Section 15: Magnetic properties of materials

Definition of fundamental quantities

When a material medium is placed in a magnetic field, the medium is magnetized. This magnetization is described by the *magnetization vector* **M**, the dipole moment per unit volume. Since the magnetization is induced by the field, we may assume that **M** is proportional to **H**. That is,

$$\mathbf{M} = \chi \mathbf{B}. \tag{1}$$

The proportionality constant χ is known as the *magnetic susceptibility* of the medium. Note that the magnetic susceptibility χ bears no physical relationship to the electric susceptibility, although the same symbol is used for both. Note also that our discussion assumes that the medium is magnetically isotropic. But real crystals are anisotropic, and the susceptibility is represented by a second-rank tensor. In order to avoid mathematical complications, however, we shall ignore anisotropic effects in our treatment.

Note, that in Eq. (1) we assumed that **M** is proportional to **B**, the external field, and in doing so we ignored such things as demagnetization field, which were included in the electric case. The neglect of these factors is justifiable in the case of paramagnetic and diamagnetic materials because **M** is very small compared to **B** (typically $\chi = \mathbf{B}/\mathbf{M} \sim 10^{-5}$), unlike the electric case, in which $\chi \sim 1$. But when we deal with ferromagnetic materials, where **M** is quite large, this omission is no longer tenable, and the above effects must be included. Because of small value of the magnetic susceptibility we will not make distinction between magnetic field and magnetic induction.

Note also that χ in Eq.(1) can be dependent on the applied magnetic field. In this case, we can define the magnetic susceptibility as follows

$$\chi = \frac{\partial M}{\partial B}. \tag{2}$$

The magnetization can be defined as

$$M = -\frac{\partial E}{\partial B}, \tag{3}$$

where E is the total energy of the system. Definitions (2) and (3) are more general and can be used in calculations.

Classification of materials

All magnetic materials may be grouped into three magnetic classes, depending on the magnetic ordering and the sign, magnitude and temperature dependence of the magnetic susceptibility. We will discuss properties of five classes of materials: diamagnetic, paramagnetic, ferromagnetic, antiferromagnetic and ferrimagnetic. There is no magnetic order at any temperature in diamagnetic and paramagnetic materials, whereas there is a magnetic order at low temperatures in ferromagnetic, antiferromagnetic and ferrimagnetic materials.

In *diamagnetic* materials the magnetic susceptibility is negative. Usually its magnitude is of the order of -10^{-6} to -10^{-5}. The negative value of the susceptibility means that in an applied magnetic field diamagnetic materials acquire the magnetization, which is pointed opposite to the applied field. In diamagnetic materials the susceptibility nearly has a constant value independent of temperature.

Ionic crystals and inert gas atoms are diamagnetic. These substances have atoms or ions with complete shells, and their diamagnetic behavior is due to the fact that a magnetic field acts to distort the orbital motion. Another class of diamagnetic materials is noble metals.

All the other classes of materials have positive susceptibility. Within these classes the magnitude of the susceptibility varies over a very wide range. However, at sufficiently high temperatures the susceptibility decreases with increasing temperature for all materials in these classes. It was found experimentally that all these materials follow the relationship

$$\chi = \frac{C}{T \pm T_C} \qquad (4)$$

more or less exactly for sufficiently high T. Here C and T_C are positive constants independent of temperature and different for each material.

It was found that in some materials T_C=0 and this equation is obeyed down to the lowest temperatures at which measurements have been made. This class of materials is called *paramagnetic*. In paramagnetic materials χ is positive - that is, for which **M** is parallel to **B**. The susceptibility is however is also very small: 10^{-4} to 10^{-5}. The best-known examples of paramagnetic materials are the ions of transition and rare-earth ions. The fact that these ions have incomplete atomic shells is what is responsible for their paramagnetic behavior.

In all other materials equation (4) breaks down as temperature decreases. They all have a *critical temperature* below which the variation of susceptibility with temperature is very different from its variation above this temperature.

In *ferromagnetic materials* the critical temperature is called the *Curie temperature*. Above the Curie temperature the susceptibility follow relationship (4) with a negative sign. When temperature approaches T_C the magnetic susceptibility tends to be infinite. An infinite susceptibility means that a finite magnetization can exist even in zero applied field, which is the case in permanent magnets. The problem is that the magnetization of ferromagnetic materials in zero field can have a range of different values and consequently cannot be regarded as a property of the material. However, it is found that if a relatively small magnetic field is applied to these materials, the magnetization tends to a constant value, which is called the saturation magnetization M_S or spontaneous magnetization. Below Curie temperature $M_S(T)$ against T follows a universal curve: it tends to a constant value as T=0; as T increases, the spontaneous magnetization decreases more and more rapidly. At the Curie temperature the magnetization disappeared.

Ferrimagnetic materials have non-zero magnetization below the Curie temperature which is similar to ferromagnetic materials. However, significant departures from (4) occur over a range of temperatures. This behaviour is only followed at temperatures large compared with the Curie temperature. Another difference between ferrimagnets and ferromagnets is that in ferrimagnetic materials the saturation magnetization against temperature behave in a more complicated way. For

example, for some ferrimagnets the magnetization can increase with increasing temperature and then drops down.

Antiferromagnetic materials have small positive susceptibilities at all temperatures. At high temperatures they follow eq. (4) with T_C usually having a positive sign. A critical temperature in this case is called Neel temperature. Below the Neel temperature the susceptibility generally decreases with decreasing temperature. There is no spontaneous magnetization in antiferromagnetic materials.

Calculation of atomic susceptibilities

In the presence of a uniform magnetic field the Hamiltonian of an ion (atom) is modified in the two major ways:

(1) In the total kinetic energy term the momentum of each electron is replaced by

$$\mathbf{p} \to \mathbf{p} + \frac{e}{c}\mathbf{A}, \tag{5}$$

where **A** is the vector potential associated with the magnetic field such that

$$\mathbf{B} = \nabla \times \mathbf{A}. \tag{6}$$

We assume that the applied field is uniform so that

$$\mathbf{A} = -\frac{1}{2}\mathbf{r} \times \mathbf{B}. \tag{7}$$

(2) The interaction energy of the field with each electron spin must be added to the Hamiltonian:

$$H_{spin} = 2\mu_B \mathbf{BS}, \tag{8}$$

where μ_B is the Bohr magneton

$$\mu_B = \frac{e\hbar}{2mc} = 0.58 \cdot 10^{-8} eV/G. \tag{9}$$

As the result the total energy of electrons will have a form

$$H = \frac{1}{2m}\sum_i \left(\mathbf{p}_i - \frac{e}{2c}\mathbf{r}_i \times \mathbf{B}\right)^2 + 2\mu_B \mathbf{BS}. \tag{10}$$

We denote by T_0 the kinetic energy in the absence of the applied field, i.e.

$$T_0 = \frac{1}{2m}\sum_i \mathbf{p}_i^2. \tag{11}$$

The cross term is the brackets can be rewritten taking into account that

$$\mathbf{p}_i \cdot (\mathbf{r}_i \times \mathbf{B}) = -\mathbf{B} \cdot (\mathbf{r}_i \times \mathbf{p}_i). \tag{12}$$

We note that also **r** and **p** are quantum-mechanical operators, here we can work with these quantities as with classical variables because only non-diagonal components enter this product (i.e.

there no terms which contain, e.g., x components of both **r** and **p** which do not commute). Note: $\left[r_\mu, p_\nu\right] = i\hbar\delta_{\mu\nu}$.

Assuming that the field is along z direction, we can rewrite

$$\left(\mathbf{r}_i \times \mathbf{B}\right)^2 = B^2\left(x_i^2 + y_i^2\right). \tag{13}$$

Finally we find for the field-dependent correction to the total Hamiltonian:

$$\Delta H = H - T_0 = \mu_B(\mathbf{L} + 2\mathbf{S})\cdot\mathbf{B} + \frac{e^2}{8mc^2}B^2\sum_i\left(x_i^2 + y_i^2\right), \tag{14}$$

where **L** is the total orbital momentum:

$$\hbar\mathbf{L} = \sum_i\left(\mathbf{r}_i \times \mathbf{p}_i\right). \tag{15}$$

The energy correction due to the applied electric field is small compared to electron energies. For example, 1T= $\mu_B \cdot 1Tesla = 0.58\cdot 10^{-4} eV$. Therefore one can compute the changes in the energy levels induced by the field with ordinary perturbation theory.

Equation (14) is the basis for theories of the magnetic susceptibility of individual atoms, ions, or molecules.

Langevin diamagnetism

Let us now apply these results to a solid composed of ions or atoms with all electronic shells filled. Such atoms have zero spin and orbital angular momentum in its ground state, i.e.

$$\langle 0|\mathbf{S}|0\rangle = \langle 0|\mathbf{L}|0\rangle = 0. \tag{16}$$

Consequently only last term in eq.(14) contributes to the field-induced shift in the ground state energy:

$$E = \langle 0|H|0\rangle = \frac{e^2}{8mc^2}B^2\langle 0|\sum_i\left(x_i^2 + y_i^2\right)|0\rangle = \frac{e^2}{12mc^2}B^2\langle 0|\sum_i r_i^2|0\rangle, \tag{17}$$

where the last form follows from the spherical symmetry of the closed-shell ion,

$$\langle 0|\sum_i x_i^2|0\rangle = \langle 0|\sum_i y_i^2|0\rangle = \langle 0|\sum_i z_i^2|0\rangle = \frac{1}{3}\langle 0|\sum_i r_i^2|0\rangle. \tag{18}$$

It is conventional to define a mean square ionic radius by

$$\left\langle r^2\right\rangle = \frac{1}{Z}\langle 0|\sum_i r_i^2|0\rangle, \tag{19}$$

where Z is the total number of electrons in an ion. We obtain then for the magnetization induced by the applied magnetic field, according to (3):

$$M = -\frac{\partial E}{\partial B} = -\frac{e^2 NZ\left\langle r^2 \right\rangle}{6mc^2} B, \tag{20}$$

which implies a negative magnetic susceptibility:

$$\chi = -\frac{e^2 NZ\left\langle r^2 \right\rangle}{6mc^2}, \tag{21}$$

where N is the number of atoms per unit volume.

Diamagnetism is associated with the tendency of electrical charges partially to shield the interior of a body from an applied magnetic field. In electro-magnetism we are familiar with Lenz's law: when the magnetic energy flux through an electrical circuit is changed, an induced current is set up in such a direction as to oppose the flux change.

Formula (21) can be derived classically.

Consider an electron rotating about the nucleus in a circular orbit, and let a magnetic field be applied perpendicular to the plane of the paper, as shown in Fig. 1. Before this field is applied, we have, according to Newton's second law,

$$F_0 = m\omega_0^2 r \tag{22}$$

where F_0 is the attractive Coulomb force between the nucleus and the electron, and ω_0 is the angular velocity.

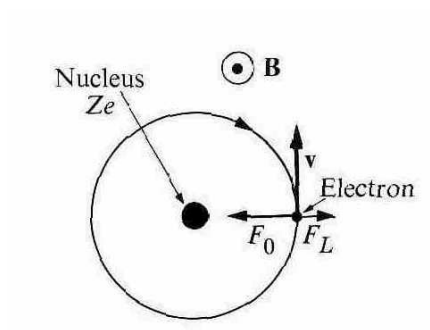

Fig. 1 Atomic origin of diamagnetism. The Lorentz force F_L opposes the Coulomb force F_0; **v** is the electron velocity.

When the field is applied, an additional force starts to act on the electron: the *Lorentz force* $-e/c\left(\mathbf{v}\times\mathbf{B}\right)$. For the geometry of Fig.1, the effect is to produce a radially outward force given by $eB\omega_0 r/c$, and Eq. (22) should therefore be amended to

$$F_0 - \frac{e}{c} B\omega_0 r = m\omega^2 r\,. \tag{23}$$

Assuming that B is small we can look for a solution is a form

$$\omega = \omega_0 + \Delta\omega. \tag{24}$$

Substituting (24) in the right-hand part of the Eq.(23) we find

$$\Delta\omega = -\frac{eB}{2mc}, \tag{25}$$

which shows that the rotation of the electron has been slowed down. This reduction in frequency produces a corresponding change in the magnetic moment. This can be calculated as follows. The change in the frequency of rotation is equivalent to the change in the current around the nucleus, which is

I = (charge) x (revolutions per unit time) = $(-Ze)\left(\frac{1}{2\pi}\frac{eB}{2mc}\right)$.

The magnetic moment μ of a current loop is given by the product (current) x (area of the loop)/c, where c appears due to CGS units. The area of the loop of radius r is πr^2. We have then

$$\mu = (-Ze)\left(\frac{1}{2\pi}\frac{eB}{2mc}\right)\frac{\pi\langle r^2\rangle}{c} = -\frac{e^2 Z\langle r^2\rangle}{4mc^2}B, \tag{26}$$

Here $\langle r^2\rangle = \langle x^2\rangle + \langle y^2\rangle$ is the mean square of the perpendicular distance of the electron from the field axis through the nucleus. The mean square distance of the electrons from the nucleus is $\langle r^2\rangle = \langle x^2\rangle + \langle y^2\rangle + \langle z^2\rangle$. For a spherically symmetrical distribution of charge we have $\langle x^2\rangle = \langle y^2\rangle = \langle z^2\rangle$, so that is $\langle r^2\rangle$ in eq.(26) should be replaced by $3/2\langle r^2\rangle$, which gives identical result to eq.(20).

Diamagnetism can be found in ionic crystals and crystals composed of inert gas atoms, because these substances have atoms or ions with complete electronic shells. Another class of diamagnetic materials is noble metals which will be discussed later.

Paramagnetism of insulators

If atoms in a solid have non-filled electronic shells than we have to take into account the first term in the Hamiltonian (14). Its contribution is then much larger than the contribution from the second term so that we can ignore it. We consider the effect of this term on an ion in a ground state which can be described by quantum numbers L, S, J and J_z, where **J** is the total angular momentum and J_z is the projection of this momentum into a quantization axis. It can be shown that

$$\langle LSJJ_z|\mathbf{L}+2\mathbf{S}|LSJJ_z'\rangle = g\langle LSJJ_z|\mathbf{J}|LSJJ_z'\rangle, \tag{27}$$

where g is the g-factor, which is given by

$$g = 1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}. \tag{28}$$

We stress that this relation is valid only within the $(2J + 1)$ dimensional set of states that make up the degenerate atomic ground state in zero field; i.e., (28) is obeyed only for matrix elements taken between states that are diagonal in J, L, and S. If the splitting between the zero-field atomic ground-state multiplet and the first excited multiplet is large compared with k_BT (as is frequently the case), then only the $(2J + 1)$ states in the ground-state multiplet will contribute appreciably to the free

energy. In that case (and only in that case) Eq. (28) permits one to interpret the first term in the Hamiltonian (14) as expressing the interaction

$$E = -\boldsymbol{\mu}\mathbf{B} \tag{29}$$

of the field with a magnetic moment that is proportional to the total angular momentum of the ion, so that

$$\boldsymbol{\mu} = -g\mu_B \mathbf{J}\,. \tag{30}$$

The applied magnetic field lifts degeneracy of the manifold of states and splits it into $2J+1$ equidistant levels, which his known as Zeeman splitting. The energies of these levels are given by

$$E_{J_z} = g\mu_B B J_z\,, \tag{31}$$

Where J_z is an integer and has values from $-J$ to J. If thermal energy is less or comparable with the Zeeman splitting, these levels will be populated differently and give a different contribution to the magnetic moment of the ion. The magnetization of the solid is determined by the average value of the magnetic moment, so that $\mathbf{M} = N\langle\boldsymbol{\mu}\rangle$, where N is the concentration of ions if the solid and $\langle\boldsymbol{\mu}\rangle$ is the value of magnetic moment averaged over the Boltzmann distribution:

$$\mathbf{M} = N\langle\boldsymbol{\mu}\rangle = -Ng\mu_B \frac{\sum_{J_z=-J}^{J} J_z e^{\frac{g\mu_B B J_z}{k_B T}}}{\sum_{J_z=-J}^{J} e^{\frac{g\mu_B B J_z}{k_B T}}}\,. \tag{32}$$

The summation can be easily performed due to geometric progression and the result for the magnetization is

$$M = NgJ\mu_B B_J(x), \tag{33}$$

where $x = \dfrac{g\mu_B JB}{kT}$ and $B_J(x)$ is the Brillouin function defined by

$$B_J(x) = \frac{2J+1}{2J}\coth\left(\frac{2J+1}{2J}x\right) - \frac{1}{2J}\coth\left(\frac{x}{2J}\right). \tag{34}$$

Figure 2 shows the dependence of the magnetization for three different ions as a function of applied magnetic field. Note that in order to reach the saturation, very low temperatures and very high magnetic fields are required.

At relatively low fields and not too low temperatures we can expand the coth in (34) assuming that x << 1, so that

$$\coth(x) \approx \frac{1}{x} + \frac{x}{3}. \tag{35}$$

We can then find for the susceptibility:

$$\chi = \frac{M}{B} = \frac{NJ(J+1)g^2\mu_B^2}{3k_BT} = \frac{Np^2\mu_B^2}{3k_BT} = \frac{C}{T}, \tag{36}$$

where p is *the effective number of Bohr magnetons* , defined as

$$p = g\left[J(J+1)\right]^{1/2}. \tag{37}$$

C is *the Curie constant* and the form (37) is known as *the Curie low*.

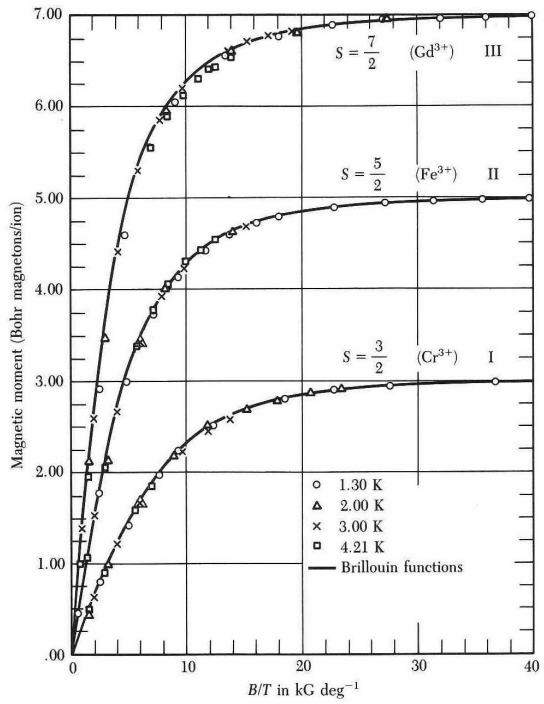

Fig.2 Magnetic moment *versus B/T* for samples of (I) potassium chromium alum, (II) ferric ammonium alum, and (III) gadolinium sulfate octahydrate. Over 99.5% magnetic saturation is achieved at 1.3 K and about 5T.

Hund Rules

The Hund rules as applied to atoms and ions affirm that electrons will occupy orbitals in such a way that the ground state is characterized by the following:

1. The maximum value of the total spin S allowed by the exclusion principle;

2. The maximum value of the orbital angular momentum L consistent with this value of S;

3. The value of the total angular momentum J is equal to $|L\text{-}S|$ when the shell is less than half full and to $L+S$ when the shell is more than half full. This due to the spin-orbit interaction the constant of which has opposite sign depending on whether is less than half full or more than half full. When the shell is just half full, the application of the first rule gives $L = 0$, so that $J = S$.

Table 1. Ground states of ions with partially filled *d*- or f-shells, as constructed from Hund's rules

d-shell ($l = 2$)										
n	$l_z = 2,$	$1,$	$0,$	$-1,$	-2	S	$L = \lvert\Sigma l_z\rvert$	J		SYMBOL
1	↓					1/2	2	3/2	$J = \lvert L - S\rvert$	$^2D_{3/2}$
2	↓	↓				1	3	2		$^3F_2$
3	↓	↓	↓			3/2	3	3/2		$^4F_{3/2}$
4	↓	↓	↓	↓		2	2	0		$^5D_0$
5	↓	↓	↓	↓	↓	5/2	0	5/2		$^6S_{5/2}$
6	⇵	↑	↑	↑	↑	2	2	4	$J = L + S$	$^5D_4$
7	⇵	⇵	↑	↑	↑	3/2	3	9/2		$^4F_{9/2}$
8	⇵	⇵	⇵	↑	↑	1	3	4		$^3F_4$
9	⇵	⇵	⇵	⇵	↑	1/2	2	5/2		$^2D_{5/2}$
10	⇵	⇵	⇵	⇵	⇵	0	0	0		$^1S_0$
f-shell ($l = 3$)										
n	$l_z = 3,$	$2,$	$1,$	$0, -1, -2, -3$		S	$L = \lvert\Sigma l_z\rvert$	J		
1	↓					1/2	3	5/2	$J = \lvert L - S\rvert$	$^2F_{5/2}$
2	↓	↓				1	5	4		$^3H_4$
3	↓	↓	↓			3/2	6	9/2		$^4I_{9/2}$
4	↓	↓	↓	↓		2	6	4		$^5I_4$
5	↓	↓	↓	↓	↓	5/2	5	5/2		$^6H_{5/2}$
6	↓	↓	↓	↓	↓ ↓	3	3	0		$^7F_0$
7	↓	↓	↓	↓	↓ ↓ ↓	7/2	0	7/2		$^8S_{7/2}$
8	⇵	↑	↑	↑	↑ ↑ ↑	3	3	6	$J = L + S$	$^7F_6$
9	⇵	⇵	↑	↑	↑ ↑ ↑	5/2	5	15/2		$^6H_{15/2}$
10	⇵	⇵	⇵	↑	↑ ↑ ↑	2	6	8		$^5I_8$
11	⇵	⇵	⇵	⇵	↑ ↑ ↑	3/2	6	15/2		$^4I_{15/2}$
12	⇵	⇵	⇵	⇵	⇵ ↑ ↑	1	5	6		$^3H_6$
13	⇵	⇵	⇵	⇵	⇵ ⇵ ↑	1/2	3	7/2		$^2F_{7/2}$
14	⇵	⇵	⇵	⇵	⇵ ⇵ ⇵	0	0	0		$^1S_0$

Rare-earth ions

Experiments on rare-earth ions in crystals show that they obey the Curie law, with an effective number of magnetons in agreement with the theory of spin-orbit interaction. Table 2 confirms this. In these ions, therefore, the angular momenta L and S are strongly coupled, and the moment of the ion can respond freely to the external field.

Table 2. Effective Number of Magnetons for Rare-Earth Ions

Ion	Ground state	Theory $p = g\sqrt{j(j+1)}$	Experiment (Eq. 9.43) p
La^{3+}	$^1S_0$	0	Diamagnetic
Pr^{3+}	$^3H_4$	3.58	3.6
Nd^{3+}	$^5I_{9/2}$	3.62	3.6
Dy^{3+}	$^6H_{15/2}$	10.6	10.6

This result is not surprising. In these ions - from La to Lu in the periodic table - the 4f shell is incompletely filled. The outer 5p shell is completely filled, while the 5d and 6s shells which are still further out are stripped of their electrons to form the ionic crystal. Thus the only incomplete shell is the 4f shell, and this is the one in which the magnetic behavior occurs. Since electrons in this shell lie deep within the ion, screened by the outer 5p and 5d shells, they are not appreciably affected by other ions in the crystal. Magnetically their behavior is much like that of a free ion. Another reason why the free-ion treatment applies to the rare-earth ions is that the spin-orbit interaction is strong in these substances, because this interaction is proportional to Z, the atomic number of the element concerned, and all the rare-earth ions have large Z's. Typical values for the spin-orbit and the crystal-field interactions in these materials are 10^{-1} eV and 10^{-2} eV, respectively.

Iron-group ions

Table 3 shows that iron-group ions behave magnetically as if $J = S$, that is, only the spin moment can contribute to magnetization. We can see this by means of the following argument. The magnetic properties of this group of elements are due to the electron in the incomplete 3d shell. Since electrons in this outermost shell interact strongly with neighboring ions, the orbital motion is essentially destroyed, or *quenched*, leaving only the spin moment to contribute to the magnetization. In other words, in these ions, the strength of the crystal field is much greater than the strength of the spin-orbit interaction, just the reverse of the situation in rare-earth ions. Typical strengths of the crystal field and spin-orbit interactions in the iron group are 1 eV and 10^{-2} eV, respectively.

Table 3. Iron-Group Ions

Ion	Ground state	Theory $p = g\sqrt{j(j+1)}$	Theory $p = 2\sqrt{s(s+1)}$	Experiment (Eq. 9.43) p
K^+, Ca^{3+}	$^1S_0$	0	0	Diamagnetic
Ti^{3+}, V^{4+}	$^2D_{3/2}$	1.55	1.73	1.7
V^{3+}	$^3F_2$	1.63	2.83	2.8
V^{2+}, Cr^{3+}, Mn^{4+}	$^4F_{3/2}$	0.77	3.87	3.8
Mn^{2+}, Fe^{3+}	$^6S_{5/2}$	5.92	5.92	5.9
Fe^{2+}	$^5D_4$	6.70	4.90	5.4
Ca^{2+}	$^2D_{5/2}$	3.55	1.73	1.9

In the case of the transition metal ions from the iron group (partially filled *3d* shells) the crystal field is very much larger than the spin-orbit coupling. This perturbation will not lift the spin degeneracy, since it depends only on spatial variables and therefore commutes with S, but it can completely lift the degeneracy of the orbital L-multiplet, if it is sufficiently asymmetric. The result will then be a ground-state multiplet in which the mean value of every component of $\mathbf{L}$ vanishes (even though $\mathbf{L}^2$ still has the mean value $L(L + 1)$). One can interpret this classically as arising from a precession of the orbital angular momentum in the crystal field, so that although its magnitude is unchanged, all its components average to zero.

Paramagnetism of conduction electrons

Spin paramagnetism arises from the fact that each conduction electron carries a spin magnetic moment which tends to align with the field. An electron has spin ½. One might expect that the conduction would make a Curie-type paramagnetic contribution (36) to the magnetization of the metal with $J=S=1/2$:

$$\chi = \frac{N\mu_B^2}{k_B T}, \tag{38}$$

This shows that the susceptibility is inversely proportional to temperature. Experiments show, however, that spin susceptibilities in metals are essentially independent of temperature. The observed values are also considerably smaller than those predicted by (38). These facts clearly cast strong doubts on the applicability of (36) to the conduction electrons. The source of the difficulty lies in the fact that Eq. (36) was derived on the basis of localized electrons obeying the Boltzmann distribution, whereas the conduction electrons are delocalized and satisfy the Fermi distribution.

The proper treatment, taking this into account, is illustrated in Fig.4. In the absence of the field, half the electrons have spins pointing in the positive z-direction, and the other half in the negative direction (Fig. 4a), resulting in a vanishing net magnetization. When a field is applied along the z-direction, the energy of the spins parallel to **B** is lowered by the amount $\mu_B B$, while the energy of spins opposite to **B** is raised by the same amount (Fig.4b). The situation which ensues is energetically unstable, and hence some electrons near the Fermi level begin to transfer from the opposite-spin half to the parallel-spin one, leading to a net magnetization. Note that only relatively few electrons near the Fermi level are able to flip their spins and align with the field. The other electrons, lying deep within the Fermi distribution, are prevented from doing so by the exclusion principle.

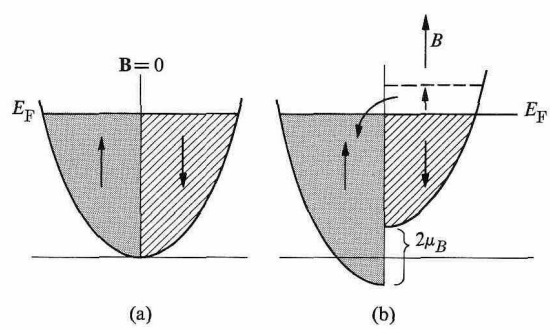

Fig. 4. (a) When B = 0, the two halves of the Fermi-Dirac distribution are equal, and thus $M = 0$; (b) When a field B is applied, spins in the antiparallel half flip into the parallel half, resulting in a net parallel magnetization.

We can now estimate the magnetic susceptibility. The electrons participating in the spin flip occupy an energy interval of $\mu_B B$ (Fig.4). Thus their concentration is given by $N_{eff} = ½D(E_F)\mu_B B$, where $D(E_F)$ is the density of states at the Fermi energy level [the factor ½ is inserted because $D(E_F)$ as defined us earlier includes both spin directions, while in the present circumstances only one spin direction is involved in the flipping]. Since each spin flip increases the magnetization by $2\mu_B$ (from $-\mu_B$ to $+\mu_B$), it follows that the net magnetization is given by

$$M = N_{eff}\, 2\mu_B = \mu_B^2 D(E_F)B\,, \tag{39}$$

leading to a paramagnetic susceptibility

$$\chi = \mu_B^2 D(E_F) \tag{40}$$

The susceptibility is thus determined by the density of states at the Fermi level, $D(E_F)$. According to eq. (40), χ is essentially independent of temperature. This is seen from the fact that temperature has only a small effect on the Fermi-Dirac distribution of the electrons, and consequently the derivation leading to (40) remains valid. If we apply the results for free electrons for which $D(E_F) = 3N/2E_F = 3N/2k_BTF$, eq.(40) then leads to

$$\chi = \frac{3N\mu_B^2}{2k_BT_F}\,, \tag{41}$$

where T_F the Fermi temperature ($E_F = k_BT_F$). Since T_F is very large, often 30,000°K or higher, we can see that (41) is smaller than (36) by factor of 10^2 - in agreement with experiment.

In transition metals, the paramagnetic susceptibility is exceptionally large, because $D(E_F)$ is large, by virtue of the narrow and high 3d band.

Diamagnetism

Conduction electrons also exhibit diamagnetism on account of the cyclotron motion they execute in the presence of the magnetic field. Each electron loop is equivalent to a dipole moment whose direction is opposite to that of the applied field. Classical treatment shows that the total diamagnetic contribution of all electrons is zero. Quantum treatment however shows that for free electrons this causes a diamagnetic moment equal to –1/3 of the paramagnetic moment. Therefore the total susceptibility of a free electrons gas is

$$\chi = \frac{N\mu_B^2}{k_BT_F} \tag{42}$$

The net response is therefore paramagnetic. In comparing theoretical results with experiment, one must also include the diamagnetic effect of the ion cores. Table 4 gives the results for some metals.

Table 4. Susceptibilities of Some Monovalent and Divalent Metals x 10^6 (Room Temperature)

			Experimental	Theoretical
Element	χ_{total} (expt)	χ_{core}	$\chi_{electron} = \chi_{total} - \chi_{core}$	$\chi_{electron} = \chi_{spin} + \chi_{orbit}$
K	0.47	− 0.31	0.76	0.35
Rb	0.33	− 0.46	0.79	0.33
Cu	− 0.76	− 2.0	1.24	0.65
Ag	− 2.1	− 3.0	0.9	0.60
Au	− 2.9	− 4.3	1.4	0.60
Mg	0.95	− 0.22	1.2	0.65
Ca	1.7	− 0.43	2.1	0.5