

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.

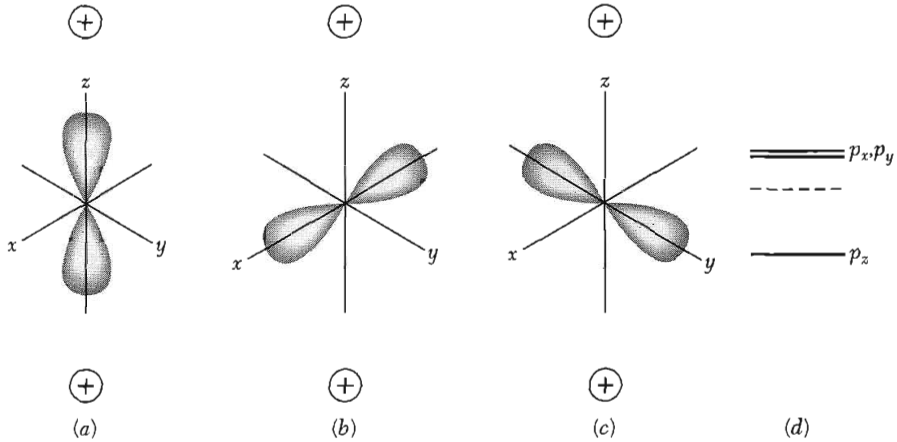


Figure 6 Consider an atom with orbital angular momentum $L = 1$ placed in the uniaxial crystalline electric field of the two positive ions along the z axis. In the free atom the states $m_L = \pm 1, 0$ have identical energies—they are degenerate. In the crystal the atom has a lower energy when the electron 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