Advanced Physics 1/2

Theory of Magnetism

2019, terms 3/4

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Sources

This lecture is based on the books “Lecture Notes on Electron Correlation and Magnetism” by Patrik Fazekas and “Quantum Theory of Magnetism” by Wolfgang Nolting and Anupuru Ramakanth. In parts, it follows the lecture notes “Theory of Magnetism” by Carsten Timm. Original papers are used as cited in the footnotes.

1. Introduction

1.1 Magnetism as an effect of the electron-electron interaction

Since antiquity it was known that there is an attraction between lodestone (magnetite, Fe_3O_4) and iron. Plato and Aristotle mention permanent magnets. They are also mentioned in Chinese texts of the 4th century BC. Use of a magnetic compass for navigation was first mentioned in a Chinese text dated 1040-1044 AD but a much earlier use is possible. Apparently the magnetic compass was first used for orientation on land, not on the sea.

Thus, magnetism at first referred to the long-range interaction between ferromagnetic macroscopic entities. However, in this course we will focus on the microscopic origin of the magnetic order in solids; one of these orders is ferromagnetism.

Initially, we want to describe the effect of an external magnetic field H on the behavior of a solid. For a weak field, the relevant response function is the susceptibility

$$\chi = \frac{M}{H}$$

with the magnetization density H. The probing field can be space and time dependent. Consequently, if we introduce Fourier components of H and M, we find in general a wave vector and frequency dependent generalized susceptibility $\chi(\vec{q}, \omega)$ which fully characterizes the behavior of the systems in weak fields. Calculating the magnetization requires solving a quantum mechanical eigenvalue problem where the interaction of the external field with the system is added to the microscopic Hamiltonian. The energy scale of this interaction is $\mu_B H$ with the Bohr magneton

$$\mu_B = \begin{cases} \frac{e\hbar}{2mc} \approx 9.27 \cdot 10^{-21} \frac{\text{erg}}{\text{G}} \text{ in cgs units} \\ \frac{e\hbar}{2m} \approx 9.27 \cdot 10^{-24} \frac{\text{J}}{\text{T}} \text{ in SI units}\,, \end{cases} \tag{1.1}$$

and with Gauss (G) and Tesla (T). μ_B is nearly equal to the spin moment of an electron in vacuum.

Now how large is this energy scale $\mu_B H$? In condensed matter physics, a common energy unit is electron Volt $1\,\mathrm{eV} = 1.6 \cdot 10^{-19}\,\mathrm{J}$, and equivalent temperatures are obtained using the Boltzmann constant $k_B = 1.38 \cdot 10^{-23}\,\frac{\mathrm{J}}{\mathrm{K}} = 8.6 \cdot 10^{-5}\,\frac{\mathrm{eV}}{\mathrm{K}}$. This means that $1\,\mathrm{eV}$ corresponds to the temperature $11605\,\mathrm{K}$. A standard laboratory field of $5\,\mathrm{T} = 5 \cdot 10^4\,\mathrm{G}$ then corresponds to an interaction energy of $\mu_B H = 3\,\mathrm{K}$. Comparing to other solid state energy scales, this is rather small: band widths can be of the order $1 - 10\,\mathrm{eV} \sim 10^4 - 10^5\,\mathrm{K}$; Coulomb matrix elements are of similar size, and phonons are characterized by Debye temperatures of $\Theta_D = 100 - 1000\,\mathrm{K}$. Even spin orbit coupling is usually stronger than $\mu_B H$. $\mu_B H$ is of the order of the superconducting T_c of conventional superconductors; it is well known that sufficiently strong magnetic fields can suppress superconductivity.

It would however be wrong to assume that because of the small energy scales, no drastic change in the behavior of solids is to be expected. One possibility is a situation of degeneracies in a system with competing energy scales where a magnetic field can trigger strong effects. Also, if strong correlations lead to very narrow effective bands and therefore very small Fermi energies, as in heavy Fermion materials, laboratory fields can have dramatic effects.

Conventionally, weak magnetism denotes the situation when the magnetization of a material is induced by an external field and vanishes when the field is turned off. Strong magnetism means that a material shows a spontaneous magnetization also in the absence of an external field. Formally, a divergent static susceptibility $\chi(\vec{q}, \omega = 0)$ indicates the onset of magnetic ordering.

While field induced magnetization can be attributed to a weak perturbation, this is not anymore true for the origin of spontaneous magnetic order. Realizable magnetic fields are rather weak, and dipole fields of atomic moments at interatomic distances are even weaker. Let's consider if the magnetism of iron could be due to classical moments that align by sitting in each others fields. In ferromagnetic iron, the moments are $\mu_{at} = 2.1\mu_B$, and nearest neighbor distances are $a = 2.55\,\text{Å} \approx 5a_B$ (with Bohr radius $a_B = \frac{\hbar^2}{me^2}$). The fine structure constant is $\alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137}$, and a Rydberg is $1\,\mathrm{Ry} = \frac{e^4 m}{2\hbar^2} \approx 13.6\,\mathrm{eV}$. Then the dipole-dipole interaction can be estimated as $\frac{\mu_{at}^2}{a^3} = \left(\frac{\mu_{at}}{\mu_B}\right)^2 \left(\frac{a}{a_B}\right)^{-3} \frac{\alpha^2}{2}\,\mathrm{Ry} \approx 10^{-5}\,\mathrm{eV} \approx 0.1\,\mathrm{K}$. This clearly cannot account for a Curie temperature of $1043\,\mathrm{K}$.

Spontaneous magnetic order is, in most cases, a consequence of strong electron-electron interactions, rather than a secondary effect due to a weak perturbation. The magnetism of strongly magnetic materials arises from large terms in the Hamiltonian. Whenever band theory indicates a metal with narrow conduction bands, magnetism arises in a natural manner (*i.e.* it is one of the leading instabilities). Then the material often turns out to be a magnetic insulator rather than a metal. Magnetic instabilities are closely related to the problem of metal insulator transitions. Not all materials loose their metallicity upon becoming magnetic, though: Other circumstances like band filling play a role. There are the famous ferromagnetic metals Fe, Co, Ni, magnetic rare earth metals Gd and Dy or the ferromagnetic metallic oxide CrO_2.

Magnetism will be discussed here in the context of electron-electron interactions. Once these are strong, systems can become magnetic, they can distort structurally, they can show metal insulator transitions, and they might even become unconventional superconductors. The focus will here be on the microscopic mechanisms of magnetism.

1.2 Magnetic field sources

The phenomena that can be observed experimentally are determined by the available magnetic fields, and new field induced effects are discovered with each progress in available magnetic field strengths. The cgs unit of magnetic field H is Oersted, and conversion to SI is by $10\,\mathsf{Oe} = \frac{10^3}{4\pi}\,\frac{\mathsf{A}}{\mathsf{m}}$. The unit of the field $B = H + 4\pi M$ is the same by value and dimension but it is called Gauss. The SI unit is $1\,\mathrm{Tesla} = 10^4\,\mathrm{G}$. The field of the earth is about 0.5 G. Simple iron based permanent magnets provide a few hundred Gauss, and powerful permanent magnets like samarium-cobalt ($SmCo_5$) or neodymium-iron-boron ($Nd_2Fe_{14}B$) have fields of 3000-4000 G. Large fields for research are produced by electromagnets; fields of 5-30 T are routine. There are limits to the fields that can be produced by currents through coils because the force exerted by the field on the coil eventually exceeds the tensile strength of the material. Resistive heating through the current is another limiting factor. This can be avoided by the use of superconducting coils; however, superconductivity breaks down when the magnetic field exceeds the critical field of the superconductor. Hybrid magnets with resistive electromagnets inside a superconducting magnet can reach higher fields, $\sim 45\,\mathrm{T}$. For many experiments, it is sufficient to have an intense field for milliseconds or microseconds; fields up to 100 T can be produced with non-destructive pulsed magnets. Self-destructing pulsed magnets can produce an order of magnitude larger fields, for example very recently 1200 T at ISSP, University of Tokyo, and constitute a very active field of research.

1.3 Some concepts at the example of magnetite

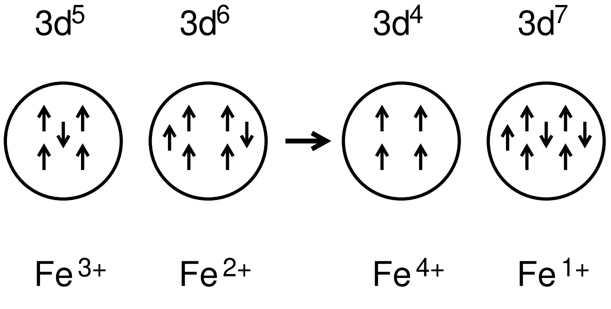
Even though magnetite was known to most ancient civilizations, it is a complicated substance and a topic of research even today. By way of an introduction we will learn about some of the questions that can be asked, but not about all the answers

1.3.1 Charge states

Magnetite is an iron oxide with the formula Fe_3O_4; besides it, there are also the iron oxides FeO and Fe_2O_3 (hematite). We can use them to analyze the ionic bonding: We have divalent iron in $Fe^{2+}O^{2-}$ and trivalent iron in $Fe_2^{3+}O_3^{2-}$. Now in magnetite, both divalent and trivalent iron are present: $Fe^{2+}Fe_2^{3+}O_4^{2-}$. It is called a mixed valent oxide. We can try to imagine what these charge states of iron would mean in terms of a band picture. Fe^{2+} and Fe^{3+} both have partially filled d shells, $3d^5$ for Fe^{3+} and $3d^6$ for Fe^{2+}. Now we can try to think of the resulting band as a tight binding band with nearest neighbor hopping. For a pair of $3d^5$ and $3d^6$ sites, we can think of this hopping event between sites i and j:

$$\left|3d^5\right\rangle_i\left|3d^6\right\rangle_j \rightarrow \left|3d^4\right\rangle_i\left|3d^7\right\rangle_j \tag{1.2}$$

This can be realized by a minority spin electron jumping away from a $3d^5$ site:



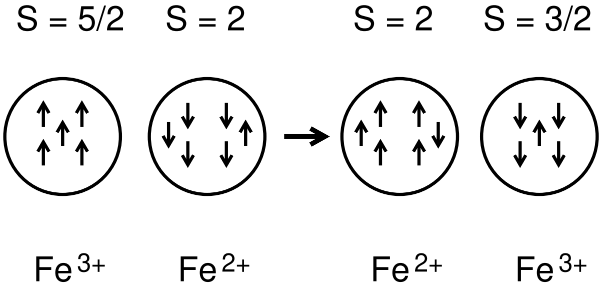
If such a hopping process would be realized, we would also expect monovalent Fe^+ and tetravalent Fe^{4+} ions to appear. However, this is contrary to our chemical picture that magnetite contains only divalent and trivalent iron; at least, independent electron theory seems to give us a too high fraction of other valences. Mixed valence is rather common in transition metals and rare earths and means that a substance is dominated by two valence states at the exclusion of others. Thus, in magnetite we should somehow restrict hopping to processes that interchange Fe^{2+} and Fe^{3+}:

$$\left|3d^5\right\rangle_i\left|3d^6\right\rangle_j \to \left|3d^6\right\rangle_i\left|3d^5\right\rangle_j \tag{1.3}$$

Restricting hopping in this way is an example of correlated motion rather than the usual band motion of electrons.

1.3.2 Spin states

Even equation 1.3 is still too permissive because we have not yet taken into account the spin state. Fe^{2+} and Fe^{3+} are magnetic ions and will retain the total spin (the magnetic moment) that they would have in free space. First of all, we need to understand why free Fe^{2+} ions have total spin $S = 2$, and Fe^{3+} ions have total spin $S = \frac{5}{2}$. Then we need to study if and how this survives in the solid state.
So let us consider the hopping process



This is consistent with equation 1.3 but we would consider it forbidden because it would lead to a low spin state of Fe^{3+}, $S = \frac{3}{2}$. Physically, the reason to exclude such processes is the same as in the case of the valence restriction above: It would lead from a low energy subspace to a high energy subspace. Later, both the reason for the energetic separation of subspaces and the way to introduce such constraints formally will be discussed.
For the special case of magnetite, it is possible to give a simple form both to the valence constraint and to the restriction to high spin states. Magnetite is ferrimagnetic, with an ordering temperature $T_N = 858$ K. If we consider temperatures of $T < 200$ K, we can approximate the electron motion as hopping on the background of a frozen pattern of spin order. Magnetite has an inverse spinel structure (Figure 1.1), AB_2O_4 with two crystallographically inequivalent iron sites. Below T_N, spins on the two inequivalent lattice sites are polarized in the opposite way. The tetrahedrally coordinated A site has one Fe^{3+} ion, the octahedrally coordinated B site has one Fe^{3+} ion, one Fe^{2+} ion. While the opposite moment Fe^{3+} ions compensate each

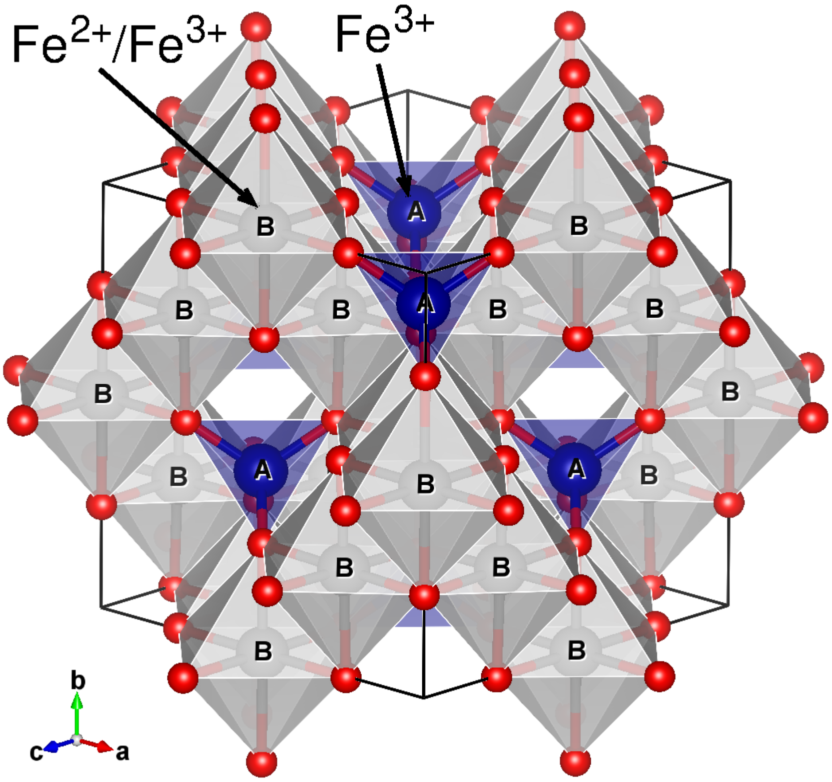
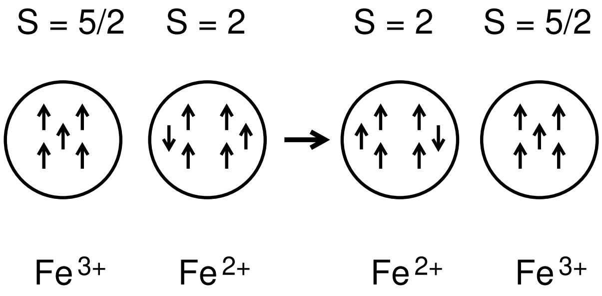


Figure 1.1: Inverse spinel structure AB_2O_4 of Fe_3O_4: Fe^{3+} ions occupy the tetrahedral A sites as well as half of the octahedral B sites; the other B sites are occupied by Fe^{2+} ions.

other, a residual ferrimagnetic moment of Fe^{2+} on the B site remains. At sufficiently low temperature when magnetic ordering is nearly perfect, the only allowed hopping is that of minority spin electrons that switch Fe^{2+} and Fe^{3+} sites:



This means that after fixing the spin order, we can forget about the spin degree of freedom and focus only on the mobile electrons which are now “spin free”. The problem is reduced to nearest neighbor hopping of spin-less Fermions in a half-filled band:

$$H_{\text{hop}} = -t \sum_{\langle ij \rangle} \left(c_i^\dagger c_j + c_j^\dagger c_i \right) \tag{1.4}$$

Here, $c_i^\dagger$ creates an electron at lattice site i, c_i annihilates an electron. t is an energy and represents the hopping amplitude.

1.3.3 Charge order

So far, the problem of 16 d electrons in the chemical unit cell of Fe_3O_4 has been reduced to a half-filled band of spin-less Fermions moving on the the B sublattice of the inverse spinel. For a half-filled band, we would now expect a metallic ground state. However, the resistivity of Fe_3O_4 shown in Figure 1.2 clearly doesn't show a metallic temperature dependence and is rather high at all temperatures.

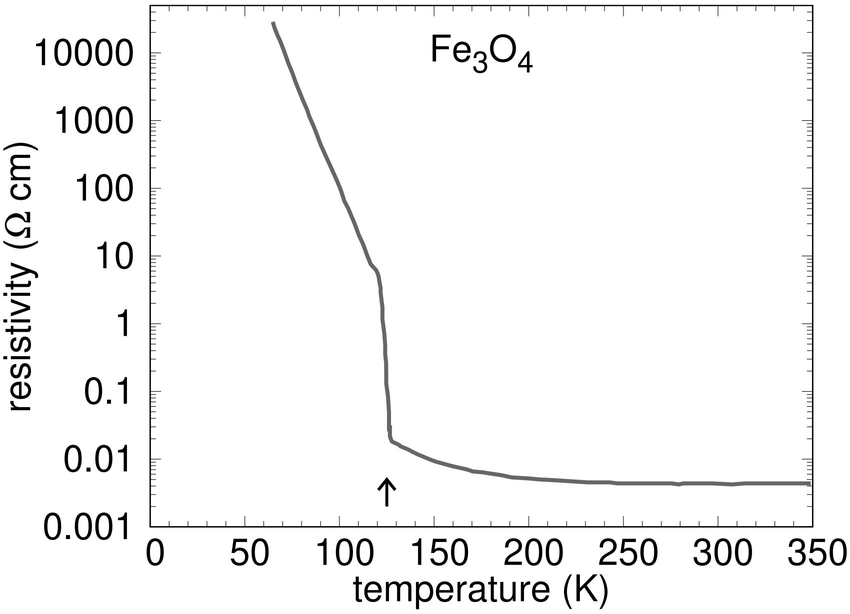


Figure 1.2: Resistivity of Fe_3O_4 as function of temperature[a]. The temperature of the Verwey transition is indicated by an arrow.

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[a] V. V. Shchennikov, S. V. Ovsyannikov, J. Phys.: Condens. Matter **21**, 271001 (2009).

In particular, resistivity jumps up by two orders of magnitude when Fe_3O_4 is cooled below the so-called Verwey temperature $T_V \approx 125$ K. Even though it is a transition from a semiconducting to an insulating state, it can be considered an example of a correlation-driven metal-insulator transition. We have accounted for substantial parts of the electron-electron repulsion by restricting the valence states to Fe^{2+} and Fe^{3+} and by assigning definite, maximum spins to these valence states. However, an important part is missing. In the spin-less Fermion model, the electrons are prohibited by the Pauli principle to share the same site but there is so far nothing preventing them from sitting at nearest neighbor sites. However, the associated Coulomb energy is large at $V = \frac{e^2}{a}$ with lattice spacing a. We should add this term to the Hamiltonian:

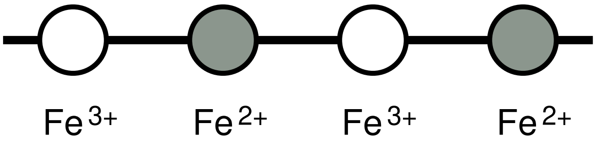
$$H = H_{\text{hop}} + H_{\text{e-e}} = -t \sum_{\langle ij \rangle} \left(c_i^\dagger c_j + c_j^\dagger c_i \right) + V \sum_{\langle ij \rangle} \hat{n}_i \hat{n}_j \tag{1.5}$$

with site occupation operator $\hat{n}_i = c_i^\dagger c_i$. This is of course a very simplified band model but it contains some essential aspects of the Verwey transition.

It is an example of how model Hamiltonians are devised. The two terms of the Hamiltonian stand for competing tendencies. For small V, the first, kinetic energy term dominates and essentially a half-filled band with little suppression of simultaneous occupation of neighboring sites is obtained. On the other hand, setting $t = 0$ results in

$$H_{\text{e-e}} = V \sum_{\langle ij \rangle} \hat{n}_i \hat{n}_j \,. \tag{1.6}$$

This energy would be minimized by a state in which only every other site is occupied:



This could be called a large amplitude charge density wave. It has also been interpreted as an example of Wigner crystallization, the formation of an electron crystal. This is a prime example of the meaning of a strongly correlated state: The electrons do their utmost to avoid each other in direct space, and it is clear that this is an insulating state. It is also interesting that this state does not have the full translational invariance of the underlying crystal. An important effect of strong electronic correlations is the appearance of symmetry breaking ground states, ground states whose symmetry is lower than that of the Hamiltonian.