

BASICS AND MAGNETIC MATERIALS

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1 – INTRODUCTION

1 – 1 History of magnetism [1,2]

In ancient China as well as Europe (i.e. Greece) it had been recognized that pieces of iron are attracted by loadstone (Fe_3O_4). A further fundamental behaviour of such magnets is that if delicately suspended they align with respect to the meridians of earth, which has been used to construct the compass. The earliest European treatises on magnetism are written by P. Peregrinus (1269) and W. Gilbert (1600). R. Descartes (1596–1650) marks the transition divorcing physics from metaphysics. In 1820 H.C. Oersted found that electric currents have the same effect on a compass needle as a piece of loadstone. M. Faraday discovered the magnetic induction in 1831 and was the first who used the term *magnetic field*. This line of investigation culminated in the beautiful equations bearing the name of J.C. Maxwell (1873) who had not only summarized all what was known at that time about electric and magnetic fields and their interactions with matter but also introduced the displacement current completing the electric current in the equations which now could describe electromagnetic waves such as light and the radio waves then discovered by H.R. Hertz in 1888. After H.A. Lorentz had established his theory of electrons in electromagnetic fields it was expected that combining Maxwell's equations and Lorentz's theory would

allow to reproduce the properties of magnetic materials and to confirm the hypothesis of A.M. Ampere (1775-1836) that ferromagnetism is caused by (molecular) currents. However N. Bohr (1911) and J.H. van Leeuwen (1919) showed that, according to this classical theory, *at any finite temperature, and all finite applied electric or magnetic fields, the magnetization of a collection of electrons in thermal equilibrium vanishes identically*, which demonstrates the need for modifying the theory by quantization. This has been successfully done in the 20th century.

1 – 2 Magnetism and magnetic materials in our daily life [3,4]

We are exposed to the earth's field and to natural electromagnetic waves. Many things we are daily concerned with as e.g. TV, radio, portable phone etc. are based on the prediction and the invention of Maxwell and Hertz. Magnetism is applied in various domains of great economic importance such as energy, traffic, telecommunication, information technologies, home devices and medicine. Enhanced effort can also be observed in studies of basic magnetism and in interdisciplinary branches related to magnetism such as geomagnetism and biomagnetism.

The magnetic field is one of the primary parameters of quantum and thermodynamic states. The extension of the range of fields available for research belongs to the important new experimental approaches. Measurements in higher fields often resulted in the discovery of novel effects in physics. Prominent examples are the quantum Hall effects.

2 – MAGNETIC MOMENT AND MAGNETIZATION [5-12]

2 – 1 Magnetization in Maxwell's equations

The microscopic form of Maxwell's equations (in the SI system of units) is

$$\nabla \times \mathbf{h} = \varepsilon_0 \dot{\mathbf{e}} + \mathbf{i} \quad (1) \qquad \nabla \cdot \mathbf{h} = 0 \quad (2)$$

$$\nabla \times \mathbf{e} = -\mu_0 \dot{\mathbf{h}} \quad (3) \qquad \nabla \cdot \varepsilon_0 \mathbf{e} = \mathbf{r} \quad (4)$$

$$\dot{\mathbf{i}} + \nabla \cdot \mathbf{i} = 0 \quad (5)$$

where \mathbf{h} and \mathbf{e} are the magnetic and the electric field, \mathbf{i} is the current density, \mathbf{r} the charge density. ε_0 and μ_0 are the electric permittivity and the magnetic permeability of the vacuum. Microscopic parts of \mathbf{i} (those as proposed by Ampere) can be expressed by the curl of a vector \mathbf{M} and microscopic contributions to \mathbf{r} by the divergence of a vector $-\mathbf{P}$ i.e.

$$\mathbf{r} = \rho - \nabla \cdot \mathbf{P} \quad (6) \qquad \mathbf{i} = \mathbf{j} + \nabla \times \mathbf{M} + \dot{\mathbf{P}} \quad (7)$$

Thus the above equations (1) and (4) take the form

$$\nabla \times (\mathbf{h} - \mathbf{M}) = \varepsilon_0 \dot{\mathbf{e}} + \dot{\mathbf{P}} + \mathbf{j} \quad (1')$$

$$\nabla \cdot (\varepsilon_0 \mathbf{e} + \mathbf{P}) = \rho \quad (4')$$

where ρ and \mathbf{j} represent the macroscopic charge and current densities. The corresponding averages of $\mu_0 \mathbf{h}$ and \mathbf{e} are designated as \mathbf{B} and \mathbf{E} , respectively. The macroscopic fields \mathbf{H} and \mathbf{D} are introduced by the definitions $(\mathbf{B} - \mu_0 \mathbf{M}) = \mu_0 \mathbf{H}$ and $(\varepsilon_0 \mathbf{E} + \mathbf{P}) = \mathbf{D}$. Consequently, the macroscopic form of Maxwell's equations (1) to (5) is

$$\nabla \times \mathbf{H} = \dot{\mathbf{D}} + \mathbf{j} \quad (1'') \qquad \nabla \cdot \mathbf{B} = 0 \quad (2'')$$

$$\nabla \times \mathbf{E} = -\mu_0 \dot{\mathbf{H}} \quad (3'') \qquad \nabla \cdot \mathbf{D} = \rho \quad (4'')$$

$$\dot{\rho} + \nabla \cdot \mathbf{j} = 0 \quad (5'')$$

A dipole moment of the magnetic "charge density" $\nabla \cdot \mathbf{H} = -\nabla \cdot \mathbf{M}$ can be introduced by

$$\mathbf{m} = -\int_V d\tau \mathbf{r} (\nabla \mathbf{M}) = \int_V d\tau \mathbf{M} \quad (8)$$

(\mathbf{M} vanishes outside of the volume V). Thus \mathbf{M} is the magnetic-moment density.

2 – 2 Magnetic moment and angular momentum

Eq. (8) can be transformed into

$$\mathbf{m} = \frac{1}{2} \int_V d\tau \mathbf{r} \times (\nabla \times \mathbf{M}) \quad (9)$$

where the *Amperian molecular current density* $\nabla \times \mathbf{M}$ appears. If we attribute $\nabla \times \mathbf{M}$ to the motion of electrons characterized by their (negative) charge e , their charge density ρ , mass m and velocity \mathbf{v} we obtain

$$\mathbf{m} = \frac{e}{2m} \int_V d\tau \rho_m \mathbf{r} \times \mathbf{v} = \frac{e}{2m} \mathbf{L} \equiv g \frac{e}{2m} \mathbf{L} \quad (10)$$

where $\rho_m = \rho m/e$ is the mass density and \mathbf{L} is the angular momentum of the electron under consideration. The experiment of A. Einstein and W.J. de Haas (in 1915) revealed that the g factor is nearly 2 instead of 1. This was a strong hint that the microscopic description of the electrons has to be modified (towards relativistic quantum theory).

2 – 3 Quantization and relativity; diamagnetism

Maxwell's equations are not sufficient to determine the fields and their sources. Additional equations are needed that describe the motion of the electrons. However classical mechanics fails in describing the majority of the experimental results on solid state magnetism. The results of Einstein and de Haas and those of W. Gerlach and O. Stern (1922) and G. Uhlenbeck and G. Goudsmit (1925) brought to light that the electron has an intrinsic angular momentum \mathbf{S} characterized by the spin quantum number $s = 1/2$, and g in Eq. (10), with \mathbf{S} instead of \mathbf{L} , is close to 2. This could be well described by a quantum-relativistic equation found by P. Dirac (1928). If a homogeneous magnetic field \mathbf{B} of strength B is applied parallel to the z direction Dirac's Hamiltonian for one electron in a potential \mathcal{V} can be approximately written as

$$\mathcal{H} = \mathcal{H}_0 - \frac{e}{2m} (\mathbf{L} + 2\mathbf{S}) \mathbf{B} + \frac{e^2}{2m} \frac{B^2}{4} (x^2 + y^2) - \lambda (\mathbf{L} \mathbf{S}) \quad (14)$$

The last term is the spin-orbit interaction with λ depending on details of the potential \mathcal{V} . \mathcal{H}_0 does not depend on \mathbf{B} . The magnetic moments and the susceptibility have to be calculated by

$$\mathbf{m} = \langle \boldsymbol{\mu} \rangle = -\partial \langle \mathcal{H} \rangle / \partial \mathbf{B} \quad \chi_{ij} = -\mu_0 \mathcal{N} \partial^2 \langle \mathcal{H} \rangle / \partial B_i \partial B_j \quad (15)$$

where $\langle \dots \rangle$ are quantum mechanical expectation values with respect to the eigenstates (in particular the ground state) of \mathcal{H} and \mathcal{N} is the number of magnetic moments per unit volume. The third term in (14) results in a negative susceptibility. This *diamagnetic susceptibility* is small (typically 10^{-6} to 10^{-5}). However it dominates if the moments resulting from the second term in (14) vanish. Examples of χ values (in 10^{-6}): H_2O : -9 , copper: -1.1 , alcohol: -7.2 .

2 – 4 Magnetization in thermodynamics

In a thermodynamic description of magnetic material the field \mathbf{H} appears as a state variable. However there are some difficulties. One problem is that we often (e.g. in dealing with permanent magnets) are interested in thermodynamically metastable states connected with hysteresis phe-

nomena whereas, strictly speaking, the laws of thermodynamics only hold for states of true thermal equilibrium. Also the magnetic material experiences not only the applied field generated by an external source but also the field generated by its own magnetization. Confusion exists as how to define a correct expression for magnetic work. Statistical thermodynamics defines the internal energy of a system described by a Hamiltonian \mathcal{H} as $\langle \mathcal{H} \rangle$ where $\langle \dots \rangle$ now means averaging over an appropriate statistical ensemble. Consequently the first law of thermodynamics reads

$$d\langle \mathcal{H} \rangle = \delta Q - \mu_0 \mathbf{m} d\mathbf{H} \quad (17)$$

The second term on the right hand side of (17) is the work done on the system described by \mathcal{H} and δQ is the heat provided to the system. \mathbf{H} in (17) is the external field. It is common to use an alternative definition of the internal energy of the magnetic material

$$U = \langle \mathcal{H} \rangle + \mu_0 \mathbf{H} \mathbf{m} \quad (18)$$

and, consequently, of the magnetic work:

$$dU = \delta Q + \mu_0 \mathbf{H} d\mathbf{m} = \delta Q + \mu_0 \int_V d\tau \mathbf{H} d\mathbf{M} \quad (19)$$

This does not change the predictions for experimental results. Insofar both definitions of magnetic work, the last terms in (19) and (17), are correct. An additional difficulty in the thermodynamics of magnetized materials results from the fact that the magnetostatic interaction is long range.

2 – 5 Localized vs. itinerant electron magnetism in solids

In isolated atoms or ions with incompletely filled electron shells the electron-electron interaction results in the formation of magnetic moments in the quantum mechanical ground state, which are governed by the three famous Hund's rules. For small fields H the magnetization of a system of such atoms is given by

$$\mathbf{M} = \chi \mathbf{H} \quad \text{with} \quad \chi = C/T \quad (21)$$

where C is the Curie constant of the considered system.

If such atoms form a solid the behaviour of the electrons differs in different materials. Two main types can be distinguished. If the density of the electrons is large as e.g. in Li- or Na-metal the electrons are delocalized and itinerant. The Hund's rule magnetic moment disappears, resulting in a small, nearly temperature independent susceptibility χ (see below). For small electron densities the electrons are strongly correlated and, therefore, they can be localized and carry a magnetic moment as e.g. in MnO, FeO, CoO, CuO (antiferromagnets) and EuO, CrCl₃ (ferromagnets).

2 – 6 Itinerant electron magnetism

The itinerant electrons can be described as weakly interacting Landau quasiparticles. Their susceptibility is approximately temperature independent and is given by

$$\chi = 2\mu_0 \mu_B^2 N(E_F) \left(1 - \frac{1}{3} \frac{m^2}{m^{*2}}\right) \quad \text{with} \quad \mu_B = \frac{|e| \hbar}{2m} \quad (22)$$

where μ_B is the quantum of magnetic moments, called Bohr's magneton, $N(E_F)$ is the density of states at the Fermi level E_F , \hbar is Planck's constant and m^* is the effective mass of the considered quasiparticles. Eq. (22) is the combination of the paramagnetic contribution of the spins of the quasiparticles (W. Pauli 1927) and of their diamagnetic orbital contribution (L.D. Landau 1930). Thus metals with large or moderate m^* (e.g. Na: $m/m^* \approx 1$) are Pauli paramagnets, $\chi > 0$, whereas those with small m^* are Landau diamagnets, $\chi < 0$, as e.g. Bi ($m/m^* \approx 10^2$).

According to Slater (1936) and Stoner (1938) the interaction between itinerant electrons in a solid manifests itself as an exchange interaction. This effect has been used to explain the ferromagnetism in systems like Ni or MnSi. If $IN(E_F) < 1$ where I is the strength of the exchange interaction the paramagnetic state remains stable. Then the susceptibility is given by

$$\chi = \frac{2\mu_0\mu_B^2 N(E_F)}{1 - IN(E_F)} \quad (24)$$

describing the exchange enhancement of the Pauli susceptibility in (22). A particularly strong enhancement of this type is observed in Pd.

3 – LOCALIZED ELECTRON MAGNETISM [1, 6 – 17]

There is a rich variety of materials with electrons being localized by correlation and carrying a magnetic moment. In most cases these moments result from 3d or 4f electrons. However moments from other unfilled shells (e.g. 5f or 2p) are also known. Examples for 2p-type magnetic materials are solid O₂ (an antiferromagnet) and TDAE-C₆₀ (an organic ferromagnet).

3 – 1 Effects of crystalline electric fields

In a solid the localized electrons are in the electrostatic field stemming from the atomic neighbours, usually called crystalline electric fields (CEF). Depending on the symmetry in the solid and the strength of the CEF the contribution of the orbital angular momentum \mathbf{L} to the local magnetic moment will be reduced or even totally "quenched" which is the reason, why often (e.g. in the iron bar of the Einstein-de Haas experiment) only spin magnetic moments are observed.

The CEF cause a mixing of the eigenfunctions of L_z and a splitting of their energy eigenvalues. If this splitting is large compared to the Hund's-rule-one interaction, a reduction of the Hund's rule value S of the total spin may occur. This is called High-spin–Low-spin transition.

A sufficiently strong spin-orbit interaction (see part 3 –2) prevents the quenching of \mathbf{L} and the Hund's rule total angular momentum \mathbf{J} survives at the site. Typical examples for this are ions of 4f elements. Then the CEF will mix the eigenfunctions of J_z and split their energy levels. In certain cases such zero-field splitting results in a singlet ground state. If the energy gap between such a singlet and the excited states is large enough the site is "non-magnetic" i.e. it has no magnetic moment in small applied fields \mathbf{H} although it has well defined quantum numbers L , S and J .

If the exchange interaction (see part 3 –4) is strong compared to the CEF the quenching and zero-field-splitting effects can be overcome. This effect is called *induced-moment magnetism*. Small moments can also be induced by an applied magnetic field which mixes the non-magnetic ground state singlet with excited CEF states. This small effect is the *Van Vleck paramagnetism*.

H.A. Kramers (1930) showed that in a localized atomic site containing an odd number of electrons all energy levels will have an even degeneracy. Such sites can never be in singlet states i.e. be non-magnetic, independent of the strength of the CEF.

If finite magnetic moments survive at the atomic sites in the solid (in spite of the CEF) the CEF cause magnetic anisotropy which will be discussed in part 4.

3 – 2 Spin orbit interaction

The spin-orbit interaction is magnetic in its nature. It governs the third Hund's rule i.e. the mutual alignment of \mathbf{L} and \mathbf{S} in atoms and ions. In less than half filled atomic electron shells the parameter λ in (14) is positive i.e. the resulting total angular momentum is $J = |L - S|$ whereas for more than half filled shells we have $\lambda < 0$ and $J = L + S$. In solids the \mathbf{S} - \mathbf{L} -interaction in 4f ions is strong compared to the CEF interaction whereas in 3d ions the CEF dominate, resulting in the

above discussed **L-** or **S-**quenching. The **S-L**-interaction is essential for the magnetic anisotropy because it couples the direction of the spin based magnetization to the spatial wave function of the electrons that is stabilized in the solid, due to CEF (see part 4).

3 – 3 Dipolar interaction

The magnetostatic energy of a pair of magnetic dipoles \mathbf{m}_i and \mathbf{m}_j is given by

$$E_{\text{dip}}(i, j) = \mu_0 \frac{(\mathbf{m}_i \mathbf{m}_j) r^2 - 3(\mathbf{m}_i \mathbf{r})(\mathbf{m}_j \mathbf{r})}{4\pi r^5} \quad (25)$$

where \mathbf{r} is the displacement vector from \mathbf{m}_i to \mathbf{m}_j . This interaction is omnipresent and is relatively weak, resulting in magnetic ordering temperatures of typically 1 K only. On the other hand the long range character of this interaction has far-reaching consequences: The total dipolar energy of a material is the sum of (25) over all pairs (i,j). In a continuum description this is

$$E_{\text{dip}} = -\frac{\mu_0}{2} \int_V d\tau \mathbf{H}'(\mathbf{r}) \mathbf{M}(\mathbf{r}) \quad (26)$$

where $\mathbf{M}(\mathbf{r})$ is the magnetization at position \mathbf{r} and $\mathbf{H}'(\mathbf{r})$ is the field generated by $\mathbf{M}(\mathbf{r})$ according to the field equation (2''), i.e. $\nabla \mathbf{H}'(\mathbf{r}) = -\nabla \mathbf{M}(\mathbf{r})$. The integral in (26) is only semiconvergent i.e. it depends on the shape of the sample and the thermodynamic limit $V \rightarrow \infty$ cannot be simply considered. In homogeneously magnetized samples, $\mathbf{M}(\mathbf{r}) = \mathbf{M} = \text{const.}$, (26) can be written as

$$E_{\text{dip}} = \frac{\mu_0}{2} V \sum_{i,j} D_{i,j} M_i M_j \quad \sum_i D_i = 1 \quad (27)$$

where $(D_{i,j})$ is the demagnetization tensor which is symmetric. D_i ($i = 1,2,3$) are the non-negative eigenvalues of $(D_{i,j})$, called demagnetization factors. The volume-average of the components of $\mathbf{H}'(\mathbf{r})$, often called demagnetizing fields, are given by

$$\langle H'_i(\mathbf{r}) \rangle_V = -D_i M_i \quad (29)$$

3– 4 Exchange interaction

The simplest form of exchange interaction between two ions is

$$\mathcal{H}_{\text{ex}}(i,j) = -J \mathbf{S}_i \cdot \mathbf{S}_j \quad (30)$$

This Hamiltonian describes the combined effect of electrostatic interaction (here – between localized electrons on different positions, i and j) and Pauli's exclusion principle. Therefore this interaction is isotropic. In the simplest form of exchange interaction, the *direct exchange* by overlap of electron wave functions of neighbours in a solid (W. Heisenberg 1928), is the same physical mechanism as the (covalent) chemical bond. In ionic compounds the exchange of the magnetic ions (e.g. Cu^{++} in cuprates) is mediated by wave functions of non-magnetic anions (e.g. O^-). This indirect exchange is called *superexchange* mostly resulting in antiferromagnetism (see 5 –1). If additionally to the localized magnetic electrons itinerant electrons are present, as e.g. in 4f elements, an alternative form of indirect exchange (called *RKKY interaction*) is observed: now a given localized electron interacts not only with its nearest neighbours but the interaction (mediated by the itinerant electrons) is long range and even oscillates, changing its strength and sign. In mixed valence materials such as $(\text{La,Sr})\text{MnO}_3$ mobile Mn-3d electrons mediate the exchange between neighbouring Mn magnetic ions. This so called *double exchange* results in ferromagnetism.

4 – ANISOTROPY AND DIMENSIONALITY [7 – 18]

4 – 1 Types of magnetic anisotropy

The most important form of magnetic anisotropy is the dependence of the energy on the direction of the magnetization where the magnitude of latter can be assumed to be (approximately) inde-

pendent of the direction. In a microscopic description the most common mechanism for this type of anisotropy is the *single ion anisotropy* which in lowest order in the components of the total spin of a given position in the solid, in case of an orthorhombic system, is

$$\mathcal{H}_{\text{sia}} = \tilde{\mathbf{D}}\mathbf{S}_z^2 + \tilde{\mathbf{E}}(\mathbf{S}_y^2 - \mathbf{S}_x^2) \quad (31)$$

Here $\tilde{\mathbf{D}}$ and $\tilde{\mathbf{E}}$ are parameters that depend on the strength of the CEF (see 3 –1) and of the **S-L**-interaction (see 3 –2), and x, y, z represent the crystallographic axes.

The combination of exchange interaction (see 3 –4) with CEF and **S-L**-interaction (3 –2) can be treated in a perturbational approach which results in the so called *anisotropic exchange* interaction. For a pair (i,j) of positions in the solid it is given by

$$\mathcal{H}_{\text{ae}} = \mathbf{S}_i \hat{\mathbf{D}}_{ij} \mathbf{S}_j \quad (32)$$

where ($\hat{\mathbf{D}}_{ij}$) is a symmetric tensor. It should be noted that the dipolar interaction (25) has the same form as (32), if $\mathbf{m}_i, \mathbf{m}_j$ in (25) are identified with the local spin operators $\mathbf{S}_i, \mathbf{S}_j$. Therefore (32) is sometimes called *pseudodipolar interaction*. In uniformly magnetized bodies the dipolar interaction can be macroscopically described by (27). There the anisotropy of the dipolar interaction is expressed by the demagnetization tensor (\mathbf{D}_{ij}) and is called *shape anisotropy*.

For certain symmetries the synergistic effects of exchange, CEF and **S-L**-interaction result in a second form of anisotropic exchange

$$\mathcal{H}_{\text{DM}} = \mathbf{d} (\mathbf{S}_i \times \mathbf{S}_j) \quad (33)$$

where the magnitude of the vector \mathbf{d} is a measure of the strength of this *antisymmetric or Dzyaloshinsky-Moriya* interaction and \mathbf{d} also defines a preferred direction in the considered solid.

Localized magnetic moments with $S = \hbar/2$ (e.g. Cu^{++}) cannot experience single site anisotropy of type (31) because $S_x^2 = S_y^2 = S_z^2 = \hbar^2/4$ are constants. In such cases a further form of anisotropy can be of relevance, the *anisotropy of the g-factor* also caused by CEF and **S-L** interaction.

Magnetic anisotropy prefers axes but not directions i.e. the energy is not changed if all magnetic moments in a material are inverted. Nevertheless forms of *unidirectional magnetic anisotropy* have been reported in literature. The most prominent example is the *exchange anisotropy* (W.H. Meiklejohn and C-P. Bean 1957). If a ferromagnet is exchange-coupled to one magnetic sublattices of an antiferromagnet (e.g. on the surface of the latter) the exchange interaction tends to align the magnetization of the ferromagnet along the direction of that sublattice magnetization of the antiferromagnet. Such preferred direction can be approximately considered as unchangeable.

As expected from the third term in (14) *diamagnetism* of localized electrons can also be strongly anisotropic. In graphite the ratio of susceptibilities measured parallel and perpendicularly to the hexagonal axis is as large as 53.

4 – 2 Magnetic anisotropy and coercivity

In a continuum theory called micromagnetism ferromagnetic materials are described by a free energy which – in simplest cases – is given by

$$F = \int_{\mathbf{v}} d\tau \left[A \frac{(\nabla \mathbf{M})^2}{M_s^2} - K \frac{(\mathbf{nM})^2}{M_s^2} - \frac{\mu_0}{2} \mathbf{MH}' - \mu_0 \mathbf{MH} \right] \quad (35)$$

where M_s is the magnitude of the (saturation) magnetization assumed to be temperature dependent but independent of the applied field \mathbf{H} . The first term is the exchange energy. Thus A is related to

J in (30). The second term is the anisotropy energy where K is related to \tilde{D} in (31) or (\hat{D}_{ij}) in (32) and \mathbf{n} is the direction preferred by the magnetic anisotropy. The third term in (35) is the self energy (26) and the last is the Zeeman energy. A particularly simple case is that \mathbf{n} in (35) is parallel to one of the principal axes of the demagnetization tensor (27) and \mathbf{H} is parallel to \mathbf{n} . For large $H = |\mathbf{H}|$ the body will be uniformly magnetized with $\mathbf{M} = \mathbf{n} M_s$. If now H is reduced to become negative, at $H = 0$ there is a first order phase transition where \mathbf{M} changes to $-\mathbf{n} M_s$. It was shown by W.F. Brown (1963) that, for spherically shaped samples, this jump in magnetization should not occur at $H = 0$ but at the coercive field $H = -jH_c$ with

$$jH_c \geq H_A \quad (36)$$

because for $-jH_c < H < 0$ the magnetized state is metastable. In this formula $H_A = 2K/M_s$ is the anisotropy field of the material. In most cases the observed values of jH_c are orders of magnitude smaller than predicted in (36), $jH_c \ll H_A$. This contradiction is called *Brown's paradox*. Brown's paradox is due to the presence of imperfections in the solid state structure in length scales of nanometers or even smaller as well as thermal fluctuations and quantum mechanical tunneling.

4 – 3 Magnetism in low dimensional systems

A system consisting of weakly interacting chains of magnetic moments that are strongly coupled within the chains, or weakly interacting planes of strongly coupled moments can be considered as quasi-one or quasi-two dimensional, respectively. They are strongly anisotropic systems because the strength of interaction is different along different directions. As discussed in part 4 – 1 the magnetic anisotropy in the magnetic properties of such systems will manifest itself via CEF and **L-S**-interaction. However, even if the CEF and the **L-S**-interaction are neglected and only the Heisenberg Hamiltonian (30) is taken into account (with J strong for pairs i,j within the low dimensional subsystem, and $J \rightarrow J_\perp$ is small for i,j from pairs of different neighbour subsystems), the behaviour of such systems is very different for different quasi-dimensionality d because fluctuations make cooperative phenomena very sensitive to dimensionality. The detailed behaviour of low- d systems depends on details of the interaction and on the size of the total spin \mathbf{S} of the positions in the solid. An interesting case is the "spin 1/2 Heisenberg antiferromagnet" i.e. $J < 0$ and $S = \hbar/2$ in (30), because there are strong quantum fluctuations. In that case systems with $d=1, 2$ or 3 behave totally different although all of them are magnetically isotropic in spite of their anisotropic lattice. If the low- d subsystems are weakly coupled a *dimensionality crossover* may occur. For example, if $d = 2$ planes are stacked and neighbour planes are weakly coupled to each other, at a low temperature T_N this system manifests its dimensionality $d = 3$ by antiferromagnetic ordering, whereas uncoupled planes would have $T_N = 0$.

5 – PHASE TRANSITIONS AND MAGNETIZATION PROCESSES [1 – 20]

5 – 1 Types of magnetic order

The interactions discussed in part 3 result in cooperative behaviour of the localized magnetic moments, in particular in quantum mechanical ground states with long range magnetic order. If only positive exchange integrals J in (30) occur the ground state magnetic order is very simple: all individual magnetic moments will be aligned to be parallel to each other independent of the structure of the solid. Such *ferromagnetic* ground state appears also in finite clusters of atoms e.g. in a simple dimer with two spins \mathbf{S}_1 and \mathbf{S}_2 . If J in (30) is negative the situation becomes more complicated. In that case the dimer (for $S_1 = S_2 = \hbar/2$) has a singlet ground state with no magnetic moments at the sites 1 and 2 and is separated from the (ferromagnetic) triplet state by an energy gap (called *spin gap*) of width $|J|$. Antiferromagnetic order can only exist in infinitely large systems of sufficiently large dimensionality.

In the simplest type of antiferromagnetic (afm) structure: each spin is antiparallel to its nearest neighbours. Depending on the actual lattice structure, the detailed interaction, the number of dif-

ferent participating magnetic sites etc. very different types of afm structures can occur and a rich variety of them have been determined using advanced technologies as neutron scattering, x-ray magnetic scattering, Mössbauer spectroscopy, nuclear magnetic resonance (NMR) and muon spin relaxation (μ SR). In systems with sufficiently low lattice symmetry the DM-interaction (33) can lead to some canting of the moments of the afm structure, resulting in a small net magnetization (as e.g. in La_2CuO_4). This effect is called *weak ferromagnetism*. A net magnetization also arises in *ferrimagnets* where the magnetic moments are antiparallel ordered but they have different sizes, as e.g. the different iron magnetic moments in the large class of ferrites which are widely used in soft magnetic and permanent magnet materials. If the exchange between the local magnetic moments is mediated by itinerant electrons this RKKY interaction can cause spiral structures (*spin density waves*) which can be commensurate or incommensurate with respect to the lattice structure. Typical examples for this are the 4f elements and their intermetallic compounds.

If different interactions (that intend to orient a given magnetic moment in different directions) are in competition effects of *frustration* will occur. Usually the system will resolve frustration by forming more than two magnetic sublattices. Another type is geometrical frustration where even uniform nearest neighbour interaction is in competition due to the specific lattice structure (e.g. the $d = 3$ pyrochlore lattice). The ground states of such materials have no long range order and are called spin liquid, spin ice or cooperative paramagnetism. Frustration arising from competing interactions in the presence of disordered solid structures can result in a *spin glass* state with the orientations of their magnetic moments being frozen and randomly distributed.

5 – 2 Magnetic domains

In a ferromagnetic sample is governed by the first and second term in (35) *domain walls* can be formed separating uniformly magnetized domains. The *wall width* δ and the *wall energy* per unit area, γ , are given by

$$\delta \sim \sqrt{A/K} \qquad \gamma \sim \sqrt{AK} \qquad (39)$$

The magnetostatic selfenergy of the (uniformly magnetized) sample i.e. (27) or the third term in (35) can be reduced by the formation of domains. The actual domain structure is the result of the balance of the energy stored in the domain walls and of magnetostatic energy. For reasons of such energy balance, spherical particles with an diameter below the *critical single-domain size*

$$D_c \sim \sqrt{AK} / \mu_0 M_s^2 \qquad (40)$$

do not form domain structures, i.e. they are single domain. In modern rare-earth transition-metal permanent magnets δ is a few nanometers and D_c is a few hundreds of nanometers. The width of the domains depend on the sample size.

As proposed by Y. Imry and S.K. Ma (1975), in *random anisotropy* systems i.e. those with random \mathbf{n} in (35) or random orientation of local z-axes in (31), domain like structures are formed that are not caused by magnetostatic selfenergy (i.e. dipolar interactions) but by minimizing the exchange energy in the presence of the random anisotropy.

If in fine-grained hard magnetic materials the crystallites are coupled by a reduced exchange interaction or by magnetostatic interaction only, coarse magnetization structures have been found that extend over many of the crystallites. They have been called *interaction domains*.

5 – 3 Ordering and reorientation phase transitions

Simple magnetic systems characterized by exchange parameters J in (30) show a monotonic decrease of the magnetization in ferromagnets or the alternating magnetization in antiferromagnets with increasing temperature. According to L.D. Landau the change from the paramagnetic state at

high temperatures to ferromagnetism or antiferromagnetism has to be a *second order phase transition* because it separates states with different symmetries. If, however, there are significant magneto-elastic couplings in the material fluctuations in magnetization can induce distortions of the crystal lattice resulting in a *first order phase transition*. The low temperature behaviour of systems exhibiting a second order magnetic phase transition can be well described by spin waves whereas the overall temperature dependence of magnetization can rather well be reproduced by mean field approximations. If the strength of the coupling between different subsystems is only moderate these subsystems will dominate different ranges of the energy spectrum of the combined Hamiltonian and, consequently, they will reveal their own temperature scales. Therefore many different types of phase transitions may occur. Thus in $\text{GdBa}_2\text{Cu}_3\text{O}_7$ the $d = 2$ sublattice of Cu^{++} magnetic moments ($S = \hbar/2$) orders antiferromagnetically at $T_N[\text{Cu}] \approx 95$ K, whereas the $d \approx 3$ Gd sublattice orders at $T_N[\text{Gd}] \approx 2.2$ K, probably due to dipolar interaction (25). In ferrimagnets with heavy 4f elements and 3d elements often the main contribution of the magnetization at low temperatures comes from the 4f element whereas at high temperatures the contribution of the 3d magnetic moment dominates. Since 4f magnetic moments stronger decrease with increasing temperature than the 3d moments the total magnetic moment of such materials disappears at a certain temperature, the *compensation temperature* T_{comp} . In GdCo_4B the ordering temperature is $T_C = 505$ K and T_{comp} is as high as 410 K.

Another class of phase transitions, the *spin reorientation transitions* appear if the contributions of different subsystems to magnetic anisotropy are different in sign and have a different temperature dependence. Thus in $\text{Nd}_2\text{Fe}_{14}\text{B}$ the contribution of Nd and Fe to K in (35) compensate at $T = T_{\text{SRT}} \approx 135$ K i.e. the anisotropy constant K changes its sign at T_{SRT} and consequently the material changes its type of magnetic anisotropy from "easy axis" at high temperatures to "easy cone".

5 – 4 Metamagnetic transitions

The concept of *metamagnetic transitions* is now used to describe the large class of field-induced magnetic phase transitions. They are characterized by a jump or at least an upward curvature in the field dependence of magnetization. In a *spin-flip transition* the antiparallel magnetic moments in antiferromagnets are reversed by the field \mathbf{H} (applied parallel to the axis of the magnetic moments) if the anisotropy constant K is large enough. At some critical field both sublattices become suddenly parallel to \mathbf{H} . Examples are TbCu_2 and DyCo_2Si_2 at low temperatures. If in the same experiment K would have been sufficiently small (classical example: $\text{CuCl}_2 \cdot \text{H}_2\text{O}$) the axis of oppositely aligned afm sublattice magnetizations would suddenly rotate at some critical field to become nearly perpendicular to \mathbf{H} , which results in a jump in the magnetic susceptibility. This is a *spin flop transition*. Upon further increasing $|\mathbf{H}|$ the sublattice magnetizations change their direction continuously until, at an upper critical field, they are parallel to \mathbf{H} . In ferrimagnets a similar flopping phenomenon occurs even at zero K because at small \mathbf{H} the axis of the two sublattice magnetizations will be parallel to \mathbf{H} . *First order magnetization processes* (FOMPs) occur if in an applied field the effects of different (higher order) anisotropy constants are in competition.

Paramagnetic metamagnetism: as discussed in part 3 – 1 if in systems strong CEF dominate the magnetic properties the ground state can be a singlet resulting in a very weak (Van Vleck) paramagnetism. In a large field so called level crossing may occur i.e. magnetic CEF energy levels will become lower than the mentioned singlet. Consequently the susceptibility jumps to become as large as in Langevin-Curie paramagnets (examples: TmSb , PrNi_5 , Pr).

E.P. Wohlfarth and P. Rhodes (1962) predicted the phenomenon of collective electron metamagnetism later often called *itinerant electron metamagnetism* (IEM). This is a transition from Pauli paramagnetism to ferromagnetism if a sufficiently large field \mathbf{H} is applied. Meanwhile many materials are known that exhibit IEM, as e.g. YCo_2 , LuCo_2 , $\text{La}(\text{Fe},\text{Si})_{13}$.

5 – 5 Quantum phase transitions

Phase transitions at zero temperature are called quantum phase transitions which, in other words, are abrupt qualitative changes of the quantum mechanical ground state in dependence on external parameters such as pressure, concentration of some element, magnetic field etc. They are driven by quantum fluctuations. The paramagnetic metamagnetism and the itinerant electron metamagnetism (mentioned in part 5 –4) are simple examples of magnetic quantum phase transitions. A further example is the Ising ferromagnet LiHoF_4 in a magnetic field applied perpendicularly to its magnetic axis. At some critical field the system becomes a (quantum) paramagnet.

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