F. Atomic Origins of Magnetism

In the following we will try to get some understanding of the atomic origins of magnetism for the solid state of matter. Most of the descriptions can also be used to explain magnetic phenomena of liquids and gases. The related mathematical equations, which result from quantum mechanics in most cases, will often be written down without exact proof.

1. Magnetic Moment of the Electron

The electron shows an angular momentum **L**, which is related to its spatial movement around the atomic nucleus, see **Fig. F.1**. Classically a frequency of revolution $\omega = v/r$ belongs to this movement, where v=velocity, r=spatial radius and m_e=electron mass. This leads to the following formula or **L**:

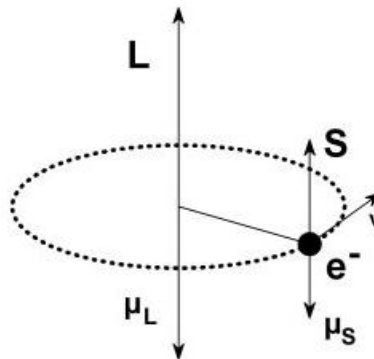$$\vec{L} = m_e \cdot r^2 \vec{\omega} \tag{F.1}$$

The magnetic moment $\mathbf{\mu_L}$ of the electron can be defined as the product of a circular electrical current I around a closed area A:

$$\vec{\mu}_L = I \cdot d\vec{A} \tag{F.2}$$

By calculating a current I from the revolving charge e, we get for the magnetic moment by the above:

$$\vec{\mu}_L = -\frac{e}{2m_e}\vec{L} \tag{F.3}$$

The same expression follows from a quantum theoretical derivation.

Fig.F1: Angular momentum **L**, spin **S** and corresponding magnetic moments for an electron which revolves around the atomic nucleus.

As first shown in past century by the experiments of Stern and Gerlach, beside the angular momentum of the movement around the nucleus there exists another momentum belonging to the electron. It is named electron spin **S** and describes an effect, which can be interpreted as a revolution of the electron around its own axis. By means of relativistic quantum theory (Dirac) it can be shown, that this spin also leads to a specific magnetic moment μ_s:

$$\vec{\mu}_s = -\frac{e}{m_e}\vec{S} \tag{F.4}$$

(F.3) and (F.4) are often expressed by use of the so called Bohr magneton, which has the unit of a magnetic moment:

$$\mu_B = \frac{e \cdot \hbar}{2m_e} \tag{F.5}$$

Here $\hbar = h/2\pi = 1.055e\text{-}34$ Js, where h is the so called Plank's constant.

By the rules of quantum mechanics for the angular momentum only the absolute value as well as one respective component in one specified direction are measurable. The same is valid for magnetic moments. The possible values for these parameter can be gained as described in the following:

For a single electron in the potential V of the nucleus the time independent Schrödinger equation has to be applied:

$$(-\frac{\hbar}{2me}\Delta + V)\psi = E\psi \tag{F.6}$$

The wave function Ψ provides discrete electron states, which can be described by quantum numbers n, l, m_l . These states can be expanded by use of the quantum number m_s that describes the components of the electron spin. For the wave function so we have:

$$\psi = \psi(n, l, m_l, m_s) \tag{F.7}$$

Measurable parameters of quantum theory are called observables and can be computed as expectation values of operators being applied to the wave functions. These expectation values in case of the magnitude of the angular momentum are given by following equation, when *L* denotes the respective operator:

$$L = \int \psi^* L\psi dV \tag{F.8}$$

Applying (F.8) to solutions of /F.6) according to (F.7) provides the expectation value of the magnitude value of **L** to:

$$L = \sqrt{l(l+1)} \cdot \hbar \tag{F.9}$$

Similarly we get for the z-component:

$$L_z = m_l \cdot \hbar \tag{F.10}$$

Here we have

$$l = 0,1.2,.....(n-1)$$

and   (F.11)

$$m_l = -l,-(l-1),....,(l-1),l$$

In (F.7) n is so the so called principle quantum number, which depicts spatial shells of separated electron clouds. Electrons with l=0,1,2,3... are denoted as s,p,d,f... electrons in minor shells. Pictorially these minor shells are different in respect to the spatial shape of probability to meet an electron there.

Analogously to (F.9) and (F.10) there a discrete expectation values for the spin:

$$S = \sqrt{s(s+1)} \cdot \hbar$$ (F.12)

and

$$S_z = m_s \cdot \hbar$$ (F.13)

For both quantum numbers s and m_s the following discrete values are true:

$$s = 1/2 \text{ und } m_s = +/-1/2$$ (F.14)

If there is an external field **H** applied to an atom, by its direction we will define the z-direction of the following depiction. **Fig. F2** shows the possible components of the angular momenta **L** and **S** in field direction. **L** is depicted here by using the value 2. In case of trying to interpret this, one often speaks about a precession of the momentum around the field axis.
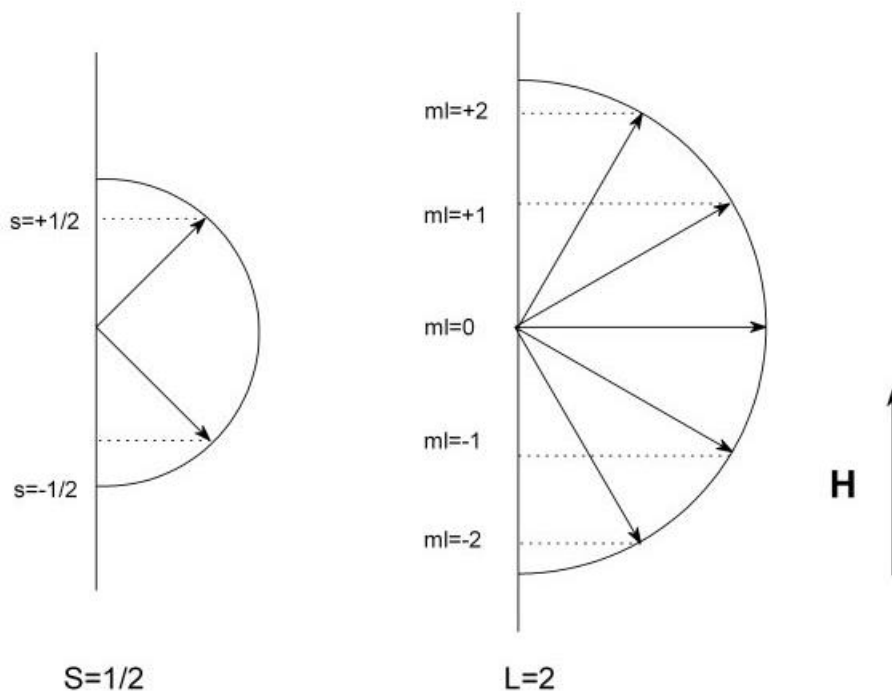
Fig. F2.: Discrete states for the spin **S** and angular momentum **L** of the electron in an external field.

Based on (F.3) and (F.4) the quantization of the angular momentum results analogously for the magnetic moments.

$$\mu_L = -\mu_B \cdot \sqrt{l(l+1)}$$

and

$$\mu_{LH} = -\mu_B \cdot m_l$$

(F.15)

For the spin moment we have:

$$\mu_S = -2 \cdot \mu_B \cdot \sqrt{s(s+1)}$$

and

$$\mu_{SH} = -2 \cdot \mu_B \cdot m_S$$

(F.16)

2. **Magnetic Moment of Atoms**

In atoms the single momenta of the electrons add up to form a total angular momentum. Analogously we have a summation of magnetic moments which build up the total magnetic moment of the atom. But caused by quantum mechanics the sum is neither a result of a simple addition of vectors, nor are the specific states realizable by the same probabilities.

For the total angular momentum of the atom **J** in most cases the rules for the coupling follow the so called Russel-Saunders rules. Here first the orbital momenta couple and the same do the spins. Then we have a coupling of both resultants to the total momentum:

$$\vec{J} = \vec{L}_t + \vec{S}_t$$

(F.17)

An alternative way of coupling happens for very heavy atoms and is called spin-orbit coupling. Here first each single electron couples its orbital and its spin moment and finally all single electron momenta sum up to the total angular momentum of the atom. A qualitative description is given by the rules of Hund. For the absolute value and the z-component of the angular momentum in case of the Russel-Saunders coupling we have:

$$\left| \vec{J} \right| = \sqrt{J(J+J)} \cdot \hbar$$

(F.18)

and

$$J_z = m_j \cdot \hbar$$

(F.19)

where $m_j = -J, -(J-1), -(J-2), \ldots J-2, J-1, J$ analogously to the behavior of the orbital momentum.

For the respective magnetic moment we get:

$$\mu = -g \cdot \mu_B \cdot \sqrt{J(J+1)}$$

and

$$\mu_z = -g \cdot \mu_B \cdot m_j$$

(F.20)

where the so called Lande-Faktor g takes the following values:

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \tag{F.21}$$

3. Dia-, Para- and Ferromagnetism

Under external fields the magnetic moments of the atoms are oriented in respect to the field direction. Quantum mechanically this can be identified with a higher probability of specific discrete states in comparison to others. The resulting differences between dia- para- and ferromagnetism can be explained by use of the field dependence of the resulting magnetic moments:

In case of diamagnetism we have systems, where the atoms a dominated by orbital momenta **L**. Here those states are preferred energetically, which lead to a counteracting orientation of **μ** and **H** and by this also to an antiparallel orientation of magnetization **M** and **H**. By this effect Lenz's rule is fulfilled, which says that charged particles counteract any change of magnetic flux.
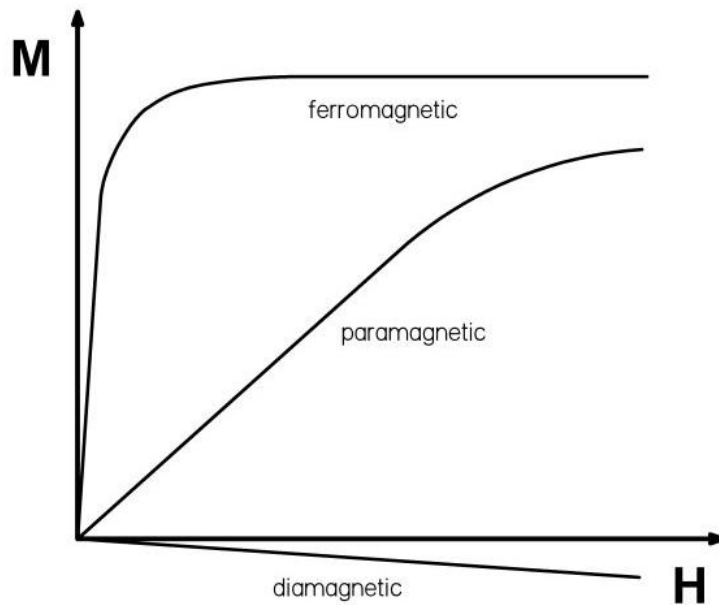
Fig.F.3: Magnetic moment as a function of external field for different bodies with dia- para- and ferromagnetic behavior, schematic.

In case of paramagnetism states of angular momentums are preferred, which determine a parallel orientation of the magnetic moments **μ** or the magnetization **M** and the external field **H**. The angular momenta here are often dominated by **S** or **J.** In case of very high fields the total magnetic moment converges to a saturation value, which results when all magnetic moments are oriented in parallel direction. The H-dependence can be derived by analyzing the fractional population of the different m_j-states in the field using Boltzmann statistics. For M we get by this:

$$M = M_{sat} \cdot B_J \left(\frac{\mu_0 g J \mu_B H}{k_B T} \right) \tag{F.22}$$

k_B here is the so called Boltzmann constant, M_{sat} is the maximum possible magnetization, i.e. the saturation magnetization and B_j is the Brillouin function for the state j:

$$B_j(x) = \frac{2j+1}{2j}\coth(\frac{2j+1}{2j}x) - \frac{1}{2j}\coth(\frac{x}{2j})$$

The ferromagnetic case shall be inspected in more detail. Here in most cases a very fast orientation parallel to the field can be observed. While in dia- or paramagnetic substance only isolated electrons or atoms interchange with the field, in case of ferromagnetism there is an additional force between the atoms or electrons: The so called exchange interaction. The respective energy operator of quantum mechanics is often expressed in the following way:

$$H_{ij} = -2I\vec{S}_i \cdot \vec{S}_j \qquad\qquad (F.23)$$

I denotes the exchange integral, which stands for the strength of exchange interaction.

In case of positive exchange integrals a parallel orientation of the spin is preferred energetically. When an eternal field is applied, the exchange interaction causes a much faster orientation of the moments as in case of paramagnetism. This leads to the steep increase of M as indicated schematically in **Fig. F3**.

When I is negative, an anti parallel orientation of magnetic moments to each other is prefered, which leads to so called antiferromagnetism. Antiferromagnetic materials shall not be treated here, but it should mentioned that nowadays such material can be of high technical importance, e.g. in GMR sensors.

By watching a single atom using (F.23) and summing over all neighbored magnetic moments, the effect of the surroundings of the atom can be expressed by introducing a field H_m, which is proportional to the magnetization around the atom:

$$H_m = \alpha M \qquad\qquad (F.24)$$

This approximation is called molecular field approximation. Setting (F.24) into (F.22) as an additional field, one gets for ferromagnets the temperature dependence of magnetization as:

$$M_s = M_{sat} \cdot B_j(\frac{\mu_0 g J \mu_B (H + \alpha M_s)}{k_B T}) \qquad\qquad (F.25)$$

By the index s the so called spontaneous magnetization is denoted, which means that magnetization, which builds up only by the exchange interaction within one magnetic domain. Numerical solution of this equation for Ms under the assumption $H \ll \alpha M$ provides a dependence like in **Fig.F4**. Here Tc is the Curie temperature, which describes the temperature of phase transition between the states ferromagnetic and paramagnetic.

4. Summary

The atomic origins of the magnetic phenomena in solids, liquids and gases can be found in the angular moments of the electrons. These show an orbital angular momentum as well as a spin momentum. By the help of quantum theory it can be shown that these angular momenta lead to respective magnetic moments. The angular momenta of the single electrons of one atom couple to discrete states of total momenta due to quantum mechanic rules. By this also the magnetic moments couple to a total moment.
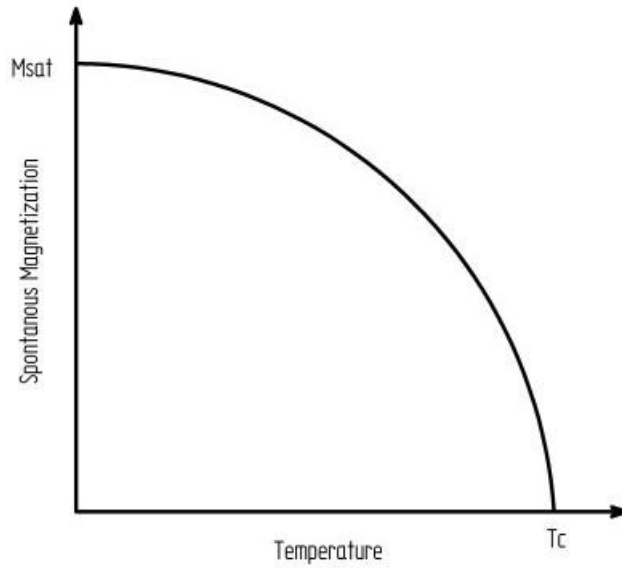
Fig.4: Spontaneous magnetization in ferromagnetic domains as a function of temperature.

The phenomenon of paramagnetism can be explained by the orientation of isolated magnetic moments in an external field. In ferromagnetic materials in addition to the external field the so called exchange interaction plays an important role. The exchange interaction forces the single magnetic moments to orient themselves parallel to each other. This leads to a fast and steep increase of magnetization in an external field. In addition it determines the built up of a spontaneous magnetization, which decreases with temperature and vanishes at the Curie point.

Diamagnetism can be explained by orbital angular momenta, where states are preferred which lead to an antiparallel orientation of the respective magnetic moments and the applied field.

The above explanations depict the existence of the phenomenon which is called ferro-magnetism. They do not explain the division into hard and soft magnetic materials. Simplified, the origin for hard magnetic materials can be found in the coupling of magnetic moments with the crystal lattice and microscopic structure of the respective solid. By this a change of magnetization is suppressed once the material is polarized into one specific direction. This leads to the phenomenon of hysteresis, which will be treated in more detail in another chapter.

The above has been mainly concerned with magnetic moments that are bound to single atoms. Models which are based on free or quasi free electrons have been neglected here, but can be found in literature.