

11

Diamagnetism and Paramagnetism

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NOTATION: In the problems treated in this chapter the magnetic field B is always closely equal to the applied field B_a , so that we write B for B_a in most instances.

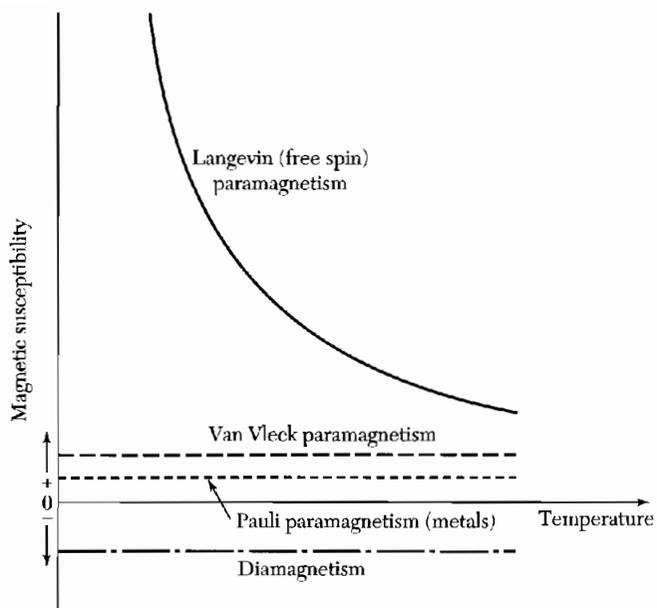


Figure 1 Characteristic magnetic susceptibilities of diamagnetic and paramagnetic substances.

CHAPTER 11: DIAMAGNETISM AND PARAMAGNETISM

Magnetism is inseparable from quantum mechanics, for a strictly classical system in thermal equilibrium can display no magnetic moment, even in a magnetic field. The magnetic moment of a free atom has three principal sources: the spin with which electrons are endowed; their orbital angular momentum about the nucleus; and the change in the orbital moment induced by an applied magnetic field.

The first two effects give paramagnetic contributions to the magnetization, and the third gives a diamagnetic contribution. In the ground $1s$ state of the hydrogen atom the orbital moment is zero, and the magnetic moment is that of the electron spin along with a small induced diamagnetic moment. In the $1s^2$ state of helium the spin and orbital moments are both zero, and there is only an induced moment. Atoms with all filled electron shells have zero spin and zero orbital moment: finite moments are associated with unfilled shells.

The magnetization M is defined as the magnetic moment per unit volume. The **magnetic susceptibility** per unit volume is defined as

$$\text{(CGS)} \quad \chi = \frac{M}{B}; \quad \text{(SI)} \quad \chi = \frac{\mu_0 M}{B} \quad (1)$$

where B is the macroscopic magnetic field intensity. In both systems of units χ is dimensionless. We shall sometimes for convenience refer to M/B as the susceptibility without specifying the system of units.

Quite frequently a susceptibility is defined referred to unit mass or to a mole of the substance. The molar susceptibility is written as χ_M ; the magnetic moment per gram is sometimes written as σ . Substances with a negative magnetic susceptibility are called **diamagnetic**. Substances with a positive susceptibility are called **paramagnetic**, as in Fig. 1.

Ordered arrays of magnetic moments are discussed in Chapter 12; the arrays may be ferromagnetic, ferrimagnetic, antiferromagnetic, helical, or more complex in form. Nuclear magnetic moments give rise to **nuclear paramagnetism**. Magnetic moments of nuclei are of the order of 10^{-3} times smaller than the magnetic moment of the electron.

LANGEVIN DIAMAGNETISM EQUATION

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

In a superconductor or in an electron orbit within an atom, the induced current persists as long as the field is present. The magnetic field of the induced current is opposite to the applied field, and the magnetic moment associated with the current is a diamagnetic moment. Even in a normal metal there is a diamagnetic contribution from the conduction electrons, and this diamagnetism is not destroyed by collisions of the electrons.

The usual treatment of the diamagnetism of atoms and ions employs the Larmor theorem: In a magnetic field the motion of the electrons around a central nucleus is, to the first order in B , the same as a possible motion in the absence of B except for the superposition of a precession of the electrons with angular frequency

$$\text{(CGS)} \quad \omega = eB/2mc ; \qquad \text{(SI)} \quad \omega = eB/2m. \quad (2)$$

If the field is applied slowly, the motion in the rotating reference system will be the same as the original motion in the rest system before the application of the field.

If the average electron current around the nucleus is zero initially, the application of the magnetic field will cause a finite current around the nucleus. The current is equivalent to a magnetic moment opposite to the applied field. It is assumed that the Larmor frequency (2) is much lower than the frequency of the original motion in the central field. This condition is not satisfied in free carrier cyclotron resonance, and the cyclotron frequency of the carriers is twice the frequency (2).

The Larmor precession of Z electrons is equivalent to an electric current

$$\text{(SI)} \quad I = (\text{charge})(\text{revolutions per unit time}) = (-Ze) \left(\frac{1}{2\pi} \cdot \frac{eB}{2m} \right). \quad (3)$$

The magnetic moment μ of a current loop is given by the product (current) \times (area of the loop). The area of the loop of radius ρ is $\pi\rho^2$. We have

$$\text{(SI)} \quad \mu = -\frac{Ze^2B}{4m} \langle \rho^2 \rangle, \qquad \text{(CGS)} \quad \mu = -\frac{Ze^2B}{4mc^2} \langle \rho^2 \rangle. \quad (4)$$

Here $\langle \rho^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle$ 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 $\langle r^2 \rangle = \frac{3}{2} \langle \rho^2 \rangle$.

From (4) the diamagnetic susceptibility per unit volume is, if N is the number of atoms per unit volume,

$$(CGS) \quad \chi = \frac{N\mu}{B} = -\frac{NZe^2}{6mc^2} \langle r^2 \rangle ; \quad (5)$$

$$(SI) \quad \chi = \frac{\mu_0 N \mu}{B} = -\frac{\mu_0 N Z e^2}{6m} \langle r^2 \rangle .$$

This is the classical Langevin result.

The problem of calculating the diamagnetic susceptibility of an isolated atom is reduced to the calculation of $\langle r^2 \rangle$ for the electron distribution within the atom. The distribution can be calculated by quantum mechanics.

Experimental values for neutral atoms are most easily obtained for the inert gases. Typical experimental values of the molar susceptibilities are the following:

	He	Ne	Ar	Kr	Xe
χ_M in CGS in $10^{-6} \text{ cm}^3/\text{mole}$:	-1.9	-7.2	-19.4	-28.0	-43.0

In dielectric solids the diamagnetic contribution of the ion cores is described roughly by the Langevin result. The contribution of conduction electrons in metals is more complicated, as is evident from the de Haas-van Alphen effect discussed in Chapter 9.

QUANTUM THEORY OF DIAMAGNETISM OF MONONUCLEAR SYSTEMS

We give the quantum treatment of the classical Langevin result. From Appendix (G.18) the effect of a magnetic field is to add to the Hamiltonian the terms

$$\mathcal{H} = \frac{ie\hbar}{2mc} (\nabla \cdot \mathbf{A} + \mathbf{A} \cdot \nabla) + \frac{e^2}{2mc^2} A^2 ; \quad (6)$$

for an atomic electron these terms may usually be treated as a small perturbation. If the magnetic field is uniform and in the z direction, we may write

$$A_x = -\frac{1}{2}yB, \quad A_y = \frac{1}{2}xB, \quad A_z = 0, \quad (7)$$

and (6) becomes

$$\mathcal{H} = \frac{ie\hbar B}{2mc} \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) + \frac{e^2 B^2}{8mc^2} (x^2 + y^2). \quad (8)$$

The first term on the right is proportional to the orbital angular momentum component L_2 if \mathbf{r} is measured from the nucleus. In mononuclear systems

this term gives rise only to paramagnetism. The second term gives for a spherically symmetric system a contribution

$$E' = \frac{e^2 B^2}{12mc^2} \langle r^2 \rangle, \quad (9)$$

by first-order perturbation theory. The associated magnetic moment is diamagnetic:

$$\mu = -\frac{\partial E'}{\partial B} = -\frac{e^2 \langle r^2 \rangle}{6mc^2} B, \quad (10)$$

in agreement with the classical result (5).

PARAMAGNETISM

Electronic paramagnetism (positive contribution to χ) is found in:

1. Atoms, molecules, and lattice defects possessing an odd number of electrons, as here the total spin of the system cannot be zero. Examples: free sodium atoms; gaseous nitric oxide (NO); organic free radicals such as triphenylmethyl, $C(C_6H_5)_3$; F centers in alkali halides.

2. Free atoms and ions with a partly filled inner shell: transition elements; ions isoelectronic with transition elements; rare earth and actinide elements. Examples: Mn^{2+} , Gd^{3+} , U^{4+} . Paramagnetism is exhibited by many of these ions even when incorporated into solids, but not invariably.

3. A few compounds with an even number of electrons, including molecular oxygen and organic biradicals.

4. Metals.

QUANTUM THEORY OF PARAMAGNETISM

The magnetic moment of an atom or ion in free space is given by

$$\mu = \gamma \hbar \mathbf{J} = -g \mu_B \mathbf{J}, \quad (11)$$

where the total angular momentum $\hbar \mathbf{J}$ is the sum of the orbital $\hbar \mathbf{L}$ and spin $\hbar \mathbf{S}$ angular momenta.

The constant γ is the ratio of the magnetic moment to the angular momentum; γ is called the **gyromagnetic ratio** or **magnetogyric ratio**. For electronic systems a quantity g called the g factor or the spectroscopic splitting factor is defined by

$$g \mu_B \equiv -\gamma \hbar. \quad (12)$$

For an electron spin $g = 2.0023$, usually taken as 2.00. For a free atom the g factor is given by the Landé equation

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}. \quad (13)$$

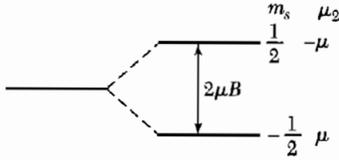


Figure 2 Energy level splitting for one electron in a magnetic field B directed along the positive z axis. For an electron the magnetic moment μ is opposite in sign to the spin S , so that $\mu = -g\mu_B S$. In the low-energy state the magnetic moment is parallel to the magnetic field.

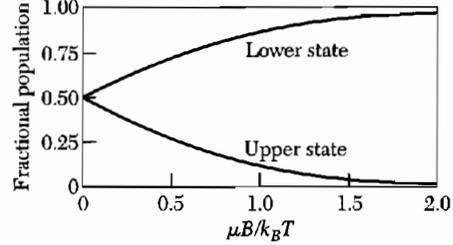


Figure 3 Fractional populations of a two-level system in thermal equilibrium at temperature T in a magnetic field B . The magnetic moment is proportional to the difference between the two curves.

The **Bohr magneton** μ_B is defined as $e\hbar/2mc$ in CGS and $e\hbar/2m$ in SI. It is closely equal to the spin magnetic moment of a free electron.

The energy levels of the system in a magnetic field are

$$U = -\boldsymbol{\mu} \cdot \mathbf{B} = m_j g \mu_B B, \quad (14)$$

where m_j is the azimuthal quantum number and has the values $J, J-1, \dots, -J$. For a single spin with no orbital moment we have $m_j = \pm \frac{1}{2}$ and $g = 2$, whence $U = \pm \mu_B B$. This splitting is shown in Fig. 2.

If a system has only two levels the equilibrium populations are, with $\tau \equiv k_B T$,

$$\frac{N_1}{N} = \frac{\exp(\mu B/\tau)}{\exp(\mu B/\tau) + \exp(-\mu B/\tau)}; \quad (15)$$

$$\frac{N_2}{N} = \frac{\exp(-\mu B/\tau)}{\exp(\mu B/\tau) + \exp(-\mu B/\tau)}; \quad (16)$$

here N_1, N_2 are the populations of the lower and upper levels, and $N = N_1 + N_2$ is the total number of atoms. The fractional populations are plotted in Fig. 3.

The projection of the magnetic moment of the upper state along the field direction is $-\mu$ and of the lower state is μ . The resultant magnetization for N atoms per unit volume is, with $x = \mu B/k_B T$,

$$M = (N_1 - N_2)\mu = N\mu \cdot \frac{e^x - e^{-x}}{e^x + e^{-x}} = N\mu \tanh x. \quad (17)$$

For $x \ll 1$, $\tanh x \approx x$, and we have

$$M \approx N\mu(\mu B/k_B T). \quad (18)$$

In a magnetic field an atom with angular momentum quantum number J has $2J + 1$ equally spaced energy levels. The magnetization (Fig. 4) is given by

$$M = NgJ\mu_B B_J(x), \quad (x = gJ\mu_B B/k_B T), \quad (19)$$

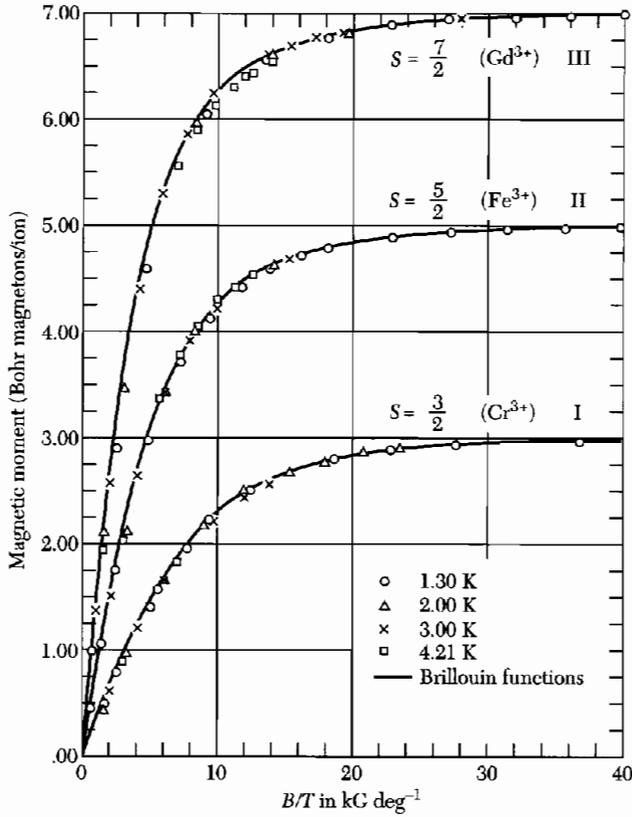


Figure 4 Plot of magnetic moment versus B/T for spherical samples of (I) potassium chromium alum, (II) ferric ammonium alum, and (III) gadolinium sulfate octahydrate. Over 99.5% magnetic saturation is achieved at 1.3 K and about 50,000 gauss (5T). After W. E. Henry.

where the **Brillouin function** B_J is defined by

$$B_J(x) = \frac{2J+1}{2J} \operatorname{ctnh} \left(\frac{(2J+1)x}{2J} \right) - \frac{1}{2J} \operatorname{ctnh} \left(\frac{x}{2J} \right). \quad (20)$$

Equation (17) is a special case of (20) for $J = \frac{1}{2}$.

For $x = \mu_B/k_B T \ll 1$, we have

$$\operatorname{ctnh} x = \frac{1}{x} + \frac{x}{3} - \frac{x^3}{45} + \dots, \quad (21)$$

and the susceptibility is

$$\frac{M}{B} \cong \frac{NJ(J+1)g^2\mu_B^2}{3k_B T} = \frac{Np^2\mu_B^2}{3k_B T} = \frac{C}{T}. \quad (22)$$

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

$$p \equiv g[J(J+1)]^{1/2}. \quad (23)$$

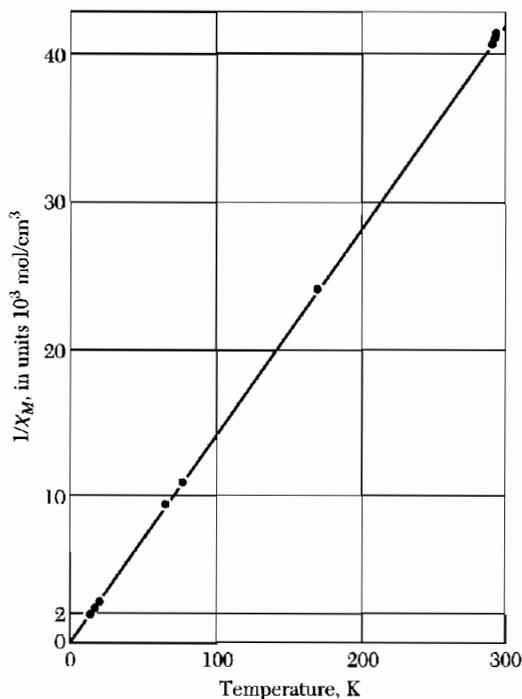


Figure 5 Plot of $1/\chi$ vs T for a gadolinium salt, $\text{Gd}(\text{C}_2\text{H}_3\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$. The straight line is the Curie law. (After L. C. Jackson and H. Kamerlingh Onnes.)

The constant C is known as the **Curie constant**. The form (19) is known as the Curie-Brillouin law, and (22) is known as the **Curie law**. Results for the paramagnetic ions in a gadolinium salt are shown in Fig. 5.

Rare Earth Ions

The ions of the rare earth elements (Table 1) have closely similar chemical properties, and their chemical separation in tolerably pure form was accomplished only long after their discovery. Their magnetic properties are fascinating: The ions exhibit a systematic variety and intelligible complexity. The chemical properties of the trivalent ions are similar because the outermost electron shells are identically in the $5s^25p^6$ configuration, like neutral xenon. In lanthanum, just before the rare earth group begins, the $4f$ shell is empty; at cerium there is one $4f$ electron, and the number of $4f$ electrons increases steadily through the group until we have $4f^{13}$ at ytterbium and the filled shell $4f^{14}$ at lutetium. The radii of the trivalent ions contract fairly smoothly as we go through the group from 1.11 Å at cerium to 0.94 Å at ytterbium. This is known as the “lanthanide contraction.” What distinguishes the magnetic behavior of one ion species from another is the number of $4f$ electrons compacted in the inner shell with a radius of perhaps 0.3 Å. Even in the metals the

Table 1 Effective magneton numbers p for trivalent lanthanide group ions

(Near room temperature)				
Ion	Configuration	Basic level	$p(\text{calc}) = g[J(J+1)]^{1/2}$	$p(\text{exp}),$ approximate
Ce ³⁺	4f ¹ 5s ² p ⁶	² F _{5/2}	2.54	2.4
Pr ³⁺	4f ² 5s ² p ⁶	³ H ₄	3.58	3.5
Nd ³⁺	4f ³ 5s ² p ⁶	⁴ I _{9/2}	3.62	3.5
Pm ³⁺	4f ⁴ 5s ² p ⁶	⁵ I ₄	2.68	—
Sm ³⁺	4f ⁵ 5s ² p ⁶	⁶ H _{5/2}	0.84	1.5
Eu ³⁺	4f ⁶ 5s ² p ⁶	⁷ F ₀	0	3.4
Gd ³⁺	4f ⁷ 5s ² p ⁶	⁸ S _{7/2}	7.94	8.0
Tb ³⁺	4f ⁸ 5s ² p ⁶	⁷ F ₆	9.72	9.5
Dy ³⁺	4f ⁹ 5s ² p ⁶	⁶ H _{15/2}	10.63	10.6
Ho ³⁺	4f ¹⁰ 5s ² p ⁶	⁵ I ₈	10.60	10.4
Er ³⁺	4f ¹¹ 5s ² p ⁶	⁴ I _{15/2}	9.59	9.5
Tm ³⁺	4f ¹² 5s ² p ⁶	³ I ₆	7.57	7.3
Yb ³⁺	4f ¹³ 5s ² p ⁶	² F _{7/2}	4.54	4.5

4f core retains its integrity and its atomic properties: no other group of elements in the periodic table is as interesting.

The preceding discussion of paramagnetism applies to atoms that have a $(2J + 1)$ -fold degenerate ground state, the degeneracy being lifted by a magnetic field. The influence of all higher energy states of the system is neglected. These assumptions appear to be satisfied by a number of rare-earth ions, Table 1. The calculated magneton numbers are obtained with g values from the Landé result (13) and the ground-state level assignment predicted below by the Hund theory of spectral terms. The discrepancy between the experimental magneton numbers and those calculated on these assumptions is quite marked for Eu³⁺ and Sm³⁺ ions. For these ions it is necessary to consider the influence of the high states of the $L - S$ multiplet, as the intervals between successive states of the multiplet are not large compared to $k_B T$ at room temperature. A multiplet is the set of levels of different J values arising out of a given L and S . The levels of a multiplet are split by the spin-orbit interaction.

Hund Rules

The Hund rules as applied to electrons in a given shell of an atom 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 $|L - S|$ when the shell is less than half full and to $L + S$ when the shell is more than half full. When the shell is just half full, the application of the first rule gives $L = 0$, so that $J = S$.

The first Hund rule has its origin in the exclusion principle and the coulomb repulsion between electrons. The exclusion principle prevents two electrons of the same spin from being at the same place at the same time. Thus electrons of the same spin are kept apart, further apart than electrons of opposite spin. Because of the coulomb interaction the energy of electrons of the same spin is lower—the average potential energy is less positive for parallel spin than for antiparallel spin. A good example is the ion Mn^{2+} . This ion has five electrons in the $3d$ shell, which is therefore half-filled. The spins can all be parallel if each electron enters a different orbital, and there are exactly five different orbitals available, characterized by the orbital quantum numbers $m_L = 2, 1, 0, -1, -2$. These will be occupied by one electron each. We expect $S = \frac{5}{2}$, and because $\sum m_L = 0$ the only possible value of L is 0, as observed.

The second Hund rule is best approached by model calculations. Pauling and Wilson,¹ for example, give a calculation of the spectral terms that arise from the configuration p^2 . The third Hund rule is a consequence of the sign of the spin-orbit interaction: For a single electron the energy is lowest when the spin is antiparallel to the orbital angular momentum. But the low-energy pairs m_L, m_S are progressively used up as we add electrons to the shell; by the exclusion principle when the shell is more than half full the state of lowest energy necessarily has the spin parallel to the orbit.

Consider two examples of the Hund rules: The ion Ce^{3+} has a single f electron; an f electron has $l = 3$ and $s = \frac{1}{2}$. Because the f shell is less than half full, the J value by the preceding rule is $|L - S| = L - \frac{1}{2} = \frac{5}{2}$. The ion Pr^{3+} has two f electrons; one of the rules tells us that the spins add to give $S = 1$. Both f electrons cannot have $m_l = 3$ without violating the Pauli exclusion principle, so that the maximum L consistent with the Pauli principle is not 6, but 5. The J value is $|L - S| = 5 - 1 = 4$.

Iron Group Ions

Table 2 shows that the experimental magneton numbers for salts of the iron transition group of the periodic table are in poor agreement with (23). The values often agree quite well with magneton numbers $p = 2[S(S + 1)]^{1/2}$ calculated as if the orbital moment were not there at all.

Crystal Field Splitting

The difference in behavior of the rare earth and the iron group salts is that the $4f$ shell responsible for paramagnetism in the rare earth ions lies deep

¹L. Pauling and E. B. Wilson, *Introduction to quantum mechanics*, McGraw-Hill, 1935, pp. 239–246. See also Dover Reprint.

Table 2 Effective magneton numbers for iron group ions

Ion	Configuration	Basic level	$p(\text{calc}) = g[J(J+1)]^{1/2}$	$p(\text{calc}) = 2[S(S+1)]^{1/2}$	$p(\text{exp})^a$
Ti ³⁺ , V ⁴⁺	3d ¹	² D _{3/2}	1.55	1.73	1.8
V ³⁺	3d ²	³ F ₂	1.63	2.83	2.8
Cr ³⁺ , V ²⁺	3d ³	⁴ F _{3/2}	0.77	3.87	3.8
Mn ³⁺ , Cr ²⁺	3d ⁴	⁵ D ₀	0	4.90	4.9
Fe ³⁺ , Mn ²⁺	3d ⁵	⁶ S _{5/2}	5.92	5.92	5.9
Fe ²⁺	3d ⁶	⁵ D ₄	6.70	4.90	5.4
Co ²⁺	3d ⁷	⁴ F _{3/2}	6.63	3.87	4.8
Ni ²⁺	3d ⁸	³ F ₄	5.59	2.83	3.2
Cu ²⁺	3d ⁹	² D _{5/2}	3.55	1.73	1.9

^a Representative values.

inside the ions, within the 5s and 5p shells, whereas in the iron group ions the 3d shell responsible for paramagnetism is the outermost shell. The 3d shell experiences the intense inhomogeneous electric field produced by neighboring ions. This inhomogeneous electric field is called the **crystal field**. The interaction of the paramagnetic ions with the crystal field has two major effects: The coupling of **L** and **S** vectors is largely broken up, so that the states are no longer specified by their *J* values; further, the 2*L* + 1 sublevels belonging to a given *L* which are degenerate in the free ion may now be split by the crystal field, as in Fig. 6. This splitting diminishes the contribution of the orbital motion to the magnetic moment.

Quenching of the Orbital Angular Momentum

In an electric field directed toward a fixed nucleus, the plane of a classical orbit is fixed in space, so that all the orbital angular momentum components L_x , L_y , L_z are constant. In quantum theory one angular momentum component, usually taken as L_z , and the square of the total orbital angular momentum L^2 are constant in a central field. In a noncentral field the plane of the orbit will move about; the angular momentum components are no longer constant and may average to zero. In a crystal L_z will no longer be a constant of the motion, although to a good approximation L^2 may continue to be constant. When L_z averages to zero, the orbital angular momentum is said to be quenched. The magnetic moment of a state is given by the average value of the magnetic moment operator $\mu_B(\mathbf{L} + 2\mathbf{S})$. In a magnetic field along the *z* direction the orbital contribution to the magnetic moment is proportional to the quantum expectation value of L_z ; the orbital magnetic moment is quenched if the mechanical moment L_z is quenched.

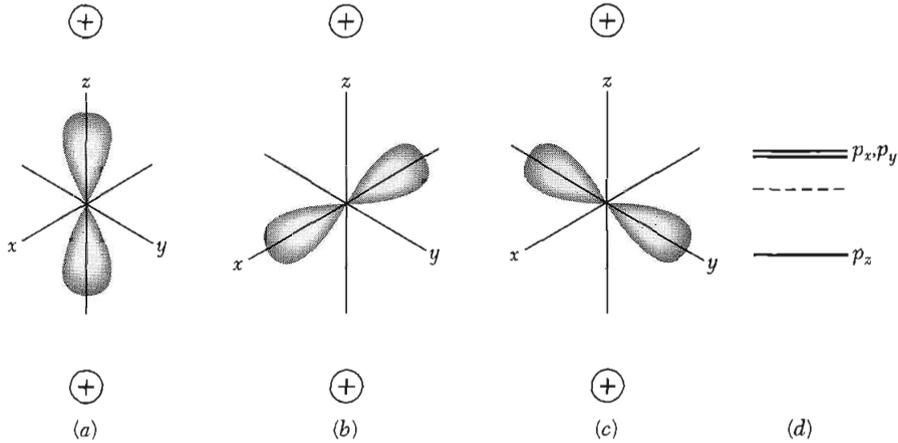


Figure 6 Consider an atom with orbital angular momentum $L = 1$ placed in the uniaxial crystalline electric field of the two positive ions along the z axis. In the free atom the states $m_L = \pm 1, 0$ have identical energies—they are degenerate. In the crystal the atom has a lower energy when the electron cloud is close to positive ions as in (a) than when it is oriented midway between them, as in (b) and (c). The wavefunctions that give rise to these charge densities are of the form $zf(r)$, $xf(r)$ and $yf(r)$ and are called the p_z , p_x , p_y orbitals, respectively. In an axially symmetric field, as shown, the p_x and p_y orbitals are degenerate. The energy levels referred to the free atom (dotted line) are shown in (d). If the electric field does not have axial symmetry, all three states will have different energies.

As an example, consider a single electron with orbital quantum number $L = 1$ moving about a nucleus, the whole being placed in an inhomogeneous crystalline electric field. We omit electron spin.

In a crystal of orthorhombic symmetry the charges on neighboring ions will produce an electrostatic potential φ about the nucleus of the form

$$e\varphi = Ax^2 + By^2 - (A + B)z^2, \quad (24)$$

where A and B are constants. This expression is the lowest degree polynomial in x , y , z which is a solution of the Laplace equation $\nabla^2\varphi = 0$ and compatible with the symmetry of the crystal.

In free space the ground state is three-fold degenerate, with magnetic quantum numbers $m_L = 1, 0, -1$. In a magnetic field these levels are split by energies proportional to the field B , and it is this field-proportional splitting which is responsible for the normal paramagnetic susceptibility of the ion. In the crystal the picture may be different. We take as the three wavefunctions associated with the unperturbed ground state of the ion

$$U_x = xf(r); \quad U_y = yf(r); \quad U_z = zf(r). \quad (25)$$

These wavefunctions are orthogonal, and we assume that they are normalized. Each of the U 's can be shown to have the property

$$\mathcal{L}^2 U_i = L(L+1)U_i = 2U_i, \quad (26)$$

where \mathcal{L}^2 is the operator for the square of the orbital angular momentum, in units of \hbar . The result (26) confirms that the selected wavefunctions are in fact p functions, having $L = 1$.

We observe now that the U 's are diagonal with respect to the perturbation, as by symmetry the nondiagonal elements vanish:

$$\langle U_x | e\varphi | U_y \rangle = \langle U_x | e\varphi | U_z \rangle = \langle U_y | e\varphi | U_z \rangle = 0. \quad (27)$$

Consider for example,

$$\langle U_x | e\varphi | U_y \rangle = \int xy |f(r)|^2 \{Ax^2 + By^2 - (A+B)z^2\} dx dy dz; \quad (28)$$

the integrand is an odd function of x (and also of y) and therefore the integral must be zero. The energy levels are then given by the diagonal matrix elements:

$$\begin{aligned} \langle U_x | e\varphi | U_x \rangle &= \int |f(r)|^2 \{Ax^4 + By^2x^2 - (A+B)z^2x^2\} dx dy dz \\ &= A(I_1 - I_2), \end{aligned} \quad (29)$$

where

$$I_1 = \int |f(r)|^2 x^4 dx dy dz; \quad I_2 = \int |f(r)|^2 x^2 y^2 dx dy dz.$$

In addition,

$$\langle U_y | e\varphi | U_y \rangle = B(I_1 - I_2); \quad \langle U_z | e\varphi | U_z \rangle = -(A+B)(I_1 - I_2).$$

The three eigenstates in the crystal field are p functions with their angular lobes directed along each of the x, y, z axes, respectively.

The orbital moment of each of the levels is zero, because

$$\langle U_x | L_z | U_x \rangle = \langle U_y | L_z | U_y \rangle = \langle U_z | L_z | U_z \rangle = 0.$$

The level still has a definite total angular momentum, since \mathcal{L}^2 is diagonal and gives $L = 1$, but the spatial components of the angular momentum are not constants of the motion and their time average is zero in the first approximation. Therefore the components of the orbital magnetic moment also vanish in the same approximation. The role of the crystal field in the quenching process is to split the originally degenerate levels into nonmagnetic levels separated by energies $\gg \mu H$, so that the magnetic field is a small perturbation in comparison with the crystal field.

At a lattice site of cubic symmetry there is no term in the potential of the form (24), that is, quadratic in the electron coordinates. Now the ground state of an ion with one p electron (or with one hole in a p shell) will be triply

degenerate. However, the energy of the ion will be lowered if the ion displaces itself with respect to the surroundings, thereby creating a noncubic potential such as (24). Such a spontaneous displacement is known as a **Jahn-Teller effect** and is often large and important, particularly with the Mn^{3+} and Cu^{2+} ions and with holes in alkali and silver halides.

Spectroscopic Splitting Factor

We suppose for convenience that the crystal field constants, A, B are such that $U_x = xf(r)$ is the orbital wave function of the ground state of the atom in the crystal. For a spin $S = \frac{1}{2}$ there are two possible spin states $S_z = \pm\frac{1}{2}$ represented by the spin functions α, β , which in the absence of a magnetic field are degenerate in the zeroth approximation. The problem is to take into account the spin-orbit interaction energy $\lambda \mathbf{L} \cdot \mathbf{S}$.

If the ground state function is $\psi_0 = U_x \alpha = xf(r)\alpha$ in the zeroth approximation, then in the first approximation, considering the $\lambda \mathbf{L} \cdot \mathbf{S}$ interaction by standard perturbation theory, we have

$$\psi = [U_x - i(\lambda/2\Delta_1)U_y]\alpha - i(\lambda/2\Delta_2)U_z\beta, \quad (30)$$

where Δ_1 is the energy difference between the U_x and U_y states, and Δ_2 is the difference between the U_x and U_z states. The term in $U_z\beta$ actually has only a second-order effect on the result and may be discarded. The expectation value of the orbital angular momentum to the first order is given directly by

$$\langle \psi | L_z | \psi \rangle = -\lambda/\Delta_1,$$

and the magnetic moment of the state as measured in the z direction is

$$\mu_B \langle \psi | L_z + 2S_z | \psi \rangle = [-(\lambda/\Delta_1) + 1]\mu_B.$$

As the separation between the levels $S_z = \pm\frac{1}{2}$ in a field H is

$$\Delta E \approx g\mu_B H = 2[1 - (\lambda/\Delta_1)]\mu_B H,$$

the g value or spectroscopic splitting factor (12) in the z direction is

$$g = 2[1 - (\lambda/\Delta_1)]. \quad (31)$$

Van Vleck Temperature-Independent Paramagnetism

We consider an atomic or molecular system which has no magnetic moment in the ground state, by which we mean that the diagonal matrix element of the magnetic moment operator μ_z is zero.

Suppose that there is a nondiagonal matrix element $\langle s | \mu_z | 0 \rangle$ of the magnetic moment operator, connecting the ground state 0 with the excited state s of energy $\Delta = E_s - E_0$ above the ground state. Then by standard perturbation theory the wavefunction of the ground state in a weak field ($\mu_2 B \ll \Delta$) becomes

$$\psi'_0 = \psi_0 + (B/\Delta)\langle s | \mu_z | 0 \rangle \psi_s, \quad (32)$$

and the wavefunction of the excited state becomes

$$\psi'_s = \psi_s - (B/\Delta)\langle 0|\mu_z|s\rangle\psi_0 . \quad (33)$$

The perturbed ground state now has a moment

$$\langle 0'|\mu_z|0'\rangle \cong 2B|\langle s|\mu_z|0\rangle|^2/\Delta , \quad (34)$$

and the upper state has a moment

$$\langle s'|\mu_z|s'\rangle \cong -2B|\langle s|\mu_z|0\rangle|^2/\Delta . \quad (35)$$

There are two interesting cases to consider:

Case (a). $\Delta \ll k_B T$. The surplus population in the ground state over the excited state is approximately equal to $N\Delta/2k_B T$, so that the resultant magnetization is

$$M = \frac{2B|\langle s|\mu_z|0\rangle|^2}{\Delta} \cdot \frac{N\Delta}{2k_B T} , \quad (36)$$

which gives for the susceptibility

$$\chi = N|\langle s|\mu_z|0\rangle|^2/k_B T . \quad (37)$$

Here N is the number of molecules per unit volume. This contribution is of the usual Curie form, although the mechanism of magnetization here is by polarization of the states of the system, whereas with free spins the mechanism of magnetization is the redistribution of ions among the spin states. We note that the splitting Δ does not enter in (37).

Case (b). $\Delta \gg k_B T$. Here the population is nearly all in the ground state, so that

$$M = \frac{2NB|\langle s|\mu_z|0\rangle|^2}{\Delta} . \quad (38)$$

The susceptibility is

$$\chi = \frac{2N|\langle s|\mu_z|0\rangle|^2}{\Delta} , \quad (39)$$

independent of temperature. This type of contribution is known as Van Vleck paramagnetism.

COOLING BY ISENTROPIC DEMAGNETIZATION

The first method for attaining temperatures much below 1 K was that of isentropic, or adiabatic, demagnetization of a paramagnetic salt. By its use, temperatures of 10^{-3} K and lower have been reached. The method rests on the fact that at a fixed temperature the entropy of a system of magnetic moments is lowered by the application of a magnetic field.

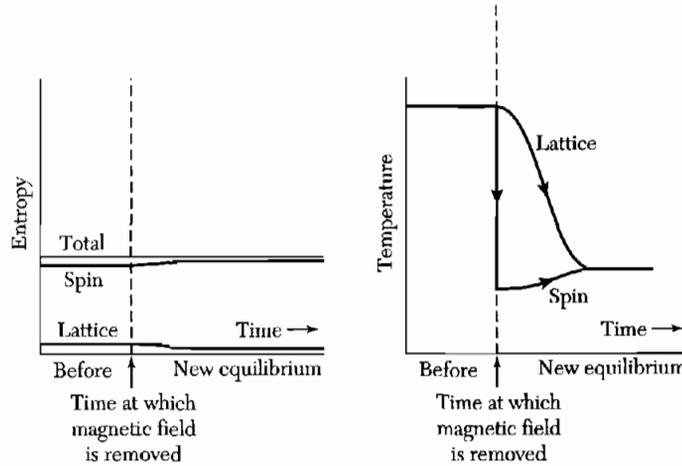


Figure 7 During isentropic demagnetization the total entropy of the specimen is constant. For effective cooling the initial entropy of the lattice should be small in comparison with the entropy of the spin system.

The entropy is a measure of the disorder of a system: the greater the disorder, the higher is the entropy. In the magnetic field the moments will be partly lined up (partly ordered), so that the entropy is lowered by the field. The entropy is also lowered if the temperature is lowered, as more of the moments line up.

If the magnetic field can then be removed without changing the entropy of the spin system, the order of the spin system will look like a lower temperature than the same degree of order in the presence of the field. When the specimen is demagnetized at constant entropy, entropy can flow into the spin system only from the system of lattice vibrations, as in Fig. 7. At the temperatures of interest the entropy of the lattice vibrations is usually negligible, thus the entropy of the spin system will be essentially constant during isentropic demagnetization of the specimen. Magnetic cooling is a one-shot operation, not cyclic.

We first find an expression for the spin entropy of a system of N ions, each of spin S , at a temperature sufficiently high that the spin system is entirely disordered. That is, T is supposed to be much higher than some temperature Δ which characterizes the energy of the interactions ($E_{\text{int}} \equiv k_B \Delta$) tending to orient the spins preferentially. Some of these interactions are discussed in Chapter 12. The definition of the entropy σ of a system of G accessible states is $\sigma = k_B \ln G$. At a temperature so high that all of the $2S + 1$ states of each ion are nearly equally populated, G is the number of ways of arranging N spins in $2S + 1$ states. Thus $G = (2S + 1)^N$, whence the spin entropy σ_S is:

$$\sigma_S = k_B \ln (2S + 1)^N = Nk_B \ln (2S + 1) . \quad (40)$$

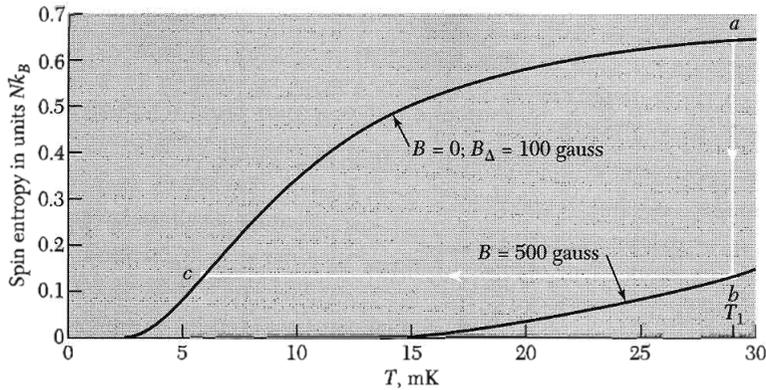


Figure 8 Entropy for a spin $\frac{1}{2}$ system as a function of temperature, assuming an internal random magnetic field B_{Δ} of 100 gauss. The specimen is magnetized isothermally along ab , and is then insulated thermally. The external magnetic field is turned off along bc . In order to keep the figure on a reasonable scale the initial temperature T_1 is lower than would be used in practice, and so is the external magnetic field.

This spin entropy is reduced by a magnetic field if the lower levels gain in population when the field separates the $2S + 1$ states in energy.

The steps carried out in the cooling process are shown in Fig. 8. The field is applied at temperature T_1 with the specimen in good thermal contact with the surroundings, giving the isothermal path ab . The specimen is then insulated ($\Delta\sigma = 0$) and the field removed, the specimen follows the constant entropy path bc , ending up at temperature T_2 . The thermal contact at T_1 is provided by helium gas, and the thermal contact is broken by removing the gas with a pump.

The population of a magnetic sublevel is a function only of $\mu B/k_B T$, hence of B/T . The spin-system entropy is a function only of the population distribution; hence the spin entropy is a function only of B/T . If B_{Δ} is the effective field that corresponds to the local interactions, the final temperature T_2 reached in an isentropic demagnetization experiment is

$$T_2 = T_1(B_{\Delta}/B) \quad , \quad (41)$$

where B is the initial field and T_1 the initial temperature.

Nuclear Demagnetization

Because nuclear magnetic moments are weak, nuclear magnetic interactions are much weaker than similar electronic interactions. We expect to reach a temperature 100 times lower with a nuclear paramagnet than with an electron paramagnet. The initial temperature T_1 of the nuclear stage in a nuclear spin-cooling experiment must be lower than in an electron spin-cooling

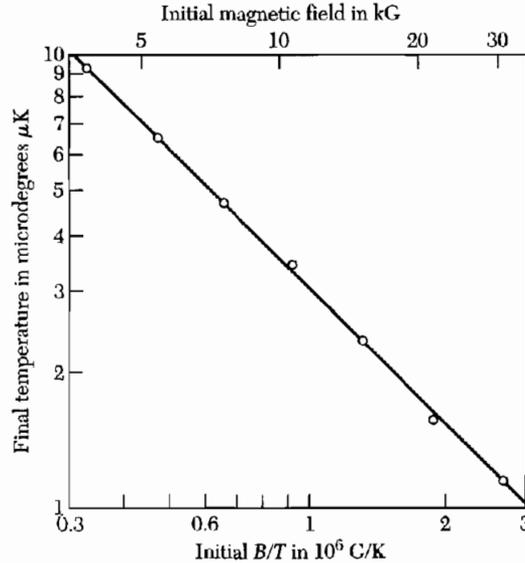


Figure 9 Nuclear demagnetizations of copper nuclei in the metal, starting from 0.012 K and various fields. (After M. V. Hobden and N. Kurti.)

experiment. If we start at $B = 50$ kG and $T_1 = 0.01$ K, then $\mu B/k_B T_1 \approx 0.5$, and the entropy decrease on magnetization is over 10 percent of the maximum spin entropy. This is sufficient to overwhelm the lattice and from (41) we estimate a final temperature $T_2 \approx 10^{-7}$ K. The first nuclear cooling experiment was carried out on Cu nuclei in the metal, starting from a first stage at about 0.02 K as attained by electronic cooling. The lowest temperature reached was 1.2×10^{-6} K.

The results in Fig. 9 fit a line of the form of (41): $T_2 = T_1(3.1/B)$ with B in gauss, so that $B_\Delta = 3.1$ gauss. This is the effective interaction field of the magnetic moments of the Cu nuclei. The motivation for using nuclei in a metal is that conduction electrons help ensure rapid thermal contact of lattice and nuclei at the temperature of the first stage.

PARAMAGNETIC SUSCEPTIBILITY OF CONDUCTION ELECTRONS

We are going to try to show how on the basis of these statistics the fact that many metals are diamagnetic, or only weakly paramagnetic, can be brought into agreement with the existence of a magnetic moment of the electrons.

W. Pauli, 1927

Classical free electron theory gives an unsatisfactory account of the paramagnetic susceptibility of the conduction electrons. An electron has associated with it a magnetic moment of one Bohr magneton, μ_B . One might expect that

the conduction electrons would make a Curie-type paramagnetic contribution (22) to the magnetization of the metal: $M = N\mu_B^2 B/k_B T$. Instead it is observed that the magnetization of most normal nonferromagnetic metals is independent of temperature.

Pauli showed that the application of the Fermi-Dirac distribution (Chapter 6) would correct the theory as required. We first give a qualitative explanation. The result (18) tells us that the probability an atom will be lined up parallel to the field B exceeds the probability of the antiparallel orientation by roughly $\mu_B B/k_B T$. For N atoms per unit volume, this gives a net magnetization $\approx N\mu_B^2 B/k_B T$, the standard result.

Most conduction electrons in a metal, however, have no possibility of turning over when a field is applied, because most orbitals in the Fermi sea with parallel spin are already occupied. Only the electrons within a range $k_B T$ of the top of the Fermi distribution have a chance to turn over in the field; thus only the fraction T/T_F of the total number of electrons contribute to the susceptibility. Hence

$$M \approx \frac{N\mu_B^2 B}{k_B T} \cdot \frac{T}{T_F} = \frac{N\mu_B^2}{k_B T_F} B, \quad (42)$$

which is independent of temperature and of the observed order of magnitude.

We now calculate the expression for the paramagnetic susceptibility of a free electron gas at $T \ll T_F$. We follow the method of calculation suggested by Fig. 10. An alternate derivation is the subject of Problem 5.

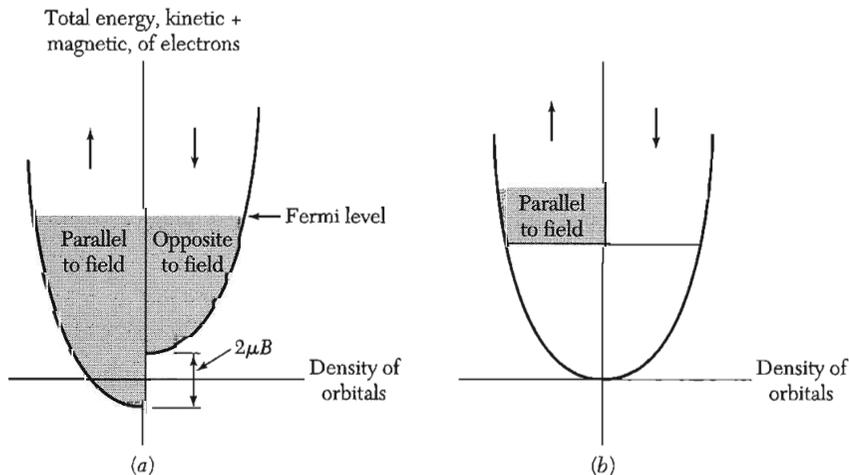


Figure 10 Pauli paramagnetism at absolute zero; the orbitals in the shaded regions in (a) are occupied. The numbers of electrons in the “up” and “down” band will adjust to make the energies equal at the Fermi level. The chemical potential (Fermi level) of the moment up electrons is equal to that of the moment down electrons. In (b) we show the excess of moment up electrons in the magnetic field.

The concentration of electrons with magnetic moments parallel to the magnetic field is

$$N_+ = \frac{1}{2} \int_{-\mu B}^{\epsilon_F} d\epsilon D(\epsilon + \mu B) \cong \frac{1}{2} \int_0^{\epsilon_F} d\epsilon D(\epsilon) + \frac{1}{2} \mu B D(\epsilon_F) , \quad (43)$$

written for absolute zero. Here $\frac{1}{2}D(\epsilon + \mu B)$ is the density of orbitals of one spin orientation, with allowance for the downward shift of energy by $-\mu B$. The approximation is written for $k_B T \ll \epsilon_F$.

The concentration of electrons with magnetic moments antiparallel to the magnetic field is

$$N_- = \frac{1}{2} \int_{\mu B}^{\epsilon_F} d\epsilon D(\epsilon - \mu B) \cong \frac{1}{2} \int_0^{\epsilon_F} d\epsilon D(\epsilon) - \frac{1}{2} \mu B D(\epsilon_F) . \quad (44)$$

The magnetization is given by $M = \mu(N_+ - N_-)$, so that

$$M = \mu^2 D(\epsilon_F) B = \frac{3N\mu^2}{2k_B T_F} B , \quad (45)$$

with $D(\epsilon_F) = 3N/2\epsilon_F = 3N/2k_B T_F$ from Chapter 6. The result (45) gives the **Pauli spin magnetization** of the conduction electrons, for $k_B T \ll \epsilon_F$.

In deriving the paramagnetic susceptibility, we have supposed that the spatial motion of the electrons is not affected by the magnetic field. But the wavefunctions are modified by the magnetic field; Landau has shown that for free electrons this causes a diamagnetic moment equal to $-\frac{1}{3}$ of the paramagnetic moment. Thus the total magnetization of a free electron gas is

$$M = \frac{N\mu_B^2}{k_B T_F} B . \quad (46)$$

Before comparing (46) with the experiment we must take account of the diamagnetism of the ionic cores, of band effects, and of electron-electron interactions. In sodium the interaction effects increase the spin susceptibility by perhaps 75 percent.

The magnetic susceptibility is considerably higher for most transition metals (with unfilled inner electron shells) than for the alkali metals. The high values suggest that the density of orbitals is unusually high for transition metals, in agreement with measurements of the electronic heat capacity. We saw in Chapter 9 how this arises from band theory.

SUMMARY

(In CGS Units)

- The diamagnetic susceptibility of N atoms of atomic number Z is $\chi = -Ze^2 N \langle r^2 \rangle / 6mc^2$, where $\langle r^2 \rangle$ is the mean square atomic radius. (Langevin)
- Atoms with a permanent magnetic moment μ have a paramagnetic susceptibility $\chi = N\mu^2 / 3k_B T$, for $\mu B \ll k_B T$. (Curie-Langevin)

- For a system of spins $S = \frac{1}{2}$, the exact magnetization is $M = N\mu \tanh(\mu B/k_B T)$, where $\mu = \frac{1}{2}g\mu_B$. (Brillouin)
- The ground state of electrons in the same shell have the maximum value of S allowed by the Pauli principle and the maximum L consistent with this S . The J value is $L + S$ if the shell is more than half full and $|L - S|$ if the shell is less than half full.
- A cooling process operates by demagnetization of a paramagnetic salt at constant entropy. The final temperature reached is of the order of $(B_\Delta/B)T_{\text{initial}}$, where B_Δ is the effective local field and B is the initial applied magnetic field.
- The paramagnetic susceptibility of a Fermi gas of conduction electrons is $\chi = 3N\mu^2/2\epsilon_F$, independent of temperature for $k_B T \ll \epsilon_F$. (Pauli)

Problems

1. **Diamagnetic susceptibility of atomic hydrogen.** The wave function of the hydrogen atom in its ground state ($1s$) is $\psi = (\pi a_0^3)^{-1/2} \exp(-r/a_0)$, where $a_0 = \hbar^2/me^2 = 0.529 \times 10^{-8}$ cm. The charge density is $\rho(x, y, z) = -e|\psi|^2$, according to the statistical interpretation of the wave function. Show that for this state $\langle r^2 \rangle = 3a_0^2$, and calculate the molar diamagnetic susceptibility of atomic hydrogen (-2.36×10^{-6} cm³/mole).
2. **Hund rules.** Apply the Hund rules to find the ground state (the basic level in the notation of Table 1) of (a) Eu^{++} , in the configuration $4f^7 5s^2 p^6$; (b) Yb^{3+} ; (c) Tb^{3+} . The results for (b) and (c) are in Table 1, but you should give the separate steps in applying the rules.
3. **Triplet excited states.** Some organic molecules have a triplet ($S = 1$) excited state at an energy $k_B \Delta$ above a singlet ($S = 0$) ground state. (a) Find an expression for the magnetic moment $\langle \mu \rangle$ in a field B . (b) Show that the susceptibility for $T \gg \Delta$ is approximately independent of Δ . (c) With the help of a diagram of energy levels versus field and a rough sketch of entropy versus field, explain how this system might be cooled by isentropic magnetization (not demagnetization).
4. **Heat capacity from internal degrees of freedom.** (a) Consider a two-level system with an energy splitting $k_B \Delta$ between upper and lower states; the splitting may arise from a magnetic field or in other ways. Show that the heat capacity per system is

$$C = \left(\frac{\partial U}{\partial T} \right)_\Delta = k_B \frac{(\Delta/T)^2 e^{\Delta/T}}{(1 + e^{\Delta/T})^2}.$$

The function is plotted in Fig. 11. Peaks of this type in the heat capacity are often known as **Schottky anomalies**. The maximum heat capacity is quite high, but for $T \ll \Delta$ and for $T \gg \Delta$ the heat capacity is low. (b) Show that for $T \gg \Delta$ we have $C \cong k_B (\Delta/2T)^2 + \dots$. The hyperfine interaction between nuclear and electronic magnetic moments in paramagnetic salts (and in systems having electron spin order) causes

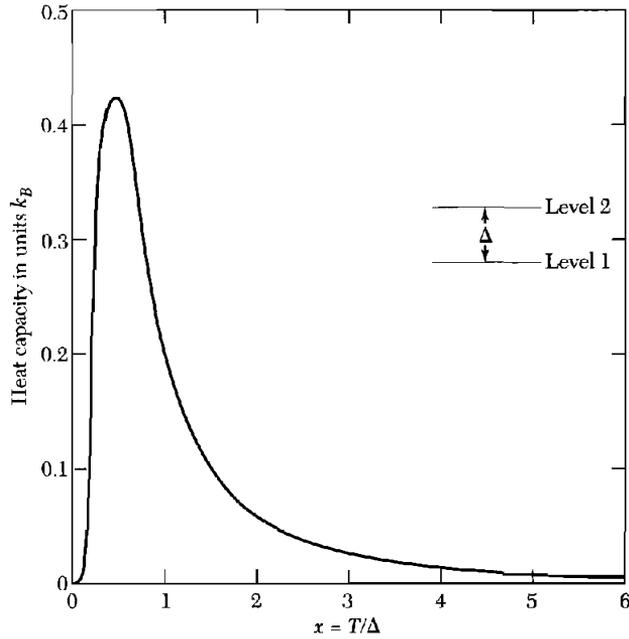


Figure 11 Heat capacity of a two-level system as a function of T/Δ , where Δ is the level splitting. The Schottky anomaly in the heat capacity is a very useful tool for determining energy level splittings of ions in rare-earth and transition-group metals, compounds, and alloys.

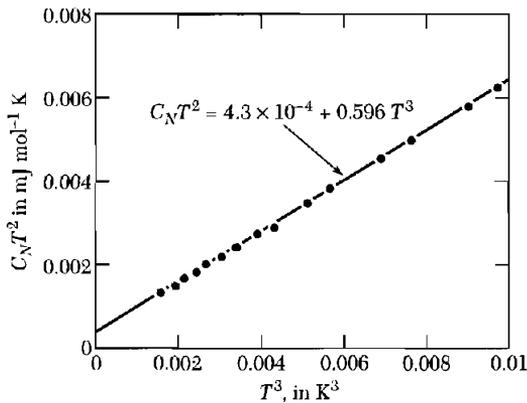


Figure 12 The normal-state heat capacity of gallium at $T < 0.21$ K. The nuclear quadrupole ($C \propto T^{-2}$) and conduction electron ($C \propto T$) contributions dominate the heat capacity at very low temperatures. (After N. E. Phillips.)

splittings with $\Delta \approx 1$ to 100 mK. These splittings are often detected experimentally by the presence of a term in $1/T^2$ in the heat capacity in the region $T \gg \Delta$. Nuclear electric quadrupole interactions with crystal fields also cause splittings, as in Fig. 12.

5. Pauli spin susceptibility. The spin susceptibility of a conduction electron gas at absolute zero may be approached by another method. Let

$$N^+ = \frac{1}{2}N(1 + \zeta) ; \quad N^- = \frac{1}{2}N(1 - \zeta)$$

be the concentrations of spin-up and spin-down electrons. (a) Show that in a magnetic field B the total energy of the spin-up band in a free electron gas is

$$E^+ = E_0(1 + \zeta)^{5/3} - \frac{1}{2}N\mu B(1 + \zeta) ,$$

where $E_0 = \frac{3}{10}N\epsilon_F$, in terms of the Fermi energy ϵ_F in zero magnetic field. Find a similar expression for E^- . (b) Minimize $E_{\text{total}} = E^+ + E^-$ with respect to ζ and solve for the equilibrium value of ζ in the approximation $\zeta \ll 1$. Go on to show that the magnetization is $M = 3N\mu^2 B / 2\epsilon_F$, in agreement with Eq. (45).

- 6. Conduction electron ferromagnetism.** We approximate the effect of exchange interactions among the conduction electrons if we assume that electrons with parallel spins interact with each other with energy $-V$, and V is positive, while electrons with antiparallel spins do not interact with each other. (a) Show with the help of Problem 5 that the total energy of the spin-up band is

$$E^+ = E_0(1 + \zeta)^{5/3} - \frac{1}{8}VN^2(1 + \zeta)^2 - \frac{1}{2}N\mu B(1 + \zeta) ;$$

find a similar expression for E^- . (b) Minimize the total energy and solve for ζ in the limit $\zeta \ll 1$. Show that the magnetization is

$$M = \frac{3N\mu^2}{2\epsilon_F - \frac{3}{2}VN} B ,$$

so that the exchange interaction enhances the susceptibility. (c) Show that with $B = 0$ the total energy is unstable at $\zeta = 0$ when $V > 4\epsilon_F/3N$. If this is satisfied, a ferromagnetic state ($\zeta \neq 0$) will have a lower energy than the paramagnetic state. Because of the assumption $\zeta \ll 1$, this is a sufficient condition for ferromagnetism, but it may not be a necessary condition. It is known as the **Stoner condition**.

- 7. Two-level system.** The result of Problem 4 is often seen in another form. (a) If the two energy levels are at Δ and $-\Delta$, show that the energy and heat capacity are

$$U = -\Delta \tanh(\Delta/k_B T) ; \quad C = k_B (\Delta/k_B T)^2 \operatorname{sech}^2(\Delta/k_B T) .$$

(b) If the system has a random composition such that all values of Δ are equally likely up to some limit Δ_0 , show that the heat capacity is linearly proportional to the temperature, provided $k_B T \ll \Delta_0$. This result was applied to the heat capacity of dilute magnetic alloys by W. Marshall, Phys. Rev. **118**, 1519 (1960). It is also used in the theory of glasses.

- 8. Paramagnetism of $S = 1$ system.** (a) Find the magnetization as a function of magnetic field and temperature for a system of spins with $S = 1$, moment μ , and concentration n . (b) Show that in the limit $\mu B \ll kT$ the result is $M \cong (2n\mu^2/3kT)B$.