MAGNETISM OF MATTER
BASIC INTERACTIONS AND MAGNETISATION PROCESSES

D. Givord
Laboratoire Louis Néel, CNRS, 25 avenue des Martyrs, B.P. 166, 38042 – Grenoble –cedex 9

Contents

1 - PHYSICS OF BASIC PHENOMENA

1-1 Formation of a moment at the atomic scale

At the atomic scale, the existence of an orbital moment is associated with the motion of the individual electrons on their orbits. The electrons have also a spin moment of purely quantum nature. The progressive filling of a given atomic shell is determined by electron correlations (repulsive electrostatic repulsion between electrons) when account is taken of the Pauli principle. The result is the well-know Hund's rules. Unfilled shells bear a spin and orbital moments, which are linked by spin-orbit coupling (λLS).

1-2 From atom to solid : localised versus itinerant electrons

Unfilled shells are of outer character. In solids, they tend to form bands (in metals) or covalent bonds (in insulators). The resulting delocalisation of the electrons reduce the influence of the correlations, which are intimately linked to the onset of magnetism. In most cases, magnetism is not stable anymore. Magnetism is essentially characteristic of two main transition series, the 3d and 4f series. It arises from the relatively localised character of the corresponding electron shells.

1-3 Exchange interactions

The electron correlations, at the origin of moment formation at the atom level, may couple moments on different atoms. This is the phenomenon of exchange interactions. For strictly localised electrons, the interatomic correlations are very weak. They are much larger when the same electrons are shared by several atoms. This is the case in itinerant electrons systems (3d transition metals) and in insulators where covalence is involved leading to super-exchange (e.g. transition metal oxides).

1-4 Anisotropy

The electron orbitals are coupled to the crystal lattice. The associated orbital moment, and the spin moment through λLS coupling, are oriented along a well-defined direction, termed the easy magnetisation direction. This is the phenomenon of magnetocrystalline anisotropy. In an ordered crystalline structure, the anisotropy establishes the parallel alignement of the moments up to the macroscopic scale. It is responsible, through this mechanism for long range magnetic order. The strength of the magnetocrystalline anisotropy results from the competition between different energy terms : λLS coupling, exchange interactions and interactions of the electrons orbitals with the crystal lattice through Crystalline Electric Field (CEF) interactions. The magnetorystalline anisotropy may be very large in rare earth-based magnetic systems.

1-5 Magnetostriction

Linear magnetostriction is characterised by a deformation of the crystal lattice, in which the loss in elastic energy is compensated by a gain in CEF interactions.Ddifferent deformations of the crystal lattice are asociated with different orientations of the 4f shell, thus allowing the electrostatic interactions between magnetic electrons and surrounding charges to be minimized. As above for magnetocrystalline anisotropy, magnetriction may be very large in 4f electron systems.

2 - MODELS AND FORMALISMS

2-1 Paramagnetism of localised moments without interactions

The mean magnetisation of a system of classical moments, under a magnetic field H and at the temperature T is :

$$M = N\, m_0\, \mathbf{L}\,(H/T) \qquad (1)$$

where m_0 is the intrinsic magnetic moment, N the number of atoms per unit volume and $\mathbf{L}$ the Langevin function. For a quantum system :

$$M = N\, m_0\, \mathbf{B}_J\,(H/T) \qquad (2)$$

Where $\mathbf{B}_J$ is the Brillouin function associated with the quantum momentum J.
A high temperature development leads to :

$$M = \chi_0\, H \qquad (3)$$

Where χ_0 is the magnetic susceptibility, expressed as :

$$\chi_0 = C/T \qquad (4)$$

Where C is the Curie constant.

2-2 Interactions between localised moments – Molecular field model

The central hypothesis in the molecular field model is to assume that the magnetic exchange interactions are proportional to the mean magnetisation (ferromagnetism) or, more generally, to the mean magnetisation on a given magnetic sublattice.
Let us restrict ourselves to the ferromagnetic case. The molecular field is :

$$H_m = - nM \qquad (5)$$

Where n is the molecular field coefficient. The magnetisation under the applied field H is :

$$M = \chi_0 \, (H + H_m) \qquad (6)$$

Relations (5) and (6) lead to :

$$M(1 - n\chi_0) = \chi_0 \, H \qquad (7)$$

At high temperature, $0 < (1 - n\chi_0) < 1$, and thus :

$$M = \chi \, H, \qquad (8)$$

where :

$$\chi = \chi_0 / (1 - n\chi_0) \qquad (9)$$

is the susceptibility enhanced by exchange interactions :

$$\chi = C / (T - T_C) \qquad (10)$$

where T_C is the Curie temperature.

At temperatures $T > T_C$, the susceptibility follows a Curie-Weiss law. At the Curie temperature, $(1 - n\chi_0) = 0$, χ diverges. Below T_C, a spontaneous magnetisation, M_s, exists in the absence of an externally applied field. M_s is obtained by expressing that (1), (2) and (5) are simultaneously satisfied.

2-3 The Stoner model of itinerant electrons

In general, modelling of magnetic exchange interactions should take into account separately the intra-atomic interactions which lead to the existence of a local moment and the inter-atomic exchange interactions which lead to the coupling between moments.

In the Stoner model, the electrons are assumed to be fully delocalised and such a distinction between intra-atomic and inter-atomic interactions disappears. The exchange interactions between itinerant electrons are represented by :

$$E_M = U \, n\!\uparrow n\!\downarrow \qquad (11)$$

where $n\!\uparrow$ and $n\!\downarrow$ are the number of electrons for each spin state (the total number of electrons, $n = n\!\uparrow + n\!\downarrow$). The change in energy associated with the onset of a band splitting may be expressed as :

$$\Delta E_M = U \, n\!\uparrow n\!\downarrow - (1/4) \, U n^2 = - (1/4) \, U n^2 m^2 \qquad (12)$$

Where $m = (n\!\uparrow - n\!\downarrow) / n$. To this energy gain, an energy loss, ΔE_c is opposed, resulting from the occupancy of higher kinetic energy states in the band. For small splitting δE, one obtains to first order :

$$\Delta E_c = (1/2) \, \delta E \, n \, m \qquad (13)$$

Let $n(E_F)$ be the density of states at the Fermi level for each spin state. It is deduced that :

$$\Delta E_M + \Delta E_c = [(n^2 m^2) / 4 \, n(E_F)] \, [(1 - U \, n(E_F)] \qquad (14)$$

The conditions for the stability of magnetism is determined by the so-called Stoner criterion :

- For $(1 - U \, n(E_F)) > 0$, the lowest energy state corresponds to m=0. Pauli paramagnetism is observed under applied field. The susceptibility, enhanced by the interactions between electrons is :

$$\chi = \chi_0 / (1 - U\, n(E_F)) \qquad (15)$$

where :

$$\chi_0 = 2mn(E_F) \qquad (16)$$

is the susceptibility without interactions.

- For $(1 - U\, n(E_F)) < 0$, a band splitting appears which lead to ferromagnetism at low temperature. The magnetic properties may be calculated in the case where $(1 - U\, n(E_F)) <\cong 0$. This is the very Weak Itinerant Ferromagnetism limit (WIF).

2-4 Descriptions of anisotropy and magnetostriction.

A quantitative description of the various phenomena leading to the existence of magnetocrystalline anisotropy and magnetostriction is not possible. Phenomenological developments are often used which are based on the fact that the symmetry of these phenomena is equal to or higher than the crystal symmetry.

For example, the anisotropy in cubic symmetry may be expressed as :

$$E_K = K_1(\alpha_1^2\alpha_2^2 + \alpha_2^2\alpha_3^2 + \alpha_3^2\alpha_1^2) + K_2\,(\alpha_1^2\alpha_2^2\alpha_3^2 + \ldots) \qquad (17)$$

where α_1, α_2 and α_3 are the direction cosines of the magnetisation direction and K_1 and K_2 are anisotropy constants.

In systems of local moments, e.g. in rare-earth compounds, a phenomenological description of the CEF may be used. The anisotropy can then be discussed in terms of phenomenological microscopic parameters which describe the strength of the crystalline electric field. Similar phenomenological parameters which represent the striction dependence of the CEF interactions are deduced from analysis of the magnetostriction.

3- SPECIFIC SYSTEMS

3-1 3d transition metals and their alloys [1]

The 3d electrons which are responsible for magnetism in 3d metals, are distributed in a relatively narrow band. On a given atom site, intra-atomic electron correlations favour the formation of a local moment, as observed experimentally. Interatomic correlations are very weak and cannot account for the large ordering temperatures observed in particular in Fe (1043K), Co (1393K) or Ni (631K). The electrons may however hop from one site to another. In this process, the on-site exchange interactions are transferred to the neighbouring atoms and magnetic ordering is established.

The magnetic properties of Fe, Co and Ni alloys with another transition element are essentially determined by the differences in electronegativity between the solute and the solvent atoms. As discussed by Friedel [2], when a solute atom is introduced into a metallic matrix, the excess nuclear charge Z displaces locally the mobile electrons (i.e. the electrons close to the Fermi level) until the displaced charges screens out the nuclear charge exactly. This effect occurs around the solute atom over distances of the order of the interatomic distances, i.e. the screening is strongly localized. In Co and Ni which are strong ferromagnets, the screening is provided by spin-down d electrons almost uniquely (there are no spin_up electrons close to EF). It result that the magnetic moment can be simply evaluated :

$$\mu_{solvent} = \text{constant} \qquad (18)$$

and

$$\mu_{solute} = \mu_{matrix} - Z\,\mu_B \qquad (19)$$

3-2 Rare-earth metals [3]

The 4f electrons are highly localised. The arguments presented above to explain the coupling between 3d moments do not apply. It must be considered however that the 5d conduction electrons of these metals mediate the indirect interactions between 4f moments. The interaction between a conduction electron spin, s, and a 4f spin, S, may be expressed as :

$$\mathbf{H}_{sS} = \Gamma(r-R)\ s(r)\ \ S \qquad (20)$$

where $\Gamma(r-R)$ is the interaction constant assumed to be ponctual ($\Gamma(r) = \Gamma\ \delta(r)$). The polarisation of the conduction electrons, as determined by relation (20), is transmitted to the other local 4f moments, leading to the so-called indirect RKKY coupling. The coupling between moments is formally of the Heisenberg-type :

$$\mathbf{H}_{T} = -\ J(R_{ij})\ J_i\ J_j \qquad (21)$$

where $J(R_{ij})$ may be expressed in terms of band structure parameters of the 5d itinerant electrons. $J(R_{ij})$ contains an oscillatory term $F(2k_F\ (R_i\text{-}R_j))$. This gives account for the long-range nature of the interactions and the various types of magnetic orders which may occur.

3-3 Rare earth – transition metal alloys [4]

Transition metals moments : Rare-earth transition metal (R-M) alloys and compounds present a series of original properties which result in their use as permanent magnet and magnetic recording materials.

3d magnetism in these systems can be discussed by considering alloys with a non-magnetic R element (e.g. Y). The variation of the magnetic moment as a function of the percentage of Y introduced can be discussed by considering that Y (and any other R element) is an early transition element. One shows that the magnetic moment is :

$$\mu_{matrix} = (10 - N_v + N_{sp})\ \mu_B \qquad (22)$$

where N_v is the number of matrix valence electrons and N_{sp} is the number of electrons in the s and p bands, assumed to be unpolarised. It follows that :

$$\bar{\mu} = [10(1-c) - N_v - Z_c + N_{sp}]\ \mu_B = Z_m + N_{sp} \qquad (23)$$

where Z_m is a parameter termed the magnetic valence.

Curie temperatures : In Y-Co and Y-Ni compounds, ferromagnetic ordering is observed with high Curie temperatures. In Y-Fe compounds, the ordering temperatures tend to be weaker and the Curie temperature is higher in the Fe-poor compounds than in the Fe-rich ones. These properties may be related to the fact that strongly positive interactions are expected at the end of a transition series, and on the opposite, negative interactions tend to appear in the middle of a series. In fact, when plotted as a function of the 3d band filling, the ordering temperatures in all compounds can be shown to follow a unique curve [5].

R-M coupling : In systems where both the R and M atoms bear a moment, the R-M coupling scheme may be described in terms of antiparallel coupling between R and M spins as shown above, combined with positive 5d-4f exchange interactions at the R sites.

The experiment shows that the exchange interaction between the R and M spins are strong. This can be understood by considering that thecoupling between itinerant 3d and 5d electrons. To first order, the strength of the R-M interactions follows the de Gennes law, which expresses that coupling occurs between spins. The interactions, however, are enhanced for R elements at the beginning of the 4f series. This is due to the higher strengths of the 4f-5d on-site interactions, and may be discussed by considering the changes in the relative extension of the 5d and 4f shells across the R series.

Anisotropy and magnetostriction : A very large anisotropy may be observed in R-M compounds with uniaxial structures. The CEF interactions acting on the R sites determine the low temperature anisotropy. A specific property of these compounds is the fact that the anisotropy remains high at room temperature. Actually, the splitting of the multiplet is determined by both CEF and R-M interactions. Both interactions do not vary very much up to room temperature. The variation of anisotropy is determined by the progressive thermal population of the excited levels, in a scheme of levels which is approximately temperature independent, and is not renormalised by the decrease in R-R exchange interactions as it occurs in rare-earth alloys.

3-4 Magnetism in oxides [6,7]

In systems where the magnetic d electrons have a localised character the mechanism by which exchange takes place in metals does not apply. It remains that the interatomic interactions are small and coupling takes place by superexchange as described by Anderson.

Considering that (i) the electron spin is conserved during electron transfer from one site to another and (ii) that Pauli exclusion principle imposes that 2 electrons on the same orbital are antiparallel, the transfer integrals may be written :

$$t_{nm} = b_{nm} \sin(\theta_{nm}/2) \qquad (24)$$

The energy U is required for such a transfer and the energy gained associated with transfer is :

$$\Delta E = - \sum_{m,n} t_{nm}^2 / U = Cte + (b_{nm}^2 / 2U) \cos\theta_{nm} \qquad (25)$$

This energy leads to a coupling which is formally equivalent to Heisenberg exchange. In most cases, the coupling is indirect mediated by the anions. The sign and the strength of the coupling is then determined by the nature of the cation states which are hybridized with the anion states as well as by number of electrons on the d-shells. This may be qualitatively described by the Goodenough-Kanamori rules. The coupling is often antiferromagnetic.

The magnetic structures and ordering temperatures in transition metal oxides are semi-quantitatively described within this model.

A specific property of oxides is the fact that the Fermi level often crosses the d-band state. These materials tend to show metallic conductivity. In half-filled bands, insulating behaviours are found due to the correlations which separate the states with different spin orientation ; the materials are Mott insulators. This is the case of $LaMnO_3$. The Mn ions are in octahedral site ; the t_{2g} low energy CEF states are approximately 2 eV below the excited e_g states. The t_{2g} states are fully occupied with 3 up-spin d electrons, the e_g orbitals are occupied by 1 up-spin d electron. In $(La_{1-x}Ca_x)MnO_3$, Mn ions may be in a 3^+ or 4^+ states. The e_g states partially filled form a band, i.e. the d electrons have a certain delocalised character and metallic conductivity is observed. This itinerant character of the d electrons leads to a ferromagnetic coupling term between Mn ions, termed double exchange and which competes with super-exchange, hence the complex magnetic structures which may be observed. The interplay between magnetic and transport properties leads to drastic variations in transport properties at the Curie temeprature on the one hand, under applied field (colossal magnetoresistance) on the other hand.

4- DIPOLAR INTERACTIONS AND THEIR CONSEQUENCES

4-1 Dipolar interactions

The exchange interactions, described in the above sections are very large but short ranged. At large distances, the coupling between moments is influenced by long-range dipolar interactions, which are negligible at the atomic scale, but dominant at large distances. These can be expressed as :

$$E_D = \frac{m_0}{4p} \frac{m_i m_j}{r_{ij}^3} - \frac{m_0}{4p} \frac{3(m_i r_{ij})(m_j r_{ij})}{r_{ij}^5} \qquad (28)$$

The dipolar interactions, between 2 dipoles at a distance r, vary as $1/r^3$, the number of dipoles at a distance r from a central atom increases as r^3, thus the dipolar interactions acting involve atoms up to the macroscopic scale.

In a uniformly magnetised material, dipolar interactions are the source of the demagnetising field. They lead to shape anisotropy in an aspherical shape sample.

4-2 Domains and walls

In a ferromagnetic material, exchange interactions and dipolar interactions are competing. The balance between them leads to a magnetisation state in which the macroscopic magnetisation is zero, but an almost parallel alignment of the moments is preserved at short distances. In the absence of magnetocrystalline anisotropy, a gradual rotation of the moments occur. In the more general case, the material splits into several zones, the magnetic domains. Within each domain, the moments are parallel as required by exchange, the magnetisation is directed along a well defined easy direction, as required by anisotropy. From one domain to another, the magnetisation direction changes so that the global magnetisation vanishes.

Between two domains, a progressive rotation of the moments takes place which defines a Bloch wall. A Bloch wall has a characteristic thickness, δ, for which its energy per unit area, γ, is minimum. δ and γ are given by :

$$\delta = \pi \sqrt{A/K} \quad \text{and} \quad \gamma = 4\sqrt{AK}$$

where A, the exchange constant expressed in J/m, characterises the strength of the exchange interactions and K is the anisotropy constant expressed in J/m^3. δ varies from typically 50 nm in the 3d metals to 3 nm in high-anisotropy compounds ($SmCo_5$, $Nd_2Fe_{14}B$).

In general, the division of a ferromagnetic material into domains separated by walls occurs spontaneously. In a homogeneous material, the wall energy does not depend on the wall position. Under an applied field H, the initial magnetisation variation is such as to minimise the Zeeman energy and the dipolar energy. In a system of cubic symmetry, the susceptibility is equal to the inverse of the demagnetising field slope, it is determined by the sample shape and not linked to the material intrinsic properties. During this process, the magnetisation variation occurs by growing of the domains which are favoured by the applied field, at the expense of others. At larger field, the material is in the single domain state, magnetisation variation occurs by moment rotation.

4-3 Coercivity[8]

In this section, we analyse the properties of a uniaxial ferromagnet which has been submitted to a large enough applied field and is in the saturated single domain state. Let us assume that a field is applied, along the easy magnetisation direction but antiparallel to the magnetisation. Neglecting dipolar interactions, 2 main terms determine the equilibrium configuration of this system :

The magnetocrystalline anisotropy which may be written to first order as :

$$E_A = K_1 \sin^2 \theta \tag{29}$$

where θ is the angle of the moments with respect to the initial easy direction. The Zeeman energy which describes the coupling of the moments with the applied field, H_0, is:

$$E_Z = - \mu_0 M_s H_0 \cos(\pi-\theta). \tag{30}$$

The lowest energy state corresponds to the moments being aligned along the easy magnetisation direction and parallel to the applied field. However, the magnetisation is confined in low fields along its initial direction because any rotation away from it will cost some anisotropy energy. An energy barrier separates the two energy minimum. The barrier vanishes when the applied field reaches the value of the anisotropy field ($H_A = 2K_1/M_s$). This defines the coercive field, H_c, which is thus theoretically equal to H_A.

This discussion of magnetisation reversal is due to Stoner and Wohlfarth [9]. It is implicitely assumed that magnetisation reverses uniformly. The question then arises, whether other processes exist which would allow reversal in lower fields. It turns out that in a system with strong magnetocrystalline anisotropy, uniform rotation is theoretically of lowest energy.

In real systems, the coercive field is in general much lower than H_A. This difference between theory and experiment is ascribed to the existence of local defects which allow local nucleation of reversed domains. These can easily move under an applied field and lead to full magnetisation reversal. It remains, that, even if coercivity is much weaker than its theoretical value, a close link is found with anisotropy. The high performance modern magnets are based on rare earth – transition metal high anisotropy compounds. Modern media used for magnetic recording are also based on high anisotropy materials.

REFERENCES

[1] E.P. Wohlfarth, Iron, Cobalt and Nickel, in Ferromagnetic Materials, vol.1, E.P. Wohlfarth ed. , North Holland, Amsterdam, (1988)
[2] J. Friedel, Nuovo Cim. Suppl. 7 (1958) 287
[3] B. Coqblin, The Electronic Structure of Rare-Earth Metals and Alloys : the Magnetic Heavy Rare Earths, Academic Press, London (1977)
[4] J.J.M. Franse and R.J. Radwanski, Magnetic Properties of Binary Rare-Earth 3d-Transition-Metal Intermetallic Compounds, in Handbook of Magnetic Materials, vol. 7, K.H.J. Buschow ed., Elsevier, Amsterdam (1995)
[5] D. Courtois and D. Givord, J. Magn. Magn. Mater., (1999)
[6] J. B. Goodenough, Metallic Oxides, Pergamon Press Ltd., (1971) ; Magnetism and the Chemical Bond, Interscience and Wiley, New York (1963)
[7] M. Imada, A. Fujimori and Y. Tokura, Rev. Mod. Phys., 70 (1998) 1040
[8] D. Givord and M. F. Rossignol, Coercivity, in Rare-earth-Iron Permanent Magnets, J.M.D. Coey ed., Clarendon Press, Oxford (1996)
[9] E.C. Stoner and E.P. Wohlfarth, Phil. Trans. Roy. Soc. London 240A (1948) 599