ENERGY RELEVANT MATERIALS:

INVESTIGATIONS BASED ON FIRST PRINCIPLES

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Doctoral Thesis
School of Industrial Engineering and Management, Department of Materials Science and Engineering, KTH, Sweden, 2012
Akademisk avhandling som med tillstånd av Kungliga Tekniska Högskolan framlägges till offentlig granskning för avläggande av doctorsexamen fredagen den 23 Mars 2012 kl 10:00 i sal F3, Lindstedtsvägen 26, Kungliga Tekniska Högskolan, Stockholm.

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Abstract

Energy production, storage and efficient usage are all crucial factors for environmentally sound and sustainable future technologies. One important question concerns the refrigeration industry, where the energy efficiency of the presently used technologies is at best 40% of the theoretical Carnot limit. Magnetic refrigerators offer a modern low-energy demand and environmentally friendly alternative. The diiron phosphide-based materials have been proposed to be amongst the most promising candidates for working body of magnetic refrigerators. Hydrogen is one of the most promising sources of renewable energy. Considerable international research focuses on finding good solid state materials for hydrogen storage. On the other hand, hydrogen gas is obtained from hydrogen containing chemical compounds, which after breaking the chemical bonds usually yield to a mixture of different gases. Palladium-silver alloys are frequently used for hydrogen separation membranes for producing purified hydrogen gas. All these applications need a fundamental understanding of the structural, magnetic, chemical and thermophysical properties of the involved solid state materials. In this thesis ab initio electronic structure methods are used to study the magnetic and crystallographic properties of Fe$_2$P based magneto-caloric compounds and the thermophysical properties of Pd-Ag binary alloys.

The nature of magnetism and the strong sensitivity of the Curie temperature of the Fe$_2$P$_{1-x}$T$_x$ ($T =$ boron, silicon and arsenic) are investigated. Using first principles theory, the change in the average magnetic exchange interactions upon doping is decomposed into chemical and structural contributions, the latter including the $c/a$ and volume effects. It is demonstrated that for the investigated alloys the structural effect can be ascribed mainly to the $c/a$ ratio that strengthens the magnetic exchange interactions between the two Fe sublattices. On the other hand, it is shown that the two types of Fe atoms have a very complicated co-dependency, which manifests in a metamagnetic behavior of the FeI sublattice. This behavior is strongly influenced by doping the P sites.

Lattice stability of pure Fe$_2$P and the effect of Si doping on the phase stability are presented. In contrast to the observation, for the ferromagnetic state the hexagonal structure ($hex$, space group $P6_2/m$) has no the lowest energy. For the paramagnetic state, the $hex$ structure is shown to be the stable phase and the computed total energy versus composition indicates a $hex$ to $bco$ (body centered orthorhombic, space group $Imm2$) crystallographic phase transition with increasing Si content. The mechanisms responsible for the structural phase transition are discussed in details.

The magnetic properties of Fe$_2$P can be subtly tailored by Mn doping. It was shown experimentally that Mn atoms preferentially occupy one of the two different Fe sites of Fe$_2$P. Theoretical results for the Mn site occupancy in MnFeP$_{1-x}$Si$_x$ are presented.


The single crystal elastic constants, the polycrystalline elastic moduli and the Debye temperature of disordered Pd$_{1-x}$Ag$_x$ binary alloys are calculated for the whole range of concentration, $0 \leq x \leq 1$. It is shown that the variation of the elastic parameters of Pd-Ag alloys with chemical composition strongly deviates from the simple linear trend. The complex electronic origin of these anomalies is demonstrated. The effect of long range order on the single crystal elastic constants of Pd$_{0.5}$Ag$_{0.5}$ alloy is also investigated.

Within this thesis most of the calculations were performed using the Exact Muffin-Tin Orbitals method. The chemical and magnetic disorder are treated via the Coherent Potential Approximation. The paramagnetic phase is modeled by the Disordered Local Magnetic Moments approach.
Sammanfattning


Magnetismens natur och den starka känsligheten för Curie-temperaturen hos Fe₂P₁₋ₓTₓ (T=bor, kisel, arsenik) undersöks. Genom ab initio-teori uppdelas förändringen i den genomsnittliga magnetiska växelverkan genom dopning i kemiska och strukturella bidrag, den senare inbegripande c/a och volymen. Det visas att för de undersökta legeringarna kan den strukturella effekten tillskrivas främst c/a-förhållandet som stärker den magnetiska växelverkan mellan två Fe-delgitter. Å andra sidan visas det att de två typerna av järnatomer har ett komplicerat medverkande, vilket visar sig i ett metamagnetiskt beteende hos FeI-delgittert. Detta beteende är starkt influerat av P-dopning.

Gitterstabiliteten hos rent Fe₂P och effekten av kiseldopning på fasstabiliteten presenteras. I motsats till det som observerats har, för det ferromagnetiska tillståndet, den hexagonala strukturen (hex, rymdgrupp P62m) inte den lägsta energin. För det paramagnetiska tillståndet visas att hex-strukturen är den stabila fasen, och den beräknade totala energin mot sammansättning indikerar att en hex till bco (kroppscenrerad ortorombisk, rymdgrupp Immm) kristallografisk fasomvandling sker med ett ökande kiselinnehåll. De magnetisk-strukturella effekterna och mekanismerna bakom den strukturella fasomvandlingen diskuteras i detalj.

De magnetiska egenskaperna hos Fe₂P kan modifieras med Mn-dopning. Det har visats experimentellt att Mn-atomer föredrar att upptä en av två olika Fe-positioner hos Fe₂P. Teoretiska resultat för Mn-placeringen i MnFeP₁₋ₓSₓ presenteras.
De enkel- och polykristallina elastiska konstanterna och Debye-temperaturen hos oordnade $Pd_{1-x}Ag$ legeringar är beräknade för alla sammansättningar, $0 \leq x \leq 1$. Det visar sig att ändringen av de elastiska parametrarna hos Pd-Ag legeringar genom ändring av den kemiska sammansättningen starkt skiljer sig från den enkla förväntade trenden. Det komplexa elektroniska ursprunget för dessa anomalier demonstreras. Effekten av långdistansordning på de enkelkristallina elastiska konstanterna hos $Pd_{0.5}Ag_{0.5}$ undersöks också.


Preface

List of included publications:

I Magnetic exchange interactions in B, Si and As doped Fe$_2$P from first principles theory

II A microscopic theory of the magnetism of the large spin-entropy material Fe$_2$P$_{1-x}$T$_x$ (T=B and Si)

III *Ab initio* study of structural and magnetic properties of Si-doped Fe$_2$P

IV Order-disorder induced magnetic structures of FeMnP$_{0.75}$Si$_{0.25}$

V Strongly enhanced magnetic moments in ferromagnetic FeMnP$_{0.5}$Si$_{0.5}$

VI *Ab initio* study of the elastic anomalies in Pd-Ag alloys

VII Effect of long-range order on elastic properties of Pd$_{0.5}$Ag$_{0.5}$ alloy from first principles
Comment on my own contribution

**Paper I:** literature survey, all of the EMTO calculations, data analysis, writing the manuscript.

**Paper II:** literature survey, all of the EMTO calculations, data analysis; the manuscript was written jointly.

**Paper III:** literature survey, all of the EMTO calculations, data analysis; the manuscript was written jointly.

**Paper IV:** all of the EMTO calculations, data analysis; the manuscript was written jointly.

**Paper V:** all of the EMTO calculations, data analysis; the manuscript was written jointly.

**Paper VI:** literature survey, all of the EMTO calculations, data analysis; the manuscript was written jointly.

**Paper VII:** literature survey, all of the EMTO calculations, data analysis; the manuscript was written jointly.

Publications not included in the thesis:

**VIII** Assessing common density functional approximations for the *ab initio* description of monovacancies in metals

**IX** Density functional study of vacancies and surfaces in metals
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Chapter 1

Introduction

Nowadays the environmental protection is becoming more and more important. The focus of many scientific studies is on subjects related to the greenhouse effect, the protection of ozone layer and reduction of the global energy consumption. Energy production, storage and efficient usage are all crucial factors for environmentally sound and sustainable future technologies. One of the recent subjects concerns the refrigeration technologies. Magnetic refrigeration offers the most advanced alternative for the widespread energy inefficient approaches. In magnetic refrigeration the magneto-caloric materials play the key role as working body. Another important research field deals with the hydrogen usage as energy carrier, for which purified hydrogen is needed. Palladium-silver alloy membranes are amongst the most important devices in the hydrogen separation and purification process.

Magnetic refrigeration techniques are based on the magneto-thermodynamic phenomenon known as magneto-caloric effect (MCE). The MCE is simply heat absorption or emission by a magnetic material under varying magnetic field.

The magnetic refrigeration cycle, as illustrated in Fig. 1.1, contains the following steps:

1. a magnetic field aligns the initially randomly oriented magnetic moments, resulting in heating of the magnetic material (with temperature $T_0$), $T_1 = T_0 \rightarrow T_2 > T_0$;

2. using heat transfer this heat is removed from the magnetic material to the ambience, $T_2 \rightarrow T_3 \sim T_0$;

3. on removing the field, the magnetic moments are randomized, which leads to cooling of the magnetic material below ambient temperature, $T_3 \rightarrow T_4 < T_0$

4. heat from the system to be cooled is then extracted by the magnetic material using a heat-transfer medium.
Using magneto-caloric material as working body of the refrigerator the inefficient compressor of the conventional refrigerator is removed. Another advantage of the magneto-caloric refrigerators is the environmentally friendly cooling functioning: magnetic refrigerators use a solid refrigerant and environmentally sound heat transfer fluids as water, water-alcohol solution, air, helium - depending on the operating temperature. Within this field, the primary goal is to find the adequate working material for given operating conditions.

Theoretical simulations propose a direction for the experimental work or give a deeper atomic-scale explanation of the experimental results. Analysis of the compositional dependence of the crystal structure, magnetic properties (for example: Curie temperature, magnetic entropy change) is important for technological applications. This research field represents a true challenge for the theoretical research. The reason for this is that handling of magnetic and/or chemical disorder are only partially solved [1, 2, 3] and there is no unified description of the magnetism especially in weak ferromagnetic solids often found as promising MCE materials.

Magnetic and crystallographic properties of Fe$_2$P and its alloys were in focus of many experimental studies. A strong sensitivity of the Fe$_2$P Curie temperature to the presence of Fe vacancy, stress and pressure was reported by Lundgren et. al. [4]. They show that $T_C$ correlates with the anomalous change of the lattice parameters. This finding holds for the Si doped system too [5]. Theoretically Fe$_2$P was analyzed early on by Wohlfart [6], Moriya and Usami [7], in terms of itinerant magnetism. Based on the band

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**Figure 1.1.** Schematic picture of the magnetic refrigeration cycle (figure based on BASF future business). For the explanation of the process phases see the text.
theory, first principles calculations reproduced the magnetic moments with acceptable agreement [8, 9]. Yamada and Terao [10] showed that the first order magnetic transition in Fe$_2$P can be attributed to the appearance of a metamagnetic transition for one of the Fe sites.

The effect of structural (hexagonal axial ratio and volume) changes and composition on the magnetic interactions of Fe$_2$P$_{1-x}$T$_x$ (T = boron, silicon and arsenic) is investigated here and the results are included in Paper I. The effect of doping on the metamagnetic behavior is investigated, and results are included in Paper II. Crystallographic properties of Si doped Fe$_2$P in paramagnetic phase are studied (Paper III). Results obtained for manganese doped Fe$_2$P$_{1-x}$Si$_x$ are presented and included in Papers IV and V.

Palladium-silver alloys were discovered by Heraeus in 1931. They first were applied in dentistry as bridges and crowns due to their nobility and resistance to tarnishing. These alloys are also ductile and have good electrical conductivity, therefore they are used in conductive films and pastes, multilayer capacitors or as contacts. The hydrogen separation membrane is the most recent application [11]. Hydrogen can be used as an environmentally friendly energy carrier. A high quantity of hydrogen in the Earth can be found in chemical compounds. To obtain pure hydrogen, first, chemical bonds have to be broken which leads to a mixture of gases. From this multi-component mixture hydrogen can be extracted and purified using palladium-silver membranes. All the above mentioned applications of Pd-Ag alloys need adequate mechanical properties. Therefore, it is important to know the thermophysical properties of Pd-Ag alloys as a function of composition.

The Fermi surface geometry [12, 13] and mixing enthalpy [14] for the whole composition range are well known for Pd-Ag alloys. Five electronic topological transitions (ETT) were detected which should be reflected in several physical properties. It was a big challenge to catch up the effect of ETTs in the elastic properties of this alloy. Results are included in Paper VI.

Muller and Zunger suggested three ordered structures at low temperatures: the L1$_2$ (Cu$_3$Au-type) structure for Pd$_3$Ag, the L1$_1$ (CuPt-type) structure for the equiatomic Pd-Ag and the L1$_1^+$ structure for PdAg$_3$ [15]. The effect of long range ordering on the single crystal elastic constants of Pd$_{0.5}$Ag$_{0.5}$ alloy is published in Paper VII.

The structure of the thesis is the following:

- **Chapter II–Magnetism**: gives a short overview of the magneto-caloric effect and the itinerant electron magnetism,

- **Chapter III–Elastic properties of solids**: contains the theoretical description of the elasticity,

- **Chapter IV–Theoretical tool**: introduces into the density functional theory and the exact muffin-tin orbital formalism,
• Chapter V–Fe$_2$P based materials: presents results obtained for Fe$_2$P and its alloys,

• Chapter VI–Thermophysical properties of Pd-Ag binary alloys: includes results obtained for PdAg binary alloys.

Results are summarized and Papers I to VII are attached to the end of the thesis.

First principles studies were performed by the author using the Exact Muffin-Tin Orbital method. The Curie temperatures were estimated using Monte Carlo simulations based on the Metropolis algorithm as implemented in the UppASD program in combination with the cumulant crossing method, simulations done by Dr. Lars Bergqvist. The relaxed crystal structures were obtained with Projector Augmented Wave (PAW) method as implemented in the Vienna ab initio simulation package, calculations were done by Dr. Marko P. J. Punkkinen. The full potential results are calculated by Dr. Qing-Miao Hu with Full-Potential Augmented Plane Wave plus local orbital method implemented in WIEN2k program package.
Chapter 2

Magnetism in magnetocaloric materials

2.1 Magneto-caloric effect (MCE)

2.1.1 General aspects of MCE

The phenomenon in which a magnetic material changes heat under the action of an alternating external magnetic field is called magneto-caloric effect (MCE). The MCE was discovered by Warburg in 1881 in the case of iron [16]. Its physical explanation was given by Weiss and Piccard [17]. A first application was proposed independently by Debye [18] and Giauque [19] in the 1920s. In 1933 Giauque and MacDougall [20] used for the first time the adiabatic demagnetization to reach 0.25 K in the Gd$_2$(SO$_4$)$_3 \times 8$H$_2$O paramagnetic salt.

The MCE can be measured by a magnetic entropy change ($\Delta S_m$) through isothermal application and by a temperature change ($\Delta T_{ad}$) via an adiabatic application of a magnetic field to a magnetic material (Fig. 2.1).

The magnetic entropy change ($\Delta S_m$) can be obtained from measurements. Namely, using the thermodynamic Maxwell relation (Eq. (2.1)), the magnetic entropy can be determined from magnetization measurements made at discrete temperature intervals (Eq. (2.2) at constant pressure $p$) or from direct calorimetric measurement of the field dependence of the heat capacity (Eq. (2.3)).

\[
\left(\frac{\partial S}{\partial H}\right)_{T,p} = \left(\frac{\partial M}{\partial T}\right)_{H,p} \quad (2.1)
\]

\[
\Delta S_m = \int_{H_i}^{H_f} \left(\frac{\partial M}{\partial T}\right)_{H,p} dH \quad (2.2)
\]
CHAPTER 2. MAGNETISM IN MAGNETOCALORIC MATERIALS

\[ \Delta S_m = \int_{T_i}^{T_f} \frac{C(T, H_f) - C(T, H_i)}{T} dT. \]  \hspace{1cm} (2.3)

In these expressions \( M \) stands for the magnetization, \( H \) is the magnetic field, \( C \) is the temperature dependent heat capacity at given magnetic field, \( T \) is the temperature, indices \( i \) and \( f \) stands for the initial and the final state, respectively.

Alternatively one may make use of the theory based on statistical [21] and mean-field models of the magnetic materials [21, 22].

![Figure 2.1. Entropy versus temperature diagram illustrating the magneto-caloric potentials \( \Delta S_m \) and \( \Delta T_{ad} \) [23].](image)

The adiabatic temperature change (\( \Delta T_{ad} \)) can be integrated numerically using the measured or theoretically predicted magnetization and heat capacity (Eq. (2.4)).

\[ \Delta T_{ad} = -\int_{H_i}^{H_f} \frac{T}{C(H, p)} \left( \frac{\partial M}{\partial T} \right)_{H, p} dH. \]  \hspace{1cm} (2.4)

The MCE is large when the specific heat is small and the entropy change is large. Large entropy change is obtained usually in the vicinity of magnetic and structural phase transitions.

Nowadays the aim of the research is to find such magnetic materials which show huge MCE, adequate magnetic properties (narrow hysteresis, suitable \( T_C \)), and environmentally friendly and cheap constituents.
2.1. MAGNETO-CALORIC EFFECT (MCE)

Experimental groups reported that the \( \text{FeMnP}_{1-x}\text{As}_x \) compounds are good candidates for magneto-caloric cooling applications near the room temperature \([24, 25, 26, 27]\). The Curie temperature \( (T_C) \) can be tailored as a function of concentration, \( x \) \([28, 29]\). Arsenic can be replaced by Si, Ge, Sb, which affects the \( T_C \) and ultimately the MCE. \( \text{Fe}_2\text{P} \) is the base compound for these magneto-caloric materials.

2.1.2 Physical background

Entropy is the number of possible microscopic configurations of a system. It is the measure of the disorder in the material. The total entropy \( (S) \) of a magnetic material can be decomposed into lattice \( (S_l) \), magnetic \( (S_m) \) and electronic \( (S_e) \) entropies as follows

\[
S(H,T,x) = S_l(H,T,x) + S_m(H,T,x) + S_e(H,T,x).
\]

(2.5)

Lattice entropy \( (S_l) \) is related to the lattice degrees of freedom of a system, which in turn are connected to phonon excitations and depend on the crystal structure. Magnetic entropy \( (S_m) \) is related to the spin degrees of freedom, and reaches its maximum when the local magnetic moments have completely random orientation. This is the case in the paramagnetic phase, \( i.e. \) above the magnetic ordering temperature. Accordingly, the magnetic entropy change obtains its maximum at the magnetic phase transition. The phase transition has to be reversible for applications, and the reversible processes may show hysteresis. Electronic entropy \( (S_e) \) has a minor contribution at the temperatures of interest (around or slightly above the room temperature).

To understand the reason of magneto-caloric phenomenon we should analyze the effect of an adiabatically applied magnetic field to a paramagnetic spin system near the magnetic phase transition temperature. Applying a magnetic field to the paramagnetic system decreases the magnetic entropy, because the previously randomly oriented local magnetic moments will align corresponding to the external magnetic field. In an \textit{adiabatic} process the total entropy of a material is kept constant. Therefore, a decreasing in the magnetic entropy will lead to an increase of the other entropy terms. Especially the phonon entropy will increase due to the spin-lattice coupling. Since in an adiabatic process there is no heat transfer to the medium the phonon entropy increase will manifest in temperature increase of the system. The opposite process, the adiabatic demagnetization will lead to the cooling of the system.

Generally, all entropy contributions can vary as a function of magnetic field \( (H) \), temperature \( (T) \) and other thermodynamic parameters \( (x) \), for example pressure \( (P) \). For materials which possess localized magnetic moments, like rare earth materials, the entropy contributions can be separated from each other. For the \( 3d \) itinerant magnetic materials they cannot be separated, due to the strong coupling between different contributions.
When the spin-lattice coupling is strong, the magnetic phase transition is accompanied by the crystallographic phase transition. Compounds can show low [30, 31, 32] or large [32] thermal hysteresis. There are cases when the magnetic phase transition is coupled with the crystallographic one [33, 34]. The $T_T$ and MCE can be tuned with the composition [28, 29, 34, 35]. The MCE can be increased with pressure [36]. All these features indicate that it is necessary to know the details of the electronic structure and of the magnetic properties to understand and describe the magneto-caloric effect and to find the adequate magnetic material for some preassigned purposes.

First principles calculations can give a detailed understanding of the changes of the electronic structure which leads to magnetic and crystallographic phase transitions and entropy changes.

### 2.2 Itinerant electron magnetism

The non-integer magnetic moments of the transition metals and their alloys can be understood by means of itinerant electron magnetism. The carriers of the magnetism in transition metals and their alloys are the electrons which also contribute to the bonding between the atoms. The atomic $sp$ and $d$ states overlap forming a band, therefore the electrons are not localized and the Hund’s rules fail to describe the magnetism in such systems.

The first attempt to describe the itinerant magnetism was made by Stoner in the 1930’s [37, 38]. Stoner derived a condition for the appearance of a spontaneous magnetization which reads as

$$\text{DOS}(\varepsilon_F) I_s \geq 1,$$

where $\text{DOS}(\varepsilon_F)$ is the density of states at the Fermi level for the paramagnetic phase and $I_s$ is the Stoner parameter. The ground state is ferromagnetic (FM) if the $\text{DOS}(\varepsilon_F)$ is large or the molecular field is strong ($I_s$ is large). This condition is equivalent to

$$(-\chi_0)^{-1} \sim \left(\frac{\partial^2 E(M)}{\partial M^2}\right)_{M_0} < 0,$$

where $\chi_0$ is the paramagnetic susceptibility, $E(M)$ is the total energy and $M$ is the magnetization ($M_0 \equiv M = 0$).

In the 1960’s Wohlfarth, Rhodes [39] and Shimizu [40, 41] showed that the Stoner condition is a sufficient condition for a ferromagnetic ground state. Furthermore, the magnetic energy may show a minimum at finite $M$ even if the Stoner criteria is not fulfilled, meaning that $\left(\frac{\partial^2 E(M)}{\partial M^2}\right)_{M_0} > 0$. Figure 2.2.1 presents the most important behaviors of $E(M)$. 
2.2. ITINERANT ELECTRON MAGNETISM

Figure 2.2. Schematic picture of: 1. magnetic energy ($E(M)$) as a function of magnetization ($M$). 2. magnetization as a function of magnetic field ($H$).

- a and b ferromagnetism;
- c and d paramagnetism with a metastable FM state;
- e and f paramagnetism.

To discuss in more detail Fig. 2.2.1 the magnetic energy is expanded in even powers of the magnetization ($M$)

$$E(M) = \frac{1}{2} AM^2 + \frac{1}{4} BM^4 + \frac{1}{6} CM^6 + \ldots, \tag{2.8}$$

where $A$, $B$ and $C$ are the expansion coefficients. Six different cases are distinguished at $T = 0$ K, constant volume and zero magnetic field, in accordance with Fig. 2.2.1:

- a. $A < 0$ - strong ferromagnetism, the Stoner criteria is fulfilled (solid black line a of Fig. 2.2.1). The magnetic moment cannot increase to infinity, therefore $C$ must be positive.

  When $A > 0$, $B < 0$ and $C > 0$ the ground state can be either ferromagnetic or paramagnetic. One can distinguish different paramagnetic phases. The $\kappa \equiv AC/B^2$ dimensionless parameter is introduced to describe the different magnetic phases.
b. $\kappa < 3/16$ [42, 43] - weak ferromagnetism. The $E(M)$ curve has a positive curvature at $M = 0$, but a minimum at an $M$ finite value (black dashed line $b$ of Fig. 2.2.1).

c. $\kappa = 3/16$ [42, 43] - the FM and PM states are degenerate (solid green line $c$ of Fig. 2.2.1). The FM state can be stabilized by an external magnetic field ($H$).

d. $3/16 < \kappa < 9/20$ [44] - paramagnetic phase, with an inflection point at finite $M$ (dashed green line $d$ of Fig. 2.2.1). The finite moment state can be stabilized too by applying an external magnetic field.

e. and f. $\kappa \geq 9/20$ - the system is paramagnetic at any field [45]. These paramagnetic phases are marked by orange lines ($e$ and $f$) of Fig. 2.2.1.

The magnetization as a function of $H$ is presented in Figure 2.2.2. The magnetization curve show hysteresis for the $b$ type of ferromagnetism and for the $c$ and $d$ type of paramagnetism leading to a discontinuity in the susceptibility ($\chi = dM/dH$). The hysteresis disappears for the $f$ type of paramagnetism.

Transitions between the different magnetic phases is a first order phase transition and can be achieved by increasing/decreasing the temperature [45], applying a pressure [46] or turning on/off an external magnetic field [39]. In theoretical descriptions of phase transitions one has to take into account the temperature, volume and/or magnetic field dependence of the magnetization and the expansion coefficients ($M(T,V,H)$ and $A(T,V,H)$, $B(T,V,H)$, $C(T,V,H)$, respectively). This will lead to the well known Landau theory of phase transitions.

The zero Kelvin expansion coefficients for constant $V$ and $H$ can be calculated by fixed spin moment (FSM) calculations.

### 2.3 Magnetic exchange constants

Thermodynamic properties of ferromagnets can be obtained within a two step approach. In the first step the zero temperature electronic structure is calculated and the total energy is mapped onto an effective classical Heisenberg Hamiltonian

$$H_{\text{eff}} = - \sum_{i \neq j} J_{ij} \mathbf{e}_i \cdot \mathbf{e}_j,$$

where $J_{ij}$ is the magnetic exchange constant between magnetic atoms on site $i$ and $j$, $\mathbf{e}_i$ is the unit vector of the magnetic moment. The magnitude of the magnetic moments are included in $J_{ij}$ by construction. Positive/negative $J_{ij}$ corresponds to ferromagnetic/antiferromagnetic coupling. In the present work the exchange constants are calculated within the multiple-scattering theory (see section 4.2.3).

In the second step the Hamiltonian is solved using statistical mechanics methods.
Chapter 3

Elastic properties of solids

The main difference between single-crystal alloys and real materials is the inherent disorder. Solid materials have a hierarchical buildup of which the bottom level is made up of atoms. Atoms are arranged in a periodic array forming a crystal lattice. The most frequent source of disorder is the breakdown of the long-range order of the crystal lattice. Materials are often built up by nano- or micrometer sized single crystal grains, which are separated by stacking faults, interphase boundaries, etc.

The elastic properties of materials, considered isotropic on a large scale, can be completely described by the polycrystalline elastic moduli, like the bulk modulus \( B \), the shear modulus \( G \), the Young’s modulus \( E \) and the Poisson ratio \( \nu \). They are interconnected quantities, two of them uniquely describe the investigated system.

The bulk modulus \( B \) being the second order derivative of the total energy with respect to the volume can be determined by fitting a general function, called the equation of state, to the \textit{ab initio} total energies for a set of atomic volumes. The most commonly used equations of state are the Murnaghan [47], the Birch-Murnaghan [48] and the Morse [49] type. The shear modulus \( G \) can be derived from the single crystal elastic constants using suitable averaging methods based on statistical mechanics.

3.1 Single crystal elastic constants

The elastic properties of single crystals are investigated using small, uniform distortions (strain, \( e_{ijkl} \)) to the lattice and calculating the energy change due to the strain as a function of the strain magnitude. For small deformations the Hooke’s law is satisfied: the strain is directly proportional to the stress. The components of the strain tensor are linear combinations of the stress tensor components and vice versa. The proportionality factors in the first case are the elastic compliance constants \( s_{ijkl} \) and in the second case the elastic stiffness constants \( c_{ijkl} \), referred to as elastic constants.
The adiabatic $c_{ijkl}$ elasticity tensor [50] (Eq. (3.1)) is the second order derivative of the internal energy with respect to the strain tensor $e_{kl}$. $i, j, k$ and $l$ run from 1 to 3, indicating the three space direction: 1, 2 and 3 stand for $x$, $y$ and $z$, respectively.

$$
c_{ijkl} = \frac{1}{V} \frac{\partial^2 E}{\partial e_{ij} \partial e_{kl}}. \tag{3.1}
$$

The fourth-rank elasticity tensor contains 81 elements. Due to the lattice symmetry the elasticity tensor reduces to a 6x6 matrix, containing at most 21 different elements with two indices $\alpha$ and $\beta$. According to the Voigt notation $\alpha, \beta=1, 2, 3$ when $ij= 11, 22, 33$, $\alpha, \beta= 4$ for $ij= 23$ or $32$, $\alpha, \beta= 5$ for $ij= 13$ or $31$ and $\alpha, \beta= 6$ for $ij= 12$ or $21$. In the following the Voigt notation is used, and for simplicity $\alpha$ and $\beta$ are replaced by $i$ and $j$, respectively.

The energy change ($\Delta E$) upon a general strain (Eq. (3.3)) is given by

$$
\Delta E = E(e_i)_{i=1,6} - E(0) = \frac{1}{2} V \sum_{i,j=1}^{6} c_{ij} e_i e_j + O(e^f) \tag{3.2}
$$

where $E(0)$ and $V$ is the energy and the volume of undistorted lattice, respectively, $O(e^f)$ denotes the higher order terms ($f \geq 3$), and the general strain cast as follows

$$
\mathcal{D}(e) = \left( \begin{array}{c}
e_1 \\
\frac{1}{2}e_6 \\
\frac{1}{2}e_5 \\
\frac{1}{2}e_4 \\
\frac{1}{2}e_5 \\
\frac{1}{2}e_4 \\
\frac{1}{2}e_3
\end{array} \right). \tag{3.3}
$$

Usually, the total energy changes much more strongly with the volume than with a general (volume preserving) strain. Therefore, to eliminate the strong volume-dependent energy change, which could overcome the strain effect to the total energy, volume conserving deformations are employed for the elastic constants calculations. $\det(\mathcal{D}(e)+\mathcal{I}) = 1$ is the criterion for a volume conserving deformation. As a consequence, the distortion matrix is rewritten as a function of a single parameter $\varepsilon$, and result in a particular combination of the elastic constants.

### 3.1.1 Elastic constants of cubic lattices

For a lattice with cubic symmetry, there are three independent elastic constants: $c_{11}$, $c_{12}$ and $c_{44}$. Two of these cubic elastic constants are derived from the bulk modulus ($B$)

$$
B = \frac{c_{11} + 2c_{12}}{3} \tag{3.4}
$$

and from the tetragonal shear modulus ($c'$)
3.1. SINGLE CRYSTAL ELASTIC CONSTANTS

3.1.1 Single Crystal Elastic Constants

\[ c' = \frac{c_{11} - c_{12}}{2}. \] (3.5)

The bulk modulus can be obtained from the equation of state, as mentioned before. In order to calculate the two cubic shear moduli, \( c' \) and \( c_{44} \), the following orthorhombic and monoclinic volume conserving deformations can be applied on the conventional cubic unit cell, respectively

\[
\mathcal{D}_o + \mathcal{I} = \begin{pmatrix} 1 + \varepsilon_o & 0 & 0 \\ 0 & 1 - \varepsilon_o & 0 \\ 0 & 0 & \frac{1}{1 - \varepsilon_o} \end{pmatrix} \quad \text{and} \quad \mathcal{D}_m + \mathcal{I} = \begin{pmatrix} 1 & \varepsilon_m & 0 \\ \varepsilon_m & 1 & 0 \\ 0 & 0 & \frac{1}{1 - \varepsilon_m} \end{pmatrix}. \] (3.6)

The energy change \( \Delta E(\varepsilon) = E(\varepsilon) - E(0) \) in response to these distortions is given by

\[
\Delta E(\varepsilon_o) = 2Vc'\varepsilon_o^2 + O(\varepsilon_o^4) \quad \text{and} \quad \Delta E(\varepsilon_m) = 2Vc_{44}\varepsilon_m^2 + O(\varepsilon_m^4) \] (3.7)

for orthorhombic and monoclinic deformations, respectively.

3.1.2 Elastic Constants of Hexagonal Lattices

For a hexagonal lattice there are five independent elastic constants, \( c_{11}, c_{12}, c_{13}, c_{33} \), and \( c_{44} \). The relations between \( c_{11}, c_{12}, c_{13} \), and \( c_{33} \) are given by the bulk modulus \( B \), the dimensionless quantity \( R \), and \( c_s \), as follows

\[
B = \frac{c_{33}(c_{11} + c_{12}) - 2c_{13}^2}{c_s}, \] (3.8)

where

\[
c_s \equiv c_{11} + c_{12} + 2c_{33} - 4c_{13}, \] (3.9)

and

\[
R = \frac{c_{33} - c_{11} - c_{12} + c_{13}}{c_s}. \] (3.10)

The hexagonal axial ratio \((c/a)\) may change with the volume. The volume dependence of the equilibrium hexagonal axial ratio \( (c/a)_0 = (c/a)_0(V) \) is related to the difference in the linear compressibilities along the \( a (K_a) \) and \( c (K_c) \) axis, which in turn gives the dimensionless quantity \( R \) as
\[ R = B(K_a - K_c) = -\frac{d \ln(c/a) \partial V}{d \ln V}. \]  

(3.11)

The ratio of the direction dependent compressibilities is given by [51]

\[ \frac{K_a}{K_c} = \frac{c_{11} + c_{12} - 2c_{13}}{c_{33} - c_{13}}. \]  

(3.12)

The elastic constant from Eq. (3.9), \( c_s \), is obtained from the second order derivative of \( E(V, c/a) \) at the global equilibrium \( c/a \)

\[ c_s = \frac{9(c/a)^2}{2V} \frac{\partial^2 E(V, c/a)}{\partial(c/a)^2} \bigg|_{c/a=(c/a)g}. \]  

(3.13)

Finally, \( c_{44} \) and \( c_{66} = (c_{11} - c_{12})/2 \) are determined from a volume conserving monoclinic and orthorhombic deformations (Eq. (3.14)), respectively, applied on the hexagonal unit cell.

\[ D_m + I = \begin{pmatrix} 1 & 0 & \varepsilon_m \\ 0 & 1 - \varepsilon_m & 0 \\ \varepsilon_m & 0 & 1 \end{pmatrix} \quad \text{and} \quad D_o + I = \begin{pmatrix} 1 + \varepsilon_o & 0 & 0 \\ 0 & 1 - \varepsilon_o & 0 \\ 0 & 0 & 1 - \varepsilon_o \end{pmatrix}, \]  

(3.14)

The energy change \( \Delta E(\varepsilon) = E(\varepsilon) - E(0) \) in response to these distortions is given by

\[ \Delta E(\varepsilon_m) = 2Vc_{44}\varepsilon_m^2 + O(\varepsilon_m^4) \quad \text{and} \quad \Delta E(\varepsilon_o) = 2Vc_{66}\varepsilon_o^2 + O(\varepsilon_o^4) \]  

(3.15)

for monoclinic and orthorhombic deformations, respectively.

### 3.1.3 Transformation between coordinate systems

The single crystal elastic constants are defined respective to the principal axes of a given crystal. These axes define different coordinate systems for different type of crystals. The relation between two sets of elastic constants defined within different coordinate systems can be established by applying the tensor transformation rules to the components of the fourth-rank elastic tensor, viz.

\[ \epsilon'_{ijkl} = \sum_{m,n,o,p=1}^{3} T_{im}T_{jn}T_{ko}T_{lp}c_{mnop}, \]  

(3.16)

where \( \epsilon'_{ijkl} \) and \( c_{mnop} \) denotes the elastic constants defined in the final and initial coordinate system, respectively, and \( T_{\alpha\beta} \) are the elements of the tensor transformation matrix \( T \).
3.1. SINGLE CRYSTAL ELASTIC CONSTANTS

Figure 3.1. Steps of the Euler’s rotation of a coordinate system [52]:

a). rotation by an angle Φ around the z-axis;
b). rotation by an angle Θ around the x’ axis;
c). rotation by an angle Ψ about the z’ axis.

The elements of the tensor transformation matrix $T$ can be obtained by applying Euler’s rotation theorem [52] to the initial coordinate system. The transition from the initial coordinate system to the final one involves three angles, called Euler angles, denoted by Φ, Θ and Ψ shown in Figure 3.1. The steps shown in Figure 3.1 are known as the ”x-convention” of the rotation of the coordinate system and involve counter-clockwise rotations. The elements of the rotation matrix according to the ”x-convention” cast as

$$
T = \begin{pmatrix}
T_{11} & T_{12} & T_{13} \\
T_{21} & T_{22} & T_{23} \\
T_{31} & T_{32} & T_{33}
\end{pmatrix},
$$

(3.17)

where

$$
\begin{align*}
T_{11} &= \cos \Psi \cos \Phi - \cos \Theta \sin \Phi \sin \Psi, \\
T_{12} &= \cos \Psi \sin \Phi + \cos \Theta \cos \Phi \sin \Psi, \\
T_{13} &= \sin \Psi \sin \Theta, \\
T_{21} &= -\sin \Psi \cos \Phi - \cos \Theta \sin \Phi \cos \Psi, \\
T_{22} &= -\sin \Psi \sin \Phi + \cos \Theta \cos \Phi \cos \Psi, \\
T_{23} &= \cos \Psi \sin \Theta, \\
T_{31} &= \sin \Theta \sin \Phi, \\
T_{32} &= -\sin \Theta \cos \Phi, \\
T_{33} &= \cos \Theta.
\end{align*}
$$

(3.18)
CHAPTER 3. ELASTIC PROPERTIES OF SOLIDS

3.2 Polycrystalline elastic moduli

Isotropic elastic constants may be obtained by averaging the single crystal elastic constants. The most widely used methods are the Voigt and Reuss bounds, the Hashin-Shtrikman bounds, Hershey average and Hill average. In the following a short overview of the Voigt and Reuss bounds and Hill average is given for cubic solids, quantities derived from single and polycrystalline elastic constants are presented.

3.2.1 The Voigt and Reuss bounds, Hill average for cubic crystals

The Voigt method is based on applying a uniform strain, and is formulated using the elastic constants \( c_{ij} \). The Reuss method assumes a uniform stress, and is formulated using the elastic compliances \( s_{ij} \). The Voigt and Reuss bounds are given for a cubic solid in terms of elastic constants as follows

\[
B_V = \frac{c_{11} + 2c_{12}}{3}; \quad G_V = \frac{c_{11} - c_{12} + 3c_{44}}{5}; \quad B_R = B_V; \quad G_R = \frac{5(c_{11} - c_{12})c_{44}}{4c_{44} + 3(c_{11} - c_{12})}
\]

(H3.19)

Hill [53] showed that the best average shear modulus can be estimated using the Voigt and Reuss bounds, which represent a rigorous upper and lower bounds, as follows

\[
G_H = \frac{G_V + G_R}{2}.
\]

(H3.20)

Instead of the arithmetic average one can use the geometric one. For an isotropic material the \( G_V \) and \( G_R \) are equal.

3.2.2 Isotropic polycrystalline aggregates

Single crystal elastic constants are macroscopically valid only for monocrystalline materials. A polycrystalline material consist of monocrystalline grains, which are randomly oriented. On a large scale, such systems can be considered to be quasi-isotropic or isotropic. An isotropic system is completely described by the bulk modulus \( B \) and the shear modulus \( G \). The Young’s modulus \( E \) and Poisson ratio \( \nu \) are connected to \( B \) and \( G \) by relations

\[
E = \frac{9BG}{3B + G}; \quad \nu = \frac{3B - 2G}{6B + 2G}.
\]

(H3.21)

The longitudinal \( (v_L) \) and transversal \( (v_T) \) sound velocities are given in terms of \( B \) and \( G \)
3.2. POLYCRYSTALLINE ELASTIC MODULI

\[
\rho v_L^2 = B + \frac{4}{3} G ; \quad \rho v_T^2 = G
\]  

(3.22)

where \( \rho \) is the density. The average sound velocity \((v_m)\) is used to calculate the Debye temperature

\[
\Theta = \frac{\hbar}{k_B} \left( \frac{6\pi^2}{V} \right)^{1/3} v_m,
\]  

(3.23)

where \( V \) is the average atomic volume, \( \hbar \) and \( k_B \) are Planck’s and Boltzmann’s constants, respectively, and the average sound velocity is given by

\[
\frac{3}{v_m^3} = \frac{1}{v_L^3} + \frac{2}{v_T^3}.
\]  

(3.24)
Chapter 4

Theoretical tool

There are many ways to calculate the properties of materials. Some methods are based on empirical parameters, others need as input parameters only the nuclear charges. The latter is called first principles or \textit{ab initio} calculation and it is based on solving the many-body Schrödinger equation

\[ \mathcal{H} \Psi = E \Psi, \]  

where the Hamiltonian (\( \mathcal{H} \)) for an interacting ion-electron system may be written as

\[ \mathcal{H} = -\frac{\hbar^2}{2} \sum_k \frac{\nabla R_k^2}{M_k} - \frac{\hbar^2}{2m_e} \sum_i \nabla r_i^2 - \sum_i \sum_k \frac{e^2 Z_k}{4\pi\epsilon_0|r_i - R_k|} + \]  

\[ + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{4\pi\epsilon_0|r_i - r_j|} + \frac{1}{2} \sum_{k \neq l} \frac{e^2 Z_k Z_l}{4\pi\epsilon_0|R_k - R_l|}. \]  

(4.2)

Here \( \hbar \) is the reduced Planck constant \( (\hbar = h/2\pi) \), \( R_k/r_i \) is the nuclear/electronic position vector for \( k' \)-th/\( i' \)-th nucleus/electron, \( M_k \) and \( m_e \) are the corresponding masses, \( Z_k \) are the nuclear charges. \( \Psi \) is the many-body wave function and \( E \) is the energy eigenvalue for interacting particles. The first two terms in Eq. (4.2) are the kinetic energy operators for nuclei and electrons, respectively. The third term describes the electron-nucleus interaction, the fourth the electron-electron one and the last term the nucleus-nucleus one. \( \Psi \) is the wave function for electrons and nuclei, being function of all positions.

Without approximations the Schrödinger equation cannot be solved for solid systems containing thousands of atoms. Because the nuclei are much heavier than the electrons \( (m_e/M_k \sim 10^{-3} - 10^{-5}) \), the electrons can be considered moving in stationary orbits in
the external potential generated by the fixed nuclei. Therefore, the electronic part of the Schrödinger equation can be separated from that one which describes the motion of the nuclei. This is known as the Born-Oppenheimer approximation [54]. The nuclear motion and the resulting energy contribution to the total Gibbs’ energy of the system are treated within phonon theory.

The Hamiltonian for the interacting electron gas becomes

$$H = -\frac{\hbar^2}{2m_e} \sum_i \nabla^2 r_i - \sum_i \sum_k \frac{e^2 Z_k}{4\pi\epsilon_0 |r_i - R_k|} + \frac{1}{2} \sum_{i\neq j} \frac{e^2}{4\pi\epsilon_0 |r_i - r_j|}$$

where $T$ stands for the kinetic energy of electrons, $V_{\text{ext}}$ is the external potential, i.e. the Coulomb potential from the interactions between electrons and nuclei, and $W$ is the electron-electron Coulomb potential.

Unfortunately, the Schrödinger equation with the simplified Hamiltonian (Eq. (4.3)) is still far too complicated to be solved for any realistic solid. Therefore, further simplifications are needed to turn the above many-body problem into a solvable problem.

### 4.1 Density Functional Theory

#### 4.1.1 General aspects

The basic idea behind the Density Functional Theory (DFT) was first given by Thomas [55], according to that the total energy of the system can be described merely by the electron density. In the Thomas-Fermi theory a homogeneous electron gas was assumed. This theory fails to reproduce any physical parameter of a realistic material.

In 1964 Hohenberg and Kohn [56] reformulated the Thomas-Fermi theory. The total energy (Eq. (4.4)) was written as a functional of the electron density ($n(r)$)

$$E = \langle \Psi_i(r) | H | \Psi_i(r) \rangle = T + W + \int V_{\text{ext}}(r)n(r)dr.$$  

By separating terms which do not depend on the external potential, i.e. the kinetic energy ($T$) and the electron-electron interaction energy ($W$), Eq. (4.4) can be recast as follows

$$E[n] = F[n] + \int V_{\text{ext}}(r)n(r)dr.$$  

The following statements form the basis of this reformulation:
CHAPTER 4. THEORETICAL TOOL

1. the external potential uniquely determines the ground state density,
2. the exact ground state density minimizes the total energy functional
\[ \frac{\delta E[n]}{\delta n(r)} = 0 \] (4.6)
3. the functional \( F[n] \) does not depend on the external potential \( (V_{ext}) \). Therefore it may be considered to be a universal functional.

The universal functional \( F[n] \) contains the kinetic energy term for non-interacting electrons \( (T_s) \), the classical electron-electron Coulomb interaction, i.e. the Hartree term \( (E_H[n]) \) and the exchange-correlation term \( (E_{xc}[n]) \). The last one includes the energy contributions due to the Pauli exclusion principle (exchange) and all the other energy contributions due to the many particle interaction not included in the other terms.

\[ F[n] = T_s + E_H[n] + E_{xc}[n] \] (4.7)

The \( W + V_{ext} \) terms in the Eq. (4.3) can be replaced by an effective potential, \( V_{eff} \), which leads to the so-called Kohn-Sham [57] single-electron equation

\[ \mathcal{H}_{eff}(r) \psi_i(r) = \left[ -\frac{\hbar^2}{2} \nabla^2 + V_{eff}(r) \right] \psi_i(r) = \epsilon_i \psi_i(r) \] (4.8)

where

\[ V_{eff} = V_{ext} + V_H([n]; r) + \frac{\delta E_{xc}[n]}{\delta n(r)} \] (4.9)

with the Hartree potential

\[ V_H([n]; r) = \frac{1}{4\pi\epsilon_0} \int \frac{n(r)}{|r - r'|} dr'. \] (4.10)

The Kohn-Sham equation is a Schrödinger type one-electron equation. The ground-state density for an \( N \) electron system is given by the single electron wave functions

\[ n(r) = \sum_{i=1}^{N} |\psi_i(r)|^2. \] (4.11)

The sum runs over all Kohn-Sham states up to the Fermi level accomplishing that the total number of electrons have to be constant: \( N_e = \int n(r) dr \). For a spin polarized
system the single electron wave functions are calculated separately for spin up and spin
down components and leads to a total density composed from spin up and spin down
densities: \( n(\mathbf{r}) = n^\uparrow(\mathbf{r}) + n^\downarrow(\mathbf{r}) \).

The exact value for the Kohn-Sham non-interacting electron kinetic energy may be cal-
culated from the electron density and one-electron energies \( \epsilon_j \) appearing in the one-
electron equations

\[
T_s = \sum_{\epsilon_j < \epsilon_F} \epsilon_j - \int V_{\text{eff}}([n]; \mathbf{r}) n(\mathbf{r}) d\mathbf{r}.
\]

The total energy of the electronic system then is obtained as

\[
E_{\text{tot}} = \sum_{\epsilon_j < \epsilon_F} \epsilon_j - \int V_{\text{eff}}([n]; \mathbf{r}) n(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int V_{\text{H}}([n]; \mathbf{r}) n(\mathbf{r}) d\mathbf{r} +
\]

\[
+E_{xc}[n] + \int V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \sum_{k \neq l} \frac{e^2 Z_k Z_l}{4\pi \epsilon_0 |\mathbf{R}_k - \mathbf{R}_l|}
\]

(4.13)

using the total density given in Eq. (4.11).

The only unknown factor in the Kohn-Sham equation (Eq. (4.9)) is the exchange-correlation
functional, \( E_{xc}[n] \). The exchange part due to the Pauli exclusion principle may be calcu-
lated exactly [58] within the Hartree-Fock approximation, but this is demanding within
DFT. The correlation part includes all interactions which cannot be calculated exactly.
Therefore, instead of calculating separately the exact exchange and approximating the
correlation there are several approximations which treat these energy contributions
jointly as a functional of the electron density \( n(\mathbf{r}) \). The exchange-correlation energy
can be obtained by integrating the single electron exchange \( (\epsilon_x([n]; \mathbf{r})) \) and correlation
\( (\epsilon_c([n]; \mathbf{r})) \) energies

\[
E_{xc}[n] = E_x[n] + E_c[n] = \int \epsilon_x([n]; \mathbf{r}) n(\mathbf{r}) d\mathbf{r} + \int \epsilon_c([n]; \mathbf{r}) n(\mathbf{r}) d\mathbf{r}.
\]

(4.14)

The first approximation for the exchange-correlation functional was obtained consid-
ering a special model system, the uniform electron gas with density \( n(\mathbf{r}) \). It is called
Local Density Approximation, LDA. The corresponding exchange-correlation potential
\( V_{xc}^{\text{LDA}} = \delta(n \epsilon_{xc}^{\text{LDA}}) / \delta n \) is a local potential, meaning that it depends only on the elec-
tron density in the actual point.

Several expressions for \( \epsilon_{xc}^{\text{LDA}}([n]; \mathbf{r}) \) were developed. The most commonly used is the
parametrization for the correlation energy \( (\epsilon_c^{\text{LDA}}(n)) \) made by Perdew and Wang [59]
based on Monte Carlo calculations of Ceperley and Alder [60]. The LDA one-electron
exchange energy is given by: \( \varepsilon_z^{LDA}(n) = -3/2(3/\pi)^{1/3}n^{2/3} \) in atomic Rydberg units. The LDA overestimates the bonding, which leads to an underestimation of the equilibrium volume. Therefore, improvements over the LDA are needed.

Inclusion of gradient corrections to the electron density leads to a group of functionals, which use Generalized Gradient Approximation, GGA. The exchange-correlation energy is expressed as a local functional of the density and the magnitude of its gradient: \( \varepsilon_{xc}^{GGA}[n(r), |\nabla n(r)|] \). Two versions of the GGA are commonly implemented in DFT computational programs: the first one was developed by Perdew, Burke and Ernzerhof (PBE) [61] and the second is a revision of the PBE for solids and surfaces (PBEsol) [62]. The PBE works better than the LDA for bulk properties of 3d metals.

4.1.2 Computational remarks

The Kohn-Sham equation (Eq. (4.8)) must be solved by self-consistent iterations. The first step can be guessing an initial value for the charge density \( n(r) \). Than the following steps can be performed:

1. construct the effective potential \( V_{\text{eff}} \),
2. calculate a new density,
3. if the solution is not converged continue with the 1\textsuperscript{st} step.

There are different computational methods for solving the Kohn-Sham equation. The major difference coming from the structure of the effective potential and the basis set. In general the desired quantities (charge density, total energy, etc.) are calculated within the possible smallest basic unit of the investigated system, than integrated up for the whole system. The smallest basic unit is called the Wigner-Seitz cell.

Results presented here were obtained using the Exact Muffin-Tin Orbital (EMTO) method to solve the Kohn-Sham equation.

4.2 The Exact Muffin-tin Orbital method

4.2.1 General aspects

In the muffin-tin approximations the space is divided into spheres around the atomic sites and the interstitial region between the spheres. In the EMTO method the potentials are constructed using optimized overlapping spherical potentials and the Kohn-Sham equation is solved exactly for these potentials. The effective single-electron potential, called muffin-tin potential (\( V_{\text{mt}} \)), is approximated by a spherically symmetric potential
4.2. THE EXACT MUFFIN-TIN ORBITAL METHOD

\( (V_R(r - R)) \) centered on lattice site \( R \), plus a constant potential \( V_0 \) for the interstitial region

\[
V_{\text{eff}}(r) \approx V_{\text{mt}}(r) \equiv V_0 + \sum_R [V_R(r - R) - V_0]. \tag{4.15}
\]

The final optimized overlapping muffin-tin potential is constructed from the optimal \( V_R(r - R) \) and \( V_0 \). Their optimal value is obtained by minimizing the mean of the squared deviation between \( V_{\text{eff}} \) and \( V_{\text{mt}} \). This optimization is done self-consistently within the Spherical Cell Approximation (SCA). In the SCA the Wigner-Seitz cell is replaced by a sphere with radius \( w \), the sphere having equal volume with the cell. \( V_R(r - R) \) includes the attractive electron-nuclei (\( V_{\text{ext}} \) in Eq. (4.9)) and the repulsive electron-electron (or Hartree, \( V_H \) in Eq. (4.9)) electrostatic potentials, both having long range. To obtain the charge neutrality, \( V_{\text{ext}} \) and \( V_H \) are separated to intra cell and inter cell contributions. According to this separation, \( V_R(r - R) \) is constructed as follows:

\[
V_R(r - R) = V^I_R(r - R) + V^M_R + \Delta V^\text{SCA}_R + \mu_{xc}(r - R) \tag{4.16}
\]

were \( V^I_R(r - R) \) stands for the spherical part of the intra-cell electrostatic potential, \( V^M_R \) is the spherically symmetric part of the Madelung potential, \( \Delta V^\text{SCA}_R \) is the SCA correction, \( \mu_{xc}(r - R) \) is the spherically symmetric part of the exchange-correlation potential.

Solutions of the Kohn-Sham equation (Eq. (4.8)) are expressed by linear combination of the exact muffin-tin orbitals \( (\bar{\psi}^a_{RL}) \)

\[
\Psi_j(r) = \sum_{RL} \bar{\psi}^a_{RL}(\epsilon, r - R) v^a_{RL,j}. \tag{4.17}
\]

The expansion coefficients \( v^a_{RL,j} \) are determined in a way that \( \Psi_j(r) \) to be solution for Eq. (4.8) in the entire space. This is realized by the so-called kink cancelation equation.

The exact muffin-tin orbitals are constructed using different basis functions inside the potential sphere \( (r - R < s_R) \) and in the interstitial region \( (r - R > s_R) \). The \( s_R \) is the radius of the potential sphere centered at site \( R \).

Inside the potential sphere the basis functions, so-called partial waves \( (\phi^a_{RL}) \), are constructed as a product of the real harmonics \( (Y_L(\vec{r} - \vec{R})) \) and solutions of the scalar-relativistic, radial Dirac equation for the spherical potential \( (\phi_{RL}) \)

\[
\phi^a_{RL}(\epsilon, r - R) = N_{RL}(\epsilon)\phi_{RL}(\epsilon, r - R)Y_L(\vec{r} - \vec{R}). \tag{4.18}
\]

The normalization factor \( N_{RL}(\epsilon) \) assures a proper matching (equal value and slope) at the potential sphere boundary \( (s_R) \) to the basis function outside of the potential sphere.
In the interstitial region the basis functions, called screened spherical waves \( \psi_{RL}^a(\kappa^2, r - R) \) \( (\kappa^2 = \epsilon - V_0) \), are solutions of the free electron Schrödinger equation. The boundary condition is given in conjunction with non-overlapping spheres, called hard spheres, centered at lattice site \( R \) with radius \( a_R \). The screened spherical waves behave as real harmonics on their own \( a \)-spheres centered at site \( R \) forming a complete basis set (first term of Eq. (4.19)), and can be expanded around any site \( R' \) in real harmonics (second term of Eq. (4.19)).

\[
\psi_{RL}^a(\kappa^2, r - R) = f_{RL}^a(\kappa^2, r - R)Y_L^\dagger(r - R)\delta_{R' R} + \sum_{L'} t_{RL}^a(\kappa^2, r - R')Y_L^\dagger(r - R')S_{RL' RL}^a(\kappa^2), \tag{4.19}
\]

where \( f_{RL}^a \) and \( t_{RL}^a \) are the value (head) and the slope (tail) functions, respectively. The expansion coefficients \( S_{RL' RL}^a(\kappa^2) \) is called slope matrix.

The partial waves and the screened spherical waves must join continuously and differentiable at \( a_R \). This is realized by additional free electron wave functions \( \varphi_{RL}^a(\epsilon, r - R) \)

\[
\varphi_{RL}^a(\epsilon, r - R) = f_{RL}^a(\kappa^2, r - R) + t_{RL}^a(\kappa^2, r - R)D_{RL}^a(\epsilon) \tag{4.20}
\]

were \( D_{RL}^a(\epsilon) \) is the logarithmic derivative of \( \varphi_{RL}^a(\epsilon, r - R) \) at \( r - R = a_R \), also known as single-site scattering matrix. \( \varphi_{RL}^a(\epsilon, r - R) \) joins continuously and differentiable to the partial wave at \( s_R \) and continuously to the screened spherical wave at \( a_R \). The slope cancelation between the screened spherical waves and free electron solutions is provided by the kink cancelation equation

\[
\sum_{RL} K_{RL'} RL^a(\epsilon_j)\varphi_{RL'}^a \equiv \sum_{RL} a_R \{ S_{RL' RL}^a(\kappa_j^2) - \delta_{R' R} \delta_{L' L} D_{RL}^a(\epsilon_j) \}\varphi_{RL'}^a = 0. \tag{4.21}
\]

were \( a_R \) is the fixed slope of the tail functions \( t_{RL}^a \) at the hard spheres.

In the present method, the Green’s function formalism is employed to obtain the total charge density, the total number of states and the total energy. Solutions of Eq. (4.21) are as well solutions of the Kohn-Sham equation (Eq. (4.8)) in the entire space and can be obtained from the poles of the path operator \( g_{RL' RL}^a(z) \) defined for a complex energy \( z \) by

\[
\sum_{RL', L''} K_{RL' RL''}^a(z)g_{RL' RL''}^a(z) = \delta_{R' R} \delta_{L' L}. \tag{4.22}
\]

For further details the reader is referred to Ref. [63].

The total charge density is obtained by summation of the one-center densities, which may be expanded in terms of real harmonics around each lattice site

\[
n(r) = \sum_{R} n_R(r - R) = \sum_{RL} n_{RL}(r - R)Y_L^\dagger(r - R). \tag{4.23}
\]

The total energy of the system is obtained via full charge density (FCD) technique using the total charge density. The space integrals over the Wigner-Seitz cells in Eq. (4.13)
is solved via the shape function technique. The FCD total energy is decomposed in following terms

\[ E_{\text{tot}} = T_s[n] + \sum_{R} (F_{\text{intra}R}[n_R] + E_{\text{xc}R}[n_R]) + F_{\text{inter}}[n] \] (4.24)

where \( T_s[n] \) is the kinetic energy, \( F_{\text{intra}R} \) is the electrostatic energy due to the charges inside the Wigner-Seitz cell, \( F_{\text{inter}} \) is the electrostatic interaction between the cells (Madelung energy) and \( E_{\text{xc}R} \) is the exchange-correlation energy.

### 4.2.2 EMTO-CPA

In a substitutionally disordered alloy each alloy component can occupy any atomic site within the lattice. In the Coherent Potential Approximation (CPA) [64, 65], the alloy is replaced by an ordered effective medium in which the alloy components are embedded. Within the EMTO-CPA method the real alloy potential and the path operator is replaced by a coherent potential \( \tilde{P} \) and a coherent path operator \( \tilde{g} \), respectively. The fluctuations of the real alloy potential are neglected (single-site approximation). For each alloy component with \( c_i \) atomic fraction a single-site path operator is introduced \( g_i \). The coherent potential is introduced via the single-site scattering matrix \( \tilde{D} \). The single-site path operator satisfies:

\[ \tilde{g} = \sum_i c_i g_i \] (all are dependent on position and energy).

Due to the single-site treatment of the impurity a new term/potential is added to the expression of the effective potential in Eq. (4.16)

\[ \Delta V_{\text{SIM},i}^R = -\frac{2\alpha_c}{w}(Q_i^s - Q_s) \] (4.25)

where \( V_{\text{SIM},i}^R \) is the potential shift for the \( i^{th} \) alloy component, \( \alpha_c \) is a dimensionless parameter which match the CPA charge transfer to the real charge transfer, \( w \) is the Wigner-Seitz radius, \( Q_{s,i}^r \) is the difference between the number of electrons of \( i^{th} \) alloy component \( Q_{s,i}^r \) and the average number of electrons \( Q_s^r \) both defined inside the potential sphere with radius \( s \).

The EMTO-CPA total energy cast as:

\[ E_{\text{tot}} = T_s[n] + \sum_{R} \sum_i c_i (F_{\text{intra}R}^i[n_R^i] + E_{\text{xc}R}^i[n_R^i]) + F_{\text{inter}}[Q] + \Delta E_{\text{SIM}} \] (4.26)

where \( \Delta E_{\text{SIM}} \) is an additional energy shift due to the single-site treatment of the impurity. The other terms are the same as in Eq. (4.26), the only difference being that the intra cell electrostatic energy \( F_{\text{intra}R}^i[n_R^i] \) and the exchange-correlation energy \( E_{\text{xc}R}^i[n_R^i] \) is defined for each alloy component and scales with the concentration \( c_i \). In the expression
of $\Delta E^{SIM}$

$$\Delta E^{SIM} = -\sum_i c_i \alpha'_c \frac{1}{w} (Q_R^{i,s} - Q_R^s)^2$$  \hspace{1cm} (4.27)

$\alpha'_c$ is a dimensionless parameter which assures that the total energy obtained by CPA match with the total energy of a real alloy. Both, the potential and the energy shifts ($V_R^{SIM,i}$ and $\Delta E^{SIM}$, respectively), as well as the parameters $\alpha_c$ and $\alpha'_c$ are taken into account within the screened impurity model by Korzhavyi et al. [66, 67].

### 4.2.3 Calculation of $J_{ij}$ within the EMTO method

The magnetic exchange constants for a multi component system $J_{ij}^{QQ'}$ ($i, j$ and $Q, Q'$ denoting atomic positions and types, respectively), are calculated based on the magnetic force theorem [68, 69] implemented in the EMTO method as follows:

$$J_{ij}^{QQ'} = \frac{1}{4\pi} \text{Im} \int_C dz \text{Tr}_L \left[ \left( (D_i^{Q,\uparrow})^{-1} - (D_i^{Q,\downarrow})^{-1} \right) \tilde{g}_{ij}^{QQ',\uparrow} \left( (D_j^{Q',\uparrow})^{-1} - (D_j^{Q',\downarrow})^{-1} \right) \tilde{g}_{ji}^{Q'Q,\downarrow} \right],$$

where $D_i^{Q,s}$ and $\tilde{g}_{ij}^{QQ',s}$ ($s = \uparrow, \downarrow$) are the spin-projected single-site scattering matrices and the matrices of the average scattering path operator, respectively. Note, that the trace is taken in angular momentum space, $L = (\ell, m)$, and the occurring scattering matrices are energy dependent.

$J_{ij}$ scales with the concentration of the alloy components

$$J_{ij} = \sum_{Q,Q'} c_Q c_{Q'} J_{ij}^{QQ'}.$$  \hspace{1cm} (4.29)

### 4.3 Disordered Local Moment approach

The Disordered Local Magnetic Moment (DLM) approach is one way to model the paramagnetic phase in theoretical calculations [70, 71]. Within this approach an $AB$ binary system where $A$ is magnetic and $B$ is non-magnetic, can be represented as a ternary alloy: $A_{0.5}^\uparrow A_{0.5}^\downarrow B$ with a random mixture of two magnetic states of $A$. This approximation describes accurately the paramagnetic state with randomly oriented local magnetic moments. In this thesis the zero-temperature DLM state is meant when referring to the theoretical paramagnetic state.
Chapter 5

Fe$_2$P based materials

The diiron phosphide (Fe$_2$P) based materials have attracted numerous MCE research recently. The largest MCE can be obtained around the magnetic transition temperature which is the Curie temperature ($T_C$) for a ferromagnetic to paramagnetic transition. The $T_C$ of Fe$_2$P is around 215 K [72, 73, 74]. The $T_C$ can be tuned by replacing part of the Fe atoms with manganese (Mn) and part of the P atoms with T = boron (B), silicon (Si) or arsenic (As). The Mn addition leads to a decrease in the $T_C$ in MnFe(P,As) system [29, 75] and by T addition increases the $T_C$ in Fe$_2$(PT) [76, 5, 77]. Both, Fe$_2$(PSi) and (MnFe)$_2$P show crystallographic phase transitions too [5, 78].

In this thesis the magnetic and the crystallographic properties of Fe$_2$P, Fe$_2$P$_{1-x}$T$_x$ and MnFeP$_{0.75}$Si$_{0.25}$, MnFeP$_{0.5}$Si$_{0.5}$ are studied.

5.1 Magnetic properties of Fe$_2$P based alloys

A remarkably steep increase of the magnetic transition temperature of Fe$_2$P by partial replacement of P by B [76], Si [5] or As [77] was found experimentally. A strong sensitivity of the Fe$_2$P Curie temperature to the presence of Fe vacancy, stress and pressure was also reported by Lundgren et. al. [4]. They showed that $T_C$ correlates with the anomalous change of the lattice parameters ($c$ increases with the temperature when $a$ decreases, both having a discontinuity at $T_C$). This anomalous cell axis behavior and its correlation with $T_C$ was also found by Si doping. In brief, the strong sensitivity of $T_C$ was related to the structural change ($c/a$). Yamada and Terao [10] showed that the first order magnetic transition in Fe$_2$P can be attributed to the appearance of a metamagnetic transition for one of the Fe sites. How the metamagnetic behavior is affected by doping, and the relation between the metamagnetic behavior and the anomalous lattice parameter change are not known.

In the following the driving force behind the complex magnetic behavior is investigated.
CHAPTER 5. FE$_2$P BASED MATERIALS

for Fe$_2$P$_{1-x}$T$_x$ calculating the magnetic exchange interactions as a function of composition and structure. The metamagnetic behavior is discussed for the pure and B and Si doped Fe$_2$P.

The investigated Fe$_2$P$_{1-x}$T$_x$ (x = 0, x = 8% for B, x = 10% for Si and x = 10% for As) alloys crystallize in a hexagonal (hex) crystal structure with space group $P\bar{6}2m$. The hex unit cell contains nine atoms distributed in four crystallographically different sites as follows: three-three Fe atoms occupy the $3f$ and $3g$ triple-degenerate sites. They are labeled as FeI and FeII, respectively. Two phosphorus atoms (PI) are in the $2c$ site, which is double-degenerate, and the $1c$ site is non-degenerate containing one phosphorus atom (PII). The FeI atom is surrounded by two PI and two PII atoms which form a tetrahedron around FeI. Therefore this site is called tetrahedral site. Around the FeII atom one PII and four PI atoms form a pyramid. This site is called pyramidal site. The environment of Fe atoms is presented in Fig. 5.1. The relation between the pyramidal and tetrahedral

![Figure 5.1: The environment of iron atoms in the $P\bar{6}2m$ structure. a: Relation between the pyramidal and tetrahedral sites. Rhombohedral projection in 2D. b: Hexagonal arrangement of rhombohedral subcells. (Based on Ref. [73].) ](image)

sites is presented in Fig. 5.1a. The P atoms form a channel around the Fe atoms. These pyramidal-tetrahedral channel pairs build up the hexagonal arrangement as shown in Fig. 5.1b.
5.1. MAGNETIC PROPERTIES OF Fe₂P BASED ALLOYS

Doping led to a volume (\(V\)) and \(c/a\) ratio change within the hexagonal phase. The composition dependent lattice parameters are listed in Table 5.1.

Table 5.1. Experimental volume (\(V\)) and \(c/a\) ratio for Fe₂P [79] and Fe₂P₁₋ₓTx (T= B, Si, As) [76, 5, 77]. Note the decrease in \(c/a\) ratio as we go from pure Fe₂P to the B, Si and As doped systems.

<table>
<thead>
<tr>
<th></th>
<th>(V) (Å(^3))</th>
<th>(c/a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂P</td>
<td>103.10</td>
<td>0.589</td>
</tr>
<tr>
<td>Fe₂P₀.₉₂B₀.₀₈</td>
<td>102.14</td>
<td>0.570</td>
</tr>
<tr>
<td>Fe₂P₀.₉Si₀.₁</td>
<td>103.92</td>
<td>0.578</td>
</tr>
<tr>
<td>Fe₂P₀.₉As₀.₁</td>
<td>104.63</td>
<td>0.580</td>
</tr>
</tbody>
</table>

The present calculations were performed using the experimentally determined lattice parameters and assuming a uniform doping on the two P sites.

There are some relevant theoretical findings which are not included in details in the thesis:

- The experimentally known anomalous cell axes behavior is detected theoretically too. After optimizing the \(c/a\) ratio of the \(\text{hex}\) lattice for ferromagnetic and paramagnetic (DLM) phases a 0.5% volume decrease is found upon the ferromagnetic-paramagnetic phase transition. The theoretical lattice parameter \(a\) decreases and \(c\) increases. Further details can be found in Paper III.

- The total energy difference between the ferromagnetic and paramagnetic phases calculated at fixed structure as a function of Si content leads to an about 4% increase in \(T_C\) with 10 at. % of Si. Results included in Paper III.

5.1.1 Structural effects on magnetic properties

The magnetic exchange constants (\(J_{ij}\)) were calculated as a function of volume, \(c/a\) ratio and doping elements in order to identify their impact to the magnetic ordering in these alloys. In the present section the most important and interesting features are discussed, for completeness the reader is referred to Paper I.

First, a detailed analysis of the Fe₂P \(J_{ij}\) was done. The Fe atoms in the 3\(f\) and 3\(g\) positions are labeled by 1–3 and 4–6, respectively. For a given distance, if appropriate, there are identical interactions, and they can be cast into the following six groups: \(J_{11}, J_{12}, J_{14}, J_{15}, J_{44}\) and \(J_{45}\). The group interactions show an oscillatory behavior, which falls off with the distance. The strongest interactions turned out to be between the different nearest neighbor FeII atoms in 3\(g\) positions: \(J_{45}\). The next strongest interactions are between FeI-FeII atoms in 3\(f\) - 3\(g\) positions, e.g. \(J_{14}, J_{15}\). The \(J_{11}, J_{12}\) and
The different group interactions show different V and c/a dependence for Fe₂P, some of them increase, others decrease with increasing V (c/a). Therefore a \( J_{av} \) is introduced as a qualitative description of the interactions, and it is investigated how it behaves as a function of V, c/a and composition. At this point this simplification is reasonable, because calculation of \( T_C \) is not intended. A general structural trend is concluded as follows: by increasing c/a the \( J_{av} \) decrease and by increasing the volume the \( J_{av} \) increase. This \( J_{av}(V) \) trend is in line with the results of the pressure experiment, which showed that \( T_C \) decreases with the pressure [73].

When going from Fe₂P to Fe₂P\(_{1-x}T_x\) first the composition is changed, the induced difference in \( J_{av} \) meaning the chemical effect. Then the structure is changed in two steps, which corresponds to the c/a and V effect, respectively. The total effect is the sum of the different contributions.

It turned out that B has the largest chemical effect (\( \Delta J_{av}(chem)(B)=0.33\Delta J_{av}(tot)(B) \)), which strengthens the magnetic interactions. For Si and As the chemical effect is minor, 3\% and -2\%, respectively.

The experimental c/a ratio decreases for all alloys relative to the c/a of Fe₂P. In agreement with the general structural trend formulated for Fe₂P the \( J_{av} \) increases, when the c/a ratio is changed for a fixed composition.

The experimental V decreases for the B doped alloy, and increases for the others (Fe₂P\(_{0.9}Si_{0.1}\), and Fe₂P\(_{0.9}As_{0.1}\)) relative to the V of Fe₂P. In agreement with the observation for Fe₂P, the \( J_{av} \) decreases for Fe₂P\(_{0.92}B_{0.08}\) and increases for the Si and As doped systems.

Analyzing the chemical, volume and c/a effect on the different groups of \( J_{ij} \)'s it turned out that the more robust FeII-FeII interactions are less affected and the main player is how the interactions between the two sublattices are changed by alloying. The total change in the \( J_{15} \) give the largest contribution (67/62/71\%) to the total change in \( J_{av} \).

Summing up the different contributions it is found that the total change in the \( J_{av} \) is also in line with the experimental findings: B has an almost twice as large effect on the Curie temperature as Si, and As has the smallest effect. The total change of \( J_{av} \) upon doping with B (Si, As) represents just 18 (11, 7)\% increase, which is not comparable quantitatively with the experimental findings: \( T_C \) increases by 82 (60, 56)\%. This finding suggest that no accurate \( T_C \) can be computed if the present \( J_{ij} \)'s are employed in a Monte Carlo study.

Taking into account the structural modifications upon doping and applying a more advanced approach, namely the \( J_{ij} \) calculation, we are able to improve our previous predictions for Fe₂P\(_{0.9}Si_{0.1}\): 11\% increase in \( J_{ij} \) with 10\% Si addition instead of 4\%, indicating that the structural effects are important.

For Fe₂P, \( J_{45} \) are positive and large (~1.5 mRy) indicating a strong ferromagnetic coupling between the FeII atoms. That is, the FeII sublattice is ferromagnetic. However, none of the interactions between the FeI atoms are large, meaning that this sublattice has a less strong tendency to order.
5.1. MAGNETIC PROPERTIES OF Fe₃P BASED ALLOYS

5.1.2 Metamagnetism in Fe₃P and its alloys

Based on the expansion of magnetic energies discussed in detail in section 2.2, the magnetic behavior of the different Fe sublattices in Fe₃P₁₋ₓTx (x = 0, x = 0.08 when T = B and x = 0.1 when T = Si) can be evaluated. Total energies as a function of the total magnetic moment \( M \) were calculated. The magnetic energies coming from the two different types of Fe atoms are separated as follows

\[
E(m_1, m_2) = \frac{1}{2}a_1m_1^2 + \frac{1}{4}b_1m_1^4 + \frac{1}{6}c_1m_1^6 + \frac{1}{2}a_2m_2^2 + \frac{1}{4}b_2m_2^4 - Jm_1m_2, \tag{5.1}
\]

where \( m_1 \) and \( m_2 \) are the local magnetic moments for Fe-I and Fe-II, respectively, \( a_1, b_1, c_1 \) and \( a_2, b_2 \) are the corresponding expansion coefficients, and \( J \) is the exchange constant between the two types of magnetic sites. The expansion coefficients were estimated by fitting the magnetic energy calculated as a function of \( M = m_1 + m_2 \), with the constraint

\[
\left( \frac{\partial E(m_1, m_2)}{\partial (m_1 - m_2)} \right)_{M = 0} = 0.
\]

The calculated coefficients show that the FeII sublattice has a ferromagnetic ground state, i.e. \( a_2 < 0 \) and \( b_2 > 0 \), for all systems. The FeI sublattice has \( a_1 > 0, b_1 < 0 \) and \( c_1 > 0 \) for all alloys, meaning that FeI can be either ferromagnetic or paramagnetic, depending on the dimensionless parameter \( \kappa \equiv a_1c_1/b_1^2 \) (see section 2.2). The estimated \( \kappa \) values are: 0.263 for Fe₃P, 0.247 for Fe₃P₀.₉₂Si₀.₁ and 0.208 for Fe₃P₀.₉₂B₀.₀₈. These values are between the barriers 3/16 (0.19) and 9/20 (0.45), meaning that the FeI sublattice is paramagnetic in the absence of the exchange interaction between \( m_1 \) and \( m_2 \). Fe₃P has the largest \( \kappa \), which means that the finite-moment state of the Fe-I sublattice (when the interaction with the Fe-II site is neglected) is the least stable, compared to that of the doped systems. For Fe₃P₀.₉₂B₀.₀₈, \( \kappa \) is close to the FM limit 3/16, indicating that the stability of the finite-moment state of Fe-I is significantly increased by B doping. For the Si-doped system, \( \kappa \) is in between that of pure and B-doped Fe₃P.

For a more detailed analysis, the magnetic energy as a function of \( m_1 \) is monitored, shorting out the interaction with the exchange field from the Fe-II atoms (Fig. 5.2). The magnetic energy has a minimum at \( m_1 = 0 \) for all three systems, and an inflection point/minimum at \( m_1 \sim 1 \) for the pure Fe₃P/doped systems. In all alloys considered, the magnetic ordering of the Fe-I sublattice is stabilized by the exchange field created by the Fe-II sublattice, when the exchange coupling to the Fe-II reaches a critical value. This happens when the average magnetic moment of the Fe-II sublattice is sufficiently large, say above a critical value \( m_c \). A finite temperature reduces the average moment of the Fe-II site (as well as the Fe-I site) so that with increasing temperature one approaches from above \( m_c \). This happens for Fe₃P as well as for B or Si doping. However, since the value of \( m_c \) is smaller for B and Si doped samples (due to the fact that Fe-I has a stronger internal tendency to form a finite moment state - see Fig.2.1), it should be possible to reach higher ordering temperatures in these cases.

For the present study the experimental structures were used, meaning that the composition and the structure were changed simultaneously. To which extent the structural
change and the chemical effect is responsible for the stabilization of the finite-moment state with doping is not known yet. Further investigations are under way.

The microscopic picture presented above suggests that the magnetic exchange interactions calculated for a FM state of Fe$_2$P based systems, with an accompanying large moment of the FeI, does not represent well the state of affairs close to the ordering temperature. This is due to that fluctuations on FeII atoms diminish (or remove) the exchange interaction between Fe-I and Fe-II moments, which brings forth the metamagnetic behavior of the Fe-I moment at (or close to) the ordering temperature. An approach which can take into account the metamagnetic behavior of the FeI site is promising to give the good theoretical Curie temperature.

### 5.1.3 Curie temperature

Magnetic exchange interactions were calculated in ferromagnetic and constrained DLM (cDLM) states. Within the constrained DLM approach the FeI sublattice is forced to keep the DLM phase leading to a zero average magnetic moment of FeI. The local magnetic moment on FeI and moments on FeII are relaxed freely. This approach is used to model the metamagnetic behavior of the FeI sublattice. The Curie temperature is calculated, with both $J_{ij}$, using statistical methods. Results for Fe$_2$P and Fe$_2$P$_{1-x}$B$_x$, together with the available experimental data, are listed in Table 5.2. Starting from a ferromagnetic state the $T_C$ is considerably overestimated. The cDLM approach gives theoretical $T_C$ in
good agreement with the experimental data.

Table 5.2. Theoretical Curie temperatures (K) calculated for $\text{Fe}_2\text{P}_{1-x}\text{B}_x$ ($x = 0 - 0.15$) in ferromagnetic (FM) and cDLM states together with the experimental (exp) data [76]. Deviation from the experimental data in percentage is given in parenthesis.

<table>
<thead>
<tr>
<th></th>
<th>exp</th>
<th>FM</th>
<th>cDLM</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Fe}_2\text{P}$</td>
<td>219</td>
<td>426 (95%)</td>
<td>241 (10%)</td>
</tr>
<tr>
<td>$\text{Fe}<em>2\text{P}</em>{0.96}\text{B}_{0.04}$</td>
<td>360</td>
<td>535 (49%)</td>
<td>270 (-25%)</td>
</tr>
<tr>
<td>$\text{Fe}<em>2\text{P}</em>{0.92}\text{B}_{0.08}$</td>
<td>452</td>
<td>579 (29%)</td>
<td>375 (-17%)</td>
</tr>
<tr>
<td>$\text{Fe}<em>2\text{P}</em>{0.85}\text{B}_{0.15}$</td>
<td>520</td>
<td>652 (25%)</td>
<td>560 (8%)</td>
</tr>
</tbody>
</table>

5.2 Stability of hexagonal $\text{Fe}_2\text{P}$

The final refinement of the $\text{Fe}_2\text{P}$ crystal structure was done by Carlsson et al. in 1973 [80] and later on by Fujii et al [79]. According to these experimental results $\text{Fe}_2\text{P}$ crystallizes in a hexagonal crystal structure (space group $P\bar{6}2m$) in both, ferromagnetic and paramagnetic, phases. Crystallographic phase transition may be induced by substitution of Fe / P atoms or by applied pressure at high temperature. A hexagonal ($P\bar{6}2m$) - orthorhombic ($I\text{mm}2$) transition is induced by $\sim 8\%$ Si addition near 0 K [5, 81]. Another orthorhombic structure ($P\text{nma}$) forms when $\text{Fe}_2\text{P}$ is doped with Mn in the intermediate concentration range, e.g. $0.31 \leq x \leq 0.62$ [82]. Recently, a hexagonal ($P\bar{6}2m$) - orthorhombic ($I\text{mm}2$) transition was published for Mn rich $\text{Mn}_x\text{Fe}_{1.95-x}\text{P}_{0.5}\text{Si}_{0.5}$ off-stoichiometric compounds [83]. The applied pressure induces $P\bar{6}2m$ - $P\text{nma}$ transition [84, 85]. These pressure experiments show that the metastable $P\text{nma}$ structure may be stabilized in ambient conditions after quenching [84, 85]. 0 K DFT calculations done by Wu and Qin [86] show that the $P\text{nma}$ and the $P\bar{6}2m$ structures are almost degenerate in energy, the stable being the $P\text{nma}$ structure.

In the present lattice stability study three structures, namely the $P\bar{6}2m$, $I\text{mm}2$ and $P\text{nma}$ structures, are involved. The experimental structures were relaxed for the $\text{Fe}_2\text{P}$ composition using the Projector Augmented Wave (PAW) method. The relative stability of the different structures is demonstrated via PAW and Full-Potential Augmented Plane Wave plus local orbital (FPAPW) results too besides the EMTO results.
5.2.1 Crystal structures

The hexagonal (hex) $P_{62m}$ structure is presented in detail in section 5.1.

The $Imm_2$ orthorhombic structure

![Diagram of $Imm_2$ orthorhombic structure with atom positions labeled (a) and (b).]

The body centered orthorhombic (bco) unit cell contains 18 atoms: 12 Fe and 6 P atoms, and may be represented as a double hex cell. The site correspondence between the hex and bco unit cells [81, 87] is given in Table 5.3. The correspondence between the lattice parameters $a$, $b$, $c$ is given for a simple orthorhombic cell with 32 atoms (built up by four hex cell) [81]. The orthorhombic structure is shown in the Fig. 5.3a.

**Table 5.3.** Site correspondences between hex and bco structures [81, 87]. Site projected Wigner-Seitz radii ($r_{WS}/w$) for hex and hypothetical bco Fe$_2$P.

<table>
<thead>
<tr>
<th>hex</th>
<th>bco</th>
<th>Site</th>
<th>$r_{WS}/w$</th>
<th>Site</th>
<th>$r_{WS}/w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeI</td>
<td>Fe1, Fe2</td>
<td>3f (FeI)</td>
<td>0.992</td>
<td>8e (Fe1)</td>
<td>0.999</td>
</tr>
<tr>
<td>FeII</td>
<td>Fe3, Fe4, Fe5, Fe6</td>
<td>4c (Fe2)</td>
<td>0.997</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PI</td>
<td>P1</td>
<td>3g (FeII)</td>
<td>1.035</td>
<td>4d (Fe3)</td>
<td>1.031</td>
</tr>
<tr>
<td>PII</td>
<td>P2, P3</td>
<td></td>
<td></td>
<td>4d (Fe4)</td>
<td>1.023</td>
</tr>
<tr>
<td>$2c_{hex}$ $\approx a_{so}$</td>
<td>2e (PI)</td>
<td>0.977</td>
<td></td>
<td>8e (P1)</td>
<td>0.983</td>
</tr>
<tr>
<td>$\sqrt{3}a_{hex}$ $\approx b_{so}$</td>
<td>1b (PII)</td>
<td>0.956</td>
<td></td>
<td>2b (P2)</td>
<td>0.948</td>
</tr>
<tr>
<td>$a_{hex}$ $\approx c_{so}$</td>
<td></td>
<td></td>
<td></td>
<td>2a (P3)</td>
<td>0.954</td>
</tr>
</tbody>
</table>
5.2. STABILITY OF HEXAGONAL Fe\textsubscript{2}P

The site projected Wigner-Seitz (WS) radii in units of the average WS radii ($r_{WS}/w$) are listed in Tab. 5.3 for the $\text{hex}$ and the hypothetical $\text{bco}$ Fe\textsubscript{2}P, respectively. The relaxed crystal structure analysis show that the WS sphere around 3$f$ site is smaller than that around 3$g$, and the WS sphere around 2$c$ is larger than that around 1$b$ for the $\text{hex}$ phase. For $\text{bco}$ the largest WS sphere is around the P1 sites amongst P sites. This becomes important when Fe and P atoms are replaced by other ones. In the $\text{hex}$ phase roman numbers and in the $\text{bco}$ phase arabic numbers are used for site representation.

The $Pnma$ orthorhombic structure

The $Pnma$ structure contains 12 atoms in the unit cell, 8 / 4 Fe/P atoms, respectively. All atoms occupy the 4$c$ position. 4 / 4 Fe atoms and all P atoms are crystallographically equivalent. There is similar arrangement of P atoms around the Fe I and Fe II atoms as in the case of the hexagonal structure: the 4 nearest neighbor P atoms form a tetrahedron around the Fe I, and Fe II atoms have 5 nearest P atoms in a pyramidal arrangement. $Pnma$ and $P62m$ structures differ from each other by the orientation of the rhombohedral subcells. The orthorhombic arrangement of rhombohedral subcells is shown in Fig. 5.3b [78, 88].

5.2.2 Lattice stability

Lattice stability in the ferromagnetic phase

In the present work the total energies for the relaxed, ferromagnetic $\text{hex}$ ($P62m$), and $\text{bco}$ ($I\text{m}m2$) structures were calculated using the PAW, FPAPW and EMTO methods. Results show that the $\text{hex}$ and $\text{bco}$ phases are almost degenerated, the ferromagnetic total energy difference $\Delta E_{FM} = E_{FM}^{\text{bco}} - E_{FM}^{\text{hex}}$ being -0.13 / -0.02 mRy for PAW / FPAPW, meaning that the $\text{bco}$ phase is the stable one. The EMTO results for $\Delta E_{FM}$ is equal with the PAW result. This is in contradiction with the experimental findings [80, 79]. To find the effects which are not included in the ab initio calculations and could stabilize the $\text{hex}$ phase, the zero-point energies were investigated. For details about the zero-point phonon contribution and the zero-point spin fluctuation contribution the reader is referred to Paper III. A short summary is given below.

The energy contribution coming from the zero-point phonon vibration is not enough to overcome the structural energy difference. This term can stabilize the $\text{hex}$ structure only if there are soft phonon modes in the $\text{hex}$ phase. This question needs to be investigated in the future. In a weak ferromagnet, as in Fe\textsubscript{2}P, the magnetic moments are not localized to a given site, a fluctuation in the magnitude of the magnetic moment and in the orientation may be observed. Previously the appearance of such “spin waves” was ascribed to thermal excitations [89]. It was shown recently, that spin fluctuations can appear even at 0 K [90]. This term can stabilize the ferromagnetic $\text{hex}$ phase at 0 K.
CHAPTER 5. FE$_2$P BASED MATERIALS

The 0 K, ferromagnetic total energies calculated with the PAW and FPAPW methods show that the \textit{Pnma} structure is the most stable structure between the three investigated structures. The energy difference $E_{\text{Pnma}}^{FM} - E_{\text{hex}}^{FM}$ is -0.8 mRy. Regarding the \textit{hex} ($P\overline{6}2m$) - \textit{Pnma} crystallographic phase stability, results presented here are in line with the previous DFT findings [86]. As a summary can be concluded that DFT calculations predict that the \textit{hex} phase is not the stable structure for the ferromagnetic Fe$_2$P. Further investigations are needed.

Lattice stability in the paramagnetic phase

The crystallographic phase stability in the paramagnetic phase is investigated using the EMTO method in combination with the DLM approach. Within this approximation the magnetic moments are allowed to be randomly oriented, thus corresponding to a high temperature paramagnetic phase. It is found that in the paramagnetic phase the \textit{hex} structure is the stable one with 0.865 mRy/atom against the \textit{bco}.

5.3 Si induced crystallographic phase transition of Fe$_2$P$_{1-x}$Si$_x$

According to the experiment [5] at low temperature (near 10 K) Fe$_2$P$_{1-x}$Si$_x$ adopts the \textit{hex} crystal structure up to 10-12\% of Si. By increasing the Si content a phase transition is induced from the \textit{hex} (space group $P\overline{6}2m$) to the \textit{bco} (space group $I\overline{mmm}$) [5] crystal structure. Experimental measurements give the room temperature crystal parameters of Fe$_2$P and Fe$_2$P$_{0.75}$Si$_{0.25}$. First the equilibrium crystal structures were determined for Si free \textit{hex} and \textit{bco} structures. Relaxation was done with the PAW method at 0 K in ferromagnetic phase. These relaxed, rigid crystal structures were used to investigate the structural stability in both magnetic phases. The paramagnetic phase is modeled by the DLM approach.

This section gives an overview for the Si site preference and the effect of Si doping. For details the reader is referred to Paper III.

5.3.1 Si site preference

Rundqvist [91] proposed that the substitution of P by a non-metallic element should show a site preference driven by the size of the substitutional atom: atoms larger than P (e.g. arsenic, As or silicon, Si) should occupy the 2\textit{c} position while smaller (e.g. boron, B) the 1\textit{b} one. This statement was confirmed experimentally for the As [77] and B [76] substitution, but not for Si [5]. As mentioned previously (see Tab. 5.3) the Wigner-Seitz sphere around the PI (2\textit{c}) site is larger than around the PII (1\textit{b}). The atomic volume
of Si is larger than the atomic volume of P by 13% [92]. Liu and Altounian showed a Si/2c preferential occupation in the case of MnFeP$_{2/3}$Si$_{1/3}$ [93]. Therefore, a possible site preference cannot be excluded for Fe$_2$P$_{1-x}$Si$_x$ either.

In the present study, this problem was investigated for ferromagnetic Fe$_2$P$_{2/3}$Si$_{1/3}$ stoichiometric compound with the PAW method. The results show that in both, hex and bco structures the first P position, 2c and 8e for hex and bco, respectively, is the preferred one for Si substitution. This is in accordance with the larger empty space around these positions (see Table 5.3). The stabilizing effect due to the site preference of the substitutional atoms is more accentuated for the bco (2.41 mRy) structure than for the hex one (0.54 mRy).

### 5.3.2 The effect of Si doping

#### Debye temperature and magnetic properties

The calculated bulk modulus of the hex (bco) phase increases from 161 GPa (170 GPa) to 175 GPa (181 GPa) as the Si content increases from zero to 40%. The trend of the bulk modulus turns out to be the dominant term in the Debye temperature, yielding $\Theta^\text{hex}_D < \Theta^\text{bco}_D$ for all $x$ values considered here.

Magnetic properties as a function of the Si content are investigated in the paramagnetic phase of the hex and bco Fe$_2$P$_{1-x}$Si$_x$. In both structures, the local magnetic moments increase with increasing Si content. This increase is more accentuated for the bco phase.

#### Structural phase transition in Fe$_2$P$_{1-x}$Si$_x$

Experimental investigations showed that the crystal structure transition temperature increases with increasing Si content and occurs within a narrow two-phase field [5].

The lattice stability of Fe$_2$P$_{1-x}$Si$_x$ is investigated in the paramagnetic phase modeled by the DLM approach. The structural energy difference ($E^\text{bco}_x - E^\text{hex}_x$), calculated using the relaxed total energies obtained for the rigid lattice and taking into account the site preference, is shown in Fig. 5.4. The hex total energy remains below the bco total energy up to $\sim 23\%$ Si. According to that the stability field of the hex/bco phase is located below/above $x \approx 0.23$. This is consistent with high temperature experimental result [5]. Using the common tangent technique one can see a wide two-phase field which is in disagreement with the experimental findings. Note that the presented energy difference does not include the temperature effect. In the inset of Fig. 5.4 the configurational entropy is included at 700 K. One can notice that the two-phase field becomes narrower. One can conclude that to establish a good theoretical phase diagram one should take into account the
temperature effect. This is a huge task, especially to calculate the phonon entropy for a disordered multicomponent system.

Using simple models (the Debye model for phonon entropy and the mean-field model for the magnetic entropy) the effect of phonon and magnetic entropies are assessed. Results are shown in Fig. 5.5. In these studies a uniform doping of Si is assumed.

Figure 5.5. Effect of magnetic and phonon entropy on the structural energy difference (mRy) in paramagnetic Fe$_2$P$_{1-x}$Si$_x$.

a. Effect of magnetic entropy

b. Effect of phonon entropy
The magnetic entropy stabilizes the \textit{bco} phase. This is in accordance with the higher magnitude of local magnetic moments. The phonon entropy stabilizes the \textit{hex} phase, which is in accordance with the lower Debye temperature of the \textit{hex} phase. The phonon stabilizing effect is stronger. This is the reason for the increasing transition temperature with Si addition.

The site preference has an effect on the lattice stability too. The stabilizing effect of the site preference is more accentuate for the \textit{bco} structure than for the \textit{hex} one. One can realize this by comparing Figures 5.4 and 5.5. In Fig. 5.4 the total energy difference is shown for Fe$_2$P$_{1-x}$Si$_x$ taking into account the site preference. The stability field of \textit{bco} is above $x \approx 0.23$. In Fig. 5.5 the site preference is not taken into account and one can see that the stability of \textit{bco} is above $x \approx 0.30$ at 0K.

\textbf{Chemical effect of Si}

The total electrostatic energy and the one-electron kinetic energy are investigated. The average electrostatic energy of paramagnetic Fe$_2$P is slightly smaller in the \textit{bco} phase than in the \textit{hex} phase. The kinetic energy (plus the exchange-correlation term) is smaller for the \textit{hex} phase than for the \textit{bco} phase. In other words the electrostatic energy favors the \textit{bco} phase, the kinetic energy the \textit{hex} one. Silicon doping changes the bonding in such a way that the kinetic (plus exchange-correlation) energy decreases, \textit{i.e.} both structures become more stable kinetically. This effect is more pronounced for the \textit{hex} structure than for the \textit{bco} structure. The electrostatic energy shows the opposite trend: for both structures the electrostatic energy increases with Si doping. This is in line with the observation that the average interstitial charge density decreases for both structures. Note that Si has less electrons than P. This change is more pronounced for the \textit{hex} structure. Hence, the electrostatic destabilization effect of Si is larger in the \textit{hex} structure than in the \textit{bco} structure, which together with the kinetic energy change leads to the stabilization of the \textit{bco} phase against the \textit{hex} phase with Si addition.
5.4 Mn site preference and magnetic properties of MnFeP$_{1-x}$Si$_x$

Site preference

It was shown experimentally that Mn preferentially occupy the pyramidal ($3g$) sites in FeMnP [82]. In this thesis the Mn site preference is investigated theoretically in ferromagnetic MnFeP$_{0.75}$Si$_{0.25}$ and MnFeP$_{0.5}$Si$_{0.5}$ compounds, where the hex Fe$_2$P structure is assumed according to Cam Thanh et al. [27]. Three different phases are investigated:

1. Mn-pyramidal: Fe occupies the $3f$ site and Mn the $3g$ site
2. Disordered: both, $3f$ and $3g$, sites are equally occupied by Fe and Mn atoms
3. Fe-pyramidal: Fe occupies the $3g$ site and Mn the $3f$ site

![Graph showing total energy curves for MnFeP compounds]

**Figure 5.6.** Total energy curves for three possible arrangement. The dashed lines stands for the experimental Wigner-Seitz radii.

Total energy curves are shown for each compound in Fig. 5.6. For both compounds the Mn-pyramidal arrangement has the lowest energy by 7-10 mRy relative to the other two possibilities. The deviation between the experimental and theoretical Wigner-Seitz radii ($w$) is 0.20% and 0.47% for MnFeP$_{0.75}$Si$_{0.25}$ and MnFeP$_{0.5}$Si$_{0.5}$, respectively. The experimental results are included in Paper IV and Paper V for MnFeP$_{0.75}$Si$_{0.25}$ and MnFeP$_{0.5}$Si$_{0.5}$, respectively.

Manganese preferentially occupies the $3g$ pyramidal position. A reasonable explanation can be found by analyzing the atomic radius of Mn and the Wigner-Seitz spheres around
each position: Mn, having a 3.2% larger atomic radius than Fe [92], prefers to occupy the largest 3g site (see Tab. 5.3). In the present investigation a uniform occupation of P sites by Si atoms was assumed.

**Magnetic properties**

Site projected magnetic moments for Fe and Mn atoms in all phases are listed in Tab. 5.4. Comparing the magnitude of magnetic moments at different sites one can see that higher moments appears in atoms belonging to the pyramidal 3g site. For both composition the largest magnetic moment has Mn at the 3g site, which tempting to explain the stabilization of the Mn-pyramidal phase to be due to the larger exchange energy between magnetic atoms in this phase. This is in line with the theoretical finding that the ferromagnetic state in the Mn-pyramidal phase is more stabilized (by ~ 3.5 - 5 mRy) against the non-magnetic state compared to the other phases.

<table>
<thead>
<tr>
<th>site atom</th>
<th>Mn-pyramidal</th>
<th>Disordered</th>
<th>Fe-pyramidal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MnFeP$<em>{0.75}$Si$</em>{0.25}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3f Fe</td>
<td>1.44</td>
<td>1.43</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>3g Fe</td>
<td>-</td>
<td>2.29</td>
</tr>
<tr>
<td></td>
<td>3g Mn</td>
<td>2.81</td>
<td>2.79</td>
</tr>
<tr>
<td>$\mu_{FM}$</td>
<td>4.11</td>
<td>4.15</td>
<td>4.25</td>
</tr>
<tr>
<td></td>
<td>MnFeP$<em>{0.5}$Si$</em>{0.5}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3f Fe</td>
<td>1.65</td>
<td>1.70</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>3g Fe</td>
<td>-</td>
<td>2.37</td>
</tr>
<tr>
<td></td>
<td>3g Mn</td>
<td>2.81</td>
<td>2.78</td>
</tr>
<tr>
<td>$\mu_{FM}$</td>
<td>4.30</td>
<td>4.30</td>
<td>4.46</td>
</tr>
</tbody>
</table>
Chapter 6

Thermophysical properties of Pd-Ag binary alloys

Palladium-silver alloys are frequently used for hydrogen separation membranes for producing purified hydrogen gas [11]. A fundamental understanding of the composition dependence of the thermophysical properties is needed for this application. According to the experimental phase diagram [94] Pd and Ag form a continuous solid solution within the face-centered-cubic (fcc) crystallographic phase. The alloying effects in Pd-Ag binary alloys were also in the focus of theoretical investigations. In the middle of the 90’s Bruno et al. [12] reported that electronic topological transitions (ETT) may occur by alloying Pd with Ag. In 2001 Muller and Zunger suggested three ordered structures at low temperatures: the L12 (Cu3Au-type) structure for Pd3Ag, the L11 (CuPt-type) structure for the equiatomic Pd-Ag and the L11+ structure for PdAg3 [15]. Experimentally was shown that the ordering has a minor effect on the single crystal elastic constants for Cu3Au [95]. Such experimental study does not exist for PdAg. In this work the EMTO method is used to investigate the thermophysical properties of disordered Pd$_{1-x}$Ag$_x$ alloys within the fcc phase, the effect of ETTs and long range ordering.

6.1 Disordered Pd$_{1-x}$Ag$_x$ alloys

6.1.1 Lattice parameter and formation energies

The accuracy of the used method is discussed in details in Paper VI. Here the lattice parameters, entropies, enthalpies of formation and Gibbs energies of the disordered Pd$_{1-x}$Ag$_x$ presented in Fig. 6.1 together with the available experimental data [14, 96]. Despite that, the reported long and short range ordering [15, 97] was not taken into account, a good agreement between the experimental and theoretical results is found. One
can expect that the ordering has only minor impact on the thermophysical properties of Pd-Ag alloys at room temperature and above. Therefore, electronic structure and elastic properties of disordered alloys in \textit{fcc} phase are investigated first.

**Figure 6.1.** a. Theoretical and experimental equilibrium lattice parameters for Pd-Ag alloys plotted as a function of Ag concentration [96]. b. Comparison between theoretical (present results) and experimental [14] mixing enthalpy ($\Delta H$), Gibbs energy of formation ($\Delta G$) and excess entropy of formation ($\Delta S_{\text{vib}}$, and $\Delta S_{\text{xs}}$) for Pd-Ag alloys as a function of Ag concentration (1200 K).

### 6.1.2 Electronic structure

The first detailed electronic structure calculation for Pd$_{1-x}$Ag$_x$ alloys was done by Bruno \textit{et al.} [12] using the fully relativistic KKR-CPA method. Calculating the composition dependent Fermi surfaces (FS), they have found the following five electronic topological transitions (ETT):

1. a neck disruption for $x = 0.06$,
2. disappearance of a hole pocket centered at $L$ for $x = 0.2$,
3. disappearance of the first hole pocket centered at $X$ for $x = 0.35$,
4. disappearance of the second hole pocket centered at $X$ for $x = 0.53$, and
5. a neck opening at $L$ for $x=0.7$. 
To detect separately this five different ETTs a very accurate investigation is needed, because they are blurred by the substitutional disorder. Bruno et al. claim that the ETT at $x = 0.35$ is undetectable within the non-relativistic treatment [13].

![Figure 6.2.](image)

**Figure 6.2.** Total density of states (dotted line), $s + p$ partial DOS (solid line) and $d + f$ partial DOS (dashed line) of $\text{Pd}_1 - x\text{Ag}_x$. The Fermi level is indicated by a vertical dashed line.

In the following the density of states (DOS) and FSs of pure elements and the detected ETTs are discussed for $\text{Pd}_1 - x\text{Ag}_x$ alloys based on results obtained with scalar-relativistic EMTO-CPA method. A full coincidence with the relativistic results is not expected due to the differences between the methods.

![Figure 6.3.](image)

**Figure 6.3.** Fermi surfaces of Pd and Ag, respectively.
6.1. DISORDERED PD$_{1-X}$AG$_X$ ALLOYS

For pure Pd, the Fermi level lies within the $d$ band, while for Ag in the $sp$ band, shown in Fig. 6.2. This leads to a completely different Fermi surface shape for the pure elements. The Pd FS consists of the following parts:

1. an octahedron electron pocket centered at the $\Gamma$ point with $sp$ character,
2. an ellipsoid hole pocket centered at the $X$ point having $d$ character, and
3. a hole jungle-gym structure which is connected at the point $L$, also having $d$ character. This connection of the jungle-gym structures was not detected in the earlier work of Andersen [98], but it is found by Bruno et al. [13].

The Ag FS is noble-metal-like with an octahedron electron pocket centered at the $\Gamma$ point with broken necks at the $L$ points and a belly centered at $\Gamma$ lying on the $\Gamma - X$ line. The FS intersection with the $\Gamma KLUX$ plane is presented in Fig. 6.3 for Pd and Ag. When increasing the Ag content (adding electrons) first the hole pockets get filled at low Ag concentrations, then at higher Ag content a neck will appear at the $L$ point. These changes in the FS topology may arise continuously or suddenly.

The FS evolution going from Pd to Ag is presented in Fig. 6.4 for some interesting concentrations. Already at 10 at. % Ag addition induces changes in the jungle-gym hole pockets at point $L$. This FS change may be compared with the 1$^{st}$ ETT found by Bruno et al.. At 20 at. % of Ag the jungle-gym hole structure completely disappears. One can observe that there is already one single hole pocket at $X$, which still exist at $x = 0.5$ but suddenly disappears at $x = 0.55$ (4$^{th}$ ETT). At 65 at. % of Ag the neck centered at $L$ is opening and completely appeared at $x = 0.8$. Four FS topology change are detected with the scalar-relativistic EMTO method. These results are comparable with the previous theoretical findings.

Bruno et al. claimed that physical parameters can be affected by the Fermi surface topology change. The effect of ETTs was connected to the anomalous, non-linear composition dependence of the lattice parameters in the present alloys. The largest deviation from the linear behavior is around the equiatomic concentration [13], where the disappearance of the ellipsoid hole pocket centered at $X$ point happens. A similar composition dependence of the lattice constants is found using the EMTO method presented in Paper VI. In the following section the composition dependence of the elastic properties is investigated from the ETT point of view.

6.1.3 Effect of ETTs on the elastic properties

As it was discussed in the previous section, to find all five ETTs for distinct concentrations is a difficult task even for the undistorted $fcc$ Pd-Ag alloys. Due to their closeness the effects of ETTs may overlap. The relativistic treatment is also helpful, but very demanding computationally. Furthermore, elastic constants calculations involves lattice
Figure 6.4. Fermi surfaces of Pd$_{1-x}$Ag$_x$ alloys.
6.1. DISORDERED PD$_{1-x}$AG$_x$ ALLOYS

- $X$

\[
\begin{align*}
B & (\text{GPa}) \\
c_{11} & (\text{GPa}) \\
c_{12} & (\text{GPa}) \\
c_{44} & (\text{GPa}) \\
\phi & (\text{K}) \\
\nu & \\
\Theta & (\text{K}) \\
\end{align*}
\]

\[
\begin{align*}
0 & \quad 20 & \quad 40 & \quad 60 & \quad 80 & \quad 100 \\
\text{at.\% Ag} & \quad \text{at.\% Ag} & \quad \text{at.\% Ag} & \quad \text{at.\% Ag} & \quad \text{at.\% Ag} \\
\end{align*}
\]

\[
\begin{align*}
\Delta B & (\text{GPa}) \\
\Delta c_{11} & (\text{GPa}) \\
\Delta c_{12} & (\text{GPa}) \\
\Delta c_{44} & (\text{GPa}) \\
\Delta \phi & \\
\Delta \nu & \\
\Delta \Theta & (\text{K}) \\
\end{align*}
\]

\[
\begin{align*}
0 & \quad 20 & \quad 40 & \quad 60 & \quad 80 & \quad 100 \\
\text{at.\% Ag} & \quad \text{at.\% Ag} & \quad \text{at.\% Ag} & \quad \text{at.\% Ag} & \quad \text{at.\% Ag} \\
\end{align*}
\]

\[
\begin{align*}
\Delta G & (\text{GPa}) \\
\Delta E & (\text{GPa}) \\
\Delta \nu & \\
\Delta \Theta & (\text{K}) \\
\end{align*}
\]

\[
\begin{align*}
0 & \quad 20 & \quad 40 & \quad 60 & \quad 80 & \quad 100 \\
\text{at.\% Ag} & \quad \text{at.\% Ag} & \quad \text{at.\% Ag} & \quad \text{at.\% Ag} & \quad \text{at.\% Ag} \\
\end{align*}
\]

a. Theoretical single and polycrystalline elastic moduli and Debye temperature of Pd-Ag alloys as a function of the Ag concentration.

b. Deviations from the linear behavior of the theoretical single and polycrystalline elastic moduli and Debye temperature of Pd-Ag alloys as a function of the Ag concentration.

distortions, which can smear the ETT effects. Therefore, while looking for anomalies in the elastic properties of alloys caused by FS topology change one cannot expect full coincidence with the simpler lattice constant case.

Figure 6.5a presents the calculated single crystal and polycrystalline elastic constants and Debye temperatures of disordered Pd$_{1-x}$Ag$_x$ alloys as a function of the Ag content. $B$ and the elastic constants $c_{11}$, $c_{12}$ and $c_{44}$ show a nearly linear composition dependence. The deviation from the linear behavior is more accentuated for the shear modulus $G$, Young’s modulus $E$ and Debye temperature $\Theta_D$ than for single crystal elastic constants. A break in the linear dependence appears near 40 and 60 at. % Ag content. The Poisson ratio $\nu$ also exhibits a non-monotonous behavior with a minimum at 50 and 60 at. % Ag.

The non-linear contribution to the concentration dependence of the investigated physical parameters is separated and plotted in Fig. 6.5b. One observes a strong deviation from the linear behavior. $B(x)$ and $c_{12}(x)$ follow a nearly parabolic trend with a first-order derivative discontinuity at $\sim 30$ and $\sim 60$ at. % Ag, $c_{44}(x)$ has a blurred breakpoint at $x = 0.6$, and $\Delta c_{44}(x)$ changes sign around $x = 0.8$. $c_{11}(x)$ has a double minimum structure, with a sharp first order discontinuity between 50 and 60 at. % of Ag and a breakpoint at $x \approx 0.6$. The strong non-linear trends in the elastic constants are well
reflected in the polycrystalline elastic moduli and the Debye temperature. $G(x)$, $E(x)$ and $\Theta_D(x)$ have large positive deviations, while $\nu(x)$ has a negative one. $\Delta\Theta_D(x)$ has maxima at 50 and 60 at. % Ag content.

The elastic parameters show a strong non-linear, non-monotonous concentration dependence, the largest deviation being around 50 at. % Ag for all investigated parameters. The pronounced anomalous behavior can be related to the disappearance of a hole pocket centered at $X$ which has $d$ character.

### 6.2 Effect of long-range order in Pd$_{0.5}$Ag$_{0.5}$

The above presented chemically random description is definitely appropriate for the elastic properties of the Pd$_{1-x}$Ag$_x$ alloys at high temperatures, but the physical state at low temperatures might be different as suggested by recent investigations [15, 97]. The ordering in turn may have a marked impact on the bulk properties (lattice constant, bulk modulus) and the elastic parameters of the Pd-Ag system. The ordering effect on the elastic properties of the Pd$_{0.5}$Ag$_{0.5}$ alloy is in the focus of the present section. The elastic parameters of the Pd$_{0.5}$Ag$_{0.5}$ alloy are calculated for the predicted low temperature structure and they are related to the cubic elastic constants.

The predicted low temperature structure is the L1$_1$ structure with alternating Pd and Ag layers along the [111] direction of the fcc lattice ($(\text{Pd})_1/(\text{Ag})_1$) shown in Fig. 6.6. The structure can be represented as a hexagonal lattice, having the $c$ axis along the cubic [111] direction and with 6 atoms (each representing a layer) per hexagonal unit cell.

**Figure 6.6.** The L1$_1$ structure with alternating Pd and Ag layers along the fcc [111] direction.

The bulk parameters and single crystal elastic constants of the Pd$_{0.5}$Ag$_{0.5}$ alloy are calculated within the hexagonal representation as a function of the degree of ordering which
6.2. EFFECT OF LONG-RANGE ORDER IN PD\textsubscript{0.5}AG\textsubscript{0.5}

is controlled by modifying the layer composition \((\text{Pd}_{1-x}\text{Ag}_x)/(\text{Pd}_x\text{Ag}_{1-x})\): \(x\) changing from 0.5 (corresponding to the completely disordered system) to 1 (corresponding to the completely ordered system). Results for three different phases are considered here:

1. completely disordered phase (labeled as \(H_d\)), where the Pd and Ag atoms are distributed with equal probabilities within the layers of the \(L1_1\) structure,

2. partially ordered phase (\(H_{po}\)), where the Pd and Ag atoms are mixed with certain probabilities (\(x=20\%\) of Ag in a Pd layer and vice versa) within the layers,

3. ordered phase (\(H_o\)) stands for the layered structure where the different type of atoms occupy alternating layers.

The three independent elastic constants for the disordered cubic phase (labeled in the following by \(F_d\)) are transformed into hexagonal ones by applying the tensor transformation rules presented in general in Chapter 3. For the present case, the Euler’s rotation (details in Chapter 3) involves only two rotations with \(\Phi=135^\circ\) and \(\Theta=\arctan\sqrt{2}\) shown in Figure 6.7, \(\Psi\) being equal to zero. The obtained transformation matrix is

\[
T = \begin{pmatrix}
-\frac{\sqrt{2}}{4} & \frac{\sqrt{2}}{2} & 0 \\
-\frac{\sqrt{2}}{4} & -\frac{\sqrt{2}}{2} & \frac{\sqrt{6}}{3} \\
\frac{\sqrt{2}}{4} & -\frac{\sqrt{2}}{2} & \frac{\sqrt{3}}{3}
\end{pmatrix},
\]

which leads to the following relations between the \(fcc\) and hexagonal elastic constants:

\[
\begin{align*}
\frac{c_{11}^H}{2} &= \left(\frac{c_{11}^F + c_{12}^F + 2c_{44}^F}{2}\right) \\
\frac{c_{12}^H}{6} &= \left(\frac{c_{11}^F + 5c_{12}^F - 2c_{44}^F}{6}\right) \\
\frac{c_{13}^H}{3} &= \left(\frac{c_{11}^F + 2c_{12}^F - 2c_{44}^F}{3}\right) \\
\frac{c_{33}^H}{3} &= \left(\frac{c_{11}^F + 2c_{12}^F + 4c_{44}^F}{3}\right) \\
\frac{c_{44}^H}{3} &= \left(\frac{c_{11}^F - c_{12}^F + c_{44}^F}{3}\right).
\end{align*}
\]

Results listed in Table 6.1 show that, in agreement with the earlier prediction [15], the \(L1_1\) structure is the stable one for Pd\textsubscript{0.5}Ag\textsubscript{0.5} alloy. The hexagonal representation of the disordered Pd\textsubscript{0.5}Ag\textsubscript{0.5} alloy (\(H_d\)) reflects well the bulk and elastic properties calculated for the disordered cubic (\(F_d\)) system. The overall deviation is 0.09\% for the bulk parameters and 4.5\% for the elastic parameters. The differences can be attributed to the different \(k\)-point samplings and numerical instabilities which accompany the elastic constants calculations. Further on the ordering effect is investigated within the hexagonal phase to avoid the errors coming from the different representations.

The average ordering effect on the bulk and elastic parameters of the hexagonal Pd\textsubscript{0.5}Ag\textsubscript{0.5}, listed in the last three columns of Table 6.1, is 0.31 and 0.65 %, respectively. Section V


Figure 6.7. Euler’s rotation applied to the fcc phase. Green arrows indicate the cubic (x^C, y^C, z^C) coordinate axes, blue arrows show the hexagonal (x^H, y^H, z^H) axes.

Table 6.1. Theoretical (EMTO-PBEsol) results for bulk parameters ((c/a)$_g$, r$_{WS}$, B, E), elastic parameters ($R$, $c_s$, single crystal elastic constants) and linear compressibilities of Pd$_{0.5}$Ag$_{0.5}$ as a function of representation (fcc and hex) and ordering.

<table>
<thead>
<tr>
<th>(c/a)$_g$ (two layers)</th>
<th>$F_d$</th>
<th>$F_d'$</th>
<th>H$_d$</th>
<th>H$_{p0}$</th>
<th>H$_o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6330</td>
<td>1.6332</td>
<td>1.6333</td>
<td>1.6353</td>
<td></td>
<td></td>
</tr>
<tr>
<td>r$_{WS}$ (Bohr)</td>
<td>2.9344</td>
<td>2.9341</td>
<td>2.9335</td>
<td>2.9322</td>
<td></td>
</tr>
<tr>
<td>B (GPa)</td>
<td>155.11</td>
<td>154.85</td>
<td>155.59</td>
<td>156.93</td>
<td></td>
</tr>
<tr>
<td>E (mRy)</td>
<td>0.077</td>
<td>-0.201</td>
<td>-0.620</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R$</td>
<td>0.003</td>
<td>0.006</td>
<td>0.017</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$c_s$ (GPa)</td>
<td>563</td>
<td>547</td>
<td>547</td>
<td>537</td>
<td></td>
</tr>
<tr>
<td>$c_{11}$ (GPa)</td>
<td>182</td>
<td>256</td>
<td>245</td>
<td>247</td>
<td>249</td>
</tr>
<tr>
<td>$c_{12}$ (GPa)</td>
<td>137</td>
<td>116</td>
<td>124</td>
<td>124</td>
<td>121</td>
</tr>
<tr>
<td>$c_{13}$ (GPa)</td>
<td>92</td>
<td>94</td>
<td>95</td>
<td>98</td>
<td></td>
</tr>
<tr>
<td>$c_{33}$ (GPa)</td>
<td>280</td>
<td>277</td>
<td>279</td>
<td>280</td>
<td></td>
</tr>
<tr>
<td>$c_{44}$ (GPa)</td>
<td>94</td>
<td>46</td>
<td>47</td>
<td>47</td>
<td>45</td>
</tr>
<tr>
<td>$c_{66} = (c_{11} - c_{12})/2$ (GPa)</td>
<td>70</td>
<td>61</td>
<td>62</td>
<td>64</td>
<td></td>
</tr>
<tr>
<td>$K_a$ (1/GPa)</td>
<td>0.00216</td>
<td>0.00216</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_c$ (1/GPa)</td>
<td>0.00214</td>
<td>0.00205</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

of Paper VII demonstrate that the ordering has negligible effect on the trend obtained for the concentration dependence. Despite this, one can notice interesting features here: e.g. the difference between the in plane compressibility, represented here with the component along the a axis ($K_a$), and the linear compressibility along the c axis ($K_c$). $K_a$ and $K_c$ are equal for H$_d$ certifying the isotropy of this phase. H$_o$ is anisotropic: it is
more compressible along the $a$ axis than along the $c$ one. The ordering has a small effect on the in plane compressibility, but a large one along the $c$ direction. This effect is due to the differences between the nearest neighbor (NN) interactions of $H_d$ and $H_o$. For the disordered phase, there are Pd-Pd, Ag-Ag and Pd-Ag interactions along the 12 NN with equal probabilities. Since the NN interactions in $H_d$ involve all tree types of bonds, the compressibilities in different directions are expected to be equal. For the ordered case, on the other hand, there are only either Pd or Ag atoms within an atomic layer perpendicular to the $c$ axis. Therefore the average compressibility in the $x - y$ plane involves the 6 (3+3) Pd-Pd and Ag-Ag bonds, and with lesser extent also the 6 out-of plane Pd-Ag bonds. This situation is not so different from that found in the case of $H_d$, which explains why $K_a$ is not sensible to the ordering (layering) effect. However, along the $c$ axis the situation is very different: there are only Pd-Ag type of interactions along the $c$ axis for $H_o$. Therefore, the compressibility is much more affected by the ordering along the $c$ axis.
In this thesis, the magnetic properties of the pure and B, Si and As doped Fe$_2$P are investigated. The total effect on the change in the average magnetic exchange interactions is decomposed into chemical and structural effects, the latter including the $c/a$ and volume effects. The chemical effect turned out to be less significant compared with the structural effects. An important observation is that in Fe$_2$P, the FeII - FeII interactions are positive and large ($\sim 1.5$ mRy) indicating a strong ferromagnetic coupling within the FeII sublattice. That is, the FeII sublattice is ferromagnetic. However, none of the interactions between the FeI atoms are large, meaning that this sublattice has a less strong tendency to order. The structural effects, mainly the decreased $c/a$, strengthen the intra layer magnetic interactions for the doped systems relative to the pure Fe$_2$P.

The nature of magnetism of the two sublattices is studied for Fe$_2$P$_{1-x}$T$_x$ (T = B, Si) by expanding the magnetic energy in even powers of the magnetization. It turned out that the FeII sublattice is ferromagnetic with or without the magnetic interactions between the two sublattices. Instead, the FeI sublattice is paramagnetic, with a metastable finite moment state. The finite moment state is stabilized by the exchange field created by the FeII atoms. Silicon and B stabilize the metastable state of FeI atoms. To which extent the composition and the structural change are responsible for the stabilization of the metastable finite moment state of FeI is not known yet.

Based on above results it is stated that no reasonable Curie temperature can be calculated without taking into account the metamagnetic behavior of the FeI sublattice. It is proposed a constrained DLM approach, as a model which takes into account the metamagnetic behavior of FeI. Curie temperatures are calculated for FM and cDLM phases. Both give reasonable good concentration dependence for the B doped system, but the FM results considerably overestimate the $T_C$. The cDLM results are in good agreement with the experimental data especially for Fe$_2$P and Fe$_2$P$_{0.85}$B$_{0.15}$.

The crystallographic structure stability of pure Fe$_2$P is investigated. Theory predicts that at low temperature the Fe$_2$P does not adopt the $hex$ crystal structure as the stable structure. The $hex$ structure could be stabilized against the $bco$, if the energy contribution to the free energy coming from the zero-point spin fluctuation is taken into account. The reason of the $Pnma$ structure stability is unknown.

The crystallographic phase transition induced by Si in the Fe$_2$P$_{1-x}$Si$_x$ is described in the
6.2. EFFECT OF LONG-RANGE ORDER IN PD$_{0.5}$AG$_{0.5}$

paramagnetic phase, but the narrow two-phase field is not reproduced by first principles calculations. Entropy effects are assessed using simple models. The Si site preference in Fe$_2$(PSi) and the Mn site preference in MnFeP$_{1-x}$Si$_x$ is investigated in detail.

Thermophysical properties of Pd-Ag binary alloys are described by first-principles calculations. The calculated lattice parameters, excess entropy, enthalpy of formation, Gibbs energy for alloys, elastic constants and polycrystalline elastic moduli for Ag and Pd are in good agreement with the available experimental data. Strong deviations from the linear behavior are found for the lattice constant, elastic constants, polycrystalline elastic moduli and Debye temperature as a function of concentration. These deviations may be related to the Fermi surface topological transitions. Here four ETTs, obtained with the EMTO method, are discussed. Results are in reasonable agreement with the previous theoretical findings.

The effect of long range ordering on the bulk and elastic properties of Pd$_{0.5}$Ag$_{0.5}$ alloy is discussed. The L1$_1$ is the stable structure for the equiatomic composition. The long range ordering has minor effect on the elastic properties. Trends obtained for the composition dependence assuming a random fcc solid solution are not affected.

Within my future plans there is to find out what is the main reason behind the stabilization effect on the metastable state of FeI in doped Fe$_2$P. Is the stabilization related to the structural change? I would like to extend the above mentioned magnetic studies to the systems doped on the Fe sites. How the metamagnetism of FeI is affected by doping with magnetic or non-magnetic elements on the two Fe sites? What is the reason behind the instability of the $hex$ phase of Fe$_2$P? Is this a failure of DFT? Methods beyond DFT can resolve the contradiction between experiment and theory?
I would like to investigate the effect of long range ordering in other non-magnetic and also magnetic systems.
Acknowledgements

First of all, I am grateful to my supervisor Professor Levente Vitos for giving me the opportunity to join to the AMP group in KTH, for always showing a great interest to my work and for professional guidance. My appreciation also goes to Professor Kalevi Kokko, my co-supervisor. Thank you for the useful and interesting discussions. I would like to express my sincere gratitude to Professor Börje Johasson.

I would like to thank Professor Olle Eriksson for encouragement, scientific discussions and fruitful collaboration. Dr. Lars Berqvist, Dr. Marko P. J. Punkkinen thank you for the collaboration and encouraging discussions. Cooperations with Dr. Zsolt Gercsi, Prof. Qing-Miao Hu, discussions and joint work with members of the magneto-caloric group in Uppsala are greatly acknowledged.

Dr. L. Chioncel thank you for your support. Dr. K. Kádas, Prof. M. Richter, Prof. A. V. Ruban, Dr. P. A. Korzhavyi: many thanks for helpful discussions. I would like to thank to Dr. S. Schönecker and A. Östlin for your help.

Colleagues, Noura, Chunmei, Hualei, Xiaoqing, Song, Wei, Guiseng, Fuyang, Moshiour, Vitaly, Volya, Gustavo: thank you for discussions, joking, happy lunch time and summer and Christmas parties, and for broadening my knowledge about different nations and beliefs.

I would like to thank all the members of the AMP group and MSE for creating an inspiring environment for my study.

The Swedish Energy Agancy, Swedish Research Council, European Research Council (Grant No. 228074 ALPAM), Swedish Foundation for International Cooperation in Research and Higher Education are acknowledged for financial support. Swedish National Infrastructure Computing (UPPMAX and Matter) are acknowledged for computer resources.

Special thanks go to the opponent and comity members.

Last but not least, I would like to express my deepest thanks to my husband, Lorand, for his support and love and to my parents and sister for support and encouragement.
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