Nanocrystalline Fe-Pt alloys: phase transformations, structure and magnetism

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Synopsis

This work has been devoted to the study of phase transformations involving chemical ordering and magnetic properties evolution in bulk Fe-Pt alloys composed of nanometer-sized grains. Nanocrystalline $\text{Fe}_{100-x}\text{Pt}_x$ ($x = 40-60$) alloys have been prepared by mechanical ball milling of elemental Fe and Pt powders at liquid nitrogen temperature. The as-milled Fe-Pt alloys consist of ~100 $\mu$m sized particles constituted by randomly oriented grains having an average size in the range of 10-40 nm. Depending on the milling time, three major microstructure types have been obtained: samples with a multilayer-type structure of Fe and Pt with a thickness of 20-300 nm and a very thin (several nanometers) A1 layer at their interfaces (2 h milled), an intermediate structure, consisting of finer lamellae of Fe and Pt (below approximately 100 nm) with the A1 layer thickness reaching several tens of nanometers (4 h milled) and alloys containing a homogeneous A1 phase (7 h milled).

Subsequent heat treatment at elevated temperatures is required for the formation of the L1$_0$ FePt phase. The ordering develops via so-called combined solid state reactions. It is accompanied by grain growth and thermally assisted removal of defects introduced by milling and proceeds rapidly at moderate temperatures by nucleation and growth of the ordered phases with a high degree of the long-range order. The mechanism of ordering into the L1$_0$ structure depends on the alloy composition and the precursor microstructure. Heating of the $\text{Fe}_{100-x}\text{Pt}_x$ ($x = 40; 45; 50; 55$) alloys with the initial A1 structure induces the A1 $\rightarrow$ L1$_0$ transformation, whereas in the $\text{Fe}_{50}\text{Pt}_{50}$ powders with the multilayer-type microstructure, the L1$_0$ formation proceeds via a metastable state according to the sequence: $\text{Fe/Pt precursor} \rightarrow \text{L1}_0 + \text{L1}_2 \rightarrow \text{L1}_0$. The results based on the in-situ neutron powder diffraction and differential scanning calorimetry measurements show that for the equiatomic composition the A1 $\rightarrow$ L1$_0$ transformation rate is fastest and a deviation from the equiatomic concentration significantly decelerates the ordering.

The combination of the chemically highly ordered L1$_0$ FePt and L1$_2$ Fe$_3$Pt and/or FePt$_3$ phases, formed after an isothermal heat treatment of the $\text{Fe}_{100-x}\text{Pt}_x$ ($x = 40 - 60$) powders with multilayer-type microstructure, yields a wide range of magnetic phenomena. In these alloys, the nanometer scale multilayer structure is preserved after annealing. In Pt-rich alloys, the decoupling of the L1$_0$ FePt lamellae by paramagnetic L1$_2$ FePt results in the increased coercivity. In heat treated Fe-rich $\text{Fe}_{100-x}\text{Pt}_x$ powders, composed of the high magnetisation L1$_2$ Fe$_3$Pt and hard magnetic L1$_0$ FePt phases, adjusting the microstructure of the as-milled alloys modifies the extent of exchange coupling between the phases. In the 2 h milled and subsequently annealed Fe-rich Fe-Pt alloys, despite small grains, only a weakly pronounced exchange coupling is observed between the L1$_2$ Fe$_3$Pt and L1$_0$ FePt phases. Due to rather thick Fe$_3$Pt layers in terms of the soft magnetic phase domain-wall parameter, only those Fe$_3$Pt grains that are located at the interface between the Fe$_3$Pt and L1$_0$ lamellae are exchange-coupled to the hard magnetic L1$_0$ phase. In these powders, the lower (than predicted for non-interacting randomly oriented particles) remanence may be explained by the presence of dipolar interactions leading to magnetisation reversal already in positive applied fields. Due to the presence of the soft magnetic Fe$_3$Pt and/or A1 phases, weakly
coupled to the hard magnetic L1₀, the magnetisation reversal in these powders is noncooperative.

The phases in the annealed Fe₅₀-xPtₓ powders milled for 4 h are distributed in the form of very fine lamellae. This nanometer-scale microstructure gives rise to large effects of exchange interactions between crystallites of the phases. As a result, the demagnetisation curves of the heat treated Fe-rich Fe₅₀-xPtₓ samples show a single-phase magnetic behaviour, although several magnetic phases are present in the powders, and in both equiatomic and Fe-rich Fe₅₀-xPtₓ alloys a significant remanence enhancement is observed. As a result of remanence enhancement, much improved energy density (BH)ₘₐₓ values (up to 121 kJ/m³) are obtained in the heat treated Fe-rich Fe₅₀-xPtₓ powders milled for 4 h.

In the heat treated Fe₅₀-xPtₓ powders milled for 4 h, due to the strong intergrain exchange coupling magnetisation reversal is more uniform compared to that in the 2 h milled and annealed powders. The demagnetisation curves of the former alloys are highly reversible. Nevertheless, the open recoil loops of the Fe-rich powders indicate deviations from the ideal exchange-spring-magnet behaviour. The recoil loop area decreases with decreasing soft magnetic phase fraction and no recoil hysteresis is observed in the essentially single L1₀-phase Fe₅₀Pt₅₀ sample. In a two-particle interaction model elaborated in the present work, the existence of hysteresis in recoil loops has been shown to arise from insufficient coupling between the low- and the high-anisotropy particles. The recoil loop area turns out to be a function of the interaction strength, anisotropy of the particles, i.e. switching field distribution, and the fraction of the low-anisotropy component. The model reveals the main features of magnetisation reversal processes observed experimentally in exchange-coupled systems. In particular, it has been shown that if two particles interact, a reversible magnetisation rotation is possible also when the easy axes of the particles are parallel to each other and to the applied field, provided additional conditions are fulfilled.

Neutron diffraction has been used for the investigation of the magnetic structure of ordered and partially ordered nanocrystalline Fe-Pt alloys. It has been shown that the Fe moment in L1₀-type Fe-Pt alloys is sensitive to composition and almost insensitive to the degree of order in the investigated compositional range. In particular, the Fe moments decrease with increasing Fe content, which is primarily a consequence of the lattice volume reduction.
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**Introduction**

Permanent magnets find application in a wide variety of devices, from everyday appliances like loudspeakers and quartz watches to motors, data storage and medical (e.g. magnetic resonance imaging) devices. From a point of view of applications, magnetic materials may be divided into three groups: soft magnetic materials used e.g. for magnetic flux guidance in electromagnetic devices; semi-hard magnets used for magnetic data storage and hard magnetic materials exploited in static applications [Coe96]. The division of magnetic materials into these three categories is achieved on the basis of their coercive force (coercivity). Apart from the fact that the coercivity is to a great extent determined by a particular microstructure, a high magnetic anisotropy is a prerequisite for achieving high coercivities. Modern permanent magnet materials are based on intermetallic compounds of rare-earths and 3d transition metals with very high magnetocrystalline anisotropy, such as Nd$_2$Fe$_{14}$B and SmCo$_5$ [Coe96].

A figure of merit of permanent magnet performance is its maximum energy density $(BH)_{\text{max}}$ – a measure of the maximum magnetostatic energy available from a magnet of optimal shape. To obtain large $(BH)_{\text{max}}$ both high coercivity and high remanent magnetisation (remanence) are required. For most applications, a permanent magnet should have not only optimised magnetic properties, but also appropriate nonmagnetic properties (electrical, mechanical, corrosion behaviour etc.). Distinct advantages of Fe-Pt alloys are, as opposed to the rare-earth-transition-metal-based compounds, that they are very ductile and chemically inert. Since the mid-1930s Fe-Pt alloys are known to exhibit high coercivities due to high magnetocrystalline anisotropy of the L1$_0$ FePt phase [Gra35], but the high price prevented widespread applications of these alloys. The main intrinsic magnetic properties of this itinerant-electron ferromagnet are reported to be $T_c = 750$ K (Curie temperature), $J_s =1.43$ T (spontaneous magnetisation at room temperature) and $K_1 = 6.6$ MJ/m$^3$ (first anisotropy constant at room temperature) [Iva73, Kus50]. The magnetic properties of the Fe-Pt alloys will be treated in detail in Section 1.4. Due to the unique combination of excellent intrinsic magnetic properties and good corrosion resistance, L1$_0$-based thin films and nanoparticles are promising candidates for ultra-high-density magnetic storage media [Sun00, Wel00]. In bulk form, their high cost limits L1$_0$-based permanent magnets to very specialised applications such as in magnetic micro-electromechanical systems (magnetic MEMS) or in aggressive environments, for instance, in dentistry, where they are used as magnetic attachments to retain dental prostheses in the oral cavity.

Various preparation techniques are used to obtain the ordered L1$_0$ phase. Typically, the synthesis starts with the preparation of the disordered A1 phase followed by annealing at elevated temperatures [Iva73, Wat83, Yer90, Zha92, Ris99, Sun00, Xia02]. In thin film-form,
the L10 FePt phase can be directly prepared by deposition onto heated substrates [Ceb94, Wei04]. Ordered FePt thin films have also been prepared by subsequent annealing of multilayers produced by sequential deposition of Fe and Pt layers of thickness in the order of several nanometers [Liu98]. A review of fabrication techniques and properties of thin film L10-based alloys has been given by Cebollada et al. [Ceb02]. Nanoparticulate systems can be produced by chemical synthesis [Sun00] leading to self-organised magnetic arrays or by a gas-phase based process [Rel03]. Cold deformation [Hai03a] is used to make FePt foils and electrodeposition [Rhe03] can be employed to prepare layers of several microns. Because of the ductility of the Fe-Pt alloys, a powder-metallurgical route, often used for producing permanent magnet materials [Sch87], is not easily adaptable here. It will be demonstrated that mechanical alloying of elemental Fe and Pt powders, performed at liquid-nitrogen temperature, can be successfully used to prepare nanocrystalline Fe100-xPtx (x = 40-60) powders (Chapter 4).

The mechanisms of phase formation and ordering, and thus magnetic properties of Fe-Pt alloys, differ depending on the used approach. Very high coercivities exceeding 4 T can be obtained in ultrathin films consisting of magnetically isolated L10 grains, whereas in continuous L10-based films the coercivity is in the range of 1-2 T [Shi02]. In conventionally processed relatively coarse grained bulk Fe-Pt alloys, the dominant mechanism contributing to coercivity, which usually does not exceed 0.5 T, is domain wall pinning at different types of planar defects (twin and/or antiphase boundaries) [Kam82, Zha92]. Improved coercivity values (up to about 1.0 T) were obtained for alloys subjected to mechanical deformation followed by annealing at temperatures below the order-disorder transformation [Iva73, Kle03, Hai03a]. This processing leads simultaneously to a decrease of defect density, nucleation and growth of the new phases concurrent with the ordering process. As a result, the microstructure is drastically changed and material mostly consisting of fine L10 FePt grains is obtained. However, the macroscopic isotropy of these materials results in a relatively low remanence.

The material design on a nanoscale is one of the possibilities to improve the magnet performance. For instance, Fe-based (Finemet) alloys composed of nanometer-sized randomly distributed crystallites exhibit a superior soft magnetic behaviour compared to that of conventional coarse-grained materials [Yos88, Her89]. The coercivity reduction due to random anisotropy is undesired in permanent magnets. On the other hand, the reduction of grain size in polycrystals is advantageous for improving the remanence by favouring parallel spin arrangement in neighbouring grains (remanence enhancement). Enhancement of remanence and so-called exchange-spring hysteresis behaviour of nanocomposite magnets are caused by exchange coupling between grains of different magnetic phases (Section 1.5).

Several attempts have been undertaken to improve the performance of L10-based magnets, both in thin film and bulk form. The combination of hard magnetic L10 FePt and soft magnetic Fe3Pt yields a significant remanence enhancement in Fe3Pt/FePt nanocomposites prepared by chemical synthesis [Zen02a]. Very high remanence values obtained in rapidly annealed thin-film Fe/Pt multilayers have also been reported [Liu98], although the resulting nanocomposite film no longer exhibited the original multilayer structure. On the other hand, exchange spring-magnet behaviour does not occur if the
crystallite size in a L1₀ FePt/L1₂ Fe₃Pt two-phase system is too large [Hai03a]. Remanence enhancement has also been found in annealed bulk Fe₅₉.₇₅Pt₃₉.₅Nb₀.₇₅ [Xia04]. However, no typical spring-magnet behaviour was observed in these alloys, which was mainly attributed to an insufficient degree of chemical order in the L1₀ phase. This confirms that despite the crystallographic simplicity of the L1₀ phase, its formation and the accomplishment of complete chemical long-range order require sophisticated preparation procedures, which are not yet investigated in full detail.

A common feature of materials prepared by sputtering [Ris99, Liu98], melt-spinning [Yer90], mechanical alloying (Chapter 4) and nanoparticle synthesis [Sun00, Zen02a] is a high density of crystal defects (vacancies, dislocations, grain boundaries and interfaces). The understanding of the L1₀ phase formation and ordering kinetics, as well as their dependence on the precursor structure and composition (with respect to stoichiometry controversial data have been reported [Sek03, Bar04]) would assist in the development of Fe-Pt materials with optimised magnetic properties.

In this work, a comprehensive study of phase transformations and ordering in Fe-Pt alloys is performed by a combination of in-situ neutron powder diffraction and thermal analysis (Chapter 4). The dependence of ordering processes on the alloy composition and initial microstructure (homogeneous A1 phase or multilayer-type) is established. Through the use of mechanical alloying and subsequent heat treatment it has been possible to achieve the formation of chemically highly ordered L1₀ FePt and, in the case of the Fe-rich and Pt-rich compositions, L1₂ Fe₃Pt and FePt₃ phases, respectively. Whereas in Pt-rich alloys the decoupling effect of the FePt₃ phase leads to coercivity improvement, in Fe-rich nanocomposites a peculiar nanometer scale multilayer structure gives rise to remanence enhancement due to large effects of exchange interactions between the crystallites of the phases. In Chapter 5, the structure, magnetic properties and magnetisation reversal processes of these alloys are investigated. Experimentally observed phenomena are understood on the basis of a simple two-particle interaction model (Chapter 2). Neutron diffraction has also been used for the investigation of the magnetic structure of ordered and partially ordered nanocrystalline Fe-Pt alloys (Chapter 6). It has been shown that the magnetic moment of Fe atoms in L1₀-type Fe-Pt alloys is sensitive to the compositional order. The results are compared to density functional calculations.
Chapter 1

Fundamentals

In this chapter, the Fe-Pt phase diagram and approaches to obtain ordered phases (Section 1.1) as well as their crystallographic types (Section 1.2) will be presented. Long-range chemical order and techniques for its quantitative determination will be introduced on the example of binary alloys (Section 1.3). Section 1.4 is devoted to the intrinsic magnetic properties of the Fe-Pt alloys and in Section 1.5 magnetisation processes in nanometer-scaled materials will be introduced.

1.1. Fe-Pt phase diagram

According to the Fe-Pt phase diagram (Fig. 1.1), at high temperatures an fcc solid solution of the components is observed. At temperatures below 1300 °C, alloys close to the equiatomic concentration exhibit a disorder-order transformation from the disordered face-centred cubic A1-type structure to the tetragonal L1₀-type superstructure. The existence

![Equilibrium phase diagram of the Fe-Pt system](image)

Fig. 1.1. Equilibrium phase diagram of the Fe-Pt system (adapted from [Mas90]). Shown schematically are crystallographic structures of the phases in the corresponding phase equilibrium regions (see Section 2.1.2 for details).
region of the L1\(_0\) structure extends from approximately 35 to 55 atomic percent Pt. In Fe\(_{100-x}\)Pt\(_x\) alloys deviating from the 35 ≤ x ≤ 55 stoichiometry, formation of the stable cubic superstructures FePt\(_3\) (L1\(_2\)) and Fe\(_3\)Pt (L1\(_2\)) is expected at temperatures below 850 °C and 1350 °C, respectively. An eutectoid reaction A1 \→ L1\(_0\) + L1\(_2\) is located at approximately 1160 °C at the composition of the A1 phase of about 55 at. % Pt. Further, there exist two-phase regions in Pt-rich alloys (A1 + L1\(_2\) FePt\(_3\)) and in Fe-rich alloys (A1 + L1\(_2\) Fe\(_3\)Pt).

Since the chemical ordering in conventional bulk alloys becomes prohibitively slow at low temperatures, the phase diagram data are confined to temperatures above 600 °C. Nevertheless, the region below 400 °C was extensively investigated for the Fe-rich compositions (20 ≤ x ≤ 35), as these alloys show the Invar effect [Was90] and undergo a martensitic transformation at temperatures close to and below room temperature [Sum83]. The phase diagram around the stoichiometric composition Fe\(_3\)Pt is shown in Fig. 1.2. In the ordered state, the L1\(_2\) Fe\(_3\)Pt phase is stable down to approximately 60 K, whereas the disordered Fe\(_3\)Pt starts to transform to a bcc martensite already at room temperature. The martensite in L1\(_2\)-type ordered Fe-Pt alloys near the composition Fe\(_3\)Pt was reported to have a bct structure [Tad75].

The particular phase composition and microstructure that can be obtained in Fe-Pt alloys depend both on the concentration and specific kinetic regimes. For instance, the disordered A1 structure can be stabilised by (rapid) quenching from high temperatures or by deformation [Yer85, Mag70]. In thin film-form, the A1 phase can be prepared by sputtering onto room-temperature or slightly heated (about 200 °C) substrates [Ris99, Pyn76]. It can also be produced by a chemical synthesis of nanoparticles [Sun00]. A typical approach to obtain the ordered phase (L1\(_0\) or L1\(_2\)) is a heat treatment of the A1 precursor.

In coarse-grained alloys, the mechanism of the cubic A1 \→ tetragonal L1\(_0\) transformation involves the precipitation of the ordered phase within a grain. Any of the three <100> axes of the cubic matrix may be chosen as the tetragonal one, i.e. there exist three possible orientations of the c-axis for the ordered L1\(_0\) phase. Appreciable internal elastic strains arise due to the difference in the lattice parameters of the phases (see Table 1.1). These stresses affect the A1 \→ L1\(_0\) transformation, which results in a structural self-organisation by two mechanisms. A metastable state is initially formed with
1 > c/a > (c/a)\text{equilibrium} and by the formation of six types of highly disperse anti-phase domains (APD), i.e. the APDs with all three orientations of the tetragonal c-axis. This stage corresponds to the so-called “tweed” contrast in TEM images (Fig. 1.3(a)). The strain energy can be further decreased by the stress-induced growth of the ordered phase. The microstructure in this case consists of regular stacks of plate-like misoriented crystallites-twins (Fig 1.3(b)). These adjacent ordered bands contact each other coherently along invariant [110] planes. The tetragonal c-axes of the L1\textsubscript{0} phase are, thus, misoriented by an angle close to π/2. In addition to polytwinning, the microstructures often contain a high density of antiphase boundaries in the ordered bands (Fig 1.3(c)). The polytwinned microstructure in relatively coarse grained materials is beneficial for achieving hard magnetic properties, as the mentioned planar defects act as pinning centres for magnetic domain walls [Kan82, Zha92, Vla00].

If prior to the ordering treatment a high density of crystal defects is introduced into the alloy, the transformation scenario may change drastically. In the alloys driven away from equilibrium, so-called “combined” solid state reactions may occur that take place when thermodynamical equilibrium is approached by more than one elementary reaction [Hor79]. In the case of Fe-Pt alloys with a high density of defects (such as vacancies, dislocations, grain boundaries and interfaces) the ordering process may be assisted by a simultaneous decrease of defect density, growth of new phases and sintering. As a result of the combined reactions, the microstructure is drastically changed and material mostly consisting of fine L1\textsubscript{0} FePt grains is obtained.

1.2. Crystallographic structures of Fe-Pt phases

Figure 1.4 illustrates schematically the chemically ordered L1\textsubscript{0} and L1\textsubscript{2} structures, as well as the disordered A1 structure. The different chemical species appear as dark and light spheres.

In the L1\textsubscript{0} structure (Fig. 1.4(a)), common for alloys of equiatomic compositions (e.g. FePt), the cubic symmetry is broken due to the stacking of alternate planes of the 3\textit{d} element.
Crystallographic structures of Fe-Pt phases

If the chemical ordering into the L1₀ structure would take place without any lattice distortion the ratio of the lattice parameters in the tetragonal unit cell would be \( c^*/a^* = 1.414 \). In reality, however, \( c^*/a^* \) of L1₀ FePt is 1.363 [Ceb02]. If a \( tP4 \) (Pearson symbol) pseudocell with the lattice parameters \( c = c^* \) and \( a = \sqrt{2} a^* \) is used instead of the real \( tP2 \) unit cell the experimental \( c/a \) ratio is 0.96 (see Table 1.1). It should be noted that L1₀ structures without the above mentioned lattice distortions, i.e. for identical in-plane and out-of-plane atomic distances, \( c/a = 1 \) (as e.g. in FeNi [Rav01]), are nevertheless clearly tetragonal with \( c^*/a^* = \sqrt{2} \).

In figure 1.4(b) the L1₂ ordered structure is shown. This is a cubic phase that can form around a 1:3 stoichiometry. In Fe₃Pt (FePt₃), the Pt (Fe) atoms occupy the cube corners and the Fe (Pt) atoms occupy the face-centre positions.

Figure 1.4(c) shows the face-centered cubic (A1), chemically disordered structure. The iron and platinum atoms occupy each lattice site randomly.

1.3. Long-range chemical order

The ordered structures considered in Section 1.2 represent the case of a perfect long-range order (LRO), e.g. all the Pt-sites are occupied by Pt atoms and the Fe-sites by Fe atoms. However, the chemical order may not be perfect and to characterise the degree of
disorder one may use the parameters $r_{\text{Pt}}$ and $r_{\text{Fe}}$, which are the fractions of Pt- and Fe-sites occupied by a correct atom, Pt or Fe, respectively. Using these parameters, the degree of long-range chemical order can be quantified by defining the following expression for the LRO parameter, $S$ [War90]:

$$S = r_{\text{Pt}} + r_{\text{Fe}} - 1 = (r_{\text{Pt}} - c_{\text{Pt}})/(y_{\text{Fe}} - c_{\text{Fe}})/y_{\text{Pt}},$$

(1.1)

where $c_{\text{Pt(Fe)}}$ is the atom fractions of Pt(Fe) and $y_{\text{Pt(Fe)}}$ is the fraction of Pt(Fe) sites. When the order is perfect, the order parameter $S$ reaches unity, while for a completely random atom arrangement $S$ is equal to zero. Thus, the order parameter can reach its maximum ($S = 1$) only for a stoichiometric composition. For nonstoichiometric compositions, $S$ is always less than unity. The maximum value for the LRO parameter is, thus, a function of the composition of the alloy and for L1$_0$-type ordering has been defined as $S_{\text{max}} = 1 - 2|\Delta x|$, where $\Delta x$ is the compositional deviation in atom fraction from 0.5 [Ceb02]. It has to be noted, that the above definition for $S$ is derived for homogeneous materials. Frequently, however, materials consist of regions having a high degree of chemical order and regions being nearly or completely disordered. In this case, as an additional parameter, the volume fraction of the chemically ordered phase, should be used to quantify the order in such inhomogeneous materials.

Being the most direct technique, powder diffraction is frequently used to characterise the long-range chemical order in alloys. As an example, figure 1.5(a) shows a calculated x-ray diffraction pattern for the A1 phase revealing the presence of the fundamental reflections (111), (200) and (220). As a result of ordering, splitting of the fundamental reflection occurs due to lowering of the symmetry and additional reflections called superstructure reflections appear in powder diffraction patterns (Fig. 1.5(b)).

The integrated intensity of a Bragg reflection is given by the expression:

$$I_k = cL_k|F_k|^2 e^{-2M}P_k A$$

(1.2)

where $k$ represents the Miller indices, $hkl$, for a Bragg reflection, $c$ is constant in the recording of the diffraction pattern, $L_k$ contains the Lorentz, polarisation and multiplicity factors, $F_k$ is a structure factor for the $k$th reflection, $e^{-2M}$ is the thermal displacement factor,
$P_k$ is the preferred orientation function ($P_k = 1$ indicates the absence of a preferred orientation) and $A$ is an absorption factor \([\text{Uma82}]\). The structure factor $F_k$ is determined by a structural model, i.e. it takes into account the dependence of intensity on the type of atoms and their position in a cell and is defined by the lattice basis:

$$F_k = \sum_j r_j f_j \exp \left[2\pi i (hx_j + ky_j + lz_j)\right],$$

where $r_j$ is the site occupation parameter, $f_j$ is the atomic scattering factor and $x_j$, $y_j$ and $z_j$ are the position parameters of the $j$th atom in the unit cell.

For the $L1_0$-type ordering, the structure factors for fundamental $F_f$ and superstructure $F_{ss}$ reflections are calculated as

$$F_f = 4(c_{\text{Pt}} f_{\text{Pt}} + c_{\text{Fe}} f_{\text{Fe}})$$

(1.4a)

$$F_{ss} = 2S(f_{\text{Pt}} - f_{\text{Fe}}).$$

(1.4b)

From Eq. (1.4) it follows that $F_f$ is independent of the degree of order, whereas the structure factor of the superstructure reflections is proportional to the LRO parameter. The latter can be determined by comparing the integrated intensity of a superstructure reflection with that of a fundamental reflection. However, as mentioned above, it is important to distinguish between partially ordered and inhomogeneous alloys. If several phases coexist, overlapping peaks of the different phases complicate the determination of the integrated intensities. This problem may be solved by e.g. using the Rietveld analysis \([\text{Rie69, You93}]\) of diffraction data. In this work, the fractions of the sites occupied by a correct atom $r_j$ extracted from a Rietveld refinement were used for the LRO parameter determination.

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**Fig. 1.5.** Calculated x-ray diffraction patterns for (a) disordered A1 FePt and (b) completely ordered $L1_0$ FePt phase.
1.4. Magnetic properties

1.4.1. Magnetic moment

The necessary condition for the appearance of a magnetic moment is the existence of partially filled shells. Ferromagnetic order follows from the interplay between the exchange (Coulomb) interactions and the Pauli principle. The origin of the spin magnetic moment ($\mu_s$) in the materials considered here can be understood on the basis of the itinerant ferromagnetism model. In this theory, often called Stoner model, the ferromagnetism arises due to spontaneously spin-split bands. The difference between the centres of gravity $\Delta E$ determines the exchange-splitting of the bands with the corresponding parameter $I = \Delta E / \mu_s$ [Woh80]. The so-called Stoner criterion for ferromagnetism

$$IN(E_F) \geq 1,$$

(1.5)

which requires strong exchange interactions and a large density of states at the Fermi energy $N(E_F)$, for pure elements is met only for Fe, Co and Ni. The resulting spin magnetic moment is directly given by

$$\mu_s = \mu_B (n_\uparrow - n_\downarrow) = -2\mu_B \langle S_z \rangle / h $$

(1.6)

where $n_\uparrow$ and $n_\downarrow$ are the number density of spin-up and spin-down electrons, respectively, and $\langle S_z \rangle$ is the expectation value of the spin operator along the z-direction.

Figure 1.6 shows the spontaneous splitting of energy bands for bcc Fe. The majority-spin $3d^\uparrow$ levels are only partially occupied, thus Fe is classified as a weak ferromagnet (Co and Ni are strong ferromagnets) despite its relatively large magnetic moment. In the Fe-Pt compounds, iron can be considered to be dense-packed. In the fcc local environment, the Fe moment is highly sensitive to interatomic spacing and lattice volume (Table 1.2). This large magnetovolume anomaly is associated with the weak ferromagnetism of iron [Pin86].

In agreement with the Stoner criterion (1.5) the Pt metal is paramagnetic (Table 1.2). However, exchange-enhanced paramagnetism is a well-known feature of Pt metal [Blu01] and thus Pt atoms can significantly contribute to the magnetic properties of intermetallic compounds.

In Fe-Pt alloys, both Fe and Pt atoms carry a magnetic moment. The origin of the induced magnetic moment on the Pt sites, as well as of the enhanced magnetic moment on the Fe sites can be understood in the following scheme [Daa91]. The enhanced Fe moment is a consequence of the hybridisation between the $3d(Fe)$ and $5d(Pt)$ states, as well as the hybridisation between both $d$ states and the free-electron-like $sp$ states. The bandwidths are 2.7 eV for the majority-spin ($3d^\uparrow$) and 2.0 eV for the minority-spin ($3d^\downarrow$) Fe bands and 2.7 eV for both $5d^\uparrow$ and $5d^\downarrow$ Pt bands. The exchange splitting of the Fe $d$ bands is 2.6 eV, thus the top of the Fe $3d^\uparrow$ and the bottom of the Fe $3d^\downarrow$ bands are separated by a small energy gap. Since the centre of gravity of the Pt $d$ bands is about 3.0 eV below that of the minority Fe $d$ bands, the $3d^\uparrow$ of Fe and both $5d$ bands of Pt are completely filled. Assuming no hybridisation
between the $d$ and $sp$ states and using Eq. (1.6) one would obtain a magnetic moment of Fe of $4 \mu_B$. In reality, it has a value of about $2.8 \mu_B$ (Table 1.2).

The hybridisation between the Fe $d$ and Pt $d$ states causes a significant broadening of the Fe and Pt majority-spin bands because they coincide in energy. The minority $d$ bands of Fe and Pt have a greater separation in energy and the hybridisation between their minority $d$ bands is weak. The minority-spin band remains small and the hybridisation introduces $0.4$ Pt $d$ holes. The oppositely magnetised free-electron-like $sp$ states reduce this spin moment to a value of $0.35 \mu_B$, as obtained by electronic structure calculations [Daa91, Sol95].

The total magnetic moment of Fe, as well as of Pt in the FePt compounds, is dominated by the spin component (Table 1.2). Nevertheless, there exist a small orbital moment

$$\mu_i = -\mu_0 \langle L_z \rangle / \hbar,$$

(1.7)

which arises due to a net orbital current from the $d$-electron motion around the nucleus. The motion of the orbiting electron should be larger in one than in the opposite direction. In magnetic materials, such a symmetry breaking is caused by spin-orbit (SO) coupling.

**Table 1.2.** Ground-state properties of Fe and Pt metals and L1$_0$ FePt: spin $\mu_S$, orbital $\mu_L$ and total $\mu_{tot}$ magnetic moments, spin-orbit splitting $\xi$, exchange-splitting $I$ and $IN(E_F)$ parameters. The values are taken from Refs. [Shi96, Sig94, Woh80, Daa91, Sol95, Gun76]. For $\gamma$-Fe, the magnetic moments calculated for different lattice parameters are given [Pin86].

<table>
<thead>
<tr>
<th></th>
<th>Lattice constant, Å</th>
<th>Magnetic moment, $\mu_0$</th>
<th>$\xi$, eV</th>
<th>$I$, eV</th>
<th>$IN(E_F)$</th>
</tr>
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<tbody>
<tr>
<td>Fe</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha$-Fe (bcc)</td>
<td>ferro</td>
<td>2.866</td>
<td>2.23</td>
<td>0.043</td>
<td>2.273</td>
</tr>
<tr>
<td>$\gamma$-Fe (fcc)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.07</td>
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<tr>
<td></td>
<td></td>
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<td></td>
<td></td>
<td>0.92</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.5-1.7</td>
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<tr>
<td>Pt</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<td></td>
<td>0.4</td>
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<td></td>
<td></td>
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<td>0.5</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>FePt</td>
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</tbody>
</table>

*Fig. 1.6. Calculated density of states for $\alpha$-Fe showing spontaneous splitting of energy bands. The $\uparrow$ density is plotted positive and $\downarrow$ negative (adapted from [Coey 1996]).*
connected with the presence of polarised spins. The \( d \)-electron orbits may be anisotropic by
bonding alone, but without SO coupling they will possess time reversal symmetry \([Stö95]\).
The size of the orbital moment in different directions depends, therefore, on the crystal
symmetry and the size of the SO coupling. In the 3\( d \) metals, the small value of the orbital
moment is a consequence of the crystal-field quenching of the orbital moment and small SO
coupling parameter \( \xi \) \([Eri90]\). In the heavy Pt metal, the SO coupling is an order of
magnitude larger than that in iron (Table 1.2).

### 1.4.2. Magnetocrystalline anisotropy

The magnetocrystalline anisotropy (MCA) is the difference in the free energy, when
the magnetisation direction changes from the magnetically easy axis to the magnetically
hard axis. MCA arises through SO interaction, which couples the isotropic spin moment to
the crystal lattice \([Van37]\). The reason for the strong MCA in L\( 1_0 \) FePt is the large spin-orbit
coupling in Pt and the 5\( d \)(Pt)-3\( d \)(Fe) hybridisation, both transforming the effect of the
tetragonal lattice on the orbital electron wave functions into a strong dependence of the free
energy on the direction of magnetisation \( M_s \) \([Daa91, Ost03, Sta04]\).

In a simple phenomenological description \([Von71]\) the MCA is characterised by the
anisotropy constant

\[
K_1 = \frac{H_A J_s}{2},
\]

where \( H_A \) is the anisotropy field and \( J_s = \mu_0 M_s \) is the spontaneous polarisation. The first
anisotropy constant of L\( 1_0 \) FePt \( K_1 = 6.6 \text{ MJ/m}^3 \) (Table 1.3) is larger than that of some rare-
earth transition-metal compounds used in modern permanent magnets, Nd\(_2\)Fe\(_14\)B (4.9 \text{ MJ/m}^3) and Sm\(_2\)Co\(_{17}\) (3.3 \text{ MJ/m}^3) \([Coe96]\). Both experimental data and electronic
structure calculations indicate a correlation between the degree of the LRO within the L\( 1_0 \)
phase and the MCA: the latter increases linearly with the LRO parameter \([Kam99, Oka02,
Sta04, May89]\). As pointed out in Section 1.2, the tetragonal symmetry of the L\( 1_0 \) structure is
mainly caused by chemical ordering of the cubic A\( 1 \) structure. The MCA will be influenced
by this chemical ordering as well as by an additional distortion of the lattice resulting in a
change of the tetragonal lattice parameters (Section 1.2). However, because these
phenomena are strongly correlated with each other it is difficult to experimentally separate
their influences on MCA. In the literature this topic has been discussed controversially.
Whereas Weller et al. \([Wel00]\) consider the lattice distortion as the main reason for the large
MCA, Ostanin et al. \([Ost03]\) and Opahle et al. \([Opa05]\) conclude from results of electronic
structure calculations that the lattice distortion has a much smaller effect on MCA than the
effect of chemical ordering. Assuming the first scenario, even small deviations of the \( c/a \)
ratio in the nanocrystalline compound from its bulk value would have a strong influence on
the MCA, disregarding the chemical ordering. In the second scenario, such effects would
have only a moderate influence on the MCA.
Magnetic properties

The MCA of the cubic ferromagnetic phases of the Fe-Pt system is orders of magnitude smaller than that of $L1\text{\textsubscript{0}}$ FePt. This is a consequence of different scaling laws of the MCA energy with the SO-parameter. Whereas in cubic systems the MCA energy scales with $\xi^4$, in tetragonal systems the strength of SO interaction is a second order contribution in terms of perturbation theory [Ric98].

### 1.4.3. Magnetic order

In the disordered state, the intermetallic compounds of the Fe-Pt system are ferromagnetic and their total magnetic moment obeys a law of mixing of atomic moments of Fe and Pt, equal to $2.75 \mu_B$ and $0.3 \mu_B$, respectively [Men74]. In Fe$_{100-x}$Pt$_x$ alloys for $x \leq 25$ the martensitic transformation takes place at room temperature and above (Fig. 1.2). The $L1\text{\textsubscript{2}}$ ordered Fe$_3$Pt compound is ferromagnetic with a high value of room-temperature saturation magnetisation and a Curie temperature $T_c$ of about 410 K [Men75, Sum78]. The alloys around the Fe$_3$Pt stoichiometry are also known to reveal the Invar effect [Was90]. The ordered $L1\text{\textsubscript{0}}$ FePt is ferromagnetic with relatively high values of $T_c = 750$ K and $J_s = 1.43$ T. $L1\text{\textsubscript{2}}$ FePt$_3$ is paramagnetic at room temperature and can exhibit two types of antiferromagnetic order below 160 K [Bac63, Maa01]. Such a wide variation of the magnetic structure types in the Fe-Pt alloys is evidently a consequence of various atomic configurations around Fe atoms, which, in turn, has a considerable effect on the electronic structure of these alloys.

In a local-moment description of ferromagnets, the Curie temperature is determined by the strength of exchange interactions between the atoms. Such a description works

Table 1.3. The room temperature magnetic behaviour (\textit{para} – paramagnetic; \textit{ferro} – ferromagnetic; \textit{af} – antiferromagnetic) and magnetic properties of the main phases in the Fe-Pt system: the Curie temperature $T_c$, the anisotropy constant $K_i$, the anisotropy field $H_A = 2K_i/\mu_0 M_s$, the saturation magnetisation $M_s$, the upper limit of energy density $(BH)_{\text{max}} = \mu_0 M_s^2/4$, the domain wall width $\delta_w$, the exchange length $l_{\text{ex}}$ and the critical single-domain particle size $D_c$. The values are taken from Refs. [Kus50, Bac62, Iva73, Men74, Men75, Sum78, Kne91, Sko99a, Vla00, Maa01, Hai03b].

<table>
<thead>
<tr>
<th></th>
<th>$T_c$ (K)</th>
<th>$K_1$ (MJ/m$^3$)</th>
<th>$\mu_0 H_A$ (T)</th>
<th>$\mu_0 M_s$ (T)</th>
<th>$\mu_0 M_s^2/4$ (kJ/m$^3$)</th>
<th>$\delta_w$ (nm)</th>
<th>$l_{\text{ex}}$ (nm)</th>
<th>$D_c$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FePt</td>
<td>para</td>
<td>585</td>
<td>1.5</td>
<td>448</td>
<td>≈ 15</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Disordered FePt</td>
<td>ferro</td>
<td>428</td>
<td>0.8</td>
<td>127</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FePt$_3$</td>
<td>ferro</td>
<td>410</td>
<td>1.8</td>
<td>645</td>
<td>≈ 15</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ordered FePt</td>
<td>ferro</td>
<td>750</td>
<td>11.5</td>
<td>510</td>
<td>6.3</td>
<td>2.0</td>
<td>560</td>
<td></td>
</tr>
<tr>
<td>FePt$_3$</td>
<td>para (af at T &lt; 160 K)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha$-Fe</td>
<td>ferro</td>
<td>1043</td>
<td>0.046</td>
<td>2.16</td>
<td>928</td>
<td>30</td>
<td>1.5</td>
<td>7</td>
</tr>
</tbody>
</table>

The values are taken from Refs. [Kus50, Bac62, Iva73, Men74, Men75, Sum78, Kne91, Sko99a, Vla00, Maa01, Hai03b].
rather well also in most of itinerant-electron dominated magnetic materials [Mor85, Moh03]. Chemical ordering changes the local environment by changing the relative number of different types of nearest-neighbour atomic pairs. Moreover, the interatomic exchange interactions depend on the distance between atoms. For instance, in L1_0 FePt, Fe-Fe interactions are ferromagnetic in (001) Fe planes and antiferromagnetic along the [001] direction, while Fe-Pt interactions are ferromagnetic [Mry04]. In the disordered alloys around the Fe3Pt stoichiometry, Fe-Pt interactions are ferromagnetic, whereas Fe-Fe and Pt-Pt interactions are antiferromagnetic [Nik74]. The Fe-Pt exchange interactions are responsible for the stabilisation of ferromagnetic order in Fe-Pt alloys [Nik74, Mry04, Lin83]. Thus, chemical ordering is expected to influence $T_c$, which is indeed observed [Lin83, May89, Oka02, Zen02b]. In contrast, the saturation magnetisation of the L1_0 phase was reported to be largely independent of the degree of order at a fixed composition, whereas the total magnetisation was found to increase with Fe content [Oka02, May89]. The interpretation of the magnetisation data is, however, complex and the data do not provide sufficient information about the individual atomic moments. In this work, it will be shown that, unexpectedly, the Fe moment decreases with increasing Fe content (Chapter 6).

The Stoner model of itinerant ferromagnetism usually gives a good description of the magnetic ground state at 0 K. At finite temperatures, however, the magnetic moment vanishes, as the exchange-splitting $\Delta E$ goes to zero and the Curie temperature, $T_c$, is much overestimated [Woh80, Ric98]. Somewhat improved theoretical $T_c$ values are obtained by taking into account spin-flip Stoner excitations and collective long-wavelength spin fluctuations [Moh87]. In the above mentioned local-moment description, the Hamiltonian is given by

$$\hat{H} = -\frac{1}{2} \sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$$

in the nearest neighbour Heisenberg model, where the constant $J_{ij}$ is the exchange integral (positive for ferromagnetic and negative for antiferromagnetic coupling) and $\mathbf{S}_i$ is the spin. The Heisenberg model can be solved in the mean-field approximation (nearest-neighbour pair interaction model [Von71]), which provides a satisfactory agreement with experiment [Miz73, Nik74, May89, Lin83, Hal97]. Apparently, interaction between more distant pairs of atoms, the dependence of the exchange integral on the interatomic distance, as well as the directional anisotropy of exchange interactions (in L1_0 FePt [Zen02b]) should be considered for a better description of the $T_c$ variation in Fe-Pt alloys.

The mean-field theory is able to account for the existence and the approximate temperature dependence of spontaneous magnetisation $M_s(T)$, but cannot reproduce all the details of its behaviour below $T_c$, in particular, in the two limiting cases, $T/T_c \to 0$ and $T/T_c \to 1$. To describe the dependence $M_s(T)$ in the full temperature range, the following function was proposed [Kuz05]:

$$\frac{M_s(T)}{M_s(0)} = \left[ 1 - \gamma \left( \frac{T}{T_c} \right)^{3/2} \right] - (1 - \gamma) \left( \frac{T}{T_c} \right)^{5/2} \right]^{1/3},$$

(1.10)
where \( M_s(0) \) is the magnetisation at 0 K and \( \gamma \) is a so-called shape parameter. Eq. (1.10) is constructed to obey Bloch’s 3/2 power law at low temperatures \( T/T_c \to 0 \), \( M_s(T)/M_s(0) = 1 - a T^{3/2} \), whereas \( M_s(T)/M_s(0) \sim (T_c - T)^{1/3} \) in the critical region \( T/T_c \to 1 \), as obtained from the critical behaviour of the Heisenberg model [Blu01]. The shape parameter \( \gamma \) is determined by the dependence of the intensity of the exchange interaction, including its sign, on the interatomic distance [Kuz06].

1.5. Magnetisation processes of nanocomposite systems

1.5.1. Hard/soft nanocomposites

The interactions on the atomic scale discussed in Section 1.4 determine the intrinsic magnetic properties of a material, such as the spontaneous magnetisation \( M_s \), the Curie temperature \( T_c \) and the magnetocrystalline anisotropy constant \( K_1 \). The extrinsic magnetic properties, e.g. remanent magnetisation (remanence) \( M_r \) and coercive force (coercivity) \( H_c \), are related to magnetic hysteresis (the dependence of the magnetisation as a function of the applied magnetic filed) and are determined to a great extent by the microstructure. Another key characteristic of a permanent magnet is the energy product \( (BH)_{\text{max}} \), which is twice the maximum magnetostatic energy available from a magnet of optimal shape. The energy product increases both with increasing coercivity and remanence. However, for materials with sufficiently high \( H_c \) (\( H_c \geq M_r/2 \)), the energy product can never exceed the value \( \mu_0 M_s^2 / 4 \). Driven by this limitation, research has focused on developing new high anisotropy materials with high \( M_s \) and \( T_c \) [Coe96]. Nevertheless, the magnetisation values \( \mu_0 M_s \) of the modern hard magnetic intermetallic compounds are still significantly lower than those of \( \alpha \)-Fe (2.16 T), Co (1.8 T) or Fe\(_{65}\)Co\(_{35}\) (2.43 T).

The remanent magnetisation of real magnets is usually below its saturation value (mostly due to lack of grain alignment). In particular, the remanence-to-saturation ratio \( M_r/M_s \) is limited to 0.5 for magnets composed of non-interacting uniaxial randomly oriented particles. The processing route for obtaining an anisotropic magnet is in general more sophisticated than that for a non-textured magnet, thus justifying the efforts to obtain a better \( M_r/M_s \) ratio in the latter. It has been possible to achieve remanence enhancement in the so-called exchange-spring or exchange-coupled magnets [Coe88, Eck90, Kne91]. In general, remanence enhancement in this type of magnets is attributed to intergrain coupling via exchange interaction. This coupling causes the magnetisation of neighbouring grains to deviate from their particular easy axis resulting in a magnetisation increase parallel to the direction of the applied field.

One may distinguish between assemblies of high anisotropy (hard magnetic) grains (see, e.g. [Cle88, Man91]) termed single-phase exchange-coupled magnets and a combination of a less anisotropic (soft magnetic) phase with a high anisotropy phase called nanocomposite exchange-coupled magnets. The latter class of materials presents the basic idea of the exchange-spring principle: adding the less anisotropic phase with its high magnetisation enhances the remanence, while the high magnetic anisotropy of the hard
magnetic phase ensures a sufficiently large coercivity. The result should be a nanocomposite permanent magnet with the highest possible energy product \((BH)_{\text{max}}\). However, in order to profit from the combination of the beneficial properties of the constituent phases the demagnetisation behaviour of the composite material must be magnetically single phase (compare Fig. 1.7). Therefore, the soft magnetic phase should be exchange-coupled to the hard magnetic one and the microstructure has to be on the nanoscale \([\text{Kne91}]\). Remanence enhancement, single-phase demagnetisation behaviour and rather steep recoil loops \([\text{Eck90}]\) are general criteria for the presence of exchange-spring behaviour. The large reversible portion of the demagnetisation curve corresponds to an energy recovery, as in the case of a mechanical spring, from which the term “exchange-spring magnet” is derived.

A starting point for the development of exchange-coupled permanent magnets was a publication by Coehoorn et al. \([\text{Coe88}]\) reporting remanence-enhancement in a nanocomposite magnet consisting of the hard magnetic Nd\(_2\)Fe\(_{14}\)B phase and soft magnetic Fe\(_3\)B and \(\alpha\)-Fe. Various combinations of hard magnetic phases with soft magnetic phases have been synthesised including RzFe\(_{14}\)B/\(\alpha\)-Fe (R = Nd, Pr), Sm\(_2\)Fe\(_{17}\)N(C)/\(\alpha\)-Fe, Sm-Co/\(\alpha\)-Fe(Co) and FePt/Fe\(_3\)Pt exchange-coupled nanocrystalline bulk magnets \([\text{Coe88, Man93, Din93, Feu96, Hir97, Had99, Bol02}]\), as well as thin films and multilayers \([\text{Par96, Alo95, Ful99, Liu98, Zen02a}]\). The exchange-coupling concept has its origin in the random-anisotropy theory \([\text{Imr75, Cal77}]\). Kneller and Hawig \([\text{Kne91}]\) have proposed a one-dimensional model of the micromagnetic structure of the exchange-coupled nanocomposite material. The simplified model assumes a uniaxial anisotropy of both phases. The reversal process was supposed to occur by (reversible) magnetisation reversal starting in the soft magnetic phase. The field at which the reversal mode penetrates the hard magnetic phase is called the nucleation or switching field, \(H_n\), and corresponds to an irreversible magnetisation reversal. A number of theoretical approaches have been addressed to analyse the magnetisation reversal of exchange-spring magnets, either bulk or multilayer \([\text{Sko93, Sch94, Lei97a, Fis98a, Ful98, Sab98}]\). A review of these methods has been given by Solzi et al. \([\text{Sol02}]\). In general, these approaches find that the most important parameters are dimensions, relative amounts and distribution of ferromagnetic phases with small and large magnetocrystalline anisotropy (Section 1.5.3).
1.5.2. Micromagnetic parameters

In equilibrium, the configuration of a ferromagnetic body follows from a complex interplay between the various contributions to the free energy. For instance, a large particle may subdivide into differently oriented magnetic domains, regions spontaneously magnetised to saturation, to minimise its magnetostatic energy. Nevertheless, the system must spend an energy to create the domain boundaries, domain walls, and for small particles the cost of creating a domain wall exceeds the gain in magnetostatic energy. For spherical particles with uniaxial anisotropy, a rough estimate of the critical single-domain diameter gives \[ D_c = \frac{72\sqrt{AK_1}}{\mu_0 M_s^2}, \] where \( A \) is the exchange stiffness constant. The critical single-domain diameter \( D_c \) is an equilibrium property. In contrast, hysteresis is a nonequilibrium phenomenon caused by energy barriers. Furthermore, equilibrium domains are qualitatively different from the nonuniform magnetisation states occurring during magnetisation reversal.

The magnetisation process represents the response of a ferromagnetic material to an external magnetic field \( H \). This corresponds to an addition of the field interaction term \( E_{ext} = -\mu_0 M \cdot H \) to the free energy of the system in the continuum description of magnetism, usually called micromagnetism [Bro62]. The particular mechanism of magnetisation reversal and the details of magnetic hysteresis depend again on the competition among different energy contributions. In general, the ferromagnetic exchange favours the parallel alignment of the magnetic moments, irrespective of their direction; the anisotropy promotes alignment of the moments along specific directions (easy axes); the magnetostatic energy favours configurations for which the magnetisation follows closed paths inside the sample to avoid stray fields. To deduce the magnetisation configuration realised in the system one has to minimise the micromagnetic total free energy functional

\[
\delta G = \delta \int_V (E_{ex} + E_A + E_d + E_{ext}) dV = 0, \tag{1.12}
\]

where \( E_{ex} = A(\nabla m)^2 \) is the exchange energy density (\( m(r) = M(r) / M_\text{r} \) is the vector of magnetisation direction), \( E_A \) represents the anisotropy energy density, containing any crystal and/or structural contributions, and \( E_d \) is the magnetostatic energy density.

The origin of the magnetostatic energy is a long-range magnetic dipolar interaction. The so-called stray field is defined as the magnetostatic field generated by the divergence of magnetisation \( \nabla \cdot H_d = -\nabla \cdot M \) [Sol02]. Inside the sample volume, \( H_d \) is termed demagnetising field, since usually its direction is opposite to that of \( M \). In homogeneous ellipsoids of revolution magnetised along the axis of revolution the demagnetising field is equal to
\[ H_d = -NM, \quad (1.13) \]

where \( N \) is the **demagnetising factor**, a symmetric tensor with eigenvalues \( N_i \) \((i = 1; 2; 3)\) that obeys: \( \sum N_i = 1; N_i \geq 0 \) [Osb45]. A situation, when a magnet is magnetised homogeneously, is rarely encountered in practice. Often demagnetising-field irregularities are ascribed to inhomogeneous magnetic fields naturally occurring in real magnets. However, exchange interactions and particle size may also contribute to the demagnetising behaviour (Section 1.5.3). The exchange contribution is particularly relevant in nanocomposite magnets [Sko99b]. A common practice to account for the demagnetising field is using the shearing procedure to correct the hysteresis loops measured in open-circuit measurements. The procedure consists in considering skewed reference curves \( M(H-NM) \) instead of \( M(H) \). Inhomogeneous magnetisation states, often encountered in nanostructured materials, cannot be described in terms of macroscopic demagnetising factors and the shearing procedure may yield an overskewing of the loops. For instance, by applying the shearing procedure to e.g. a thin film with the “appropriate” out-of-plane \( N = 1 \) often leads to an unphysical loop shape, overskewing [Sko00a, Han04]. An approximate skewing procedure, based on the assumption of an infinite slope \( dM/dH = \infty \) at \( H = H_c \), results in \( N = 0.5 \) for thin films [Han04, Liu98] and \( N = 0.33-0.4 \) for epoxy-bonded powders investigated in the present work (see Appendix A).

Dimensional analysis of Eq. (1.12) yields two fundamental length scales. The competition between exchange and magnetostatic energy is expressed in terms of the exchange length

\[ l_{ex} = \frac{A}{\mu_0 M_s^2}. \quad (1.14) \]

It determines, for example, the transition from coherent rotation to curling (Section 1.5.3) and the grain size below which the hysteresis loops of two- or multi-phase magnets show a single-magnetic-phase behaviour (Fig. 1.7). The comparison between exchange and anisotropy may be expressed by means of the wall-width parameter

\[ \delta_w = \sqrt{A/K_1}, \quad (1.15) \]

which determines the thickness of the domain wall separating magnetic domains and the spatial response of the magnetisation to local perturbations [Sko03]. The values of \( l_{ex} \) and \( \delta_w \) for \( L_1 \) FePt and \( \alpha \)-Fe are listed in Table 1.3 and are typical for hard and soft magnetic materials, respectively.

**1.5.3. Magnetisation reversal**

The Stoner-Wohlfarth theory [Sto48] substantially overestimates the coercivity \( H_c \). A key problem of coercivity theory is to determine \( H_c \) for real microstructures [Aha60]. A
widely used phenomenological way of discussing magnetisation reversal is the analysis based on the equation \[Adl85, Dur85, Kro88\]

\[ H_c = \alpha_K \frac{2K_1}{\mu_0 M_s} - N_{eff} M_s, \]  

(1.16)

where \(\alpha_K\) is a real-structure dependent parameter (less than unity), describing the reduction of anisotropy by defects and misaligned grains, and \(N_{eff}\) is an effective demagnetising factor, which can be larger than unity. The values \(\alpha_K\) and \(N_{eff}\) depend on the mechanism responsible for coercivity, either nucleation or pinning \([Giv96]\). Nucleation-controlled magnets are, ideally, defect- and domain-free and the coercivity is essentially given by a nucleation field (in micromagnetism, the term nucleation refers to the instability of a remanent state in a reverse magnetic field \(H = -H_n\)). In contrast, pinning-type magnets contain pronounced inhomogeneities, which ensure coercivity by impeding the motion of domain walls.

In structurally homogeneous (\(\alpha_K = 1\) in Eq. (1.16)) ellipsoids of evolution with an easy axis parallel to the axis of revolution, there are two exact solutions \([Sko99a]\). If the ellipsoid’s radius \(R\) is smaller than a coherence radius \(R_{coh}\), the dominating exchange interactions yield coherent (uniform) rotation or Stoner–Wohlfarth reversal (Fig. 1.8(a)). For radii larger than \(R_{coh}\), magnetostatic interactions give rise to an incoherent curling mode (Fig. 1.8(c)). For spheres and long cylinders \(R_{coh} = 5l_{ex}\) and \(R_{coh} = 3.7l_{ex}\), respectively. Coherent rotation and curling yield the following nucleation fields

\[ H_n = \frac{2K_1}{\mu_0 M_s} - \frac{1}{2} (3N - 1)M_s, \]  

(1.17)

and

\[ H_n = \frac{2K_1}{\mu_0 M_s} - \left( N - \frac{c(N)A}{\mu_0 M_s^2 R^2} \right) M_s, \]  

(1.18)

respectively \([Sko99a]\). Here \(c(N)\) is a factor depending on particle geometry. The multiplier before \(M_s\) is the effective demagnetising factor \(N_{eff}\) in Eq. (1.16). An attempt to use the

![Fig. 1.8. Nucleation modes in spheres surrounded by a hard-magnetic shell: (a) coherent rotation, (b) bulging, (c) curling and (d) clamped curling. The figures are top views on the equator plane and the arrows show \(m(r)\) for the core phase (white) and in the hard magnetic environment (grey) \(m(r) = 0\). (adapted from [Sko03]).](image-url)
nucleation fields (1.17) and (1.18) as an estimate for the coercivity of real magnets fails, because already a single nanoscale inhomogeneity may initiate the magnetisation reversal of the whole magnet. This localised nucleation leads to a strong reduction of $H_n$ and explains Brown’s paradox [Bro57], according to which the observed coercivity is often considerably smaller than predicted by (1.17)-(1.18).

A further reversal mode postulated recently is called the bulging nucleation mode [Sko99b], which may occur in spherical soft magnetic particles surrounded by a very hard-magnetic matrix (Fig. 1.8(b)). This condition is particularly relevant for nanocomposite hard/soft bulk magnets. The bulging mode exhibits the same radial angular symmetry of the coherent mode, but the exchange between the soft and the hard magnetic phases generates a radial inhomogeneity of the magnetisation. As a consequence, the nucleation field depends in this case on the exchange stiffness and on the particle size, as for the curling mode:

$$H_n = \frac{2K_1}{\mu_0 M_s} + 2\pi^2 \frac{A}{\mu_0 M_s^2 R^2 M_s},$$  \hspace{1cm} (1.19)$$

and is highest for smaller soft magnetic inclusions in the hard matrix. For larger inclusion diameters ($R \sim l_\text{ex}$) a clamped curling mode is realised (Fig. 1.8(d)), that is, $\mathbf{m}(r) = 0$ at the soft/hard interface.

The nucleation fields (1.17)-(1.19) are obtained without taking into account the morphology of real magnets, which gives rise to random stray fields and local variations of anisotropy in both strength and direction. The two factors contribute to the strong reduction of the nucleation field and make the hysteresis loops nonrectangular. The spin structure of isotropic magnets has been studied in the context of the random-field problem, where individual magnetic moments or particles are assumed to be subject to a local (anisotropy) field with random orientation [Imr75, Her89]. The number of correlated spins was found to depend on the competition between the random (anisotropy) field and exchange energies. Based on this model, a dimension $R \sim \delta_s$ was obtained, below which the exchange energy starts to balance the anisotropy energy, i.e. grains yield intergranular correlations. As a consequence, the macroscopic anisotropy $K_{\text{eff}}$ of an assembly of interacting grains with mean dimension $R$ and random fluctuating anisotropy $K_1$ scales down as

$$K_{\text{eff}} \sim \frac{K_1^4}{A^3} R^6.$$ \hspace{1cm} (1.20)$$

It is evident that there is a very strong reduction of the anisotropy with decreasing grain size. This effect was exploited to reduce the coercivity of nanocrystalline soft magnetic materials [Yos88, Her89]. The random anisotropy model, with some modifications, has also been applied to nanocrystalline hard magnetic materials to account for the observed coercivity [Sun90]. One has to note, however, that the macroscopic anisotropy reduction does not necessarily imply a similar reduction of coercivity, which is determined by a particular microstructure [Gie92, Sol02].
The coercivity reduction due to random anisotropy is undesired in permanent magnets. On the other hand, the grain size reduction in polycrystalline materials is advantageous for improving the remanence by favouring parallel spin arrangement in neighbouring grains (remanence enhancement with respect to an ensemble of noninteracting particles). The remanence enhancement is a consequence of the competitive effects of magnetocrystalline anisotropy within each grain and exchange interactions between neighbouring grains.

The macroscopic parameters, such as $J_r$, $H_n$ and $(BH)_{\text{max}}$, of nanocomposite systems can be described by using a simplified one-dimensional model of a triple layer (Fig. 1.9) [Lei97a]. In particular, it was shown that the nucleation field for irreversible magnetisation reversal $H_n$ is a function of the soft layer thickness $d_s$. For soft layers thinner than the hard-magnetic wall-width parameter $\delta_w^h$, the nucleation field is independent of $d_s$ and is identical to $H_n$ of the hard magnetic phase. The magnetisation reversal takes place by homogeneous rotation. For $d_s = (1-10)\delta_w^h$, the nucleation field decreases steeply with increasing $d_s$. Consequently, a nonhomogeneous (irreversible) rotation mechanism dominates the magnetisation reversal, although a reversible process still coexists due to exchange coupling [Lei97b]. The hysteresis loop is no longer rectangular in shape and one can distinguish a kink denoting the presence of a soft magnetic phase. Nevertheless, the hysteresis behaviour of the system can be considered single-phase. For very thick soft layers ($d_s \gg \delta_w^s$), the hard and soft magnetic phases are decoupled, and the hysteresis loop is typical of a two-phase system with two different nucleation fields (Fig. 1.7). The magnetisation reversal takes place by inhomogeneous rotation of the moments independently in the hard and soft magnetic phases. With regard to the remanence, the critical parameter is the wall-width parameter of the soft phase $\delta_w^s$. For a soft layer thickness $d_s < \delta_w^s$, the easy direction of the hard magnetic layer determines the orientation of the magnetisation of the whole system (i.e. the soft layer anisotropy is negligible), whereas for $d_s > \delta_w^s$, the remanence depends on the direction of the easy axis of the soft magnetic phase. If $d_s < \delta_w^h$, $(BH)_{\text{max}}$ will be of the same order of magnitude or higher than that of the pure hard magnetic phase. The maximum gain in $(BH)_{\text{max}}$ can be achieved if the
hard layer thickness is equal to $d_s$. Therefore, to exploit at best the exchange-spring behaviour, one has to adjust the hard-to soft volume ratio.

A disadvantage of the above described model is a restriction to simple geometries and disregard of stray-field effects. Numerical micromagnetic simulations based on the finite-element method effectively take into account the microstructure of the system, including magnet shape and details of irregular grain structure [Sch94, Fis96, Fis98b, Sch98]. They enabled a quantitative description of the correlation between the microstructure and the magnetic properties of two- and three-dimensional isotropic soft/hard nanocomposites and single-phase exchange-coupled magnets. It was shown that the magnetisation reversal is mainly determined by short-range exchange and long-range dipolar interactions. Exchange interactions are responsible for remanence enhancement and coercivity reduction. Due to the short-range character of exchange interactions ($\sim \delta_w$), the spatial extension of the soft magnetic phase plays a decisive role in the magnetisation reversal process. In order to obtain the maximum remanence in nanocomposite magnets, the nucleation of the moments of the soft magnetic phase should be avoided for positive applied external fields, which corresponds to the condition

$$d_s \leq 2\delta_w \quad (H \geq 0).$$

The maximum coercivity is obtained by suppressing the magnetisation reversal of the hard magnetic phase induced by the reversed moments of the soft magnetic phase. That means,

$$d_s \leq 2\delta_w \quad (H \approx H_c).$$

Therefore, the optimised grain structure of composite magnets consists of soft magnetic grains smaller than $2\delta_w$ embedded into the hard-magnetic matrix. For larger soft magnetic inclusions, the remanence reduces, the coercivity initially increases and eventually reduces, as the volume fraction of the soft magnetic phase becomes too high [Sch94, Fis96]. With increasing dimensions of the soft magnetic phase, as well as with a degradation of microstructure homogeneity, long-range magnetostatic interactions start to considerably influence the magnetisation processes. Local stray fields lead to strongly nonuniform magnetisation distributions, e.g. create magnetic vortex structures within soft magnetic regions [Fis98b], and, therefore, assist the magnetisation reversal. Consequently, the increased stray fields further reduce the coercivity.

### 1.5.4. Intergrain interactions

As discussed in Section 1.5.3, in materials consisting of small particles in close contact with each other, magnetisation reversal is influenced by magnetic interactions (of exchange or dipolar origin) between grains or particles. As a result of intergranular correlations, the magnetic microstructure of nanostructured materials changes as well and a formation of so-called interaction domains extending across a large number ($\sim 10^{1-3}$) of grains is observed [Cra60, Cra69, Cre01, Xu01].
The micromagnetic mean-field model \[\text{Sko01}\], the Preisach model \[\text{Von71}\] and approaches based on Wohlfarth’s remanence relation \[\text{Woh58}\], such as Henkel- and \(\Delta M\)-plots \[\text{Hen64, May91}\], are often used to describe interaction between particles or grains. In the mean-field approach, the influence of neighbouring grains or particles is treated in terms of an effective field

\[
H_{\text{eff}} = H + \Lambda M , \tag{1.23}
\]

where \(\Lambda\) is a coupling parameter. However, the mean-field method does not correctly estimate the effect of magnetic interactions on e.g. the nucleation field \[\text{Bro62, Cal77}\].

Wohlfarth’s remanence relation

\[
J_d(H) = J_r - 2J_r(H) \tag{1.24}
\]

predicts the remanent polarisation \(J_d(H)\) acquired after dc saturation in one direction and subsequent removal of a reverse field \(H\) as a function of the isothermal (non-saturated) remanent polarisation \(J_r(H)\) measured after the field \(H\) had been applied to the (thermally or ac-field-) demagnetised sample and then the field has been removed. Consequently it follows \(J_r(\infty) = J_r\) as the (saturated) remanence of the material. The applicability of Eq. (1.24) is limited to noninteracting single-domain particles with uniaxial anisotropy. In the case of interactions, it is suitable to use the Henkel plot, where \(J_r(H)\) is plotted against \(J_d(H)\) and Eq. (1.24) yields a straight line for a system, where the validity requirements are verified. Alternatively, one can plot the quantity \(\Delta J(H)\) defined as

\[
\Delta J(H) = \frac{J_d(H) - [J_r - 2J_r(H)]}{J_r} , \tag{1.25}
\]

and known as delta-\(M\) or delta-\(J\) plot. Non-vanishing \(\Delta J(H)\) values are considered to be indicative for the presence of magnetic interactions. Positive \(\Delta J(H)\) values are interpreted as being due to exchange (magnetising type) interactions and negative \(\Delta J(H)\) values to magnetostatic (demagnetising type) interactions \[\text{May91, Che00}\]. Deviations from Eq. (1.25) are not necessarily due to interparticle interactions, but may also be due to multidomain and incoherent rotation effects \[\text{Woh58, Sko01}\].

One of the characteristics of exchange-spring magnet materials is the (nearly) reversible rotation of the magnetically soft component of magnetisation at fields below the switching field of the hard magnetic phase. The reversible portion of the change of polarisation is given by \[\text{Kne91}\]

\[
\Delta J_{\text{rev}}(H) = \left[ J_d(H) - J(H) \right] / J_r , \tag{1.26}
\]

while the irreversible portion of polarisation change,

\[
\Delta J_{\text{irr}}(H) = \left[ J_r - J_d(H) \right] / 2J_r , \tag{1.27}
\]

is the change in remanent polarisation after the reverse field has been removed. Here \(J(H)\) is the polarisation obtained after saturation and subsequent application of the reverse field \(H\).
A way to interpret magnetisation processes is to consider the degree of their cooperativity [Sko03]. The term cooperative refers to the involvement of two or more particles, as opposed to an ensemble of noninteracting particles. Cooperative effects can be useful in permanent magnets, where they suppress the effect of anisotropy field fluctuations resulting e.g. in the vanishing of the two-phase behaviour of hysteresis loops (Fig. 1.7). By definition, the coherent-rotation and curling modes are cooperative. Weakly interacting particles and grains are cooperative from the point of view of intraparticle magnetisation processes, but noncooperative from the point of view of interparticle interactions.

The nucleation behaviour of a system consisting of interacting particles can be obtained from the analysis of the switching field distribution (SFD), given by

$$\chi_{\text{irr}} = d(\Delta J_{\text{irr}})/dH.$$  

In a simple interaction model [Sko01], one may consider two particles, $A$ and $B$, coupled by an exchange or magnetostatic interaction and characterised by nonequal switching fields (anisotropy constants) $H_A (K_A)$ and $H_B (K_B)$, where $H_B \geq H_A (K_B \geq K_A)$. For $K_B \gg K_A$ a broad switching field distribution is obtained, whereas for $K_B = K_A$ and a switching field distribution is narrow. In the case of a broad SFD the magnetic reversal is noncooperative, and the particles $A$ and $B$ switch at different reversed fields $H$ (Fig. 1.10(b)). By contrast, for $K_B = K_A$ the magnetisation reversal is cooperative (Fig. 1.10 (c,d)).

In this work, it has been shown that there exist further reversal modes in addition to the rotation mechanisms shown in Fig. 1.10. Rigorous calculations and an analysis of a two-particle interaction model will be presented in Chapter 2.
Chapter 2

A two-particle interaction model

The reversal behaviour of a system consisting of magnetically interacting particles is greatly complicated by interactions between them. Exact solutions are possible only in a few simple cases and have been obtained e.g. for the case of dipole interaction between two identical uniaxial particles [Bro62, Che92]. Switching fields for a system consisting of two particles coupled by a certain interaction were obtained by Skomski and Sellmyer [Sko01], but no rigorous analysis has been made with respect to whether further reversal modes additional to those shown in Fig. 1.10 may exist. In this chapter, the appearance of a noncollinear reversal mode, corresponding to the exchange-spring reversal mode, will be demonstrated on the basis of a very simple interaction model. In the Stoner-Wohlfarth model, reversible rotation of the magnetisation is observed for particles with easy axes oriented at random [Sto48]. Here it will be shown that if two particles interact, a reversible magnetisation rotation is possible also when the easy axes are parallel to each other and to the applied field, provided additional conditions are fulfilled.

2.1. Model and critical fields

Let us consider two single-domain particles with a uniaxial anisotropy having identical volumes \( V \). The particles have different first anisotropy constants \( K_1 \) and \( K_2 \) (here always \( K_1 > K_2 \)) and are coupled by a ferromagnetic exchange interaction (magnetostatic interaction is not considered here at all). The easy axes of the particles are parallel (Fig. 2.1). After saturation in positive fields, both moments are aligned along their easy axes (\( \theta_1 = \theta_2 = 0 \)). If a reverse field \( H \) is applied in the direction parallel to the easy axes, magnetisation reversal starts at some critical (switching) field. Generally, the exchange interaction is given by

\[
E_W \sim -W(\cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos(\phi_1 - \phi_2)),
\]

where \( W \) is the coupling constant and \( \phi \) is the azimuth angle. For any \( \theta_1 \) and \( \theta_2 \) choosing \( \phi_1 - \phi_2 \neq 0 \) results

![Fig. 2.1. Two interacting single-domain particles.](image-url)
in an increase of the exchange energy (for $W > 0$). Thus, during magnetisation reversal the two moments and the applied field form a common plane and it is sufficient to minimize the following energy:

$$\frac{E}{V} = K_1 \sin^2 \theta_1 + K_2 \sin^2 \theta_2 + J_s H \cos \theta_1 + J_s H \cos \theta_2 - W \cos (\theta_1 - \theta_2), \quad (2.1)$$

where $J_s$ is the spontaneous polarisation (for simplicity, assumed to be identical for both particles). The angles $\theta_1$ and $\theta_2$ vary between 0 and $\pi$. The equilibrium conditions

$$\frac{\partial E}{\partial \theta_1} = K_1 \sin 2\theta_1 - J_s H \sin \theta_1 + W \sin (\theta_1 - \theta_2) = 0, \quad (2.2a)$$

$$\frac{\partial E}{\partial \theta_2} = K_2 \sin 2\theta_2 - J_s H \sin \theta_2 - W \sin (\theta_1 - \theta_2) = 0 \quad (2.2b)$$

yield three straightforward solutions, the stability of which has to be investigated

(I) $\theta_1 = \theta_2 = 0$;

(II) $\theta_1 = 0$ and $\theta_2 = \pi$;

(III) $\theta_1 = \theta_2 = \pi$.

The solution (III) is trivial, is stable and obviously reached for sufficiently large $H$. The stability conditions

$$\frac{\partial^2 E}{\partial \theta_1^2} \frac{\partial^2 E}{\partial \theta_2^2} - \left( \frac{\partial^2 E}{\partial \theta_1 \partial \theta_2} \right)^2 > 0 \quad \text{and} \quad \frac{\partial^2 E}{\partial \theta_2^2} > 0 \quad (2.4)$$

are satisfied simultaneously for the starting solution (I), $\theta_1 = \theta_2 = 0$, if

$$H > H_{11}^{(1)} \equiv \frac{K_1 + K_2 + W}{J_s} + \sqrt{\frac{(K_1 - K_2)^2 + W^2}{J_s^2}}, \quad (2.5)$$

$$H < H_{11}^{(2)} \equiv \frac{K_1 + K_2 + W}{J_s} - \sqrt{\frac{(K_1 - K_2)^2 + W^2}{J_s^2}}, \quad (2.6)$$

$$H < H_{11}^{(3)} \equiv \frac{2K_2 + W}{J_s}, \quad (2.7)$$

whereas the solution (II) can be stable for

$$H < H_{12}^{(1)} \equiv \frac{K_1 - K_2}{J_s} + \sqrt{\frac{(K_1 + K_2)^2 - 2W(K_1 + K_2)}{J_s^2}}, \quad (2.8)$$

$$H > H_{12}^{(2)} \equiv \frac{K_1 - K_2}{J_s} - \sqrt{\frac{(K_1 + K_2)^2 - 2W(K_1 + K_2)}{J_s^2}}, \quad (2.9)$$
where the indices $\uparrow \uparrow (\equiv \theta_1 = \theta_2 = 0)$ and $\uparrow \downarrow (\equiv \theta_1 = 0, \theta_2 = \pi)$ denote the stability of the corresponding magnetisation direction of the particles with respect to the applied reverse field. In deriving the stability regions of magnetisation states the foremost significance has the lower field, as this will be the critical field, at which a given state becomes unstable.

Because of the existence of solution (II) it is not trivial, in which way the magnetisation reversal occurs. There exist several limits of interest. The first one, $W \ll K_1 - K_2$, representing the case of weak interactions, yields the critical fields

$$H^{(3)}_{\uparrow \uparrow} = \frac{-2K_2 + W}{J_s}, \quad \text{(2.10)}$$

From (2.11) and $K_1 > K_2$ it follows that instability in the parallel alignment of the moments of the particles is determined by the critical field $H^{(2)}_{\uparrow \downarrow} (= H^{(3)}_{\uparrow \uparrow})$. For applied fields below $H^{(2)}_{\uparrow \downarrow}$ no reversal occurs. If one assumes that the state $\uparrow \downarrow$ is realised, then, as the applied field is increased further, the particles switch at different fields $H^{(2)}_{\uparrow \downarrow} = (2K_2 + W)/J_s$ and $H^{(1)}_{\uparrow \downarrow} = (2K_1 - W)/J_s$, i.e. magnetisation reversal occurs by noncooperative rotation.

In the limit of strong interactions, $W >> (K_1 + K_2)/2$, the conditions (2.4) resulting in the critical fields (2.8) and (2.9) cannot be fulfilled. The state $\uparrow \uparrow$ becomes unstable if $H$ exceeds the smallest field among those given by Eq. (2.5)-(2.7), which for $W > 0$ is always $H^{(2)}_{\uparrow \downarrow}$. In the limit of strong interactions, the reversal is cooperative.

Magnetisation reversal is cooperative and coherent, i.e. occurs by a simultaneous rotation of the two moments through equal angles in the same direction, if the anisotropies of both particles are equal, $K_1 = K_2 = K$. The stability analysis yields

$$H^{(1)}_{\uparrow \uparrow} = \frac{2K + 2W}{J_s} \quad \text{and} \quad H^{(2)}_{\uparrow \uparrow} = \frac{2K}{J_s}, \quad (\theta_1 = \theta_2 = 0), \quad \text{(2.13)}$$

$$H^{(1)}_{\uparrow \downarrow} = \frac{2K}{J_s} \sqrt{1 - \frac{W}{K}} \quad \text{and} \quad H^{(2)}_{\uparrow \downarrow} = \frac{-2K + W}{J_s}, \quad (\theta_1 = 0; \theta_2 = \pi). \quad \text{(2.14)}$$

The instability of the $\theta_1 = \theta_2 = 0$ state is determined by $H^{(2)}_{\uparrow \downarrow}$ of Eq. (2.13), since the critical field given by Eq. (2.14) is below those in Eq. (2.13). In the model considered here, the interaction constant $W$ is positive and the particles will reverse at the common switching field $H^{(2)}_{\uparrow \downarrow} = 2K/J_s$, independent of the interaction strength.

It is important to underline here that the term cooperative reversal merely means that both particles reach their final reversed state together, while noncooperative reversal leads to switching of one of the particles and the second particle remains in the initial state. Thus,
the cooperative reversal may proceed by both coherent and incoherent rotation. Further, in order to prove that the reversal is coherent, a study of the dynamic behaviour at finite angles is necessary [Bro62].

2.2. Magnetic phase diagram

In Section 2.1, the critical fields and stability regions of the corresponding magnetisation states have been derived. Knowledge of the critical fields is a necessary, but not a sufficient condition for predicting the way in which the magnetisation reversal occurs. The actual mechanism of reversal may depend on the anisotropy magnitude, interaction and external magnetic field strength, as well as on the magnetic prehistory. Furthermore, the existence of additional non-trivial solutions, beyond those given by Eq. (2.3), cannot be excluded. In this section, magnetic phase diagrams and energy surfaces are examined numerically for particular parameters and related to the discussed effects. The results are given on the basis of stability diagrams, which show the contour lines $H_1^{(1)}$, $H_1^{(2)}$ and $H_1^{(2)}$ in a $H-W$ plane. The magnetic phases follow from a discussion, given for certain examples.

2.2.1. Case 1: $K_1 = 7.0 \text{ MJ/m}^3$ and $K_2 = 1.0 \text{ MJ/m}^3$

From the detailed analysis of energy surfaces it follows that for sufficiently strong $K_2$ (with respect to $K_1$) the stability diagram is also a magnetic phase diagram, i.e. it predicts the mechanism, by which magnetisation reversal occurs. As an example, in figure 2.2, the critical field contours (Eq. (2.6), (2.8) and (2.9)) are plotted showing the regions of cooperative and noncooperative reversal for particular $J_s$, $K_1$ and $K_2$ values. The values $K_1 = 7.0 \text{ MJ/m}^3$ and $J_s = 1.43 \text{ T}$ correspond to the room temperature anisotropy constant and saturation magnetisation of the L1$_0$ FePt phase, respectively ([Iva73], Table 2.1).

Let us start from a saturated state ($\theta_1 = \theta_2 = 0$) in zero external field. As the reverse field is applied, the particles remain in the initial state until the reverse field intensity

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig22}
\caption{Stability diagram for two interacting single domain particles showing the regions of cooperative and noncooperative reversal for $K_1 = 7.0 \text{ MJ/m}^3$, $K_2 = 1.0 \text{ MJ/m}^3$ and $J_s = 1.43 \text{ T}$. The upper boundary of the shaded area gives a stability of the $\uparrow\uparrow$ configuration when increasing $H$ from zero, whereas the lower one limits the $\uparrow\downarrow$ stability region on decreasing $H$ provided the maximum reversed field was below $H_{\uparrow\downarrow}^{(1)}$ (compare Fig. 2.4).}
\end{figure}
reaches $H_{1\uparrow}^{(2)}$. When the interaction is small ($W < 3.9$ MJ/m$^3$, e.g. guideline $\odot$ in Fig. 2.2), an increase of the external field above $H_{1\uparrow}^{(2)}$ will lead to noncooperative rotation, i.e. the particle with smaller anisotropy ($K_2$) will reverse, whereas the high anisotropy particle ($K_1$) will remain in the initial state. As the external field reaches $H_{1\uparrow}^{(1)}$, the high anisotropy particle will reverse as well. The switching fields for both particles are modified by the interaction: as the interaction strength $W$ increases, the field $H_{1\uparrow}^{(2)}$, at which the smaller anisotropy particle reverses, increases, whereas smaller fields are required to reverse the high anisotropy particle. When the interaction strength exceeds some limit (e.g. $W > 3.9$ MJ/m$^3$, e.g. guideline $\odot$ in Fig. 2.2), cooperative reversal is observed.

The magnetisation state of these two single-domain particles depends not only on interaction strength, anisotropy and external magnetic fields, but also upon the magnetic prehistory. For instance, in the limit of strong interactions (when the reversal is cooperative, guideline $\odot$ in Fig. 2.2), starting from the reversed state ($\theta_1 = \theta_2 = \pi$) and reducing the reversed field to zero again, will not bring the system to the state $\theta_1 = \theta_2 = 0$, but the spins will remain in the $\theta_1 = \theta_2 = \pi$ configuration. The same is true for the case of small and moderate interaction strength (noncooperative reversal, e.g. guideline $\odot$ in Fig. 2.2), if the maximum reversed applied field has exceeded $H_{1\uparrow}^{(1)}$. For small and moderate interaction strength, reducing the reversed field, which is above $H_{1\uparrow}^{(2)}$ but below $H_{1\uparrow}^{(1)}$, to zero again will result in the appearance of hysteresis. That means, the particle with smaller anisotropy will

**Table 2.1.** Spontaneous polarisation $J_s$ anisotropy field $H_a$ and first anisotropy constant $K_1$ determined from the fit of magnetisation curves (maximum field 16 T) using the law of approach to saturation [And97] for highly ordered ($S = 0.97$) L1$_0$ FePt. Measurements were performed on Fe$_{50}$Pt$_{50}$ powder milled for 4 h and annealed at 450 °C/336 h.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$J_s$ (T)</th>
<th>$\mu_0 H_a$ (T)</th>
<th>$K_1$ (MJ/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1.5(1)</td>
<td>14.8(5)</td>
<td>8.7(9)</td>
</tr>
<tr>
<td>300</td>
<td>1.39(5)</td>
<td>13.0(5)</td>
<td>7.0(7)</td>
</tr>
</tbody>
</table>

Fig. 2.3. Energy profile versus rotation angle of the low anisotropy particle ($\theta_2$) for increasing reverse field $H$ from 0 MA/m to 2.0 MA/m and to 3.2 MA/m (closed symbols) and subsequently decreasing reverse field to 1.8 MA/m and to 1.0 MA/m (open symbols). The parameters used in the calculation are: $J_s = 1.43$ T, $K_1 = 7.0$ MJ/m$^3$, $K_2 = 1.0$ MJ/m$^3$ and $W = 3.0$ MJ/m$^3$. $\theta_1$ is always zero for the considered fields.
return to the initial state \( \theta_2 = 0 \) not in the field \( H_{1\uparrow}^{(2)} \) (upper limit of the shaded area in Fig. 2.2), but in a smaller one, i.e. \( H = H_{1\uparrow}^{(2)} \) (lower limit of the shaded area in Fig. 2.2).

The hysteresis is also revealed in the energy profile plots (Fig. 2.3). For the given interaction strength \( W = 3 \, \text{MJ/m}^3 \), the particles remain in the initial state \( \theta_1 = \theta_2 = 0 \) for reversed fields up to \( H = H_{1\uparrow}^{(2)} \approx 3 \, \text{MA/m} \), as could be inferred from the existence of the energy barriers for fields below 3 MA/m. In a maximum applied reversed field of 3.2 MA/m, the magnetisation of the particle with smaller anisotropy reverses. Since this field is below the field, at which the high anisotropy particle switches, \( H_{1\downarrow}^{(1)} \), the latter will not rotate, i.e. for the considered reverse fields \( \theta_i \) is always zero. Subsequent reduction of the reversed field will bring the system into the initial state \( \theta_1 = \theta_2 = 0 \), not at the critical field \( H_{1\uparrow}^{(2)} \), but in a smaller field equal to \( H_{1\uparrow}^{(2)} \approx 1.4 \, \text{MA/m} \).

In terms of the hysteresis loop, this situation is illustrated in Fig. 2.4(a) and corresponds to the so-called recoil loop measurements (see, for instance, the description of the measurement procedure required for obtaining Wohlfarth’s remanence relation (1.23)). Indeed, recoil hysteresis is often observed experimentally in hard/soft nanocomposite magnets [Bol02, Emu00, Gol98, see also Section 5.3].

In the absence of interactions, for a maximum applied field larger than the switching field of the low anisotropy particle \( (H_{1\uparrow}^{(2)}) \), but below the switching field of the high anisotropy particle \( (H_{1\downarrow}^{(1)}) \), the low anisotropy particle reverses, while the high anisotropy particle remains in the initial state. If the reverse field is subsequently reduced, the low anisotropy particle follows its hysteresis loop (Fig. 2.4(a)). In order to reverse the low anisotropy particle, application of the positive field equal to \( 2K_2/J_s \) is required. That means, in the absence of interactions for applied fields below the switching field of the high anisotropy particle a minor loop arising from the low anisotropy particle hysteresis is observed. Interaction between the particles shifts the minor loop to higher reversed fields, producing the open recoil loop (Fig. 2.4(b)). According to the model, the recoil loop area decreases with increasing interaction strength and it vanishes in the limit of strong interactions.
interactions (compare Fig. 2.2 and Fig. 2.4). Interaction between the particles modifies the fields $H^{(2)}_{1\uparrow\uparrow}$ and $H^{(1)}_{1\uparrow\downarrow}$, nevertheless, the low anisotropy particle switches irreversibly. It is possible that in a system consisting of randomly oriented particles, the magnetisation of the low anisotropy particles making an angle with the applied reverse field will rotate reversibly for fields below the switching field of the high anisotropy particles.

### 2.2.2. Case 2: $K_1 = 7.0 \, MJ/m^3$ and $K_2 = 0.1 \, MJ/m^3$

The stability diagram for the case of $K_1 = 7.0 \, MJ/m^3$ and $K_2 = 0.1 \, MJ/m^3$ shown in Fig. 2.5 indicates that there exists a critical region (shaded area in Fig. 2.5), where the states $\theta_1 = \theta_2 = 0$ and $\theta_3 = \pi$ are not stable. A question arises, whether the $\theta_1 = \theta_2 = \pi$ state is stable. By inspecting the energy surface curves, a further reversal mode, additional to the reversal modes given by (2.3), has been observed (see Fig. 2.6). This reversal mode is a reversal mechanism as found in exchange-spring (ES) nanocomposite magnets [Sol02]. With increasing reverse field above $H^{(2)}_{1\uparrow\uparrow}$, the particles do not switch but start to rotate nonuniformly from the easy direction. For simplicity, the direction of the magnetisation of both particles at a given reverse field is also schematically shown in figure 2.6. Provided the external field is below $H^{(1)}_{1\uparrow\downarrow}$, the rotation is fully reversible. The reverse field $H = H^{(1)}_{1\uparrow\downarrow}$ promotes the irreversible switching of both particles. Thus, depending on the interaction strength three major reversal modes can be distinguished: poorly coupled magnet (PCM) region, where the low- and high-anisotropy particles behave almost independently, ES region for sufficiently strong coupling and high-anisotropy-particle dominated, magnetically rigid composite magnet (RM), region (Fig. 2.5). In Fig. 2.5 the sketched boundaries between the ES and RM behaviour are approximate.

In the ES regime, the low- and high-anisotropy particles rotate noncollinearly. As the reverse field increases, the turn angle of the low anisotropy particle ($\theta$) increases faster than that of the high anisotropy particle (Fig. 2.7). Whereas $\theta_2$ increases steadily with $H$, the angle $\theta_1$ first increases and then relaxes to zero again if $\theta_2$ goes to $\pi$. Obviously, the high anisotropy particle is perturbed by the rotation of the low anisotropy particle.

![Stability diagram for two interacting single domain particles showing poorly coupled (PCM), exchange-spring (ES) and rigid-magnet (RM) reversal mode regions for $K_1 = 7.0 \, MJ/m^3$, $K_2 = 0.1 \, MJ/m^3$ and $J_s = 1.43 \, T$. The boundaries between the noncollinear reversal mode and $\theta_1 = \theta_2 = \pi$, as well as between ES and RM behaviour are approximate (indicated by zigzag lines).](image)
A two-particle interaction model

With increasing interaction strength, higher reverse fields are required to switch the low anisotropy particle. However, when the interaction exceeds some limit, given by $H_{1}^{(1)} = H_{1}^{(2)}$, the high anisotropy particle does not relax to the initial state but the noncollinear reversible rotation is followed by the irreversible switching of both particles ($W = 4.0 \text{ MJ/m}^3$ in Fig. 2.7). Thus, also in the ES regime the switching of both particles can be either cooperative or noncooperative depending on the interaction strength. For $K_1 = 7.0 \text{ MJ/m}^3$ and $K_2 = 0.1 \text{ MJ/m}^3$, the cooperative switching by the ES noncollinear mechanism is observed in the interaction strength range of approximately $3.55 \text{ MJ/m}^3 < W < 6.0 \text{ MJ/m}^3$ and for stronger interactions the particles switch simultaneously, as discussed in Section 2.2.1.

Fig. 2.6. Energy surface contour plots of two interacting particles for the reverse field increasing from 1.5 MA/m to 2.9 MA/m ($J_s = 1.43 \text{T}$, $K_1 = 7.0 \text{ MJ/m}^3$, $K_2 = 0.1 \text{ MJ/m}^3$ and $W = 3.0 \text{ MJ/m}^3$). Arrows show schematically the direction of the magnetisation of the particles at the corresponding reverse field.
Figure 2.8 summarises schematically possible reversal modes observed in the system consisting of two interacting particles. In the case of equal anisotropy constants as well as in the RM region, a transition from the $\theta_1 = \theta_2 = 0$ to $\theta_1 = \theta_2 = \pi$ state occurs by a simultaneous switching. This conclusion is made on the basis of the equilibrium equations (2.2). However, to follow the details of the reversal, one would require a study of the dynamic behaviour. Noncooperative switching is observed in the case of weak, PCM region, or absent interaction. In the ES region, reversible magnetisation rotation is followed by irreversible switching. Depending on the interaction strength, reversal can be either noncooperative (ES 1) or cooperative (ES 2).

Figure 2.9 shows simulated (quasistatic) demagnetisation curves of two interacting particles as a function of interaction strength. In the limit of weak interactions (for instance, $W = 1 \text{ MJ/m}^3$), the particles switch almost independently. With increasing interaction, the demagnetisation curve is not rectangular in shape and one can distinguish the first critical field, at which noncollinear reversible rotation starts, and the second critical field, at which the high anisotropy particle switches irreversibly. The switching field for irreversible rotation decreases dramatically with increasing the interaction strength. In the limit of very strong interactions, the demagnetisation curve is rectangular again, with a single critical field, being substantially smaller than that of the noninteracting high anisotropy particle,
and the magnetisation reversal is coherent.

### 2.3. Summary

For a simple two-particle model the magnetic phase diagrams were derived in terms of magnetic field, interaction and anisotropy strength. These diagrams provide information about the reversal mechanisms and critical fields, at which the reversal takes place. This simple model predicts the existence of a noncollinear reversal mode, typical for exchange-spring magnets. Depending on the interaction strength, the reversal may be cooperative or noncooperative also in the exchange-spring regime, (see Fig. 2.7). Noncollinear reversal modes have also been observed by Fullerton et al. [Ful98] and Amato et al. [Ama99], where exchange-spring soft/hard layers consisting of hundreds of spins were studied using a one-dimensional discrete model qualitatively similar to (2.1). It is striking that the existence of the noncollinear reversal mode can be obtained considering interactions between only two particles with parallel easy axes, thus suggesting that the exchange-spring behaviour is a very general phenomenon.

The described model suggests that the existence of hysteresis in recoil loops is due to insufficient coupling between low- and high-anisotropy particles (time-dependent hysteresis due to magnetic viscosity [Giv96] is not considered here). The origin of the recoil hysteresis is very similar to the bias caused by exchange anisotropy, i.e. the shift of the hysteresis loop of a ferromagnetic phase along the field axis, which arises due to exchange interaction at the interface between ferromagnetic and antiferromagnetic materials [Mei57, Nog05]. The recoil loop area is also determined by the difference in anisotropies of the particles: as the anisotropy difference increases, the recoil loop area is reduced (compare Fig. 2.5 and Fig. 2.2). Obviously, if the anisotropies of both particles are equal, no recoil hysteresis is observed, since the particles switch at a single field $2K/J_s$.

It can be shown that the degree of recoil hysteresis depends not only on the interaction strength and anisotropy distribution, but also on the particle volume and magnetisation. In Eq. (2.1), we assumed the particles to have equal volumes and magnetisation. Stability analysis of the solutions (2.3) obtained from minimisation of the free energy

---

**Fig. 2.9.** Simulated demagnetisation curves of two interacting particles as a function of the interaction strength $W$ ($K_1 = 7.0 \text{ MJ/m}^3$, $K_2 = 0.1 \text{ MJ/m}^3$ and $J_s = 1.43 \text{T}$)
where $V_i$ is the volume, $K'_i = V_i K_i$ and $J_{s,i}$ is the magnetisation of the respective particle ($i = 1$ or $2$), shows that the difference between $H_1^{(2)}$ and $H_1^{(1)}$ depends on the magnetisation and the volume of the particles (see Fig. 2.10). Thus, the area of the recoil loop is a function of the magnetisation and the volume of the particles. For a fixed interaction strength, the recoil loop area increases, when the volume and/or magnetisation of the low anisotropy particle becomes larger. The larger magnetisation of the low anisotropy particle is analogous to the increase of the soft magnetic phase fraction, that means, in soft/hard nanocomposites the area of the recoil loop depends on the volume fraction of the soft magnetic phase. A similar dependence of the recoil loop area on the (mean field) interaction strength, on the switching field distribution, as well as on the soft magnetic phase fraction has also been obtained by McCallum [McCal06], where an exchange-spring magnet was modelled in a mean-field approximation. Nevertheless, mean-field theory results should be taken with care, as the mean-field model delivers unsatisfactory results in the description of interacting systems [Bro62, Cal77].

On the other hand, decreasing the volume of the low anisotropy particle may be regarded analogous to increasing the degree of dispersion or “nanostructurisation” in hard/soft layers [Ama99]. From figure 2.9 it follows that with decreasing volume of the low anisotropy particle, the transition to the exchange spring regime occurs for smaller $W$ and the critical field $H_1^{(2)}$ increases substantially. That means, the exchange spring and rigid magnet configurations are more favoured, since the coupling of the low anisotropy particle with smaller volume $V_2$ to the larger high anisotropy particle becomes more effective. The same effects are observed with decreasing magnetisation of the low-anisotropy particle. Thus, the two-particle model (2.15) conceptually predicts the dependence of magnetisation reversal modes on dimensions and relative amounts of the particles. Although simple, the presented model predicts many phenomena observed in hard/soft nanocomposite magnets.
Chapter 3

Experimental details

In this chapter, material preparation and characterisation methods at different processing stages will be introduced. The material preparation involved powder processing by mechanical ball milling. To develop hard magnetic properties, the milling was followed by a heat treatment. Since the processing route results in a random orientation of the crystallites, the obtained permanent magnet material is macroscopically isotropic.

3.1. Mechanical ball milling

Mechanical alloying, or more generally mechanical ball milling, is the process when mixtures of powders (of different metals or alloys/compounds) are milled together. Frequently the term mechanical alloying is used to emphasise the fact that material transfer is involved during processing, whereas milling of (already alloyed) powders having uniform composition with the aim of e.g. crystallite size reduction and/or mechanically inducing other transformations is termed mechanical milling [Sur01]. A variation of milling is cryomilling in which the milling operation is carried out at cryogenic temperatures. The method is indispensable for processing powders of ductile components, where the effect of cold welding between the powder particles and the grinding medium should be minimised. It allows to avoid the use of process control agents often leading to powder contamination.

For the preparation of Fe_{100-x}Pt_x, appropriate mixtures of elemental Fe and Pt powders with a purity of 99.9 % and a particle size less than 80 µm were mechanically ball-milled at liquid nitrogen and room temperatures. The starting powders, together with hardened steel balls were sealed in a hardened steel vial under an argon atmosphere and milled for 1-9 h in a Misuni vibration mill at a vibration frequency of 12 Hz. A ball-to-powder weight ratio (BPR) of 15:1 and balls with different diameters, i.e. 10 mm and 5 mm, were used. The combination of balls with different diameters was reported to minimise the amount of cold welding and to increase the collision energy, which, in turn, accelerates alloying [Tak94, Sur01]. For the low-temperature milling liquid nitrogen was supplied continuously during the milling process.

For obtaining a desired structure, a subsequent heat treatment of the as-milled powders was carried out in a sealed quartz tube. In the case of the Fe_{100-x}Pt_x powders, the heat treatment was carried out under an argon pressure of 500 mbar and at temperatures between 300 °C and 550 °C.
3.2. Thermal analysis

Differential scanning calorimetry (DSC) was used to study phase transformations and for the analysis of the thermal properties of the materials. By determining the rate of heat flow into a sample, DSC provides quantitative thermodynamic and kinetic information about physical or chemical changes occurring in the material. In the present work, the thermal behaviour was examined by using a Perkin Elmer DSC 7 system. Dynamic (non-isothermal) DSC measurements were performed by continuous heating with heating rates of 5-40 K/min over the temperature range of 50-700 °C under flowing argon.

The Perkin Elmer system is a power-compensated DSC. In this technique, the sample and the reference are thermally insulated from one another and each is provided with its own individual heater and temperature sensor. The instrument is based on the “zero-balance” principle of measurement, in which the energy absorbed or evolved by the sample is compensated by adjusting the power going to the respective heaters in such a way that the temperature of the sample and the reference follows a particular temperature program. The compensation is carried out by increasing or decreasing the heater power of a differential temperature control circuit. The output of the differential temperature control circuit is used to generate a DSC curve.

3.3. X-ray diffraction

The phase composition and the structural and microstructure parameters of the powder samples (unless specified additionally) were investigated by x-ray diffraction. Rietveld analysis [Rie69, You93] was used for a quantitative phase analysis and for lattice constants, profile parameters and site occupation determination. The Rietveld refinement was performed using the X’Pert Plus software developed by Philips Analytical BV. Average crystallite size \( <D> \) and microstrain \( <\varepsilon> \) were determined using an “average size-strain” method of Langford [Lan92]. In the following sections a brief description of the above mentioned methods will be given. Requirements to the data collection for a reliable x-ray diffraction analysis as well as measurement conditions selected in the present work are given below.

Obtaining a high quality diffraction pattern implies first of all obtaining undistorted diffraction profiles and precise Bragg peak positions. The use of divergence slits fitted in the incident beam path and receiving slits allows to reduce peak aberrations, eliminate Bragg peak shifts and control the measured x-ray beam intensity. The sensitivity of the phase analysis relies on the detection of the peaks with small intensities. This can be achieved by increasing the x-ray beam intensity or by a reduction of the background intensity. The background arises mainly due to the presence of the continuous radiation in the x-ray tube spectrum, scattering by the diffractometer details, the air scatter, the sample fluorescent radiation and incoherent scatter. Anti-scatter slits fitted in the diffracted beam path reduce the air scatter and thus the background radiation. However, the most efficient
way of reducing the background intensity is the usage of a diffracted beam monochromator.

Measurements were performed using a Philips X’Pert diffractometer equipped with a diffracted beam graphite monochromator. The following measurement conditions were used: Co-K$_\alpha$ radiation (weighted average wavelength $\lambda_{K\alpha} = 1.7902$ Å); the voltage and the current of the x-ray tube of 40 kV and 40 mA, respectively; a fixed divergence slit with an aperture size of 0.25 ° (incident beam), an antisccatter slit with an aperture size of 2 ° and a receiving slit with a height of 0.5 mm. X-ray diffraction patterns were collected in the 2$\theta$ angle range between 20 and 140 degrees with a step size of 0.05 ° and time per step of 7...20 s. The sample in-plane rotation was enabled to improve the particle statistics.

3.3.1. Rietveld analysis

Traditionally phase identification is based on a comparison of the observed data with interplanar spacings $d$ and relative intensities $I$ of known phases. Quantitative phase analysis assumes that the integrated intensity of Bragg reflections is proportional, among all the intensity factors, to the volume fraction of a phase in a multi-phase mixture. The analysis is, however, extremely complicated or not possible at all when a severe overlap of diffraction peaks and/or peaks of different phases occurs. Evidently, these reasons complicate an extraction of detailed crystal structure information as well. Hence, the determination of peak position and intensity independently of each other is not an appropriate approach in these cases. Rietveld [Rie69] proposed a whole-pattern fitting with parameters of a model function depending on the crystallographic structure, instrument features and some numerical parameters. With such an approach, even the overlapping peaks contribute information about the structure to the refinement. The Rietveld analysis, originally developed to refine structures from data obtained by fixed wavelength neutron diffraction, has become generally accepted in x-ray powder diffraction as well [You93]. Hill and Howard [Hil87] introduced the basis of a quantitative phase analysis using Rietveld refinement. The main advantage of this method is that no calibration standard is required to determine the phase abundance, since the weight (volume) fraction is derived from the scale factors obtained during the refinement.

In the Rietveld refinement, the calculated intensity $y_{ci}$ at any arbitrary point at the pattern $I$ is determined by summing of the calculated contributions from neighbouring Bragg reflections and the background. When more than one phase is present, a summation over contributing phases $p$ is performed additionally:

$$y_{ci} = y_{bi} + \sum_p s_p \sum_k I_k \phi(2\theta_i - 2\theta_k),$$

(3.1)

where $s_p$ is the scale factor (proportional to the volume fraction of the phase $p$), $k \equiv hkl$, $I_k$ is the integrated intensity given by Eq. (1.2), $\phi$ is the reflection profile function and $y_{bi}$ is the background intensity at the $i$th step. The positions of the reflections from each phase are determined by their respective set of cell dimensions according to the Bragg equation ($2d_{HKL}\sin\theta = \lambda$), whereas the intensity is determined by the content of the unit cell.
The reflection profile function $\phi$ approximates the effects produced by both instrumental and sample-related features. The knowledge of this function allows, in turn, to extract information about the microstructure parameters with respect to size and strain effects (see Section 3.3.2). In this work, the peak shape was modelled by using the pseudo-Voigt ($pV$) function, which is a linear combination of the Lorentzian and Gaussian functions:

\[
pV = \gamma \frac{\sqrt{4}}{\Gamma \pi} \left[ 1 + 4 \left( \frac{2\theta_i - 2\theta_k}{\Gamma} \right)^2 \right]^{-1} + (1 - \gamma) \frac{\sqrt{4} \ln 2}{\Gamma \sqrt{\pi}} \exp \left[ -4 \ln 2 \left( \frac{2\theta_i - 2\theta_k}{\Gamma} \right)^2 \right],
\]

where $\gamma$ ($0 \leq \gamma \leq 1$) is the $pV$ mixing parameter and $\Gamma$ is the full-width-at-half-maximum (FWHM) intensity. Both the mixing parameter $\gamma$ and the FWHM can be varied across the pattern by application of the functions

\[
\Gamma^2 = U \tan^2 \theta + V \tan \theta + W, \quad (3.3)
\]
\[
\gamma = \gamma_0 + \gamma_1 (2\theta) + \gamma_2 (2\theta)^2, \quad (3.4)
\]

where $U$, $V$, $W$ and $\gamma_0$, $\gamma_1$, $\gamma_2$ are refinable parameters.

The aim of the Rietveld analysis is to find a set of parameters that describe the observed diffraction pattern as good as possible. During the least-squares refinement the following quantity is minimised:

\[
U(\xi) = \sum_i \frac{1}{y_i} (y_i - y_{i,\xi})^2 \quad (3.5)
\]

and the minimum satisfies the condition

\[
\frac{\partial U}{\partial \xi} = 0, \quad (3.6)
\]

where $y_i$ is the observed intensity at the $i^{th}$ step and $\xi$ represents the refined parameters (see Table 3.1). Once, good starting global, unit-cell and profile parameters were obtained, the Rietveld refinement of structural parameters was performed. The crystal structure refinement was carried out for the L1$_0$ ordered phase with the aim of order parameter determination. The atom positions $x_j$, $y_j$, and $z_j$ were kept constant, whereas the site occupation $r_j$ was varied. The fractions $r_j$ extracted from the Rietveld refinement were used for the determination of the long-range order parameter $S$ of L1$_0$ FePt, as defined in Eq. (1.1). In the powders containing along with L1$_0$ FePt the L1$_2$ (Fe$_3$Pt and FePt$_3$) phases the structure of the latter was refined provided the fraction of these additional phases was high enough (about 40 vol. %).

Although the difference plot is the most useful indicator for the evaluation of the refinement, the fit of the calculated pattern to the observed data can also be given numerically. This can be done in terms of agreement indices, so-called $R$-values. The weighted-profile value $R_{wp}$ is defined as
where $\sum_{i=1}^{N} y_{i}^2 = 0$.

Ideally, the final $R_{wp}$ should approach the statistically expected $R$-value,

$$R_{exp} = \frac{\sum_{i} w_i (y_i - y_{ci})^2}{\sum_{i} w_i y_i^2}.$$  

(3.8)

where $N$ is the number of observations and $P$ the number of parameters. The ratio between the two (“goodness-of-fit”)

$$\chi^2 = R_{wp} / R_{exp}$$  

(3.9)

should approach unity. The Bragg-intensity $R$-value can be used to monitor the improvement in the structural model

$$R_{Bragg} = \frac{\sum_{k} |I_{k}^i - I_{k}^c|}{\sum_{k} |I_{k}^i|}.$$  

(3.10)

The majority of samples investigated in the present work contain more than one phase. As a rule, diffraction lines of the phases suffer from a severe overlap due to the nanocrystalline nature of the materials and/or rather close cell dimensions (compare Appendix B). As an example, figure 3.1 shows a Rietveld refinement plot for a Fe$_{55}$Pt$_{45}$ powder. Qualitatively, the experimental diffraction profile allows for identification of the L$_{10}$ FePt phase. However, if the profile is modelled considering the L$_{10}$ phase only, the difference plot clearly reveals the presence of additional phases (“shoulders” marked by

Table 3.1. Rietveld refinement parameters.

<table>
<thead>
<tr>
<th>Global</th>
<th>For each phase present</th>
</tr>
</thead>
<tbody>
<tr>
<td>2θ correction (includes both a zero offset and sample displacement)</td>
<td>Scale factor $s_p$</td>
</tr>
<tr>
<td>Background parameters $B_m$ *)</td>
<td>Lattice parameters</td>
</tr>
<tr>
<td></td>
<td>Profile parameters $U_i$, $V_i$, $W_i$ and $\gamma_i$ **)</td>
</tr>
<tr>
<td></td>
<td>Overall temperature factor</td>
</tr>
<tr>
<td></td>
<td>Preferred orientation $P_k$ ***)</td>
</tr>
<tr>
<td></td>
<td>Site occupation parameter $r_i$</td>
</tr>
</tbody>
</table>

*) Background was refined by a polynomial approximation $y_{bi} = \sum_{m=1}^{4} B_m (2\Theta_i)^m$.

**) Values of $\gamma_1$ and $\gamma_2$ (initially set as zero) have not changed during the refinement.

***) $P_k$ was, as a rule, equal to unity for powder samples.
arrows in Fig. 3.1). Further refinement indicates a coexistence of the L1\textsubscript{0} FePt and A1 FePt, Fe\textsubscript{3}Pt and FePt\textsubscript{3} phases. Therefore, without the use of the Rietveld analysis the detection of minority phases would be extremely complicated or even impossible.

### 3.3.2. Grain size and lattice strain determination

The broadening of x-ray diffraction lines arises due to so-called physical (specimen-related) and instrumental (geometrical) factors [Klu54, Uma82]. In general, the former contains contributions from the small size of the crystallites (coherently scattering domains) and lattice strain (often denoted as microstrain or lattice distortion) caused by e.g. the presence of lattice defects. Instrumental broadening arises due to wavelength distribution and geometrical aberrations and is treated as characteristic of the particular instrument.

The observed diffraction profile \( h(2\theta) \) is a convolution of the physical \( f(2\theta) \) and instrumental \( g(2\theta) \) profiles:

\[
h(2\theta) = \int f(y)g(2\theta - y)\,dy ,
\]

(3.11)

where \( 2\theta = (2\theta_1 - 2\theta_k ) \) and \( y \) is the variable of integration in the same 2\( \theta \) domain. The physical profile \( f(2\theta) \) can be, in turn, represented as a convolution of the size and strain components. Prior to analysis of the diffraction line broadening, correction of the observed line profiles for instrumental effects should be made. Several methods exist that are based on a deconvolution operation of Eq. (3.11) [Klu54, Uma82]. However, these methods require well separated diffraction peaks and are not appropriate when the peaks
severely overlap. In this case, the methods of integral breadths can be used, since these methods require assumptions only about the functional form of the peak shapes [Kei83, Lan92, Bal93].

The integral breadth $\beta$ of a diffraction peak is defined as following:

$$
\beta = \frac{\int \phi(2\theta)d(2\theta)}{\phi_{\text{max}}},
$$

(3.12)

where $\phi_{\text{max}}$ is the peak intensity. In turn, the mixing parameter of the pseudo-Voigt function $\gamma$ is defined as the ratio of FWHM, $\Gamma$, to the integral breadth [Lan78]:

$$
\gamma = \frac{\Gamma}{\beta}.
$$

(3.13)

and, obviously,

$$
\frac{\Gamma}{\beta} = \gamma \frac{\Gamma_G}{\beta_G} + (1 - \gamma) \frac{\Gamma_L}{\beta_L}.
$$

(3.14)

Thus, the integral breadths $\beta$ of the $pV$ function can be determined using the expression [Lan78, Kei83]

$$
\beta = \frac{\pi/2}{(\gamma + (1 - \gamma)\sqrt{\pi \ln 2})\Gamma}.
$$

(3.15)

The line profile parameters, extracted from the Rietveld refinement of the observed diffraction pattern were corrected for the instrumental broadening. As a standard reference material (SRM), a LaB$_6$ powder specimen has been used. Since the reflections of the SRM are at different angles from those of a sample, it was necessary to interpolate $\Gamma$ of the SRM profile by function (3.3). For the correction, the $pV$ functions of the geometrical $g(2\theta)$ and experimental $h(2\theta)$ profiles were decomposed into Lorentz ($L$) and Gaussian ($G$) parts (as described in [Kei83]) and the integral breadths of these parts were corrected with the formulae

$$
\beta'^{L} = \beta^{L} - \beta^{G}
$$

(3.16)

$$
(\beta'^{G})^2 = (\beta^{L})^2 - (\beta^{G})^2,
$$

(3.17)

where the indices $f$, $h$, and $g$ refer to physical, experimental and instrumental profiles, respectively. Subsequently, the corrected profiles were recomposed to the $pV$ function with the integral breadth $\beta$ (Eq. (3.15)).

Once the instrumental broadening is “removed”, the analysis of the physically broadened line profile can be made. In order to separate the contributions to the overall breadth from crystallite size and lattice strain the modified Williamson-Hall analysis [Wil53], the so-called “average size-strain” method of Langford [Lan92] was applied. In the
“average size-strain” method the integral peak breadths $\beta$ are given in terms of reciprocal units: $\beta^* = \beta \cos \theta / \lambda$. Characterisation of the diffraction peaks is achieved by the application of a Voigt function, which is a convolution of Lorentzian and Gaussian functions. Significant mathematical simplification is obtained by using a pseudo-Voigt function, which is a close approximation to the Voigtian and fits obtained by using these functions are frequently identical [You82, Lan92]. In the “average size-strain” method it is assumed that the integral breadth of the Lorentzian component $\beta^*_L$ is attributed solely to size effects:

$$\beta^*_L = 1 / \varepsilon,$$  \hfill (3.18)

and $\beta^*_G$ of the Gaussian component arises from strain:

$$\beta^*_G = \eta d^*/2,$$  \hfill (3.19)

where $\varepsilon$ is an average apparent grain size, $\eta$ is a measure of the strain and $d^* = 2\sin \theta / \lambda$ is an inverse $d$-spacing. These assumptions, combined with the approximation that the diffraction peaks can be described by the Voigt (pseudo-Voigt) function give the following expression for the integral breadth:

$$\beta^2 = \beta^*_L \beta + \beta^*_G,$$  \hfill (3.20)

which, in turn, can be written as

$$(\beta^*/d^*)^2 = \varepsilon^{-1} \beta^*/(d^*)^2 + (\eta/2)^2.$$  \hfill (3.21)

From Eq. (3.21), the intercept of the plot $(\beta^*/d^*)^2$ versus $\beta^*/(d^*)^2$ gives the mean value of $\eta$, and the slope gives the average apparent size $\varepsilon$. If the line breadths show no $hkl$ dependence, the “true” grain size $<D>$ can be obtained from the apparent spherical particle size by multiplying $\varepsilon$ by 1.333. If the definition of the root mean square (rms) strain $<\varepsilon>$ is

![Fig. 3.2. Average size-strain plot for a powder with the nominal composition Fe$_{50}$Pt$_{50}$ consisting of two phases: $\alpha$-Fe and Pt (milled for 1 h at 77 K). The data points are identified by the Bragg peak indices.](image-url)
used, then \(<e> = \eta/2\sqrt{2\pi}\).

The effect of stacking faults to the peak broadening was not considered in this study. However, no peak displacements produced by deformation faulting were detected for the FePt powders studied.

As an example, figure 3.2 shows the “average size-strain” plot for a Fe-Pt powder containing two phases: \(\alpha\)-Fe and Pt. The line breadths for both \(\alpha\)-Fe and Pt show no \(hkl\) dependence, therefore grains may be regarded as being spherical with the diameter \(<D>\) indicated in the inset. Clearly, the peak broadening arises from both crystallite size and strain contributions. Moreover, the values of the rms strain \(<e>\) are considerable. That means, neglecting this contribution, i.e. assuming that the size of the coherently scattering domains is the only contribution to the peak breadth, would substantially underestimate the grain size. For instance, the well-known Scherrer formula \([Klu54]\) gives an estimation for the crystallite size \(<D>\) for \(\alpha\)-Fe of about 15 nm only.

### 3.4. Neutron diffraction

\textit{In-situ} neutron powder diffraction was used for a direct observation of the phase transformations in Fe-Pt alloys, as well as for a magnetic structure investigation of heat treated Fe-Pt alloys. The neutron powder diffraction has been preferred to x-ray diffraction because of the large penetration depth of thermal neutrons. The results are thus representative for the whole sample volume.

Neutrons are scattered by the atomic nuclei, but due to a non-zero magnetic moment they also interact, through dipolar forces, with unpaired electrons, thus enabling the investigation of magnetic structures. For unpolarised neutrons, the intensities of the magnetic and nuclear scattering add and the structure factor is given by

\[
|F_k| = \sum_j r_j b_j \exp\left[2\pi(ihx_j + kvy_j + lz_j)\right] + \sum_j r_j p_j \mu_j \exp\left[2\pi(ihx_j + kvy_j + lz_j)\right], \quad (3.22)
\]

where \(b_j\) is the scattering length of the nucleus \(j\). The magnetic scattering length \(p\) is defined as \(p = 1.91 r_j(Sf_S + 0.5Lf_L)\), if both spin and orbital moments are present and \(f_S\) and \(f_L\) are the corresponding magnetic form factors. The magnetic form factor reflects the density of uncompensated magnetic moments, i.e. the difference in the electron density with spin-up and spin-down directions. The magnetic interaction vector \(\mu\) is given by \(\mu = em - k(e_m)/k^2\), where \(e_m\) is a unit vector in the direction of the magnetic moment.

The neutron scattering length varies as an irregular function of the atomic number \(z_j\). This is in contrast to x-ray scattering, where the x-ray beam interacts with the electron cloud and the x-ray scattering factor relates directly to the number of electrons \(f_i = z_i\). In contrast to the x-ray atomic scattering factors of Pt and Fe, the neutron coherent scattering lengths of the two elements are so similar \((b_{Pt} = 9.60 \times 10^{-15} \text{ m} \text{ and } b_{Fe} = 9.45 \times 10^{-15} \text{ m} [Sea92])\) that the concentration waves of iron and platinum contribute only a negligible intensity to the
superlattice reflections. Therefore, in neutron diffraction from Fe-Pt alloys the intensity of
the superlattice reflections is due to the magnetic scattering only.

Neutron diffraction measurements were performed on the high-flux two-axis
diffractometer D1B at the Institut Laue-Langevin (ILL) in Grenoble, France (Fig. 3.3).
Diffraction patterns were recorded over the angular range of $35^\circ \leq 2\theta \leq 115^\circ$ with a step of
0.2° using a 400 cell curved position sensitive $^3$He multidetector. The neutron wavelength
was $\lambda = 2.52 \text{Å}$, as selected by the (002) reflection of a pyrolytic graphite monochromator. In
order to access a wider reciprocal space domain a wavelength of 1.28 Å selected by a
germanium monochromator has also been used for room temperature measurements. The
powders were filled into a cylindrical vanadium container and heated up to 660 °C with a
rate of 0.8 °C/min under vacuum. The exposure time per pattern was 5 min.

The data was analysed by Rietveld refinement using the FULLPROF program [Rod93].
The neutron patterns collected during the heating were refined sequentially, as the
variation of structure parameters was continuous in the majority of the cases. Since no
essential changes were observed below 300 °C, the data analysis was performed for
temperatures above this temperature. In the analysis of the data collected on heating only
nuclear scattering was taken into account. Whereas the Curie temperature of the A1 phase
is in the range of 330-260 °C for Pt concentrations $x = 40-55$ [Kus50], the Curie temperature
of the L$_1^0$ phase in the studied alloys is in the range of 430-472 °C (Table 4.2). However,
eglecting magnetic scattering for L$_1^0$ FePt is expected to have only a minor effect on the
results of the refinement. For instance, at 330 °C, the analysis shows that the magnetic
contribution to the intensity of the (111) and (002) Bragg peaks is as small as 1.95 % and
1.53 %, respectively. This contribution is expected to decrease upon increasing temperature
and is neglected in the treatment of data obtained on heating. The analysis of the magnetic

Fig. 3.3. D1B instrument layout at the
Institut Laue-Langevin (ILL), Grenoble,
France.
scattering was performed using neutron diffraction patterns collected during subsequent cooling of the samples from 660 °C to room temperature.

### 3.5. Scanning electron microscopy

Scanning electron microscopy (SEM) investigations using a field emission gun scanning electron microscope FEGSEM LEO Gemini 1530 apparatus equipped with energy dispersive x-ray (EDX) analysis were performed in cooperation with K. Berger and K. Khlopkov. The secondary electron mode was used for the study of the morphology of powder particles dispersed onto a conducting sample holder. The samples for the investigation of the size and distribution of different phases within the material were prepared by embedding the powder particles into epoxy followed by polishing on a cloth-covered wheel using diamond paste with water-free lubricant. The use of backscattered electrons allows to detect the contrast between areas with different chemical compositions. Since the x-ray atomic scattering factors of iron and platinum differ significantly, it can readily be distinguished between areas with different image regions with various average atomic numbers.

### 3.6. Characterisation of magnetic properties

For characterisation of the magnetic properties, specimens were produced by embedding the powder particles in epoxy resin. The shape of thus prepared samples was a cylinder with a diameter being approximately equal to its height (= 3 mm). The values of the magnetisation were normalised to the volume of the powder in the bonded magnet. Hysteresis loops were corrected for demagnetising field effects (see Appendix A).

The room temperature measurements were performed using a Superconducting Quantum Interference Device (SQUID Quantum Design MPMS-5S) in fields up to 5 T. A vibrating sample magnetometer (VSM) with a maximum applied field of 6 T was used for measurements in the temperature range of 295-750 K. For magnetocrystalline anisotropy determination, magnetisation curves have also been measured at 5 K and 300 K in an extraction magnetometer with fields up to 16 T. A detailed description of the used magnetisation measurement techniques can be found e.g. in Ref. [Blu01].

### 3.7. Magnetic force microscopy

Magnetic domains were observed using a magnetic force microscope (MFM). The MFM technique is based on the detection of the magnetostatic interaction between a sample and a small ferromagnetic tip. The tip probe is carried by a cantilever, whose deflection, caused by the interaction force, can be detected by various sensors [Wie92, Por98].

The MFM measurements have been carried out by K. Khlopkov using a Digital Instruments Nanoscope 3100 scanning probe microscope operating in the Tapping/Lift
mode \textit{[tap, Alk98].} In this mode the cantilever is vibrated at its resonance frequency (~100 kHz) in the direction normal to the sample surface and is brought close to the sample surface. The magnetic and topographic data are separated by scanning twice for each scan line. The first scan is very close to the sample surface (\textit{tapping mode} atomic force microscopy) and yields information about the sample topography. The second scan follows the recorded topography, but at an increased scan height to avoid the van der Waals forces that provided the topographic data (\textit{lift mode} magnetic force microscopy). The shift in the resonance vibration frequency due to the magnetic and/or the van der Waals interactions between the tip and the sample is monitored via a laser beam reflected off the back of the cantilever. In this way, by scanning the selected area in a raster pattern, both the topographic (van der Waals interaction) and the magnetic force gradient images can be obtained.

A commercially available CoCr coated tip with high coercivity (MESP-HC) was used. The signal measured by the MFM tip with high coercivity provides information on the phase shift being directly proportional to the second derivative of the vertical component of the sample stray fields. Thus, the magnetic contrast observed by MFM originates from the perpendicular component of oppositely polarised magnetic domains. MFM images of the powder particles were obtained at a scan height of 100 nm.
Chapter 4

Phase formation in nanocrystalline Fe-Pt alloys

In this chapter, the solid state reactions and structural evolution in nanocrystalline Fe\textsubscript{100-x}Pt\textsubscript{x} (x = 40; 45; 50; 55; 60) alloys during mechanical ball milling are investigated using x-ray diffraction and scanning electron microscopy. The ordering of the as-milled alloys is studied by neutron powder diffraction during \textit{in-situ} heat treatment and by differential scanning calorimetry. The influence of stoichiometry and initial microstructure on the transformation to the L1\textsubscript{0} phase is investigated. The neutron diffraction results are related to the thermodynamic and kinetic properties of the alloys.

4.1. Structure evolution during milling of Fe-Pt alloys

4.1.1. Milling at liquid nitrogen temperature

Figure 4.1 shows x-ray diffraction patterns of Fe-Pt powders with a nominal composition of Fe\textsubscript{50}Pt\textsubscript{50} prior to and after milling at liquid nitrogen temperature for different time intervals. Considerable changes in the phase composition and microstructure are observed after short milling times. Initially sharp x-ray diffraction lines are appreciably broadened after only 1 hour of milling. The “average size-strain” plot for the 1 h milled Fe/Pt powder yields a grain size \(<D>\) of about 29 nm for Pt and 43 nm for \(\alpha\)-Fe, i.e. a substantial reduction in the grain sizes compared to the starting microcrystalline powders is observed. The rms strain \(<\varepsilon>\) for Pt and \(\alpha\)-Fe was estimated to be about 0.16 % and 0.21 %, respectively.

The progress of alloying is illustrated in figure 4.2, which shows a change in the phase composition and crystallite size of the phases in powders with the overall stoichiometry of Fe\textsubscript{50}Pt\textsubscript{50} as a function of milling time. Rietveld refinement reveals the presence of the A1 FePt phase having dimensions of \(\sim 5\) nm after already 2 h of milling. Thus, alloying starts to occur at this milling stage. The following phase contents were determined for the 2 h milled powder: \(\alpha\)-Fe (\(\approx 31\) vol. %), Pt (\(\approx 36\) vol. %) and A1 FePt (\(\approx 33\) vol. %). The crystallites of the phases are refined (\(<D>_{\text{Pt}} = 23\) nm and \(<D>_{\alpha\text{-Fe}} = 17\) nm) and an increase of the rms strain to 0.27 % for Pt and 0.55 % for \(\alpha\)-Fe is observed. High resolution scanning electron microscope (SEM) investigation reveals that the microstructure of the powder milled for 2 h is a lamellar structure of the constituent elements having a thickness of about 20-300 nm (Fig. 4.3(left)). The fine contrast within the Pt lamellae confirms the nanocrystalline nature of the powders.
An SEM image of the 4 h milled Fe$_{50}$Pt$_{50}$ powder (Fig. 4.3(right)) reveals three types of compositional contrasts, which are attributed to Pt, Fe and FePt. The Pt and Fe lamellae are thinner compared to those in the 2 h milled powders and the A1 layer thickness reaches several tens of nanometers. Quantitative phase analysis using Rietveld refinement confirms that the powder is a mixture of $\alpha$-Fe, Pt and A1 FePt. The amount of the A1 phase ($\approx$ 60 vol. %) is substantially larger than that in the 2 h milled alloy and the crystallites of the phases are $\sim$ 10 nm.

As the milling time increases, the $\alpha$-Fe and Pt fractions are reduced, whereas the amount of A1 FePt increases (Fig. 4.2(left)). After 5 h of milling the grain sizes of $\alpha$-Fe and Pt reduce to approximately 7 nm and 9 nm, respectively. However, at this minimum grain size the strain is not at its maximum value: the rms strain of $\alpha$-Fe and Pt reduces to about 0.25 %. That is, the rms strain increases rapidly at the first stage of the milling, but for longer milling times it decreases. A similar behaviour was observed for low energy ball-
Phase formation in nanocrystalline Fe-Pt alloys

milled pure metals [Ole96]. The grain size and the lattice strain of the A1 phase after milling for 5 h were determined to be about 15 nm and 0.65 %, respectively.

After 7 h of milling at liquid nitrogen temperature the A1 FePt fraction reaches 84.4(7) vol. %, the rest being α-Fe. The grain size of the A1 phase is almost unchanged, although the lattice strain decreases to 0.49 %. The SEM investigation revealed the presence of almost equiaxed iron inclusions (~1 µm large), thus implying that the observed α-Fe is due to the iron from the balls and vial walls, which is usually observed in powders milled with steel as a grinding medium [Sur01].

Similar trends in the structure evolution with milling time are observed in Fe\(_{100-x}\)Pt\(_x\) powders with the compositions \(x = 40; 45; 55; 60\). As an example, figure 4.4 shows the phase fraction and grain size evolution with milling time for powders with an Fe\(_{60}\)Pt\(_{40}\) stoichiometry. Consistent with the stoichiometry, the amount of Pt is lower and the α-Fe fraction is higher at the initial stages of milling. The A1 phase formation starts after 2 h of milling, similarly to Fe\(_{50}\)Pt\(_{50}\). After 7 h of milling Pt is no more observed. The fraction of the A1 phase reaches 85 vol. % and that of α-Fe 15 vol. %. As the milling time increases, a higher amount of iron from the milling media is incorporated into the powders. Thus, a further increase of milling time is undesirable, since it leads to a reduction of the A1

![Fig. 4.3. High resolution SEM images (backscattered electron mode) of Fe\(_{50}\)Pt\(_{50}\) powder milled at liquid nitrogen temperature for 2 h (left) and 4 h (right).](image_url)

![Fig. 4.4. Phase composition (left) and crystallite size (right) of the phases in the Fe\(_{60}\)Pt\(_{40}\) powders milled at 77 K in dependence on milling time. The lines are guides to the eye.](image_url)
fraction in the sample.

The microstructure evolution in Fe$_{60}$Pt$_{40}$ is also similar to that in Fe$_{50}$Pt$_{50}$. The crystallites of Pt and α-Fe are rapidly refined at the early stages of milling and approach a steady-state value of approximately 7 nm after 4 h of milling (Fig. 4.4). Figure 4.5 shows SEM images for the Fe$_{60}$Pt$_{40}$ powders milled for 2 and 4 h. Similar to Fe$_{50}$Pt$_{50}$, the bright contrast is due to Pt, the dark one arises from α-Fe and the grey areas (for the 4 h milled powder) have a stoichiometry of FePt. After 7 h of milling the grain size of the A1 phase is about 15 nm and the rms strain $<\varepsilon>$ equals to 0.4 ± 0.1 %.

Fig. 4.5. High resolution SEM image (backscattered electron mode) of Fe$_{60}$Pt$_{40}$ powders milled at liquid nitrogen temperature for 2 h (left) and 4 h (right).

Fig. 4.6. Particle morphology (secondary electron mode) for Fe$_{50}$Pt$_{50}$ powder milled at liquid nitrogen temperature for 2 h (a) and 4 h (b, c) and for Fe$_{60}$Pt$_{40}$ powder milled for 9 h (d).
The particle morphology after different milling times is illustrated in figure 4.6. After 2 h of milling, a broad range of particle sizes develops, with a majority of particles being larger than the starting powder particles. The particles tend to be welded into larger pieces, which is typical for mechanically alloyed materials [Sur01]. The average particle size of the agglomerated particles reduces after 4 h of milling and is in the range of 100-150 µm. After 9 h of milling the average particle size increases again to approximately 200 µm and the particle size distribution at this stage is narrower (Fig.4.6(d)). Apparently, no substantial reduction of the particle size should be expected with further increase of milling time.

**4.1.2. Milling at room temperature**

For comparison, milling at room temperature has been performed as well. In figure 4.7, the x-ray diffraction patterns of the Fe\textsubscript{50}Pt\textsubscript{50} powders milled at room temperature are shown. The formation of A1 FePt is observed already after 1 h of milling. The A1 FePt fraction rapidly increases with milling time and reaches about 96 vol. % after 5 h of milling.

These results indicate that the formation of the A1 phase occurs faster when milling is performed at room temperature. Room temperature milling for 1 h refines the grains of α-Fe and Pt to about 17 nm and 23 nm, respectively. After milling for 2 h the average grain size reaches ~7 nm for α-Fe and 15 nm for Pt. The rms strain of α-Fe and Pt is lower compared to the low temperature milled FePt powders: about 0.12 % after 1 h and 0.15 % after 2 h of milling. The crystallite size (20 nm) for the A1 FePt phase formed by 5 h of milling at room temperature is higher than that obtained by milling at 77 K. The yield of the powder after room temperature milling is extremely low due to the cold welding of the material onto the milling media.
4.1.3. Discussion

The structure evolution observed during ball milling of elemental Fe and Pt powders is consistent with the mechanism of alloying in a system with two different ductile components [Sur01]. The yield of the powder is much higher after milling at 77 K compared to that at room temperature due to the minimised cold welding of the powder onto the milling media. When milling is performed at liquid nitrogen temperature, the formation of the A1 phase starts later compared to room temperature milling. This allows to adjust the microstructure of the Fe-Pt powders and, depending on the aim, to finish with either a lamellar structure of the constituent elements with a thin (~ 5 nm) A1 layer at their interfaces (multilayer-type), disordered A1 FePt phase or an intermediate structure, consisting of refined lamellae of Fe and Pt with the A1 layer formed at their interfaces. In the 4 h milled powders, the A1 layer thickness reaches several tens of nanometers. In the powders with the lamellar structure the crystallites of the phases are substantially smaller than the layer thickness.

For clarity, table 4.1 illustrates the three different types of microstructure obtained by milling of the Fe-Pt powders at liquid nitrogen temperature. The structure evolution during milling is qualitatively similar for Fe_{100-x}Pt_x powders with different stoichiometries (x = 40; 45; 50; 55; 60). For samples with the homogeneous A1 phase (7 h milled), microstructure parameters do not differ significantly. The lattice constant of the A1 phase increases with Pt concentration (Fig. 4.8), what can be immediately understood from the difference in the atomic radii of Fe and Pt. From thermodynamic considerations, the negative deviation of the lattice parameter-versus-composition-curve from a linear behaviour (Vegard’s law) is expected for a system with negative enthalpy of mixing (like the Fe-Pt system). In the composition range investigated here, the data are not in disagreement with these considerations. Nevertheless, for a definite conclusion, a broader composition range needs to be investigated.

The obtained Fe-Pt alloys consist of ~ 100 µm sized particles constituted by randomly

Table 4.1. Microstructures obtained by milling of Fe-Pt powders for 2, 4 and 7 h at liquid nitrogen temperature. The following compositional contrasts can be distinguished: bright contrast – Pt, dark contrast – Fe (2 h milled); bright, gray and dark contrasts correspond to Pt, Fe_{50}Pt_{50} and Fe, respectively, in the 4 h milled alloy; in the 7 h milled powders, gray contrast corresponds to Fe_{50}Pt_{50} and dark contrast to Fe.

<table>
<thead>
<tr>
<th>Milling time</th>
<th>2 h</th>
<th>4 h</th>
<th>7 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microstructure type</td>
<td>Fe/Pt multilayer</td>
<td>Fe/A1/Pt</td>
<td>A1</td>
</tr>
<tr>
<td>SEM image</td>
<td><img src="image1" alt="200 nm image" /></td>
<td><img src="image2" alt="200 nm image" /></td>
<td><img src="image3" alt="200 nm image" /></td>
</tr>
</tbody>
</table>
oriented crystallites having an average size in the range of 10-40 nm. Further, the lamellae do not show any preferential orientation throughout one agglomerate.

4.2. Ordering of nanocrystalline Fe-Pt alloys

To produce the desired L1\textsubscript{0} phase, a heat treatment of the as-milled powders is required. In this section, the influence of stoichiometry and initial microstructure on the transformation to the L1\textsubscript{0} phase is studied by neutron powder diffraction during an \textit{in-situ} heat treatment. Two series of samples were investigated: powders with the equiatomic composition milled for 2, 4 and 7 h and powders with nonequiatomic compositions milled for 7 h.

4.2.1. Alloys with equiatomic composition

Figure 4.9 shows the evolution of the neutron diffraction patterns recorded during heating with a rate of 0.8 K/min for Fe\textsubscript{50}Pt\textsubscript{50} powder milled for 2 h. Initially, diffraction peaks due to Pt, \(\alpha\)-Fe and the A1 phase are observed, which is in consistence with the x-ray diffraction results (Section 4.1). At approximately 300 °C, a phase transformation occurs. It is apparent that along with the L1\textsubscript{0} diffraction peaks, the reflections due to the FePt\textsubscript{3} and Fe\textsubscript{3}Pt phases are present. Although the similar neutron coherent scattering lengths of Fe and Pt do not allow to differentiate between the ordered and disordered structures, the two phases have presumably the L1\textsubscript{2} structure. This is confirmed by x-ray diffraction investigation of isothermally treated 2 h milled powders (Chapter 5).

With increasing temperature, the intensities, as well as the width of the Pt and \(\alpha\)-Fe peaks are reduced, as obtained from pattern refinement, and eventually the reflections disappear. The integrated intensity of the L1\textsubscript{0} FePt peaks increases with temperature. The width of the L1\textsubscript{0} peaks narrows indicating some degree of grain growth. At the end of this process, the L1\textsubscript{0} crystallite size\(\langle D\rangle\) is equal to \(\approx 40\) nm.
Fig 4.9. Three-dimensional plots of neutron diffraction patterns recorded at a heating rate of 0.8 K/min as a function of temperature for Fe$_{50}$Pt$_{50}$ powders milled for (a) 2 h, (b) 4 h and (c) 7 h. Indicated are the diffraction peaks corresponding to the phases observed. A kink around 63° is an instrument artefact.
The results of the quantitative phase analysis for the 2 h milled Fe\textsubscript{50}Pt\textsubscript{50} are presented in figure 4.10(a). With increasing temperature, the \(\alpha\)-Fe and Pt fractions are reduced, whereas the L\textsubscript{10} fraction steadily increases. The amount of the A1 phase remains almost constant. The FePt\textsubscript{3} fraction reaches a maximum of about 27 wt. % at 410 °C and a further increase of temperature leads to its reduction. The FePt\textsubscript{3} weight fraction is substantially higher than that of Fe\textsubscript{3}Pt, the same is true for the volume fractions. Apparently, the Fe\textsubscript{3}Pt fraction also passes through a maximum. It is likely that the Fe\textsubscript{3}Pt phase appears at similar temperatures as the L\textsubscript{10} and FePt\textsubscript{3} phases, however, a reliable estimation is complicated due to the low phase amount.

As an example, the quality of the fit at the initial and intermediate stages of the transformation is illustrated in figure 4.11, showing a good agreement between the observed and calculated patterns. At intermediate temperatures, an adequate fit of the observed pattern requires several phases: L\textsubscript{10}, FePt\textsubscript{3} and Fe\textsubscript{3}Pt, as well as Pt, \(\alpha\)-Fe and A1. At e.g. 438 °C no magnetic contribution to the L\textsubscript{10} superstructure reflections is observable despite the fact that the temperature is below the Curie temperature of the L\textsubscript{10} phase ([\textit{Kus50}], also Table 1.3). At 660 °C, no residual \(\alpha\)-Fe or Pt could be detected and the diffraction pattern is fully ascribed to the four phases: L\textsubscript{10}, FePt\textsubscript{3}, Fe\textsubscript{3}Pt and A1.

In the 4 h milled Fe\textsubscript{50}Pt\textsubscript{50} alloy, three phases, Pt, \(\alpha\)-Fe and A1, are observed at the beginning of the process (Fig. 4.9(b)). The crystallites of the phases (<\textit{D}> \sim 10 nm) are finer and the amount of the A1 phase (= 80 wt. %) is considerably higher compared to that in the
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The formation of the L1$_0$ phase starts at about 300 °C. Rietveld refinement of the neutron diffraction patterns shows that, additionally to the L1$_0$ phase, the FePt$_3$ phase is formed on heating (Fig. 4.10(b)). Apparently, the Fe$_3$Pt phase forms as well but its amount is too small to be detected. With increasing temperature, the Pt, α-Fe and A1 phase fractions reduce, with most of α-Fe and Pt being consumed below approximately 450 °C. The FePt$_3$ fraction reaches a maximum of about 10 wt. % at 420 °C and the FePt$_3$ phase eventually disappears at about 550 °C. The L1$_0$ fraction increases reaching a value of about 99 wt. % at 650 °C, with the rest being A1 FePt.

Heating of the Fe$_{50}$Pt$_{50}$ powder milled for 7 h induces the A1 → L1$_0$ transformation (Fig. 4.9(c)). The fundamental reflections of the L1$_0$ phase are detected at about 300 °C. In the temperature range of 340-440 °C, a (110) superstructure reflection due to the ferromagnetic ordering is observed. At lower temperatures, the intensity of the (110) peak is apparently too low to be detected both due to the small L1$_0$ fraction and to the low magnetic intensity.
Figure 4.10(c) shows the evolution of the phase composition with temperature in the 7 h milled Fe$_{50}$Pt$_{50}$ powder. The A1 $\rightarrow$ L1$_0$ transformation is essentially completed below 400 °C. Further heating leads to a change in the lattice parameters and a reduction of the peak widths, as obtained from the refinement of the corresponding neutron diffraction patterns. From the correlation between the LRO parameter and the lattice constants (in particular, the $c/a$ ratio), it is concluded that the change in the lattice constants indicates an increase in the degree of long-range chemical order (see Section 4.2.2). At higher temperatures, $\alpha$-Fe (present in the as-milled powder in the amount of about 5 wt. %) reacts with the rest of the sample. However, at temperatures below approximately 550 °C, it does not play a major role in the L1$_0$ formation.

The L1$_0$ fractions transformed on heating of the Fe$_{50}$Pt$_{50}$ powders milled for various times are summarised in figure 4.12(a). In the 7 h milled powder, complete ordering is not achieved in the studied temperature range: the amount of the L1$_0$ phase saturates at 90 wt. %, the rest being disordered A1 phase. The L1$_0$ order parameter, $S$, reaches a value of 0.96 ± 0.04, as determined from the refinement of x-ray diffraction data obtained from the reacted samples using Eq. (1.1). The L1$_0$ fraction in the 4 h milled Fe$_{50}$Pt$_{50}$ powders reaches about 99 wt. %, with the LRO parameter $S = 0.99$ ± 0.04. However, below approximately 450 °C, the temperature required for the achievement of a particular L1$_0$ fraction is higher compared to that for the 7 h milled powders, but lower than that for the 2 h milled Fe$_{50}$Pt$_{50}$. Similarly for all the powders, the peak widths are slightly decreased with increasing temperature and at the end of the process the L1$_0$ crystallites are in the range of 30-40 nm.

4.2.2. Fe$_{100-x}$Pt$_x$ ($x = 40; 45; 50; 55$) alloys

Figure 4.13 shows details of neutron diffraction patterns for Fe$_{100-x}$Pt$_x$ powders milled for 7 h recorded during heating to 660 °C. Below 300 °C, the (002) diffraction peak of the A1 phase is observed. At 410 °C, the (002) peak is split, which is a result of the A1 to L1$_0$ phase transformation. Whereas in the Fe$_{50}$Pt$_{50}$ alloy most of the A1 FePt phase is consumed at this
temperature, in nonequatomic alloys the A1 → L1₀ transformation is more sluggish and a peak asymmetry is observed, which is due to the A1 phase presence also at higher temperatures.

Figure 4.12(b) shows the evolution of the L1₀ fraction in Fe₁₀₀₋ₓPtₓ powders during heating. The A1 → L1₀ transformation starts at about 300 °C independent of the stoichiometry. Among the studied compositions the transformation is fastest for the equiatomic alloy: at already 350 °C the L1₀ fraction reaches about 70 wt. %. For Fe₅₅Pt₄₅, the L₁₀ fraction increase during heating is similar to that of Fe₅₀Pt₅₀. However, the initial rate of the A1 → L1₀ transformation is slightly lower compared to that for Fe₅₀Pt₅₀. For the Fe₅₃Pt₅₅ and Fe₆₀Pt₄₀ alloys, the kinetics of the ordering is altered: the L₁₀ ordering is considerably decelerated for these alloys. The transformation to the L₁₀ phase is not finished even at 660 °C.

On heating, there is a change of both the L₁₀ phase fraction and the degree of order within the L₁₀ phase. Although a direct determination of the degree of order is not possible due to similar scattering lengths of Fe and Pt, the degree of order can be estimated from the variation of the lattice constants. As an example, figure 4.14 shows the evolution of the lattice constants in Fe₅₃Pt₅₅ observed on the first heating, i.e. during the A1 → L1₀ transformation, as well as on the second heating up to 550 °C followed by cooling to room temperature. It is apparent that the change in the lattice constants on the first heating is connected with both an increase in the degree of the long-range chemical order and an anisotropic lattice expansion. On the second heating, however, the evolution of the lattice constants is dominated by the lattice expansion. The thermal expansion is different in the a-
Phase formation in nanocrystalline Fe-Pt alloys

and c-directions, an effect often observed in 3d-element containing magnetic anisotropic compounds \[\text{[And95, Was90]}\]. On the first heating a similar behaviour of the $a$ and $c$ parameters is observed for all the Fe$_{100-x}$Pt$_x$ powders independent of milling time or stoichiometry. As an example, figure 4.14 also shows the variation of the lattice constants in 4 h milled Fe$_{50}$Pt$_{50}$ on the first heating followed by cooling to room temperature.

After the separation of the thermal expansion effects, the LRO development with increasing temperature may be evaluated by using the equation \[\text{[May89]}\], which correlates the L$_1^0$ order parameter, $S$, with the lattice constants:

$$S^2 = \frac{1-c/a}{1-(c/a)_m},$$  \hspace{1cm} (4.1)

where $c/a$ is the lattice parameter ratio at a certain temperature and $(c/a)_m$ is the ratio of the lattice constants at the maximum temperature reached during heating (around 660 °C). For the alloys studied here, Eq. (4.1) gives a value of $S$ of about 0.6-0.8 at the beginning of the transformation and $S$ increases linearly with temperature. However, Eq. (4.1) only gives a rough estimation of the LRO parameter and the values obtained likewise should be regarded rather as qualitative.

4.2.3. Kinetic and thermodynamic properties

DSC curves recorded at a heating rate of 10 K/min (Fig. 4.15(a)) for the Fe$_{50}$Pt$_{50}$ powders milled for various times reveal a broad exothermic peak, which is due to the formation of the new phases (see above). With increasing milling time, the maximum of the transformation peak shifts towards lower temperatures (Table 4.2). The exothermic peak becomes narrower and the amount of heat $\Delta H$ evolved during the transformation, determined from the area under the peaks, reduces from 13.8 kJ/mol to 10.5 kJ/mol and
ordering of nanocrystalline Fe-Pt alloys

7.0 kJ/mol as the milling time increases from 2 h to 4 h and 7 h. The onset of the transformation is, however, essentially at the same temperature of about 310 °C.

For the analysis of the DSC curves, the Kissinger method [Kis57] was employed using heating rates $\beta$ between 5 K/min and 40 K/min. By using the linear relationship

$$\ln(T_m^2 / \beta) = E_a / k_B T_m$$

(4.2)

it is possible to obtain values for the activation energy $E_a$ of the processes involved in the transformations, where $T_m$ is the temperature of the transformation peak and $k_B$ is Boltzmann’s constant. The corresponding Kissinger plot is shown in figure 4.16. The obtained activation energies were found to increase with milling time from 1.03 eV for the 2 h milled powder to 1.29 eV and 1.45 eV for the powders milled for 4 h and 7 h, respectively.

DSC curves for the Fe$_{100-x}$Pt$_x$ $(x = 40; 45; 50; 55)$ powders milled for 7 h are shown in figure 4.15(b). Whereas the onset temperature of the transformation is essentially unchanged, the width of the peaks and their position $T_m$ vary depending on the Pt

**Table 4.2.** The onset temperature of the transformation $T_o$, the transformation peak temperature $T_m$, the enthalpy change $\Delta H$, the Curie temperature of the L1$_0$ phase $T_c$ determined from the DSC measurements at a rate of 10 K/min and the transformation activation energy $E_a$ for the Fe$_{100-x}$Pt$_x$ powders milled for a given time $t_{milling}$.

<table>
<thead>
<tr>
<th>Nominal composition</th>
<th>$t_{milling}$ (h)</th>
<th>$T_o$ (°C)</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H$ (kJ/mol)</th>
<th>$E_a$ (eV)</th>
<th>$T_c$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$<em>{50}$Pt$</em>{50}$</td>
<td>2</td>
<td>316</td>
<td>440</td>
<td>13.8 ± 1.3</td>
<td>1.03 ± 0.08</td>
<td>472</td>
</tr>
<tr>
<td>Fe$<em>{50}$Pt$</em>{50}$</td>
<td>4</td>
<td>306</td>
<td>383</td>
<td>10.5 ± 0.5</td>
<td>1.29 ± 0.05</td>
<td>462</td>
</tr>
<tr>
<td>Fe$<em>{50}$Pt$</em>{50}$</td>
<td>7</td>
<td>315</td>
<td>372</td>
<td>7.0 ± 0.2</td>
<td>1.45 ± 0.09</td>
<td>459</td>
</tr>
<tr>
<td>Fe$<em>{55}$Pt$</em>{45}$</td>
<td>7</td>
<td>312</td>
<td>377</td>
<td>7.1 ± 0.2</td>
<td>1.56 ± 0.09</td>
<td>458</td>
</tr>
<tr>
<td>Fe$<em>{60}$Pt$</em>{40}$</td>
<td>7</td>
<td>302</td>
<td>393</td>
<td>5.9 ± 0.7</td>
<td>2.0 ± 0.2</td>
<td>440</td>
</tr>
<tr>
<td>Fe$<em>{45}$Pt$</em>{55}$</td>
<td>7</td>
<td>318</td>
<td>425</td>
<td>7.5 ± 0.7</td>
<td>2.2 ± 0.2</td>
<td>458</td>
</tr>
</tbody>
</table>

Fig. 4.15. DSC traces for (a) Fe$_{50}$Pt$_{50}$ powders milled for 2, 4 and 7 h and (b) Fe$_{100-x}$Pt$_x$ $(x = 40; 45; 50; 55)$ powders milled for 7 h (heating rate 10 K/min).
concentration. The lowest $T_m$ among the studied compositions is that for Fe$_{50}$Pt$_{50}$ (372 °C), whereas the highest $T_m$ (425 °C) was observed for the Pt-rich powder. Within the experimental uncertainty, the enthalpy evolved during the transformation does not vary with Pt concentration (the rather large error bars are due to the uncertainty in setting the limits of integration of the signal). However, the activation energy $E_a$ for the $A1 \rightarrow L1_0$ transformation varies with Pt concentration: the smallest $E_a$ value of 1.45 eV is observed for the equiatomic composition, whereas the highest activation energy of about 2.0 eV is determined for Fe$_{60}$Pt$_{40}$ and Fe$_{45}$Pt$_{55}$.

In a second heating run, performed immediately after the first one, a small endothermic peak indicating the Curie temperature of the $L1_0$ phase was observed (Fig. 4.17). The values of the Curie temperature $T_c$ of the $L1_0$ phase determined from the DSC measurements are also listed in Table 4.2. They show a strong compositional dependence (to be discussed in Chapter 6).

### 4.2.4. Structure of the samples after heat treatment

X-ray data collected at room temperature from the samples immediately after the *in-situ* neutron diffraction experiments was used for the refinement of the crystal structure of the phases present in the powders. Consistent with the neutron diffraction data, a mixture

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Fig. 4.16. Kissinger plot for the minimum of the transformation peaks for Fe$_{50}$Pt$_{50}$ powders milled for 2 h, 4 h and 7 h.

Fig. 4.17. DSC run recorded on a second heating for 7 h milled Fe$_{50}$Pt$_{50}$ (heating rate 10 K/min).
of the L1₀ FePt, L₁₂ Fe₃Pt, L₁₂ Fe₃Pt and A₁ phases is observed in the 2 h milled Fe₅₀Pt₅₀ powder. Only the L₁₀ phase is detected in the Fe₅₀Pt₅₀ powder milled for 4 h (the L₁₀ fraction estimated from the neutron diffraction data is 98 ± 1 wt. %). The LRO parameter of the L₁₀ phase in the heat treated powders milled for 2 and 4 h is determined to be about 0.99 ± 0.05.

For the Fe₁₀₀−ₓPtₓ (x = 40; 45; 50; 55) alloys, the structure parameters together with the weight fraction of the phases are listed in Table 4.3. The fractions of the phases are in good agreement with the ones obtained from the refinement of the neutron diffraction data. The lattice constants of both the L₁₀ and A₁ phases decrease with decreasing Pt concentration. This means that the atomic composition of the phases is modified with x. The site occupation parameter rₚt is close to unity for the Pt-rich and equiatomic alloys, whereas in Fe₅₅Pt₄₅ and Fe₆₀Pt₄₀ the Pt sites are partially occupied by Fe atoms. The Fe sites are occupied predominantly by the correct atoms for all x. The refined site occupation parameters were used for the determination of the LRO parameter using Eq. (1.1). The smallest L₁₀ order parameter is observed for the Fe₆₀Pt₄₀ alloy, as might have been expected for the alloy with the composition deviating most from the equiatomic one. However, the experimental LRO parameter of the L₁₀ phase for Fe₅₅Pt₅₅ exceeds the maximum attainable order parameter S_max (see Section 1.3) for the given composition (Table 4.3). This higher value of the LRO parameter is a consequence of a change in the overall composition caused by the reaction of α-Fe with the rest of the sample at temperatures above 550 °C. The actual composition of the reacted sample with nominal x = 55 was determined by energy-

Table 4.3. Results of the crystal structure refinement for the Fe₁₀₀−ₓPtₓ alloys milled for 7 h: phase fraction f, lattice constants a and c, site occupation r(Fe), LRO parameter S and agreement factors R_Bragg and χ². Numbers in the brackets represent the error in the least significant figure to the left.

<table>
<thead>
<tr>
<th></th>
<th>Fe₄₅Pt₀₅</th>
<th>Fe₅₀Pt₅₀</th>
<th>Fe₅₅Pt₄₅</th>
<th>Fe₆₀Pt₄₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>L₁₀ FePt</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>space group</td>
<td>P4/mmm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>f (wt. %)</td>
<td>97.7(4)</td>
<td>96.0(8)</td>
<td>82.9(9)</td>
<td>77.2(8)</td>
</tr>
<tr>
<td>a (Å)</td>
<td>3.8619(4)</td>
<td>3.8549(3)</td>
<td>3.8426(5)</td>
<td>3.8247(5)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>3.7193(4)</td>
<td>3.7127(4)</td>
<td>3.7118(6)</td>
<td>3.7141(6)</td>
</tr>
<tr>
<td>c/a</td>
<td>0.963</td>
<td>0.963</td>
<td>0.966</td>
<td>0.971</td>
</tr>
<tr>
<td>rₚt</td>
<td>0.99(5)</td>
<td>0.98(4)</td>
<td>0.87(5)</td>
<td>0.8(1)</td>
</tr>
<tr>
<td>rₚt</td>
<td>0.98(5)</td>
<td>0.97(4)</td>
<td>0.98(4)</td>
<td>0.95(4)</td>
</tr>
<tr>
<td>S</td>
<td>0.97</td>
<td>0.95</td>
<td>0.85</td>
<td>0.75</td>
</tr>
<tr>
<td>R_Bragg (%)</td>
<td>8.9</td>
<td>8.4</td>
<td>7.7</td>
<td>6.2</td>
</tr>
</tbody>
</table>

| A₁ FePt     |         |         |         |         |
| space group | Fm̅3m   |         |         |         |
| f (wt. %)   | 2.3(4) | 4.0(4) | 17.1(8) | 22.8(7) |
| a (Å)       | 3.8182(9) | 3.8108(8) | 3.779(2) | 3.7828(6) |
| R_Bragg (%) | 5.9 | 4.9 | 6.7 | 3.6 |
| χ²          | 1.77 | 2.17 | 1.78 | 3.95 |

* a) The composition determined by SEM-EDX analysis of the reacted sample with nominal x = 55.
dispersive x-ray (EDX) analysis to be Fe\(_{48}\)Pt\(_{52}\), whereas no significant changes in the composition were observed for \(x = 40, 45\) and \(50\).

**4.2.5. Discussion**

In all the studied nanocrystalline Fe\(_{100-x}\)Pt\(_x\) powders, the c/a ratio of the L\(_{10}\) phase is substantially smaller than unity already at the early stages of the transformation and it decreases slightly as the temperature is increased, as revealed by *in-situ* neutron diffraction. By means of isothermal heat treatments of the 4 h and 7 h milled Fe\(_{50}\)Pt\(_{50}\) powders the dependence of the LRO parameter, \(S\), on the annealing time at 350 °C and 450 °C was obtained (Fig. 4.18). High values of the LRO parameter (= 0.7) are observed after annealing at 350 °C for 10 min only and \(S\) is slightly increasing as the annealing time is prolonged. A heat treatment at 450 °C results in higher \(S\) values, which again slightly increase with annealing time. Therefore, it is concluded that in the nanocrystalline Fe-Pt alloys, ordering proceeds by nucleation and growth of the ordered phase with a high (although not being at equilibrium at the beginning) degree of the long-range chemical order. Subsequently, the degree of LRO within the L\(_{10}\) grains slightly increases.

Heating of the Fe\(_{100-x}\)Pt\(_x\) (\(x = 40; 45; 50; 55\)) alloys milled for 7 h induces the A1 \(\rightarrow\) L\(_{10}\) transformation. In the Fe\(_{50}\)Pt\(_{50}\) powders with a multilayer-type microstructure (2 and 4 h milled) along with the L\(_{10}\) phase, the L\(_{12}\) Fe\(_3\)Pt and FePt\(_3\) phases are formed. The combination of the L\(_{10}\) and L\(_{12}\) phases is apparently only a local equilibrium state, provoked by the heterogeneous precursor material, since in equilibrium one should expect the formation of the L\(_{10}\) phase only [Mas90]. The subsequent decomposition of the FePt\(_3\) and Fe\(_3\)Pt phases at a further increase of temperature supports this assumption. At the initial stages of the transformation, the fraction of the FePt\(_3\) phase is substantially higher than that of Fe\(_3\)Pt. The driving force for the formation of the phases (given by the difference between the Gibbs free energies of the phases, \(\Delta G\)) may be estimated by

\[
\Delta G \approx \frac{\Delta H_f \Delta T}{T_{\text{crit}}},
\]

where \(\Delta H_f\) is the enthalpy of formation and \(\Delta T\) is the degree of undercooling below the critical temperature for ordering \(T_{\text{crit}}\) [Pot01]. At 300 °C, the driving force for the L\(_{12}\) Fe\(_3\)Pt formation is \(\Delta G \approx 0.5 \Delta H_f\) and that for FePt\(_3\) is \(\Delta G \approx 0.65 \Delta H_f\). Assuming similar values of \(\Delta H_f\) for Fe\(_3\)Pt and FePt\(_3\), one obtains a higher driving force for the formation of the FePt\(_3\) compound compared to that for Fe\(_3\)Pt. Strictly speaking, the assumption about similar values of the formation enthalpies for these compounds, as obtained by e.g. a quasi-chemical approximation [Gug52] treating a system as composed of structureless atoms, is not adequate. The asymmetry between the two components, evidently related to the electronic structure of the alloys, is observed experimentally and by electronic structure calculations [Alc69, Rub95]. For instance, at 850 °C the experimentally determined enthalpy of mixing for the FePt\(_3\) compound is about 15 % higher than that for Fe\(_3\)Pt. Thus, the expected difference in the driving forces for Fe\(_3\)Pt and FePt\(_3\) could be even larger.
The formation of the L1\textsubscript{2} Fe\textsubscript{3}Pt and FePt\textsubscript{3} phases has also been observed on annealing nanocrystalline Fe-Pt alloys milled for 4 h with nonequiatomic compositions (Chapter 5) and for Fe/Pt multilayers [Liu98, End01]. Thus, the transformations occurring on heating in the mechanically alloyed Fe-Pt powders with the lamellar microstructure are similar to that in sputtered multilayers.

Independent of milling time and stoichiometry, the ordering starts at temperatures around 300 °C, as revealed by both in-situ neutron powder diffraction and differential scanning calorimetry. Interdiffusion of the elements that already occurs during milling (as indicated by the presence of the A1 phase) might be responsible for similar onset temperatures of the transformation for the alloys with the A1 and the multilayer-type structure (e.g. 2 h milled). This behaviour is different to cold-rolled Fe/Pt bulk multilayers not revealing any intermixing between Fe and Pt. In these materials, a shift in the onset temperature to lower values is observed with decreasing layer thickness [Ver05].

The ordering in nanocrystalline Fe\textsubscript{100-x}Pt\textsubscript{x} powders develops via so-called combined solid state reactions [Hor79]. It is accompanied by grain growth and thermally assisted removal of defects introduced by milling, as indicated by the progressive sharpening of the peak widths of the phases initially present in the powders. Apparently, an additional small exothermic signal starting at temperatures of about 120 °C is observed in the DSC curves (Fig. 4.15) that may also be attributed to healing out of crystal defects [Ma91].

In the studied composition range, the values of the evolved enthalpy \( \Delta H \) (\( \sim 7 \text{ kJ/mol} \)) do not differ significantly for the Fe\textsubscript{100-x}Pt\textsubscript{x} powders milled for 7 h (Table 4.2) and are comparable to literature data [Bar04]. It has been reported that for 40 \( \leq x \leq 55 \), the \( \Delta G \)-versus-concentration-curve has a rather small curvature [Alc69] that may account for the observed \( \Delta H \) values.

In the Fe\textsubscript{50}Pt\textsubscript{50} alloys, the enthalpy release varies depending on the initial microstructure. The highest enthalpy change value of about 14 kJ/mol was observed for the 2 h milled Fe\textsubscript{50}Pt\textsubscript{50} and further milling results in a decrease of the heat release (Table 4.2), i.e. the driving force for the transformation is reduced upon further milling. This may be explained by the difference in the total free energy between the powders with the (remaining) Fe and Pt lamellae and the powders with the A1 structure. If one assumes a
structure consisting of the Fe and Pt layers, the Gibbs free energy of such system will be [Pot01]

\[ G_{\text{Fe/Pt}} = x_{\text{Fe}} G_{\text{Fe}} + x_{\text{Pt}} G_{\text{Pt}}, \]  

(4.4)

where \( G_{\text{Fe}} \) and \( G_{\text{Pt}} \) are the Gibbs free energies of pure Fe and Pt and \( x_{\text{Fe}} \) and \( x_{\text{Pt}} \) are the atomic concentrations of the elements. The Gibbs free energy of the solid solution of Fe and Pt, i.e. the A1 phase, given by

\[ G_{\text{A1}} = G_{\text{Fe/Pt}} + \Delta G_{\text{max}} \]  

(4.5)

is reduced by a mixing term \( \Delta G_{\text{max}} \) being the reduction of the Gibbs free energy caused by the mixing of the atoms. Thus, as the alloying progresses the free energy of the system is lowered resulting in a reduction of the driving force for ordering.

Figure 4.19 schematically illustrates the variation of the Gibbs free energy with the atom arrangement in Fe\(_{100-x}\)Pt\(_x\) powders. As discussed above, in the Fe\(_{50}\)Pt\(_{50}\) powders with the multilayer-type microstructure, the L1\(_0\) formation proceeds via a metastable state according to the sequence: Fe/Pt precursor → L1\(_0\) + L1\(_2\) → L1\(_0\), whereas the Fe\(_{100-x}\)Pt\(_x\) alloys with the A1 structure transform directly to the L1\(_0\) phase. The activation barrier is reduced in the powders with the multilayer microstructure: the values of the activation energy for the powders milled for 2 h (1.03 eV) and 4 h (1.29 eV) are lower compared to that in the 7 h milled Fe\(_{50}\)Pt\(_{50}\) alloy (1.45 eV). The lower activation energy values are apparently a result of gradient-assisted diffusion. Both factors, i.e. the higher driving force and the lower activation barrier, are expected to enhance the ordering kinetics in the alloys with the multilayer-type microstructure. The concentration gradient, however, requires diffusion over longer distances and thus higher temperatures are needed for obtaining larger

![Fig. 4.19. Hypothetical Gibbs free energy configurational coordinates for Fe\(_{100-x}\)Pt\(_x\) powders. The full curve represents the transformation progress starting from the multilayer-type Fe/Pt precursor, the dashed curve that of starting from the A1 FePt.](image)
amounts of the L1₀ phase (see Fig. 4.12(a)). This fact is also indicated by the higher values of the kinetic peak temperature $T_m$ for the alloys with the lamellar microstructure (Fig. 4.20(a)). The peak shift with increasing milling time can be attributed, first, to the finer lamellae and smaller grain size of the phases, favouring diffusion along grain boundaries and, second, to the alloying of the elements on an atomic level. Nevertheless, in the Fe₅₀Pt₅₀ powders with the initial A1 structure the ordering is not complete, whereas the as-milled Fe₅₀Pt₅₀ alloy with the lamellar Fe/A1/Pt structure is almost fully ordered.

The results obtained by in-situ neutron diffraction were compared to those obtained by isothermal heat treatments. In the Fe₅₀Pt₅₀ powders milled for 7 h, a substantial amount of the A1 FePt phase (67 %) is transformed after only 10 min of annealing at 350 °C. The transformed L1₀ fraction increases with annealing time and reaches about 89 % after a heat treatment at 350 °C for 16 h. The LRO parameter of the L1₀ phase was found to increase from $S = 0.72 \pm 0.02$ to $S = 0.87 \pm 0.03$ for the powders annealed for 10 min and 16 h, respectively (Fig. 4.18). At 450 °C, the transformation of the A1 phase into the L1₀ FePt phase is essentially finished after 10 min of annealing. The amount of L1₀ FePt reaches about 91 %. A further increase of annealing time does not lead to any substantial change in the phase composition. However, the LRO parameter of the L1₀ FePt phase slightly increases from about 0.92 to 0.97 in the powders annealed for 10 min and 48 h, respectively.

The coexistence of the A1 and L1₀ phases is evidently a consequence of the first order nature of the A1 $\rightarrow$ L1₀ transformation [Lan04] and has also been observed in sputter-deposited thin films [Ris99, Ton03, Spa03]. However, the Fe₅₀Pt₅₀ alloy with the initial lamellar Fe/A1/Pt structure (e.g., 4 h milled) is almost completely ordered upon heating to 660 °C: the L1₀ fraction reaches 99 ± 1 wt. %, with the LRO parameter of the L1₀ phase being 0.99 ± 0.04.

In the heat-treated 4 h milled Fe₅₀Pt₅₀ alloy, the higher L1₀ fraction compared to that in the 7 h milled alloy can be a consequence of a complex mechanism of the L1₀ phase formation. In the 7 h milled Fe₅₀Pt₅₀ alloy, the A1 $\rightarrow$ L1₀ transformation rate is apparently limited by nucleation, as the L1₀ crystallites were found to only slowly grow with annealing time (e.g. from 23 nm to 30 nm upon increasing the annealing time from 10 min to 48 h at 450 °C). The A1 $\rightarrow$ L1₀ ordering is accompanied by a decrease of the defect density and is fast at the initial stage of the transformation. For higher temperatures/longer annealing times it decelerates again due to a defect structure rearrangement. In the 4 h milled powders, the L1₀ phase forms both directly within the A1 matrix and as a result of the reaction at the interface between the Pt(Fe) and A1 layers. The latter leads to the formation of the L1₂ phases (Fig. 4.10(b)), thus creating a concentration gradient. In the 4 h milled Fe₅₀Pt₅₀ alloy, the concentration gradient provides an additional driving force for the L1₀ formation at higher temperatures, whereas in the 7 h milled powder no such gradient exists. Since the Fe and Pt lamellae in the 4 h milled alloy are significantly thinner than those in the 2 h milled powders, the layers of the formed phases are finer (see Chapter 5) and, thus, the diffusion paths between the phases are shorter. In the studied temperature range, the L1₂ phases fully decompose and, above 550 °C, the 4 h milled Fe₅₀Pt₅₀ alloy is essentially completely ordered. Apparently, the reduction of the layer thickness down to a few nanometers should further reduce the temperature and/or time required for the achievement of a high amount of highly ordered L1₀ phase.
Phase formation in nanocrystalline Fe-Pt alloys

The evolution of the L1\textsubscript{0} fraction in the Fe\textsubscript{100-x}Pt\textsubscript{x} powders indicates a change in the kinetics of the A1 \rightarrow L1\textsubscript{0} transformation with the Pt concentration x (Fig. 4.12(b)). Whereas the Fe\textsubscript{50}Pt\textsubscript{50} alloy transforms readily into the L1\textsubscript{0} phase, the transformation rate for Fe\textsubscript{55}Pt\textsubscript{45} is slightly reduced and the A1 \rightarrow L1\textsubscript{0} transformation decelerates substantially in the Fe\textsubscript{60}Pt\textsubscript{40} and Fe\textsubscript{45}Pt\textsubscript{55} alloys. Consistent with the neutron diffraction data, the DSC measurements reveal that the transformation peak temperature, \(T_m\), is lowest for the equiatomic composition (Fig. 4.20(b)). An excess of either Pt or Fe increases \(T_m\). In contrast, Barmak et al. [Bar04] concluded that the A1 \rightarrow L1\textsubscript{0} transformation is fastest for alloys with Fe excess, whereas the A1 \rightarrow L1\textsubscript{0} transformation temperature was found to be reduced in Pt-rich sputter-deposited Fe-Pt films [Sek03].

In the Fe\textsubscript{100-x}Pt\textsubscript{x} alloys, the peak temperature \(T_m\) correlates with the values of the activation energy for the A1 \rightarrow L1\textsubscript{0} transformation (Fig. 4.20). For the Fe\textsubscript{50}Pt\textsubscript{50} alloy the activation energy is smallest (1.45 \(\pm\) 0.09 eV) and apparently increases slightly for the Fe\textsubscript{55}Pt\textsubscript{45} alloy (1.56 \(\pm\) 0.09 eV). An appreciable increase of \(E_a\) (up to \(\sim\) 2.0 eV) is observed for the Fe\textsubscript{60}Pt\textsubscript{40} and Fe\textsubscript{45}Pt\textsubscript{55} alloys. Presumably the degree of the LRO in the final L1\textsubscript{0} phase is one of the factors determining the value of the activation energy. The experimental LRO parameter of the L1\textsubscript{0} phase in the Fe\textsubscript{45}Pt\textsubscript{55} alloy is higher than the expected equilibrium value, which is a result of the reaction of the iron milling debris with the rest of the sample at higher temperatures. This may also explain a rather high Curie temperature of the L1\textsubscript{0} phase for this alloy: 458 °C versus a literature value of about 400 °C [Kus50]. For x = 40, 45 and 50 the \(T_c\) values are consistent with literature data [Kus50, Iva73].

The \(E_a\) values obtained in the present study are significantly lower than the activation energy of 3.1 eV for interdiffusion in FePt single-crystals [Kus03] and are comparable to those obtained in sputter-deposited FePt films [Spa03, Bar04]. It was shown that in nanocrystalline materials the activation energies for phase transformations and ordering are lower than for bulk diffusion and are of the same order of magnitude as those for fast diffusion along defects [Bat99]. Evidently in the nanocrystalline Fe-Pt powders studied here the kinetics of the L1\textsubscript{0} formation is enhanced by the high density of defects introduced by milling.

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**Fig. 4.20.** Activation energy \(E_a\) and peak temperature \(T_m\) for (a) Fe\textsubscript{50}Pt\textsubscript{50} powder milled for various times and (b) Fe\textsubscript{100-x}Pt\textsubscript{x} powders milled for 7 h.
Chapter 5

Structure and Magnetic Properties

In this chapter, structure and magnetic properties of nanocrystalline Fe\textsubscript{100-x}Pt\textsubscript{x} (x = 40-60) powders are studied in dependence on stoichiometry, milling time and annealing conditions. Whereas in Section 4.2 the phase formation was studied during continuous heating, the Fe\textsubscript{100-x}Pt\textsubscript{x} powders considered in this chapter are obtained by an isothermal heat treatment of as-milled alloys. Only the powders milled for 2 h (Section 5.1) and 4 h (Section 5.2) and subsequently annealed are investigated. The Fe-Pt powders milled for 7 h are not considered in this chapter, since, after heat treatment, these alloys still contain coarse Fe precipitates attributed to the milling debris. The latter demagnetise in low reverse magnetic fields and show inferior magnetic properties. In Section 5.3, the analysis of magnetisation reversal processes in nanocomposite and nearly single-phase Fe-Pt magnets will be given.

5.1. Fe-Pt Alloys with an Initial Fe/Pt Multilayer Microstructure

5.1.1. Alloys with Equiatomic Composition

Heat treatment at 450 °C of the 2 h milled Fe\textsubscript{50}Pt\textsubscript{50} powder with the Fe/Pt multilayer microstructure (Table 4.1) induces an immediate formation of L\textsubscript{10}FePt, which is evidenced by the presence of the L\textsubscript{10} superstructure peaks and splitting of some of the fundamental peaks in the x-ray diffraction patterns (Fig. 5.1). Additionally to the L\textsubscript{10} phase the formation of the Fe\textsubscript{3}Pt (L\textsubscript{12}) and FePt\textsubscript{3} (L\textsubscript{12}) phases is observed. According to a Rietveld analysis the

![Fig. 5.1. X-ray diffraction patterns for Fe\textsubscript{50}Pt\textsubscript{50} powders as-milled (2 h) and annealed at 450 °C for different times (superstructure reflections of the L\textsubscript{10} phase are marked by arrows).](image)
Structure and magnetic properties

Fe$_{50}$Pt$_{50}$ powder annealed for 10 min contains about 53 vol. % of the L1$_0$ phase with an average grain size of about 25 nm. After this short annealing time unreacted $\alpha$-Fe (7 vol. %) and Pt (5 vol. %) as well as A1 FePt (13 vol. %) are present. Similar to the in-situ neutron diffraction results (Chapter 4.2), the amount of the L1$_2$ FePt$_3$ phase (16 vol. %) is higher than that of L1$_2$ Fe$_3$Pt (6 vol. %).

With increasing annealing time the amount of residual $\alpha$-Fe and Pt is reduced and no elemental Fe and Pt are observed upon annealing at 450 °C for 16 h and longer. At the same time, the L1$_0$ fraction increases and the Fe$_3$Pt and FePt$_3$ fractions are reduced (Fig. 5.2(a)). Rietveld refinement of x-ray diffraction patterns of the FePt powders annealed at 450 °C/48 h yields the following phase contents: about 84 vol. % L1$_0$ FePt, 9 vol. % A1 FePt, 5 vol. % FePt$_3$ and 2 vol. % Fe$_3$Pt.

An increase of the annealing temperature promotes higher reaction rates. For instance, after annealing for 10 min at 500 °C and 550 °C the amount of the L1$_0$ FePt phase is about 62 vol. % and 71 vol. %, respectively. As an example, figure 5.2(b) shows the evolution of the phase composition with annealing time at 550 °C. After heat treatment at this temperature for 10 min the fractions of the residual $\alpha$-Fe and Pt are less than 0.5 vol. %. The amount of the Fe$_3$Pt and FePt$_3$ phases is smaller and the rate of their dissolution is higher than that in powders annealed at lower temperatures. However, the L1$_2$ phases are still present in the samples annealed for 48 h. For the annealing conditions studied, the maximum L1$_0$ content is about 96 ± 1 vol. % after heat treatment at 550 °C/48 h, the rest being A1 FePt (2 vol. %) and L1$_2$ FePt$_3$ (2 vol. %).

The following lattice parameters of the L1$_0$ FePt phase in the heat treated Fe$_{50}$Pt$_{50}$ powders were determined by Rietveld analysis: $a = 3.858(2)$ Å and $c = 3.716(3)$ Å ($c/a = 0.964$), which is in good agreement with the lattice constant of bulk L1$_0$ FePt ($a = 3.852$ Å, $c = 3.713$ Å; compare [Pdf]). The lattice constants of the A1 phase are equal to $a = 3.820(3)$ Å. No significant changes in the lattice parameter of the L1$_0$ and A1 FePt phases are observed in dependence on the annealing conditions studied. The order parameter of the L1$_0$ FePt phase in the heat-treated FePt powders was found to be approximately 0.9, independent of annealing conditions. Thus, the heat treatment of the powders milled for 2 h results in the formation of the chemically highly ordered L1$_0$ FePt phase.
The high resolution SEM micrograph of the Fe<sub>50</sub>Pt<sub>50</sub> powder annealed at 450 °C for 48 h (Fig. 5.3) shows that the microstructure preserves a lamellar character after annealing. Three types of compositional contrast can be distinguished. According to EDX analysis, bright layers have a stoichiometry of Fe<sub>25</sub>Pt<sub>75</sub>. They are surrounded by Fe<sub>50</sub>Pt<sub>50</sub> layers, followed by a layer of Fe<sub>75</sub>Pt<sub>25</sub> (darkest contrast). The interfaces between the layers are sharp. The SEM image reveals as well that the size of the crystallites within the lamellae is substantially smaller than the lamellae thickness. The average grain size of the phases determined from the x-ray line broadening is about 30 nm and rms strain is in the range of 0.11-0.15 %.

Figure 5.4 shows the room temperature demagnetisation curves for the as-milled and annealed (450 °C) Fe<sub>50</sub>Pt<sub>50</sub> powder. In the as-milled state, the powder shows soft magnetic behaviour. A remarkable coercivity is developed after just 10 min annealing, though a shoulder is observed in the demagnetisation curves of the Fe<sub>50</sub>Pt<sub>50</sub> powders annealed for 10 min and 1 h, which is attributed to the presence of unreacted α-Fe. The increase of coercivity, $H_c$, with annealing time is due to the increase of the L1<sub>0</sub> fraction concurrent with the decrease of α-Fe and Fe<sub>3</sub>Pt fractions. The highest coercivity value ($\mu_0 H_c = 0.7$ T) was achieved in Fe<sub>50</sub>Pt<sub>50</sub> powder annealed at 450 °C for 48 h. The remanence $J_r$ changes with annealing time as well: it rises from 0.59 T for the 10 min annealed sample up to 0.70 T for the sample annealed for 48 h. The polarisation of the heat treated Fe<sub>50</sub>Pt<sub>50</sub> powders in a
maximum applied field of 5 T is equal to approximately 1.0 T.

Figure 5.5 shows the dependence of the coercivity \( H_c \) (left) and the grain size (right) of the \( L1_0 \) phase on annealing time at different temperatures. Whereas in the powders annealed at 450 °C the coercivity increases with annealing time, in Fe\(_{50}\)Pt\(_{50}\) heat treated at 500 °C the initial \( H_c \) increase is followed by a small drop. After 10 min of annealing at 500 °C, unreacted \( \alpha\)-Fe is still present (2 vol. %), whereas no \( \alpha\)-Fe is detected after 1 h of annealing. Moreover, the \( L1_0 \) fraction is higher and that of Fe\(_3\)Pt lower compared to the 10 min annealed Fe\(_{50}\)Pt\(_{50}\) powder. The subsequent decrease of coercivity is attributed to grain growth. Grain growth is even more pronounced at 550 °C. Heat treatment at this temperature for 48 h results in a grain size of about 40 nm, which is noticeably larger than that of the powders annealed at lower temperatures. As a result, at 550 °C the coercivity drop is substantial. At 450 °C, the grain growth is comparatively slow (Fig. 5.5). From this study it follows that the optimum heat treatment parameters are 450 °C for 48 h. Annealing at lower temperatures requires longer times for the completion of the phase transformations, whereas at higher temperatures the magnetic properties deteriorate as a result of grain growth.

### 5.1.2. \( Fe\(_{100-x}\)Pt\(_x\) (x = 40; 45; 50; 55; 60) alloys

Figure 5.6 shows x-ray diffraction patterns of optimally annealed (450 °C/48 h) \( Fe\(_{100-x}\)Pt\(_x\) powders. In the \( Fe\(_{50}\)Pt\(_{50}\) alloy, due to rather small Fe\(_3\)Pt and FePt\(_3\) fractions, it is not possible to unambiguously distinguish whether these phases have the ordered \( L1_2 \) or the disordered A1 structure. In the Pt-rich (Fe-rich) powders, distinct superstructure reflections of the \( L1_2 \) FePt\(_3\) (Fe\(_3\)Pt) phase are clearly detectable, which is due to the higher fraction of the latter. Only the superstructure reflections of the \( L1_2 \) phases not severely overlapping with those of the \( L1_0 \) phase are marked in figure 5.6 (compare Appendix B).

Figure 5.7(a) shows the results of the phase analysis for the annealed \( Fe\(_{100-x}\)Pt\(_x\) powders. The \( L1_0 \) fraction passes through a maximum at \( x = 50 \). With increasing \( x \), the FePt\(_3\) phase amount increases up to almost 40 vol. % for \( Fe\(_{40}\)Pt\(_{60}\), whereas the Fe\(_3\)Pt fraction is
Fe-Pt alloys with an initial Fe/Pt multilayer microstructure

Fig. 5.6. X-ray diffraction patterns of $\text{Fe}_{100-x}\text{Pt}_x$ powders milled for 2 h and annealed at 450 °C/48 h. Dashed lines mark the positions of some of the superstructure reflections of the $\text{L}_1_2$ FePt$_3$ (stars) and $\text{L}_1_2$ Fe$_3$Pt (diamonds) phases.

reduced from 38 vol. % for $\text{Fe}_{60}\text{Pt}_{40}$ to about 2 vol. % for $\text{Fe}_{50}\text{Pt}_{50}$. The content of the A1 phase is about 6-10 vol. %, relatively independent of x. The crystallite size <D> of $\text{L}_1_0$ FePt for various x is in the range of 28-35 nm.

In order to estimate the phase fractions in the optimally annealed $\text{Fe}_{100-x}\text{Pt}_x$ powders, it is assumed that the heat treatment of the as-milled alloys results in a phase separation. In the case of the powders with $x \neq 50$ this might result in a combination of the FePt$_3$ (for $x > 50$)/Fe$_3$Pt (for $x < 50$) phases with the $\text{L}_1_2$ and/or A1 structure and the FePt ($\text{L}_1_0$ and/or A1) phase. For the Pt-rich powders it can be written:

Fig. 5.7. Dependence of (a) phase composition and (b) LRO parameter of the $\text{L}_1_0$ phase ($S_{\text{L}_1_0}$) and average order parameter ($S_{\text{ave}}$) on Pt concentration in $\text{Fe}_{100-x}\text{Pt}_x$ powders milled for 2 h and annealed at 450 °C/48 h.
Structure and magnetic properties

\[ \text{Fe}_{a_0}\text{Pt}_{b_0} = a\text{Fe}_{30}\text{Pt}_{50} + b\text{Fe}_{25}\text{Pt}_{75}, \]

where \( a \) and \( b \) are the volume fractions of the FePt and Fe₃Pt phases, respectively. From Eq. (5.1) one obtains \( a = 0.6 \) and \( b = 0.4 \), which is in very good agreement with the observed volume fractions (Fig. 5.7(a)).

Table 5.1 lists the fractions of Pt(Fe) sites occupied by the correct atom, \( r_{\text{Pt(Fe)}} \), in dependence on Pt concentration. The fraction of the correctly occupied sites in L1₀ FePt is high for all the powders, with \( r_{\text{Pt}} \) being somewhat higher for the Pt-rich powders. Consequently, the LRO parameter of the L1₀ phase was found to be approximately 0.9 for the \( \text{Fe}_{100-x}\text{Pt}_{x} \) (\( x = 40; 45; 50 \)) powders, whereas \( S \) for the Pt-rich powders (\( x = 55; 60 \)) is close to unity (Fig. 5.7(b)). Since the material is multiphase, an average order parameter \( S_{\text{ave}} \) of the sample can be calculated by

\[ S_{\text{ave}} = f_0 S, \]

where \( f_0 \) is the volume fraction and \( S \) the LRO parameter of the L1₀ phase. The variation of \( S_{\text{ave}} \) in the \( \text{Fe}_{100-x}\text{Pt}_{x} \) powders conforms to that of the L1₀ volume fraction: it reaches a maximum at \( x = 50 \) (Fig. 5.7(b)).

The distribution of the phases in the heat treated \( \text{Fe}_{100-x}\text{Pt}_{x} \) powders has a strongly pronounced layered character independent of the stoichiometry. As an example, figure 5.8 shows the microstructure of the Fe-rich and Pt-rich powders. For the Fe-rich powder, the bright areas in the SEM image have the stoichiometry of \( \text{Fe}_{50}\text{Pt}_{50} \) and the dark ones that of \( \text{Fe}_{75}\text{Pt}_{25} \), whereas for \( \text{Fe}_{40}\text{Pt}_{60} \) the bright contrast is due to \( \text{Fe}_{25}\text{Pt}_{75} \) and the dark one is due to \( \text{Fe}_{50}\text{Pt}_{50} \). Moreover, the high resolution SEM image confirms the crystallite size of the phases determined from the x-ray line broadening.

**Table 5.1.** Site occupation \( r_{\text{Pt(Fe)}} \) in the L1₀ FePt phase as a function of composition \( x \) in \( \text{Fe}_{100-x}\text{Pt}_{x} \) powders.

<table>
<thead>
<tr>
<th>Site occupation</th>
<th>( x = 40 )</th>
<th>( x = 45 )</th>
<th>( x = 50 )</th>
<th>( x = 55 )</th>
<th>( x = 60 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r_{\text{Pt}} )</td>
<td>0.93(2)</td>
<td>0.91(1)</td>
<td>0.91(1)</td>
<td>0.99(1)</td>
<td>0.97(2)</td>
</tr>
<tr>
<td>( r_{\text{Fe}} )</td>
<td>1.00(2)</td>
<td>1.00(1)</td>
<td>1.00(2)</td>
<td>0.99(2)</td>
<td>0.99(2)</td>
</tr>
</tbody>
</table>

Fig. 5.8. SEM image (backscattered electron mode) of \( \text{Fe}_{35}\text{Pt}_{65} \) (left) and \( \text{Fe}_{60}\text{Pt}_{40} \) (right) powders annealed at 450 °C for 48 h.
Fe-Pt alloys with an initial Fe/Pt multilayer microstructure

Figure 5.9 summarises room temperature demagnetisation curves of the Fe\textsubscript{100-x}Pt\textsubscript{x} powders. Whereas the samples of equiatomic and Pt-rich compositions are characterised by a one-phase demagnetisation behaviour, the shoulders in the demagnetisation curves of Fe\textsubscript{55}Pt\textsubscript{45} and Fe\textsubscript{60}Pt\textsubscript{40} indicate the presence of the soft magnetic phases being poorly exchange-coupled to the hard magnetic L1\textsubscript{0} (to be discussed in Section 5.3).

Room temperature magnetic properties of the Fe\textsubscript{100-x}Pt\textsubscript{x} powders are summarised in figure 5.10. The coercivity $H_c$ in Fe\textsubscript{100-x}Pt\textsubscript{x} increases steadily with $x$ from 0.33 T ($x = 40$) to 0.95 T ($x = 60$). Up to $x = 50$, the increase of $H_c$ can be attributed to the increase of the L1\textsubscript{0} fraction and concurrent decrease of the L1\textsubscript{2} Fe\textsubscript{3}Pt phase content. The grains of the Fe\textsubscript{3}Pt phase, which is characterised by a low magnetocrystalline anisotropy, may serve as sites, where the magnetisation can be relatively easily reversed. The increase of $H_c$ for $x > 50$ can be attributed to the specific lamellar microstructure formed in the Pt-rich Fe\textsubscript{100-x}Pt\textsubscript{x} powders. The paramagnetic FePt\textsubscript{3} phase decouples the grains of the L1\textsubscript{0} phase, which leads to the increase of $H_c$. The LRO parameter of L1\textsubscript{0} FePt is higher for Pt-rich Fe\textsubscript{100-x}Pt\textsubscript{x} powders. The magnetic anisotropy in L1\textsubscript{0} compounds was shown to increase linearly with the LRO parameter $S$ [May89, Kam99, Kan00, Sta04], which should lead to an increase of $H_c$ in samples with a comparable microstructure. Therefore, for $x > 50$, along with the specific microstructural features, $H_c$ might be influenced by the chemical order in L1\textsubscript{0} FePt.

Remanence ($J_r$) and polarisation in the maximum applied field of 16 T ($J_{16}$) reduce
with increasing $x$. $J_r$ decreases from 0.83 T ($x = 40$) to 0.40 T ($x = 60$), $J_{16}$ from 1.60 T ($x = 40$) to 0.78 T ($x = 60$). For $x < 50$ the decrease of $J_r$ and $J_{16}$ is due to the reduction of the Fe$_3$Pt content. A further reduction of the polarisation for $x > 50$ is caused by the reduction of the L$_{10}$ FePt fraction concurrent with the increase of the paramagnetic L$_{12}$ FePt$_3$ phase content.

### 5.1.3. Discussion

**Fe$_{50}$Pt$_{50}$ powders**

The influence of the annealing conditions on the structure and the magnetic properties of the Fe$_{50}$Pt$_{50}$ powders milled for 2 h at liquid nitrogen temperature can be summarised as follows. Heat treatment of the powders results in the formation of the chemically highly ordered L$_{10}$ FePt phase with a LRO parameter of $\sim$ 0.9. An increase of annealing time at a given temperature, as well as an increase of annealing temperature result in a higher amount of the L$_{10}$ FePt phase. For the annealing conditions studied, the maximum L$_{10}$ fraction was about 96 vol. % (550 °C/48 h). The A1 FePt fraction ($\sim$ 10 vol. %) remains almost unchanged with annealing time. Additionally to the L$_{10}$ phase, the formation of the L$_{12}$ FePt$_3$ and Fe$_3$Pt phases is observed. Their amount is reduced with annealing time and the reduction is more effective at higher annealing temperatures. The observation is consistent with the conclusions drawn in Chapter 4.2. Nevertheless, the FePt$_3$ phase is still present in the samples annealed at 550 °C for 48 h.

The variation of the extrinsic magnetic properties with annealing conditions may be well understood on the basis of structure evolution. For short annealing times, the inferior magnetic properties could be explained by the incompleteness of the phase transformations. At 450 °C, the increase of annealing time leads to a higher L$_{10}$ fraction and, thus to an improvement of the magnetic properties. Optimum values are obtained in the samples annealed for 48 h at this temperature. The increase of annealing time and temperature leads to grain growth. Grain growth is most pronounced at 550 °C, which could explain the substantial drop in coercivity at higher temperatures. At lower annealing temperatures, grain growth is less pronounced. Thus, the possibility to form the L$_{10}$ phase at lower temperatures (450 °C) compared to annealing temperatures above 600-700 °C typical for coarse-grained alloys [Shu68, Kle03] is advantageous for obtaining optimum magnetic properties. Similar trends in the structure evolution are observed in Fe$_{100-x}$Pt$_x$ for $x = 40; 45; 50; 60$. An optimum heat treatment of 450 °C for 48 h was established for the temperatures and times studied.

**Fe$_{100-x}$Pt$_x$ (x = 40; 45; 50; 55; 60) powders**

A heat treatment (450 °C/48 h) of the Fe$_{100-x}$Pt$_x$ ($x = 40; 45; 55; 60$) powders also results in the formation of the chemically highly ordered L$_{10}$ FePt phase. The maximum amount of the L$_{10}$ phase is about 85 vol. % for Fe$_{50}$Pt$_{50}$. On the Fe-rich side, the L$_{12}$ Fe$_3$Pt phase in an amount of 38 vol. % (Fe$_{60}$Pt$_{40}$) is present, whereas in the Pt-rich powders L$_{12}$ FePt$_3$ phase is observed (40 vol. % for Fe$_{40}$Pt$_{60}$). This supports the assumption (Chapter 4.2) that it is more favourable to form the chemically highly ordered L$_{10}$ and L$_{12}$ phases, rather than a
Fe-Pt alloys with an initial Fe/Pt multilayer microstructure

nonequatomic L1₀ phase with an order parameter of, consequently, less than unity. The layer distribution of the phases in the annealed Fe₁₀₀₋ₓPtₓ powders (Fig. 5.8) is also a consequence of the heterogeneity of the as-milled material. Thus, the preparation method gives a possibility to obtain various combinations of the phases for concentrations, where, according to the equilibrium phase diagram (Fig. 1.1), only one phase region exists.

In literature, the coercivity of the L1₀-type alloys is frequently correlated to the fraction of the ordered phase (or the average order parameter $S_{\text{ave}}$) and maximum $H_c$ values are obtained in samples containing essentially the L1₀ phase [Shu68, Shu71, Ris99, Ton03]. Such an approach could be indeed justified for samples containing a mixture of the hard magnetic L1₀ and soft magnetic A1 phases, where the latter phase is treated as a defect favouring magnetisation reversal. Obviously, in the presence of additional phases, e.g. L₁₂ Fe₃Pt or FePt₃, one has to consider the magnetic ordering type of these additional phases (e.g. ferro-, antiferro- or paramagnetic) and, more importantly, the particular microstructure.

In the studied Fe₁₀₀₋ₓPtₓ powders the maximum coercivity $H_c$ does not correspond to the maximum L1₀ fraction: it increases steadily with Pt concentration $x$ and reaches 0.95 T in Fe₄₀Pt₆₀ (compare Fig. 5.7 and Fig. 5.10). The increased coercivity in Pt-rich samples can be attributed to the decoupling of the L1₀ FePt lamellae by paramagnetic L₁₂ Fe₃Pt and, apparently, to the improved degree of order in the L1₀ phase. The coercivity increase is achieved, however, at the expense of magnetisation (Fig. 5.10). As a result of the opposite dependence of coercivity and remanence on $x$, the highest energy product is achieved for Fe₅₀Pt₅₀ and is equal to $(BH)_{\text{max}} = 73$ kJ/m³ (Fig. 5.11). In the Fe-rich samples, the reduction of $(BH)_{\text{max}}$ is also a consequence of the two-phase demagnetisation behaviour. The magnetisation reversal of these powders will be treated in Section 5.3.

5.2. Fe-Pt alloys with an initial Fe/A1/Pt multilayer microstructure

In this section, the evolution of structure and magnetic properties in heat treated Fe₁₀₀₋ₓPtₓ ($x = 40; 45; 50; 55; 60$) alloys milled for 4 h is investigated. The as-milled alloys have the Fe/A1/Pt multilayer microstructure (Table 4.1). The heat treatment of the as-milled powders was performed at 450 °C for 48 h and 336 h.
Structure and magnetic properties

Figure 5.12 shows the dependence of the phase composition on Pt concentration \( x \) in the heat-treated \( \text{Fe}_{100-x}\text{Pt}_x \) powders (450 °C/48 h). Similar to the 2 h milled \( \text{Fe}_{100-x}\text{Pt}_x \) alloys treated at the same annealing conditions, the dominant phase identified in all the powders is \( \text{L1}_0 \) FePt. Its fraction reaches a maximum of about 97-98 vol. % in the \( \text{Fe}_{50}\text{Pt}_{50} \) powder, the rest being A1 phase. The average grain size \( <D> \) of the \( \text{L1}_0 \) phase determined from the x-ray data is about 30-35 nm. In the Fe-rich powders, along with the \( \text{L1}_0 \) and A1 phases, the \( \text{Fe}_3\text{Pt} \) phase was detected, whereas in the Pt-rich alloys \( \text{FePt}_3 \) is observed. In the Fe-rich samples, the amount of the \( \text{Fe}_3\text{Pt} \) phase is only slightly reduced compared to the 2 h milled alloys: its fraction is about 30 vol. % in \( \text{Fe}_{50}\text{Pt}_{40} \) and 6 vol. % in \( \text{Fe}_{55}\text{Pt}_{45} \). The amount of the \( \text{FePt}_3 \) phase in the Pt-rich powders is slightly higher than that in the 2 h milled alloys. At the same time, the \( \text{L1}_0 \) fraction is reduced and the A1 fraction increases considerably.

An increase of the soft magnetic phase fraction is also reflected in a substantial decrease of the coercivity and in the appearance of a shoulder in the demagnetisation curve of the \( \text{Fe}_{40}\text{Pt}_{60} \) sample (Fig. 5.13). For this sample, it was possible to determine the site occupation parameters in the \( \text{L1}_2 \) \( \text{FePt}_3 \) phase using Rietveld refinement: the Pt sites were

Figure 5.12. Dependence of the phase composition on Pt concentration in \( \text{Fe}_{100-x}\text{Pt}_x \) powders milled for 4 h and annealed at 450 °C/48 h. The compositional stability ranges of the phases at 600 °C according to the equilibrium phase diagram (compare Fig. 1.1) are marked as well.

Figure 5.13. Room temperature demagnetisation curves of \( \text{Fe}_{100-x}\text{Pt}_x \) powders milled for 4 h and annealed at 450 °C for 48 h (open symbols) and for 336 h (solid symbols) in dependence on the Pt concentration \( x \).
Fe-Pt alloys with an initial Fe/A1/Pt multilayer microstructure

Fe-Pt alloys with an initial Fe/A1/Pt multilayer microstructure have been investigated. It was found that the Fe sites were not fully occupied by Pt atoms ($r_{Pt} = 1$), whereas the fraction of the correctly occupied Fe sites was equal to $r_{Fe} = 0.69(5)$. This corresponds to a chemical composition of Fe$_{34.5}$Pt$_{65.5}$. Alloys with this composition show a ferromagnetic behavior at temperatures only below 250 K [Bac63]. That means that the shoulder in the demagnetization curve is most probably due to the increased fraction of the A1 phase, thus supporting the results of the phase analysis.

The FePt$_3$ phase in Pt-rich alloys has the L1$_2$ structure, as could be inferred from the existence of superstructure reflections e.g. in the Fe$_{40}$Pt$_{60}$ sample (Fig. 5.14). Owing to the relatively small Fe$_3$Pt volume fraction in Fe-rich alloys and very similar lattice parameters of the phases it is difficult to unambiguously distinguish whether the observed Fe$_3$Pt phase has the ordered L1$_2$ or the disordered A1 structure. Nevertheless, Rietveld refinement of the

![Fig. 5.14. X-ray diffraction patterns of Fe$_{100-x}$Pt$_x$ powders milled for 4 h and annealed at 450 °C/48 h. Dashed lines mark the positions of some of the superstructure reflections of the L1$_2$ FePt$_3$ (stars) and L1$_2$ Fe$_3$Pt (diamonds) phases.](image)

![Fig. 5.15. Lattice parameters of the L1$_2$ phase, $a$ and $c$, (left) and A1 phase (right) in dependence on Pt concentration $x$ in Fe$_{100-x}$Pt$_x$ powders milled for 4 h and annealed at 450 °C for 48 h (open symbols) and 336 h (solid symbols). For the L1$_2$ phase, the error bar is within the symbol size.](image)
x-ray diffraction spectra of the Fe-rich Fe\(_{100-x}\)Pt\(_{x}\) powders allows an identification of two cubic phases with different lattice parameters. The first one, presumably L\(_{12}\) Fe\(_3\)Pt, has almost identical lattice parameters in both Fe\(_{60}\)Pt\(_{40}\) and Fe\(_{55}\)Pt\(_{45}\) powders: \(a = 3.775(1)\) Å and \(a = 3.774(2)\) Å, respectively. At the same time, the lattice constant of the disordered A1 FePt phase increases with Pt concentration (Fig. 5.15). This means that the atomic composition of the A1 phase is slightly modified with \(x\). The lattice parameters of the L\(_{10}\) phase change with Pt concentration as well. The parameter \(a\) increases with \(x\), whereas \(c\) first decreases for \(x \leq 50\) and for \(x > 50\) it increases again. Obviously, the atomic composition of the L\(_{10}\) phase is also modified with Pt concentration.

Rietveld analysis was thus employed for the investigation of site occupation parameters in the L\(_{10}\) phase and their evolution with Pt concentration in the Fe\(_{100-x}\)Pt\(_{x}\) powders. The fractions of the Pt(Fe) sites occupied by the right atom \(r_{\text{Pt(Fe)}}\), extracted from the Rietveld refinement, were used for the determination of the long-range order parameter \(S\) of L\(_{10}\) FePt, as defined in Eq. (1.1). The fractions of correctly occupied sites and the order

Fig. 5.16. Fractions \(r_{\text{Pt}}\) and \(r_{\text{Fe}}\) of Pt and Fe sites, respectively, occupied by the correct atom and the order parameter \(S\) of the L\(_{10}\) phase in the Fe\(_{100-x}\)Pt\(_{x}\) powders milled for 4 h and annealed at 450 °C for 48 h (open symbols) and for 336 h (solid symbols) vs. Pt concentration.

Fig. 5.17. Dependence of the phase composition on Pt concentration in Fe\(_{100-x}\)Pt\(_{x}\) powders milled for 4 h and annealed at 450 °C/336 h.
Fe-Pt alloys with an initial Fe/A1/Pt multilayer microstructure

The site occupation fractions are high for all the powders. The fraction of the correctly occupied Pt sites in the L1\textsubscript{0} structure increases from $r_{\text{Pt}} = 0.85(5)$ for Fe\textsubscript{60}Pt\textsubscript{40} to $r_{\text{Pt}} = 0.99(3)$ for Fe\textsubscript{40}Pt\textsubscript{60}. Such an opposite dependence of $r_{\text{Fe}}$ and $r_{\text{Pt}}$ is consistent with the alloy stoichiometry. Consequently, the LRO parameter of the L1\textsubscript{0} phase reaches its maximum of 0.92 for the equatomic composition.

By increasing the annealing time to 336 h, no considerable differences in the lattice parameters (Fig. 5.15) and volume fractions of the phases (Fig. 5.17) are observed. The site occupation $r_{\text{Pt}}$ in the L1\textsubscript{0} phase and, accordingly, the L1\textsubscript{0} order parameter slightly increases (solid symbols in Fig. 5.16). The LRO parameter $S$ reaches a maximum value of 0.97(1) for the Fe\textsubscript{50}Pt\textsubscript{50} powder annealed at 450 °C for 336 h.

With increasing Pt concentration $x$, the coercivity of the Fe\textsubscript{100-x}Pt\textsubscript{x} powders annealed at 450 °C for 48 h passes through a maximum of 0.9 T at $x = 55$, whereas the remanence $J_r$ decreases from 1.04 T to 0.52 T for $x$ increasing from 40 to 60 (Fig. 5.18). The maximum energy density $(BH)_{\text{max}}$ is highest for Fe\textsubscript{50}Pt\textsubscript{50} (Fig. 5.19). In the Fe\textsubscript{50}Pt\textsubscript{50} and Fe-rich samples, an increase of the annealing time to 336 h influences the values of remanence and coercivity.

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**Fig. 5.18.** Room temperature coercivity $H_c$ (left) and remanence $J_r$ (right) in dependence on Pt concentration $x$ in Fe\textsubscript{100-x}Pt\textsubscript{x} milled for 4 h and annealed at 450 °C for 48 h (open symbols) and 336 h (solid symbols).

**Fig. 5.19.** Energy density $(BH)_{\text{max}}$ in dependence on $x$ in Fe\textsubscript{100-x}Pt\textsubscript{x} powders milled for 4 h and annealed at 450 °C for 48 h (open symbols) and 336 h (solid symbols).
only slightly (an extension of the annealing time to 336 h does not lead to any noticeable grain growth). The coercivity increase is somewhat more pronounced in the Pt-rich samples. Nevertheless, the maximum energy density of the Fe$_{100-x}$Pt$_x$ ($x = 40; 45; 55; 60$) powders increases markedly (Fig. 5.19).

### 5.2.1. Discussion

Similarly to the 2 h milled alloys, heat treatment of 4 h milled Fe$_{100-x}$Pt$_x$ ($x = 40; 45; 50; 55; 60$) results in highly ordered L1$_0$ FePt and additional L1$_2$ Fe$_3$Pt and L1$_2$ FePt$_3$ phases. However, the formation of the L1$_2$ phases is observed for nonequatomic concentrations only and the Fe$_{50}$Pt$_{50}$ powder is essentially single-phase (about 98 vol. % of L1$_0$ FePt was detected, the rest being A1 FePt).

The amount of the A1 phase is considerably increased in the heat treated Fe$_{40}$Pt$_{60}$ alloy, as follows from the refinement of the x-ray data. In equilibrium, the composition range $56 \leq x \leq 59$ is a two-phase (L1$_0$ + L1$_2$) stability region and the FePt$_3$ compound is a stable phase for concentrations $x > 59$ (Fig. 1.1). After 4 h of milling, the fraction of the A1 phase is substantial and reaches 60-70 vol.% (Fig. 4.2 and Fig. 4.4). During Rietveld refinement the lattice parameters of the A1 phase were not fixed. Nevertheless, a precise determination of the lattice parameters of the A1 phase is impossible due to extreme peak overlap of the phases (Fig. 5.20). However, with varying Pt concentration $x$, a change in the composition of the A1 phase in the 4 h milled Fe$_{100-x}$Pt$_x$ powders is expected (compare, e.g. Fig. 4.8). Thus, it is likely that the formation of the L1$_2$ FePt$_3$ phase occurs not only in the Pt-rich regions provoked by the heterogeneity of the as-milled material, but also within the A1 matrix having a composition $x > 56$. This assumption is also confirmed by the Rietveld refinement of the site occupation parameters of the L1$_0$ and L1$_2$ phases. Whereas in the heat treated (450 °C/48 h) Fe$_{40}$Pt$_{60}$ powders milled for 2 h the compositions of the L1$_0$ and L1$_2$ phases of Fe$_{50}$Pt$_{51}$ and Fe$_{28.7}$Pt$_{71.3}$ are close to stoichiometric values, in the heat treated 4 h milled Fe$_{40}$Pt$_{60}$ the L1$_0$ and L1$_2$ phases have the composition of Fe$_{46.2}$Pt$_{53.8}$ and Fe$_{34.5}$Pt$_{65.5}$, respectively. Thus, the phases L1$_0$ and L1$_2$ may simultaneously appear within the disordered A1 matrix, which in turn leads to a change in the transformation kinetics and a

![Fig. 5.20. Observed (circles) and calculated (full line) x-ray diffraction profiles and difference between the observed and calculated intensities (lower line) for Fe$_{40}$Pt$_{60}$ powder milled for 4 h. The vertical bars represent the Bragg reflection positions of the observed phases (from top to bottom: Pt, α-Fe and A1).](image-url)
Fe-Pt alloys with an initial Fe/A1/Pt multilayer microstructure

higher residual A1 fraction in the heat treated 4 h milled Pt-rich alloys (compare Section 4.2). For instance, in coarse-grained alloys, the A1 → L1₀ + L1₂ transformation leads to a formation of complex microstructures consisting of regular arrays of L1₀ and L1₂ domains with a particular topology [Ler91], which are different from microstructures obtained during the A1 → L1₀ transformation [Zha92, Kle95].

The phases in the annealed Fe₁₀₀₋ₓPtₓ powders milled for 4 h are distributed in a form of fine lamellae, i.e. the nanometer scale multilayer structure is preserved even after annealing. As an example, figure 5.21 shows a high resolution SEM image of the Fe₅₅Pt₄₅ powder (450 °C/48 h), where two types of contrast are observed. These areas have the stoichiometry of Fe₇₅Pt₂₅ and Fe₅₀Pt₅₀, as identified by EDX analysis. The high resolution SEM analysis agrees with the phase analysis of the x-ray diffraction patterns by the Rietveld method. The average grain size of the L1₀ phase determined from the x-ray data is about 30-35 nm. In the Fe-rich Fe₁₀₀₋ₓPtₓ powders, the crystallite size of the Fe₃Pt phase is slightly smaller, namely about 20 nm. Such a microstructure is an excellent prerequisite for intense exchange interactions between crystallites of hard magnetic L1₀ FePt and soft magnetic L1₂ Fe₃Pt and A1 FePt phases in the Fe₁₀₀₋ₓPtₓ powders. The demagnetisation curves of the heat treated Fe-rich Fe₁₀₀₋ₓPtₓ samples do not reveal any dips or steps, i.e. the powders show a single-phase magnetic behaviour, although several magnetic phases are present in the powders. As a result, much improved energy density values are obtained in the Fe-rich Fe₁₀₀₋ₓPtₓ samples (compare Fig. 5.11 and 5.19). An increase of annealing time to 336 h leads to a further improvement of energy density and the highest \((BH)_{max} = 121\ \text{kJ/m}^3\) is obtained for moderately off-stoichiometric powders, \(x = 45\).

The increase of \((BH)_{max}\) with extending the annealing time to 336 h can be attributed to the increase of the LRO parameter \(S\) of the L1₀ phase, resulting in an increase of the MCA \([May89, Kam99, Kan00, Sta04]\). The increase of the L1₀ anisotropy together with the exchange coupling between the soft and the hard phases results in an improved squareness of the demagnetisation curves (Fig. 5.13) and, as a consequence, in a higher energy density \((BH)_{max}\). In Fe₅₀Pt₅₀ powders, where the fraction of the soft magnetic A1 FePt phase is negligible, the shape of the hysteresis loop remains unchanged, i.e. the increase of \(S\) does not influence the effect of intergrain coupling in this essentially single-phase hard magnetic material.

Fig. 5.21. High resolution SEM image (backscattered electron mode) of the Fe₅₅Pt₄₅ powder (annealed at 450 °C/48 h). Bright contrast areas have a stoichiometry of Fe₅₀Pt₅₀, dark contrast areas are Fe₇₅Pt₂₅.
5.3. Magnetisation processes

5.3.1. Remanence analysis

For an assembly of non-interacting ferromagnetic randomly oriented particles, the remanence-to-saturation ratio \( J_r/J_s \) is equal to 0.5 for uniaxial magnetocrystalline anisotropy and \( J_r/J_s = 0.832 \) in the case of cubic symmetry (for an anisotropy constant \( K_1 > 0 \)). Accordingly, the remanent polarisation \( J_r \) of \( \text{Fe}_{100-x}\text{Pt}_x \) powders, if consisting of non-interacting particles of \( \text{L}_{10} \text{FePt}, \text{L}_{12} \text{Fe}_3\text{Pt} \) and \( \text{A}_1 \text{FePt} \), can be calculated using

\[
J_r = 0.5 J_s^{\text{L}_{10}} f_{\text{L}_{10}} + 0.832 (J_s^{\text{Fe}_3\text{Pt}} f_{\text{Fe}_3\text{Pt}} + J_s^{\text{A}_1} f_{\text{A}_1}), \tag{5.3}
\]

where \( J_s^{\text{L}_{10}} = 1.43 \) T, \( J_s^{\text{Fe}_3\text{Pt}} \approx 1.8 \) T and \( J_s^{\text{A}_1} \approx 1.5 \) T (Table 1.3) are the room temperature values of the spontaneous polarisation of the three phases and \( f_{\text{L}_{10}}, f_{\text{Fe}_3\text{Pt}} \) and \( f_{\text{A}_1} \) are the volume fractions of these phases. For the heat treated \( \text{Fe}_{100-x}\text{Pt}_x \) powders milled for 2 and 4 h, the remanence calculated using Eq. (5.3) is presented in figure 5.22. A considerable difference between the estimated and the experimental values is observed. Whereas the calculated curve is above the experimental values for the 2 h milled and subsequently annealed \( \text{Fe}_{100-x}\text{Pt}_x \) alloys, the experimental values for the heat treated alloys milled for 4 h are larger than expected. This indicates the presence of interactions in both systems. The difference between the estimated and experimental \( J_r \) values is increased with reducing Pt content, i.e. with the increase of the \( \text{Fe}_3\text{Pt} \) fraction.

To characterise the interactions in the \( \text{Fe}_{100-x}\text{Pt}_x \) alloys, remanence curve analysis was performed. Figure 5.23 shows demagnetisation curves and recoil loops of the 2 h milled and subsequently annealed \( \text{Fe}_{100-x}\text{Pt}_x \) powder for \( x = 40, 45 \) and 50. The \( \text{Fe}_{50}\text{Pt}_{50} \) powder is characterised by an almost single-phase demagnetisation behaviour. The recoil loops of the Fe-rich powders show a fairly high susceptibility. However, the shoulders observed in the

![Fig. 5.22. Room temperature remanence \( J_r \) of (a) \( \text{Fe}_{100-x}\text{Pt}_x \) powders milled for 2 h and annealed at 450 °C/48 h and of (b) 4 h milled \( \text{Fe}_{100-x}\text{Pt}_x \), annealed at 450 °C for 48 h (open symbols) and for 336 h (solid symbols) in dependence on the Pt concentration \( x \). Solid lines correspond to \( J_r \) values calculated using Eq. (5.3).](image-url)
Magnetisation processes

Demagnetisation loops of Fe$_{55}$Pt$_{45}$ and Fe$_{60}$Pt$_{40}$ indicate the presence of the soft magnetic phases (L$_{12}$ Fe$_3$Pt and A1 FePt) being poorly exchange-coupled to the hard magnetic L$_{10}$ phase. The shoulder is more pronounced in Fe$_{60}$Pt$_{40}$ containing the highest amount of Fe$_3$Pt (see Fig. 5.7). The average grain size $<D>$ of the Fe$_3$Pt phase is estimated to be about 22(3) nm $\leq 2\delta_w$, i.e. the dimensions of the soft magnetic phase are small enough for exchange-spring behaviour to be effective (as follows from Eq. (1.21) and Table 1.3). However, due to the specific lamellar microstructure (Fig. 5.8), only a limited amount of the soft magnetic Fe$_3$Pt grains, i.e. the grains at the boundary of the L$_{10}$ phase, can participate in exchange-coupling. Such an arrangement (Fig. 5.24) leaves an inner layer of the Fe$_3$Pt lamellae that can almost freely rotate under the action of an applied field. In the case of Fe$_{55}$Pt$_{45}$, where the content of Fe$_3$Pt is reduced compared to Fe$_{60}$Pt$_{40}$, a higher fraction of Fe$_3$Pt grains can be exchange-coupled to the L$_{10}$ grains. Therefore, magnetisation reversal takes place at higher fields.

In fact, magnetisation reversal in Fe-rich Fe$_{100-x}$Pt$_x$ samples starts already in positive applied fields ($\equiv$ negative reverse field), as can be concluded from the switching field distribution (SFD) function presented in Fig. 5.25. In Fe$_{60}$Pt$_{40}$ and Fe$_{55}$Pt$_{45}$, $\chi_{irr}$ values are

---

**Fig. 5.23.** Room temperature demagnetisation curves and recoil loops of Fe$_{100-x}$Pt$_x$ ($x = 40; 45; 50$) powders (milled for 2 h and annealed at 450 °C/48 h).

**Fig. 5.24.** Schematic representation of the hypothetical “magnetic” structure of the heat-treated Fe-rich Fe-Pt powders (2 h milled).
nonzero for zero applied field and fraction of reversed grains in Fe$_{60}$Pt$_{40}$ is higher compared to that in Fe$_{55}$Pt$_{45}$ (the hysteresis loops have been corrected for demagnetisation effects, see Appendix A). Nevertheless, a reversible rotation of the magnetically soft component of magnetisation still coexists at fields below the switching field of the hard magnetic L1$_0$ phase (Fig. 5.26). The reversible portion of the polarisation change $\Delta J_{\text{rev}}(H)$ was found to increase with increasing soft magnetic phase fraction.

A more intimate mixture of the crystallites of the different phases is achieved in the heat treated 4 h milled Fe$_{100-x}$Pt$_x$ powders (Fig. 5.21). Figure 5.27 shows demagnetisation curves and recoil loops of the Fe$_{100-x}$Pt$_x$ ($x = 40, 45, 50$) powders milled for 4 h and annealed at 450 °C/48 h. The demagnetisation curves indicate a single-phase demagnetisation behaviour. Moreover, the recoil loops of the Fe-rich powders are rather steep and, at the same time, are fairly reversible, i.e. they indicate exchange-spring-magnet behaviour (Section 1.5.1). Different from ideal exchange-spring-magnet behaviour (see Chapter 2), the

**Figure 5.25.** Irreversible susceptibility $\chi_{\text{irr}}$, defined by Eq. (1.28), as a function of the reversed field for Fe$_{100-x}$Pt$_x$ powders milled for 2 h and annealed at 450 °C/48 h, representing the switching field distribution (SFD).

**Figure 5.26.** Variation of the reversible ($\Delta J_{\text{rev}}$) portion of the change in polarisation, defined by Eq. (1.26), as a function of the maximum applied reverse magnetic field $H$ in Fe$_{100-x}$Pt$_x$ powders milled for 2 h and annealed at 450 °C/48 h.

<table>
<thead>
<tr>
<th></th>
<th>$\mu_0 H_n$ (T)</th>
<th>HW (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$<em>{60}$Pt$</em>{40}$</td>
<td>0.443(3)</td>
<td>0.260(9)</td>
</tr>
<tr>
<td>Fe$<em>{55}$Pt$</em>{45}$</td>
<td>0.574(2)</td>
<td>0.253(6)</td>
</tr>
<tr>
<td>Fe$<em>{50}$Pt$</em>{50}$</td>
<td>0.702(2)</td>
<td>0.268(9)</td>
</tr>
</tbody>
</table>

Table 5.2. Room temperature SFD parameters of Fe$_{100-x}$Pt$_x$ powders milled for 2 h and annealed at 450 °C/48 h. HW is the full-width-at-half-height parameter of the SFD, defined by Eq. (1.28). The SFD has its maximum at the nucleation field $H_n$. 

![Graph](image-url)
Magnetisation processes

recoil loops of the Fe$_{60}$Pt$_{40}$ powder are slightly open.

The SFDs for the heat treated 4 h milled Fe$_{100-x}$Pt$_x$ powders, represented by the irreversible susceptibility $\chi_{irr}$, are shown in Fig. 5.28. The single peak in $\chi_{irr}$ at the nucleation field $H_n$ suggests a one-stage magnetisation reversal process and manifests the single-phase magnetic behaviour, mentioned above. A shift in the mean value $H_n$ to higher values occurs with increasing $x$, i.e. with decreasing soft magnetic phase fraction. Moreover, the SFD's are narrowed with increasing $x$ (see Table 5.3). The increase of annealing time from 48 h to 336 h has only a minor influence on the SFD parameters.

![Fig. 5.27. Demagnetisation curves and recoil loops of Fe$_{100-x}$Pt$_x$ (x = 40; 45; 50) powders (milled for 4 h and annealed at 450 °C/48 h).](image)

![Fig. 5.28. Irreversible susceptibility $\chi_{irr}$, defined by Eq. (1.28), as a function of the reverse field for Fe$_{100-x}$Pt$_x$ powders milled for 4 h and annealed at 450 °C/336 h, representing the SFD.](image)

<table>
<thead>
<tr>
<th></th>
<th>$t_{\text{anneal}} = 48$ h</th>
<th>$t_{\text{anneal}} = 336$ h</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_0 H_n$ (T)</td>
<td>$HW$ (T)</td>
<td>$\mu_0 H_n$ (T)</td>
</tr>
<tr>
<td>Fe$<em>{60}$Pt$</em>{40}$</td>
<td>0.456(2)</td>
<td>0.17(1)</td>
</tr>
<tr>
<td>Fe$<em>{55}$Pt$</em>{45}$</td>
<td>0.718(1)</td>
<td>0.124(4)</td>
</tr>
<tr>
<td>Fe$<em>{50}$Pt$</em>{50}$</td>
<td>0.860(1)</td>
<td>0.01(1)</td>
</tr>
</tbody>
</table>
The SFD dependence on x in the heat treated Fe\textsubscript{100-x}Pt\textsubscript{x} powders milled for 4 h is different to that in the 2 h milled powders, where the width of the SFD function almost does not change with Pt concentration (Table 5.2). Moreover, the SFDs of the heat treated Fe\textsubscript{100-x}Pt\textsubscript{x} alloys milled for 4 h are substantially narrower (compare Tables 5.2 and 5.3). In these alloys, magnetisation rotation is almost fully reversible up to negative applied fields of about 0.1 T for Fe\textsubscript{60}Pt\textsubscript{40} and 0.3 T for Fe\textsubscript{55}Pt\textsubscript{45}. In Fe\textsubscript{50}Pt\textsubscript{50}, no irreversible magnetisation changes are observed in the reversed fields up to 0.45 T. This high degree of magnetisation reversibility is indicative for the exchange-spring-magnet behaviour.

### 5.3.2. Intergrain interactions

The presence of intergrain interactions in the heat-treated Fe\textsubscript{100-x}Pt\textsubscript{x} alloys is also manifested by the appearance of interaction domains (Section 1.5.4) in the magnetic domain structure. Figure 5.29 shows magnetic force microscopy (MFM) images of the 4 h milled and subsequently annealed, thermally demagnetised Fe\textsubscript{50}Pt\textsubscript{50} and Fe\textsubscript{60}Pt\textsubscript{40} powders. In Fe\textsubscript{50}Pt\textsubscript{50}, a homogeneous magnetic microstructure, consistent with the phase analysis (see Fig. 5.12), is observed. The strong magnetic contrast comprised of elongated domains is due to the L\textsubscript{10} phase. In Fe\textsubscript{60}Pt\textsubscript{40}, the magnetic contrast is inhomogeneous (varying darkness in Fig. 5.29(right)). According to the quantitative phase analysis, the powder consists of a mixture of the L\textsubscript{10} FePt, L\textsubscript{12} Fe\textsubscript{3}Pt and A1 FePt phases (see Fig. 5.12). All constituent phases are ferromagnetic at room temperature and a magnetic contrast is observed in the whole image. However, the presence of less anisotropic L\textsubscript{12} Fe\textsubscript{3}Pt and A1 FePt may lead to magnetic flux closure at the sample surface and hence to a decreased phase shift, as can be inferred from the varying darkness in parts of figure 5.29(right).

The reduction of the phase shift is more pronounced for the Fe\textsubscript{60}Pt\textsubscript{40} sample milled for 2 h and subsequently annealed (Fig. 5.30(left)). As discussed in Section 5.3.1, only those grains of Fe\textsubscript{3}Pt that are located at the L\textsubscript{10} layer boundary can be exchange-coupled to the L\textsubscript{10} phase. Thus, the magnetisation of most of the soft magnetic grains lies along their easy axes. A seeming absence of a magnetic contrast in some parts of figure 5.30 (left) does not mean that these sample areas are non-ferromagnetic, as the phase shift is still non-zero for these areas. Also in the middle of the L\textsubscript{10} lamellae the magnetic contrast is highly inhomogeneous.

In order to confirm that the soft magnetic Fe\textsubscript{3}Pt and the A1 FePt are responsible for the reduction of the phase shift, Pt-rich Fe\textsubscript{40}Pt\textsubscript{60} powder was also studied by MFM (Fig. 5.30(right)). In Fe\textsubscript{40}Pt\textsubscript{60} (2 h milled and subsequently annealed, see Fig. 5.7 for the phase composition), the magnetic contrast is comprised of elongated interaction domains due to the L\textsubscript{10} phase, interrupted by the layers of the paramagnetic FePt\textsubscript{3} phase, the latter showing no magnetic contrast. The lamellar distribution of the phases observed in the MFM image is in agreement with the results of the high-resolution scanning electron microscopy (Fig. 5.8). A phase shift identical to that measured for the Fe\textsubscript{50}Pt\textsubscript{50} sample was observed in Fe\textsubscript{40}Pt\textsubscript{60}. Since in both Fe\textsubscript{40}Pt\textsubscript{60} and Fe\textsubscript{50}Pt\textsubscript{50} phases, the magnetic contrast is largely due to the highly anisotropic L\textsubscript{10} phase, similar phase shift patterns should indeed be expected for these samples. In Fe\textsubscript{40}Pt\textsubscript{60}, the interaction domains within the L\textsubscript{10} lamellae tend to align
Magnetisation processes

perpendicular to the interface of the adjacent lamellae and have a feature size of about 200-300 nm. The resolution of the MFM is in the range of 30-50 nm, i.e. it is comparable to the crystallite size in the Fe-Pt powders. Nevertheless, the width and the length of the magnetic domains are substantially larger than the crystallite size of the phases, thus indicating a strong magnetic interaction between the individual grains.

The analysis of the interparticle interactions in the Fe$_{100-x}$Pt$_x$ powders was carried out using $\Delta J$ curves, given by Eq. (1.25). Predominantly positive values of $\Delta J(H)$ are observed in the Fe$_{100-x}$Pt$_x$ powders milled for 4 h and subsequently annealed (Fig. 5.31). Similarly, only positive $\Delta J(H)$ deviations are observed for the Fe-rich Fe$_{60}$Pt$_{40}$ powder milled for 2 h and subsequently annealed, whereas for the Pt-rich powder, the positive deviation is followed by a small negative $\Delta J(H)$ (Fig. 5.31(b)). The remanence curves and the MFM analysis suggest that the positive $\Delta J(H)$ values may be due to dominant exchange interactions between crystallites within the L1$_0$ lamellae. On the other hand, the decoupling effect of the
FePt$_3$ layers may lead to the situation that the magnetostatic interaction between the L1$_0$ layers becomes significant.

### 5.3.3. Discussion

In the heat treated Fe$_{100-x}$Pt$_x$ powders, magnetisation reversal processes are strongly influenced by structure and microstructure characteristics, as is usually observed in permanent magnet materials. By heat treatment of the powders with different initial microstructures, multilayer Fe/Pt (2 h milled) or Fe/A1/Pt (4 h milled), one can modify the degree of exchange-coupling between the grains.

In the case of the Fe-rich Fe$_{100-x}$Pt$_x$ powders, a realisation of a microstructure, where the high magnetisation Fe$_3$Pt phase and the hard magnetic L1$_0$ FePt phase coexist is possible. In the powders milled for 2 h and subsequently annealed, despite small grains, only a weakly pronounced exchange coupling was observed. This is attributed to the specific lamellar distribution of the phases, where only those Fe$_3$Pt grains that are located at the interface between the Fe$_3$Pt and L1$_0$ lamellae are exchange-coupled to the hard magnetic L1$_0$ phase (figures 5.24 and 5.30). In these powders, the lower than predicted by Eq. (5.2) remanence (Fig. 5.22(a)) can be explained by the presence of dipolar interactions leading to magnetisation reversal already in positive applied fields [Hai03a]. This is the case for those soft magnetic grains, which are not exchange-coupled to hard magnetic ones. The substantial amount of grains reversed in positive fields is also reflected in the switching field distribution functions of the Fe-rich Fe$_{100-x}$Pt$_x$ powders (negative reverse fields in Fig. 5.25) having finite values at zero field. The width of the SFD function is merely dependent on $x$: the distribution of switching fields in Fe$_{50}$Pt$_{50}$ is as broad as that in the Fe-rich samples (see Table 5.2). According to the phase analysis (Fig. 5.7), the total amount of the soft magnetic phases (Fe$_3$Pt and A1) in Fe$_{50}$Pt$_{50}$ is about 15 vol.%. The existence of the soft component in Fe$_{50}$Pt$_{50}$ is also reflected in slightly open recoil loops (Fig. 5.23). Thus, the broad SFD functions in the 2 h milled and subsequently annealed Fe$_{100-x}$Pt$_x$ indicate the

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**Fig. 5.31.** Room temperature $\Delta J(H)$ plots for (a) Fe$_{100-x}$Pt$_x$ ($x =$ 40; 45; 50) powders milled for 4 h and annealed at 450 °C/336 h and (b) Fe$_{50}$Pt$_{40}$ and Fe$_{50}$Pt$_{60}$ powders milled for 2 h and annealed at 450 °C/48 h.
noncooperative regime of magnetisation reversal, which is due to the presence of the soft magnetic Fe$_3$Pt and A1 phases weakly coupled to the hard magnetic L1$_0$ grains.

The distribution of switching fields in the 4 h milled and subsequently annealed Fe$_{100-x}$Pt$_x$ powders is significantly narrower than that of the heat treated 2 h milled powders (Tables 5.2 and 5.3). Obviously, in the former alloys, magnetisation reversal is more uniform due to the strong intergrain exchange coupling. The more effective exchange coupling in the heat treated Fe$_{100-x}$Pt$_x$ powders milled for 4 h is due to a finer distribution of the phases (compare Fig. 5.8 and 5.21). The demagnetisation curves of these alloys show a single-phase behaviour and are almost completely reversible in fields up to about 0.1 T for Fe$_{60}$Pt$_{40}$, 0.3 T for Fe$_{55}$Pt$_{45}$ and 0.45 T for Fe$_{50}$Pt$_{50}$. For higher reverse fields, the hard magnetic grains unfavourably oriented to the field direction start to switch irreversibly, as reflected in nonzero values of the irreversible susceptibility $\chi_{irr}$ (Fig. 5.28). For instance, in the Stoner-Wohlfarth model, irreversible rotation of the magnetisation takes place first in particles with easy axes making an angle of $\pi/4$ with the applied field and then for increasingly smaller and higher angles [Sto48], whereas the nucleation field of magnetostatically and/or exchange-coupled particles decreases steadily with increasing degree of misalignment [Kro94]. Thus, in essentially single phase Fe$_{50}$Pt$_{50}$ the distribution of the switching fields is mainly a consequence of the random orientation of the L1$_0$ crystallites.

In the Fe-rich powders a broader switching field distribution may also be attributed to a broad anisotropy distribution arising from the presence of the soft magnetic Fe$_3$Pt and A1 phases additionally to the hard magnetic L1$_0$ (Fig. 5.12). The SFD function is significantly narrowed with increasing Pt concentration (Fig. 5.28 and Table 5.3), indicative of a more uniform switching as the soft magnetic phase fraction is reduced. A shift in the mean value of the nucleation field $H_n$ to higher values occurs with increasing Pt concentration, i.e. with decreasing soft magnetic phase fraction. These observations show that the soft phases not only increase the remanence, but due to the intergrain exchange coupling, they also strongly modify the switching behaviour of the hard magnetic grains.

Recoil loops of the heat treated Fe$_{50}$Pt$_{50}$ sample milled for 4 h do not show any significant hysteresis (Fig. 5.27), whereas in the Fe-rich powders a significant recoil hysteresis is observed. The recoil loop area increases with increasing soft magnetic phase fraction. Obviously, the switching behaviour of the soft magnetic crystallites is also
Structure and magnetic properties

The switching behaviour, but also the intrinsic magnetic properties of the soft magnetic phases are modified by the exchange interaction with the hard magnetic grains. In the Fe-rich Fe\textsubscript{100-x}Pt\textsubscript{x} powders, i.e. in the hard L1\textsubscript{0}/soft L1\textsubscript{2} Fe\textsubscript{3}Pt and A1 FePt nanocomposites, a single common Curie temperature, close to the Curie temperature of the L1\textsubscript{0} phase, is observed (Fig. 5.32). This is consistent with calculations showing that the Curie temperature of nanocomposite materials is close to $T_c$ of the phase with the strongest exchange interaction \cite{Sko00b}. The apparent absence of a discontinuity at the $T_c$ of the Fe\textsubscript{3}Pt phase can also be due to disorder and a smear-out effect of the applied magnetic field, since in the vicinity of the Curie temperature the field dependence of the spontaneous magnetisation has a strongly nonlinear character \cite{Bel56}.Nevertheless, in Fe-rich Fe\textsubscript{100-x}Pt\textsubscript{x} powders, the shape of the magnetisation curve is markedly different from that of Fe\textsubscript{50}Pt\textsubscript{50}. In particular, in Fe\textsubscript{60}Pt\textsubscript{40}, containing the highest soft magnetic phase fraction, a change in the slope is observed above approximately the Curie temperature of the Fe\textsubscript{3}Pt phase (Table 1.3).

In R$_2$Fe$_{14}$B/α-Fe (R = Nd, Pr) exchange-spring nanocomposites the Curie temperature of the hard magnetic R$_2$Fe$_{14}$B compound (which is below $T_c$ of α-Fe) is slightly enhanced by exchange interactions with α-Fe grains, but the magnetisation versus temperature curves still show a distinct discontinuity at the $T_c$ of R$_2$Fe$_{14}$B \cite{Lew97, Neu98, Che99}. In nanocomposite Fe\textsubscript{100-x}Pt\textsubscript{x} alloys, the absence of a discontinuity at the $T_c$ of Fe\textsubscript{3}Pt implies that exchange interactions may propagate through paramagnetic grains of the soft phase at temperatures above $T_c$ of the soft magnetic phases. Exchange interactions between ferromagnetic layers through paramagnetic spacers have been evidenced in thin multilayers and nanocrystalline materials provided the thickness of the paramagnetic

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**Fig. 5.33.** Irreversible susceptibility $\chi_{irr}$ at 293, 473 and 600 K as a function of the reverse field for Fe\textsubscript{60}Pt\textsubscript{40} powders milled for 4 h and annealed at 450 °C/48 h.

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**Table 5.4.** SFD parameters measured at different temperatures for Fe\textsubscript{60}Pt\textsubscript{40} powders milled for 4 h and annealed at 450 °C for 48 h. HW is the full-width-at-half-height parameter of the SFD, defined by Eq. (1.28). The SFD has its maximum at the nucleation field $H_n$.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$\mu_0 H_n$ (T)</th>
<th>HW (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>0.456(2)</td>
<td>0.17(1)</td>
</tr>
<tr>
<td>473</td>
<td>0.388(3)</td>
<td>0.175(9)</td>
</tr>
<tr>
<td>600</td>
<td>0.346(2)</td>
<td>0.168(7)</td>
</tr>
</tbody>
</table>

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modified by the exchange interaction with hard magnetic grains.

Not only the switching behaviour, but also the intrinsic magnetic properties of the soft magnetic phases are modified by the exchange interaction with the hard magnetic grains. In the Fe-rich Fe\textsubscript{100-x}Pt\textsubscript{x} powders, i.e. in the hard L1\textsubscript{0}/soft L1\textsubscript{2} Fe\textsubscript{3}Pt and A1 FePt nanocomposites, a single common Curie temperature, close to the Curie temperature of the L1\textsubscript{0} phase, is observed (Fig. 5.32). This is consistent with calculations showing that the Curie temperature of nanocomposite materials is close to $T_c$ of the phase with the strongest exchange interaction \cite{Sko00b}. The apparent absence of a discontinuity at the $T_c$ of the Fe\textsubscript{3}Pt phase can also be due to disorder and a smear-out effect of the applied magnetic field, since in the vicinity of the Curie temperature the field dependence of the spontaneous magnetisation has a strongly nonlinear character \cite{Bel56}.Nevertheless, in Fe-rich Fe\textsubscript{100-x}Pt\textsubscript{x} powders, the shape of the magnetisation curve is markedly different from that of Fe\textsubscript{50}Pt\textsubscript{50}. In particular, in Fe\textsubscript{60}Pt\textsubscript{40}, containing the highest soft magnetic phase fraction, a change in the slope is observed above approximately the Curie temperature of the Fe\textsubscript{3}Pt phase (Table 1.3).

In R$_2$Fe$_{14}$B/α-Fe (R = Nd, Pr) exchange-spring nanocomposites the Curie temperature of the hard magnetic R$_2$Fe$_{14}$B compound (which is below $T_c$ of α-Fe) is slightly enhanced by exchange interactions with α-Fe grains, but the magnetisation versus temperature curves still show a distinct discontinuity at the $T_c$ of R$_2$Fe$_{14}$B \cite{Lew97, Neu98, Che99}. In nanocomposite Fe\textsubscript{100-x}Pt\textsubscript{x} alloys, the absence of a discontinuity at the $T_c$ of Fe\textsubscript{3}Pt implies that exchange interactions may propagate through paramagnetic grains of the soft phase at temperatures above $T_c$ of the soft magnetic phases. Exchange interactions between ferromagnetic layers through paramagnetic spacers have been evidenced in thin multilayers and nanocrystalline materials provided the thickness of the paramagnetic
regions is in the order of the exchange-field penetration length \([\text{Wan92, Bov98, Her94}]\). Such an exchange-field penetration originates from the spin polarisation of the paramagnetic regions by the ferromagnetic phase.

If the magnetic behaviour of the soft magnetic phases were not modified by the exchange interactions with hard magnetic grains, then at temperatures above \(T_c\) of the Fe\(_3\)Pt and/or A1 phases the switching behaviour of the sample would be determined by the hard magnetic grains only. That means, the width of the SFD function should decrease, as the Fe\(_3\)Pt and A1 phases become paramagnetic. In practice, no change in the width of the SFD functions is observed with increasing temperature (Fig. 5.33 and Table 5.4).

The exchange polarisation of the soft magnetic phase at elevated temperatures is also reflected in the recoil loop measurements. In particular, the recoil loops for Fe\(_{60}\)Pt\(_{40}\) measured at 473 K are still open, indicative of the presence of a soft magnetic component (Fig. 5.34). Apparently, as the magnetisation of the L1\(_0\) phase is reduced with temperature, the exchange penetration becomes less effective (a consequence of the temperature dependence of the penetration length \([\text{Sko00b}]\)). Nevertheless, even at 600 K (above the Curie temperature of the Fe\(_3\)Pt and A1 phases) a clear recoil hysteresis is still observed.

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**Fig. 5.34.** Demagnetisation curves and recoil loops at 293, 473 and 600 K of Fe\(_{60}\)Pt\(_{40}\) powders milled for 4 h and annealed at 450 °C/48 h.

**Fig. 5.36.** \(\Delta J(H)\) plots at 293 K and 473 K for Fe\(_{60}\)Pt\(_{40}\) powder milled for 4 h and annealed at 450 °C/48 h.
The combined analysis of remanence curves and MFM data suggests that exchange interactions between crystallites may apparently be reflected in positive $\Delta J(H)$ values, whereas a negative $\Delta J(H)$ could be an indication of magnetostatic interactions. However, this conclusion is only tentative. For certain types of short-range order in an assembly of magnetostatically interacting particles $\Delta J(H)$ can be positive as well (Fig. 5.35). Furthermore, strictly speaking, the Wohlfarth relation (Eq. (1.24)) can only be used to analyse interactions between magnetic particles if these are single-domain and of uniaxial type of magnetic anisotropy. Hence non-homogeneous magnetisation modes such as magnetic domain structures and easy-plane as well as cubic magnetic anisotropy have to be excluded. At the same time, most of the soft grains will not contribute to finite values of $\Delta J(H)$. This is also reflected in qualitatively similar $\Delta J(H)$ plots for single phase Fe$_{50}$Pt$_{50}$, as well as for nanocomposite powders with both weak and strong exchange coupling between the soft and hard magnetic grains (Fig. 5.31). On the other hand, $\Delta J(H) = 0$ does not necessarily imply the absence of magnetic interactions between the particles.

Despite being normalised to the saturated remanence of the sample, $J_r$, the positive $\Delta J(H)$ deviations seem to correlate with the magnetisation of the hard magnetic component (Fig. 5.31, Fig. A.3, A.4 in Appendix A and also Fig. 5.36). In Fig. 5.31(a), the amplitude of the positive $\Delta J(H)$ is smaller for Fe-rich powders, since the remanence $J_r$ of the sample is larger and the L1$_0$ volume fraction is lower compared to that in Fe$_{50}$Pt$_{50}$. In Fe$_{60}$Pt$_{40}$, a slight shift of the peak position to lower fields and the reduced $\Delta J(H)$ amplitude at 473 K are due to lower magnetocrystalline anisotropy and magnetisation of the L1$_0$ phase, respectively (Fig. 5.36). Such a variation of the hard magnetic phase magnetisation may be regarded as a variation in the mean-field interaction strength. Setting various demagnetisation factors is also equivalent to varying the mean field parameter $\Lambda$ in Eq. (1.23). If the demagnetising factor is chosen inappropriately, the $\Delta J(H)$ plot may even change its sign (see Appendix A). Furthermore, the effective demagnetising factor cannot describe inhomogeneous magnetisation states existing in real materials. Thus, on the basis of the $\Delta J(H)$ plot only, definite conclusions about the type of interactions present in the system should be taken with care.

**Fig. 5.35.** Types of short-range order in an assembly of magnetostatically interacting particles favouring (a) magnetised state and (b) demagnetised state.
Chapter 6

Magnetic moments of ordered Fe-Pt alloys

In this chapter, the dependence of the magnetic moments on the compositional order in L1\textsubscript{0}-type Fe\textsubscript{100-x}Pt\textsubscript{x} alloys is studied by neutron powder diffraction. Both experimental data and theoretical calculations indicate a correlation between the degree of order within the L1\textsubscript{0} phase and fundamental properties, such as magnetcocrystalline anisotropy and Curie temperature \cite{May89, Kam99, Kan00, Sta04}. In contrast, the saturation magnetisation of the L1\textsubscript{0} phase was reported to be largely independent of the degree of order at a fixed composition \cite{Oka02, May89}. The interpretation of the magnetisation data is, however, complex and the data do not provide sufficient information about the individual atomic moments. Moreover, a possible coexistence of several phases can further complicate the analysis. In contrast, by using Rietveld refinement of neutron powder diffraction data it is possible to determine the magnetic moments of individual atoms in the L1\textsubscript{0} compound also in the presence of additional phases.

6.1. Neutron diffraction

The analysis of the magnetic scattering was performed during cooling of the as-milled samples after heating to 930 K (see Section 4.2). Powders with starting compositions of Fe\textsubscript{60}Pt\textsubscript{40}, Fe\textsubscript{55}Pt\textsubscript{45} and Fe\textsubscript{45}Pt\textsubscript{55} were milled for 7 h and those of Fe\textsubscript{50}Pt\textsubscript{50} for 4 h. The actual compositions after heat treatment were determined by EDX analysis in a scanning electron microscope to be Fe\textsubscript{59}Pt\textsubscript{41}, Fe\textsubscript{55}Pt\textsubscript{45}, Fe\textsubscript{48}Pt\textsubscript{52} and Fe\textsubscript{50}Pt\textsubscript{50}, respectively.

![Fig. 6.1. Evolution of the neutron diffraction patterns with decreasing temperature for an Fe\textsubscript{50}Pt\textsubscript{50} powder. The diffraction peaks of the L1\textsubscript{0} FePt phase are marked; arrows indicate the position of the magnetic superstructure peaks.](image-url)
Figure 6.1 shows the evolution of the neutron diffraction patterns for the Fe$_{50}$Pt$_{50}$ powder recorded during cooling from 920 K. At 920 K, only the fundamental (111), (200) and (002) diffraction peaks due to the L1$_0$ phase are observed. As the temperature is lowered, the intensity of the fundamental reflections increases and at about 725 K, i.e. below the Curie temperature of the L1$_0$ phase (Table 1.3), the (110) and (201) superstructure reflections are clearly observed. The intensity of these superstructure reflections is due to magnetic scattering only, since the intensities of the chemical superstructure peaks are negligible due to almost identical coherent neutron scattering lengths of Pt and Fe.

In contrast to the neutron coherent scattering lengths, the x-ray atomic scattering factors of Pt and Fe differ significantly, which enables a determination of the site occupations using x-ray diffraction. Therefore, prior to the refinement of the magnetic structure, the crystal structure parameters were refined using x-ray diffraction data. The x-ray patterns of the samples were recorded at room temperature after the neutron diffraction measurements (Section 4.2.3). No significant changes in either peak widths or fractions of the phases were observed by neutron diffractometry upon cooling, thus justifying the use of the room temperature crystal structure parameters in the refinement of the neutron

Table 6.1. Parameters obtained by refinement of x-ray data: volume fraction of the phases $f$ (also compared to neutron data), lattice constants $a$ and $c$, unit cell volume $V$, fraction of the Pt(Fe) sites occupied by the correct atom $r_{Pt(Fe)}$, order parameter $S$. Values of the magnetic moment of iron $\mu_{Fe}$ obtained from the refinement of neutron diffraction data collected at 2.52 Å are given together with the corresponding agreement factors. The magnetic moment of Pt was fixed at 0.3 $\mu_B$ per atom.

<table>
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<tr>
<th></th>
<th>Fe$<em>{48}$Pt$</em>{52}$</th>
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<th>Fe$<em>{55}$Pt$</em>{45}$</th>
<th>Fe$<em>{59}$Pt$</em>{41}$</th>
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<tr>
<td>$f$ (vol. %)</td>
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<td>100</td>
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<td></td>
<td>neutron</td>
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<td>$a$ (Å)</td>
<td>3.8619(4)</td>
<td>3.8600(2)</td>
<td>3.8426(5)</td>
<td>3.8247(5)</td>
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<td>$c$ (Å)</td>
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<td>3.7131(3)</td>
<td>3.7118(6)</td>
<td>3.7141(6)</td>
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<tr>
<td>$c/a$</td>
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<td>0.962</td>
<td>0.966</td>
<td>0.971</td>
</tr>
<tr>
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<td>55.324</td>
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<td>$r_{Pt}$</td>
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<td>1.00(4)</td>
<td>0.86(5)</td>
<td>0.8(1)</td>
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<td>$r_{Fe}$</td>
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<td>0.98(5)</td>
<td>0.95(4)</td>
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<td>0.99</td>
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<tr>
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<td>2.2</td>
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<th>Fe$<em>{55}$Pt$</em>{45}$</th>
<th>Fe$<em>{59}$Pt$</em>{41}$</th>
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<td>2.1(2)</td>
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<td>$R_N$ (%)</td>
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<td>1.9</td>
<td>1.7</td>
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<tr>
<td>$R_{MAC}$ (%)</td>
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<td>13.8</td>
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<tr>
<td>$\chi^2$</td>
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<td>2.6</td>
<td>3.0</td>
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<th>A1 FePt (Fm 3 m)</th>
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<td>$a$ (Å)</td>
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</tr>
<tr>
<td>$R_{Bragg}$ (%)</td>
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* At 352 K.
Neutron diffraction data. Results of the refinements are listed in Table 6.1. The Fe\textsubscript{50}Pt\textsubscript{50} alloy was found to be essentially single L\textsubscript{10} phase. In Fe\textsubscript{48}Pt\textsubscript{52}, Fe\textsubscript{55}Pt\textsubscript{45} and Fe\textsubscript{59}Pt\textsubscript{41}, along with the L\textsubscript{10} phase the A1 phase was detected (the residual A1 phase is a result of different ordering mechanisms in Fe-Pt alloys milled for various times (Section 4.2)). The volume fractions of the phases are in excellent agreement with those obtained from the refinement of the neutron diffraction data (Table 6.1). The average crystallite size of the L\textsubscript{10} phase is about 35-40 nm, as determined from the x-ray line broadening after separation of size and lattice strain effects.

In Fe\textsubscript{50}Pt\textsubscript{50} and Fe\textsubscript{48}Pt\textsubscript{52}, almost all the Fe and Pt sites in L\textsubscript{10} FePt are occupied by the correct atoms (Table 6.1). For Fe\textsubscript{55}Pt\textsubscript{45} and Fe\textsubscript{59}Pt\textsubscript{41} a particular L\textsubscript{10} structure is observed: the Fe sites are almost exclusively occupied by the correct atoms and about 15 % and 20 %, respectively, of the Pt sites are occupied by iron atoms. The obtained atomic site occupation parameters \( r_{\text{Pt(Fe)}} \) were subsequently used in the refinement of the neutron diffraction data, as well as for the determination of the LRO parameter \( S \) of L\textsubscript{10} FePt, defined in Eq. 1.1.

Magnetic structure refinement requires knowledge of the magnetic form factors of the elements. The Fe magnetic form factor used in this study is the one given in the International Tables for Crystallography [Pri04]. The magnetic form factor of Pt in ordered Fe-Pt alloys has not been precisely experimentally determined so far. However, alloying Pt with a magnetic 3d transition metal element induces a magnetic moment on Pt (see Section 1.4.1). Thus, one has to consider a possible contribution of the induced Pt magnetic moment to the neutron scattering. LSDA calculations with Slater exchange [Wat77] have been used by Brown et al. [Bro04] to fit the magnetic behaviour of Pt in an ordered Fe\textsubscript{72}Pt\textsubscript{28} single crystal, as probed by polarised neutron diffraction. The same magnetic form factor of Pt corresponding to a spherical average of the form factors given by Watson-Yang et al. [Wat77] has been used in this work to fit the neutron diffraction data. However, a simultaneous refinement of the Fe and Pt moments, \( \mu_{\text{Fe}} \) and \( \mu_{\text{Pt}} \), yields unreasonably high values for \( \mu_{\text{Pt}} \). On the other hand, fixing the Pt moment at any value between 0.2-0.4 \( \mu_\text{B} \) results in a variation of the Fe moment within ±2 %, which is comparable to the experimental error bar. Thus, in the final refinement of the magnetic structure the Fe
Magnetic moments of ordered Fe-Pt alloys

moments were not fixed, while $\mu_{\text{Pt}}$ was set to 0.3 $\mu_B$. This value is in agreement with electronic structure calculations [Opa06] and also with the literature [Men74]. In the refinement, a parallel alignment of the moments on the Fe and Pt sites of the L1$_0$ phase was assumed. Refinement of the patterns assuming an opposite direction of the Fe and Pt moments (as suggested previously [Bro04]) leads to worse agreement factors. For instance, the magnetic $R$-factor for the structure with the oppositely aligned Pt moment is $R_{\text{MAG}} = 3.5\%$ versus 2.6\% ($R_{\text{MAG}}$ for Fe$_{50}$Pt$_{50}$ in Table 6.1) for the structure with a parallel alignment of the Fe and Pt moments.

In order to access a wider reciprocal space domain, a wavelength of 1.28 Å has been used for room temperature measurements (Fig. 6.2). The refinement of neutron diffraction data collected at this wavelength enabled the determination of isotropic displacement factors $B_{\text{iso}}$: 0.50(6) Å$^2$ for Fe and 0.15(8) Å$^2$ for Pt, which agree well with literature [Bro04]. The displacement factors for Fe and Pt of 0.5 Å$^2$ obtained on a single crystal by Brown et al. [Bro04] for elevated temperatures were used in this work for the refinement of the patterns at higher temperatures.

The neutron diffraction patterns, as well as the results of the magnetic structure refinement for the Fe$_{48}$Pt$_{52}$, Fe$_{50}$Pt$_{50}$, Fe$_{55}$Pt$_{45}$ and Fe$_{59}$Pt$_{41}$ alloys are presented in Fig. 6.3 and

![Neutron diffraction patterns](image-url)
Table 6.1, respectively. The large $R_{\text{MAG}}$ values for Fe$_{55}$Pt$_{45}$ and Fe$_{59}$Pt$_{41}$ are caused by a reduced amount of the L1$_0$ phase in this sample. For Fe$_{55}$Pt$_{45}$ and Fe$_{59}$Pt$_{41}$ it was not possible to refine the magnetic moment of Fe on the Pt sites and the observed moment is an average over all Fe atoms. At room temperature, the magnetic moment of the Fe atoms in the L1$_0$ phase amounts to about $2.7 \, \mu_B$ in Fe$_{50}$Pt$_{50}$. It is somewhat reduced in the Fe$_{48}$Pt$_{52}$ alloy and it is substantially reduced in Fe-rich alloys (by about 20\%).

Figure 6.4 shows the thermal evolution of the magnetic moment of Fe obtained from the analysis of the neutron diffraction patterns collected during cooling. In order to evaluate the Fe moment at zero temperature, $\mu_{\text{Fe}}(0)$, the temperature dependence of the Fe moment was fitted using Eq. (1.10). The evaluated parameters are listed in Table 6.2. From the fit, a value $\mu_{\text{Fe}}(0) = 2.8 \, \mu_B$ was obtained for Fe$_{50}$Pt$_{50}$ and Fe$_{48}$Pt$_{52}$, whereas $\mu_{\text{Fe}}(0) = 2.4 \, \mu_B$ for Fe$_{59}$Pt$_{41}$. The experimental error in the individual data points is about $\pm 0.2 \, \mu_B$ (Fig. 6.4). This error is reduced to $\pm 0.05 \, \mu_B$, if the temperature dependence is fitted according to Eq. (1) (see Table 6.2). The total error including the discussed uncertainty of the Pt moments is estimated to be $\pm 0.1 \, \mu_B$. The values of the Curie temperature obtained from the fit agree well with differential scanning calorimetry results (Table 4.2) and with literature data [Iva73, Kus50]. The Curie temperature of the L1$_0$ phase is very sensitive to the composition and, thus to the degree of order: it decreases from about 739 K to 726 K and to 675 K, as the order parameter reduces from 0.99 to 0.97 and to 0.75. Thus, equiatomic well ordered Fe-Pt alloys are more suitable for hard magnetic applications, as they possess the highest Curie temperature.

**Table 6.2.** Parameters obtained from a fit of the data presented in Fig. 6.4 using Eq. (1.10): magnetic moment ($\mu_0$) of iron at $T = 0$, $\mu_{\text{Fe}}(0)$, Curie temperature, $T_c$, and shape parameter, $\gamma$. $S$ is the experimental order parameter.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$S$</th>
<th>$\mu_{\text{Fe}}(0)$</th>
<th>$T_c$ (K)</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$<em>{58}$Pt$</em>{52}$</td>
<td>0.97</td>
<td>2.85(2)</td>
<td>726(1)</td>
<td>1.40(5)</td>
</tr>
<tr>
<td>Fe$<em>{50}$Pt$</em>{50}$</td>
<td>0.99</td>
<td>2.84(4)</td>
<td>739(1)</td>
<td>0.7(1)</td>
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<tr>
<td>Fe$<em>{59}$Pt$</em>{41}$</td>
<td>0.75</td>
<td>2.38(6)</td>
<td>675(3)</td>
<td>1.3(2)</td>
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6.2. Magnetisation measurements

For comparison, room temperature magnetisation measurements were performed on samples after the neutron diffraction (Fig. 6.5). Obviously, both the magnetisation measured in 5 T and the remanence increase with decreasing Pt concentration. However, the interpretation of the magnetisation measurements is complicated by several reasons. First, the Fe$_{100-x}$Pt$_x$ powders are not single phase for x = 39; 45 and 52 (Table 6.1). Not only the magnetisation of the L1$_0$ phase, but also that of A1 depends on the composition (see Section 1.4.3). Apparently, with decreasing x in the Fe$_{100-x}$Pt$_x$ powders the total magnetisation of the A1 phase should increase as a result of the Fe concentration increase, as indicated by the lattice parameter evolution with x (compare Table 6.1 and Fig. 4.8). From the values of the lattice parameters it is, however, not possible to reliably determine the atomic composition of the A1 phase. Second, the magnetisation measured in a field of 5 T is by no means the saturation magnetisation. The remanence values cannot be used for the evaluation of the magnetisation of the phases either, since the nanometer-range crystallites in both Fe$_{50}$Pt$_{50}$ and Fe-rich Fe$_{100-x}$Pt$_x$ powders are exchange-coupled, thus leading to remanence enhancement. The latter is increasing with the increase of the soft magnetic phase fraction (see Fig. 5.22). Therefore, the magnetisation measurements do not provide reliable means for the determination of the magnetisation of the L1$_0$ phase.

6.3. Discussion

The magnetic moments of Fe in Fe$_{100-x}$Pt$_x$ (x = 39; 45; 50; 52) alloys depend on the compositional order, as obtained from neutron diffraction data. For alloys with almost perfect L1$_0$-type long-range order the experimental value of the Fe magnetic moment was determined to be $2.8 \pm 0.1 \mu_B$ (extrapolated to zero temperature). The Fe moment decreases with increasing Fe concentration. This surprising behaviour is in contrast to the well-known
Fe-Al system, where increasing Fe content enhances the magnetism [Bes75]. Moreover, in Fe-Al alloys, the Fe moments increase with the reduction of the chemical order. In order to establish to which extent the chemical composition and the degree of order influence the magnetic moments of the considered Fe-Pt alloys, density functional calculations using the local spin-density approximation (LSDA) were additionally performed (calculations by I. Opahle, details can be found in [Lyu06]).

Table 6.3 shows the calculated spin moments of L1₀ FePt for the particular compositions. Listed are the calculated moments of Fe and Pt atoms on the correct site and the total moment per primitive unit cell containing two sites (see Fig. 1.4). Since the measured Fe moments are averaged over all Fe atoms, the experiment should be compared to the corresponding averaged iron moment $\mu_\text{Fe}^{\text{ave}}$ in the calculation. Calculations were performed for both the experimental lattice parameters given in Table 6.1 and the theoretical LSDA volumes obtained by minimisation of the total energy. During this minimisation, the $c/a$-ratios were kept fixed to the respective experimental value given in Table 6.1. The order parameter in the calculations was chosen in accordance with the experimental data.

The calculations reproduce the experimental dependence of the Fe moment on the composition. The calculated Fe moment for the stoichiometric alloy Fe₅₀Pt₅₀ agrees very well with the measured one. For the Pt-rich Fe₄₈Pt₅₂ alloy, the small non-stoichiometry has only a minor influence on the iron moment. In the case of the iron rich Fe₅₀Pt₄₁, the calculations yield a substantial reduction of the Fe moment compared to the stoichiometric compound, in agreement with experiment. For the calculations performed at the experimental lattice parameters ($\mu_\text{Fe}^{\text{ave}} = 2.63 \mu_\text{B}$), this reduction is less pronounced than in the experiment, while the Fe moments calculated at the theoretical volumes ($\mu_\text{Fe}^{\text{ave}} = 2.45 \mu_\text{B}$) are in almost perfect agreement with the measurements. Additional calculations at different

### Table 6.3

<table>
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<tr>
<th>Composition</th>
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<th>Lattice parameter</th>
<th>$\mu_\text{Fe}^{t}$</th>
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lattice constants show that there is primarily one mechanism responsible for the smaller Fe moment in the Fe-rich compound: The smaller volume leads to a reduction of the moment, as is usual for itinerant magnets. Further contributions to this effect result from the change of the electronic structure with composition. Disorder in the lattice smoothens the density of states, which on one hand reduces the magnetic moments for fixed lattice parameters. However, on the other hand increasing disorder also leads to an increase of the volume, which in turn increases the magnetic moments. For well ordered Fe$_{50}$Pt$_{41}$ alloys with order parameter $S > 0.6$ both effects strongly compensate, and the iron moments are only weakly affected by a change of the order parameter for a fixed composition.
Conclusions and outlook

This work has been devoted to the study of phase transformations involving chemical ordering and magnetic properties evolution in bulk Fe-Pt alloys composed of nanometer-sized grains. These alloys provide model systems for fundamental studies of a number of physical phenomena not easily accessible in thin film systems. The improved understanding of the mechanisms of phase formation and magnetic behaviour should be equally valuable for other Fe-Pt alloys consisting of fine crystallites and contribute to the design and optimisation of materials based on the L1$_0$ phase.

Nanocrystalline Fe$_{100-x}$Pt$_x$ (x = 40-60) alloys investigated in the present work have been produced by mechanical ball milling of elemental Fe and Pt powders at 77 K. The as-milled Fe-Pt alloys consist of ~100 µm sized particles constituted by randomly oriented grains having an average size in the range of 10-40 nm. Depending on the milling time, three major microstructure types have been obtained: samples with a multilayer-type structure of Fe and Pt with a thickness of 20-300 nm and a very thin A1 (~5 nm) layer at their interfaces (2 h milled), an intermediate structure, consisting of finer lamellae of Fe and Pt (below approximately 100 nm) with the A1 layer thickness reaching several tens of nanometers (4 h milled) and alloys containing a homogeneous A1 phase (7 h milled). With respect to microstructure, the mechanically alloyed materials provide a counterpart to deposited Fe/Pt multilayers [Liu98, End01] and homogeneous A1 thin films produced by co-sputtering and nanoparticle synthesis [Yer85, Ris99, Sun00], as well as melt-spun alloys [Yer85].

Subsequent heat treatment at elevated temperatures is required for the formation of the L1$_0$ FePt phase. By neutron powder diffraction performed during in-situ heat treatment and by differential scanning calorimetry (DSC) it has been shown that independent of milling time and stoichiometry the onset of ordering is at around 300 °C. The ordering develops via so-called combined solid state reactions [Hor79]. It is accompanied by grain growth and thermally assisted removal of defects introduced by milling and proceeds rapidly at moderate temperatures by nucleation and growth of the ordered phases with a high degree of the long-range order (LRO). The mechanism of ordering into the L1$_0$ structure depends on the alloy composition and the precursor microstructure. Heating of the Fe$_{100-x}$Pt$_x$ (x = 40; 45; 50; 55) alloys with the initial A1 structure induces the A1 → L1$_0$ transformation, whereas in the Fe$_{50}$Pt$_{50}$ powders with the multilayer-type microstructure, the L1$_0$ formation proceeds via a metastable state according to the sequence: Fe/Pt precursor → L1$_0$ + L1$_2$ → L1$_0$. The ordering kinetics in the studied nanocrystalline Fe-Pt powders is enhanced compared to that in coarse-grained alloys, as indicated by the reduced values of the activation energy. The results based on the in-situ neutron powder diffraction and DSC measurements suggest that for the equiatomic composition the A1 → L1$_0$ transformation rate is fastest and a deviation from the equiatomic concentration
significantly decelerates the ordering. The activation energy for the $A1 \rightarrow L1_0$ transformation can be correlated with the degree of the LRO in the final $L1_0$ phase. The higher driving force and lower activation barrier further enhance the ordering kinetics in the Fe-Pt alloys with the lamellar microstructure. The additional driving force may be explained by a higher total Gibbs free energy of the powders with the (remaining) Fe and Pt lamellae, whereas the lower activation energy values are apparently a result of gradient-assisted diffusion. Thus, for the accomplishment of the highly ordered state a fine multilayer-type microstructure should be favoured.

In the Fe-Pt alloys, due to almost identical neutron coherent scattering lengths of Fe and Pt it was not possible to directly observe the development of the long-range order, i.e. the distribution of Fe and Pt atoms over positions in the $L1_0$ lattice. For a direct observation of the LRO evolution within the $L1_0$ phase by neutron diffractometry, Co-Pt and Fe-Pd alloys appear to be suitable candidates. Moreover, it would be of interest to compare in-situ the phase formation and the ordering in Co-Pt and Fe-Pd alloys to that in Fe-Pt, as the kinetic and thermodynamic properties of these alloys have been reported to be significantly different [Bar02].

The phase transformations occurring in the nanocrystalline Fe-Pt powders are similar to that in sputter-deposited FePt films with regard to the temperature range and the activation energy of the ordering process [Bar04, End01, Spa03]. Whereas in particulate $L1_0$-based thin film samples the decrease of defect density, grain growth and sintering result in microstructures not useful for magnetic recording [Kle03], in bulk nanocrystalline magnets and, apparently, in thick films for MEMS applications, combined solid state reactions are beneficial for the enhancement of the ordering kinetics.

An isothermal heat treatment of the $Fe_{100-x}Pt_x$ ($x = 40; 45; 50; 55; 60$) powders with multilayer-type microstructure at moderate temperatures leads to a large amount of the highly ordered $L1_0$ FePt phase and additional $L1_2$ Fe$_3$Pt and $L1_2$ FePt$_3$ phases. This preparation technique gives the possibility to obtain various combinations of phases for concentrations, where, according to the equilibrium phase diagram, only one phase region exists. The specific lamellar distribution of the phases in the annealed $Fe_{100-x}Pt_x$ powders is provoked by the heterogeneity of the as-milled precursor material. By adjusting the precursor microstructure, i.e. by varying the milling time, one can also vary the layer thickness and modify the phase composition in the heat treated $Fe_{100-x}Pt_x$ powders.

Low annealing temperatures (compared to annealing temperatures above 600-700 °C typical for coarse-grained alloys [Shu68, Kle03]) result in reduced grain growth. The average crystallite size is in the range of 20-30 nm after a treatment at 450 °C for 48 h or 336 h. In the heat treated $Fe_{100-x}Pt_x$ alloys, crystallites of the phases are randomly oriented within powder particles. In this small grain size regime, random anisotropy effects give rise to exchange-coupling behaviour. Again, the extent of exchange coupling in annealed $Fe_{100-x}Pt_x$ can be modified by adjusting the microstructure of the as-milled alloys.

In the Fe-rich $Fe_{100-x}Pt_x$ powders milled for 2 h and subsequently annealed, despite small grains, only a weakly pronounced exchange coupling was observed between the high magnetisation $L1_2$ Fe$_3$Pt and hard magnetic $L1_0$ FePt phases. This is attributed to the specific lamellar distribution of the phases. Due to rather thick Fe$_3$Pt layers in terms of the soft magnetic phase domain-wall parameter (Section 1.5.3), only those Fe$_3$Pt grains that are
located at the interface between the Fe₃Pt and L₁₀ lamellae are exchange-coupled to the hard magnetic L₁₀ phase. In these powders, the lower (than predicted for non-interacting randomly oriented particles) remanence may be explained by the presence of dipolar interactions leading to magnetisation reversal already in positive applied fields.

In the 2 h milled and subsequently annealed Fe₅₀Pt₅₀ alloys, along with the highly ordered L₁₀ FePt phase, the amount of which is about 85 vol. %, the formation of L₁₂ Fe₃Pt, as well as L₁₂ FePt₃ is observed. In the Pt-rich Fe₁₀₀₋ₓPtₓ powders, the L₁₀ FePt and L₁₂ FePt₃ phases are formed. Independent of the Pt concentration, all the heat treated Fe₁₀₀₋ₓPtₓ powders milled for 2 h contain the soft magnetic A₁ phase (6-10 vol. %). Due to the presence of the soft magnetic Fe₃Pt and/or A₁ phases, weakly coupled to the hard magnetic L₁₀, the magnetisation reversal in these powders is noncooperative.

In the heat treated Fe₁₀₀₋ₓPtₓ powders milled for 2 h, the maximum coercivity does not correspond to the maximum L₁₀ fraction: it increases steadily with Pt concentration x and reaches \( H_c = 0.95 \) T in Fe₅₀Pt₅₀. The increased coercivity in Pt-rich samples can be attributed to the decoupling of the L₁₀ FePt lamellae by paramagnetic L₁₂ FePt₃ and, apparently, to the improved degree of order in the L₁₀ phase. The coercivity increase is achieved, however, at the expense of magnetisation. As a result of the opposite dependence of coercivity and remanence on x, in the heat treated Fe₁₀₀₋ₓPtₓ powders milled for 2 h, the highest energy product of \((BH)_{\text{max}}\) = 73 kJ/m³ is achieved for Fe₅₀Pt₅₀. In the Fe-rich alloys, the reduction of the maximum energy density is also a consequence of the two-phase demagnetisation behaviour. The noncooperative regime of magnetisation reversal and two-phase demagnetisation behaviour have also been predicted by a simple two-particle model for the case of weak interactions between the particles (Chapter 2).

Similarly to the 2 h milled alloys, heat treatment of the 4 h milled Fe₁₀₀₋ₓPtₓ results in the formation of highly ordered L₁₀ FePt and additional L₁₂ Fe₃Pt and L₁₂ FePt₃ phases. However, the formation of the L₁₂ phases is observed for nonequiaxial concentrations only and the Fe₅₀Pt₅₀ powder is essentially single-phase. In this powder, the amount of L₁₀ FePt is about 98 vol. %, the rest being A₁ FePt. The phases in the annealed Fe₁₀₀₋ₓPtₓ powders milled for 4 h are distributed in the form of very fine lamellae. This nanometer-scale microstructure gives rise to large effects of exchange interactions between crystallites of the phases. As a result, the demagnetisation curves of the heat treated Fe-rich Fe₁₀₀₋ₓPtₓ samples show a single-phase magnetic behaviour, although several magnetic phases are present in the powders, and in both equiatomic and Fe-rich Fe₁₀₀₋ₓPtₓ alloys a significant remanence enhancement is observed.

In the heat treated Fe₁₀₀₋ₓPtₓ powders milled for 4 h, due to the strong intergrain exchange coupling magnetisation reversal is more uniform compared to that in the 2 h milled and annealed powders. The demagnetisation curves of the former alloys are highly reversible. Nevertheless, the open recoil loops of the Fe-rich powders indicate deviations from the ideal exchange-spring-magnet behaviour. The recoil loop area decreases with decreasing soft magnetic phase fraction and no recoil hysteresis is observed in the essentially single L₁₀-phase Fe₅₀Pt₅₀ sample. In a two-particle interaction model (Chapter 2), the existence of hysteresis in recoil loops has been shown to arise from insufficient coupling between the low- and the high-anisotropy particles. The origin of recoil hysteresis is similar to exchange-bias arising from an exchange anisotropy [Mei57]. In the two-particle model,
the recoil loop area turns out to be a function of the interaction strength, anisotropy of the particles, i.e. switching field distribution, and the fraction of the low-anisotropy component. Evidently the simple model considered in Chapter 2, cannot take into account the microstructure of real materials, which always contains irregularities and imperfections. Moreover, crystallites within real materials are often randomly distributed. Nevertheless, the model reveals the main features of magnetisation reversal processes observed experimentally in exchange-coupled systems. In particular, it is striking that the existence of the noncollinear reversible magnetisation rotation mode, typical for exchange-spring magnets, can be obtained considering interactions only between two particles with the easy axes parallel to each other and to the applied field, thus suggesting that the exchange-spring behaviour is a very general phenomenon. In the Stoner-Wohlfarth model (noninteracting particles), reversible rotation of the magnetisation is observed only for particles with easy axes oriented at random [Sto48].

The model shows that the switching behaviour of both low-anisotropy and high-anisotropy particles is modified by interactions between them. The experimentally observed variation of the switching behaviour of the hard and soft magnetic phases is supported by the model predictions. For instance, with decreasing the soft magnetic phase fraction in the heat treated Fe$_{100-x}$Pt$_x$ powders milled for 4 h, a shift in the mean value of the nucleation field $H_n$ to higher values occurs and the switching is more uniform, as indicated by the narrowing of the switching field distribution function.

Not only the switching behaviour, but also the intrinsic magnetic properties of the soft magnetic phases are modified by the exchange interactions with the hard magnetic grains. In the Fe-rich Fe$_{100-x}$Pt$_x$ powders, i.e. in the hard L1$_0$/soft L1$_2$ Fe$_3$Pt and Al FePt nanocomposites, a single common Curie temperature, close to the Curie temperature of the L1$_0$ phase, is observed. The single Curie temperature suggests that exchange interactions propagate through paramagnetic grains of the soft phases even at temperatures above the Curie temperature of the soft magnetic phases. Polarisation of the soft magnetic phases through exchange interaction with hard magnetic grains has also been evidenced in the recoil loop measurements and in the distribution of switching fields.

The combined analysis of remanence curves using so-called $\Delta J(H)$-plots [Woh58, May91] and MFM data suggests that exchange interactions between crystallites may apparently be reflected in positive $\Delta J(H)$ values, whereas negative $\Delta J(H)$ could be an indication of magnetostatic interactions. Nevertheless, care should be taken when applying a $\Delta J(H)$-plot-type analysis to strongly interacting systems, as the variation of the $\Delta J(H)$ plot has a strong mean-field-type character.

As a result of remanence enhancement, much improved energy density values are obtained in the Fe-rich Fe$_{100-x}$Pt$_x$ powders milled for 4 h and annealed at 450 °C/48 h. An increase of annealing time to 336 h leads to a further improvement of energy density and the highest $(BH)_{\text{max}} = 121$ kJ/m$^3$ is obtained for moderately off-stoichiometric powders, Fe$_{55}$Pt$_{45}$. The increase of $(BH)_{\text{max}}$ with extending the annealing time to 336 h is attributed to the increase of the LRO parameter of the L1$_0$ phase. The obtained energy products are comparable to those in isotropic Nd$_2$Fe$_{14}$B/α-Fe nanocomposites and competitive to the highest values reported for bulk Fe-Pt-based alloys [Cre97, Wat83, Yer90, Hai03c, Xia04, Zha04]. In order to further improve the permanent magnet performance of nanocrystalline
Fe-Pt alloys, densification of the powders, as well as crystallographic alignment of the L10 grains, yielding textured nanocomposites, should be achieved. In this work, consolidation of the as-milled Fe\textsubscript{60}Pt\textsubscript{40} powders by hot compaction at 500 °C using pressures of about 300 MPa followed by hot deformation (at 500 °C with a deformation rate of \(\sim 10^{-4} \text{s}^{-1}\)) has been proven to be successful. The produced disc-shaped samples with a diameter of about 6 mm and a thickness of 500 \(\mu\text{m}\) were characterised by a magnetically isotropic behaviour due to the lack of crystallographic alignment. In order to induce texture at the second step of the deformation process, the ways of producing a mechanically stable compact at temperatures below 300 °C, where still no phase transformation occurs, should be explored.

A curious feature of most of the heat-treated nanocrystalline Fe-Pt alloys is the presence of the A1 phase. The A1 phase is also frequently observed in sputter deposited Fe-Pt thin films either post-annealed or deposited at elevated temperatures [\textit{Ris99, Ton03, Spa03}]. Whereas in alloys with an initial homogeneous A1 structure it can primarily be explained by kinetic effects of the A1 \(\rightarrow\) L1\textsubscript{0} transformation, a question arises with regard to the A1 phase presence after heat treatment of the multilayer-type Fe-Pt powders. Elucidating the mechanism responsible for the existence of disorder (possible sources could be untransformed A1 regions, inferior distribution of atoms on their appropriate sublattices near grain boundaries or antisite defects) would require high-resolution transmission electron microscopy investigations. Another aspect of phase transformations involving chemical ordering is a competition between the L1\textsubscript{0} and L1\textsubscript{2} phases occurring simultaneously within the disordered A1 matrix, as observed, for instance, during heat treatment of the Fe\textsubscript{40}Pt\textsubscript{60} alloy milled for 4 h. In the Fe\textsubscript{40}Pt\textsubscript{60} alloy, the composition of the A1 phase is at a Pt concentration, where the L1\textsubscript{0} and L1\textsubscript{2} phases coexist in equilibrium at low temperatures (Fig. 1.1). In coarse-grained alloys, the A1 \(\rightarrow\) L1\textsubscript{0} + L1\textsubscript{2} transformation leads to a formation of complex microstructures consisting of regular arrays of L1\textsubscript{0} and L1\textsubscript{2} domains with a particular topology [\textit{Ler91}], which are different from microstructures obtained during the A1 \(\rightarrow\) L1\textsubscript{0} transformation [\textit{Zha92, Kle95}]. It would be, thus, interesting to study how the kinetics and mechanisms of ordering in (L1\textsubscript{2}+L1\textsubscript{0}) stability regions are modified by the nanocrystalline nature of the material.

In this work, it has been shown that the Fe moment in L1\textsubscript{0}-type Fe\textsubscript{100-x}Pt\textsubscript{x} (\(x = 41; 45; 50; 52\)) alloys is sensitive to composition and almost insensitive to the degree of order in the investigated compositional range. The individual Fe and Pt moments decrease with increasing Fe content, which is primarily a consequence of the lattice volume reduction. This behaviour is in contrast to that of the magnetocrystalline anisotropy and of the Curie temperature depending on both the composition and the degree of the LRO within the L1\textsubscript{0} phase [\textit{May89, Kam99, Kan00, Oka02, Sta04}]. Furthermore, it would be of interest to investigate the influence of the stoichiometry and the degree of chemical order on the magnetic structure of L1\textsubscript{0}-based Co-Pt and Fe-Pd alloys and to compare the results to those of Fe-Pt alloys. A possibility of interstitial and substitutional modification of the L1\textsubscript{0}-type alloys and its influence on the intrinsic magnetic properties is also an intriguing question.
Appendix

A. Demagnetising field influence on remanence analysis

Hysteresis loops measured in open-circuit have to be corrected by the demagnetising contribution \(-NM\), which is achieved by applying the shearing procedure. The procedure consists in considering skewed reference curves \(M(H-NM)\) instead of \(M(H)\). The use of the demagnetising correction by \(-NM\) is an effective (mean-field) description of dipolar interactions and is limited to homogeneous uniformly magnetised ellipsoids. Generally, exchange interactions and particle size also influence the demagnetising behaviour [Sko99b]. Thus, in real samples, local magnetic fields are strongly inhomogeneous and the \(H \rightarrow H-NM\) correction gives only a very rough estimation of demagnetising fields if local switching is considered. Further, the mean-field description fails to account for cooperative phenomena [Bro62, Cal77]. Knowledge about the appropriate demagnetising factor is crucial in the remanence curves analysis, as the latter assumes the sample to be in a remanent state. In particular, measured curves not corrected for demagnetising field deliver wrong information about magnetisation reversal in the system.

Figure A.1(left) shows hysteresis loops for a heat treated Fe\(_{50}\)Pt\(_{50}\) powder prepared in a cylindrical shape by embedding the powder particles in epoxy (cylinder diameter being equal to its height). For this cylindrical sample, an appropriate demagnetising factor \(N\) has been chosen between 0.33 and 0.4 (the choice is made on the basis of the maximum susceptibility \(dJ/dH\) value, Fig. A.1(right)). Nevertheless, this demagnetising factor is only approximate and does not reflect real demagnetising fields in the sample.

As an example, figure A.2 shows \(\Delta J(H)\) plots and irreversible susceptibility \(\chi_{\text{irr}}\), defined by Eq. (1.25) and (1.28), respectively, for a Nd\(_{4.5}\)Fe\(_{77}\)B\(_{18.5}\) alloy prepared by melt-spinning and subsequent annealing at 700 °C/10 min. The alloy composition is similar to

![Fig. A.1. Hysteresis loops (left) and susceptibility \(dJ/dH\) (right) for various values of bulk demagnetisation factor \(N\) in Fe\(_{50}\)Pt\(_{50}\) powders (4 h milled and annealed at 450 °C/48 h).](image-url)
that reported by Coehoorn et al. [Coe88], i.e. it is a nanocomposite magnet showing exchange-spring behaviour (see Section 1.5.1). Rietveld analysis reveals that the heat-treated Nd$_{4.5}$Fe$_{77}$B$_{18.5}$ alloy contains the hard magnetic Nd$_2$Fe$_{14}$B phase and soft magnetic Fe$_3$B and α-Fe, in agreement with the initial report by Coehoorn et al. [Coe88]. According to our data the amount of the Nd$_2$Fe$_{14}$B phase is about 50 vol. % (in contrast to 15 vol. % reported by Coehoorn et al. [Coe88]) and is consistent with data obtained by Murakami et al. [Mur00].

The remanence analysis was performed on two types of samples: on a single ribbon with the field applied along its plane, i.e. with the appropriate $N = 0$, and on a bonded magnet prepared by embedding the ribbons crushed to powder in epoxy resin and deliberately setting $N$ to zero, despite the fact that the appropriate $N$ is unequal to zero. Consequently, as the data is recorded after application and subsequent removal of the field, the bonded magnet with $N$ set to 0 is not in a true remanent state. Thus, the $J_r(H)$ and $J_d(H)$ values are measured not at zero internal field, but in the internal field within the sample being negative. As a result, the $\Delta J(H)$ plot for the bonded powder no longer shows positive deviations and has negative values only. A similar analysis has been performed on nanocomposite R$_2$Fe$_{14}$B (R = Ce, Nd, Pr, Tb) + 25 vol. % α-Fe powders prepared by ball milling and subsequent annealing at 650 °C (600 °C for R = Ce) for 10 min. Figure A.3 summarises the magnetic properties and microstructure parameters of these materials. For R = Ce, Nd and Pr, $\Delta J(H)$ plots for bonded magnets with $N$ set to 0 show only a negative deviation, whereas for the appropriate $N = 0.33$ the positive deviation is followed by a negative one (Fig. A.4). For the Tb$_2$Fe$_{14}$B + 25 vol. % α-Fe nanocomposite, the $\Delta J(H)$ plots for $N = 0$ and 0.33 look similar, which is apparently due to the small magnetisation of the Tb$_2$Fe$_{14}$B phase. Moreover, the Tb$_2$Fe$_{14}$B compound is temperature [Coe96], which may further influence the $\Delta J(H)$ behaviour.

The irreversible susceptibility $\chi_{irr}$, representing the switching field distribution, also changes depending on whether the sample is in the true remanent state or not (Fig. A.2 and Fig. A.4). For an incorrect $N$, the width of $\chi_{irr}$ is significantly increased and $\chi_{irr}$ values are nonzero for zero applied field for the same reasons, as discussed above.

![Fig. A.2](image-url)

**Fig. A.2.** $\Delta J(H)$ plots and irreversible susceptibility $\chi_{irr}$, as a function of the reverse field for nanocomposite Nd$_{4.5}$Fe$_{77}$B$_{18.5}$ alloy prepared by melt-spinning and subsequent annealing at 700 °C/10 min.
Fig. A.3. (a) Room temperature coercivity ($H_c$), remanence ($J_r$) and polarisation in the field of 8 T ($J_{8T}$) and (b) crystallite size of the phases in nanocomposite $R_2Fe_{14}B$ ($R = Ce, Nd, Pr, Tb$) + 25 vol.% $\alpha$-Fe powders prepared by ball milling and subsequent annealing at 650 °C (600 °C for $R = Ce$) for 10 min.

Fig. A.4. $\Delta J(H)$ plots and irreversible susceptibility $\chi_{irr}$, as a function of the reverse field for nanocomposite $R_2Fe_{14}B$ ($R = Ce, Nd, Pr, Tb$) + 25 vol.% $\alpha$-Fe powders prepared by ball milling and subsequent annealing at 650 °C (600 °C for $R = Ce$) for 10 min: (a) bulk demagnetising factor $N$ set to zero and (b) $N = 0.33$. 

\[ H_c, J_r, J_{8T} \]
### B. Planar spacing

Table B. Calculated planar spacing $d_{hkl}$ and integrated intensity $I_{hkl}$ of the allowed \{hkl\} reflections for the FePt (L1$_0$ and A1), FePt$_3$ (L1$_2$) and Fe$_3$Pt (L1$_2$) compounds.

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