Thermal Expansion and Local Environment Effects in Ferromagnetic Iron-Based Alloys -A Theoretical Study

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Linköping 2009

L'heure de la fin des découvertes ne sonne jamais.
Colette

Abstract

The Nobel Prize for Physics 1920 was awarded to C.-E. Guillaume for his discovery of properties of nickel steels. He had previously observed that certain iron-nickel alloys exhibit the Invar effect i.e. an extremely low thermal expansion coefficient over a wide range of temperature. The decades since then have seen the observation of similar phenomena in other iron-based materials such as iron-platinum and iron-palladium. Moreover, there has been a great deal of theoretical work on the mechanism behind the Invar anomaly in the above-mentioned systems. However, despite many years of intensive research, a widely accepted microscopic theory of the effects is still lacking.

The present thesis aims at providing an insight into the physical nature of the thermal expansion of ferromagnetic random face-centered cubic iron-nickel, iron-platinum and iron-palladium bulk solids.

First, the thermal expansion coefficient is modeled as a function of temperature. The theory relies on the disordered local moment (DLM) formalism. However, contrary to all the previous models, the mapping between equilibrium states and partially disordered local moment (PDLM) states involves the probability that an iron-iron nearest-neighbour pair shows anti-parallel local magnetic moments, and the average lattice constant of the system at a finite temperature is calculated by minimization of an energy. The approach is applied to iron-nickel alloys. The model qualitatively reproduces several experimentally observed properties of disordered fcc iron-nickel solids. This includes Guillaume's famous plot of the thermal expansion coefficient at room temperature as a function of concentration.

Second, for the purpose of studying the origin of the anomalous expansion, the anomalous and normal contributions to the thermal expansion coefficient are defined, then evaluated for iron-nickel alloys. The results support the idea that the peculiar behaviour of the expansivity, α, originates solely from the anomalous contribution, α_a.

Subsequently, the anomalous contribution is modeled for iron-nickel systems. In formulating the model, the following observation is taken into account; the average lattice spacing of an $Fe_{100-x}Ni_x$ alloy at temperature T in a partially disordered local moment state is strongly negatively correlated with the probability that a nearest-neighbour pair has each of its two sites occupied by an iron atom and exhibits anti-ferromagnetically aligned magnetic moments (X_{FFAP}). The quantity $\alpha_a(x, T)$ is estimated for several couples of values of the parameters x and T. Model results are found to agree qualitatively and quantitatively well with data

obtained from the definition of α_a. Thus, the model can successfully explain the basic process leading to the anomalous thermal expansion. It is consistent with the theory that the coefficient α_a is controlled by the temperature derivative of X_{FFAP}. Finally, the anomalous contribution to the thermal expansion coefficient of $Fe_{72}Pt_{28}$ and $Fe_{66}Pd_{34}$ solids is modeled as that of $Fe_{65}Ni_{35}$. A good agreement between the model results and experimental data for the expansivity as a function of temperature is noted. In conclusion, the Invar effects in disordered fcc iron-nickel, iron-platinum and iron-palladium alloys may have a common origin.

Acknowledgements

Contents

Chapter 1

Background

1.1 Experiments

Figure 1.1. The linear thermal expansion coefficient of a non-magnetic fcc Cu element as a function of temperature, according to calculations [1] and experiments [2]. Black lines: direct interpolation between experimental data points.

The linear thermal expansion coefficient of a face-centered cubic (fcc) solid in metastable or stable equilibrium at temperature T and pressure P is given by $\alpha(T, P) = 1/a(T, P)(\partial a/\partial T)_P(T, P)$ where $a(T, P)$ denotes the average lattice constant. For numerous fcc metals (Cu, $Fe_{20}Ni_{80}$,...) under ambient pressure, the coefficient α increases with rising temperature and is of the order of 10^{-5} K^{-1} for room temperature. A piece of metal exhibiting a constant thermal expansion

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Figure 1.2. The linear thermal expansion coefficient of a disordered fcc $Fe_{100-x}Ni_x$ alloy at room temperature as a function of concentration in percent, according to experiments [4].

coefficient of 10^{-5} K^{-1} which is initially 10 m long increases its length by 1 mm if the temperature is raised by 10 K. Fig. 1.1 depicts the linear thermal expansion coefficient of an fcc Cu solid as a function of temperature, according to calculations [1] and experiments [2].

Around 1897, Guillaume measured the thermal expansion coefficient of an fcc $Fe_{100-x}Ni_x$ alloy at ambient conditions for various Ni concentrations [3]. He discovered that certain alloys display an extremely low thermal expansivity. For example, as seen in Fig. 1.2, the expansivity of an $Fe_{65}Ni_{35}$ solid is much smaller than 10^{-5} K^{-1} [4]. Later on, further investigations were carried out [5, 6, 7]. Fig. 1.3 displays some results obtained by Matsui *et al.*. It can be observed that the Invar effect takes place below the Curie temperature. This indicates that the anomaly is of magnetic origin.

Following the publication of Guillaume's original paper, a vast amount of experimental data concerning ferromagnetic disordered fcc Fe-Ni alloys was collected [8, 9]. It revealed the existence of other anomalous physical properties such as a downward deviation of the average lattice spacing from the value predicted by Vegard's law, a departure of the saturation magnetic moment from the Slater-Pauling curve, an unusual temperature dependence of the magnetization and the pressure-induced Invar effect (see Fig. 1.4) [10].

The Invar effect was found in other systems such as Fe-Pt and Fe-Pd [8, 9]. Fig. 1.3 displays the linear thermal expansion coefficient of ferromagnetic disordered fcc $Fe_{65}Ni_{35}$, $Fe_{72}Pt_{28}$ and $Fe_{68}Pd_{32}$ systems as a function of temperature, according to experiments [7, 11, 12]. Clearly, the expansivities are extremely low in a wide

Figure 1.3. The linear thermal expansion coefficient of a ferromagnetic disordered fcc $Fe_{65}Ni_{35}$, $Fe_{72}Pt_{28}$ and $Fe_{68}Pd_{32}$ alloy as a function of temperature, according to experiments [7, 11, 12]. The value of the Curie temperature of each system is denoted as T_c.

interval of temperature.

1.2   Theoretical Studies

There has been a great deal of theoretical work on the origin of the Invar effect in $Fe_{65}Ni_{35}$ alloys. Obviously, a negative contribution to the thermal expansion coefficient compensates at some temperature the positive contribution coming from the anharmonicity of the ionic interaction energy [7]. Moreover, there appears to be an almost universal consensus that the negative contribution is related to the magnetic properties of the alloys in question. On the issue of which magnetic models are appropriate, however, opinions differ. One strand in the literature favours the localized electron picture (Heisenberg model) in which each atom has its own permanent and temperature independent magnetic moment. A second approach is based on the itinerant electron picture (Stoner model). A few models are presented below.

In 1963, R. J. Weiss proposed the so-called 2γ-state model [13], where the iron atoms in the alloy at finite temperature can occupy two states with different magnetic moments and different volumes (one ferromagnetic high-volume state and one anti-ferromagnetic low-volume state). He also assumed that the energy difference between the two states to be a function of the Ni concentration. He chose it so that the atomic ground state in $Fe_{65}Ni_{35}$ is ferromagnetic with high-volume,

Figure 1.4. The relative volume of an $Fe_{55}Ni_{45}$ alloy for several temperatures and pressures, according to experiments [10]. Note that the system exhibits a very small thermal expansion coefficient between 291 and 500 K and for P =7.7 GPa $\left[\; \alpha(T,P) = 0.2 \; 10^{-5} \; K^{-1} \right]$. However, it shows no anomalies for P =0.4 GPa.

and the increase of population of the low-volume state with rising temperature leads to the Invar effect. Even though the model provides an explanation for the anomalous expansion of $Fe_{65}Ni_{35}$, the concept of "anti-ferromagnetic atomic state" is ill-defined. Moreover, this approach appears to be incompatible with the results of Mössbauer and neutron experiments [14, 15].

The latent anti-ferromagnetism model assumes that the exchange interaction energy of the Fe-Fe nearest-neighbour pairs is anti-ferromagnetic [16, 17]. Within this theory, the main magnetic properties (magnetization, Curie temperature, . . .) can be reproduced accurately using a nearest-neighbour Ising model [18]. The corresponding ground-state spin structure involves anti-ferromagnetically aligned Fe moments [19]. It should be noted that experiments support the idea that the ground state is collinear ferrimagnetic with a few percent of local magnetic moments that are oriented anti-parallel to the magnetization [20]. There were a few attempts to evaluate the magnetic part of the thermal expansion coefficient as a function of temperature within the latent anti-ferromagnetism model [21]. In spite of a certain success, they do not give complete satisfaction because experimental results for the pressure derivative of the Curie temperature were used as input data.

Within the class of local moments models, there has been some recent emphasis that the ground state magnetic structure of $Fe_{65}Ni_{35}$ is non-collinear and this property gives rise to the anomalous thermal expansion of the system [22]. However, the thermal expansion coefficient as a function of temperature has not been

calculated. Furthermore, experiments undertaken to detect such non-collinearity do not seem to find it [23].

It seems that an important step towards a quantitative prediction of the thermal expansion has been made a few years ago; the Debye-Grüneisen model [1] has been employed to estimate the non-magnetic lattice contribution to the thermal expansion coefficient as a function of temperature, and the partially disordered local moment formalism has been chosen for the evaluation of the anomalous contribution [24]. The PDLM model can be used to calculate by means of *ab initio* methods total energies of $Fe_{65}Ni_{35}$ in collinear magnetic states, given the fraction of Fe atoms whose spins are "up", x_{FU}, and the fraction of Ni atoms whose spins are "up", x_{NU}. A PDLM state for $x_{FU} = x_{NU} = 1$ is fully magnetized, whereas a PDLM state for $x_{FU} = x_{NU} = 0.5$ is completely disordered. Though the results of Crisan *et al.* [24] are in good agreement with experimental data, the physical origin of the Invar phenomenon remains elusive.

Later on, Khmelevskyi *et al.* applied the PDLM formalism to study the thermal expansion in Fe-Pt alloys [25]. The analysis of their results linked the Invar effect to a gradual weakening of the Fe local moments caused by the changes in the electronic structure due to temperature induced magnetic disorder.

1.3 Conclusion

In conclusion, certain ferromagnetic disordered fcc Fe-Ni, Fe-Pt and Fe-Pd alloys exhibit an anomalous thermal expansion coefficient. Apparently, recent progress in the development of computational methods for thermal expansion coefficients has been achieved. However, there is still no general consensus on the precise mechanism behind the Invar effect in $Fe_{65}Ni_{35}$. Furthermore, it is unclear whether the anomalies in $Fe_{65}Ni_{35}$, $Fe_{72}Pt_{28}$ and $Fe_{68}Pd_{32}$ have a common origin.

Chapter 2

Calculation of Thermal Expansion Coefficients

Chapter 2 presents a new model based on the DLM formalism for the thermal expansion coefficient of a ferromagnetic random face-centered cubic $Fe_{100-x}Ni_x$ alloy in metastable or stable equilibrium at temperature T as a function of temperature and concentration. The theory is directly applicable to ferromagnetic random fcc $Fe_{100-x}Pt_x$ and $Fe_{100-x}Pd_x$ systems.

2.1 Modelling the Thermal Expansion Coefficient

In the present work, the linear thermal expansion coefficient of a ferromagnetic random fcc $Fe_{100-x}Ni_x$ alloy in metastable or stable equilibrium at temperature T is modeled as:

$$\alpha(x,T) = \frac{1}{a(x,T)} \left(\frac{\partial a}{\partial T} \right)_x (x,T), \qquad (2.1)$$

where $a(x,T)$ denotes $a\big(x,T; x_{\mathrm{FU}}(x,T), x_{\mathrm{NU}}(x,T)\big)$, the equilibrium configurationally averaged lattice constant of the system at T in the partially disordered local moment (PDLM) state characterized by the pair $\big(x_{FU}(x,T), x_{NU}(x,T)\big)$. $x_{FU}(x,T)$ represents the probability that an iron spin is up and $x_{NU}(x,T)$ gives the probability that a nickel spin is up. The pair $\big(x_{FU}(x,T), x_{NU}(x,T)\big)$ is chosen so that the system in the PDLM state exhibits similar magnetic characteristics to those of the alloy in equilibrium at T; the magnetic properties include the magnetization, $M(x,T)$, the probability that an iron-iron nearest-neighbour pair shows anti-parallel local magnetic moments, $x_{\mathrm{FFAP}}(x,T)$, the probability that an iron-nickel first-neighbour pair exhibits anti-parallel moments, $x_{\mathrm{FNAP}}(x,T)$, and the probability that a nickel-nickel nearest-neighbour pair displays anti-ferromagnetically aligned moments, $x_{\mathrm{NNAP}}(x,T)$. In practice, $\alpha(x,T)$ is approximated as:

$$\alpha(x,T) \approx 1/a(x,T) \quad \Big[a\big(x, T + \delta T; x_{\text{FU}}(x, T + \delta T), x_{\text{NU}}(x, T + \delta T)\big) - \cdots$$
$$\cdots - a\big(x, T - \delta T; x_{\text{FU}}(x, T - \delta T), x_{\text{NU}}(x, T - \delta T)\big)\Big]/2\delta T.$$
$$(2.2)$$

The general procedure for the determination of the average lattice spacing $a(x,T)$ is briefly described below. (See Sections 2.3, 2.4, 2.5 and 2.6 for the details of the calculations.)

1. Certain magnetic properties of the system in equilibrium at temperature T are computed: $M(x,T)$, $x_{\text{FFAP}}(x,T)$, $x_{\text{FNAP}}(x,T)$ and $x_{\text{NNAP}}(x,T)$.

2. The characteristics $x_{\text{FU}}(x,T)$ and $x_{\text{NU}}(x,T)$ of the PDLM state that reproduces the values of $M(x,T)$, $x_{\text{FFAP}}(x,T)$, $x_{\text{FNAP}}(x,T)$ and $x_{\text{NNAP}}(x,T)$ are derived.

3. The configurationally averaged free energy of the system at temperature T in the PDLM state for the pair $\big(x_{FU}(x,T), x_{NU}(x,T)\big)$ is estimated as a function of the lattice spacing.

4. The average lattice constant $a(x,T)$ is obtained by minimization of the average free energy with respect to the lattice parameter.

It is worth emphasizing here that the model differs from all the previous models based on the DLM formalism [24, 25] in that the present mapping between equilibrium states and PDLM states involves the probability that an iron-iron nearest-neighbour pair shows anti-parallel moments, and the average lattice constant $a(x,T)$ is calculated by minimization of an energy.

2.2   Modelling the Anomalous Contribution

For the purpose of investigating the origin of the anomalous thermal expansion, the expansion coefficient is written as the sum of two contributions:

$$\alpha(x,T) = \alpha_n(x,T) + \alpha_a(x,T), \qquad (2.3)$$

where

$$\alpha_n(x,T) = \lim_{\delta T \to 0} 1/a(x,T) \Big[a\big(x, T + \delta T; x_{\text{FU}}(x, T + \delta T), x_{\text{NU}}(x, T + \delta T)\big) - \cdots$$
$$\cdots - a\big(x, T; x_{\text{FU}}(x, T + \delta T), x_{\text{NU}}(x, T + \delta T)\big)\Big]/\delta T,$$
$$(2.4)$$

and

$$\alpha_a(x,T) = \lim_{\delta T \to 0} 1/a(x,T) \left[a\big(x,T; x_{\mathrm{FU}}(x,T+\delta T), x_{\mathrm{NU}}(x,T+\delta T)\big) - \cdots \right.$$
$$\left. \cdots - a\big(x,T; x_{\mathrm{FU}}(x,T), x_{\mathrm{NU}}(x,T)\big) \right]/\delta T. \quad (2.5)$$

$\alpha_n(x,T)$ and $\alpha_a(x,T)$ are referred to as the normal contribution and the anomalous contribution. By "normal", it is meant a thermal expansion coefficient which depends on temperature similarly to that of a non-magnetic fcc Cu (see Fig. 1.1). According to Eq. 2.4, $\alpha_n(x,T)$ is expressed using the difference of two lattice constants evaluated for the same magnetic structure. However, Eq. 2.5 shows that $\alpha_a(x,T)$ is related to the difference of two lattice spacings estimated for the same temperature.

It should be mentioned that Eqs. 2.4 and 2.5 have been suggested for the first time by the author.

2.3   Calculating Magnetic Properties

To carry out point 1 of the procedure, a mean-field Ising model of the Müller-Hesse type is employed [26]. According to the adopted model, the spin at the iron sites is allowed to take only two values, $S_{\mathrm{F}}(x)$ and $-S_{\mathrm{F}}(x)$. A similar requirement is formulated for the spin at the nickel sites using the analogous quantity $S_{\mathrm{N}}(x)$. The average spin at an iron site with n like nearest-neighbours $\big(< S_i >_{\mathrm{F},n}\big)$ and the average spin at a nickel site with n unlike first-neighbours $\big(< S_i >_{\mathrm{N},n}\big)$ for all possible values of n between 0 and 12 constitute the central quantities. They verify the set of equations:

$$< S_i >_{\mathrm{F},n}(x,T) = S_{\mathrm{F}}(x) \tanh S_{\mathrm{F}}(x)\big(n J_{\mathrm{FF}}(x)< S_i >_{\mathrm{F}}(x,T) + \cdots$$
$$\cdots + (12-n) J_{\mathrm{FN}}(x)< S_i >_{\mathrm{N}}(x,T)\big)/k_{\mathrm{B}}T, \quad (2.6)$$

$$< S_i >_{\mathrm{N},n}(x,T) = S_{\mathrm{N}}(x) \tanh S_{\mathrm{N}}(x)\big(n J_{\mathrm{FN}}(x)< S_i >_{\mathrm{F}}(x,T) + \cdots$$
$$\cdots + (12-n) J_{\mathrm{NN}}(x)< S_i >_{\mathrm{N}}(x,T)\big)/k_{\mathrm{B}}T, \quad (2.7)$$

where the average spin at an iron site and the average spin at a nickel site are also given by:

$$< S_i >_{\mathrm{F}}(x,T) = \sum_{n=0}^{12} p(x,n) < S_i >_{\mathrm{F},n}(x,T), \quad (2.8)$$

$$< S_i >_{\mathrm{N}}(x,T) = \sum_{n=0}^{12} p(x,n) < S_i >_{\mathrm{N},n}(x,T), \quad (2.9)$$

and the probability that an iron site is surrounded by n like first-neighbours in the random alloy is related to the concentration:

$$p(x,n) = \sum_{n=0}^{12} \mathrm{C}_{12}^n \, (1-x)^n \, x^{12-n}. \tag{2.10}$$

Once the quantities $<S_i>_{\mathrm{F},n}(x,T)$ and $<S_i>_{\mathrm{N},n}(x,T)$ are known for all possible values of n between 0 and 12, it is straightforward to determine the magnetic properties of interest such as the average spin:

$$<S_i>(x,T) = (1-x)<S_i>_{\mathrm{F}}(x,T) + <S_i>_{\mathrm{N}}(x,T). \tag{2.11}$$

The probability that an iron-iron nearest-neighbour pair shows anti-parallel local magnetic moments is of great importance in this work. It is given by:

$$x_{\mathrm{FFAP}}(x,T) = 2 \, \frac{\sum_{n=1}^{12} \, p(x,n) \, x_{FU,n}(x,T)}{\sum_{n=1}^{12} \, p(x,n)} \, \frac{\sum_{n=1}^{12} \, p(x,n) \, \left(1 - x_{FU,n}(x,T)\right)}{\sum_{n=1}^{12} \, p(x,n)}, \tag{2.12}$$

where the probability that an iron site exhibits n like nearest-neighbours and a spin up verifies:

$$x_{FU,n}(x,T) = \frac{<S_i>_{\mathrm{F},n}(x,T) \, + \, S_{\mathrm{F}}(x)}{2 \, S_{\mathrm{F}}(x)}. \tag{2.13}$$

When combined with Eq. 2.13, Eq. 2.12 yields that if the magnetic phase of the system at temperature T is ferromagnetic then $x_{\mathrm{FFAP}}(x,T) = 0$, whereas if it is completely disordered then $x_{\mathrm{FFAP}}(x,T) = 1/2$.

Obviously, the input parameters of the Ising model for $Fe_{100-x}Ni_x$ need to be specified. The magnitude of the spin at an iron site $\left(S_{\mathrm{F}}(x)\right)$ and the magnitude of the spin at a nickel site $\left(S_{\mathrm{N}}(x)\right)$ are derived from first-principles calculations for the ferromagnetic system. For example in the case of $Fe_{65}Ni_{35}$, computations give 1.31 μ_{B} for $S_{\mathrm{F}}(x)$ and 0.31 μ_{B} for $S_{\mathrm{N}}(x)$. The exchange constants $J_{\mathrm{FF}}(x)$ (between a nearest-neighbour iron-iron pair) and $J_{\mathrm{FN}}(x)$ (between a nearest-neighbour iron-nickel pair) are tuned in such a way that the predicted saturation magnetization and the Curie temperature agree well with experimentally measured properties [9]. Moreover, the exchange constant $J_{\mathrm{NN}}(x)$ (between a nearest-neighbour nickel-nickel pair) is set to the value of J_{NN} obtained at $x=1$, 40.55 meV. These exchange constants are the only experimentally determined parameters in the model.

Table 2.1 displays the values of J_{FF}, J_{FN} and J_{NN} for x=30, 35, 45, 55, 80 and compares some calculated magnetic quantities to experimental observations [9]. Results of the temperature dependence of the fraction of iron-iron nearest-neighbour pairs that are anti-parallel in $Fe_{100-x}Ni_x$ are shown in Fig. 2.1 for several concentrations. Some interesting consequences of the model are pointed out. Contrary to that of nickel-rich alloys ($Fe_{45}Ni_{55}$, $Fe_{20}Ni_{80}$), the magnetic structure of iron-rich materials ($Fe_{70}Ni_{30}$, $Fe_{65}Ni_{35}$, $Fe_{55}Ni_{45}$) at very low temperature shows a significant fraction of local magnetic moments which are anti-ferromagnetically aligned with the magnetization. Another effect reported here is that for a fixed concentration, x_{FFAP} increases with rising temperature below $T_{\mathrm{c}}(x)$ but fully saturates

x	30	35	45	55	80
$J_{\mathrm{FF}}(x)$ (meV)	-1.77	-1	-0.8	-0.8	-0.5
$J_{\mathrm{FN}}(x)$ (meV)	14	17	21	23	21.5
$J_{\mathrm{NN}}(x)$ (meV)	40.55	40.55	40.55	40.55	40.55
$\|(M(x) - M_{\mathrm{exp}}(x))/M_{\mathrm{exp}}(x)\|$	1 %	8 %	3.5 %	2 %	1.5 %
$\|(T_{\mathrm{c}}(x) - T_{\mathrm{c,exp}}(x))/T_{\mathrm{c,exp}}(x)\|$	4 %	2 %	1 %	1 %	0.2 %

Table 2.1. The chosen exchange constants along with the absolute values of the relative deviations of predicted magnetic quantities from experimental observations for x=30, 35, 45, 55, 80 [9].

Figure 2.1. The probability that an iron-iron nearest-neighbour pair shows anti-parallel local magnetic moments in a random fcc $\mathrm{Fe_{100-x}Ni_x}$ as a function of temperature, for several concentrations in percent, according to a mean-field Ising model.

above $T_{\mathrm{c}}(x)$. The relevance of the latter comment will be established in Section 3.3, while discussing the origin of the Invar effect in Fe-Ni alloys.

2.4 Mapping between Equilibrium States and PDLM States

The second step of the approach presented in Section 2.1 deals with the evaluation of the probability that an iron spin is up, $x_{\mathrm{FU}}(x,T)$, and the probability that a nickel spin is up, $x_{\mathrm{NU}}(x,T)$, for the partially disordered local moment state exhibiting the same magnetic properties $< S_i > (x,T)$, $x_{\mathrm{FFAP}}(x,T)$, $x_{\mathrm{FNAP}}(x,T)$ and $x_{\mathrm{NNAP}}(x,T)$ as the random alloy. That is, $x_{\mathrm{FU}}(x,T)$ and $x_{\mathrm{NU}}(x,T)$ are solu-

tions to the set of equations:

$$x_{\text{FFAP}}(x,T) = 2x_{\text{FU}}(x,T)\big[1 - x_{\text{FU}}(x,T)\big], \tag{2.14}$$

$$x_{\text{FNAP}}(x,T) = x_{\text{FU}}(x,T) - 2x_{\text{FU}}(x,T)x_{\text{NU}}(x,T) + x_{\text{NU}}(x,T), \tag{2.15}$$

$$x_{\text{NNAP}}(x,T) = 2x_{\text{NU}}(x,T)\big[1 - x_{\text{NU}}(x,T)\big], \tag{2.16}$$

$$< S_i > (x,T) = (1-x)S_{\text{F}}(x)\big[2x_{\text{FU}}(x,T) - 1\big] + xS_{\text{N}}(x)\big[2x_{\text{NU}}(x,T) - 1\big]. \tag{2.17}$$

2.5   Determining Average Total Energies

The configurationally averaged total energy of a random fcc $Fe_{100-x}Ni_x$ in the PDLM state for the pair $\big(x_{\text{FU}}, x_{\text{NU}}\big) = \big(x_{\text{FU}}(x,T), x_{\text{NU}}(x,T)\big)$ is estimated as a function of the average lattice constant. Then, a Morse function [1] is fitted to the energy curve using a least-squares procedure. The parameters of the fit give the equilibrium average lattice constant for the values of x_{FU} and x_{NU} in question, $a(x; x_{\text{FU}}, x_{\text{NU}})$. They also give the bulk modulus, $B(x; x_{\text{FU}}, x_{\text{NU}})$, and the low-temperature Grüneisen constant, $\gamma_{LT}(x; x_{\text{FU}}, x_{\text{NU}})$. B and γ_{LT} can be expressed in terms of volume derivatives of the total energy:

$$B = V\frac{\partial^2 E}{\partial V^2}, \tag{2.18}$$

and

$$\gamma_{LT} = -1 - \frac{V}{2}\frac{\partial^3 E/\partial V^3}{\partial^2 E/\partial V^2}, \tag{2.19}$$

where the volume per atom, V, is related to the lattice constant by:

$$V = \frac{a^3}{4}. \tag{2.20}$$

The first-principles total energy computations are performed within the framework of the exact muffin-tin orbitals (EMTO) theory using the full charge density (FCD) technique [27]. The problem of substitutional chemical disorder is treated within the coherent potential approximation (CPA) [28]. The integration over the irreducible part of the Brillouin zone is done over approximately 500 **k**-points distributed according to the Monkhorst-Pack scheme [29]. This is sufficient to ensure that the calculated lattice constants, bulk moduli and Grüneisen constants are converged with respect to the number of **k**-points within 5 mÅ, 100 kbar, and 0.1 respectively.

Fig. 2.2 displays the average total energy per atom of $Fe_{65}Ni_{35}$ as a function of the average lattice constant, for $(x_{\text{FU}}, x_{\text{NU}})$=(0.5, 0.5), (0.9, 1). Figs. 2.3, 2.4 and 2.5 depict some predicted equilibrium average lattice spacings, bulk moduli

Figure 2.2. The average total energy per atom (relative to a reference energy) of a random fcc $Fe_{65}Ni_{35}$ in a PDLM state as a function of the average lattice constant, for $(x_{FU}, x_{NU})=(0.5, 0.5)$, $(0.9, 1)$, according to *ab initio* calculations performed by means of the EMTO method.

and Grüneisen constants plotted against the fraction of iron-iron nearest-neighbour pairs that are anti-parallel, x_{FFAP}. Surprisingly, the lattice constant for a fixed concentration is strongly negatively correlated with x_{FFAP}. This tendency of reduction of the lattice constant as x_{FFAP} is increased plays a central role in the existence of the Invar effect (see Section 3.3 for further details). Finally, note that all the bulk moduli are found to be between 1.5 and 1.9 Mbar, and all the Grüneisen constants lie between 1.5 and 1.8.

2.6 Calculating Average Lattice Constants

It is well known that thermal expansion of crystals requires the presence of anharmonic terms in the ionic interaction energy; a purely harmonic energy will not give rise to a temperature-dependent equilibrium volume. In the case of "weak" anharmonicity, its effect can be estimated via perturbation theory. It turns out that the lowest order terms determining the thermal expansion coefficient are given correctly by the quasi-harmonic approximation in which the vibrational free energy is calculated according to the harmonic approximation but the normal-mode frequencies are allowed to depend on the volume of the crystal [30]. Moruzzi *et al.* employed a quasi-harmonic Debye-Grüneisen model for the estimation of linear thermal expansion coefficients of non-magnetic elemental metals [1]. In this

Figure 2.3. The equilibrium average lattice constant of a random fcc $Fe_{100-x}Ni_x$ in a PDLM state versus the probability that an iron-iron nearest-neighbour pair shows anti-parallel local magnetic moments, x_{FFAP}. Diamonds show results of *ab initio* calculations carried out by means of the EMTO method for different pairs (x_{FU}, x_{NU}).

approach, the free energy $F(T, V)$ is given by:

$$F(T,V) = E(V) + \frac{9}{8}k_B\Theta_D(V) - k_BTD\left(\frac{\Theta_D(V)}{T}\right) + 3k_BT\ln\left(1 - e^{-\Theta_D(V)/T}\right),$$

(2.21)

where $E(V)$ denotes the total energy obtained from electronic structure calculations, k_B represents the Boltzmann constant. D is the Debye function which is defined as:

$$D(y) = \frac{3}{y^2}\int_0^y dx\frac{x^3}{e^x - 1}.$$

(2.22)

The Debye temperature $\Theta_D(V)$ is approximated as:

$$\Theta_D(V) = 41.63\left(\frac{(3V_0/4\pi)^{1/3}B_0}{M}\right)^{1/2}\left(\frac{V_0}{V}\right)^{\gamma_0},$$

(2.23)

where V_0, B_0 and γ_0 are the volume in a.u.^{3}, bulk modulus in kbar and Grüneisen constant derived from the total energy E as a function of V. Besides, M is the atomic weight.

Returning to the main point of this section, the average lattice constant $a(x, T; x_{FU}, x_{NU})$ of $Fe_{100-x}Ni_x$ is approximated as the lattice constant corresponding to the volume which minimizes a free energy. The free energy in question is given by Eqs. 2.21 and 2.23, and configurational averaging enters only

Figure 2.4. The equilibrium bulk modulus of a random fcc $Fe_{100-x}Ni_x$ in a PDLM state versus the probability that an iron-iron nearest-neighbour pair displays anti-parallel local magnetic moments, according to EMTO computations.

through the average total energy and the three parameters calculated in Section 2.5. Though uncontrolled, approximations of the same type have been made in previous studies [31, 32, 33]. Some of them lay predicted thermal expansion coefficients in qualitative agreement with experimental data.

Fig. 2.6 depicts the calculated mean lattice parameter of $Fe_{65}Ni_{35}$ for various pairs (x_{FU}, x_{NU}). It also displays the predicted lattice constant of the system at temperature T, $a\big(x, T; x_{FU}(x, T), x_{NU}(x, T)\big)$, for several temperatures below 800 K. A useful way to think of the general procedure presented in Section 2.1 is illustrated by the figure. Imagine that the magnetic configuration were fixed. Then the material would show only "normal" thermal expansion. Let us call the corresponding thermal expansion curve $a(x, T; x_{FU}, x_{NU})$; the curve for x=35, $x_{FU} = 0.90$, and $x_{NU} = 1$ is the uppermost dashed curve in Fig. 2.6. In reality, however, raising the temperature causes the material to demagnetize, and the values of x_{FFAP}, x_{FNAP} and x_{NNAP} change accordingly. One may say that the system "hops" from the curve $a(x, T; x_{FU}, x_{NU})$ to the curve $a(x, T; x'_{FU}, x'_{NU})$, resulting in a lattice spacing given by the curve $a\big(x, T; x_{FU}(x, T), x_{NU}(x, T)\big)$. This is shown as the solid line in Fig. 2.6. In the case depicted, each hop is to a curve lower than the last, cancelling the upward trend of each individual curve: this is the essence of the Invar effect.

Figure 2.5. The equilibrium Grüneisen constant of a random fcc $Fe_{100-x}Ni_x$ in a PDLM state versus the probability that an iron-iron nearest-neighbour pair exhibits anti-parallel local magnetic moments, according to EMTO computations.

2.7   Evaluating Thermal Expansion Coefficients

The thermal expansivity $\alpha(x,T)$ can be obtained from Eq. 2.2. Figs. 2.7 and 2.8 show that the model outlined in Section 2.1 qualitatively reproduces several well known properties of disordered fcc Fe-Ni alloys. This includes Guillaume's famous plot of the thermal expansion coefficient at room temperature as a function of concentration [4] and Matsui's plot of the thermal expansion coefficient of $Fe_{65}Ni_{35}$ as a function of temperature [7]. As far as the author knows, the present model is the only theory relying on a first-principles approach that reproduces qualitatively the thermal expansion coefficient of the ferromagnetic Fe-Ni alloys as a function of temperature and concentration.

To facilitate the identification of the origin of the iron-nickel alloys anomalous expansion, physicists traditionally divide the coefficient $\alpha(x,T)$ into two contributions (see for example Ref. [7]), a "normal" term coming exclusively from the anharmonicity of the ionic interaction energy and an "anomalous" term. In this study, the expansion coefficient is also written as the sum of two contributions $\alpha_n(x,T)$ and $\alpha_a(x,T)$. Both terms have been evaluated at room temperature for different Ni atomic concentrations from Eqs. 2.4 and 2.5. As observed in Fig. 2.9, α_a can be hold responsible for the anomalous behaviour of α as a function of x. In addition, Fig. 2.10 clearly shows that the peculiar T-dependence of α for $x = 35$ originates from α_a. Thus, a thorough study of the anomalous expansion coefficient α_a seems relevant.

Figure 2.6. Calculated average lattice constants of a random fcc $Fe_{65}Ni_{35}$ at several temperatures. The circles indicate the lattice constants calculated assuming the magnetic configuration to be fixed. From top to bottom, (x_{FU}, x_{NU})=(0.90, 1), (0.89, 1), (0.84, 1), (0.79, 0.97), (0.71, 0.89), (0.57, 0.64), (0.5, 0.5). The crosses show the lattice constants according to the model. The dotted line and the solid line are obtained by linear interpolation between circles and crosses respectively.

2.8　Conclusion

The thermal expansion coefficient of a ferromagnetic random face-centered cubic iron-nickel alloy has been modeled. The theory relies on the DLM formalism. The procedure for the determination of the average lattice spacing $a(x,T)$ has been described. It consists of four steps: (i) Certain magnetic properties of the system in equilibrium at temperature T are computed. (ii) The characteristics $x_{FU}(x,T)$ and $x_{NU}(x,T)$ of the PDLM state that reproduces the values of $M(x,T)$, $x_{FFAP}(x,T)$, $x_{FNAP}(x,T)$ and $x_{NNAP}(x,T)$ are derived. (iii) The configurationally averaged free energy of the system at temperature T in the PDLM state for the pair $\big(x_{FU}(x,T), x_{NU}(x,T)\big)$ is estimated as a function of the lattice spacing. (iv) The average lattice constant $a(x,T)$ is obtained by minimization of the average free energy with respect to the lattice parameter. It is worth emphasizing here that the model differs from all the previous models based on the DLM formalism. Several interesting results have emerged from the calculations. For instance, the probability that an iron-iron nearest-neighbour pair exhibits anti-parallel moments increases with rising temperature below the Curie temperature, but is constant above the critical temperature. Furthermore, the use of first-principles techniques has revealed that the predicted equilibrium average lattice constant for a PDLM state is strongly negatively correlated with x_{FFAP}. It has also been shown that the model results are in good agreement with experimental data for several well

known properties of the ferromagnetic disordered face-centered cubic iron-nickel alloys. As far as the author knows, the present model is the only theory relying on a first-principles approach that reproduces qualitatively the thermal expansion coefficient of these materials as a function of temperature and concentration.

For the purpose of studying the origin of the anomalous expansion, the anomalous and normal contributions to the coefficient have been defined, then evaluated. The results support the idea that the peculiar behaviour of the expansivity originates solely from the anomalous contribution. Consequently, an in-depth analysis of the last mentioned term has been suggested.

Figure 2.7. The linear thermal expansion coefficient of a disordered fcc $Fe_{100-x}Ni_x$ at room temperature as a function of concentration in percent, according to the model (diamonds) and experiments [4] (orange line).

Figure 2.8. The linear thermal expansion coefficient of a ferromagnetic disordered fcc $Fe_{65}Ni_{35}$ bulk solid as a function of temperature, according to the model (diamonds) and experiments [7] (orange line).

Figure 2.9. Linear thermal expansion coefficients of a random fcc $Fe_{100-x}Ni_x$ at room temperature as a function of concentration in percent, according to the model. The total expansion coefficient (black circles) can be written as the sum of a normal contribution (blue circles) and an anomalous contribution (orange circles).

Figure 2.10. Linear thermal expansion coefficients of a random fcc $Fe_{65}Ni_{35}$ as a function of temperature, according to the model. The normal contribution (blue circles) and anomalous contribution (orange circles) sum up to give the total expansion coefficient (black circles).

Chapter 3

Origin of the Invar Effect in Iron-Nickel Alloys

In Chapter 2, the linear thermal expansion coefficient of a ferromagnetic random fcc $Fe_{100-x}Ni_x$ alloy at temperature T has been estimated for different concentrations and temperatures. Moreover, its expansivity, α, has been divided into two contributions, the so-called normal term, α_n, and the so-called anomalous term, α_a. Both contributions have been evaluated. The results support the idea that only α_a contribute to the unusual temperature and concentration dependence of α. Thus, an exhaustive study of the anomalous contribution has been proposed. An investigation of the intrinsic cause of the concentration and temperature dependence of the anomalous term α_a is carried out in this chapter.

3.1 Existence of Negative Correlations

As can be seen in Eq. 2.5, the coefficient $\alpha_a(x, T)$ is related to the difference between two lattice constants evaluated for the same temperatures but two magnetic structures which can be different. This suggests an examination of the equilibrium average lattice spacing of a random fcc $Fe_{100-x}Ni_x$ alloy at temperature T in a PDLM state as a function of (x_{FU}, x_{NU}).

Figs. 3.1 and 3.2 depict the average lattice parameter plotted against X_{FFAP}, for various concentrations, temperatures and pairs (x_{FU}, x_{NU}). X_{FFAP} denotes the probability that a nearest-neighbour pair has each of its two sites occupied by an iron atom and exhibits anti-ferromagnetically aligned magnetic moments. It is explicitly given by:

$$X_{FFAP} = (1 - x/100)^2 2x_{FU}(1 - x_{FU}). \tag{3.1}$$

According to the figures, the average lattice constant of a given alloy at a fixed temperature is strongly negatively correlated with X_{FFAP}. This is true at least for $x = 35, 55, 80$ at $T = 0.01$ K and for $x = 35$ at $T = 100, 800$ K. That is, a strong

Figure 3.1. The calculated average lattice constant of a random fcc $Fe_{100-x}Ni_x$ in a PDLM state at temperature $T = 0.01$ K versus X_{FFAP}, for various concentrations and pairs (x_{FU}, x_{NU}). a_1 indicates the slope of the correlation line for each of the following concentrations $x =35, 55, 80$.

negative correlation between the average lattice parameter and the probability that a nearest-neighbour pair has each of its two sites occupied by an iron atom and shows anti-parallel moments is likewise observed in the *ab initio* data presented in Fig. 3.3. It is also remarkable that the slopes of the correlation lines differ only a little from each other. This will be taken advantage of in modelling α_a.

3.2   Origin of Negative Correlations

The mechanism behind the tendency of the average lattice parameter of a random fcc $Fe_{100-x}Ni_x$ to be reduced as X_{FFAP} is increased, is investigated in this section. Within the proposed model, the Hamiltonian H of $Fe_{100-x}Ni_x$ has the following form:

$$H = \sum_{\langle ij \rangle} E_{ij}, \tag{3.2}$$

where $E_{ij}(d_{ij}, \mathbf{e}_i, \mathbf{e}_j)$ is the interaction energy between site i and site j, d_{ij} is an intersite distance and $\mathbf{e}_i$ is a unit vector oriented in the direction of the moment at site i. The sum runs over all pairs of nearest neighbours. For each of these pairs, the interaction energy is expressed as:

$$E_{ij}(d_{ij}, \mathbf{e}_i, \mathbf{e}_j) = E_{ij}^{LJ}(d_{ij}) - J_{ij}(d_{ij}) \, \mathbf{e}_i \cdot \mathbf{e}_j, \tag{3.3}$$

Figure 3.2. The calculated average lattice spacing of a random fcc $Fe_{65}Ni_{35}$ in a PDLM state at temperature T versus X_{FFAP}, for several temperatures and pairs (x_{FU}, x_{NU}). The slope of the correlation line for a given temperature is denoted as a_1.

where $E_{ij}^{LJ}(d_{ij})$ is the chemical (nonmagnetic) part of the interaction energy and $J_{ij}(d_{ij})$ is an exchange interaction energy between the moments at sites i and j. The former is taken to be of the Lennard-Jones type:

$$E_{ij}^{LJ}(d_{ij}) = -E_{ij}^0 \left\{ 2\left(\frac{d_{ij}^0}{d_{ij}}\right)^6 - \left(\frac{d_{ij}^0}{d_{ij}}\right)^{12} \right\}. \tag{3.4}$$

d_{ij}^0 and E_{ij}^0 are two parameters which characterize E_{ij}^{LJ}. The atoms are placed at the ideal lattice sites, with the static atomic displacements not taken into account. As a consequence, all the nearest-neighbour bonds are of identical length. The input functions J_{ij}'s and the input constants d_{ij}^0's and E_{ij}^0's depend only on the chemical types of the atoms. J_{FF} denotes the exchange interaction energy between two iron sites. J_{FN} represents the exchange energy for an iron-nickel pair. J_{NN} is the same for a nickel-nickel pair. d_{FF}^0, d_{FN}^0, d_{NN}^0, E_{FF}^0, E_{FN}^0 and E_{NN}^0 are defined in an analogous way.

The model is applied to the calculation of the equilibrium average lattice spacing $a(x; x_{FU}, x_{NU})$ of the random fcc alloy in a PDLM state with the fraction of iron spins that are up, x_{FU}, and the fraction of nickel spins that are up, x_{NU}. The average lattice parameter can be expressed as:

$$a(x; x_{FU}, x_{NU}) = \sqrt{2}d(x; x_{FU}, x_{NU}), \tag{3.5}$$

where $d(x; x_{FU}, x_{NU})$ is the average nearest-neighbour bond length. Assuming that neither J_{FN} nor J_{NN} vary with the first-neighbour spacing, $d(x; x_{FU}, x_{NU})$ is

Figure 3.3. The predicted equilibrium average lattice constant of a random fcc $Fe_{100-x}Ni_x$ in a PDLM state versus X_{FFAP}, for several pairs (x_{FU}, x_{NU}) and concentrations, according to EMTO computations. The slope of the correlation line for a chosen concentration is written as a_1. This figure is a replot of the data displayed in Fig. 2.3.

found to be a solution to the following equation:

$$\left(\frac{\partial E_{AV}^{LJ}}{\partial d}\right)_x (x,d) - \left(\frac{\partial J_{FF}}{\partial d}\right)_x (x,d)\left[\left(1 - \frac{x}{100}\right)^2 - 2X_{FFAP}\right] = 0, \qquad (3.6)$$

where the weighted average of the chemical energy is given by:

$$E_{AV}^{LJ} = (1 - x/100)^2 E_{FF}^{LJ} + 2x(1 - x/100)E_{FN}^{LJ} + (x/100)^2 E_{NN}^{LJ}. \qquad (3.7)$$

Combined with Eq. 3.5, Eq. 3.6 establishes a relation between $a(x; x_{FU}, x_{NU})$ and X_{FFAP}. The latter equation is presented below for two different values of X_{FFAP}. In the case of the ferromagnetic state $\big((x_{FU}, x_{NU}) = (1, 1)\big)$, $d(x; x_{FU}, x_{NU})$ must solve:

$$\left(\frac{\partial E_{AV}^{LJ}}{\partial d}\right)_x (x,d) - \left(\frac{\partial J_{FF}}{\partial d}\right)_x (x,d)\left(1 - \frac{x}{100}\right)^2 = 0. \qquad (3.8)$$

However, if the magnetic structure is completely disordered $\big((x_{FU}, x_{NU}) = (0.5, 0.5)\big)$, $d(x; x_{FU}, x_{NU})$ is given by:

$$\left(\frac{\partial E_{AV}^{LJ}}{\partial d}\right)_x (x,d) = 0. \qquad (3.9)$$

The sum of $(\partial E_{AV}^{LJ}/\partial d)_x(x,d)$ and $-(\partial J_{FF}/\partial d)_x(x,d)\big[(1 - x/100)^2 - 2X_{FFAP}\big]$ is evaluated for various distances, concentrations and values of X_{FFAP}. The calculations are performed for $E_{FF}^0 = E_{FN}^0 = E_{NN}^0 = 11$ mRy, $d_{FF}^0 = d_{FN}^0 = d_{NN}^0 = 2.512$

Å. In addition, $(\partial J_{\mathrm{FF}}/\partial d)_x(x,d)$ is chosen to be constant between 2.5 and 2.56 Å, for $x =$35, 80. It is equal to 10 mRy/Å, the value of the derivative of J_{FF} in Ref. [34] estimated for $d = 2.544$ Å.

The predicted equilibrium average lattice parameter of $Fe_{65}Ni_{35}$ and $Fe_{20}Ni_{80}$ is plotted against X_{FFAP} for several pairs $(x_{\mathrm{FU}}, x_{\mathrm{NU}})$ in Fig. 3.4. In agreement with *ab initio* data, the model results exhibit a strong negative correlation between the lattice spacing and the probability that a nearest-neighbour pair has each of its two sites occupied by an iron atom and shows anti-parallel moments for both concentrations. Furthermore, the slopes of the correlation lines displayed in the figure are all of the same order of magnitude.

A useful way to think about the above model applied to $Fe_{100-x}Ni_x$ for $x = 35$ is shown in Fig. 3.5. If the PDLM state is such that $\left[(1 - x/100)^2 - 2X_{\mathrm{FFAP}}\right]$ cancels out, then the equilibrium average lattice spacing is given by the intersection point of the curve of $(\partial E_{\mathrm{AV}}^{\mathrm{LJ}}/\partial d)_x$ with the x-axis; the curve is the left-most curve in Fig. 3.5. Because $(\partial J_{\mathrm{FF}}/\partial d)_x(x,d)$ is strictly positive between 2.5 and 2.56 Å, raising $\left[(1 - x/100)^2 - 2X_{\mathrm{FFAP}}\right]$ causes the value of the sum of $(\partial E_{\mathrm{AV}}^{\mathrm{LJ}}/\partial d)_x(x,d)$ and $-(\partial J_{\mathrm{FF}}/\partial d)_x(x,d)\left[(1 - x/100)^2 - 2X_{\mathrm{FFAP}}\right]$ to decrease in that interval. One may say that the system "hops" from a curve to a curve lower than the last, resulting in a shift of the lattice spacing towards a bigger value. This explains the downward trend of the equilibrium average lattice parameter as X_{FFAP} is increased.

The data reported in this section are consistent with the idea that the slope of the correlation line between the equilibrium average lattice constant of a random fcc $Fe_{100-x}Ni_x$ in a PDLM state and the probability X_{FFAP} is governed by the derivative of the mean exchange energy between iron-iron first-neighbour pairs with respect to the mean nearest-neighbour bond length.

3.3   Origin of the Invar Effect

The present thesis aims at providing an insight into the physical nature of the thermal expansion of ferromagnetic fully-disordered fcc Fe-Ni alloys. To achieve such a goal, the normal contribution and the anomalous contribution to the thermal expansion coefficient of a ferromagnetic random fcc $Fe_{100-x}Ni_x$ have been defined and evaluated for several concentrations. (See Chapter 2.) The obtained results support the theory that the peculiar behaviour of the expansivity originates solely from the anomalous contribution.

For the purpose of understanding in a qualitative manner the basic process leading to a concentration and temperature dependence of α_a of $Fe_{100-x}Ni_x$, it is sufficient to consider the model below. The formulation of the model is governed by two facts. First, the equilibrium average lattice constant of the system at temperature T in a PDLM state is strongly negatively correlated with X_{FFAP}. This suggests the following derivation. If the spacing were a linear function of X_{FFAP}:

$$a(x, T; x_{\mathrm{FU}}, x_{\mathrm{NU}}) = a_1(x,T)X_{\mathrm{FFAP}} + a_0(x,T), \tag{3.10}$$

Figure 3.4. The calculated equilibrium average lattice constant of a random fcc $Fe_{100-x}Ni_x$ in a PDLM state versus X_{FFAP}, for several pairs (x_{FU}, x_{NU}) and concentrations, according to the model (circles) and *ab initio* computations (diamonds).

then $\alpha_a(x,T)$ as defined by Eq. 2.5 would be given by:

$$\alpha_a(x,T) = \frac{a_1(x,T)}{a(x,T)} \left(\frac{\partial X_{FFAP}}{\partial T} \right)_x (x,T). \tag{3.11}$$

Second, previous data support the idea that the slope a_1 and the average lattice constant a appearing in the left-most fraction on the right-hand side of the equality sign in Eq. 3.11 show a small relative variation in the domain of study ($30 \leq x \leq 80$, $0\,\mathrm{K} < T < 1000\,\mathrm{K}$). Here, the anomalous thermal expansion coefficient is modeled as:

$$\alpha_a(x,T) = \frac{a_1(x_0)}{a_{FM}(x_0)} \left(\frac{\partial X_{FFAP}}{\partial T} \right)_x (x,T), \tag{3.12}$$

where $a_1(x_0)$ and $a_{FM}(x_0)$ are two first-principles results obtained by means of the EMTO method for $x_0 = 35$. $a_1(x_0)$ corresponds to the slope of the correlation line shown in Fig. 3.3, whereas $a_{FM}(x_0)$ denotes the spacing $a(x_0; x_{FU}, x_{NU})$ for $(x_{FU}, x_{NU}) = (1,1)$. By inserting the expression of X_{FFAP} in terms of x_{FFAP}, Eq. 3.12 becomes:

$$\alpha_a(x,T) = \frac{a_1(x_0)}{a_{FM}(x_0)} \left(1 - \frac{x}{100} \right)^2 \left(\frac{\partial x_{FFAP}}{\partial T} \right)_x (x,T). \tag{3.13}$$

It is worth discussing the origin of some specific features of the thermal expansion in ferromagnetic random fcc Fe-Ni alloys with the help of Fig. 2.1 and Eq. 3.13.

Figure 3.5. The sum of $(\partial E_{\mathrm{AV}}^{\mathrm{LJ}}/\partial d)_x(x,d)$ and $-(\partial J_{\mathrm{FF}}/\partial d)_x(x,d)\big[(1-x/100)^2 - 2X_{\mathrm{FFAP}}\big]$ for random fcc $\mathrm{Fe}_{65}\mathrm{Ni}_{35}$ in a PDLM state with the probability that an iron spin is up, x_{FU}, and the probability that a nickel spin is up, x_{NU} as a function of the average nearest-neighbour bond length, for various values of X_{FFAP}, according to the model. The reader is reminded that $X_{\mathrm{FFAP}} = (1-x/100)^2 x_{\mathrm{FFAP}}$ where $x_{\mathrm{FFAP}} = 2x_{\mathrm{FU}}(1-x_{\mathrm{FU}})$. The intersection points of the curves with the x-axis give the corresponding equilibrium lattice constants.

The first two effects analyzed here deal with $\mathrm{Fe}_{65}\mathrm{Ni}_{35}$. According to Fig. 2.10, $\alpha_a(x,T)$ is negative below the Curie temperature. However, it cancels out above a temperature close to $T_c(x)$. These phenomena can be understood in the framework of the present model. Eq. 3.12 predicts that $\alpha_a(x,T)$ is negative below the critical temperature because the two terms a_1 and $(\partial x_{\mathrm{FFAP}}/\partial T)_x(x,T)$ have opposite signs. The same equation predicts that $\alpha_a(x,T)$ is zero above $T_c(x)$, due to the fact x_{FFAP} is constant in this range. There are more intriguing effects. For example, as observed in Fig. 2.9, $\alpha_a(x,T)$ evaluated at $T = 300$ K is smaller for $\mathrm{Fe}_{65}\mathrm{Ni}_{35}$ than for $\mathrm{Fe}_{20}\mathrm{Ni}_{80}$. This is consistent with the model; the quantities $(1-x/100)^2$ and $(\partial x_{\mathrm{FFAP}}/\partial T)_x(x,T)$ are bigger in the Fe-rich alloy.
In practice, $\alpha_a(x,T)$ is approximated as:

$$\alpha_a(x,T) \approx \frac{a_1(x_0)}{a_{\mathrm{FM}}(x_0)} \frac{X_{\mathrm{FFAP}}(x,T+\delta T) - X_{\mathrm{FFAP}}(x,T-\delta T)}{2\delta T}, \qquad (3.14)$$

where $\delta T = 50$ K. Figs. 3.6 and 3.7 compare the anomalous contribution to the thermal expansion coefficient of $\mathrm{Fe}_{100-x}\mathrm{Ni}_x$ at temperature T calculated via Eq. 3.14 to that given by Eq. 2.5, for various (x,T) pairs. As observed in Figs. 3.6 and 3.7, the model results agree qualitatively and quantitatively well with the rest of the data. Therefore, it is concluded that Eq. 3.12 combined with the input data

Figure 3.6. Anomalous contributions to the linear thermal expansion coefficient of a random fcc $Fe_{100-x}Ni_x$ at room temperature as a function of concentration in percent. The black circles and the orange circles show the values calculated via Eq. 3.14 and Eq. 2.5 respectively.

taken from Figs. 2.1 and 3.3 can successfully explain the basic mechanism behind the anomalous thermal expansion in ferromagnetic random fcc Fe-Ni alloys. It appears that the coefficient α_a is controlled by the derivative of X_{FFAP} with respect to temperature.

3.4   Conclusion

This chapter has been devoted to investigating the intrinsic cause of the concentration and temperature dependence of the anomalous contribution to the thermal expansion coefficient in ferromagnetic random fcc iron-nickel alloys. The process has involved several steps.

First of all, the equilibrium average lattice constant of $Fe_{100-x}Ni_x$ at temperature T in a PDLM state has been estimated and plotted against X_{FFAP}, for various pairs $(x_{\mathrm{FU}}, x_{\mathrm{NU}})$. It is strongly negatively correlated with X_{FFAP}. That is, a strong negative correlation between the equilibrium average lattice parameter and X_{FFAP} has likewise been observed in *ab initio* data. In addition, the slopes of all the regression lines differ only a little from each other.

Second, the mechanism behind the tendency of the spacing to be reduced as X_{FFAP} is increased, has been analyzed. A model system based on a Hamiltonian written as the sum of Lennard-Jones energies and a classical Heisenberg Hamiltonian has been introduced. The equilibrium average lattice parameter is a solution to an equation involving X_{FFAP}. In agreement with *ab initio* data, the model results

Figure 3.7. Anomalous contributions to the linear thermal expansion coefficient of a random fcc $Fe_{65}Ni_{35}$ as a function of temperature. The black circles and the orange circles show the values calculated via Eq. 3.14 and Eq. 2.5 respectively.

exhibit a strong negative correlation. The data are consistent with the idea that the slope of the correlation line between the equilibrium average lattice constant of a random fcc $Fe_{100-x}Ni_x$ in a PDLM state and the probability X_{FFAP} is governed by the derivative of the mean exchange energy between iron-iron first-neighbour pairs with respect to the mean nearest-neighbour bond length.

Finally, the anomalous contribution to the thermal expansion coefficient has been modeled. The formulation of the theory relies on previously described effects. The theoretical results agree qualitatively and quantitatively well with the corresponding data obtained in Chapter 2. The model can successfully explain the basic mechanism behind the anomalous thermal expansion in ferromagnetic random fcc Fe-Ni alloys. It has appeared that the coefficient α_a is controlled by the temperature derivative of the probability X_{FFAP}.

Chapter 4

The Invar Effect in Iron-Platinum and Iron-Palladium Alloys

Chapter 3 has been devoted to understanding in a qualitative manner the basic process leading to the concentration and temperature dependence of the anomalous contribution to the thermal expansion coefficient in ferromagnetic random fcc iron-nickel alloys. The anomalous contribution to the expansivity has been modeled as $\alpha_a = a_1(x_0)/a_{\mathrm{FM}}(x_0)(\partial X_{\mathrm{FFAP}}/\partial T)_x$. $\alpha_a(x, T)$ has been calculated for various concentrations and temperatures; $a_1(x_0)$ and $a_{\mathrm{FM}}(x_0)$ have been estimated by means of first-principles methods, whereas $X_{\mathrm{FFAP}}(x, T)$ is the result of a mean-field Ising model. It has been concluded that α_a in ferromagnetic random fcc iron-nickel systems seems to be governed by the derivative of X_{FFAP} with respect to temperature.

As mentioned in Chapter 1, besides ferromagnetic disordered fcc Fe-Ni materials, there are other fcc Fe-based alloys exhibiting a spontaneous magnetization, a chemical short-range order and an anomalous thermal expansion coefficient below a certain temperature. Naturally, the question arises whether it is possible that the Invar effects in $Fe_{65}Ni_{35}$, $Fe_{72}Pt_{28}$ and $Fe_{68}Pd_{32}$ have a common origin.

In this chapter, a step towards the formulation of a sensible answer to the above question is taken.

4.1 Calculating Magnetic Properties

As a starting point, the probability that an Fe-Fe nearest-neighbour pair shows anti-parallel moments (x_{FFAP}) is evaluated as a function of temperature for ferromagnetic random fcc $Fe_{72}Pt_{28}$ and $Fe_{66}Pd_{34}$ alloys. To carry out the calculations, the method described in Section 2.3 is adopted. The chosen values for the input parameters of the mean-field Ising model are reported in Table 4.1 for $Fe_{72}Pt_{28}$

S_{Fe} (μ_{B})	1.42
S_{Pt} (μ_{B})	0.16
J_{FeFe} (meV)	1.2
J_{FePt} (meV)	16
J_{PtPt} (meV)	0
$|(M - M_{\text{exp}})/M_{\text{exp}}|$	2 %
$|(T_{\text{c}} - T_{\text{c,exp}})/T_{\text{c,exp}}|$	0.25 %

Table 4.1. The chosen values for the input parameters of the mean-field Ising model for a ferromagnetic random fcc $Fe_{72}Pt_{28}$, along with the absolute value of the relative deviation of the calculated saturation magnetization and the Curie temperature from experimental results [9]. Note that the magnitude of the spin at the iron sites S_{Fe} and the platinum sites S_{Pt} are derived from first-principles calculations for the fully magnetized system. J_{FeFe}, J_{FePt} and J_{PtPt} represent the exchange constants between the nearest-neighbour iron-iron pairs, iron-platinum and platinum-platinum pairs.

and Table 4.2 for $Fe_{66}Pd_{34}$.
Fig. 4.1 shows the model results of x_{FFAP} as a function of temperature for $Fe_{72}Pt_{28}$, $Fe_{66}Pd_{34}$ and $Fe_{65}Ni_{35}$. It reveals striking similarities between the three curves. For example, for each of the three systems, x_{FFAP} increases with rising temperature below T_{c} and cancels out above the magnetic ordering temperature. In addition, it exhibits a strong dependence on temperature in a wide interval.

4.2   Existence of Negative Correlations

It is interesting to study the correlation between the equilibrium average lattice constant of a random fcc $Fe_{72}Pt_{28}$ in a PDLM state and the probability that a first-neighbour pair has each of its two sites occupied by Fe atoms and shows anti-ferromagnetically aligned magnetic moments. It is also of interest to carry out a similar analysis for a random fcc $Fe_{66}Pd_{34}$. The methods employed for the calculations are described in Section 2.5. Fig. 4.2 depicts some predicted spacings plotted against X_{FFAP}. Once more, common features can be observed in the three

S_{Fe} (μ_{B})	1.45
S_{Pd} (μ_{B})	0.15
J_{FeFe} (meV)	1.2
J_{FePd} (meV)	35.1
J_{PdPd} (meV)	0
$|(M - M_{\text{exp}})/M_{\text{exp}}|$	3 %
$|(T_{\text{c}} - T_{\text{c,exp}})/T_{\text{c,exp}}|$	0.5 %

Table 4.2. The same as in Table 4.1 but for a ferromagnetic random fcc $Fe_{66}Pt_{34}$. S_{Pd}, J_{FePd} and J_{PdPd} are the analogous quantities to S_{Pt}, J_{FePt} and J_{PtPt}. The experimental data are taken from Ref. [9].

Figure 4.1. The probability that an Fe-Fe nearest-neighbour pair shows anti-parallel moments in ferromagnetic random fcc $Fe_{72}Pt_{28}$, $Fe_{66}Pd_{34}$ and $Fe_{65}Ni_{35}$ alloys as a function of temperature, according to a mean-field Ising model.

systems. First, the average lattice parameter is strongly negatively correlated with X_{FFAP}. Second, the slope of the corresponding correlation line is in the order of 0.1 Å.

4.3   Origin of the Invar Effect

It has been shown in Sections 4.1 and 4.2 that some physical properties of ferromagnetic random fcc $Fe_{72}Pt_{28}$ and $Fe_{66}Pd_{34}$ solids are qualitatively identical to those of a ferromagnetic random fcc $Fe_{65}Ni_{35}$. This is consistent with the idea that the Invar effect has the same underlying mechanism in the three systems. To test the validity of this theory, the anomalous contribution to the thermal expansion coefficient of each of the two following materials, $Fe_{100-x}Pt_x$ for $x = 28$ and $Fe_{100-x}Pd_x$ for $x=34$, is modeled as that of $Fe_{65}Ni_{35}$:

$$\alpha_a(x,T) = \frac{a_1(x)}{a_{FM}(x)}\left(\frac{\partial X_{FFAP}}{\partial T}\right)_x (x,T), \tag{4.1}$$

where $a_1(x)$ and $a_{FM}(x)$ are estimated by means of first-principles methods. $a_1(x)$ denotes the slope of the correlation line shown in Fig. 4.2, whereas $a_{FM}(x)$ represents the equilibrium average lattice constant for the fully magnetized state. In

Figure 4.2. The predicted equilibrium average lattice constant of random fcc $Fe_{72}Pt_{28}$ and $Fe_{66}Pd_{34}$ systems in a PDLM state versus X_{FFAP}, for several pairs (x_{FU}, x_{NU}), according to EMTO computations. The slope of the correlation line for each of the systems is denoted by a_1.

practice, $\alpha_a(x, T)$ is approximated as:

$$\alpha_a(x,T) \approx \frac{a_1(x)}{a_{FM}(x)} \frac{X_{FFAP}(x, T + \delta T) - X_{FFAP}(x, T - \delta T)}{2\delta T}, \qquad (4.2)$$

where $\delta T = 50$ K. Fig. 4.3 displays the anomalous term α_a as a function of temperature for the three alloys, according to the model. As expected, α_a is negative below the Curie temperature and cancels out above T_c; this is true for the Fe-Pt alloy as well as the others.

An estimate of the thermal expansion coefficient of an $Fe_{72}Pt_{28}$ at temperature T is given by the sum of the normal term $\alpha_n(x, T)$ evaluated for a random fcc $Fe_{65}Ni_{35}$ alloy from the definition written in Section 2.2 and the anomalous term $\alpha_a(x, T)$ calculated via Eq. 4.2 for an $Fe_{72}Pt_{28}$ alloy. The thermal expansivity of an $Fe_{66}Pd_{34}$ at temperature T can be obtained in an analogous way. Calculated results are reported in Figs. 4.4 and 4.5. A good qualitative agreement between the model results and the experimental data [11, 12] is noticed. Thus, it is concluded that the Invar effects in disordered fcc $Fe_{72}Pt_{28}$, $Fe_{68}Pd_{32}$ and $Fe_{65}Ni_{35}$ may originate from the same mechanism.

Figure 4.3. The calculated anomalous contribution to the linear thermal expansion coefficient of ferromagnetic random fcc $Fe_{72}Pt_{28}$, $Fe_{65}Ni_{35}$ and $Fe_{66}Pd_{34}$ alloys as a function of temperature. The contribution for $Fe_{65}Ni_{35}$ is calculated via Eq. 3.14. The contribution for the other systems is evaluated via Eq. 4.2.

4.4   Conclusion

In a recent paper, the origin of the Invar effect in disordered fcc Fe-Pt alloys was examined by applying the DLM formalism [25]. The mechanism behind the Invar phenomenon was attributed to the weakening of the local Fe moments due to effects of thermally induced magnetic disorder.

In the present work, the DLM theory has been utilized to explain why disordered fcc Fe-Pt and Fe-Pd alloys exhibit an extremely low thermal expansion coefficient in a large temperature interval. It has been shown that some physical properties of ferromagnetic random fcc $Fe_{72}Pt_{28}$ and $Fe_{66}Pd_{34}$ are qualitatively identical to those of a ferromagnetic random fcc $Fe_{65}Ni_{35}$. These findings are consistent with the idea that the Invar effect has the same underlying mechanism in the three systems. To test the validity of this theory, the anomalous contribution to the thermal expansion coefficient of the Fe-Pt and Fe-Pd systems has been modeled as that of the Fe-Ni alloy. For all the bulk solids considered here, a good qualitative agreement between the model results and experimental data for the expansivity as a function of temperature has been observed. As a result, it has been concluded that the Invar effects in disordered fcc $Fe_{72}Pt_{28}$, $Fe_{68}Pd_{32}$ and $Fe_{65}Ni_{35}$ may have a common origin.

Figure 4.4. The linear thermal expansion coefficient of ferromagnetic disordered fcc $Fe_{72}Pt_{28}$ alloys. Results obtained by adding α_a for a random fcc $Fe_{72}Pt_{28}$ calculated via Eq. 4.2 to α_n for a random fcc $Fe_{65}Ni_{35}$ evaluated from the definition written in Section 2.2 are shown by diamonds. Experimental results are indicated by the orange line [11].

Figure 4.5. The linear thermal expansion coefficient of a ferromagnetic disordered fcc Fe-Pd alloys. Results obtained by adding α_a for a random fcc $Fe_{66}Pd_{34}$ calculated via Eq. 4.2 to α_n for a random fcc $Fe_{65}Ni_{35}$ evaluated from the definition written in Section 2.2 are shown by diamonds. Experimental results for an $Fe_{68}Pd_{32}$ are indicated by the orange line [12].

Chapter 5

Summary of Papers

5.1 Paper I: The Local Environment Effects in an FCC $Fe_{50}Ni_{50}$ Alloy

Paper I deals with the local environment effects on physical properties of a face-centered cubic $Fe_{50}Ni_{50}$ alloy. The site-projected density of states, the magnetic moment and the effective exchange parameter for an iron site in the system in a collinear magnetic state are calculated by means of *ab initio* methods [35, 36, 37]. This is done for various states and different sites exhibiting different numbers of like nearest-neighbours. As observed in Fig. 5.1, there exists a substantial dependence of the magnitude of the magnetic moment on the local chemical environment for the average lattice constant (a) of 3.45 Å. In addition, the effective exchange parameter seems to be negatively correlated with the number of iron atoms in the first coordination shell of the atom. Furthermore, upon close inspection of Fig. 5.2, one notes that the highest peak in the spin-up density of states has a tendency to shift towards the Fermi energy as the number of iron first-neighbours increases for $a =$ 3.49, 3.72 Å.

Figure 5.1. (a) The local magnetic moment and (b) the effective exchange parameter for an Fe site in an fcc $Fe_{50}Ni_{50}$ alloy in a collinear magnetic state plotted against the average lattice constant, for various sites. The legends indicate the numbers of Fe and Ni atoms in the first coordination shell of Fe atoms.

5.2   Paper II: Static Ionic Displacements in an FCC $Fe_{50}Ni_{50}$ Alloy

Paper II is concerned with the static ionic displacements in a face-centered cubic $Fe_{50}Ni_{50}$ alloy in a ferromagnetic state. The relaxed ionic positions are calculated by means of the Projected Augmented Wave method (PAW) [38] as implemented in the Vienna Ab Initio Package (VASP) [39]. Results are displayed in Fig. 5.3. According to the calculations, the effect of the structural relaxation on the mean iron-iron nearest-neighbour bond length is relatively small. However, it is found that the distance between the iron-iron first-neighbour pairs shows a large dispersion compared with the change of the average distance due to the static dis-

Figure 5.2. The site-projected density of states (DOS) for an Fe site in an fcc Fe$_{50}$Ni$_{50}$ alloy in a collinear magnetic state as a function of the energy, for various sites and average lattice spacings. $a = 3.72$ Å corresponds to a high-spin ferromagnetic state (a) and $a = 3.49$ Å corresponds to a state in a vicinity of the first spin flip transition (b). The legends indicate the numbers of Fe and Ni atoms in the first coordination shell of Fe atoms.

placements. Analogous calculations are carried out for iron-nickel and nickel-nickel pairs. Analogous conclusions are drawn.

Figure 5.3. Nearest-neighbour bond lengths in a ferromagnetic fcc $Fe_{50}Ni_{50}$ alloy. Theoretical results are shown by vertical solid lines, filled diamonds and an horizontal dashed line. Experimental results from Ref. [40] are shown by open circles and an horizontal dot-dashed line.

5.3 Paper III: Magnetic Structures in the Fe-Rich FCC Fe-Ni Alloys

Paper III investigates the total energy of face-centered cubic iron and iron-nickel alloys as a function of the average lattice constant for various magnetic states. The *ab initio* total energy calculations are carried out within the density functional theory (DFT) using two complementary techniques, one based on the Exact Muffin-Tin Orbital (EMTO) theory within the coherent potential approximation (CPA) and another one based on the Projector Augmented-Wave (PAW) method. Results for fcc Fe are displayed in Fig. 5.4, whereas results for fcc $Fe_{64}Ni_{36}$ and $Fe_{65}Ni_{35}$ are shown in Figs. 5.5 and 5.6. As observed in Fig. 5.4 and 5.5, the ground state is ferromagnetic for a "small" average lattice constant but non-magnetic for a "large" average lattice parameter. In between, there is an interval where the total energy of several magnetic states lies in a narrow energy range. The region shifts off the equilibrium volume towards lower volumes with increasing Ni concentration. The ferromagnetic state is stable for most of the compositions. The partial disordered local moment state does not compete with other configurations, so earlier works which emphasize the importance of the PDLM and DLM states for Invar alloys [43] are not supported by the present study. The most important competing magnetic states are the spin spiral state and the ferrimagnetic spin-flip state. The latter occurs as the first transition from the ferromagnetic high-spin

state at large volumes upon decreasing of the volume. Though its precise location with respect to the equilibrium volume in Invar alloys depends on the approximation to the exchange-correlation functional used, it is shown that it is quite possible that the ground state magnetic structure of the alloys is affected by the spin flipped states. The sites with flipped spins can serve as nucleation centers for the formation of the noncollinear magnetic order in the system.

Figure 5.4. The total energy of an fcc Fe as a function of the lattice parameter, for different magnetic states, according to EMTO calculations performed within the generalized gradient approximation using the parameterization of Perdew, Burke and Ernzerhof [41]. Shown are results for the nonmagnetic (open circles, solid line) and ferromagnetic states (open squares, solid line), 1**k** (diamonds) and double layer (X, solid line) AFM states, as well as for the spin spiral state (filled circles, dashed line). The latter corresponds to the planar spin spiral with the wave vector q along the Γ-X direction in the Brillouin zone which minimize the total energy for the spin spiral. The dependence of the wave vector q and magnetic moment for the spin-spiral state on the lattice parameter is shown in the inset in the figure. Also shown are the total energies for the partial disordered local moment states (dotted lines) with a relative fraction of the spin-down component 10 (triangles up), 20 (triangles left), 30 (triangles down), 40 (triangles right), and 50% (stars).

Figure 5.5. The total energy of an fcc $Fe_{64}Ni_{36}$ alloy as a function of the average lattice parameter, for different magnetic states, according to EMTO calculations.

Figure 5.6. The total energy of an fcc $Fe_{65}Ni_{35}$ alloy as a function of the average lattice parameter, for the spin flipped (SF, triangles) and ferromagnetic (FM, circles, dashed line) states, according to the PAW calculations carried out within the generalized gradient approximation using the parameterization of Perdew and Wang [42].

5.4   Paper IV: Local Magnetovolume Effects in an FCC Fe$_{65}$Ni$_{35}$ Alloy

A systematic *ab initio* study of static ionic displacements in a face-centered cubic Fe$_{65}$Ni$_{35}$ alloy is carried out. Results can be seen in Figs. 5.7, 5.8, 5.9, 5.10 and 5.11. Theoretical results for the magnitudes of the average Fe-Fe, Fe-Ni, and Ni-Ni $\langle 110 \rangle$ bond vectors agree well with experimental measurements [44]. In addition, it is observed that in collinear ferrimagnetic states, iron-iron nearest neighbour pairs with anti-parallel local magnetic moments are shorter on average than those with parallel moments. Furthermore, considering different states (ferromagnetic, non-magnetic and collinear ferrimagnetic states) for the same average lattice spacing, it is shown that the magnetic structure strongly influences some local geometrical properties of the alloy. For example, a transition from a ferromagnetic state to a collinear ferrimagnetic state induces a significant contraction of the volume associated with an iron site where the moment flips. A model system based on a Hamiltonian written as the sum of Lennard-Jones energies and a classical Heisenberg Hamiltonian is introduced. It yields structural properties which are qualitatively similar to those obtained *ab initio*. It is found that some of the phenomena can be classified as magnetovolume effects.

Figure 5.7. The magnitudes of the average Fe-Fe, Fe-Ni and Ni-Ni $\langle 110 \rangle$ bond vectors (relative to the mean distance between first neighbors) in fcc Fe-Ni alloys. Triangles: *ab initio* results for an Fe$_{65}$Ni$_{35}$ alloy in the lowest energy ferromagnetic state. Crosses: experimental results for an Fe$_{63}$Ni$_{37}$ alloy at 60 K [44].

Figure 5.8. Characteristics of the distributions of Fe-Fe, Fe-Ni, and Ni-Ni nearest neighbour bond lengths in an fcc $Fe_{65}Ni_{35}$ alloy in various states, according to *ab initio* calculations. (a): data for the lowest energy ferromagnetic state. (b): data for the lowest energy non-magnetic state.

Figure 5.9. The average Fe-Fe nearest neighbour bond lengths in a collinear ferrimagnetic fcc $Fe_{65}Ni_{35}$ alloy as functions of the average lattice constant, according to *ab initio* calculations. The Fe-Fe pairs are distinguished on the relative orientation of their moments: parallel (triangles up) or antiparallel (triangles down).

Figure 5.10. The average local volume of an Fe atom coordinated with n like nearest-neighbours as a function of n, according to first-principles calculations. Crosses, triangles up and triangles down: results for the non-magnetic, ferromagnetic and collinear ferri-magnetic state with $a = 3.583$ Å.

5.5 Paper V: Origin of the Invar Effect in Fe-Ni Alloys

Certain alloys of iron and nickel (so-called "Invar" alloys) exhibit almost no thermal expansion over a wide range of temperature. It is clear that this is the result of an anomalous contraction upon heating which counteracts the normal thermal expansion arising from the anharmonicity of lattice vibrations. This anomalous contraction seems to be related to the alloys' magnetic properties, since the effect vanishes at a temperature close to the Curie temperature. However, despite many years of intensive research, a widely accepted microscopic theory of the Invar effect in face-centered cubic Fe-Ni alloys is still lacking. Here a simple theory of the Invar effect in these alloys is presented. It is based on Ising magnetism, *ab initio* total energy calculations, and the Debye-Grüneisen model. It is shown that this theory accurately reproduces several well known properties of these materials, including Guillaume's famous plot of the thermal expansion coefficient as a function of the concentration of nickel (see Fig. 5.12). The present approach supports the idea that the average lattice constant is governed by a few parameters, including the fraction of iron-iron nearest-neighbour pairs.

Figure 5.11. The average local volume of an iron atom in a fcc $Fe_{65}Ni_{35}$ in (a) non-magnetic, (b) ferromagnetic, and (c) collinear ferrimagnetic states, versus the number of iron atoms in the first coordination shell. Green circles: model results. Blue crosses: *ab initio* results.

Figure 5.12. The linear thermal expansion coefficient of a disordered fcc $Fe_{100-x}Ni_x$ at room temperature as a function of concentration in percent, according to the model (diamonds) and experiments [4] (orange line).

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List of Publications

[I] I. A. Abrikosov, F. Liot, T. Marten and E. A. Smirnova. Magnetism in Systems with Reduced Dimensionality and Chemical Disorder: The Local Environment Effects. J. Magn. Magn. Mater. **300**, 211 (2006).

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[V] F. Liot and C. A. Hooley. A Simple Theory of the Invar Effect in Iron-Nickel Alloys. In manuscript.