

### Julia Lyubina (Autor) Nanocrystalline Fe-Pt alloys: phase transformations, structure and magnetism



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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 3*d* transition metals with very high magnetocrystalline anisotropy, such as Nd<sub>2</sub>Fe<sub>14</sub>B and SmCo<sub>5</sub> [*Coe96*].

A figure of merit of permanent magnet performance is its maximum energy density (BH)max - a measure of the maximum magnetostatic energy available from a magnet of optimal shape. To obtain large (BH)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<sub>0</sub> 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  $T_c = 750 \text{ K}$ (Curie temperature),  $J_s = 1.43$  T (spontaneous magnetisation at room temperature) and  $K_1 = 6.6 \text{ MJ/m}^3$  (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, L10based thin films and nanoparticles are promising candidates for ultra-high-density magnetic storage media [Sun00, Wel00]. In bulk form, their high cost limits L10-based permanent magnets to very specialised applications such as in magnetic microelectromechanical 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<sub>0</sub> 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 L1<sub>0</sub> 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 L1<sub>0</sub>-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 Fe<sub>100-x</sub>Pt<sub>x</sub> (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 L1<sub>0</sub> grains, whereas in continuous L1<sub>0</sub>-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) [*Kan82, 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 L1<sub>0</sub> 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 L1<sub>0</sub>-based magnets, both in thin film and bulk form. The combination of hard magnetic L1<sub>0</sub> FePt and soft magnetic Fe<sub>3</sub>Pt yields a significant remanence enhancement in Fe<sub>3</sub>Pt/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 L1<sub>0</sub> FePt/L1<sub>2</sub> Fe<sub>3</sub>Pt two-phase system is too large [*Hai03a*]. Remanence enhancement has also been found in annealed bulk Fe<sub>59.75</sub>Pt<sub>39.5</sub>Nb<sub>0.75</sub> [*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 L1<sub>0</sub> phase. This confirms that despite the crystallographic simplicity of the L1<sub>0</sub> 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 L1<sub>0</sub> 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 L1<sub>0</sub> FePt and, in the case of the Fe-rich and Pt-rich compositions, L1<sub>2</sub> Fe<sub>3</sub>Pt and FePt<sub>3</sub> phases, respectively. Whereas in Pt-rich alloys the decoupling effect of the FePt<sub>3</sub> 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 L1<sub>0</sub>-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 L1<sub>0</sub>-type superstructure. The existence



**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).



**Fig. 1.2.** Phase diagram of the Fe-Pt system around the stoichiometric composition Fe<sub>3</sub>Pt.  $M_s^{ord}$  and  $M_s^{dis}$ denote the temperatures at which the martensitic transformation starts.  $\alpha$  stands for a martensite phase and  $\gamma$  stands for the Fe<sub>3</sub>Pt (A1 or L1<sub>2</sub>) phase.  $T_c^{ord}$  and  $T_c^{dis}$  denote the Curie temperatures of the ordered and disordered phases, respectively (adapted from [*Rel95*]).

region of the L1<sub>0</sub> structure extends from approximately 35 to 55 atomic percent Pt. In Fe<sub>100-x</sub>Pt<sub>x</sub> alloys deviating from the  $35 \le x \le 55$  stoichiometry, formation of the stable cubic superstructures FePt<sub>3</sub> (L1<sub>2</sub>) and Fe<sub>3</sub>Pt (L1<sub>2</sub>) is expected at temperatures below 850 °C and 1350 °C, respectively. An eutectoid reaction A1  $\rightarrow$  L1<sub>0</sub> + L1<sub>2</sub> 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<sub>2</sub> FePt<sub>3</sub>) and in Fe-rich alloys (A1 + L1<sub>2</sub> Fe<sub>3</sub>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 ( $20 \le x \le 35$ ), 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<sub>3</sub>Pt is shown in Fig. 1.2. In the ordered state, the L1<sub>2</sub> Fe<sub>3</sub>Pt phase is stable down to approximately 60 K, whereas the disordered Fe<sub>3</sub>Pt starts to transform to a bcc martensite already at room temperature. The martensite in L1<sub>2</sub>-type ordered Fe-Pt alloys near the composition Fe<sub>3</sub>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<sub>0</sub> or L1<sub>2</sub>) is a heat treatment of the A1 precursor.

In coarse-grained alloys, the mechanism of the cubic A1  $\rightarrow$  tetragonal L1<sub>0</sub> 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<sub>0</sub> 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  $\rightarrow$  L1<sub>0</sub> transformation, which results in a structural self-organisation by two mechanisms. A metastable state is initially formed with



**Fig. 1.3.** Typical microstructures formed as a result of the  $A1 \rightarrow L1_0$  transformation in coarse-grained Fe-Pt, Fe-Pd or Co-Pt alloys which are not deformed before annealing: (a) "tweed" contrast [*Zha92*], (b) polytwin (101) structure and (c) polytwin structure with a high density of antiphase boundaries [*Kle95*].

 $1 > c/a > (c/a)_{equilibrium}$  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<sub>0</sub> phase are, thus, misoriented by an angle close to  $\pi/2$ . 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  $L1_0$  FePt grains is obtained.

#### **1.2.** Crystallographic structures of Fe-Pt phases

Figure 1.4 illustrates schematically the chemically ordered L1<sub>0</sub> and L1<sub>2</sub> structures, as well as the disordered A1 structure. The different chemical species appear as dark and light spheres.

In the L1<sub>0</sub> 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 3d element



**Fig. 1.4.** Schematical illustration of (a) the L1<sub>0</sub> structure (shown are the real cell (Pearson symbol *tP*2) and pseudo-cell (Pearson symbol *tP*4) with the lattice parameters  $a = \sqrt{2}a^*$  and  $c = c^*$ ); (b) the L1<sub>2</sub> structure and (c) the chemically disordered A1 phase. The different chemical species appear as dark and light spheres.

(Fe) and the 5*d* element (Pt) along the [001] direction. If the chemical ordering into the L1<sub>0</sub> 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 L1<sub>0</sub> 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 L1<sub>0</sub> 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 L1<sub>2</sub> ordered structure is shown. This is a cubic phase that can form around a 1:3 stoichiometry. In Fe<sub>3</sub>Pt (FePt<sub>3</sub>), 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 longrange 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

| Phase                                 | Space group       | Lattice constants, Å |
|---------------------------------------|-------------------|----------------------|
| FePt (L1 <sub>0</sub> )               | P4/mmm            | a = 3.852; c = 3.713 |
| FePt (A1)                             | $Fm\bar{3}m$      | a = 3.807            |
| Fe <sub>3</sub> Pt (L1 <sub>2</sub> ) | Pm <sup>3</sup> m | a = 3.75             |
| Fe <sub>3</sub> Pt (A1)               | $Fm\bar{3}m$      | a = 3.76             |
| FePt <sub>3</sub> (L1 <sub>2</sub> )  | $Pm\bar{3}m$      | a = 3.866            |
| FePt <sub>3</sub> (A1)                | Fm3m              | a = 3.86             |

**Table 1.1.** Crystallographic data of the structures of the Fe-Pt system.

disorder one may use the parameters  $r_{Pt}$  and  $r_{Fe}$ , 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*]:

$$S = r_{\rm Pt} + r_{\rm Fe} - 1 = (r_{\rm Pt} - c_{\rm Pt}) / y_{\rm Fe} = (r_{\rm Fe} - c_{\rm Fe}) / y_{\rm Pt}, \qquad (1.1)$$

where  $c_{Pt(Fe)}$  is the atom fractions of Pt(Fe) and  $y_{Pt(Fe)}$  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 nonstiochiometric 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<sub>0</sub>-type ordering has been defined as  $S_{max} = 1-2|\Delta x|$ , 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 xray 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,



**Fig. 1.5.** Calculated x-ray diffraction patterns for (a) disordered A1 FePt and (b) completely ordered L1<sub>0</sub> FePt phase.

 $P_k$  is the preferred orientation function ( $P_k = 1$  indicates the absence of a preferred orientation) and *A* is an absorption factor [*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:

$$F_{k} = \sum_{j} r_{j} f_{j} \exp\left[2\pi i (hx_{j} + ky_{j} + lz_{j})\right],$$
(1.3)

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<sub>0</sub>-type ordering, the structure factors for fundamental  $F_f$  and superstructure  $F_{ss}$  reflections are calculated as

$$F_{f} = 4(c_{\rm Pt}f_{\rm Pt} + c_{\rm Fe}f_{\rm Fe})$$
(1.4a)

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

#### **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

$$IN(E_{\rm F}) \ge 1\,,\tag{1.5}$$

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

$$\mu_{\rm s} = \mu_{\rm B} (n_{\uparrow} - n_{\downarrow}) = -2\mu_{\rm B} \langle S_{\rm z} \rangle /\hbar \tag{1.6}$$

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 majorityspin  $3d^{\uparrow}$  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



**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*]).

between the *d* and *sp* states and using Eq. (1.6) one would obtain a magnetic moment of Fe of 4  $\mu_{\text{B}}$ . In reality, it has a value of about 2.8  $\mu_{\text{B}}$  (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

$$\mu_{\rm l} = -\mu_{\rm B} \langle L_z \rangle / \hbar \,, \tag{1.7}$$

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<sub>0</sub> 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*].

| -          |       | Lattice     | Magnetic moment, $\mu_{\rm B}$ |              |                |               |         |                 |
|------------|-------|-------------|--------------------------------|--------------|----------------|---------------|---------|-----------------|
|            |       | constant, Å | $\mu_{ m s}$                   | $\mu_{ m l}$ | $\mu_{ m tot}$ | ξ <i>,</i> eV | l, eV   | $IN(E_{\rm F})$ |
| α-Fe (bcc) | ferro | 2.866       | 2.23                           | 0.043        | 2.273          | 0.07          | 0.92    | 1.5-1.7         |
| γ-Fe (fcc) | af    | 3.50        |                                |              | 1.0            |               |         |                 |
|            |       | 3.60        |                                |              | 1.4            |               | 0.4     | 0.5             |
|            |       | 3.70        |                                |              | 2.1            |               |         |                 |
|            | ferro | 3.60        |                                |              | 2.4            |               |         |                 |
|            |       | 3.70        |                                |              | 2.6            |               |         |                 |
| Pt (fcc)   | para  | 3.923       |                                |              |                | 0.6           | 0.3-0.8 | 0.5-0.7         |
| FePt       | ferro |             | Fe: 2.77                       | 0.06         | 2.83           |               |         |                 |
|            | -     |             | Pt: 0.35                       | 0.06         | 0.41           |               |         |                 |

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 L1<sub>0</sub> FePt is the large spin-orbit coupling in Pt and the 5d(Pt)-3d(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

$$K_1 = \frac{H_A J_s}{2},$$
(1.8)

where  $H_A$  is the anisotropy field and  $J_s = \mu_0 M_s$  is the spontaneous polarisation. The first anisotropy constant of L1<sub>0</sub> FePt  $K_1 = 6.6 \text{ MJ/m}^3$  (Table 1.3) is larger than that of some rareearth transition-metal compounds used in modern permanent magnets, Nd<sub>2</sub>Fe<sub>14</sub>B (4.9 MJ/m<sup>3</sup>) and Sm<sub>2</sub>Co<sub>17</sub> (3.3 MJ/m<sup>3</sup>) [Coe96]. Both experimental data and electronic structure calculations indicate a correlation between the degree of the LRO within the L10 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 L1<sub>0</sub> structure is mainly caused by chemical ordering of the cubic A1 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/aratio 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.

**Table 1.3.** The room temperature magnetic behaviour (*para* – paramagnetic; *ferro* – ferromagnetic; *af* – antiferromagnetic) and magnetic properties of the main phases in the Fe-Pt system: the Curie temperature  $T_c$ , the anisotropy constant  $K_1$ , the anisotropy field  $H_A = 2K_1/\mu_0 M_s$ , the saturation magnetisation  $M_s$ , the upper limit of energy density  $(BH)_{max} = \mu_0 M_s^2/4$ , the domain wall width  $\delta_w$ , the exchange length  $l_{ex}$  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*].

|            |                    |         | Т <sub>с</sub><br>(К)  | <i>K</i> <sub>1</sub><br>(MJ/m <sup>3</sup> ) | μ <sub>0</sub> H <sub>A</sub><br>(T) | μ <sub>0</sub> M <sub>s</sub><br>(T) | $\mu_0 M_s^2 / 4$ (kJ/m <sup>3</sup> ) | δ <sub>w</sub><br>(nm) | l <sub>ex</sub><br>(nm) | D <sub>c</sub><br>(nm) |
|------------|--------------------|---------|------------------------|---|--------------------------------------|--------------------------------------|--|------------------------|-------------------------|------------------------|
|            | Fe <sub>3</sub> Pt | para    |                        |   |                                      |                                      |  |                        |                         |                        |
| Disordered | FePt               | ferro   | 585                    |   |                                      | 1.5                                  | 448                                    | ≈ 15                   |                         |                        |
|            | FePt <sub>3</sub>  | ferro   | 428                    |   |                                      | 0.8                                  | 127                                    |                        |                         |                        |
|            |                    |         |                        |   |                                      |                                      |  |                        |                         |                        |
| Ordered    | Fe <sub>3</sub> Pt | ferro   | 410                    |   |                                      | 1.8                                  | 645                                    | ≈15                    |                         |                        |
|            | FePt               | ferro   | 750                    | 6.6   | 11.5                                 | 1.43                                 | 510                                    | 6.3                    | 2.0                     | 560                    |
|            | FePt <sub>3</sub>  | para (a | para (af at T < 160 K) |   |                                      |                                      |  |                        |                         |                        |
|            |                    |         |                        |   |                                      |                                      |  |                        |                         |                        |
|            | α-Fe               | ferro   | 1043                   | 0.046   |                                      | 2.16                                 | 928                                    | 30                     | 1.5                     | 7                      |

The MCA of the cubic ferromagnetic phases of the Fe-Pt system is orders of magnitude smaller than that of L1<sub>0</sub> 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<sub>100-x</sub>Pt<sub>x</sub> alloys for x  $\leq$  25 the martensitic transformation takes place at room temperature and above (Fig. 1.2). The L1<sub>2</sub> ordered Fe<sub>3</sub>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<sub>3</sub>Pt stoichiometry are also known to reveal the Invar effect [*Was90*]. The ordered L1<sub>0</sub> FePt is ferromagnetic with relatively high values of  $T_c = 750$  K and  $J_s = 1.43$  T. L1<sub>2</sub> FePt<sub>3</sub> 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