Co, ~ 1500 K for 0.66 and 1 Co per f.u.) less stable than the substitution-free Fe_2P compound (black line). The stabilizing effect of Co can therefore only be assumed for lower temperatures, while at high temperatures a decomposition back to the substitution-free Fe_2P compound is promoted.

Describing the stability by considering the binary materials FeP , FeCoP and the pure element Fe , a completely different picture for Co substitution is seen. The orthorhombic FeCoP alloy was used as a reference state, as it is considered a stable compound and would be a logical choice as a decomposition product for $\text{Fe}_{2-y}\text{Co}_y\text{P}$ materials. With these compounds as reference states, all three considered Co concentrations of 0.33, 0.66 and 1 Co (hexagonal) per f.u. are unstable with positive competition energies. This can be

4.7. Finite Temperature Phase Stabilities

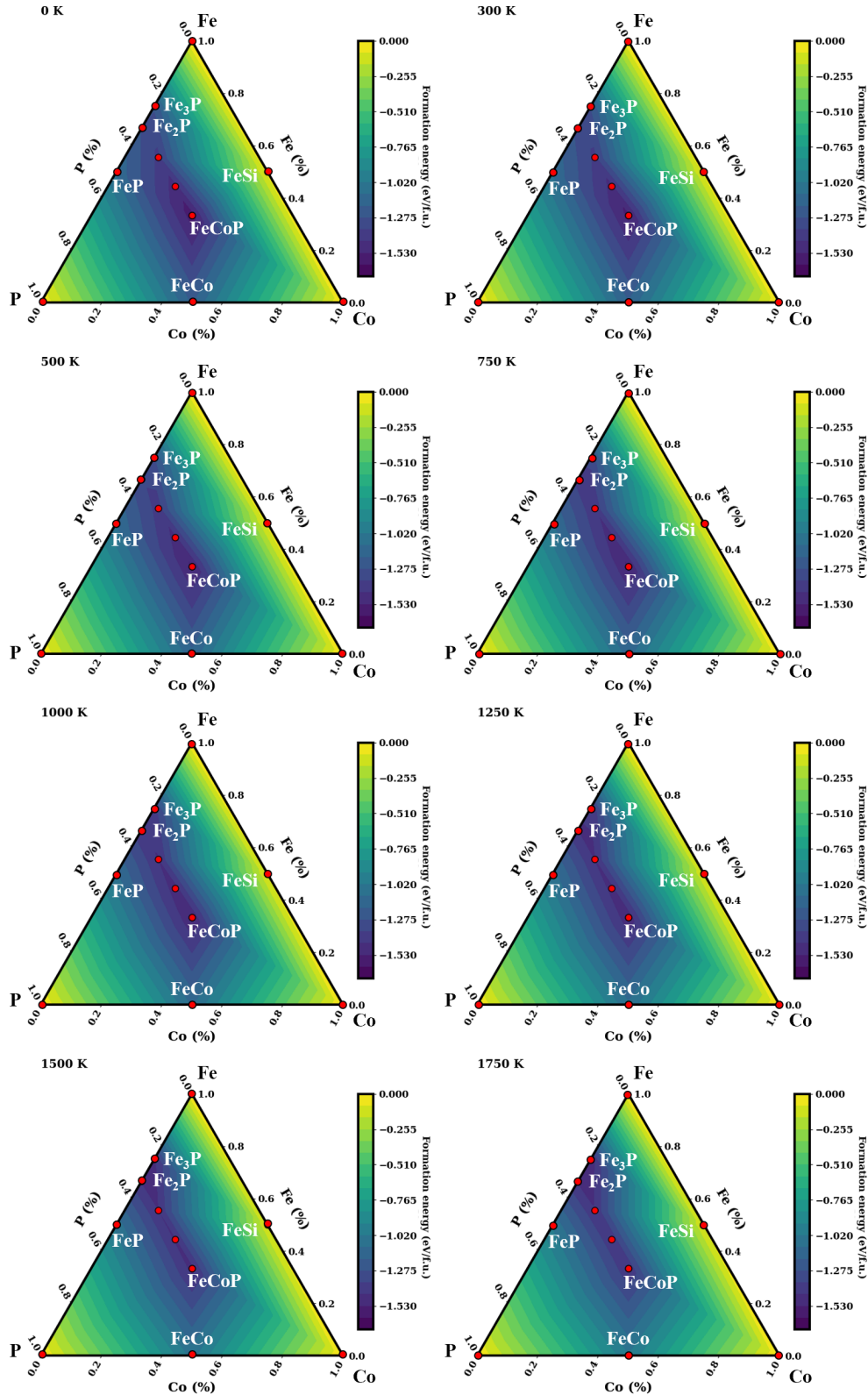


Figure 4.48: Calculated isothermic ternary phase diagrams with investigated materials marked by red dots. The unary elements Fe, Co and P are used as reference phases for the calculation of the formation energy. The diagrams are depicted for the temperatures 0, 300, 500, 750, 1000, 1250, 1500 and 1750 K. All points except the marked compounds are achieved by linear interpolation.

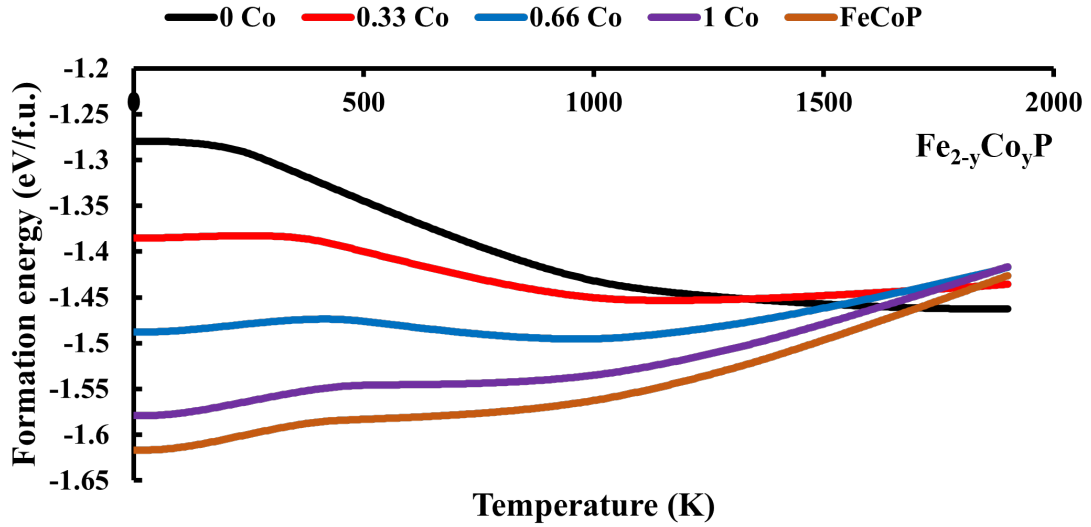


Figure 4.49: Development of the formation energy of $\text{Fe}_{2-y}\text{Co}_y\text{P}$ compounds with $y = 0, 0.33, 0.66$ and 1 Co per f.u. up to 1900 K. The primitive orthorhombic FeCoP is shown additionally for comparison of stability.

attributed to the especially high stability of the FeCoP compound (-1.62 eV/f.u. at 0 K), which also matches with the experimental data showing a transition to the primitive orthorhombic structure at 0.3 Co per f.u.

As already shown in Fig. 4.49, the orthorhombic FeCoP compound (brown line) shows a higher stability than the hexagonal 1 Co per f.u. compound in the complete temperature range. With the stability of FeCoP in mind, the positive competition energies for the ternary hexagonal $\text{Fe}_{2-y}\text{Co}_y\text{P}$ compounds are no surprise. The competition energy development with temperature for the hexagonal $\text{Fe}_{2-y}\text{Co}_y\text{P}$ compounds with $y = 0, 0.33, 0.66$ and 1 Co per f.u. is illustrated in Fig. 4.50 on the left side. In the same figure, the competition energies considering Fe_2P instead of FeP , are shown on the right side for comparison.

For both competition energy calculations positive values for hexagonal $\text{Fe}_{2-y}\text{Co}_y\text{P}$ alloys are visible. Note, that both ways of calculation yield very similar values that only differ by small margins. At 0.33 Co, the results are calculated as ~ 0.006 eV/f.u., while at 0.66 Co the values are 0.016 eV/f.u. at 0 K. With rising temperatures all three compounds increase before starting to decrease at temperature > 400 to 500 K. Nevertheless, the competition energies of all compounds are not seen to stabilize in the considered temperature range. This consequently leads to the assumption that Co substitution alone is not suited to modify the Fe_2P compound. Based on the found effects, it can be concluded that only small amounts of Co are showing the best effects in combination with temperature. In case of competition energies compounds with low Co concentrations are

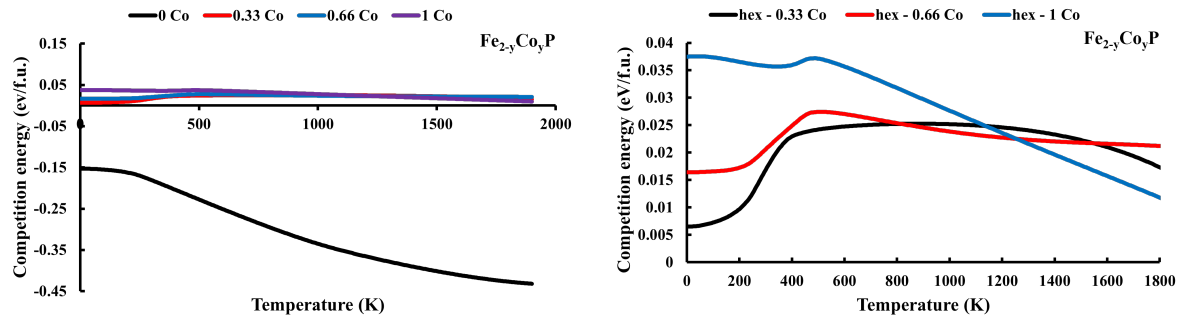


Figure 4.50: **Left:** Development of the theoretical competition energy of hexagonal $\text{Fe}_{2-y}\text{Co}_y\text{P}$ compounds with $y = 0, 0.33, 0.66$ and 1 Co per f.u. up to 1900 K, using FeP , FeCoP and Fe as reference materials for calculation. **Right:** Development of the theoretical competition energy of hexagonal $\text{Fe}_{2-y}\text{Co}_y\text{P}$ compounds with $y = 0, 0.33, 0.66$ and 1 Co per f.u. up to 1900 K, using Fe_2P , FeCoP and Fe as reference materials for calculation.

closer to the threshold of 0 eV/f.u., while higher concentrations perform worse at elevated temperatures.

4.7.5 Quaternary Phase Stabilities - Si Substitution

Based on the phase stability calculations and the identified magnetic properties for pure Si and Co substitutions, it can be derived that only small Si and Co concentrations should be implemented for an optimized Fe_2P -type magnetic material. Furthermore, the ternary phase stability investigations showed that Si promotes the transition from the hexagonal to the BCO crystal structure and complicates the manufacturing of the material. Bearing the mentioned findings in mind, the influence of simultaneous substitution of both elements into the Fe_2P material is examined next.

Phase stability calculations for the three focused Si concentrations ($0.08, 0.16$ and 0.41 Si) with additional Co substitution up to $y = 1$ Co per f.u. were performed. For $x = 0.41$ Si, Co concentrations were only considered up to $y = 0.83$ Co. Within these limits, a broad range of compounds, especially at low Si contents, was covered and the combined effect of Si and Co was investigated for both low and high Si containing hexagonal $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ materials.

To ensure a systematic understanding for the presented results, the unary formation energies with the pure elements Fe, Co, Si and P as reference materials are handled first. This is followed by the competition energies using FeP , FeSi , FeCoP and Fe . Lastly, the important competition energy values with substitution-free Fe_2P , FeSi , FeCoP and Fe as reference states for are discussed. For the unary formation energies a general assessment of the temperature effect is made, as all compounds show formation energies < 0 eV/f.u.

and can be considered as stable. In both competition energy sections, the results are discussed for each of the chosen temperatures in the diagrams, with specific details to the 0.08, 0.16 and 0.41 Si compounds. Using this methodology a systematic, clear and thorough analysis is ensured. The respective formation and competition energies for all examined Si concentrations are depicted in Fig. 4.52, 4.53 and 4.54 for the unary and binary reference states. Since with four elements it is not possible to construct a triangle diagram, two dimensional isothermic diagrams encompassing the compounds of interest were made. For a better visualization, the range of compositions in a pyramidal context is illustrated in Fig. 4.51.

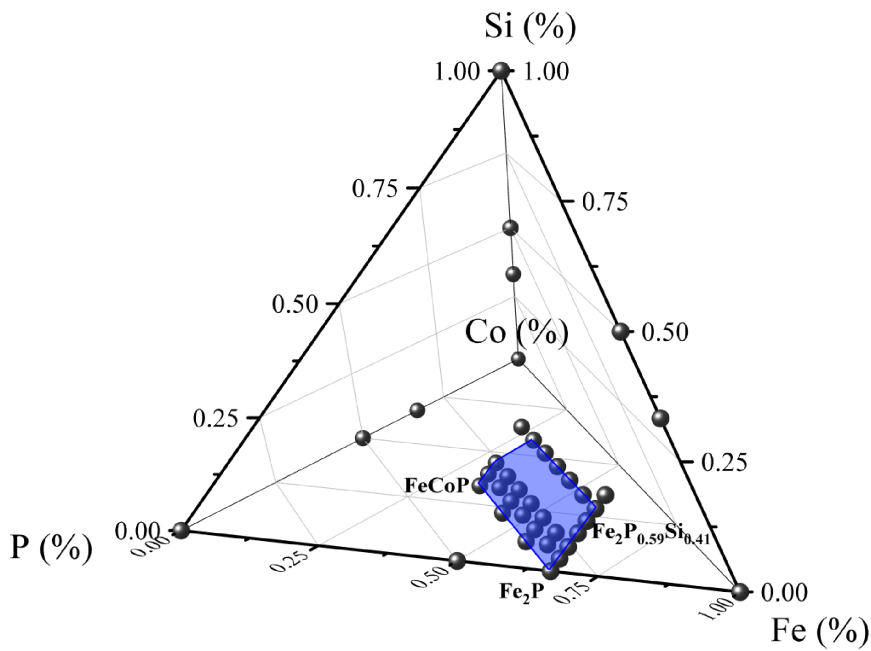


Figure 4.51: Three dimensional representation of the investigated compositional range of hexagonally structured quaternary $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ compounds.

Fe, Co, P and Si - Formation Energy

Using the pure unary elements to calculate the formation energies provides a basic evaluation of the possibility of synthesizing a compound. However, this formation energy is mostly suitable for binary compounds, as ternary and quaternary compounds are more likely to decompose into other binary materials. Nevertheless, the formation energies are still a good first investigation in a simple manner. The calculated unary formation energies for the quaternary $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ materials in Fig. 4.52 show negative E_{Form} values for all compounds. Increasing Co concentrations are seen to further diminish the formation energies independently from the temperature. This decrease is visible in all isothermic

diagrams towards FeCoP at the top left of the diagrams. These findings align with the decrease of the formation energies at 0 K (see Sec. 4.6.2). Increasing temperatures yield a general lowering for all compounds. Note, that this stabilization with temperature is less pronounced at higher Co concentrations. The reason for this stabilization is the already handled decrease of E_{Form} with Si at higher temperatures. The lower effect with higher Co contents, can be deduced from the also described increasing influence of Co with temperature. Both of these effects are visible for all three investigated Si concentrations. The combination of these effects shows therefore lower formation energies for the 0.08 Si compounds than for $x = 0.16$ and 0.41 Si per f.u. This indicates in a first assessment, that at low Si concentrations a higher stability is achieved. The highest energies and therefore less stable compounds can be seen for high Si concentrations, which exhibit noticeably higher values in the figure. This first assessment therefore concludes a higher stability for $x = 0.08$ and 0.16 Si per f.u., while $x = 0.41$ Si compounds are less stable. With higher temperatures and additional Co substitution the formation energies are further reduced.

FeP, FeSi, FeCoP and Fe - Competition Energy

In the case of the competition energies using FeP, FeSi, FeCoP and Fe (Fig. 4.53), a different development of the energies with temperature can be seen. In this investigation, not all compounds are assessed as stable and exhibit energies > 0 eV/f.u. This important threshold is plotted in the diagrams as a broader black line and the corresponding areas are labeled as stable and unstable.

Starting at 0 K, a high stability for compounds with low Si concentrations of $x = 0.08$, and 0.16 Si can be seen. This stability reaches up to Co substitutions of $y = 0.66$ and 0.5 Co per f.u. at 0.08 and 0.16 Si, respectively. With increasing temperatures the 0 eV/f.u. threshold shifts upwards indicating a stabilizing temperature effect. At 300 K, the temperature causes high Si, high Co containing compounds to reach negative E_{Comp} values. A further rise of the temperature to 750 K reduces the unstable area of compounds significantly, only excluding the $\text{Fe}_{1.16}\text{Co}_{0.83}\text{P}_{0.84}\text{Si}_{0.16}$ and $\text{FeCoP}_{0.92}\text{Si}_{0.08}$ compositions from being stable. Above 1000 K only the ternary hexagonal FeCoP compound is seen as unstable, which remains unstable up to 1750 K.

In general, the temperature decreases the competition energies and stabilizes compounds with higher Co substitution at elevated temperatures. From these first competition energy investigation using FeP, FeSi, FeCoP and Fe, it can be derived that compounds with only low contents of Si and Co are more stable than compositions including high concentrations of both elements. This is based on the fact, that low Si and Co concentrations start at negative E_{Comp} values and get further decreased with temperature. This development is also visible in the diagram.

4.7. Finite Temperature Phase Stabilities

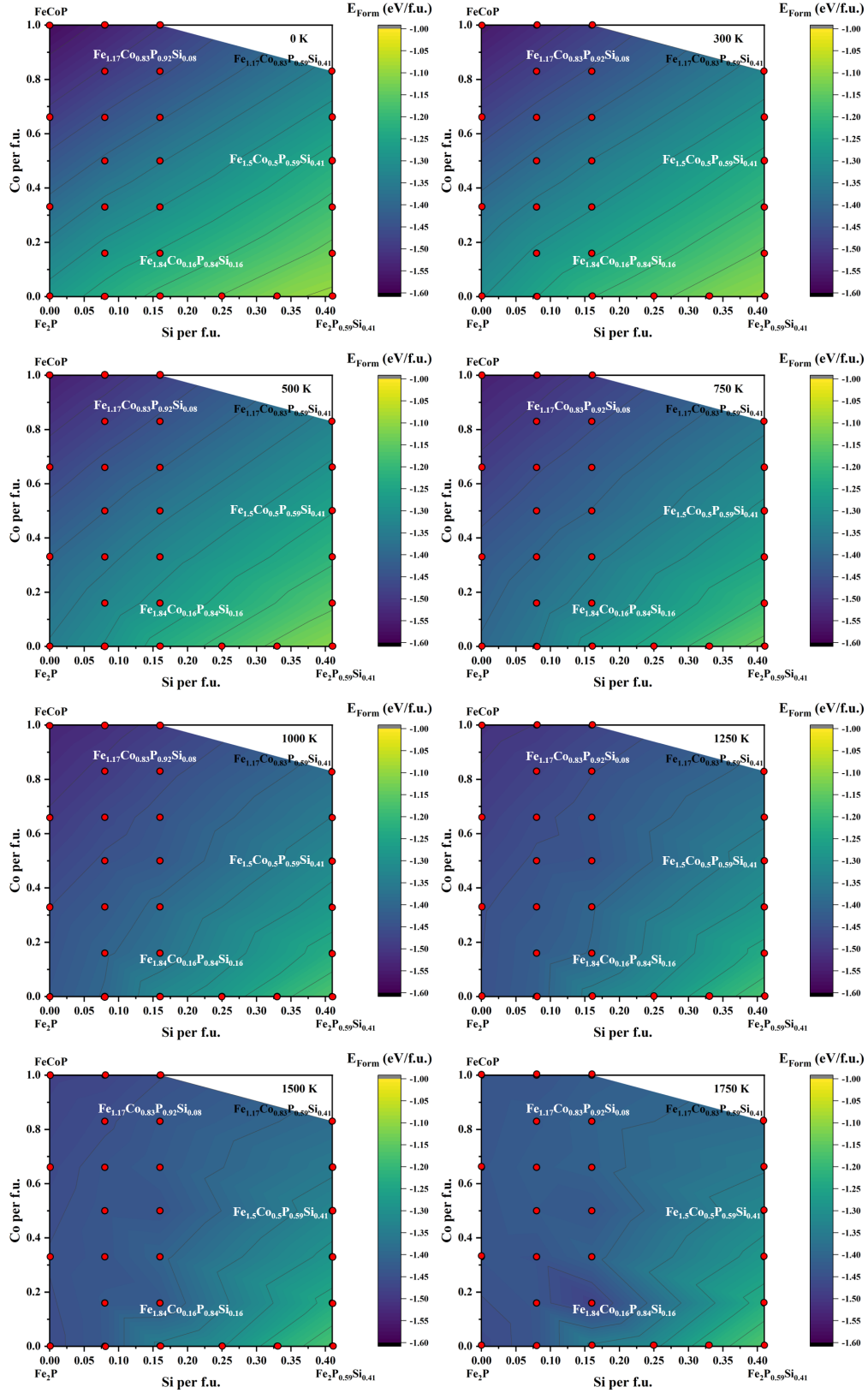


Figure 4.52: Heatmap for the formation energy of the quaternary $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ materials (red dots) in the range of $0 \leq x \leq 0.41$ Si and $0 \leq y \leq 1$ Co per f.u., except for the high Si case where y is considered up to 0.83 Co per f.u. The formation energy is color coded (yellow to dark blue) and the 0 eV/f.u. threshold is marked by a black line.

4.7. Finite Temperature Phase Stabilities

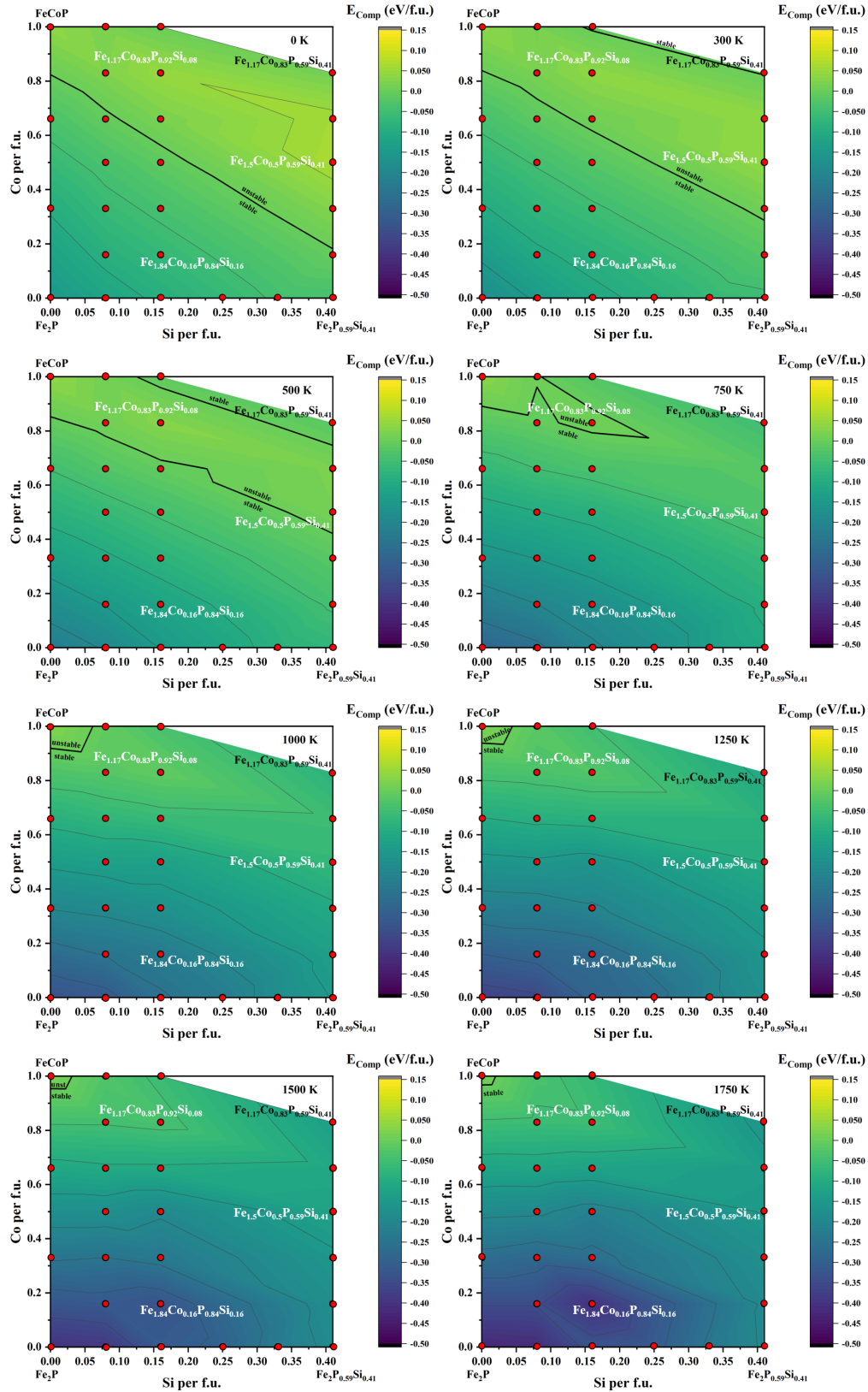


Figure 4.53: Heatmap for the competition energy using FeP, FeSi, FeCoP, Fe and Co of the quaternary $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ materials (red dots) in the range of $0 \leq x \leq 0.41$ Si and $0 \leq y \leq 1$ Co per f.u., except for the high Si case where y is considered up to 0.83 Co per f.u. The competition energy is color coded (yellow to dark blue) and the 0 eV/f.u. threshold is marked by a black line.

Fe₂P, FeSi, FeCoP and Fe - Competition Energy

The consideration of Fe₂P instead of FeP, provides a better description for the stability, as the quaternary compounds are more likely to decompose back into Fe₂P than FeP. This change drastically influences the competition energies of the Fe_{2-y}Co_yP_{1-x}Si_x materials. The resulting quaternary heatmaps with Fe₂P, FeSi, FeCoP and Fe as reference states are shown in Fig. 4.54 for each temperature.

At lower temperatures, all included alloys yield positive E_{Comp} values. Therefore, up to 500 K all compounds can be expected to be unstable and to decompose into the reference materials. First changes appear at 750 K for compounds incorporating a high amount of Si and a medium amounts of Co of $y \geq 0.5$ Co per f.u. At low Si concentrations of 0.08 and 0.16 Si per f.u., no compound is seen to exhibit negative values compared to the reference states, meaning no stabilization is achieved. A further increase of the temperature to 1000 K drastically widens the range of stable compounds. At this temperature, all quaternary 0.16 Si compounds are determined to be stable when at least $y \geq 0.16$ Co is present in the compound. Only the ternary Fe₂P_{0.84}Si_{0.16} material yields positive values above 0 eV/f.u. With 0.41 Si the stability range also expands, including the Fe_{1.67}Co_{0.33}P_{0.59}Si_{0.41} compound. For a Si concentration of 0.08 Si, the ternary base Fe₂P_{0.92}Si_{0.08} alloy yields negative E_{Comp} values and is expected to be stable at this temperature. This widening of the stability with increasing temperature can further be observed at 1250 and 1500 K. At these temperatures, the 0.08 Si compounds start to show negative energies. At 1250 K, only a Co content of $y = 0.66$ yields a positive competition energy. At 1500 K this composition is also expected to stabilize and yields a negative competition energy. In the case of a high Si concentration of 0.41 Si included in the compound, the lowest considered Co concentration of 0.16 Co, is also calculated to be a producible compound with a negative competition energy at these temperatures.

As already covered for ternary Si substitution, the Fe₂P_{0.84}Si_{0.16} material is additionally described by the mean values of the 0.08 and 0.25 Si compounds. This results in a slightly changed heatmap for the quaternaries at temperatures ≥ 1500 K. The respective diagrams for 1500 and 1750 K are shown for comparison in Fig. 4.55.

Employing the mean values for compounds incorporating 0.16 Si, the Fe₂P_{0.84}Si_{0.16} compound is seen to stabilize above 1250 K. This only affects the lower 0 eV/f.u. line and shifts it further to the right. At 1500 K, the line was shifted up to 0.2 Si per f.u., almost reaching up to 0.25 Si at 1750 K. This shows that at high temperatures the negative influence on the stability of the additional Si can be overcome.

Even with the slight deviation for the Fe₂P_{0.84}Si_{0.16} compound, the theoretical competition energies show promising results for the investigated low and high Si containing compounds. The performed calculations also match with the experimental stability inves-

4.7. Finite Temperature Phase Stabilities

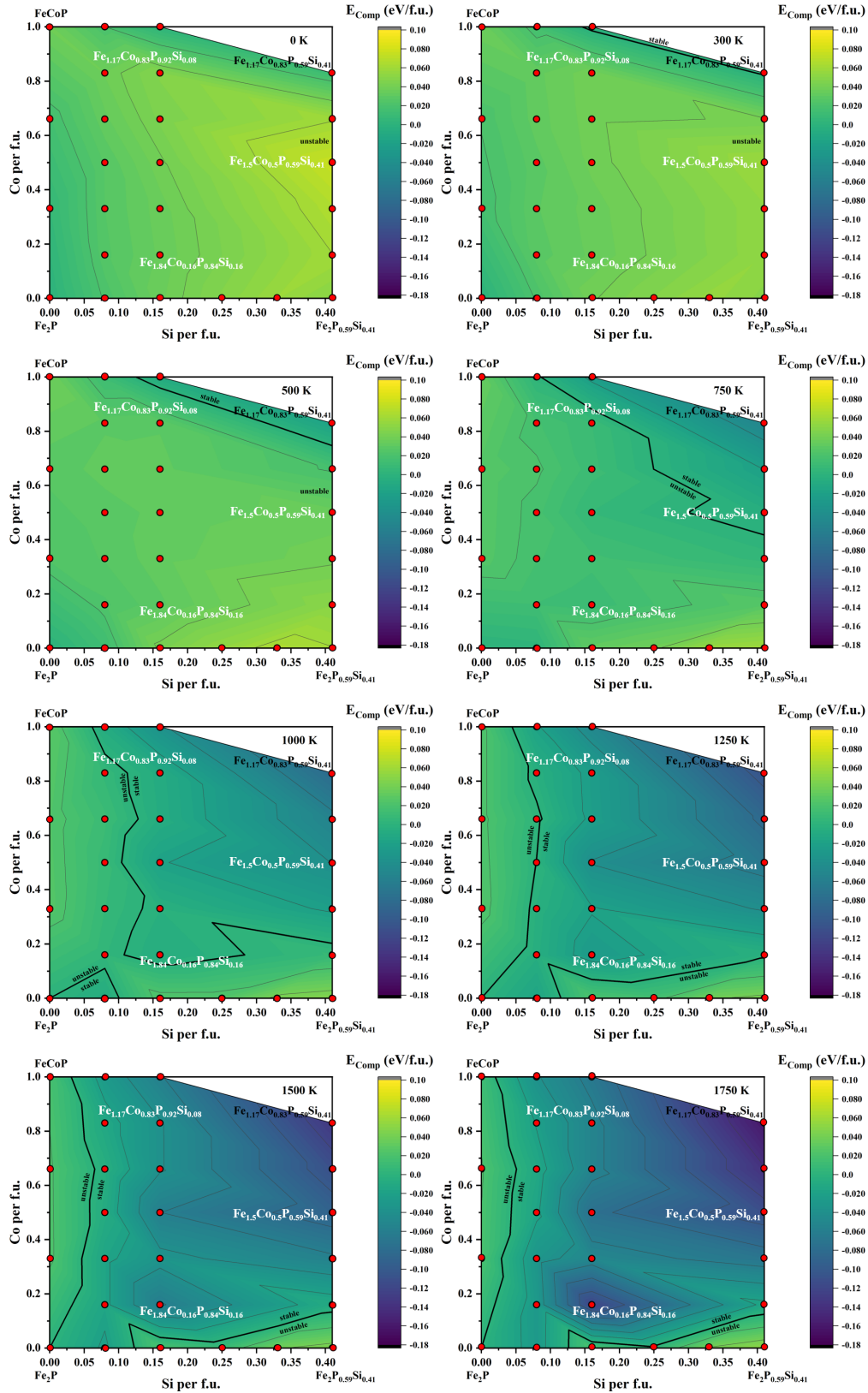


Figure 4.54: Heatmap for the competition energy using Fe_2P , FeSi , FeCoP , Fe and Co of the quaternary $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ materials (red dots) in the range of $0 \leq x \leq 0.41$ Si and $0 \leq y \leq 1$ Co per f.u., except for the high Si case where y is considered up to 0.83 Co per f.u. The competition energy is color coded (yellow to dark blue) and the 0 eV/f.u. threshold is marked by a black line.

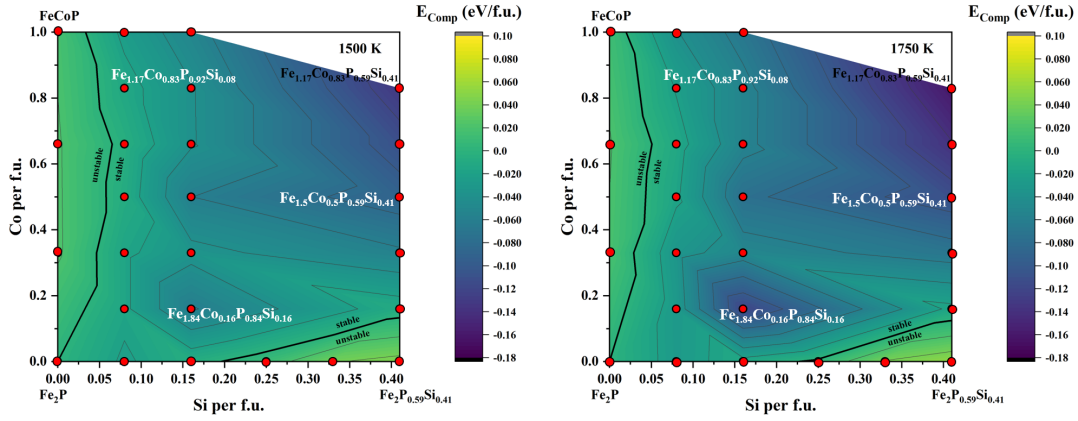


Figure 4.55: Heatmap at 1500 and 1750 K for the competition energy using Fe_2P , FeSi , FeCoP , Fe and Co of the quaternary $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ materials (red dots) in the range of $0 \leq x \leq 0.41$ Si and $0 \leq y \leq 1$ Co per f.u., except for the high Si case where y is considered up to 0.83 Co per f.u. The competition energy is color coded (yellow to dark blue) and the 0 eV/f.u. threshold is marked by a black line. For 0.16 Si the mean values between 0.08 and 0.25 Si are used for calculation.

tigations by Bao *et al.* [68], who showed an increase of the stability range for the hexagonal crystal structure for quaternary compounds. This is also visible in Fig. 4.54. Considering the mean values for $\text{Fe}_2\text{P}_{0.84}\text{Si}_{0.16}$, the higher temperature diagrams match the experimental data even better, showing an almost identical stability range. A comparison of the experimental phase diagram with the data of this work is illustrated in Fig. 4.56.

In this thesis, the finding of an increased range for the phase stability with simultaneous Si and Co substitution is supported by the negative competition energies of the quaternary $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ compounds at higher temperatures. These results emphasize that the investigated compounds can be manufactured and produced.

Nevertheless, the development of the phase stabilities depicts an interesting trend in dependence of the temperature when Fe_2P is considered instead of FeP . The ternary Si investigations have shown, that higher amounts of Si destabilize the materials at low temperatures but stabilize with rising temperatures. Meanwhile, ternary Co substitution shows decreasing energies at first, which changes to a destabilization effect at elevated temperature. However, in the quaternary $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ calculations, the first compounds that are visible to stabilize at 750 K are compounds including high Si and high Co concentrations. Only at temperatures ≥ 1000 K are compounds with lower amounts of Si seen to achieve negative competition energies. This could indicate that a combination of high Si and high Co concentrations improves the stability of the hexagonal structure and makes these compounds easier to produce. Additionally, at lower Si concentrations the substitution of Co seems to enhance the stability of the compounds even though Co

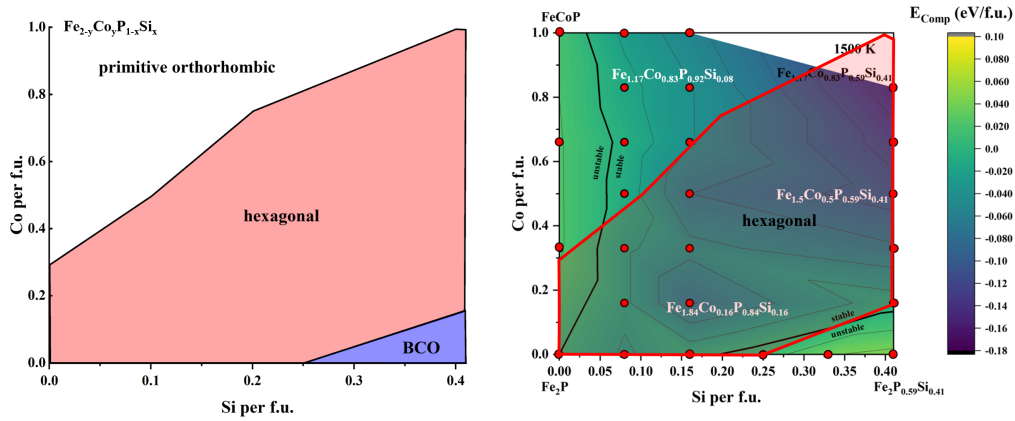


Figure 4.56: Comparison of the experimentally found phase stabilities (**left**) for quaternary $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ compounds by Bao *et al.* [68] with the calculated phase stabilities at 1500 K of this work (**right**). The experimentally found stability range of the hexagonal crystal structure is additionally depicted in the heatmap to emphasize the agreement.

alone was seen to promote a decomposition.

4.8 Combined Assessment of Stability Investigations and Magnetic Properties

With the complete investigation of the magnetic properties and the phase stabilities, an overall evaluation of the suitability of the quaternary $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ compounds is possible. As the hardness factors showed the substitutional range is limited to $x = 0.16$ Si and $y < 0.5$ Co per f.u. to provide $\kappa \geq 1$. Consequently, only compounds in this compositional range are able to exhibit the needed magnetic properties for hard magnetic materials.

On the other hand, the Curie temperature demonstrated a significant improvement with increasing Si and Co concentrations. However, the influence of Co is limited to theoretical values ~ 650 K, above which only further Si substitution can enhance the T_C . Nevertheless, even at smaller Si and Co concentrations theoretical T_C s of up to 550 K can be achieved at $x = 0.16$ Si and $y = 0.16$ Co per f.u. This may qualify these mediocre concentrations to yield an effective improvement of the Curie temperature for selected industrial applications. This is supported by experimental T_C s around 500 K for similar compounds [68].

Combining the 0 K magnetic properties with the phase stability investigations, it can be determined that the $\text{Fe}_{2-y}\text{Co}_y\text{P}_{0.92}\text{Si}_{0.08}$ and $\text{Fe}_{2-y}\text{Co}_y\text{P}_{0.84}\text{Si}_{0.16}$ materials can be expected to be producible at higher temperatures due to their negative competition energies.

If the temperature for production is limited, the 0.16 Si compounds are likely to be easier to produce than the 0.08 Si alloys. However, at 0.08 Si the magnetic properties are in general slightly higher, except for the Curie temperatures. Taking the Curie temperature as the determining measurement, the 0.16 Si compounds are preferred.

One noteworthy composition is the $\text{Fe}_{1.84}\text{Co}_{0.16}\text{P}_{0.84}\text{Si}_{0.16}$ compound that is calculated to achieve a magnetization of 1.05 T and a $|BH|_{max}$ of 221 kJ/m³. This combines with a theoretical Curie temperature of 557 K, and a K_1 of 1.83 (1.93) MJ/m³ using the GGA (LSDA) functional. This compound is expected to stabilize at temperatures ~ 1000 K and shows the highest overall stability of all compounds at ~ 1800 K. The mentioned magnetic properties summarize in an overall hardness value of ~ 1.4 .

All of these properties make this compound a very interesting alloy for consideration as a future magnetic material. Even though it shows slightly lower magnetic properties than compounds with 0.08 Si, this alloy exhibits a higher T_C and therefore addresses the main drawback of substitution-free Fe_2P . Consequently, when lower T_C s are acceptable, another promising material would be the $\text{Fe}_{1.84}\text{Co}_{0.16}\text{P}_{0.92}\text{Si}_{0.08}$ compound. It combines a theoretical T_C of 437 K with a higher anisotropy of 1.68 (1.87) MJ/m³ and an overall hardness of 1.4 (1.5). Except for the ternary $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ compounds, none of the investigated materials exhibit the required hardness factor in combination with the needed phase stability and high Curie temperature. However, the stability for these ternaries is limited to around $x = 0.25$ Si per f.u., which also restricts the improvement due to substitution. Quaternary materials with simultaneous Si and Co substitution can therefore be used, to circumvent this hurdle and enable further fine-tuning of Fe_2P .

Chapter 5

Conclusion and Outlook

Concluding this work, systematic *ab initio* investigations on the magnetic properties and phase stabilities of ternary and quaternary $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ materials were conducted, to identify suitable new hard magnetic materials. Screening calculations of *p*-block elements such as B, C, N, Al, Si, Ga, Ge and As identified Si as the best metalloid substitute for P. The best metal element for Fe exchange was found to be Co. The effects of the sole elements were examined first, before the combined effect of both were focused. The computed results were compared with available literature and a reasonable agreement was visible, strengthening the validity of the results. For quaternary $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ materials only limited experimental data was available.

Conventional DFT calculations for the magnetic properties and phase stabilities of the investigated compounds were performed and a satisfying agreement with literature was achieved. The Curie temperatures were calculated in a mean-field approximation. A systematic overestimation of the T_C for the ferromagnetic state was observed, but a good quantitative agreement of the observed trends was accomplished. The magnetocrystalline anisotropy was calculated using total energy differences and non-collinear DFT calculations.

The element Si is found to exhibit a great influence on the magnetic properties of ternary $\text{Fe}_2\text{P}_{1-x}\text{Si}_x$ materials. The magnetic moments of the Fe atoms in the $3f$ position are greatly enhanced from 0.83 to 1.5 $\mu_B/\text{f.u.}$ because of a significant magnetovolume and chemical effect. This results in increasing $\mu_0 M_S$ and $|BH|_{\text{max}}$ values up to 1.24 T and 308 kJ/m³ at 0.5 Si. KKR-MFA calculations reveal that the underlying reason for this is a strengthening of the $3f$ - $3g$ interactions, visible in a general rise of the exchange interaction energies. A detailed analysis of the J_{ij} s delivers that Si exhibits a significant volume effect that completely dominates a small negative chemical effect on the J_{ij} . This leads to increasing exchange interaction energies and consequently rising theoretical Curie temperatures up to 977 K. However, Si also diminishes the magnetocrystalline anisotropy of the compounds, visible by a lowering of K_1 and H_a . First assessments of the phase stability in connection with Si are done computing the formation and competition energy at 0 K. This results in increasing energies for both properties, with the competition energy reaching positive values ~ 0.33 Si per f.u. and thus limiting the solubility of Si in Fe_2P . With the consideration of Fe_2P in the competition energy formulation, all energy values

are determined as positive at 0 K. Rising temperatures enable the compounds to be stable up to concentrations of 0.25 Si at temperatures of 800 K (0.08 Si), 1250 K (0.16 Si) and ~ 1800 K (0.25 Si), which matches with experimental data by Severin *et al.* [123] and Jernberg *et al.* [121]. A comparison with BCO phase stabilities shows a preference for the BCO structure with increasing Si content. Nevertheless, a higher stability of the hexagonal compounds is demonstrated at high temperatures and low Si concentrations.

For ternary Co substitution in $\text{Fe}_{2-y}\text{Co}_y\text{P}$ compounds, a decrease of the magnetic moments and therefore M_S and $|BH|_{max}$ is found. A thorough analysis of the magnetic moments leads to the assumption that this decrease is connected to the inherently lower magnetic moment of Co compared to Fe. This assumption is further supported by steadily increasing exchange interaction energies with rising Co concentrations, as especially the $3g-3g$ and $3f-3g$ interactions are enhanced. These improvements of the J_{ij} s are mainly attributed to the chemical effect of Co itself and also result in higher theoretical Curie temperatures, climbing up to > 600 K. Similar to Si, Co decreases the anisotropy constant K_1 and anisotropy field H_a significantly, which is connected to the band filling of the compound. The examination of the formation and competition energy at 0 K depicts a decrease when the unary elements are considered. Taking the binary and ternary compounds as reference phases, an increase of E_{Comp} is observed. Combining this with finite temperature calculations, none of the compounds are expected to stabilize enough to reach negative values even at elevated temperatures. This matches with literature that describes a limited stability in the hexagonal phase only up to 0.3 Co per f.u. [68, 194], which is below the lowest investigated concentration of 0.33 Co per f.u.

Combining Si and Co substitution, both trends of an increase with Si and a decrease with Co can be seen in the compounds. Noteworthy is the influence of both compounds on the magnetocrystalline anisotropy, where a higher Si concentration makes the compound more resilient to the loss of the uniaxial anisotropy with increasing Co concentration. This phenomenon can be connected to the band filling of the compound, as Si and Co both compensate each other in that regard and enable an optimal band filling with electrons. Phase stabilities of quaternary $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ are first calculated at 0 K, revealing a decrease of the formation energy with Co and an increase with Si. Using two approaches for the competition energy with FeP and Fe_2P , the competition energy is seen to increase until a change of the equation is necessary. This change of equation is caused due to the higher amount of Co than P and the material FeCoP being unable to further describe the increase of Co concentration. With the second equation the competition energy is seen to decrease again. This can very well be seen as a point for future improvement and can cause deviation at higher Si and Co concentrations.

The important Curie temperature is overall increased with both Si and Co substitution,

due to improved J_{ij} interactions. Three different trends are discovered in dependence of Si concentration. At low Si, a clear increase of T_C is found, while at medium Si the T_C stagnates ~ 650 K. High Si concentrations first yield a decrease from ~ 950 K, which then transitions into oscillating values around 780 K. The underlying reason could be the combination of the positive and negative volume and chemical effects of Si and Co that partly negate each other after a certain point of substitution. For Co substitution a general maximum for the improvement of the T_C is identified around 650 K. Only the volume effect of Si is seen to improve the T_C above this point. Nevertheless, even small amounts of Si and Co substitution are already found to drastically increase the T_C for some industrial applications.

Finite temperature phase stabilities of the quaternary compounds uncover a surprising effect connected to temperature. Materials with high Si and high Co concentrations are seen to stabilize first, when Fe_2P is used as a reference state. As mentioned, this could be due to the change of the equation for the competition energy for Co concentrations above the concentration of P. Nevertheless, with rising temperatures the 0 eV/f.u. threshold continuously moves towards lower Si concentrations. The 0.41 Si compounds are therefore seen to stabilize first, followed by 0.16 and 0.08 Si compounds. This opposes the ternary Si findings of a higher stability at low Si concentrations. The combined effect of Si and Co therefore describes an significant increase of the stability range for hexagonal compounds, which corroborates with scarcely available experimental data [68].

The final assessment of the magnetic properties and the phase stability calculations reveals that all 0.08 and 0.16 Si compounds with Co concentrations $y < 0.5$ Co per f.u., can be considered as potential hard magnetic materials with an expected stabilization at elevated temperatures. All of these compounds show hardness values > 1 , reach negative competition energies and show increased theoretical Curie temperatures > 440 K. One material that should especially be highlighted is the $\text{Fe}_{1.84}\text{Co}_{0.16}\text{P}_{0.84}\text{Si}_{0.16}$ alloy that is calculated to exhibit a hardness factor ~ 1.4 , a theoretical $T_C \sim 550$ K and a phase stability that is higher than its neighboring materials.

For further verification of these theoretical findings, more experimental data for quaternary $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ materials on the magnetic properties, the Curie temperature and phase stabilities are needed. However, this work highlights some promising materials for use as hard magnets that can very well be used to reduce the dependency on RE elements in the long run. Additionally, this work can be used as an orientation for future experimental investigations, to determine which hexagonally structured ternary and quaternary $\text{Fe}_{2-y}\text{Co}_y\text{P}_{1-x}\text{Si}_x$ compounds show promising properties and stabilities. The BCO structure also shows promising magnetic and structural properties, which makes this crystal symmetry also interesting to put some focus on in following research activities.

Further research can also be put into the substitution of other elements into Fe_2P , such as Ge or B.

Appendix

A: Binary Formation Energies

To determine the most stable binary compounds consisting of Fe and P, Fe and Si and Fe and Co, the formation energy of known binary compounds is calculated. The resulting E_{Form} values are depicted in Fig. 5.1 with Fe-P compounds on the left, Fe-Si compounds in the middle and Fe-Co on the right side.

From these results, FeP was determined as the most stable binary Fe-P compound with an E_{Form} of ~ -0.59 eV/atom. Following its high stability, it is seen as the most likely decomposition product for quaternary $Fe_{2-y}Co_yP_{1-x}Si_x$ compounds, next to a decomposition back to Fe_2P . Similarly, the FeSi compound shows a high formation energy of ~ 0.49 eV/atom, making it considerably more stable than other Fe-Si binaries. Even though the Fe_2Si compound has a composition closer to Fe_2P , Fe_2Si is known to be a metastable compound that only forms under extreme conditions or in meteorites [235]. Therefore, FeSi was chosen as one of the most likely decomposition products. For the binary compounds consisting of Fe and Co, significantly lower formation energies are observed. The highest stability was calculated for the 1:1 phase FeCo with an E_{Form} of -0.019 eV/atom. Consequently, FeCo was taken as the third binary for consideration as a reference material. Compounds above the red line encompassing the materials with the lowest formation energies (such as Fe_4P , Fe_4Si and Fe_3Co) are considered as unstable. Based on these findings FeP, FeSi and FeCo, were used as reference materials for the calculation of the competition energies of compounds. The last reference material, FeCoP, was additionally chosen, as it represents the only really known stable ternary compound consisting of Fe, Co and P. It exhibits a formation energy of -0.54 eV/atom [209, 236].

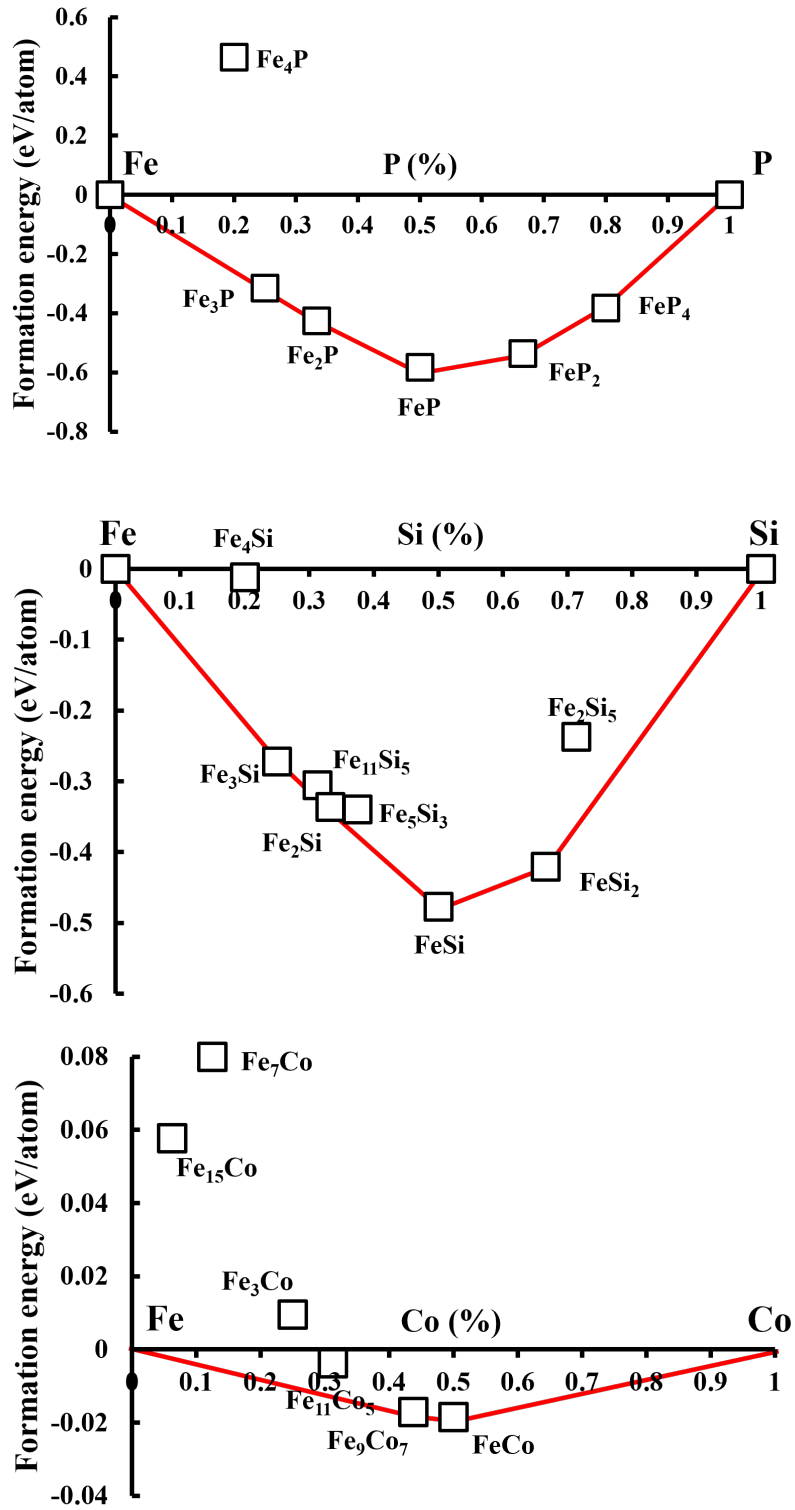


Figure 5.1: Calculated formation energies for binary compounds consisting of the elements Fe and P (**upper** image), Fe and Si (**middle** image) and Fe and Co (**lower** image) to identify the most stable binary alloys from these elements. The red line marks a stability line, that can be drawn from all stable compounds. Materials above this line are not considered as stable.

B: Density of States

For a more detailed comparison of the possible substitution-free Fe_2P crystal structures (hexagonal, body-centered-orthorhombic and primitive orthorhombic), the associated density of states were calculated and are depicted in Fig. 5.2, 5.3 and 5.4.

The calculated density of states show a few distinct differences to each other. The most obvious difference is a much higher general density of states per f.u. for the hexagonal crystal compared to BCO (max. 65 states per eV/unit cell) and prim. orthorhombic (max. 20 states per eV/unit cell). Other than this, the hexagonal cell shows around -2.6 eV a valley of the energy states. This valley is not visible in BCO and prim. orthorhombic. From -2.5 to -2.0 eV the spin down density of states decrease steadily as do the spin up states around that energy. One significant peak can be seen around -0.8 eV for the spin up states, where a maximum of ~ 80 states per eV/unit cell is reached. Above the Fermi energy a valley at the spin down states is around 0.5 to 0.8 eV calculated. No band gap is visible for the materials. The BCO crystal structure shows a consistent band of states from ~ -4 eV up to -0.5 eV in the spin up region. The spin down region is similar with a consistent set of states from -2.6 to 1 eV, showing no gaps or significant changes. The spin up states seem to be generally slightly higher compared to the hexagonal compound. However, no gap around -2.6 eV is seen for spin up. No band gap is visible for this material as well. The density of states calculation for the primitive orthorhombic symmetry shows similarities to both crystal structures. From -2.6 to 0 eV all states for the down spin are occupied similar to the hexagonal structure. Nevertheless for the spin up region, no gaps are visible which is comparable to the BCO structure. Above the Fermi energy, the prim. orthorhombic crystal shows a gap ~ 0.5 eV for spin down, which is similar to the hexagonal compound. In this compound, no band gap is visible, marking it as a metal.

All three materials show no band gap in the density of states calculation, which identifies them as metal compounds. The high similarity between the compounds, underlines the high similarity of the crystal structures. The BCO structure is described to be achievable by a slight deformation of the hexagonal structure [43]. This can also be explained by the tetrahedral and square based pyramidal environments enclosing the Fe atoms in the two different sublattices. In the primitive orthorhombic crystal similar environments for the Fe atoms are observed. Combined with the close density of states diagrams, a connection of the crystal structures by distortion can be assumed.

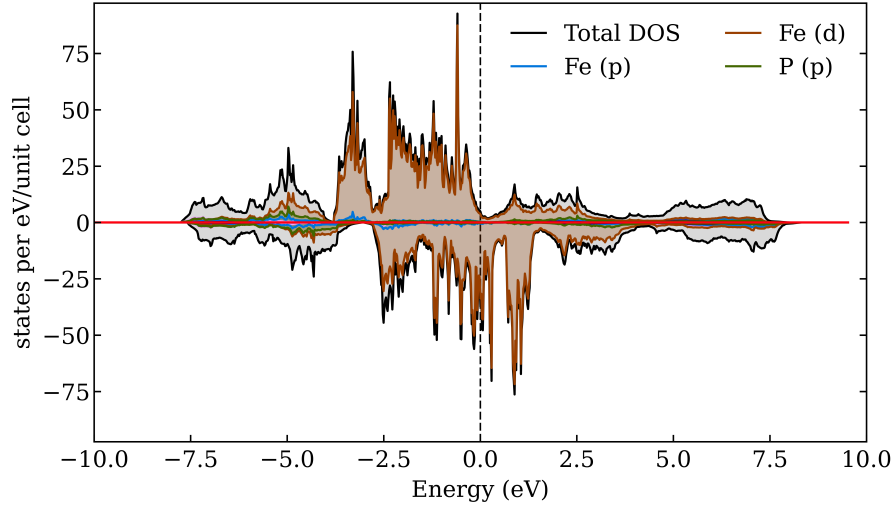


Figure 5.2: Calculated density of states for the hexagonal ($P\bar{6}2m$) Fe_2P unit cell with the contributions of each element shown in the range from -10 to 10 eV. The total DOS is shown by a black line, while the respective p and d electron contributions of Fe are colored as blue and dark yellow. The p electrons from P are seen in a green color. The Fermi energy (0 eV) is marked by a vertical dashed line.

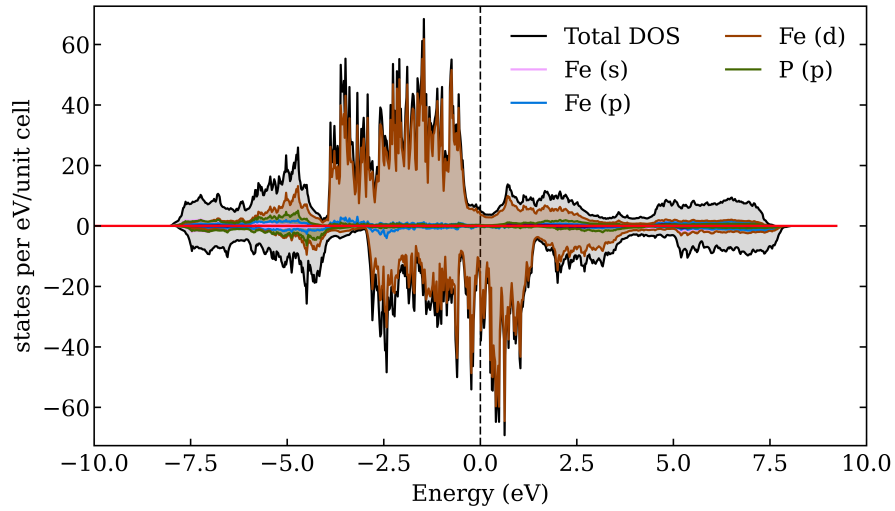


Figure 5.3: Calculated density of states for the body-centered-orthorhombic ($Imm2$) Fe_2P unit cell with the contributions of each element shown in the range from -10 to 10 eV. The total DOS is shown by a black line, while the respective s , p and d electron contributions of Fe are colored as pink, blue and dark yellow. The p electrons from P are seen in a green color. The Fermi energy (0 eV) is marked by a vertical dashed line.

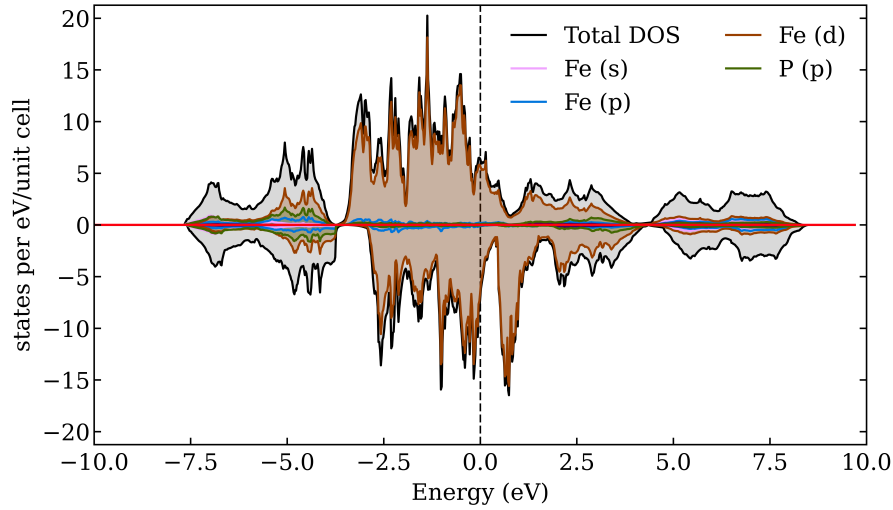


Figure 5.4: Calculated density of states for the primitive orthorhombic ($Pnma$) unit cell with the contributions of each element shown in the range from -10 to 10 eV. The total DOS is shown by a black line, while the respective s , p and d electron contributions of Fe are colored as pink, blue and dark yellow. The p electrons from P are seen in a green color. The Fermi energy (0 eV) is marked by a vertical dashed line.

C: Harmonic Phonon Dispersion Lines

The harmonic phonon dispersion lines of bcc structured Fe (Fig. 5.5), black orthorhombic P (Fig. 5.6), fcc structured Si (Fig. 5.7), fcc structured Co (Fig. 5.8), binary orthorhombic FeP (Fig. 5.9) and primitive cubic FeSi (Fig. 5.10) were calculated and compared with available experimental data to further show the agreement of the conducted calculations with literature. The calculated harmonic phonon lines show a generally good agreement with the literature data. Only slight deviations of the lines are visible, that can be explained by slight differences of the atomic positions in the crystal structure of the compounds. Nevertheless, the calculated data shows a reasonably good agreement.

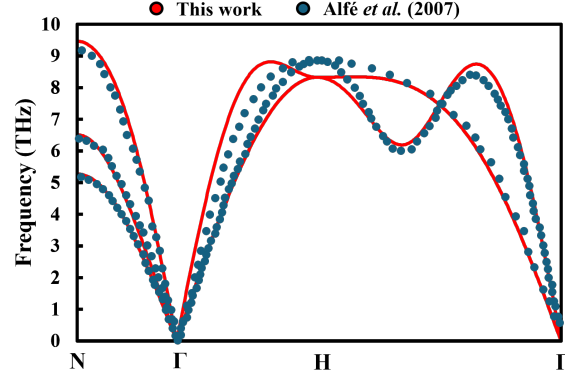


Figure 5.5: Calculated phonon dispersion lines at 0 K for bcc Fe using the phonopy program package in comparison with literature data by Alfé *et al.* [237].

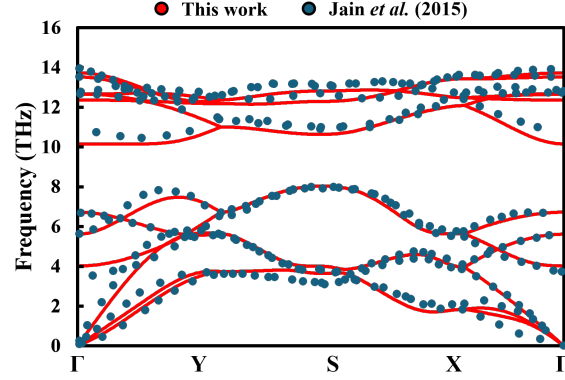


Figure 5.6: Calculated phonon dispersion lines at 0 K for black P using the phonopy program package in comparison with literature data by Jain *et al.* [238].

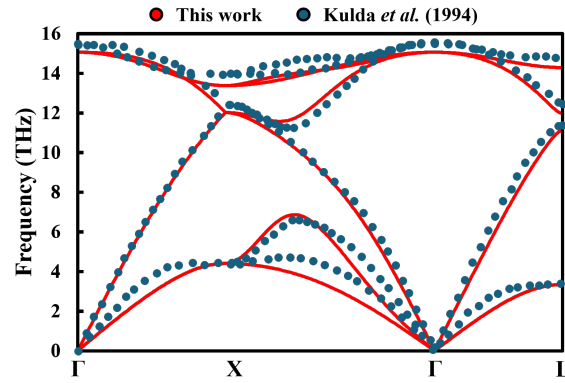


Figure 5.7: Calculated phonon dispersion lines at 0 K for fcc Si using the phonopy program package in comparison with literature data by Kulda *et al.* [239].

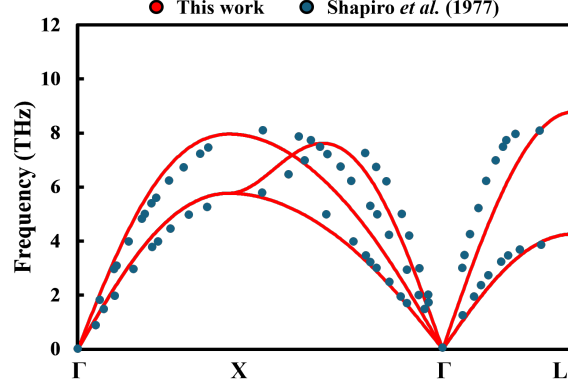


Figure 5.8: Calculated phonon dispersion lines at 0 K for fcc Co using the phonopy program package in comparison with literature data by Shapiro *et al.* [240].

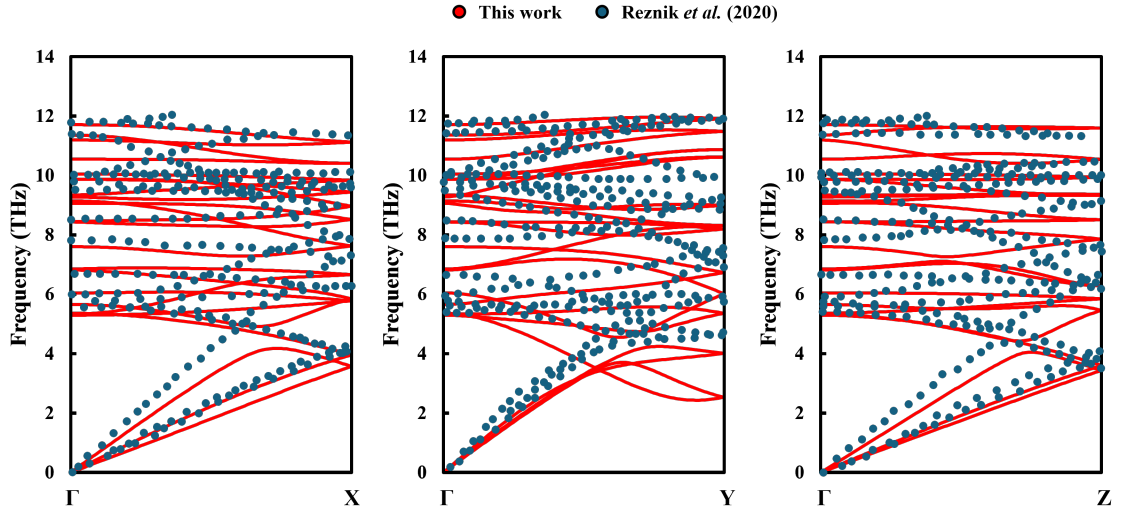


Figure 5.9: Calculated phonon dispersion lines at 0 K for orthorhombic FeP using the phonopy program package in comparison with literature data by Reznik *et al.* [241]. The high symmetry path from Γ to X, Γ to Y and Γ to Z are shown.

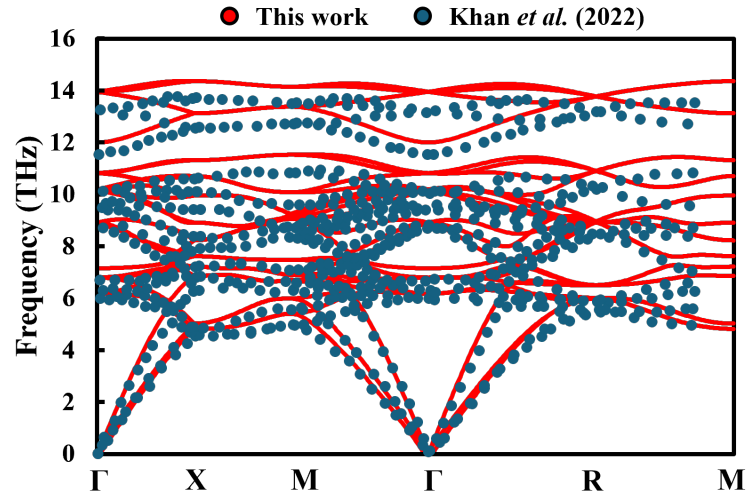


Figure 5.10: Calculated phonon dispersion lines at 0 K for primitive cubic FeSi using the phonopy program package in comparison with literature data by Khan *et al.*[242].

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List of Abbreviations

RE - Rare-earth

TM - Transition metal

m_{tot} - Total magnetic moment

μ_0 - Magnetic constant

μ_B - Bohr magneton

H - Magnetic field

H_a - Anisotropy field

H_c - Coercivity field

H_d - Internal magnetic field

M - Magnetization

M_r - Remanence magnetization

M_S - Magnetization saturation

T_C - Curie temperature

$|BH|_{max}$ - Maximum energy product

MCA - Magnetocrystalline anisotropy

MAE - Magnetocrystalline anisotropy energy

ΔE_{MAE} - Anisotropy energy

K_1 - Anisotropy constant 1st order

κ - Hardness factor

HF - Hartree-Fock

post-HF - post-Hartree-Fock

DFT - Density functional theory

DMFT - Dynamical mean field theory

LDA - Local Density Approximation

LSDA - Local Spin Density Approximation

GGA - Generalized Gradient Approximation

PW91 - Functional by Perdew and Wang

PBE - Functional by Perdew, Burke and Ernzerhof

PAW - Projector Augmented Wave

USPP - Ultrasoft Pseudopotentials

VASP - Vienna *ab initio* Simulation Package

KKR - Korringa-Kohn-Rostoker

SCF - Self-consistent field

FM - Ferromagnetic

MFA - Mean-field approximation

ASA - Atomic sphere approximation

CPA - Coherent potential approximation

MJW - Moruzzi, Janak and Williams

DOS - Density of states

bcc - Body centered cubic

fcc - Face centered cubic

BCO - Body centered orthorhombic

NM - Non-magnetic

FM - Ferromagnetic

AFM - Antiferromagnetic

f.u. - Functional unit

Curriculum Vitae

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Publications

- L.L. Bao, H. Yibole, S. Erdmann, H. İ. Sözen, T. Klüner, F. Guillou, *Solid State Sci.*, **2026**, 173, 108183.
- S. Erdmann, H. İ. Sözen, T. Klüner, *Magnetism*, **2025**, 5, 14.
- Z. Surilemu, L. L. Bao, H. Yibole, S. Erdmann, H. İ. Sözen, T. Klüner, F. Guillou, *Acta Mater.*, **2025**, 291, 120991.
- S. Erdmann, H. İ. Sözen, F. Guillou, H. Yibole, T. Klüner, *Phys. Rev. Materials*, **2024**, 8, 094401.
- N. Y. Merkt, S. Erdmann, T. Klüner, H. İ. Sözen, *J. Magn. Soc. Jpn.*, **2024**.
- S. Erdmann, A.G. Thomé, J. Wittayakun, F. Roessner, *Mol. Catal.*, **2024**, 559, 114026.
- S. Erdmann, T. Klüner, and H. İ. Sözen, *J. Magn. Magn. Mater.*, **2023**, 572, 170645.

Conferences

- 26.03. - 31.03.2023 86th DPG Spring Meeting 2023,
Dresden, Germany
Talk: Magnetic properties of rare-earth-lean ThMn₁₂-type
(Nd,X)Fe₁₁Ti (X: Y and Ce) compounds: A DFT study
- 27.02. - 01.03.2024 Workshop on Theoretical Chemistry,
Bad Hofgastein, Austria
Poster: Exploration of Rare-Earth-Free Magnetic Materials
via Active Learning from First-Principle Calculations
- 17.03. - 22.03.2024 87th DPG Spring Meeting,
Berlin, Germany
Talk: Theoretical Investigation of the Effect of Si and Co Doping
on the Physical and Magnetic Properties of
Rare-Earth-Free Fe₂P Magnets
- 02.09. - 06.09.2024 60th Symposium on Theoretical Chemistry (STC 2024),
Braunschweig, Germany
Poster: Theoretical Investigations on Fe₂P-type Magnets: Effects
of Si and Co Substitution on Physical and Magnetic Properties
- 12.11. - 13.11.2024 MSIT Seminar on Rare-Earth Materials,
Magnet Technology, Stuttgart, Germany
- 16.02. - 21.02.2025 9th MSIT Winter School on Materials Chemistry,
Castle Ebernburg, Germany
Poster: Theoretical Investigation on Fe₂P-type Magnets: Effects
of Si and Co Substitution on Physical and Magnetic Properties
- 24.08. - 29.08.2025 14th Joint European Magnetic Symposia 2025 (JEMS 2025)
Frankfurt am Main, Germany
Poster: Theoretical Effect of Si and Co Substitution
on Physical and Magnetic Properties of Fe₂P-type compounds

Declaration

This declaration is given only in German:

Hiermit versichere ich an Eides statt, dass ich diese Arbeit selbstständig verfasst und keine anderen als die angegebenen Quellen und Hilfsmittel benutzt habe.

Teile dieser Arbeit sind bereits in folgenden Publikationen veröffentlicht worden:

- S. Erdmann, H. İ. Sözen, F. Guillou, H. Yibole, T. Klüner, *Phys. Rev. Mater.*, **2024**, 8, 094401. DOI: 10.1103/PhysRevMaterials.8.094401
- S. Erdmann H. İ. Sözen, T. Klüner, *Magnetism*, **2025**, 5, 14. DOI: 10.3390/magnetism5020014
- Z. Surilemu, L. L. Bao, H. Yibole, S. Erdmann, H. İ Sözen, T. Klüner, F. Guillou, *Acta Mater.*, **2025**, 291, 120991. DOI: 10.1016/j.actamat.2025.120991

Die Ergebnisse zu den Phasenstabilitäten sind zudem geplant veröffentlicht zu werden und befinden sich im Veröffentlichungsprozess.

Diese Dissertation liegt oder lag weder in ihrer Gesamtheit noch in Teilen einer anderen wissenschaftlichen Hochschule zur Begutachtung in einem Promotionsverfahren vor. Angestrebt wird der Grad des Doktors der Naturwissenschaften (Dr. rer. nat).

Außerdem versichere ich, dass ich die allgemeinen Prinzipien wissenschaftlicher Arbeit und Veröffentlichungen, wie sie in den Leitlinien guter wissenschaftlicher Praxis der Carl von Ossietzky Universität Oldenburg festgehalten sind, befolgt habe. Im Zusammenhang mit dieser Arbeit sind keine kommerziellen Vermittlungs- oder Beratungsdienste in Anspruch genommen worden.

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