

# ELECTRON RESONANCE IN CRYSTALLINE TRANSITION-METAL COMPOUNDS

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## 1. Introduction

WHEN a solid or a liquid specimen is placed between the poles of a permanent magnet and subjected to microwave radiation, power may be absorbed by the specimen at a particular frequency or set of frequencies which depend on the strength of the permanent field. If the magnetic field is about 10,000 gauss, and resonant absorption occurs at frequencies of the order of  $1 \text{ cm.}^{-1}$ , then it is safe to attribute the resonance to unpaired electrons. This phenomenon has been variously termed "paramagnetic resonance", "electron magnetic resonance", and "electron spin resonance". The first name emphasises that pure diamagnetic substances exhibit no such resonance; the second, that it is the magnetic component of the microwave field which induces the observed transitions; and the third, that it is the spins of the unpaired electrons which make them susceptible to the applied magnetic field.

As a rule, electron-resonance measurements are made in dilute solution, solid or liquid, to minimise interference between neighbouring paramagnetic units. Though organic free radicals often exhibit electron resonance in liquid solution, it is relatively unusual for transition-metal compounds to do so. To obtain resonance spectra from such compounds it is usually necessary to grow and study dilute single crystals. It is also convenient to be able to work at very low temperatures, where line-broadening effects are reduced. Crystal studies have the compensating advantage that one can observe how the resonance spectrum depends on the orientation of the crystal in the external magnetic field; if the crystal structure is known the orbitals of the unpaired electrons may thus be identified; if not, electron resonance may provide a useful supplement to crystallographic studies. Finally, if magnetic nuclei are present it may be possible to observe "hyperfine" structure in the electron-resonance spectrum, and from this to determine how far the magnetic electrons are delocalised into the orbitals of neighbouring atoms.

For these reasons the study of inorganic crystals by electron resonance is a tool of considerable utility for the student of molecular structure. It is therefore of advantage for the inorganic chemist to know something of the theory and practical applications of the technique. There are many good reviews of the subject, some of which go deeply into the basic theory,<sup>1,2</sup> while others give comprehensive accounts of the applications of electron-

<sup>1</sup> B. Bleaney and K. W. H. Stevens, *Reports Progr. Phys.*, 1953, **16**, 108.

<sup>2</sup> K. D. Bowers and J. Owen, *Reports Progr. Phys.*, 1955, **18**, 304.

resonance spectroscopy.<sup>3,4</sup> In this article we have chosen to expound the theory by the detailed consideration of one or two representative examples, in the hope that the reader may then feel able to tackle more confidently the more advanced papers. We shall find it necessary to use the methods of quantum mechanics, and to quote general results without proof; but we shall not assume any previous knowledge of the theory of electron resonance.

A few words on notation may be helpful at this point, as it is not in all respects identical with that used in general chemical work. First, as is customary, we shall distinguish *vectors* from *scalars* by printing the former in bold type and the latter in italic type. Thus  $\mathbf{H}$ , the magnetic field, is a vector, whereas  $H_z$ , its  $z$ -component, is a scalar quantity. Secondly, we shall place a circumflex over every symbol (whether a vector or a scalar) which stands for an *operator*. Thus  $\widehat{\mathbf{L}}$  and  $\widehat{\mathbf{S}}$  (which are both vectors) denote the angular momentum *operators* associated with the orbital motion and the spin of an electron or group of electrons, measured in units of  $h/2\pi$ , while  $\widehat{L}_z$  and  $\widehat{S}_z$  are the (scalar)  $z$ -components of these operators. By contrast,  $L$ ,  $S$ ,  $M_L$  and  $M_S$  are quantum *numbers* used to label the various electronic states. Thus the symbol  $|L, M_L\rangle$  denotes a state for which  $\widehat{\mathbf{L}}^2$  has the eigenvalue  $L(L + 1)$  and  $\widehat{L}_z$  has the eigenvalue  $M_L$  (which can take any one of the  $2L + 1$  values  $-L, \dots, +L$ ). Likewise,  $|M_L, M_S\rangle$  is an eigenstate of both  $\widehat{L}_z$  and  $\widehat{S}_z$ , with eigenvalues  $M_L$  and  $M_S$  respectively (the numerical values of  $L$  and  $S$  having been previously specified). Finally, the Bohr magneton  $\beta$  has the value  $eh/4\pi mc$ , where  $-e$  and  $m$  are the charge and mass of the electron,  $c$  being the velocity of light.

## 2. General theory

An electron interacts with an external magnetic field in two ways, by virtue of its charge and by virtue of its spin. A charged particle revolving round a fixed point is equivalent to a current flowing in a loop; likewise, an electron of charge  $-e$  with angular momentum  $\widehat{\mathbf{L}}$  interacts with a magnetic field  $\mathbf{H}$  by virtue of its orbital motion. This interaction is  $-\mathbf{H} \cdot \widehat{\boldsymbol{\mu}}_L$ , where  $\widehat{\boldsymbol{\mu}}_L$  is called the orbital magnetic moment and is equal to  $-\beta \widehat{\mathbf{L}}$ , where  $\beta$  is the Bohr magneton. In addition, the spin  $\widehat{\mathbf{S}}$  confers on the electron a magnetic moment

$$\widehat{\boldsymbol{\mu}}_S = -2\beta \widehat{\mathbf{S}}$$

and this also interacts with the external magnetic field  $\mathbf{H}$ . The total interaction is therefore

$$-\mathbf{H} \cdot (\widehat{\boldsymbol{\mu}}_L + \widehat{\boldsymbol{\mu}}_S) = \beta \mathbf{H} \cdot (\widehat{\mathbf{L}} + 2\widehat{\mathbf{S}})$$

<sup>3</sup> D. J. E. Ingram, "Spectroscopy at Radio and Microwave Frequencies", Butterworths Scientific Publications, London, 1955.

<sup>4</sup> J. W. Orton, *Reports Progr. Phys.*, 1959, **22**, 204.

The simplest possible situation is that of a single electron in an s orbital, as in the hydrogen atom. Here there is no orbital angular momentum, so the interaction is simply  $2\beta\mathbf{H}\cdot\widehat{\mathbf{S}}$  which becomes  $2\beta H_z\widehat{S}_z$  if the z direction is chosen as that of the permanent field. The field  $H_z$  thus quantises the z component of the spin, whose eigenvalues  $M_S$  are well known to be  $\frac{1}{2}$  and  $-\frac{1}{2}$  for a single electron. The magnetic energies of the two corresponding levels are therefore  $\beta H_z$ ,  $-\beta H_z$  and the separation between them may be written as  $g\beta H$ , where the quantity  $g$  is called the spectroscopic splitting factor and has the value 2 (more precisely 2.0023). We have here dropped the suffix from  $H_z$  to stress the obvious fact that the Zeeman splitting is independent of the direction of the applied field; we may say that  $g$  is isotropic. In crystals, however, isotropic  $g$  values are the exception rather than the rule, as we shall see in a moment.

Having split the spin levels apart by the field  $H_z$ , we may now induce transitions between them by applying an oscillating magnetic field

$$H_x' \cos 2\pi\nu t$$

in a perpendicular direction. This is because the resulting perturbation

$$2\beta H_x' \widehat{S}_x \cos 2\pi\nu t$$

involves  $\widehat{S}_x$ , which connects, *i.e.*, has matrix elements between, eigenstates of  $\widehat{S}_z$  differing in eigenvalue  $M_S$  by 1. The selection rule is therefore, in this example,

$$\Delta M_S = \pm 1$$

and the resonance condition is, of course,

$$h\nu = g\beta H$$

The frequency of resonance is thus proportional to the magnetic field, and *vice versa*. In practice it is more convenient to vary the magnetic field than to vary the frequency of the microwave source, so the spectrum is usually presented as a relation between absorption and magnetic field for a given microwave frequency; for instance the width of a resonance line is normally quoted in gauss.

Before passing on to consider the effects of orbital motion, which are of crucial importance in crystal studies, we may interpose a word about hyperfine structure. Atomic hydrogen actually shows two electron-resonance lines and the explanation of this is that the proton, like the electron, has a spin of magnitude  $\frac{1}{2}$ , which confers on it a magnetic moment of about  $10^{-3}$  Bohr magneton. This interacts both with the external field and with the magnetic field of the electron, the latter interaction being a good deal larger than the former. If the proton spin is denoted by  $\widehat{\mathbf{I}}$ , the total magnetic interaction takes the form

$$g\beta\mathbf{H}\cdot\widehat{\mathbf{S}} + A\widehat{\mathbf{S}}\cdot\widehat{\mathbf{I}} + B\mathbf{H}\cdot\widehat{\mathbf{I}}$$

where  $B$  depends on the magnetic moment of the proton and  $A$  depends also on the probability of the electron's being at the position of the proton. Again taking  $\mathbf{H}$  to be in the  $z$  direction, we find that if  $H \gg A/g\beta$  the eigenstates of this operator are states for which  $M_S$  and  $M_I$  are both good quantum numbers, having the alternative values  $\frac{1}{2}$  and  $-\frac{1}{2}$ . Fig. 1 shows the resulting set of four energy levels (not to scale). Neglecting the term

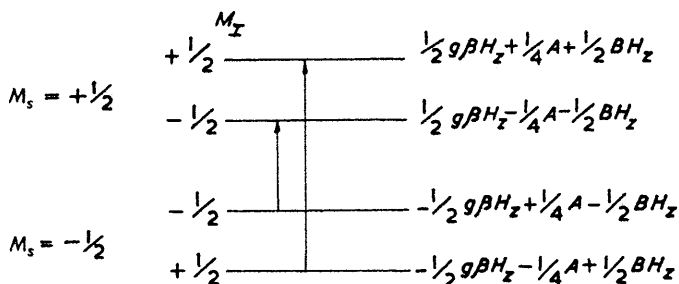


FIG. 1. Nuclear hyperfine energy levels of a 1s hydrogen atom in a magnetic field.

$BH_z$  in comparison with  $A$ , we see that the selection rules  $\Delta M_S = \pm 1$ ,  $\Delta M_I = 0$  allow the two transitions indicated, with energies  $g\beta H \pm \frac{1}{2}A$ . The two members of the hyperfine doublet are therefore separated by an amount  $A$  on the energy scale. Although such a simple discussion is seldom possible, it may be said that in general the appearance of hyperfine structure is clear evidence that the unpaired electron (or electrons) is interacting with one or more magnetic nuclei, either by direct contact as here, or through the magnetic field associated with its orbital motion.

### 3. Spin-orbit coupling

When an atom is placed in a chemical environment, the orbital motion of its electrons is strongly perturbed. To take an example: the isolated  $\text{Ti}^{3+}$  ion has a  ${}^2D$  ground term ( $L = 2$ ,  $S = \frac{1}{2}$ ) which has a five-fold orbital degeneracy ( $-L \leq M_L \leq +L$ ); but when the ion is placed in a chemical environment this degeneracy is partly lifted. Were the degeneracy completely lifted, so that finally all of the five 3d orbitals had different energies, it would be found that the expectation value of  $\hat{L}$  would vanish for each of them, and we should then say that the orbital angular momentum was completely quenched. Now there is a theorem due to Jahn and Teller<sup>5</sup> which states that, if a symmetrical non-linear molecule is in an orbitally degenerate state, then it will always distort in such a way as to lift the degeneracy. Why, then, is the orbital angular momentum of an atom or ion not always completely quenched in a chemical environment?

The answer is to be found in the phenomenon of spin-orbit coupling. Though this effect is usually insignificant in chemistry, it is vital to an

<sup>5</sup> H. A. Jahn and E. Teller, *Proc. Roy. Soc.*, 1937, *A*, 161, 220.

understanding of electron resonance. In simple terms, an electron tends to align its spin anti-parallel to its orbital angular momentum; hence, if it has orbital angular momentum, this tends to be kept going by being weakly coupled to the spin; and if it has spin, this tends to generate orbital angular momentum. There is therefore a competition between the quenching effect of the ligands—the “crystal field”—and the sustaining effect of the spin-orbit coupling. Were it not for spin-orbit coupling the orbital magnetic moment would be of no consequence in electron resonance, and we should always observe, without much interest, an isotropic  $g$  value of 2.

In the free atom or ion the most important effect of spin-orbit coupling is to split apart the different members of a particular “Russell-Saunders term” such as  ${}^2D$ . Thus in  $Ti^{3+}$  the level  ${}^2D_{3/2}$ , with  $\widehat{L}$  and  $\widehat{S}$  antiparallel, is slightly more stable than  ${}^2D_{5/2}$ , with  $\widehat{L}$  and  $\widehat{S}$  parallel. In considering only the levels which arise from a particular Russell-Saunders term it is sufficient to take the spin-orbit interaction to be of the form  $\lambda\widehat{L}\widehat{S}$ , where the parameter  $\lambda$  is an energy which depends on the number and nature of the outer electrons (for example,  $n$  3d electrons), and on the values of  $L$  and  $S$  for the term in question.  $\lambda$  also depends very strongly on the atomic number of the ion, increasing roughly as the cube of the atomic number. Values of  $\lambda$  for most of the ions of chemical interest are to be found in Condon and Shortley’s “Theory of Atomic Spectra”.<sup>6</sup> They are mostly in the range 100—1,000  $cm^{-1}$ .

#### 4. The calculation of $g$ values

When the ion is placed in a chemical environment, the orbital degeneracy characteristic of the free ion will, as already remarked, be partially lifted; but nevertheless the valency state of the bound ion may approximate quite closely to a mixture of states of the free ion, all of which arise from the same Russell-Saunders term. Thus in an octahedral environment the ground state of the  $Ti^{3+}$  ion, ( ${}^2T_{2g}$ ), and its first excited state ( ${}^2E_g$ ), both arise from the  ${}^2D$  term of the free ion, other such terms probably making insignificant contributions. If the crystal field is very strong this is no longer quite true, but for the present exposition we shall assume it to be the case, and will therefore take the spin-orbit interaction to be of the same form as it is in the related Russell-Saunders term of the free ion. In order to make the situation clearer, we shall now work through two examples, to show how the observed resonance spectra are related to the spin-orbit coupling and crystal-field splitting parameters.

(i) *The  $Ti^{3+}$  ion in a tetrahedral environment.* It is well known that if a transition-metal ion is placed in an environment with octahedral or tetra-

<sup>6</sup> E. U. Condon and G. H. Shortley, “Theory of Atomic Spectra”, Cambridge University Press, 1951, p. 197 (see also D. S. McClure, *Solid State Phys.*, 1959, **9**, 428).

hedral symmetry, the d orbitals are split into a group of three and a group of two by the electrostatic crystal field.<sup>7</sup> If the ion is tetrahedrally coordinated the orbital doublet lies *below* the orbital triplet as shown in Fig. 2, where we have indicated how a small tetragonal distortion—

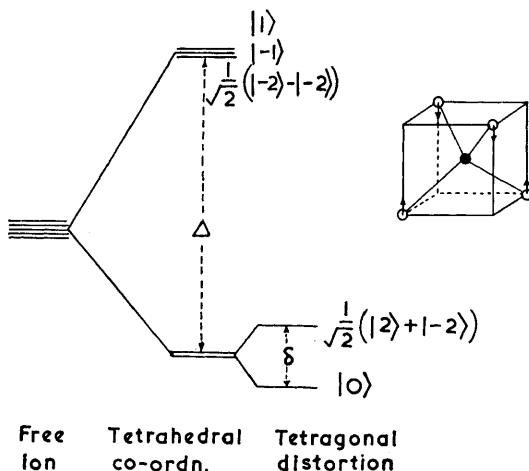


FIG. 2. Splitting of the orbitals of the  $Ti^{3+}$  ion in a tetrahedral field, with tetragonal distortion.

actually a slight flattening of the tetrahedron—further splits the orbital doublet. (We shall not need to discuss how the upper triplet is split by this additional perturbation.) We have also indicated the explicit forms of the orbitals in terms of the complex 3d orbitals;  $|M_L\rangle$  represents a 3d orbital with  $M_L$  units of angular momentum around the  $z$  axis, which is taken to be the axis along which the tetrahedron is flattened. Some such distortion is to be expected from the Jahn–Teller theorem, and we are supposing that it is such as to make the orbital  $|0\rangle$  the more stable.\*

We now fix attention on the lowest orbital and note that it contains a single electron in the ground state of the complex. If spin–orbit coupling is ignored, the ground state may be represented by the pair of symbols  $|0, \frac{1}{2}\rangle$ ,  $|0, -\frac{1}{2}\rangle$ , where the pair of numbers in each “ket” represent the values of  $M_L$  and  $M_S$  respectively, *i.e.*, the eigenvalues of  $\widehat{L}_z$  and  $\widehat{S}_z$ . When spin–orbit coupling is taken into account, however, these expressions are modified slightly by the admixture of small amounts of states with different values of  $M_L$  and  $M_S$ .

<sup>7</sup> J. S. Griffith and L. E. Orgel, *Quart. Rev.*, 1957, **11**, 381.

\* The orbitals  $|0\rangle$  and  $\sqrt{\frac{1}{2}}(|2\rangle + |-2\rangle)$  are actually the orbitals more commonly known as  $d_{z^2}$  and  $d_{x^2-y^2}$ . Of the other three orbitals  $\sqrt{\frac{1}{2}}(|2\rangle - |-2\rangle)$  is the orbital  $d_{xy}$ , and  $|1\rangle$  and  $|-1\rangle$  are the complex combinations  $\sqrt{\frac{1}{2}}(d_{xz} \pm id_{yz})$ . But as we are dealing with angular momentum it is not convenient to use the more familiar real forms for all five d orbitals.

To calculate the admixing coefficients we use first-order perturbation theory. According to this theory, the perturbation  $\lambda\widehat{\mathbf{L}}\widehat{\mathbf{S}}$  changes the state  $|0, \frac{1}{2}\rangle$  into

$$|0, \frac{1}{2}\rangle + \sum_{M_L} \sum_{M_S} |M_L, M_S\rangle \frac{\langle M_L, M_S | \lambda\widehat{\mathbf{L}}\widehat{\mathbf{S}} | 0, \frac{1}{2}\rangle}{E(0, \frac{1}{2}) - E(M_L, M_S)}$$

where the sum is over all *other* states  $|M_L, M_S\rangle$  and the denominator is the difference in energy between the unperturbed state and the state which is being mixed with it. We must therefore have a look at the values of the matrix elements  $\langle M_L, M_S | \lambda\widehat{\mathbf{L}}\widehat{\mathbf{S}} | 0, \frac{1}{2}\rangle$  and  $\langle M_L, M_S | \lambda\widehat{\mathbf{L}}\widehat{\mathbf{S}} | 0, -\frac{1}{2}\rangle$ .

First we note that the perturbation  $\lambda\widehat{\mathbf{L}}\widehat{\mathbf{S}}$  may be expanded in the form

$$\lambda(\widehat{L}_x\widehat{S}_x + \widehat{L}_y\widehat{S}_y + \widehat{L}_z\widehat{S}_z) = \frac{1}{2}\lambda(\widehat{L}_+\widehat{S}_- + \widehat{L}_-\widehat{S}_+) + \lambda\widehat{L}_z\widehat{S}_z$$

where  $\widehat{L}_\pm = \widehat{L}_x \pm i\widehat{L}_y$  and  $\widehat{S}_\pm = \widehat{S}_x \pm i\widehat{S}_y$

Therefore  $\langle M_L, M_S | \lambda\widehat{\mathbf{L}}\widehat{\mathbf{S}} | 0, \frac{1}{2}\rangle$  may be written as

$$\begin{aligned} & \frac{1}{2}\lambda\langle M_L, M_S | \widehat{L}_+\widehat{S}_- | 0, \frac{1}{2}\rangle + \frac{1}{2}\lambda\langle M_L, M_S | \widehat{L}_-\widehat{S}_+ | 0, \frac{1}{2}\rangle + \lambda\langle M_L, M_S | \widehat{L}_z\widehat{S}_z | 0, \frac{1}{2}\rangle \\ & = \frac{1}{2}\lambda\langle M_L | \widehat{L}_+ | 0\rangle \langle M_S | \widehat{S}_- | \frac{1}{2}\rangle + \frac{1}{2}\lambda\langle M_L | \widehat{L}_- | 0\rangle \langle M_S | \widehat{S}_+ | \frac{1}{2}\rangle \\ & \quad + \lambda\langle M_L | \widehat{L}_z | 0\rangle \langle M_S | \widehat{S}_z | \frac{1}{2}\rangle \end{aligned}$$

Secondly, we make use of standard formulæ for the matrix elements in the last expression. It is a standard result that the only matrix elements of these types which do not vanish are the following:

$$\begin{aligned} \langle M_L + 1 | \widehat{L}_+ | M_L\rangle &= \sqrt{[L(L + 1) - M_L(M_L + 1)]} \\ \langle M_S + 1 | \widehat{S}_+ | M_S\rangle &= \sqrt{[S(S + 1) - M_S(M_S + 1)]} \\ \langle M_L - 1 | \widehat{L}_- | M_L\rangle &= \sqrt{[L(L + 1) - M_L(M_L - 1)]} \\ \langle M_S - 1 | \widehat{S}_- | M_S\rangle &= \sqrt{[S(S + 1) - M_S(M_S - 1)]} \\ \langle M_L | \widehat{L}_z | M_L\rangle &= M_L \\ \langle M_S | \widehat{S}_z | M_S\rangle &= M_S \end{aligned}$$

From these formulæ we can see that the term  $\frac{1}{2}\lambda\widehat{L}_+\widehat{S}_-$  mixes  $|0, \frac{1}{2}\rangle$  with a little bit of  $|1, -\frac{1}{2}\rangle$ , but that  $\frac{1}{2}\lambda\widehat{L}_-\widehat{S}_+$  cannot mix  $|0, \frac{1}{2}\rangle$  with anything because  $M_S$  cannot have the value  $3/2$ , and  $\lambda\widehat{L}_z\widehat{S}_z$  is also ineffective because when  $\widehat{L}_z$  operates on  $|0, \frac{1}{2}\rangle$  it multiplies it by the eigenvalue  $M_L = 0$ . The perturbed form of  $|0, \frac{1}{2}\rangle$  is therefore

$$|0, \frac{1}{2}\rangle + c |1, -\frac{1}{2}\rangle = |^{\frac{1}{2}}\rangle, \text{ say;}$$

the admixing coefficient  $c$  is given by

$$\begin{aligned} c &= \frac{\langle 1, -\frac{1}{2} | \lambda \widehat{L}_z \widehat{S}_z | 0, \frac{1}{2} \rangle}{E(0, \frac{1}{2}) - E(1, -\frac{1}{2})} = \frac{\frac{1}{2} \lambda \langle 1, -\frac{1}{2} | \widehat{L}_+ \widehat{S}_- | 0, \frac{1}{2} \rangle}{-\Delta} \\ &= -(\lambda/2\Delta) \langle 1 | \widehat{L}_+ | 0 \rangle \langle -\frac{1}{2} | \widehat{S}_- | \frac{1}{2} \rangle \\ &= -(\lambda/2\Delta) \sqrt{(2 \times 3 - 1 \times 0)} \sqrt{(\frac{1}{2} \times \frac{3}{2} - (-\frac{1}{2}) \times \frac{1}{2})} \\ &= -\sqrt{(3/2)} \lambda / \Delta \end{aligned}$$

In a precisely similar way we can demonstrate that the unperturbed state  $|0, -\frac{1}{2}\rangle$  becomes

$$|0, -\frac{1}{2}\rangle + c | -1, \frac{1}{2} \rangle = | " -\frac{1}{2} " \rangle, \text{ say,}$$

when the effect of spin-orbit coupling is taken into account.

We now observe that the states called  $| " \frac{1}{2} " \rangle$  and  $| " -\frac{1}{2} " \rangle$  are strictly degenerate in the absence of a magnetic field, and constitute what is known as a Kramers doublet.<sup>8</sup> A magnetic field will, however, resolve this degeneracy, and we now determine the splitting produced by fields in the  $z$  or  $x$  direction. A field  $H_z$  produces a perturbation  $\beta H_z (\widehat{L}_z + 2\widehat{S}_z)$ , and we have to find the matrix elements of this between the states  $| " \pm \frac{1}{2} " \rangle$ , in order to determine how they are mixed and to find the energy separation between the resulting pair of levels.

First,  $(\widehat{L}_z + 2\widehat{S}_z)$  has no matrix element between  $| " \frac{1}{2} " \rangle$  and  $| " -\frac{1}{2} " \rangle$  because the states  $|M_L, M_S\rangle$  are eigenstates of both  $\widehat{L}_z$  and  $\widehat{S}_z$ , and there are no such states common to  $| " \frac{1}{2} " \rangle$  and  $| " -\frac{1}{2} " \rangle$ . Hence only the diagonal elements are non-zero, and these are

$$\begin{aligned} \langle " \frac{1}{2} " | \beta H_z (\widehat{L}_z + 2\widehat{S}_z) | " \frac{1}{2} " \rangle &= \beta H_z [ \langle 0, \frac{1}{2} | (\widehat{L}_z + 2\widehat{S}_z) | 0, \frac{1}{2} \rangle \\ &\quad + c^2 \langle 1, -\frac{1}{2} | (\widehat{L}_z + 2\widehat{S}_z) | 1, -\frac{1}{2} \rangle ] \\ &= \beta H_z (1 + 0) = \beta H_z \end{aligned}$$

$$\text{and likewise } \langle " -\frac{1}{2} " | \beta H_z (\widehat{L}_z + 2\widehat{S}_z) | " -\frac{1}{2} " \rangle = -\beta H_z$$

Hence if the field is applied in the  $z$  direction we obtain just the same splitting, namely  $2\beta H_z$ , as we should if only the electron spin interacted with the field. We describe this situation by saying that  $g_{\parallel} = 2$ , where the subscript  $\parallel$  means parallel to the  $z$  axis.

The situation is different, however, if the field is applied in the  $x$  direction. Now the perturbation is  $\beta H_x (\widehat{L}_x + 2\widehat{S}_x)$ , which may be written  $\beta H_x (\frac{1}{2}\widehat{L}_+ + \frac{1}{2}\widehat{L}_- + \widehat{S}_+ + \widehat{S}_-)$ . This operator has no *diagonal* elements within the pair of states  $| " \pm \frac{1}{2} " \rangle$ , since each member of the Kramers doublet comprises two terms which differ in *both*  $M_L$  and  $M_S$ . The off-

<sup>8</sup> H. A. Kramers, "Quantum Mechanics", North-Holland Publ. Co., Amsterdam, 1957, p. 384.



diagonal elements, on the other hand, do not vanish, since each term in  $|\frac{1}{2}''\rangle$  is connected with one (or both) in  $|\frac{1}{2}'\rangle$  through one of the operators  $\widehat{L}_+$ ,  $\widehat{L}_-$ ,  $\widehat{S}_+$ , or  $\widehat{S}_-$ . The two off-diagonal terms

$$\langle \frac{1}{2}'' | \beta H_x (\widehat{L}_x + 2\widehat{S}_x) | \frac{1}{2}' \rangle \text{ and } \langle \frac{1}{2}' | \beta H_x (\widehat{L}_x + 2\widehat{S}_x) | \frac{1}{2}'' \rangle$$

are both equal to

$$\begin{aligned} \beta H_x [\langle 0, \frac{1}{2} | \widehat{S}_+ | 0, -\frac{1}{2} \rangle + \frac{1}{2} c \langle 0, \frac{1}{2} | \widehat{L}_+ | -1, \frac{1}{2} \rangle + \frac{1}{2} c \langle -1, -\frac{1}{2} | \widehat{L}_- | 0, -\frac{1}{2} \rangle] \\ = \beta H_x [1 + \frac{1}{2} c(\sqrt{6} + \sqrt{6})] = \beta H_x (1 - 3\lambda/\Delta) \end{aligned}$$

The two states, therefore, split into their sum and their difference, with a separation

$$2\beta H_x (1 - 3\lambda/\Delta)$$

and we describe this by saying that  $g_{\perp} = 2(1 - 3\lambda/\Delta)$ .

Abraham and Pryce<sup>9</sup> showed that the observable behaviour of this type of system could be described by what they called a "spin hamiltonian". The two splittings we have calculated, and the splitting which occurs if the field is applied in an arbitrary direction, are precisely what one would obtain if one *ignored the orbital angular momentum* and replaced its effect by an *anisotropic* coupling between the electron spin and the external magnetic field, of the form

$$\beta \mathbf{H} \cdot \mathbf{g} \cdot \widehat{\mathbf{S}} = \beta g_{\parallel} H_z \widehat{S}_z + \beta g_{\perp} (H_x \widehat{S}_x + H_y \widehat{S}_y)$$

Physically, the orbital angular momentum induced by the spin makes the latter easier to orient in some directions than in others, and this effect is what is represented by the spin hamiltonian. It may be noted that the axes of the  $g$  tensor must coincide with the symmetry axes of the system; thus we can use the observed anisotropy of the electron-resonance spectrum to determine the orientation of a paramagnetic unit in a crystalline lattice. An outstanding example of this was the determination of the orientations of the four hæm groups in the hæmoglobin crystal,<sup>10</sup> discussed below.

(ii) *The Ti<sup>3+</sup> ion in an octahedral environment.* We work out this example as well as the previous one, because the directional effects are much more pronounced. The situation is as illustrated in Fig. 3. This time we consider the Jahn-Teller distortion to be a slight compression of the octahedron in the direction of one of its three-fold axes, which we take as the  $z$  axis. Such a distortion occurs, for instance, in the compound CsTi(SO<sub>4</sub>)<sub>2</sub>, in which the site symmetry of the octahedrally co-ordinated Ti<sup>3+</sup> ion is trigonal.<sup>11</sup> In terms of the eigenstates of  $\widehat{L}_z$ , namely  $|M_L\rangle$ , the orbitals then take the forms indicated in Fig. 3, the lowest being  $|0\rangle$ , which is axially symmetrical about the  $z$  axis.

<sup>9</sup> A. Abraham and M. H. L. Pryce, *Proc. Roy. Soc.*, 1951, *A*, **205**, 135.

<sup>10</sup> J. Bennett, J. F. Gibson and D. J. E. Ingram, *Proc. Roy. Soc.*, 1957, *A*, **240**, 67.

<sup>11</sup> B. Bleaney *Proc. Phys. Soc.*, 1950, *A*, **63**, 407.

As in the previous example, the spin-orbit interaction mixes  $|0, \frac{1}{2}\rangle$  with states involving  $|1, -\frac{1}{2}\rangle$ , and mixes  $|0, -\frac{1}{2}\rangle$  with states containing  $|-1, \frac{1}{2}\rangle$ . Now since  $\delta$  is much smaller than  $\Delta$ , the mixing of  $|0\rangle$  with the two states immediately above it will be much larger than with the two

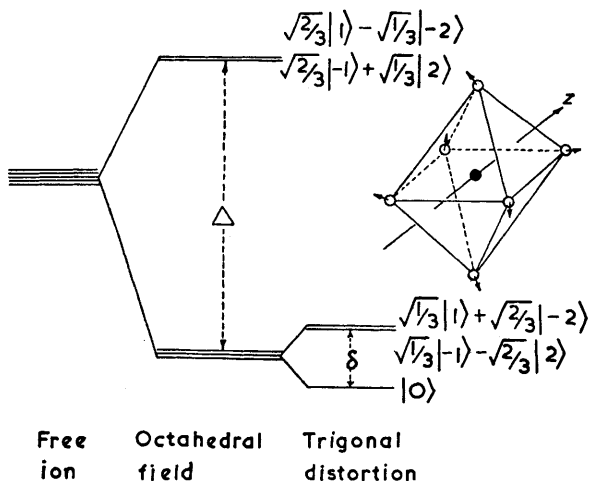


FIG. 3. Splitting of the orbitals of the  $Ti^{3+}$  ion in an octahedral field with a trigonal distortion.

states at the top of the diagram. The result is that the perturbed levels take the approximate forms

$$\sqrt{(1 - c^2)} |0, \frac{1}{2}\rangle + c[\sqrt{\frac{1}{3}} |1, -\frac{1}{2}\rangle + \sqrt{\frac{2}{3}} |-2, -\frac{1}{2}\rangle]$$

and

$$\sqrt{(1 - c^2)} |0, -\frac{1}{2}\rangle + c[\sqrt{\frac{1}{3}} |-1, \frac{1}{2}\rangle - \sqrt{\frac{2}{3}} |2, \frac{1}{2}\rangle]$$

where  $c$  is much larger than in the previous example. These states are split to different extents by magnetic fields in the  $z$  and the  $x$  direction; the corresponding  $g$ -values are found to be

$$g_{\parallel} = \frac{3(\delta + \lambda/2)}{\sqrt{[(\delta + \lambda/2)^2 + 2\lambda^2]}} - 1$$

$$g_{\perp} = \frac{(\delta - 3\lambda/2)}{\sqrt{[(\delta + \lambda/2)^2 + 2\lambda^2]}} + 1$$

In general, if the  $t_2$  shell in a distorted octahedral or tetrahedral complex is incompletely filled (but not if it is exactly half-filled) the observed splitting is much more sensitive to direction than if the odd electron (or hole) is in an  $e$  orbital.

### 5. Zero-field splittings

In the previous section we saw that for an ion with one d electron the degeneracy of the  ${}^2D$  term is largely lifted by the combined effects of the crystal field and spin-orbit coupling, but that there remains a two-fold degeneracy in each level which is only removed by an external magnetic field. Kramers<sup>8</sup> showed that this sort of degeneracy always occurs if the number of electrons is odd, because in the absence of a magnetic field a simultaneous reversal of the spin and orbital angular momenta leaves the energy unchanged. When, however, there is an even number of unpaired electrons the spin degeneracy of a triplet or quintet level may be removed entirely by the crystal field alone. We will now illustrate this effect, known as a "zero-field splitting", by the examples of the ferrate ion  $\text{FeO}_4^{2-}$ , the octahedrally co-ordinated  $\text{V}^{3+}$  ion, and the  $\text{Mn}^{2+}$  ion, in turn.

It is possible to grow single crystals of  $\text{K}_2\text{CrO}_4$  containing measurable amounts of the  $\text{FeO}_4^{2-}$  ion, and the spectrum of such a crystal shows, not a single resonance, but two resonance lines when the external magnetic field is applied in the crystallographic  $ab$  or  $ac$  planes.<sup>12</sup> Furthermore, the position of the resonance lines depends on the direction of the field relative to the crystal axes. We now discuss the interpretation of these results. Regarding the  $\text{FeO}_4^{2-}$  ion as a very strongly perturbed  $\text{Fe}^{6+}$  ion, we anticipate that its ground state has the electronic configuration  $3d^2$ . The ion is approximately tetrahedral, and the two 3d electrons will occupy the two orbitals of symmetry E, giving a  ${}^3A_2$  state. If the tetrahedral symmetry were perfect, the spin degeneracy of this triplet would be maintained, but an orthorhombic distortion is observed, which resolves the triplet into three components, with electronic spin parallel to the  $x$ ,  $y$ , and  $z$  axes of the distortion. (These symmetry arguments make it plausible that the splitting *can* occur; why it *does* occur we shall not discuss here.) Two of the axes of the distortion do not coincide with those of the crystal, but we shall indicate how the electron-resonance spectrum is determined by the directions in which the individual ions distort.

When discussing the  $\text{Ti}^{3+}$  ion we saw that it was possible to describe the behaviour of the levels by a spin hamiltonian of the form

$$\beta g_{\parallel} H_z \widehat{S}_z + \beta g_{\perp} (H_x \widehat{S}_x + H_y \widehat{S}_y)$$

We now seek a corresponding expression for the ferrate ion. In this we are guided by two considerations. First, since the effect of an external magnetic field would necessarily be isotropic if the ion were perfectly tetrahedral, we represent this interaction by the isotropic expression

$$\beta g (H_x \widehat{S}_x + H_y \widehat{S}_y + H_z \widehat{S}_z)$$

Secondly, we must have some anisotropic terms to represent the zero-field

<sup>12</sup> A. Carrington, D. J. E. Ingram, K. A. K. Lott, D. S. Schonland, and M. C. R. Symons, *Proc. Roy. Soc.*, 1960, *A*, 254, 101.

splitting, and these cannot involve  $\mathbf{H}$ . The simplest second-order expression which has the same symmetry as the orthorhombic field is

$$D_x \widehat{S}_x^2 + D_y \widehat{S}_y^2 + D_z \widehat{S}_z^2$$

We therefore adopt as our spin hamiltonian the form

$$\widehat{\mathcal{H}} = \beta g (H_x \widehat{S}_x + H_y \widehat{S}_y + H_z \widehat{S}_z) + D_x \widehat{S}_x^2 + D_y \widehat{S}_y^2 + D_z \widehat{S}_z^2$$

where  $D_x$ ,  $D_y$ , and  $D_z$  are constants with the dimensions of energy; their sum is taken to be zero. The problem is now to see what sort of electron-resonance spectrum emerges from such a spin hamiltonian.

What we must first do is to determine the possible spin states of the system and their energies. These are the eigenstates and eigenvalues of the spin hamiltonian. We therefore begin by determining the matrix elements of  $\widehat{\mathcal{H}}$  between the three levels  $|1\rangle$ ,  $|0\rangle$ , and  $|-1\rangle$  which are defined as the eigenstates of  $\widehat{S}_z$  with the eigenvalues  $M_S = 1, 0, -1$  respectively. To do this we require the matrix elements of the operators  $\widehat{S}_x$ ,  $\widehat{S}_y$ ,  $\widehat{S}_z$ ,  $\widehat{S}_x^2$ ,  $\widehat{S}_y^2$ , and  $\widehat{S}_z^2$ . We have already given expressions for determining the matrix elements of the operators  $\widehat{S}_+$  and  $\widehat{S}_-$  and the complete matrices are

$$\widehat{S}_+ = \begin{array}{c} \langle 1 | \\ \langle 0 | \\ \langle -1 | \end{array} \begin{array}{ccc} |1\rangle & |0\rangle & |-1\rangle \\ \left[ \begin{array}{ccc} 0 & \sqrt{2} & 0 \\ 0 & 0 & \sqrt{2} \\ 0 & 0 & 0 \end{array} \right] \end{array}$$

$$\widehat{S}_- = \begin{array}{c} \langle 1 | \\ \langle 0 | \\ \langle -1 | \end{array} \begin{array}{ccc} |1\rangle & |0\rangle & |-1\rangle \\ \left[ \begin{array}{ccc} 0 & 0 & 0 \\ \sqrt{2} & 0 & 0 \\ 0 & \sqrt{2} & 0 \end{array} \right] \end{array}$$

From the relations  $\widehat{S}_+ = \widehat{S}_x + i\widehat{S}_y$ ,  $\widehat{S}_- = \widehat{S}_x - i\widehat{S}_y$ , we see that  $\widehat{S}_x = \frac{1}{2}(\widehat{S}_+ + \widehat{S}_-)$  and  $\widehat{S}_y = -\frac{1}{2}i(\widehat{S}_+ - \widehat{S}_-)$ . Hence we can write down the matrices for  $\widehat{S}_x$ ,  $\widehat{S}_y$ , and  $\widehat{S}_z$ , remembering that  $|1\rangle$ ,  $|0\rangle$ , and  $|-1\rangle$  are eigenfunctions of  $\widehat{S}_z$ . These matrices are

$$\widehat{S}_x = \begin{bmatrix} 0 & 1/\sqrt{2} & 0 \\ 1/\sqrt{2} & 0 & 1/\sqrt{2} \\ 0 & 1/\sqrt{2} & 0 \end{bmatrix}$$

$$\widehat{S}_y = \begin{bmatrix} 0 & -i/\sqrt{2} & 0 \\ i/\sqrt{2} & 0 & -i/\sqrt{2} \\ 0 & i/\sqrt{2} & 0 \end{bmatrix}$$

$$\widehat{S}_z = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

The matrix elements of the operators  $\widehat{S}_x^2$ ,  $\widehat{S}_y^2$ , and  $\widehat{S}_z^2$  are obtained by simply squaring these matrices; the rules for matrix multiplication give

$$\begin{aligned}\widehat{S}_x^2 &= \begin{bmatrix} \frac{1}{2} & 0 & \frac{1}{2} \\ 0 & 1 & 0 \\ \frac{1}{2} & 0 & \frac{1}{2} \end{bmatrix} \\ \widehat{S}_y^2 &= \begin{bmatrix} \frac{1}{2} & 0 & -\frac{1}{2} \\ 0 & 1 & 0 \\ -\frac{1}{2} & 0 & \frac{1}{2} \end{bmatrix} \\ \widehat{S}_z^2 &= \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}\end{aligned}$$

We are now in a position to find the matrix elements of the spin hamiltonian. For instance, consider the matrix element  $\langle 1 | \widehat{\mathcal{H}} | 1 \rangle$ . This is expanded and evaluated as follows:

$$\begin{aligned}\langle 1 | \widehat{\mathcal{H}} | 1 \rangle &= g\beta[H_x \langle 1 | \widehat{S}_x | 1 \rangle + H_y \langle 1 | \widehat{S}_y | 1 \rangle + H_z \langle 1 | \widehat{S}_z | 1 \rangle] \\ &\quad + D_x \langle 1 | \widehat{S}_x^2 | 1 \rangle + D_y \langle 1 | \widehat{S}_y^2 | 1 \rangle + D_z \langle 1 | \widehat{S}_z^2 | 1 \rangle \\ &= g\beta[H_x \cdot 0 + H_y \cdot 0 + H_z \cdot 1] + D_x \cdot \frac{1}{2} + D_y \cdot \frac{1}{2} + D_z \cdot 1 \\ &= g\beta H_z + \frac{1}{2}(D_x + D_y) + D_z\end{aligned}$$

The other matrix elements are determined in precisely the same manner. The equation for the eigenvalues  $E$  and the eigenstates  $c_1 |1\rangle + c_0 |0\rangle + c_{-1} |-1\rangle$  therefore is

$$0 = \begin{bmatrix} g\beta H_z + \frac{1}{2}(D_x + D_y) + D_z - E, & \sqrt{\frac{1}{2}}g\beta(H_x - iH_y), & \frac{1}{2}(D_x - D_y) \\ \sqrt{\frac{1}{2}}g\beta(H_x + iH_y), & D_x + D_y - E, & \sqrt{\frac{1}{2}}g\beta(H_x - iH_y) \\ \frac{1}{2}(D_x - D_y), & \sqrt{\frac{1}{2}}g\beta(H_x + iH_y), & -g\beta H_z + \frac{1}{2}(D_x + D_y) + D_z - E \end{bmatrix} \begin{bmatrix} c_1 \\ c_0 \\ c_{-1} \end{bmatrix}$$

In principle we can now solve for the energies of the three levels but in practice it is better to examine the energies under different limiting conditions. First we consider the energy levels when no external field is applied. Putting  $H_x = H_y = 0$  and expanding the secular determinant as a cubic equation in  $E$ , we find that the three energies (and the corresponding states) are

$$\begin{aligned}D_y + D_x &: 0 \\ D_x + D_z &: \sqrt{\frac{1}{2}}(|1\rangle + |-1\rangle) \\ D_x + D_y &: \sqrt{\frac{1}{2}}(|1\rangle - |-1\rangle)\end{aligned}$$

Hence we see that the three spin levels have different energies even in zero magnetic field. We have determined these energies in terms of constants which, as we shall see shortly, are obtained from the behaviour of the spectrum in the presence of an external magnetic field.

Let us now examine the effect of a magnetic field  $H_x$  applied parallel to

the  $z$  axis ( $H_x = H_y = 0$ ). Returning to the secular equation we see that the energy of  $|0\rangle$  is unaffected by  $H_z$  whereas the other two energies are modified and are obtained by solving a quadratic equation in  $E$ . The roots of this equation are

$$E = \frac{1}{2}[2D_z + D_x + D_y \pm \sqrt{4(g\beta H_z)^2 + (D_x - D_y)^2}]$$

Provided the value of the term  $4(g\beta H_z)^2$  is large compared with that of  $(D_x - D_y)^2$ , the energies are, to a very good approximation:

$$\begin{aligned} &+ g\beta H_z + D_z + \frac{1}{2}(D_x + D_y) + (D_x - D_y)^2/8g\beta H_z \\ &- g\beta H_z + D_z + \frac{1}{2}(D_x + D_y) - (D_x - D_y)^2/8g\beta H_z \end{aligned}$$

(This approximation is equivalent to that of second-order perturbation theory.) Making use of the fact that  $D_x + D_y + D_z = 0$ , and neglecting the term  $(D_x - D_y)^2/8g\beta H_z$  we see that the energies and corresponding eigenstates are, for large values of  $H_z$ ,

$$\begin{aligned} g\beta H_z + \frac{1}{2}D_z &: |1\rangle \\ -g\beta H_z + \frac{1}{2}D_z &: |-1\rangle \\ -D_z &: |0\rangle \end{aligned}$$

and also

Now as indicated in section 2 the selection rule for transitions induced by an oscillating field perpendicular to the  $z$  axis is  $\Delta M_S = \pm 1$ . Hence the allowed transitions are, for large  $H_z$ ,

$$|0\rangle \longleftrightarrow |1\rangle \text{ and } |0\rangle \longleftrightarrow |-1\rangle$$

and their energies are, respectively,  $g\beta H_z + \frac{3}{2}D_z$  and  $g\beta H_z - \frac{3}{2}D_z$ . We now see why two absorption lines are observed for certain orientations of the crystal. (Actually the  $z$  axis turns out to be parallel to the crystallographic  $a$  axis for every  $\text{FeO}_4^{2-}$  ion in the crystal.) The general way in which the level separation varies with  $H_z$  is shown in Fig. 4. We note that when the field  $H_z$  is strong compared with the separation  $D_y - D_x$  (measured in gauss) the two resonances are separated by an amount  $3D_z$ . It is interesting that transitions between the levels whose asymptotic form is  $|1\rangle$  and  $|-1\rangle$  are induced by an oscillating field  $H'_z \cos 2\pi\nu t$  parallel to the permanent field  $H_z$  if the latter is not too strong. This is because the matrix element of  $\widehat{S}_z$  between the states  $\sqrt{\frac{1}{2}}(|1\rangle \pm |-1\rangle)$  is

$$\frac{1}{2}\langle 1|\widehat{S}_z|1\rangle - \frac{1}{2}\langle -1|\widehat{S}_z|-1\rangle = \frac{1}{2}(1 - (-1)) = 1 \neq 0$$

If, however, the permanent field becomes very strong, these transitions disappear, since  $\widehat{S}_z$  has no matrix element between the limiting forms of these states.

Our second example is the octahedrally co-ordinated  $\text{V}^{3+}$  ion, whose ground state would be one in which two electrons occupied  $t_{2g}$  orbitals

with parallel spins. We say "would be" because in fact the resulting level,  ${}^3T_{1g}$ , is orbitally degenerate and distorts in the manner indicated in Fig. 3, giving a complex of symmetry  $D_{3d}$ . The  ${}^3T_{1g}$  state therefore splits into a  ${}^3A_2$  and a  ${}^3E$  component, of which the former is the ground state (see Fig. 5).<sup>13</sup>

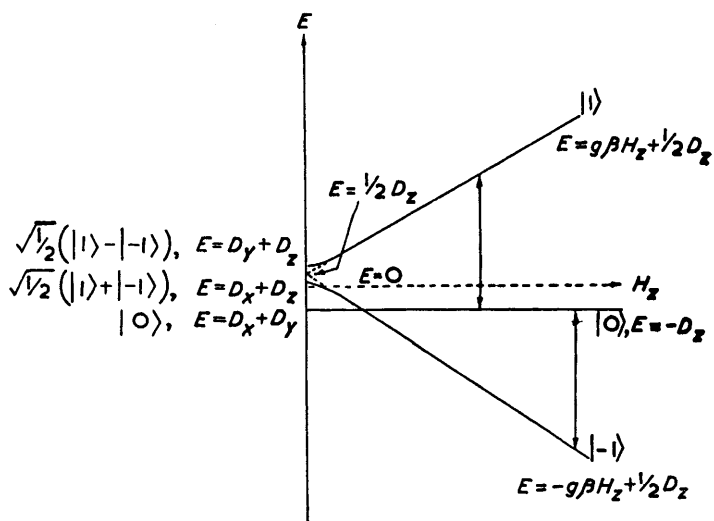


FIG. 4. Magnetic field dependence of levels of a spin triplet exhibiting a zero-field splitting.

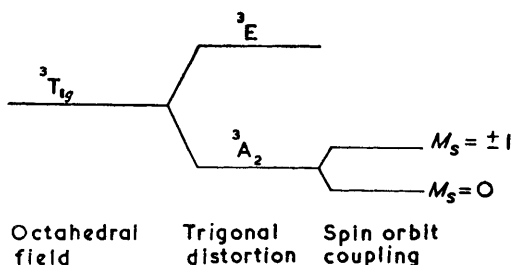


FIG. 5. Splitting of the ground state of an octahedrally co-ordinated  $V^{3+}$  ion.

Spin-orbit coupling further splits the  ${}^3A_2$  level into a non-degenerate level with  $M_S = 0$  and a doubly degenerate one with  $M_S = \pm 1$ , where the axis of quantisation of  $\hat{S}_z$  is the axis of trigonal distortion. This zero-field splitting is a good deal larger (about  $8 \text{ cm.}^{-1}$ )<sup>14</sup> than that in  $\text{FeO}_4^{2-}$  ( $D_x = 0.0504 \text{ cm.}^{-1}$ ,  $D_y = 0.0180 \text{ cm.}^{-1}$ ). The reason is that the spin-orbit

<sup>13</sup> M. H. L. Pryce and W. A. Runciman, *Discuss. Faraday Soc.*, 1958, 26, 34.

<sup>14</sup> G. M. Zverev and A. M. Prokorov, *J. Exp. Theor. Phys.*, 1958, 7, 707 (transl. of *Soviet Phys. English pagination*).

coupling operates by contaminating the  ${}^3A_2$  sublevels with the  ${}^3E$  sublevels, and this effect is large because of the small separation between the  ${}^3A_2$  and the  ${}^3E$  states; in  $\text{FeO}_4^{2-}$ , by contrast, there are no such low-lying excited states. The large zero-field splitting in  $\text{V}^{3+}$  makes impracticable the observation of electron resonance involving transitions with  $\Delta M_S = \pm 1$ ; it is possible however to observe weak transitions between the levels with  $M_S = \pm 1$  under certain rather special conditions.<sup>14</sup>

Our third example of a zero-field splitting is that of the  ${}^6S$  ( $d^5$ ) ground state of the  $\text{Mn}^{2+}$  ion in an octahedral field. We shall not go into details, but the splitting arises essentially in the following way. In the free ion spin-orbit coupling can mix together states with the same value of  $J$ ; hence the  ${}^6S_{5/2}$  state is slightly mixed with  ${}^4P_{5/2}$ , which in turn is contaminated with  ${}^2D_{5/2}$ . But a  ${}^2D$  state is split by an octahedral field for the same reason that the degeneracy of the  $d$  orbitals is lifted in such a field. This splitting reacts back on the  ${}^6S_{5/2}$  state, and this state consequently splits into a doublet and a quartet. The quartet is often found to split further into two doublets, as the result of distortion. The effect of an external magnetic field on these levels is shown in Fig. 6. The selection

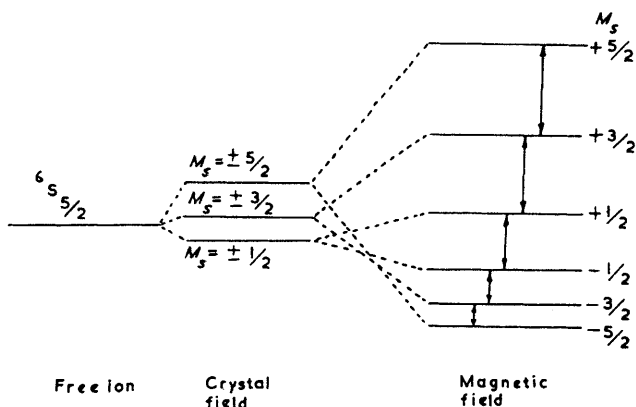


FIG. 6. Zero-field splitting in the  $\text{Mn}^{2+}$  ion, leading to fine structure in the electron-resonance spectrum.

rules permit the transitions indicated and the spectrum consists of five lines. This "fine structure" is further complicated by hyperfine structure due to interaction with the magnetic moment of the Mn nucleus.<sup>15</sup>

## 6. Rare-earth ions

The trivalent rare-earth ions have the electron configuration  $1s^2 2s^2 2p^6 \cdot 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^n 5s^2 5p^6$  where  $n$  runs from 0 ( $\text{La}^{3+}$ ) to 14 ( $\text{Lu}^{3+}$ ) and the paramagnetism thus arises from unpaired  $4f$  electrons. Although

<sup>15</sup> B. Bleaney and D. J. E. Ingram, *Proc. Roy. Soc.*, 1951, A, 205, 336.



the same perturbations as before must be introduced in order to explain the electron-resonance properties of these ions, the relative importance of these perturbations is now quite different. The 4f electrons are shielded by the outer electrons; consequently the crystal-field splittings are rather small and spin-orbit coupling is the dominant effect reducing the degeneracy of the ground state of the free ion. It will be remembered that to obtain the energy levels of the  $Ti^{3+}$  ion (which has one 3d electron) we first considered the effect of the crystal field in splitting the orbital levels apart, and only afterwards examined the effect of spin-orbit coupling in mixing levels with different spin and orbital quantum numbers. The situation with the rare-earth ions is the reverse, and as an example we consider the theory of the  $Ce^{3+}$  ion (with one 4f electron) in some detail.

The lowest electron configuration of the free  $Ce^{3+}$  ion is  ${}^2F$  ( $L = 3$ ,  $S = \frac{1}{2}$ ) which gives rise to a  ${}^2F_{5/2}$  ( $J = 3 - \frac{1}{2}$ ) and a  ${}^2F_{7/2}$  ( $J = 3 + \frac{1}{2}$ ) state, the former being the ground state. The energy separation between these two states arises from the spin-orbit coupling  $\lambda\widehat{L}\cdot\widehat{S}$  which may be written in the form

$$\lambda(\widehat{L}\cdot\widehat{S}) = \frac{1}{2}\lambda[(\widehat{L} + \widehat{S})^2 - \widehat{L}^2 - \widehat{S}^2] = \frac{1}{2}\lambda[\widehat{J}^2 - \widehat{L}^2 - \widehat{S}^2].$$

For the states  ${}^2F_{5/2}$  and  ${}^2F_{7/2}$ ,  $J$ ,  $L$ , and  $S$  are good quantum numbers, so that the expectation values of  $\widehat{J}^2$ ,  $\widehat{L}^2$ , and  $\widehat{S}^2$  are  $J(J+1)$ ,  $L(L+1)$ , and  $S(S+1)$  respectively. Hence the energy difference is just  $E({}^2F_{7/2}) - E({}^2F_{5/2}) = \frac{1}{2}\lambda[7/2(7/2+1) - 5/2(5/2+1)] = (7/2)\lambda$ , and has been found experimentally to have the value  $+2,250 \text{ cm.}^{-1}$ .

The simplest approximation that can usefully be made is to suppose that the ground state of the  $Ce^{3+}$  ion in the crystal is derived entirely from the  ${}^2F_{5/2}$  level of the free ion.<sup>16</sup> If the crystal field has the trigonal symmetry  $C_{3h}$  or  $D_{3h}$ , its effective potential splits the six-fold degenerate  ${}^2F_{5/2}$  ground state of the free ion into three Kramers doublets, which turn out to be eigenfunctions of the operator  $\widehat{J}_z$  with eigenvalues  $\pm\frac{1}{2}$ ,  $\pm\frac{3}{2}$ , and  $\pm\frac{5}{2}$  respectively. We shall not explain in detail why this happens, but merely write down the wave functions of the  $M_J = \pm\frac{1}{2}$  states, which are

$$|\frac{1}{2}\rangle = \sqrt{3/7}|0, \frac{1}{2}\rangle - \sqrt{4/7}|1, -\frac{1}{2}\rangle$$

$$\text{and } |-\frac{1}{2}\rangle = \sqrt{4/7}|-1, \frac{1}{2}\rangle - \sqrt{3/7}|0, -\frac{1}{2}\rangle$$

where the two numbers in each "ket" on the right-hand side are the eigenvalues  $M_L$ ,  $M_S$  of the operators  $\widehat{L}_z$ ,  $\widehat{S}_z$ . To calculate  $g_{\parallel}$  and  $g$  for transitions between these levels we need the matrix elements of  $\beta H_x(\widehat{L}_z + 2\widehat{S}_z)$  and  $\beta H_x(\widehat{L}_x + 2\widehat{S}_x)$ . The diagonal elements of the former are

$$\beta H_x \langle \frac{1}{2} | (\widehat{L}_z + 2\widehat{S}_z) | \frac{1}{2} \rangle = (3/7)\beta H_x$$

$$\text{and } \beta H_x \langle -\frac{1}{2} | (\widehat{L}_z + 2\widehat{S}_z) | -\frac{1}{2} \rangle = (-3/7)\beta H_x$$

<sup>16</sup> R. J. Elliott and K. W. H. Stevens, *Proc. Roy. Soc.*, 1952, A, 215, 437.

and there are no off-diagonal elements. Hence  $g_{\parallel} = 6/7 = 0.857$ . For a field applied in the perpendicular direction we have

$$\langle \frac{1}{2} | \beta H_x (\hat{L}_x + 2\hat{S}_x) | -\frac{1}{2} \rangle = (9/7)\beta H_x = \langle -\frac{1}{2} | \beta H_x (\hat{L}_x + 2\hat{S}_x) | \frac{1}{2} \rangle$$

and this time there are no diagonal elements. Hence  $g_{\perp} = 18/7 = 2.571$ .

Experimentally it is found<sup>17</sup> that a diluted single crystal of  $\text{Ce}^{3+}$  in lanthanum ethyl sulphate gives two resonances; one has  $g_{\parallel} = 0.955$ ,  $g_{\perp} = 2.185$ , and the other arises from a doublet about  $3 \text{ cm.}^{-1}$  higher, having  $g_{\parallel} = 3.72$ ,  $g_{\perp} = 0.2$ . The  $g$  values calculated for the  $M_J = \pm \frac{5}{2}$  doublet are 4.286 and 0 respectively. The situation is illustrated in Fig. 7.

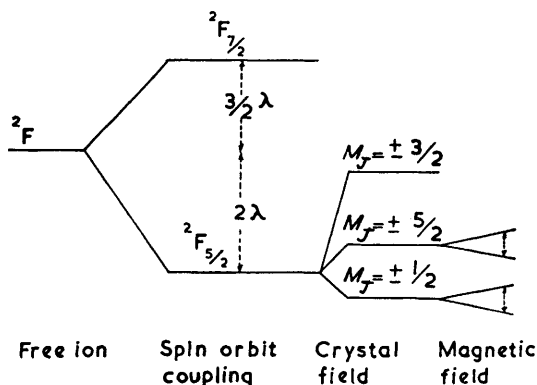


FIG. 7. Splitting of the ground state of the  $\text{Ce}^{3+}$  ion in a field of symmetry  $D_{3h}$ .

The  $M_J = \pm \frac{3}{2}$  doublet is apparently too high in energy to be appreciably populated at the temperatures of measurement.

In the foregoing paragraphs we have discussed only the very simplest rare-earth ion, with one  $4f$  electron, and have applied only the most elementary theory to it. A more accurate theory would allow for mixing of levels with different  $J$  under the influence of the crystal field.<sup>16</sup> Nevertheless, to ignore this effect in the rare earths leads only to a slightly inaccurate description, whereas in the transition-metal series it would be completely misleading to think of the ions in the crystal field as being in eigenstates of  $\hat{J}^2$ .

## 7. Nuclear hyperfine structure

As mentioned in section 2, the presence of one or more magnetic nuclei in a paramagnetic substance can impart to the electron-resonance spectrum a "hyperfine" structure in which each individual line arises from an elec-

<sup>17</sup> B. Bleaney, *Phil. Mag.*, 1951, **42**, 441.

tronic transition in which the nuclear spin (or spins) remains oriented in a particular direction. If there is one magnetic nucleus, with spin magnitude  $I$ , one may observe  $(2I + 1)$  hyperfine components since  $M_I$ , the eigenvalue of  $\hat{I}_z$ , can take any one of the  $(2I + 1)$  values  $-I, -I + 1, \dots, +I$ . These components are usually of equal intensity, and equally spaced. The magnitude of the spacing depends on two factors, (i) the resultant magnetic field and (ii) the electron spin density, at the given nucleus. These effects need separate discussion.

The magnetic field experienced by a nucleus arises from the spin and orbital angular momentum of the electrons revolving in its neighbourhood, the direct contribution of the external magnetic field being usually negligible. The contribution of a particular electron falls off inversely as the cube of its distance from the nucleus, so that electrons which do not get into the valency shell of an atom have a negligible effect on its nucleus. Another feature of this interaction is its directional character; for a given electronic level its average over all orientations of the molecule is zero. (This is why this particular interaction need not be considered in interpreting the electron-resonance spectra of paramagnetic species in liquid solution.)

The other factor determining the hyperfine spacing is the unbalance of electron spin in the immediate neighbourhood of the nucleus. This is the so-called Fermi contact interaction, and can arise only if some unpaired spin finds its way into s orbitals of the atom, because orbitals of pure p, d, and f type have vanishing amplitudes at the nucleus. When an external field is applied in a given direction, the spin of the electrons tends to become aligned in one of  $(2S + 1)$  directions (though spin-orbit coupling will partly upset this alignment), and the average direction of the electron spin near the nucleus will determine the axis of quantisation of the nuclear spin  $\hat{I}$ .

It may be noted that as far as any nucleus is concerned the effect of the external field is only to determine the manner in which the electrons move in its neighbourhood; the magnitude of the hyperfine spacing does not, therefore, depend on the strength of the external field but only on its direction (though in certain special circumstances this statement needs modification).

We have already mentioned briefly one situation in which the nuclear spin enters the hamiltonian for a paramagnetic substance; in section 2 we showed that the spin hamiltonian for the hydrogen atom could be written as

$$g\beta\mathbf{H}\cdot\hat{\mathbf{S}} + A\hat{\mathbf{S}}\cdot\hat{\mathbf{I}} + B\mathbf{H}\cdot\hat{\mathbf{I}}$$

and that the last term was negligible. Later we showed that, when allowance was made for the coupling between  $\hat{\mathbf{S}}$  and the orbital angular momen-

tum  $\widehat{\mathbf{L}}$ , the spin hamiltonian for an axially symmetrical system (excluding  $\widehat{\mathbf{I}}$ ) could be written as

$$g_{\perp}\beta(H_x\widehat{S}_x + H_y\widehat{S}_y) + g_{\parallel}\beta H_z\widehat{S}_z$$

where  $g_{\perp}$  and  $g_{\parallel}$  were not necessarily equal to one another or to 2.0023, the value for a free electron. These observations lead us to expect that in a situation in which both  $\widehat{\mathbf{L}}$  and  $\widehat{\mathbf{I}}$  enter the full hamiltonian it may still be possible to describe the spin-resonance properties of an axially symmetrical system by an effective hamiltonian of the form

$$g_{\perp}\beta(H_x\widehat{S}_x + H_y\widehat{S}_y) + g_{\parallel}\beta H_z\widehat{S}_z + A_{\perp}(\widehat{S}_x\widehat{I}_x + \widehat{S}_y\widehat{I}_y) + A_{\parallel}\widehat{S}_z\widehat{I}_z$$

This expression, suggested by analogy, can be justified by detailed analysis provided the direct effect of  $\mathbf{H}$  on the nucleus can be neglected and provided also that the nucleus has no quadrupole moment. (Terms in  $\widehat{S}_x^2$ ,  $H_z^2$ , etc., are also assumed to be negligible.) The eigenvalues of this effective hamiltonian can be found by methods similar to those already outlined.<sup>2</sup> For example, if the field  $\mathbf{H}$  is in the  $z$  direction, the spin hamiltonian becomes

$$g_{\parallel}\beta H_z\widehat{S}_z + A_{\parallel}\widehat{S}_z\widehat{I}_z + \frac{1}{2}A_{\perp}(\widehat{S}_+\widehat{I}_- + \widehat{S}_-\widehat{I}_+)$$

where  $\widehat{I}_+ = \widehat{I}_x + i\widehat{I}_y$  and  $\widehat{I}_- = \widehat{I}_x - i\widehat{I}_y$ . These operators operate on the nuclear spin states in precisely the same manner as the operators  $\widehat{S}_+$  and  $\widehat{S}_-$  operate on the electronic spin states. For an electronic doublet ( $M_S = \pm\frac{1}{2}$ ) and a nucleus of spin  $\frac{1}{2}$  ( $M_I = \pm\frac{1}{2}$ ), the matrix of the above hamiltonian within the set of states  $|M_S, M_I\rangle$  is

$$\begin{array}{c} \langle \frac{1}{2}, \frac{1}{2} | \\ \langle \frac{1}{2}, -\frac{1}{2} | \\ \langle -\frac{1}{2}, \frac{1}{2} | \\ \langle -\frac{1}{2}, -\frac{1}{2} | \end{array} \left[ \begin{array}{cccc} | \frac{1}{2}, \frac{1}{2} \rangle & | \frac{1}{2}, -\frac{1}{2} \rangle & | -\frac{1}{2}, \frac{1}{2} \rangle & | -\frac{1}{2}, -\frac{1}{2} \rangle \\ \frac{1}{2}g_{\parallel}\beta H_z + \frac{1}{4}A_{\parallel} & 0 & 0 & 0 \\ 0 & \frac{1}{2}g_{\parallel}\beta H_z - \frac{1}{4}A_{\parallel} & \frac{1}{2}A_{\perp} & 0 \\ 0 & \frac{1}{2}A_{\perp} & -\frac{1}{2}g_{\parallel}\beta H_z - \frac{1}{4}A_{\parallel} & 0 \\ 0 & 0 & 0 & -\frac{1}{2}g_{\parallel}\beta H_z + \frac{1}{4}A_{\parallel} \end{array} \right]$$

of which the eigenvalues are  $\frac{1}{4}A_{\parallel} \pm \frac{1}{2}g_{\parallel}\beta H_z$  and  $-\frac{1}{4}A_{\parallel} \pm \sqrt{[(\frac{1}{2}g_{\parallel}\beta H_z)^2 + (\frac{1}{2}A_{\perp})^2]}$ ; when  $A_{\perp} \ll g_{\parallel}\beta H_z$  the eigenvalues are therefore close to  $\pm\frac{1}{4}A_{\parallel} \pm \frac{1}{2}g_{\parallel}\beta H_z$ , as asserted in section 2.

## 8. Electron delocalisation

So far our discussion of transition-metal compounds has been based on the implicit assumption that the unpaired electrons are localised entirely in the valency shell of the metal ion. In reality, the unpaired electrons may be partly delocalised on to the ligands, or the ligand electrons may be partially delocalised into the metal orbitals. Electron resonance provides a sensitive method for the study of this effect,<sup>18,19</sup> as we shall now explain.

<sup>18</sup> K. W. H. Stevens, *Proc. Roy. Soc.*, 1953, *A*, **219**, 542.

<sup>19</sup> J. Owen, *Discuss. Faraday Soc.*, 1955, **19**, 127.

A quantitative definition of electron delocalisation may be obtained from the molecular-orbital theory, as follows. If  $\phi$  is one of the d orbitals of the metal, and  $\chi$  is a combination of ligand orbitals having the same symmetry as  $\phi$ , then a molecular orbital of the combined ion will have the form

$$\psi = \frac{\phi + \alpha\chi}{(1 + 2\alpha\sigma + \alpha^2)}$$

where  $\sigma$  is the overlap integral between  $\phi$  and  $\chi$ ;  $\alpha$  then measures the extent of delocalisation of an unpaired electron in the orbital  $\psi$ . Estimates of  $\alpha$  can be obtained in several ways, namely:

(a) *From the g values.* A convenient example is the  $\text{IrCl}_6^{2-}$  ion ( $t_{2g}^5$ ), whose electron-resonance spectrum can be observed in dilute solution in the diamagnetic crystal  $\text{K}_2\text{PtCl}_6$ .<sup>20</sup> The orbital of the "unpaired hole" is a d orbital of type  $t_{2g}$ , which can overlap  $\pi$ -wise with a suitable combination of Cl  $3p\pi$  orbitals. It has been shown that for  $\alpha = 0$ , when distortions of the ion are neglected, one should obtain an isotropic  $g$  value of 2, whereas for  $\alpha$  very large the  $g$  value would be isotropic with the value  $4/3$ . The actual value is 1.8, indicating<sup>18</sup> that  $\alpha^2/(1 + 2\alpha\sigma + \alpha^2)$  lies between 0 and 0.3. Roughly then, the extent of delocalisation  $\alpha^2$  must be about 15%.

It has been shown<sup>21</sup> that  $\sigma$ -bonding also results in a reduction of the  $g$  values. In the hydrated  $\text{Ni}^{2+}$  ion, for example, the (isotropic)  $g$  value should be

$$g = 2 - \frac{8\lambda}{(1 + \alpha^2)\Delta}$$

where  $\lambda$  is the  $\widehat{\mathbf{L}}\widehat{\mathbf{S}}$  coupling constant of the bound ion,  $\Delta$  is the crystal field splitting of the 3d orbitals and overlap has been neglected. Unfortunately this formula cannot be used to obtain a very accurate estimate of  $\alpha^2$ , since  $\lambda$  is known less accurately for the bound ion than for the free ion.

(b) *From ligand hyperfine structure.* An example of this is the electron-resonance spectrum of  $\text{IrCl}_6^{2-}$ , where electron transfer is revealed very directly by the appearance of chlorine hyperfine structure, superimposed upon the quartet hyperfine structure due to the iridium nucleus.<sup>20</sup> This phenomenon, like the reduced  $g$  value, is clearly due to partial transfer of Cl  $3p\pi$  electrons into the  $t_{2g}$  "hole" on the metal ion, resulting in a transfer of unbalanced spin in the opposite direction. For an arbitrary orientation of the  $\text{IrCl}_6^{2-}$  octahedron in the external magnetic field the Cl hyperfine structure is rather complicated, but if the field is applied along a Cl-Ir-Cl axis the two Cl nuclei on the axis split each Ir hyperfine line into a septet, whose spacing depends on  $\alpha^2$  and on the mean value of  $r^{-3}$  for an electron

<sup>20</sup> J. H. E. Griffiths, J. Owen and I. M. Ward, *Proc. Roy. Soc.*, 1953, A, 219, 526.

<sup>21</sup> M. Tinkham, *Proc. Roy. Soc.*, 1956, A, 236, 535, 549.

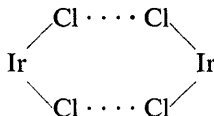
in a  $3p\pi$  Cl orbital. The value of  $\alpha^2$  obtained from the septet spacing is approximately 0.26, overlap being neglected.

(c) *From reduced metal hyperfine structure.* It is natural to suppose that delocalisation of the magnetic electrons on to the ligands will result in decreased interaction with the metal nucleus.<sup>22</sup> An example is the  $\text{Cu}(\text{H}_2\text{O})_6^{2+}$  ion, where transfer of electrons from the  $\text{H}_2\text{O}$  molecules into the  $e_g$  "hole" in the valency shell of the metal ion reduces the unpaired spin density in the neighbourhood of the Cu nucleus. Thus the Cu hyperfine spacing is appreciably smaller than would be expected from a calculation in which  $\alpha$  is set equal to zero.

Many other examples of these three effects have been found experimentally.

### 9. Exchange interaction

An important phenomenon which can be studied by electron-resonance methods is electron exchange between two paramagnetic ions in a crystal. This type of interaction has been studied<sup>23</sup> in salts of the  $\text{IrCl}_6^{2-}$  ion, the technique being to grow crystals in which 95% of the Ir atoms are replaced by diamagnetic Pt atoms. In these crystals there is an appreciable number of nearest-neighbour pairs of Ir ions which have no other Ir neighbours. The structure of such a nearest-neighbour pair can be represented diagrammatically thus:



We have already discussed the electron transfer which occurs in the  $\text{IrCl}_6^{2-}$  ion. The  $3p\pi$  electrons of the  $\text{Cl}^-$  ions spend 5% of their time on the  $\text{Ir}^{4+}$  ions and there is thus a certain definite probability of finding two chlorine atoms in neighbouring positions with spins either parallel or antiparallel; in the latter case we may think of an elongated  $\text{Cl}_2$  "molecule". The resulting energy levels are a triplet ( $S = 1$ ) at  $\frac{1}{2}K - g\beta H$ ,  $\frac{1}{4}K$ ,  $\frac{1}{4}K + g\beta H$ , and a singlet at  $-\frac{3}{4}K$ , where  $K$  is the Cl-Cl exchange energy, and one observes an electron-resonance spectrum arising from transitions between the levels of the triplet. The intensity of these transitions decreases as the temperature is lowered, indicating thermal depopulation of the triplet level. Thus the triplet lies above the singlet and the exchange is said to be antiferromagnetic.

Equally interesting examples of exchange coupling are found in some copper salts. In copper acetate<sup>24</sup> the fine structure of the spectrum is

<sup>22</sup> B. Bleaney, K. D. Bowers and M. H. L. Pryce, *Proc. Roy. Soc.*, 1955, *A*, **228**, 166.

<sup>23</sup> J. Owen, *Discuss. Faraday Soc.*, 1958, **26**, 53.

<sup>24</sup> B. Bleaney and K. D. Bowers, *Proc. Roy. Soc.*, 1952, *A*, **214**, 451.

characteristic of a triplet spin state and, in addition, the hyperfine structure shows that the odd electrons interact with two equivalent copper nuclei. This indicates that the copper ions interact strongly in pairs through exchange forces, each pair forming a paramagnetic triplet spin state and a lower diamagnetic singlet spin state. The nuclear spins of the two stable copper isotopes are both  $3/2$  and their magnetic moments are so close that, except under conditions of very high resolution, only one set of hyperfine lines is expected. This will normally consist of four lines with equal spacing and intensity. It is easy to show that two equivalent copper nuclei will give rise to seven lines with relative intensities 1:2:3:4:3:2:1 and this is just what is observed for copper acetate. The intensity of the electron-resonance spectrum again decreases as the temperature is lowered.

It is interesting to note that the deduction that the copper ions form isolated pairs was subsequently confirmed by *X*-ray crystallography; the Cu-Cu distance was found to be  $2.6\text{\AA}$ .

### 10. Univalent transition-metal ions

An interesting and recent development is the detection and study of some unipositive transition-metal ions, formed by irradiation of the bivalent ions present as impurities in single crystals such as NaF. We can best describe this by referring to one or two specific examples.<sup>25</sup>

Crystals of NaF to which  $\text{Cr}^{3+}$  has been added do not show resonance down to  $20^\circ\text{K}$ . This can be understood if the chromium is present as  $\text{Cr}^{2+}$ ; this ion, with an even number of unpaired electrons, might well not show resonance because of a large zero-field splitting of the spin quintet. However, on irradiation with  $\gamma$ -rays, *X*-rays, or high-energy electrons an isotropic spectrum appears, whose fine structure is characteristic of a  $^6\text{S}$  ground state. As in the spectrum of  $\text{Mn}^{2+}(3d^5, ^6\text{S})$ , metal hyperfine structure is observed but is found to arise from a nucleus with spin  $3/2$ , which is the spin of  $^{53}\text{Cr}$ . There is thus very good evidence that the spectrum observed is due to  $\text{Cr}^+(3d^5)$ .

Similarly when crystals of NaF containing  $\text{Fe}^{2+}$  ions are irradiated, a resonance line appears at  $20^\circ\text{K}$  with a *g* value of 4.344. This *g* value is very close to that observed for  $\text{Co}^{2+}$  in MgO crystals (4.278). However, the line observed is not due to the presence of cobalt as an impurity since the hyperfine structure characteristic of that metal is absent. The obvious conclusion is that it is due to  $\text{Fe}^+(3d^7)$  which is isoelectronic with  $\text{Co}^{2+}(3d^7, ^4\text{F})$ , but has no nuclear spin.

The Table summarises some of the available data for transition-metal-ion impurities in NaF and MgO, both of which have the NaCl crystal structure. While the *g* values are, in general, extremely sensitive to the local structure of the crystal, the results quoted have been chosen because

<sup>25</sup> W. Hayes, *Discuss. Faraday Soc.*, 1958, 26, 58.

No. of d electrons	Ion	Temp. (K)	<i>g</i> Value
d <sup>5</sup>	Mn <sup>2+</sup> (NaF)	Room temp.	2.00 ± 0.01
	Mn <sup>2+</sup> (MgO)	„	2.0014
	Fe <sup>3+</sup> (MgO)	„	2.0037
	Cr <sup>3+</sup> (NaF)	„	2.000
d <sup>6</sup>	Fe <sup>2+</sup> (MgO)	4°	3.428
	Mn <sup>2+</sup> (NaF)	Resonance not observed down to 20°K, but intensity of Mn <sup>2+</sup> spectrum decreases by 90% on irradiation	
d <sup>7</sup>	Co <sup>2+</sup> (MgO)	20°	4.278
	Co <sup>2+</sup> (NaF)	20	<i>g<sub>x</sub></i> = 4.3 <i>g<sub>y</sub></i> = 3.3 <i>g<sub>z</sub></i> = 5.7
	Fe <sup>3+</sup> (MgO)	20	4.15
	Fe <sup>3+</sup> (NaF)	20	4.344
d <sup>8</sup>	Ni <sup>2+</sup> (MgO)	77	2.227
	Co <sup>3+</sup> (NaF)	90	2.31
d <sup>9</sup>	Cu <sup>2+</sup> (MgO powder)		2.190
	Ni <sup>3+</sup> (NaF)	20	<i>g<sub>  </sub></i> = 2.766, <i>g<sub>⊥</sub></i> = 2.114

they refer to ions which probably have similar crystal environments. In these circumstances the *g* values provide strong evidence for the existence of the Cr<sup>3+</sup>, Fe<sup>3+</sup>, Co<sup>3+</sup>, and Ni<sup>3+</sup> ions in the irradiated crystals.

### 11. The investigation of crystal structures

It will by now be apparent that the electron-resonance spectrum of a compound is largely determined by its crystal structure. In some cases important features of an unknown crystal structure can be inferred from the electron-resonance spectrum. We have already quoted cupric acetate as a case in point, and another good example is provided by recent work on hæmoglobin and myoglobin and some of their derivatives.<sup>10</sup> In these substances the electron-resonance spectrum arises entirely from the co-ordinated iron atoms, so that the hæm groups can be studied without interference from the rest of the molecule. Fig. 8 represents the structure of one of the hæm units. The iron atom is centrally placed between the four nitrogen atoms; the hæm group is linked to the rest of the molecule through a fifth co-ordination point and various other groups can be attached at the sixth position (R). In the case of the "acid-met" derivative this position is occupied by a water molecule and Fig. 8 shows that the line joining the water molecule to the iron atom is an axis of local symmetry.

What one actually observes in studying "type A" myoglobin crystals is a pair of resonance lines whose *g* values depend differently upon the crystal



orientation. Each line has a minimum  $g$  value of 2.0 for one particular crystal orientation, and a maximum  $g$  value of 6.0 for any perpendicular orientation. This clearly indicates the presence of two h em groups in the unit cell, and the directions of minimum  $g$  value for the two groups may

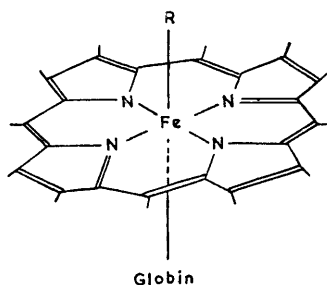


FIG. 8. *Immediate environment of an iron atom in h emoglobin.*

be identified with the Fe–R directions. The orientations of the h em groups in myoglobin and in h emoglobin were thus determined, relatively to the crystallographic axes, within an accuracy of  $2^\circ$  by electron resonance, before the recent comprehensive X-ray studies of these molecules had been completed.

## 12. Line widths

For a crystal in a perfectly uniform magnetic field, subjected to weak monochromatic microwave radiation, there are two main sources of line broadening, namely, spin–lattice and spin–spin interaction.

Spin–lattice interaction is the means whereby the magnetic energy of the paramagnetic ions is transferred to the vibrational degrees of freedom of the lattice. We have already seen that it is the spins of the electrons that mainly give rise to the magnetic energy; hence spin–lattice relaxation requires some kind of coupling between the electron spins and the varying electrostatic field due to the lattice motions. This coupling is none other than the spin–orbit interaction already discussed at some length.

If spin–lattice relaxation were the only source of line broadening, one would obtain a line of half-width  $\sim(2\pi\tau)^{-1}$  cycles where  $\tau$  is the relaxation time for transfer of energy from the spin system to the lattice. The magnitude of  $\tau$  is sensitive to two factors. First for a given substance  $\tau$  depends on the temperature, since as the temperature is raised the violence of the interatomic motion increases and the relaxation time is consequently shortened. Secondly, if we are comparing different substances,  $\tau$  will depend on the sensitivity of the  $g$  value to the geometry of the ionic environment. Thus  $\text{Mn}^{2+}$  has a long spin–lattice relaxation time, whereas the octahedrally co-ordinated  $\text{Ti}^{3+}$  ion, whose  $g$  values are sensitive to

small distortions, has a very much smaller value of  $\tau$  and only gives sharp lines at low temperatures. The sensitivity of the magnetic levels to the environment will, in general, be greater the smaller the excitation energy to higher magnetic states; hence line widths will, in general, be greater if there are low-lying excited states.

The other source of line broadening is direct interaction between different paramagnetic units. This is, of course, very small in paramagnetically dilute crystals, but becomes important in undiluted paramagnetic materials. There are two main mechanisms of spin-spin interaction; one is the direct dipole-dipole interaction between ions regarded as fixed bar magnets, and the other is exchange coupling of the electron spins, possibly mediated by intervening atoms (see section 9). Both mechanisms have the effect of replacing each  $N$ -fold degenerate state of a group of  $N$  independent ions by a set of  $N$  states differing slightly in energy. The result is that the various excitation energies are no longer exactly equal, and resonance is obtained over a range of magnetic fields. If the ions are non-equivalent, each resonance line is visibly broadened; if they are equivalent the line appears quite sharp ("exchange narrowing") but its fourth moment is actually greater than it would be if there were no exchange coupling.

It should be noted that varying the temperature has no effect upon spin-spin broadening, since the motion of the lattice does not alter significantly the distances between neighbouring ions.

One can, of course, study line widths with a view to evaluating spin-lattice relaxation times or spin-spin coupling constants. On the whole, however, the broadening of resonance lines is something that one tries to avoid experimentally, and this is best done by working with paramagnetically dilute crystals at low temperatures.