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17 Magnetic Ordering in Crystals

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In the previous two chapters, among various topics on magnetism, we have discussed the occurrence of permanent magnetic moments in crystals and their paramagnetic susceptibility. In particular we have considered the situation of well-localized electronic wavefunctions with formation of localized magnetic moments (typified by the Curie paramagnetism), as well as the alternative situation of itinerant electronic wavefunctions (typified by the Pauli paramagnetism). It is well-known that many paramagnetic materials, below a critical temperature, present magnetic order even in the absence of applied magnetic fields. The most familiar order is the ferromagnetic one, with localized moments lined up in the same direction so that a spontaneous magnetization is apparent; but several other types of magnetic ordering (antiferromagnetic, ferrimagnetic, helical, etc.) are possible.

The occurrence of magnetic ordering in crystals implies some coupling mechanism between localized or delocalized magnetic moments. Among the microscopic models of coupling between the localized moments, we focus on the Heisenberg spin Hamiltonian, because of its formal simplicity and the clear insight on the electrostatic origin of the effective spin-spin interaction. The phase transition to magnetic ordering is first studied within mean field theories; this permits a justification of the Weiss molecular field assumptions, and a reasonably simple description of some aspects of the wide and rich phenomenology accompanying magnetic ordering and phase transitions. We also consider aspects beyond mean field theories. In particular, at low temperatures, we

study with the spin-wave theory the elementary excitations (magnons) of the Heisenberg ferromagnets; universal aspects at or near the critical temperature region are examined with the renormalization group theory, which establishes the common language for quantum critical phenomena.

In paramagnetic crystals characterized by itinerant electronic wavefunctions (band paramagnetism), the occurrence of magnetic ordering suggests the importance of correlation effects among the independent particle wavefunctions, as typified by the Stoner-Hubbard model of itinerant magnetism. We close this chapter with a discussion of spin-dependent transport in bulk and layered metallic ferromagnetic structures, with the extraordinary impact of giant magnetoresistance from both fundamental and technological points of view.

The vastness of the field of magnetism makes unavoidable drastic abridgments; interesting subjects, such as surface magnetism, molecular nanomagnets, magnetic tunneling, and others have been omitted. Although the topics we cover are so limited and simplified, they should give indicative guidelines in the subject of magnetic ordering in matter.

17.1 Ferromagnetism and the Weiss Molecular Field

Phenomenological Aspects of Ferromagnetism

We begin the study of cooperative effects in magnetic materials, by considering a system in which the microscopic magnetic moments have the same magnitude and tend to line up in the same direction. A ferromagnetic specimen, at sufficiently low temperatures, exhibits spontaneous magnetization. The spontaneous magnetization $M(T)$ depends on the temperature and vanishes above a *critical temperature* T_c , called *ferromagnetic Curie temperature*. The critical temperature T_c and the *saturation magnetization* $M(T = 0)$ for some substances are reported in Table 17.1 [For further data see for instance F. Keffer, *Handbuch der Physik*, Vol. 18 Part 2 (Springer, Berlin, 1966); for Fe and Ni see also T. Tanaka and K. Miyatani, *J. Appl. Phys.* 82, 5658 (1997). For an extensive collection of experimental data on magnetism of bulk materials and nanostructures see for instance C. A. F. Vaz, J. A. C. Bland and G. Lauhoff "Magnetism in

Table 17.1 Ferromagnetic Curie temperature (in K) and saturation magnetization (in gauss) for some materials (above T_c , rare earth dysprosium makes a transition to helices).

Material	T_c	$M(T = 0)$
Fe	1043	1752
Co	1394	1446
Ni	630	510
Gd	293	1980
Dy	85	3000

ultrathin film structures" *Rep. Prog. Phys.* 71, 056501 (2008) and the rich bibliography quoted therein]. Among the elements only a few are ferromagnetic; there is instead a relatively large number of ferromagnetic alloys and oxides.

For an estimate of the order of magnitude of the saturation magnetization, consider for example a cubic crystal with a localized magnetic moment $\mu_B = e\hbar/2mc$ in every unit cell of volume $\Omega = a^3$. Assuming parallel alignment of all the microscopic magnetic moments at zero temperature, the saturation magnetization becomes

$$M(0) = \frac{\mu_B}{\Omega} = \frac{a_B^3 \mu_B}{a^3 a_B^3}, \quad (17.1a)$$

where μ_B is the Bohr magneton and a_B is the Bohr radius. For the evaluation of quantities of frequent interest in this chapter, the following relations may be useful

$$\begin{aligned} \mu_B &= 0.05788 \frac{\text{meV}}{\text{Tesla}}; \quad \frac{\mu_B^2}{a_B^3} = 0.363 \text{ meV} \implies 4.21 \text{ K}; \\ \frac{\mu_B}{a_B^3} &= 6.27 \text{ Tesla} = 62700 \text{ gauss}. \end{aligned} \quad (17.1b)$$

For typical values of the lattice parameter $a \approx 2 \text{ \AA} \approx 4 - 5 a_B$, the unit cell volume becomes $a^3 \approx 100 a_B^3$. From Eqs. (17.1), it can be seen that the expected order of magnitude of the saturation magnetization is 1000 gauss, in the range of the observed values of Table 17.1.

The spontaneous magnetization of a ferromagnetic crystal can be explained only by some interaction mechanism, which favors parallel alignment of the microscopic magnetic moments. A little reflection on the order of magnitude of the critical temperatures given in Table 17.1, shows that the *magnetic dipolar coupling cannot be the origin of such interaction*. In fact two magnetic dipoles μ_1 and μ_2 at (sufficiently large) distance \mathbf{R} interact with an energy

$$E_{\text{dip}} = \frac{1}{R^3} \left[\mu_1 \cdot \mu_2 - 3 \frac{(\mu_1 \cdot \mathbf{R})(\mu_2 \cdot \mathbf{R})}{R^2} \right]; \quad (17.2)$$

from this, the dipolar coupling energy between dipoles μ_B at the lattice sites of a cubic crystal of parameter $a \approx 4 - 5 a_B$, can be estimated as

$$E_{\text{dip}} \approx \frac{\mu_B^2}{a^3} = \frac{a_B^3 \mu_B^2}{a^3 a_B^3} \approx 10^{-5} \text{ eV} \approx 0.1 \text{ K}. \quad (17.3)$$

Thus random thermal fluctuations would destroy alignment of magnetic moments at very low temperatures, of the order of tenths of kelvin degrees, much smaller than the observed critical temperatures, which are of the order of hundred or thousand kelvin degrees. The mechanism of spin alignment must be produced by an effective interaction among spins, which is larger than the dipolar magnetic interaction by a factor $10^3 - 10^4$ or so. The origin of such a "strong" field is basically electrostatics in nature and involves orbits in real space, and not spins. However, the global antisymmetry of the electronic wavefunctions entails a stringent connection between orbital and spin states: this connection can be envisaged as an effective spin-spin coupling in several situations of interest (as discussed in Section 17.2).

The Weiss Molecular Field

Consider a crystal of volume V , formed by N equal magnetic units (atoms or ions), each of angular momentum J and magnetic moment $\mu = -g\mu_B \mathbf{J}$, localized at the sites of a periodic lattice. In the previous chapter, we have discussed the magnetization of the sample in an applied field, under the assumption that the microscopic moments are independent. For instance, from Eq. (16.17), the magnetization of a paramagnetic substance, with $J = 1/2$ and gyromagnetic factor $g = 2$, is given by the thermodynamic average

$$M = \frac{N}{V} \mu_B \frac{e^{\mu_B H/k_B T} - e^{-\mu_B H/k_B T}}{e^{\mu_B H/k_B T} + e^{-\mu_B H/k_B T}} \implies M = \frac{N}{V} \mu_B \tanh \frac{\mu_B H}{k_B T}, \quad (17.4a)$$

where H is the uniform magnetic field applied to the sample. In a paramagnetic substance, composed by independent magnetic dipoles, M is proportional to H for small H , and no spontaneous magnetization can occur in the absence of applied fields. With the approximation $\tanh x \approx x$ for small x in Eq. (17.4a), one finds that the magnetic susceptibility obeys the *Curie law*

$$\chi = \frac{M}{H} = \frac{C}{T} \quad \text{with Curie constant} \quad C = \frac{N}{V} \frac{\mu_B^2}{k_B} \quad \left(J = \frac{1}{2}; g = 2\right). \quad (17.4b)$$

In the case $J \neq 1/2$, expressions similar to Eqs. (17.4) hold with the hyperbolic tangent function replaced by the appropriate Brillouin function (and other minor changes if $g \neq 2$). For simplicity in this section we only consider paramagnetic substances with $J = 1/2$ and $g = 2$, since the generic Brillouin function $B_J(x)$ and the hyperbolic tangent function $B_{1/2}(x)$ have similar asymptotic behaviors. In the original work of Weiss the classical Langevin function $L(x) = B_{\infty}(x)$ was used.

The first phenomenological mechanism leading to magnetism was proposed by Weiss in 1907. It is based on the assumption that the effective magnetic field acting on a given dipole is given by

$$H_{\text{eff}} = H + \lambda M, \quad (17.5)$$

where H is the external magnetic field, λ is an appropriate constant, M is the magnetization, and the molecular field λM provides the cooperative effect. Originally the Weiss constant λ was considered as a phenomenological constant; the interpretation of λ in terms of microscopic quantum models appears later with the works of Heisenberg.

If we make the Weiss assumption that the effective field acting on a given dipole is $H + \lambda M$, we obtain for a ferromagnetic substance (with $J = 1/2$ and $g = 2$) the basic equation

$$M = \frac{N}{V} \mu_B \tanh \frac{\mu_B (H + \lambda M)}{k_B T}. \quad (17.6)$$

It is evident that the case $\lambda = 0$ corresponds to ordinary paramagnetism, while $\lambda > 0$ describes a ferromagnetic cooperative effect. The rest of this section is devoted to bring

out the wealth of information contained in the transcendental equation (17.6), which represents historically the first mean field approach to phase transitions.

In zero field and for $M \rightarrow 0$, Eq. (17.6) is satisfied at the "critical" temperature T_c such that

$$M = \frac{N}{V} \mu_B \frac{\mu_B \lambda M}{k_B T_c} \implies T_c = \lambda \frac{N}{V} \frac{\mu_B^2}{k_B} = \lambda C. \quad (17.7a)$$

Besides the critical temperature, it is also convenient to introduce the dimensionless magnetization m (expressed in term of saturation magnetization), so defined

$$m = \frac{V}{N} \frac{M}{\mu_B} = \frac{M}{M(0)}. \quad (17.7b)$$

Using the quantities defined in Eqs. (17.7), we can cast Eq. (17.6) in the dimensionless form

$$m = \tanh \left(\frac{\mu_B H}{k_B T} + \frac{T_c}{T} m \right). \quad (17.8)$$

The "normalized" or "reduced" magnetization m varies in the interval $0 \leq m \leq 1$. The case $m = 1$ corresponds to saturation magnetization with all the microscopic spins lined in the same direction, while the case $m = 0$ corresponds to random orientations of spins. We wish to establish the dependence of m from the temperature and from the applied magnetic field.

We begin to look for spontaneous magnetization, putting $H = 0$ in Eq. (17.8); then

$$m = \tanh \left(\frac{T_c}{T} m \right). \quad (17.9)$$

The solution of this equation is obtained plotting separately the first member (a straight line) and the second member as functions of m , and looking for the intersections between the curves; the graphical solution is shown in Figure 17.1. With the help of Figure 17.1, it is immediate to note that for $T \geq T_c$ we have only the trivial solution $m = 0$; however, below the critical temperature $T < T_c$ we have also a non-trivial solution with non-zero $m(T)$. The spontaneous magnetization $m(T)$ as a function of temperature can be obtained graphically, and its typical behavior is indicated in Figure 17.2.

Besides the graphical solution, it is instructive to obtain analytically the behavior of the magnetization for temperatures very high and very low with respect to T_c , and around the critical region.

High temperature limit. Consider first the magnetization of the ferromagnetic material for $T > T_c$, in the presence of an external magnetic field H . In the limit of sufficiently small H , also m is small, and linearization of Eq. (17.8) gives

$$m = \frac{\mu_B H}{k_B T} + \frac{T_c}{T} m \implies \frac{m}{H} = \frac{\mu_B}{k_B (T - T_c)}; \quad (17.10a)$$

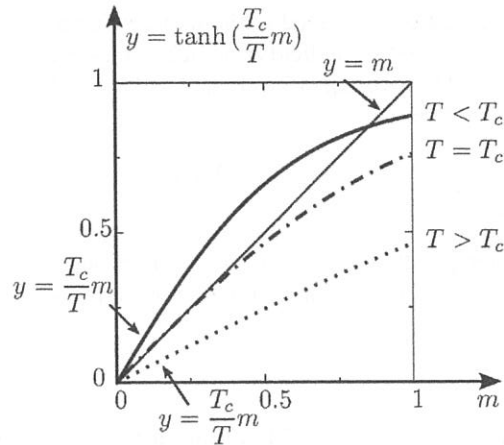


Figure 17.1 Graphical solution of the mean field equation $m = \tanh(mT_c/T)$ for the spontaneous magnetization of a ferromagnetic crystal.

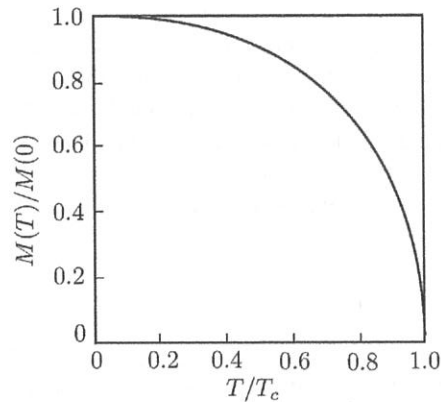


Figure 17.2 Spontaneous magnetization of a ferromagnetic crystal as function of the temperature in the mean field theory, with $J = 1/2$ in the Brillouin function.

this shows that the magnetic susceptibility follows the *Curie-Weiss law*

$$\chi = \frac{M}{H} = \frac{N}{V} \frac{\mu_B^2}{k_B(T - T_c)} = \frac{C}{T - T_c} \quad (T > T_c). \quad (17.10b)$$

Thus, in the Weiss molecular field theory, χ diverges as $(T - T_c)^{-1}$ as the temperature decreases toward the critical temperature. The tendency to parallel alignment of spins, enhances the magnetic susceptibility of the systems and leads to a phase transition below T_c .

Low temperature limit. For $T \ll T_c$ the argument of the hyperbolic tangent function in Eq. (17.9) becomes very large, and upon appropriate expansion, the spontaneous

magnetization becomes for $T \rightarrow 0$

$$m = \tanh\left(\frac{T_c}{T}m\right) \implies m = 1 - 2e^{-2(T_c/T)m} \approx 1 - 2e^{-2T_c/T}. \quad (17.11)$$

Thus, within the mean field theory, near zero temperature the spontaneous magnetization deviates from its saturation value by an exponential term; this prediction of mean field theory (as well as several others) must be appropriately corrected with treatments beyond the mean field approach.

Critical temperature region. Next, we examine the behavior near the critical temperature of the transcendental equation (17.8) in the case both H and m are small. It is convenient to elaborate Eq. (17.8) in such a way to handle functions of separate arguments H and m . For this purpose we write Eq. (17.8) in the form

$$m = \tanh(h + \tau m) \quad \text{with} \quad h = \frac{\mu_B H}{k_B T}, \quad \tau = \frac{T_c}{T};$$

then

$$m = \frac{\tanh h + \tanh(\tau m)}{1 + \tanh h \cdot \tanh(\tau m)} \implies \frac{m - \tanh(\tau m)}{1 - m \tanh(\tau m)} = \tanh h.$$

The expansion of the first member of the above equation for small m gives

$$\frac{m - \tau m + \tau^3 m^3/3 + \dots}{1 - \tau m^2 + \dots} = (1 - \tau)m + \left(\tau - \tau^2 + \frac{1}{3}\tau^3\right)m^3 \approx (1 - \tau)m + \frac{1}{3}m^3$$

(the last passage takes into account that the coefficient of m^3 is finite and equals $1/3$ for $\tau \rightarrow 1$). In summary, near the critical temperature for sufficiently small values of h and m it holds

$$(1 - \tau)m + \frac{1}{3}m^3 = h \implies \boxed{\left(1 - \frac{T_c}{T}\right)m + \frac{1}{3}m^3 = \frac{\mu_B H}{k_B T}} \quad (17.12)$$

regardless if the temperature T , near T_c , is above or below it.

We consider now the behavior of the spontaneous magnetization for T near T_c . Setting $H = 0$ in Eq. (17.12), it is seen that for $T \geq T_c$ there is only the trivial solution $m = 0$. For T near T_c from below we have the non-trivial solution

$$m^2(T) = 3 \frac{T_c - T}{T_c} \implies m(T) \propto (T_c - T)^\beta \quad \text{with} \quad \beta = \frac{1}{2}, \quad T < T_c. \quad (17.13)$$

In the mean field theory, the spontaneous magnetization goes to zero when the temperature approaches T_c from below, according to a power law with critical exponent $\beta = 1/2$.

Another critical exponent can be obtained considering the behavior of the magnetization versus the applied field at the critical temperature. Setting $T = T_c$ in Eq. (17.12), it is seen that

$$m \propto H^{1/\delta} \quad \text{with } \delta = 3. \quad (17.14)$$

Thus at the critical temperature the magnetization versus the applied field is described by a power law with critical exponent $\delta = 3$.

The critical exponent for the susceptibility can be found by differentiation of both sides of Eq. (17.12) with respect to H at constant temperature and in the zero-field limit:

$$\left(1 - \frac{T_c}{T}\right) \frac{\partial m}{\partial H} + m^2 \frac{\partial m}{\partial H} = \frac{\mu_B}{k_B T}.$$

For $T > T_c$ the magnetization at zero field vanishes, and the above equation gives

$$\frac{\partial m}{\partial H} = \frac{\mu_B}{k_B(T - T_c)} \sim (T - T_c)^{-\gamma} \quad \text{with } \gamma = 1, T \rightarrow T_c^+.$$

The same exponent results for $T \rightarrow T_c^-$; in fact using the first of Eqs. (17.13) we have

$$\left(1 - \frac{T_c}{T}\right) \frac{\partial m}{\partial H} + 3 \frac{T_c - T}{T} \frac{\partial m}{\partial H} = \frac{\mu_B}{k_B T} \quad \Rightarrow \quad \frac{\partial m}{\partial H} = \frac{1}{2} \frac{\mu_B}{k_B(T_c - T)}.$$

The above results for the susceptibility critical exponent can be summarized as follows

$$\chi \sim |T - T_c|^{-\gamma} \quad \text{with } \gamma = 1, T \rightarrow T_c. \quad (17.15)$$

The power law exponent for the magnetic susceptibility is the same for T near T_c from above or from below (although, the accompanying factors may be different in the two cases).

Another quantity of interest is the specific heat at zero field. The internal energy of the ferromagnet, contributed by the spontaneous magnetization, is $-(1/2)H_{\text{eff}} M = -(1/2)\lambda M^2$; using Eq. (17.13), it is seen that the specific heat, which is the derivative of the internal energy with respect to the temperature, is zero above the critical temperature and nearly constant just below it.

Near the critical temperature, the Weiss molecular field theory shows that several significant quantities, such as zero-field magnetization, magnetization at critical temperature, zero-field isothermal susceptibility, zero-field specific heat, follow simple power laws with appropriate exponents. Without entering in details, another significant quantity to be mentioned is the spin-spin correlation function, which is related to the probability to find the spin, at a given site, oriented in the same direction as the chosen reference spin. Near the critical point, and at large distances, the correlation function is expected to decay exponentially, with a correlation length going to infinity with a power-like dependence on temperature. At the critical temperature, it is found that the correlation function falls off much slower, in a power-like way, with increasing distance.

Table 17.2 Definition of some critical exponents for magnetic phase transitions. The values of the critical exponents in the mean field theory are given. The exact values of the two-dimensional Ising model are also reported. The approximate values for the three-dimensional Ising model and for the three-dimensional Heisenberg model, calculated with the renormalization group theory, are taken from the paper of J. C. Le Guillou and J. Zinn-Justin, Phys. Rev. B 21, 3976 (1980). It can be noticed that the critical exponents satisfy the scaling laws relations $\alpha + 2\beta + \gamma = 2$; $\gamma = \nu(2 - \eta)$; $\gamma = \beta(\delta - 1)$; $\nu d = 2 - \alpha$ (d = lattice dimensionality).

		($d=4$) Mean field	($d=2$) Ising	($d=3$) Ising	($d=3$) Heisenberg
Zero-field specific heat	$C \approx T - T_c ^{-\alpha}$	$\alpha = 0$ (Discontinuity)	$\alpha = 0$ (Logarithm)	$\alpha = 0.11$	$\alpha = -0.12$
Zero-field magnetization ($T < T_c$)	$M \approx (T_c - T)^\beta$	$\beta = 1/2$	$\beta = 1/8$	$\beta = 0.32$	$\beta = 0.37$
Zero-field isothermal susceptibility	$\chi \approx T - T_c ^{-\gamma}$	$\gamma = 1$	$\gamma = 7/4$	$\gamma = 1.24$	$\gamma = 1.39$
Magnetization at $T = T_c$	$M \approx H^{1/\delta}$	$\delta = 3$	$\delta = 15$	$\delta = 4.82$	$\delta = 4.80$
Correlation length	$\xi \approx T - T_c ^{-\nu}$	$\nu = 1/2$	$\nu = 1$	$\nu = 0.63$	$\nu = 0.71$
Pair correlation function at $T = T_c$	$\Gamma(r) \approx 1/r^{d-2+\eta}$	$\eta = 0$	$\eta = 1/4$	$\eta = 0.03$	$\eta = 0.03$

The definition and the values of the six critical exponents of more common use, mentioned in the above discussion, are summarized for convenience in Table 17.2. The critical exponents are not independent because of the scaling laws connecting them. In particular, from the knowledge of the "thermal" exponent α and of the "magnetic" exponent δ , all the other exponents can be obtained. For further details and relationships among critical point exponents see for instance the textbooks on statistical mechanics cited in the bibliography.

Inadequacies of the Weiss Molecular Field

The Weiss approach has the merit to shed light on some features of ferromagnetic behavior at the minimal technical level. However the Weiss molecular field, which is essentially a mean field theory, presents several inadequacies, that are summarized below; some aspects of the most relevant theories developed to overcome these inadequacies are outlined in the following of this chapter.

Origin of the Weiss molecular field. Historically, the more basic problem raised by the Weiss molecular field is the microscopic origin of the coupling between magnetic dipoles. We can estimate the order of magnitude of the Weiss parameter λ in terms of

T_c , using Eqs. (17.7) and the relations provided in Eq. (17.1b):

$$\lambda = \frac{V}{N} \frac{k_B T_c}{\mu_B^2} \approx \frac{a^3}{a_B^3} \frac{a_B^3}{\mu_B^2} k_B T_c \approx 10^4 - 10^5 \quad (a \approx 4 - 5a_B, \quad T_c \approx 1000 \text{ K}).$$

The phenomenological values of λ in the range $10^4 - 10^5$ exclude that the molecular field originates from magnetic dipole-dipole interactions; these dipolar interactions, once treated "mutatis mutandis" according to the Lorentz cavity field of Section 9.7.3, would give $H_{\text{eff}} = H + \lambda M$ with $\lambda \approx 4\pi/3$ (or so), a value thousand times smaller than the phenomenological values of λ . No other classical magnetic interaction can be envisaged as a source of the Weiss internal field: its origin requires a full quantum mechanical approach, as discussed in more detail in Section 17.2. The dipolar interactions, on the other hand, have a leading role in the tendency of a ferromagnetic specimen to break into "domains," so to reduce the magnetic dipole-dipole interaction energy. In the following, we will neglect this and other consequences of the dipolar interactions among spins; rather we will focus on the quantum origin of the effective coupling mechanism among the localized magnetic moments. This effective coupling can lead not only to ferromagnetism but also to other types of magnetic ordering (as discussed in Section 17.3).

Low temperature region. Near zero temperature the mean field theory predicts that spontaneous magnetization deviates from saturation by an exponential term. In contrast, experiments show a $T^{3/2}$ dependence in typical three-dimensional ferromagnets; a more accurate analysis in terms of the concepts of spin waves and magnons is needed (see Section 17.4). Another evident limit of the mean field theory is the fact that it is unable to correctly determine the effect of dimensionality on the phase transitions, as predicted for instance by the basic Mermin-Wagner theorem.

Critical temperature region. Near the critical temperature, the mean field theory shows that several significant quantities follow power-like laws. However the measured exponents of some ferromagnetic materials are rather different from the mean field result, although only minor differences seem to occur among the different materials, as seen from Table 17.3. A more detailed analysis of critical exponents is necessary in second order phase transitions; some aspects concerning this topic are discussed in Sections 17.5 and 17.6.

Table 17.3 Measured critical exponents for several ferromagnetic materials [see S. N. Kaul, J. Magn. Magn. Mater. 53, 5 (1985) and references quoted therein].

Material	Critical exponent β	Critical exponent γ
Fe	0.39	1.33
Co	0.44	1.23
Ni	0.38	1.34
Gd	0.38	1.20

Itinerant band magnetism. The description of ferromagnetism, starting from a picture of magnetic moments localized at the lattice sites, may become inadequate for transition metals and other materials, in which the interplay between band formation and magnetization is relevant; some aspects are considered in Section 17.7.

17.2 Microscopic Origin of the Coupling Between Localized Magnetic Moments

17.2.1 The Spin Hamiltonian Approach to Magnetism

The spin Hamiltonian approach is a common and fruitful short-cut approach for the description of magnetism in several materials. We consider here, at a qualitative level and without efforts to be exhaustive, different types of microscopic mechanisms that can lead to an effective coupling between pairs of spin operators. We begin this discussion with some paradigmatic models, which produce an effective interaction of the form of *scalar product of spin operators*, usually written in the form $-2JS_1 \cdot S_2$, where J is the so called exchange parameter. Needless to say in realistic situations a great variety of different microscopic mechanisms can be at work in the energy range of interest, but not more than a cursory mention to some of them will be given for brevity. For an in-depth overview of fundamental aspects of magnetism, extending from traditional bulk materials to the rapidly expanding world of molecular nanomagnets, we refer for instance to the book of Gatteschi et al., cited in the bibliography.

The origin of the effective spin-spin interaction is in essence connected to the global antisymmetry of the electron wavefunctions. Alignment or not of spins in the *spin space* imposes requirements on the wavefunctions in *real space*, where the electrostatic interactions are at work. Under appropriate circumstances, an effective spin-spin Hamiltonian may result, whose energy spectrum mimics the one of the original Hamiltonian in an appropriate energy range; in typical situations, the interaction energy J can assume values of the order of $10 \approx 100$ meV (or so), which are several orders of magnitude higher than typical magnetic dipolar interactions, estimated in Eq. (17.3). The sign of the coupling can be either positive or negative, or even oscillatory with spin distance. In the case $J > 0$ the spins tend to line up in the same direction and the coupling is said to be ferromagnetic; in the case $J < 0$ the spins tend to line up in opposite directions and the coupling is said antiferromagnetic.

It is instructive to begin our qualitative analysis considering prototype two-electron systems where an effective coupling of scalar product between the electronic spins s_1 and s_2 appears to be at work.

A model of two-electron systems has been discussed in Section 16.5.3. In the introduction to the Kondo effect, we have considered in detail the energy levels of an idealized molecule with two electrons and two orbitals, one of them of extended nature (with the possibility of double occupancy by electrons of opposite spin) and the other of localized nature (with so large Coulomb repulsive energy between electrons of opposite spin to prevent double occupancy). The hybridization between the two orbitals makes the singlet state (with total spin $S = 0$) lower in energy than the triplet state (with total spin $S = 1$); in Section 16.5.3, it has also been shown that the energy difference and