

SPIN-SPIN INTERACTION

9.1. Introduction

IN previous chapters we have been concerned primarily with the interactions of paramagnetic ions with external magnetic fields, treating them as single ions and ignoring any mutual interaction between the ions. We now consider the nature of such mutual interactions, and their effect on the paramagnetic resonance spectrum.

Since we are concerned with magnetic dipoles, the simplest and most obvious interaction between them is magnetic dipole-dipole interaction. If we know the location of each ion in the crystal lattice, and the magnetic properties of each ion, the magnetic dipole-dipole interaction between any pair can be calculated quite accurately. Unfortunately this is seldom true for interactions of other types, which may be of comparable or greater importance.

Since our magnetic moments are associated with electrically charged particles, there exists also an electrostatic interaction. It is well known that the quantum-mechanical treatment of this interaction leads to terms of two types, one of which is similar in form to the Coulomb interaction of classical physics, and which we shall call for brevity the 'Coulomb' interaction. The best known example of this is the 'electric quadrupole-quadrupole' interaction. Such interactions are of interest to us only in so far as they give an interaction energy that depends on the orientation of the magnetic dipoles. This requires that the magnetic moment be due in part to the orbital motion of the atomic electrons, since only the sub-states corresponding to different orientations of the orbital magnetic moment have different distributions of electric charge. The spin sub-states are involved only in so far as they are strongly coupled to the orbital sub-states by the spin-orbit coupling. Calculation of such 'Coulomb' interactions is handicapped by uncertainty in the magnitude of shielding (or anti-shielding) effects due to intervening ions, and by the lack of good radial electronic wave-functions. The same considerations apply to another type of multipole interaction in which one ion is coupled to another through the medium of the 'phonon radiation field' instead of the 'photon radiation field'.

Similar problems arise for a better known type of interaction, the 'exchange interaction', which involves the spin more directly. In most

cases of interest to us this interaction arises through partial electron transfer to intervening ('ligand') ions, and in magnitude the exchange interaction varies widely. If its energy is large or comparable with the microwave quantum involved in a magnetic resonance transition, the spectrum may be altered quite drastically. If the exchange energy is small compared with the microwave quantum, it affects primarily the shape and width of the resonance line. The latter is true generally for the magnetic and Coulomb interactions mentioned above, which seldom exceed 10^{-1} cm^{-1} in energy.

In §§ 9.2–9.4 we consider the form of these interactions in more detail. In the later sections we shall restrict the discussion to interactions of the form

$$\mathcal{H} = \mathbf{S}_i \cdot \mathcal{J} \cdot \mathbf{S}_j = \sum_{p,q} \mathcal{J}_{p,q} S_{ip} S_{jq}, \quad (9.1)$$

where $p, q = x, y, z$ and S_i, S_j are the effective spins for ions i, j . Obviously $\mathcal{J}_{p,q}$ may be different for every pair of ions, and suffixes (i, j) are needed but were omitted here for simplicity. The magnitude of \mathcal{J} embraces all contributions to spin-spin interaction which take the form (9.1), whatever their source.

9.2. Magnetic dipole-dipole interaction

In an ordinary paramagnetic crystal the magnetic ion is surrounded by other magnetic ions at minimum distances ~ 0.3 to 0.8 nm . There is therefore an appreciable interaction between them, since the field acting on one ion due to its neighbour is of order βr^{-3} , which may be 10^2 G or so. This interaction is known as dipole-dipole coupling, since it is in a first approximation the same as the coupling between two localized magnets. From classical theory the energy of two point magnetic dipoles \mathbf{m}_i and \mathbf{m}_j , a distance r apart, is

$$W = r^{-3} \{ \mathbf{m}_i \cdot \mathbf{m}_j - 3r^{-2} (\mathbf{m}_i \cdot \mathbf{r})(\mathbf{m}_j \cdot \mathbf{r}) \}. \quad (9.2a)$$

For a pair of isotropic electronic dipoles we can write

$$\mathbf{m}_i = -g_i \beta \mathbf{S}_i, \quad \mathbf{m}_j = -g_j \beta \mathbf{S}_j,$$

so that (9.2a) becomes, in operator form,

$$\mathcal{H} = g_i g_j \beta^2 r^{-3} \{ \mathbf{S}_i \cdot \mathbf{S}_j - 3r^{-2} (\mathbf{S}_i \cdot \mathbf{r})(\mathbf{S}_j \cdot \mathbf{r}) \}. \quad (9.2b)$$

If the direction cosines of \mathbf{r} are (l, m, n) , this can be expanded:

$$\begin{aligned} \mathcal{H} = g_i g_j \beta^2 r^{-3} \{ & S_{ix} S_{jx} (1 - 3l^2) + S_{iy} S_{jy} (1 - 3m^2) + S_{iz} S_{jz} (1 - 3n^2) - \\ & - (S_{ix} S_{jy} + S_{iy} S_{jx}) 3lm - (S_{iy} S_{jz} + S_{iz} S_{jy}) 3mn - \\ & - (S_{iz} S_{jx} + S_{ix} S_{jz}) 3nl \}, \quad (9.3) \end{aligned}$$

which is a symmetric tensor type interaction. Here it has been assumed that the dipoles are isotropic, but electronic dipoles in a solid are often anisotropic. We then require an expression for the energy of interaction of one anisotropic magnet in the field of the other (anisotropic) magnet. For a field component H_x in the x -direction the energy of such a magnet is

$$-m_x H_x = \beta H_x (g_{xx} S_x + g_{xy} S_y + g_{xz} S_z)$$

and it can be shown that (9.2a) is correct provided that for a component of a dipole moment such as m_x we write

$$m_x = -\beta (g_{xx} S_x + g_{xy} S_y + g_{xz} S_z). \quad (9.4)$$

The resultant formula can be written in the form

$$\mathcal{H} = \beta^2 r^{-3} S_{ip} S_{jq} \{g_{ips} g_{jq s} - (3st/r^2) g_{ips} g_{jq t}\}, \quad (9.5)$$

where each of the suffixes p, q, s, t takes the values x, y, z , and the usual summation rules are to be observed whenever a suffix occurs twice. This is not in general a symmetric tensor, though it may be symmetric in special cases. Two such examples are:

(a) the two ions are identical and the principal axes of their g -tensors are parallel. The tensor is symmetric provided that the coefficient of $S_{ip} S_{jq}$ is the same as that of $S_{iq} S_{jp}$; since S_i, S_j commute, interchange of (p, q) is equivalent to interchange of (i, j) , and provided that all components $g_i = g_j$, such an interchange has no effect on the coefficients of each term. This result can also be obtained directly by taking the principal axes as the (x, y, z) axes, in which case the components in (9.2a) are all of the simple form $m_x = -\beta g_x S_x$, etc., giving

$$\mathcal{H} = \beta^2 r_{ij}^{-3} \left\{ \begin{aligned} &(1-3l^2)g_{ix}g_{jx}S_{ix}S_{jx} + (1-3m^2)g_{iy}g_{jy}S_{iy}S_{jy} + \\ &+ (1-3n^2)g_{iz}g_{jz}S_{iz}S_{jz} - \\ &- 3lm(g_{ix}g_{jy}S_{ix}S_{jy} + g_{iy}g_{jx}S_{iy}S_{jx}) - \\ &- 3mn(g_{iy}g_{jz}S_{iy}S_{jz} + g_{iz}g_{jy}S_{iz}S_{jy}) - \\ &- 3nl(g_{iz}g_{jx}S_{iz}S_{jx} + g_{ix}g_{jz}S_{ix}S_{jz}) \end{aligned} \right\} \quad (9.5a)$$

which is clearly symmetric provided that $g_{ix} = g_{jx}$, etc.

(b) the two ions have parallel principal axes for their g -tensors, and the line joining them lies along one of these common principal axes. Taking the latter as the z -axis, we have $l = m = 0, n = 1$, and (9.5a) becomes

$$\mathcal{H} = \beta^2 r_{ij}^{-3} \{g_{ix}g_{jx}S_{ix}S_{jx} + g_{iy}g_{jy}S_{iy}S_{jy} - 2g_{iz}g_{jz}S_{iz}S_{jz}\} \quad (9.5b)$$

where the g -values are not necessarily the same for the two ions.

It is readily verified that (9.3) is a traceless tensor, but in general (9.5), (9.5a), and (9.5b) are not.

So far we have considered only the interaction between point dipoles, but in a magnetic ion the dipole moment is distributed, and in a magnetic complex it may be distributed over the ligands. If the distribution is spherically symmetric, as in the spin magnetism of an ion in the S -state of a half-filled shell, simple magnetostatic theory shows that its magnetic potential at exterior points is the same as that of a point dipole at the centre. If it does not have spherical symmetry, the magnetic potential can be expanded in a power series where the leading term corresponds to the potential of the equivalent point dipole. If the magnetic moment distribution has a centre of symmetry, terms in the expansion of the *potential* with odd powers in r will vanish, and the next most important term after the dipolar term in the magnetic *energy* of interaction between two ions will vary as r^{-5} . At small inter-ionic distances where this term might be significant the magnetic interaction energy is generally unobservable because of exchange interaction.

Hitherto we have assumed that the magnetic moment of an ion is given by $\mathbf{m} = -\beta(\mathbf{g} \cdot \mathbf{S})$ of which a typical component is given in eqn (9.4). This assumption is justified if only the first-order Zeeman interaction of an ion with a magnetic field is important. More generally the Zeeman interaction can be written as a power series of the form (for $S = \frac{1}{2}$)

$$W_{\pm} = \pm \frac{1}{2}g\beta H - \alpha_1 H^2 \pm \alpha_2 H^3 + \text{etc.}$$

In a resonance experiment we have for the $|+\rangle \leftrightarrow |-\rangle$ transition

$$h\nu = g\beta H + 2\alpha_2 H^3 + O(H^5)$$

and the third and higher odd-order Zeeman terms appear as small corrections to the g -factor. However the effective magnetic moment at field H is

$$-(dW/dH) = \mp \frac{1}{2}g\beta + 2\alpha_1 H \mp 3\alpha_2 H^2, \text{ etc.}$$

and in an experiment at high magnetic field the second term may well be significant, giving changes of opposite sign in the apparent magnetic moment for the $|+\rangle$ and $|-\rangle$ states. An extreme case is the Γ_3 doublet in a cubic field, such as the ground state of Dy^{2+} in CaF_2 ; this is non-magnetic ($g = 0$) at $H = 0$, but the presence of low-lying excited states gives the rather complicated Zeeman splitting shown in Fig. 5.6. Clearly the magnetic dipolar interaction of such an ion with another ion is more complex than (9.3), and in general it may be necessary to

allow for a field dependence in the ionic magnetic moment, with different effective moments in reversed orientations in the presence of an external magnetic field. Of course similar effects arise from the mutual magnetic interaction of two ions, but the magnetic field of one ion acting on a neighbouring ion is $\sim 10^3$ G, while the external field may be 10^4 to 10^5 G.

9.3. Exchange interaction

The theory of exchange interaction in insulators has been extensively reviewed by Anderson (1963), and the complexities of this subject will not be explored here. A common assumption is that the main interaction is of the form

$$\mathcal{H}_{\text{ex}} = \mathcal{J}_{ij}(\mathbf{S}_i \cdot \mathbf{S}_j), \quad (9.6)$$

where \mathbf{S}_i , \mathbf{S}_j are the true spins and not the effective spins. When $S > \frac{1}{2}$, this equation may only be the leading term of a series expansion in which higher terms (Stevens 1953*b*) such as $(\mathbf{S}_i \cdot \mathbf{S}_j)^2$ occur; the effect of such a term is considered briefly at the end of § 9.10.

In most paramagnetic crystals exchange interaction is not of the simple type arising from direct overlap of the electronic wave-functions discussed by Heisenberg and Dirac, but is due to super-exchange. The theory of Anderson (1959) has been extended by Moriya (1960) to include spin-orbit coupling, and the exchange energy then no longer takes the simple scalar form of eqn (9.6) ('isotropic exchange') but becomes 'anisotropic'. Moriya shows that in addition to the scalar term there may be other terms of the form

$$\mathbf{D} \cdot [\mathbf{S}_i \wedge \mathbf{S}_j] \quad (9.7)$$

and

$$\mathbf{S}_i \cdot \mathcal{J}_{ij} \cdot \mathbf{S}_j, \quad (9.8)$$

where the second term has the nature of a symmetrical tensor while the first is an antisymmetric tensor, with components of the form

$$D_x(S_{iv}S_{jz} - S_{iz}S_{jv}).$$

It is obvious that the form (9.1) can include both (9.6) and (9.7) if we allow \mathcal{J}_{ij} to have the form of a general tensor that is not necessarily symmetric nor traceless.

The term (9.7) was proposed on symmetry grounds by Dzialoshinski (1958) and vanishes for pairs of ions embedded in a lattice under certain symmetry conditions. Moriya showed that it is of order $(\Delta g/g)$ times the isotropic super-exchange energy, while the magnitude of the

interaction (9.8) is of order $(\Delta g/g)^2$ times the isotropic exchange, on the assumption that the ground state is an orbital singlet and the spin-orbit coupling is small compared with the crystal field splitting of the orbital states. This latter condition means that the departure Δg of the g -value from the spin-only value is rather small. However in many salts the orbital moment is far from quenched, and in these cases the anisotropic exchange interaction, expressed in terms of the effective spins, can easily become as important as the isotropic exchange, or even predominate. This can easily be seen by taking two examples.

Example 1: a rare-earth salt

We assume an isotropic interaction of the form (9.6) between the true spins. If admixture of states of different \mathbf{J} can be neglected, so that only matrix elements within the ground manifold with a single value of \mathbf{J} need be considered, the spin \mathbf{S} can be projected onto \mathbf{J} . From the equivalences $\mathbf{L} + \mathbf{S} = \mathbf{J}$, $\mathbf{L} + 2\mathbf{S} = g_J\mathbf{J}$, this projection is $(g_J - 1)\mathbf{J}$, and for a pair of identical ions the interaction may be written as

$$\mathcal{H}_{\text{ex}} = (g_J - 1)^2 \mathcal{J}_{ij}(\mathbf{J}_i \cdot \mathbf{J}_j). \quad (9.9)$$

Suppose that the crystal-field splitting leaves ground states of effective spin \mathbf{S} , with an anisotropic splitting factor \mathbf{g} , whose principal values are (g_x, g_y, g_z) . Then since we have the equivalence between the matrix elements

$$g_x \tilde{S}_x \equiv g_J J_x, \text{ etc.},$$

the exchange interaction between a pair of identical ions in the ground doublet becomes, in terms of the effective spins,

$$\mathcal{H}_{\text{ex}} = \mathcal{J}_x \tilde{S}_{ix} \tilde{S}_{jx} + \mathcal{J}_y \tilde{S}_{iy} \tilde{S}_{jy} + \mathcal{J}_z \tilde{S}_{iz} \tilde{S}_{jz} \quad (9.10)$$

where

$$\mathcal{J}_x = (g_x/g_J)^2 (g_J - 1)^2 \mathcal{J}_{ij}, \text{ etc.} \quad (9.11)$$

This interaction is of the form of eqn (9.1). It has the same principal axes as the g -tensor, but can be highly anisotropic; for example, in cases with axial symmetry, such as the ethylsulphates, we may have $g_x = g_y = 0$, while g_z^2 may be of order 100.

Example 2; a cobaltous salt

Similar relations can be deduced for salts of the iron group when the orbital momentum is not completely 'quenched'. We take as an

example a cobaltous ion, Co^{2+} , $3d^7$, in an octahedral crystal field, where the orbital degeneracy of the $L = 3$ manifold is partially lifted, leaving a Γ_4 orbital triplet as the lowest level. This triplet behaves like a manifold with effective orbital momentum $\tilde{l} = 1$ (see §§ 7.14, 19.3), and an effective orbital g -factor \tilde{g}_l , which for our purposes we can assume to have the uncorrected value $-\frac{3}{2}$. We have also a fourfold spin degeneracy, with $S = \frac{3}{2}$.

Under the action of spin-orbit coupling, the orbital triplet ($\tilde{l} = 1$) with $S = \frac{3}{2}$ splits into a doublet, a quartet, and a sextet with effective angular momenta $\tilde{J} = \frac{1}{2}, \frac{3}{2},$ and $\frac{5}{2}$ respectively. The doublet is lowest, and its Zeeman splitting corresponds to a g -factor given by an equivalent Landé formula

$$g = \frac{1}{2}(\tilde{g}_l + g_s) + \frac{(\tilde{g}_l - g_s)\{\tilde{l}(\tilde{l}+1) - S(S+1)\}}{2\tilde{J}(\tilde{J}+1)}. \quad (9.12)$$

To find the effective exchange interaction for a pair of ions both in this doublet state, we project the true spin S onto \tilde{J} , using the relations

$$\tilde{g}_l \tilde{\mathbf{I}} + g_s \mathbf{S} \equiv g \tilde{\mathbf{J}}; \quad \tilde{\mathbf{I}} + \mathbf{S} \equiv \tilde{\mathbf{J}}, \quad (9.13)$$

from which

$$\tilde{\mathbf{S}} \equiv \{(g - \tilde{g}_l)/(g_s - \tilde{g}_l)\} \mathbf{J}. \quad (9.14)$$

Using the values $\tilde{g}_l = -\frac{3}{2}$, $g_s = 2$ we find that $g = \frac{1}{3}$ and $\mathbf{S} \equiv (\frac{5}{3})\tilde{\mathbf{J}}$. The latter factor enters twice in evaluating the exchange interaction for a pair of ions, and on reverting to our usual nomenclature of effective spin $\tilde{\mathbf{S}}$ instead of $\tilde{\mathbf{J}}$ we find that we have the equivalence

$$\mathcal{J}(\mathbf{S}_i \cdot \mathbf{S}_j) = (\frac{5}{3})^2 \mathcal{J}(\tilde{\mathbf{S}}_i \cdot \tilde{\mathbf{S}}_j). \quad (9.15)$$

Thus the effective exchange interaction for the ground doublet is isotropic, as we should expect from our initial assumption of cubic (octahedral) symmetry and an isotropic exchange interaction between the true spins. The latter is not, however, necessarily correct (see below).

A multiplying factor that is so simply related to the g -factor is no longer to be expected in the presence of lower symmetry. If there is a small distortion of axial symmetry, we may write the ground state as a Kramers doublet of the general form

$$a |\mp \tilde{1}, \pm \frac{3}{2}\rangle + b |\tilde{0}, \pm \frac{1}{2}\rangle + c |\pm \tilde{1}, \mp \frac{1}{2}\rangle, \quad (9.16)$$

where each state $|\tilde{l}_z, S_z\rangle$ belongs to the Γ_4 triplet with effective orbital

angular momentum $\tilde{l} = 1$ and $S = \frac{3}{2}$. The Zeeman interaction within the doublet can be evaluated using either the usual operator $\mathbf{L} + g_S \mathbf{S}$ or its equivalent form for the Γ_4 triplet, $\tilde{g}_l \tilde{\mathbf{L}} + g_S \mathbf{S}$, with $\tilde{g}_l = -\frac{3}{2}$ and $g_S = 2$ as above. In terms of an effective spin $\tilde{S} = \frac{1}{2}$, the doublet then has the principal values for its anisotropic g -factor

$$\begin{aligned} g_{\parallel} &= 9a^2 + 2b^2 - 5c^2, \\ g_{\perp} &= 4\sqrt{3}ac + 4b^2 - 3\sqrt{2}bc. \end{aligned} \quad (9.17)$$

However to convert an exchange interaction $\mathcal{J}(\mathbf{S}_i \cdot \mathbf{S}_j)$ into the equivalent interaction in terms of the effective spins $\tilde{\mathbf{S}}$, the matrix elements of \mathbf{S} are needed. It is easily found from (9.16) that we have then

$$\begin{aligned} \mathcal{J}(\mathbf{S}_i \cdot \mathbf{S}_j) &\equiv \mathcal{J}\{(3a^2 + b^2 - c^2)^2 \tilde{S}_{iz} \tilde{S}_{jz} + \\ &\quad + (2\sqrt{3}ac + 2b^2)^2 (\tilde{S}_{ix} \tilde{S}_{jx} + \tilde{S}_{iy} \tilde{S}_{jy})\}, \end{aligned} \quad (9.18)$$

from which it is clear that the coefficients are not simply related to the g -values, unlike the formulae (9.11) for the rare-earth salt. The case of cubic symmetry is, of course, an exception; the coefficients then are $a = 1/\sqrt{2}$, $b = -1/\sqrt{3}$, $c = 1/\sqrt{6}$, for which it can be verified that (9.18) reduces to (9.15).

These two examples illustrate how an exchange interaction, isotropic in terms of the true electron spins, can become highly anisotropic when expressed in terms of the effective spins provided that the orbital momentum is not completely quenched. Under the latter circumstances it is not necessarily true that the exchange interaction is isotropic even when expressed in terms of the true spins, as can readily be seen by considering the case of direct exchange due to overlap of the orbital wave-functions of two ions. Anisotropy arises when the spin and orbit are closely coupled, so that a given component of the spin may be associated with a given orbital wave-function that has a lobe extending in the direction of a neighbouring ion, while a different spin component may be associated with an orbital wave-function with minimal extension in this particular direction. It is clear that the overlap, and hence the exchange integral itself, can then change markedly according to the orientation of the true spin, and the exchange interaction will be anisotropic in the true spins, as in eqn (9.8).

Similar remarks hold for indirect exchange. It has been shown theoretically (Judd 1959c) and experimentally (Griffiths, Owen, Park, and Partridge 1959) that, even for magnetic complexes that individually have octahedral symmetry, the exchange interaction is not

necessarily isotropic in terms either of the true or the effective spins when considerable orbital momentum is involved. The only symmetry restriction is that the exchange interaction must have a form compatible with the overall symmetry, which is necessarily less than cubic for an assembly of two complexes.

9.4. Multipole interactions

In addition to magnetic dipole and exchange interactions between a pair of ions, there may also be a 'Coulomb' interaction between them. Suppose we have two ions, i, j separated by a distance R , as in Fig. 9.1. Then each electron on ion i will be subjected to an electric field set up by the electronic and nuclear charges on ion j . The electrostatic energy of a pair of electrons, one at a point (x_i, y_i, z_i) relative to the centre of ion i , the other at a point (x_j, y_j, z_j) relative to the centre of ion j , is

$$\frac{e^2}{\epsilon\{(x_i - x_j)^2 + (y_i - y_j)^2 + (R + z_i - z_j)^2\}^{\frac{1}{2}}} \quad (9.19)$$

if for simplicity we take the line joining the centres of the two ions to lie along the z -axis of the coordinate system. In this equation ϵ is a 'dielectric constant' that allows for shielding effects due to the induced charges on intervening ions; it may be <1 , corresponding to an anti-shielding effect. If the 'medium' is anisotropic the 'dielectric constant' may also be anisotropic but this is a complication that we shall neglect.

If $R \gg x_i, x_j$, etc., we can expand (9.19) in inverse powers of R . We are, of course, interested only in those terms that vary with the magnetic sub-state of each ion. If the charge distribution on each ion does not have inversion symmetry, there may also be an electric dipole moment and an electric-dipole interaction. As an example, we take a pair of ions with non-Kramers doublets as ground states, such as Pr^{3+} in LaCl_3 . For nearest neighbours along the symmetry axis, the net interaction may be of the form

$$\mathcal{J}_\perp(S_{ix}S_{jx} + S_{iy}S_{jy}) + \mathcal{J}_\parallel S_{iz}S_{jz},$$

where the first term is due to electric dipole-dipole interaction and the last to magnetic dipole and/or exchange interaction.

The next term in the expansion of (9.19) is the quadrupole-quadrupole

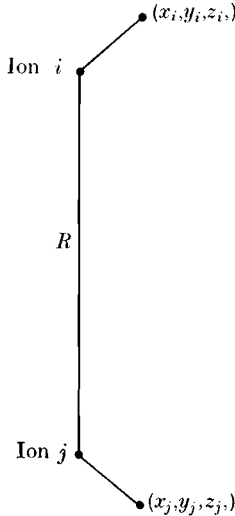


FIG. 9.1. Coordinate systems used in evaluating the electrostatic interaction between a pair of ions i, j whose centres are a distance R apart. The coordinate systems (x_i, y_i, z_i) , (x_j, y_j, z_j) have parallel axes but their origins are at the centre of each ion respectively; the z -axes are taken to be parallel to the line joining the two centres.

interaction

$$\frac{3e^2}{8\epsilon R^5} \left[\begin{aligned} &4(3z_i^2 - r_i^2)(3z_j^2 - r_j^2) - \\ &-16z_i z_j \{(x_i + iy_i)(x_j - iy_j) + (x_i - iy_i)(x_j + iy_j)\} + \\ &+(x_i + iy_i)^2(x_j - iy_j)^2 + (x_i - iy_i)^2(x_j + iy_j)^2 \end{aligned} \right]. \quad (9.20)$$

Here the interaction energy has been written in a form such that the equivalent quantum-mechanical expression can be found by replacing the spatial coordinates by angular momentum operators. For a pair of rare-earth ions, where for present purposes it is sufficient to work in terms of the ground manifold J for each ion, the Hamiltonian equivalent is

$$\mathcal{H} = A \{ 4O_{2i}^0 O_{2j}^0 - 16(O_{2i}^{+1} O_{2j}^{-1} + O_{2i}^{-1} O_{2j}^{+1}) + (O_{2i}^{+2} O_{2j}^{-2} + O_{2i}^{-2} O_{2j}^{+2}) \}, \quad (9.21)$$

where

$$O_2^0 = 3J_z^2 - J(J+1), \quad O_2^{\pm 1} = \frac{1}{2}(J_z J_{\pm} + J_{\pm} J_z), \quad O_2^{\pm 2} = J_{\pm}^2. \quad (9.22)$$

The value of the coefficient A is

$$A = \frac{3e^2 \langle r_i^2 \rangle \langle r_j^2 \rangle \langle J_i \| J_j \rangle}{8\epsilon R^5}, \quad (9.23)$$

where $\langle r^2 \rangle$ is the mean square radius of the $4f$ ions on each ion, and $\langle J \parallel \alpha \parallel J \rangle$ is the numerical coefficient of Elliott and Stevens listed in Table 20.

The terms given above and higher-order terms, arising either from exchange or from other multipole interactions, are conveniently summarized in spin operator form by Birgeneau, Hutchings, Baker, and Riley (1969).

The terms in (9.20), (9.21) do not change sign under the parity operation, or under time reversal, and are thus essentially different from the interactions considered in §§ 9.2 and 9.3. They give rise to no first-order effect for ions whose states are Kramers doublets, or non-Kramers doublets in which each state has the same electric charge distribution. On the other hand, a first-order effect may occur for the non-Kramers doublet Γ_3 , where the two states have electric quadrupole moments of opposite sign. First-order effects may arise also between ions in states of higher degeneracy, such as triplet states (Γ_4 , Γ_5) or quadruplet (Γ_8) states in ions with cubic symmetry. Possible examples arise in the lanthanide nitrides and analogous compounds with the NaCl structure; UO_2 , NpO_2 , and similar compounds of the $5f$ group with the CaF_2 structure; and ions of the $3d$ group with unquenched orbital angular momentum such as Fe^{2+} in MgO . In accidental cases of near degeneracy, such as cerium ethylsulphate with two low-lying doublet states, the quadrupole-quadrupole interaction energy may be of the same order as the separation between the two doublets, giving first-order effects (Bleaney 1961).

Second-order effects may arise in ions whose ground states are doublets, but which have fairly low-lying excited states, provided that (9.21) has matrix elements between the ground and excited states. The resultant interaction is similar in form to anisotropic exchange interaction, making it difficult to distinguish unambiguously between the two (Baker 1964b). At first sight it would seem possible to calculate accurately the size of the coefficient A in eqn (9.21), but this is hampered by lack of reliable values of $\langle r^2 \rangle$ for the $4f$ ions, and of shielding (or anti-shielding) effects due to the intervening ions.

All the spin-spin interactions considered hitherto have arisen through electro-magnetic interactions between the ions. Sugihara (1959) has suggested that another type of spin-spin interaction may arise by coupling through the 'phonon field', corresponding to the virtual emission and absorption of phonons. When the coupling between the magnetic ions and the lattice waves or phonon field is quadrupolar

in form, the 'virtual phonon interaction' may resemble a quadrupole-quadrupole interaction, and McMahon and Silsbee (1964) have shown that for a pair of Fe^{2+} ions in MgO the interaction Hamiltonian has the same form as eqn (9.21). A further theoretical treatment of the virtual phonon interaction is given by Orbach and Tachiki (1967).

Although we have primarily considered above the quadrupole-quadrupole interaction, in the case of ions (such as the $4f$, $5f$ ions) with large amounts of unquenched orbital momentum there may well be interactions involving other multipole moments (including those of odd degree). These may result from the 'Coulomb' interaction (see, for instance, Wolf and Birgeneau (1968)) or from the 'exchange' interaction (Levy 1964, 1968; Elliott and Thorpe 1968). The experimental problem of distinguishing between interactions that have the same form in the effective spin Hamiltonian but arise from different sources (including virtual phonon effects) is illustrated in the work of Wickersheim and White (1962), Baker and Mau (1966), Allen (1968), and Baker, Birgeneau, Hutchings and Riley (1968).

9.5. Interaction between a pair of similar ions

The general problem of magnetic resonance in a system of many interacting ions is extremely complicated and before discussing it in §§ 9.7–9.11 we consider the much simpler problem of a pair of interacting ions. Not only does this yield some useful insight into the more general problem, but the spectra of such pairs are themselves a direct method of investigating the nature of the spin-spin interaction, and almost the only method by which quantitative measurements of this interaction can be obtained. In this section we consider an isolated pair of identical ions, each with effective spin $S_i = S_j = \frac{1}{2}$ and with g -tensors

TABLE 9.1

Normalized states and energy levels for a pair of identical interacting ions with the spin Hamiltonian (9.24). The normalization coefficients are given by $\tan 2\alpha = (\mathcal{J}_x - \mathcal{J}_y)/4G_z$

<i>Symmetric states</i>	<i>Energy levels</i>
$\cos \alpha ++\rangle + \sin \alpha --\rangle$	$+\frac{1}{4}\mathcal{J}_z + \{G_z^2 + \frac{1}{16}(\mathcal{J}_x - \mathcal{J}_y)^2\}^{\frac{1}{2}}$
$(1/\sqrt{2}) +-\rangle + (1/\sqrt{2}) -+\rangle$	$-\frac{1}{4}\mathcal{J}_z + \frac{1}{4}(\mathcal{J}_x + \mathcal{J}_y)$
$\sin \alpha ++\rangle - \cos \alpha --\rangle$	$+\frac{1}{4}\mathcal{J}_z - \{G_z^2 + \frac{1}{16}(\mathcal{J}_x - \mathcal{J}_y)^2\}^{\frac{1}{2}}$
<i>Antisymmetric state</i>	<i>Energy level</i>
$(1/\sqrt{2}) +-\rangle - (1/\sqrt{2}) -+\rangle$	$-\frac{1}{4}(\mathcal{J}_x + \mathcal{J}_y + \mathcal{J}_z)$

whose principal values and principal axes are the same. We further simplify the problem by assuming that the spin-spin interaction has the simple form given in eqn (9.10), whose principal axes (x, y, z) are the same as the principal axes of the g -tensors. If the system is subjected to an external field \mathbf{H} directed along one of these principal axes (which we take to be the z -axis), the appropriate Hamiltonian for the pair of ions is

$$\mathcal{H} = g_z \beta H_z (S_{iz} + S_{jz}) + \mathcal{J}_x S_{ix} S_{jx} + \mathcal{J}_y S_{iy} S_{jy} + \mathcal{J}_z S_{iz} S_{jz}. \quad (9.24)$$

This Hamiltonian gives the energy matrix

$$\begin{array}{c|cccc} |++\rangle & +G_z + \frac{1}{4}\mathcal{J}_z & 0 & 0 & \frac{1}{4}(\mathcal{J}_x - \mathcal{J}_y) \\ |+-\rangle & 0 & -\frac{1}{4}\mathcal{J}_z & \frac{1}{4}(\mathcal{J}_x + \mathcal{J}_y) & 0 \\ |-+\rangle & 0 & \frac{1}{4}(\mathcal{J}_x + \mathcal{J}_y) & -\frac{1}{4}\mathcal{J}_z & 0 \\ |--\rangle & \frac{1}{4}(\mathcal{J}_x - \mathcal{J}_y) & 0 & 0 & -G_z + \frac{1}{4}\mathcal{J}_z \end{array} \quad (9.25)$$

in which $G_z = g_z \beta H_z$, and a state such as $|+-\rangle$ is one in which ion i is in the $S_{iz} = +\frac{1}{2}$ state and ion j in the $S_{jz} = -\frac{1}{2}$ state, etc. The diagonal states and energy levels are given in Table 9.1. This table shows that the four states of the two ions can be classified into three symmetric states and one antisymmetric state; it is convenient to refer to these as the 'triplet' and 'singlet' respectively, though the triplet levels are not degenerate in zero magnetic field unless the exchange interaction is isotropic. Magnetic resonance transitions are allowed only between states belonging to the triplet, and no singlet-triplet transitions are allowed, because the perturbation Hamiltonian is symmetric with respect to interchange of the two ions; that is,

$$\mathcal{H} = \beta \{\mathbf{H}_1 \cdot \mathbf{g} \cdot (\mathbf{S}_i + \mathbf{S}_j)\} \quad (9.26)$$

where \mathbf{H}_1 is the amplitude of an oscillatory magnetic field used to produce resonance transitions.

The division into symmetric and anti-symmetric states suggests that the system can be regarded as having two spectroscopic states, one a triplet with total effective spin $T = 1$, the other a singlet with total spin $T = 0$. This can be shown formally to be correct as follows.

Let T_x, T_y, T_z be the components along each of the three axes of the total effective spin of the system, so that $(S_{ix} + S_{jx}) = T_x$, etc. Then each of the terms in the exchange interaction can be transformed in the following way:

$$\begin{aligned} \mathcal{J}_x S_{ix} S_{jx} &= \frac{1}{2} \mathcal{J}_x \{(S_{ix} + S_{jx})^2 - S_{ix}^2 - S_{jx}^2\} \\ &= \frac{1}{2} \mathcal{J}_x T_x^2 - \frac{1}{4} \mathcal{J}_x, \end{aligned} \quad (9.27)$$

where we have used the fact that the values of S_{ix}^2 , S_{jx}^2 are each $\frac{1}{4}$; similar expressions hold for the y , z components. Hence the Hamiltonian becomes

$$\mathcal{H} = g_z \beta H_z T_z + \frac{1}{2}(\mathcal{J}_x T_x^2 + \mathcal{J}_y T_y^2 + \mathcal{J}_z T_z^2) - \frac{1}{4}(\mathcal{J}_x + \mathcal{J}_y + \mathcal{J}_z). \quad (9.28)$$

If we now write

$$\mathcal{J}_x = \mathcal{J}'_x + \mathcal{J}, \text{ etc., where } \mathcal{J} = \frac{1}{3}(\mathcal{J}_x + \mathcal{J}_y + \mathcal{J}_z), \quad (9.29)$$

we can regard \mathcal{J} as the 'isotropic' part of the interaction, and \mathcal{J}' the 'anisotropic' part, for which the trace is zero:

$$\mathcal{J}'_x + \mathcal{J}'_y + \mathcal{J}'_z = 0. \quad (9.30)$$

Then, since $T_x^2 + T_y^2 + T_z^2 = T(T+1)$, the Hamiltonian becomes

$$\mathcal{H} = g_z \beta H_z T_z + \frac{1}{2}(\mathcal{J}'_x T_x^2 + \mathcal{J}'_y T_y^2 + \mathcal{J}'_z T_z^2) + \frac{1}{2}\mathcal{J}\{T(T+1) - \frac{3}{2}\}. \quad (9.31)$$

The allowed values of T are $T = 0$, a singlet level at $-3\mathcal{J}/4$, and a triplet $T = 1$ whose behaviour is identical with that of a spin triplet, the mean energy of the three levels being $+\mathcal{J}/4$.

If the exchange is isotropic, $\mathcal{J}'_x = \mathcal{J}'_y = \mathcal{J}'_z = 0$ and the second term in (9.31) vanishes. All three triplet levels have the same energy $(+\mathcal{J}/4)$ in zero magnetic field, and are equally spaced by $g_z \beta H_z$ when a field is applied, as shown in Fig. 9.2. The allowed transitions within the triplet are found from the oscillatory Hamiltonian

$$\mathcal{H} = \beta(\mathbf{H}_1 \cdot \mathbf{g} \cdot \mathbf{T}), \quad (9.32)$$

which is obtained from (9.26) by writing $\mathbf{T} = \mathbf{S}_i + \mathbf{S}_j$. The allowed transitions are of the usual type $\Delta T_z = \pm 1$, and occur at

$$h\nu = g_z \beta H_z. \quad (9.33)$$

This is independent of the value of \mathcal{J} , showing that isotropic exchange has no effect on the spectrum except at temperatures where $kT \sim \mathcal{J}$, when the intensity will no longer vary inversely as the absolute temperature because of the triplet-singlet splitting. If \mathcal{J} is positive, and $\mathcal{J} \gg g_z \beta H_z$, the triplet states lie higher in energy and their populations will tend to zero at sufficiently low temperatures where $kT \ll \mathcal{J}$, so that the spectrum will then decline in intensity and ultimately vanish as the temperature is lowered. If \mathcal{J} is negative, the singlet state is the higher in energy, and will become depopulated at sufficiently low temperatures; if $g_z \beta H_z \ll kT \ll \mathcal{J}$, the intensity of the spectrum line at $h\nu = g_z \beta H_z$ will be greater by a factor $\frac{4}{3}$ when the singlet state is completely depopulated than it would have been in the absence of the

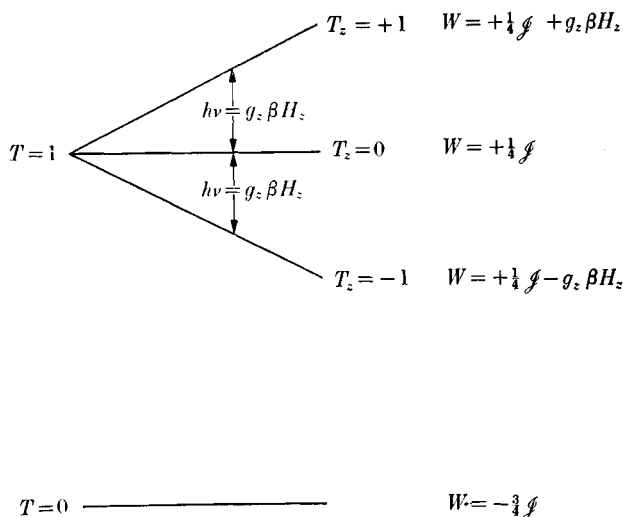


FIG. 9.2. Energy levels and allowed transitions for a pair of ions each with $S = \frac{1}{2}$ and coupled by isotropic exchange interaction:

$$\mathcal{H} = g_z \beta H_z (S_{iz} + S_{jz}) + \mathcal{J} (\mathbf{S}_i \cdot \mathbf{S}_j).$$

exchange interaction. Thus intensity measurements in the region where $kT \sim \mathcal{J}$ can be used to estimate the value of \mathcal{J} .

When the exchange interaction contains anisotropic components, the second term in (9.31) does not vanish and gives an initial splitting of the triplet levels in zero field similar to the 'fine structure' splitting discussed in § 3.5. This splitting arises only from the anisotropic part of the exchange, and is the same as that given by eqn (3.25) if we write

$$D_x = \mathcal{J}'_x/2, \text{ etc.} \quad (9.34)$$

If $g_z \beta H_z \gg \mathcal{J}'$, the allowed transitions are just those within the triplet for which $\Delta T_z = \pm 1$, and occur at (in first approximation)

$$h\nu = g_z \beta H_z \pm \frac{3}{4} \mathcal{J}'_z. \quad (9.35)$$

Hence the magnitude of \mathcal{J}'_z can be found from the separation of the two resonance lines under these conditions, and similarly \mathcal{J}'_x , \mathcal{J}'_y can be found from measurements with the external magnetic field along the axes x , y . If $g_z \beta H_z$ is comparable with \mathcal{J} , the spectrum is more complicated in its behaviour as discussed in § 3.5, but the values of \mathcal{J}'_x , \mathcal{J}'_y , \mathcal{J}'_z can be found by fitting it to the Hamiltonian (9.31). The value of the isotropic part of the interaction \mathcal{J} can be found only by intensity measurements as a function of temperature in the region

where $kT \sim \mathcal{J}$, as mentioned above. Thus the isotropic and anisotropic parts of the spin-spin interaction produce significantly different effects in the spectrum of a pair of identical ions.

The spectrum of copper acetate

A spectrum of this type was discovered in copper acetate monohydrate, $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ by Bleaney and Bowers (1952*a, b*) and Abe and Shimada (1953, 1957). The cupric ion, $3d^9, {}^2D$ is expected to have a doublet ground state, but the spectrum observed corresponded to that for an effective spin of 1. It was suggested by Bleaney and Bowers that the copper ions must occur in isolated pairs in this salt, and this was later verified by an X-ray determination of the structure by van Niekerk and Schoening (1953), which showed that the copper-copper distance in a pair is only 0.264 nm.

The constants of the triplet spectrum in copper acetate and of the doublet spectrum in zinc-doped copper acetate are given in Table 9.2. The 'fine structure' constants D , E follow the customary nomenclature for a spin 1 spectrum (eqn (3.26)), and are related to the anisotropic parts of the exchange interaction discussed above:

$$D = 3\mathcal{J}'_z/4; \quad E = \frac{1}{4}(\mathcal{J}'_x - \mathcal{J}'_y). \quad (9.36)$$

The intensity of the triplet spectrum passes through a maximum, and declines rapidly at temperatures below 90°K. From this intensity

TABLE 9.2

Parameters of the triplet spectrum of copper acetate and of the doublet spectrum in zinc-doped copper acetate

Effective spin Temperature	$\text{Cu}_2\text{Ac}_4 \cdot 2\text{H}_2\text{O}$		$\text{ZnCuAc}_4 \cdot 2\text{H}_2\text{O}$
	$T = 1$ 90°K	$T = 1$ 300°K	$S = \frac{1}{2}$ 77°K
g_x	2.08(3)	2.053(5)	2.052(7)
g_y	2.08(3)	2.093(5)	2.082(7)
g_z	2.42(3)	2.344(10)	2.344(5)
$ D $ (cm^{-1})	0.34(3)	0.345(5)	—
E (cm^{-1})	0.010(5)	0.005(3)	—
A_x (cm^{-1})	<0.001		<0.0018
A_y (cm^{-1})	<0.001		<0.0023
A_z (cm^{-1})	0.008		0.0147(6)
Ref.	BB, 1952	AS, 1957	KAG, 1965

References: BB, Bleaney and Bowers (1952*b*).

AS, Abe and Shimada (1957).

KAG, Kokoszka, Allen, and Gordon (1965).

variation an estimate of $(260 \pm 50) \text{ cm}^{-1}$ was obtained for the singlet-triplet splitting, which is equal to \mathcal{J} . A more accurate value of $(310 \pm 15) \text{ cm}^{-1}$ is obtained by fitting the susceptibility measurements

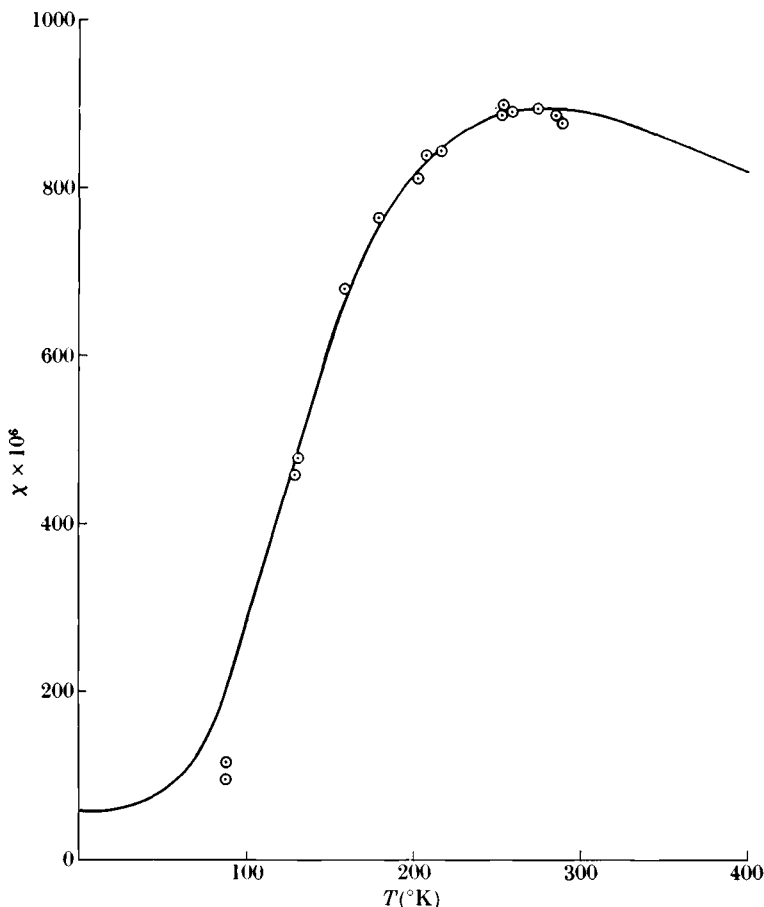


FIG. 9.3. The susceptibility of copper acetate monohydrate (per g mol of copper). The continuous line is the function

$$\chi = \frac{4C}{T\{3 + \exp(\mathcal{J}/kT)\}} + \alpha,$$

where C is the Curie constant and α the temperature-independent susceptibility. The experimental points are those of Foex, Karantissis, and Perakis (1953).

(see Fig. 9.3). Thus the anisotropic part of the exchange interaction (measured by D , E) is very small compared with the isotropic part.

The g -values of Abe and Shimada (which are almost certainly more accurate than those of Bleaney and Bowers) for the triplet state agree very closely with those of isolated copper ions in copper-zinc pairs

obtained from zinc-doped copper acetate by Kokoszka, Allen, and Gordon (1965). This supports a treatment (Bleaney and Bowers 1952*b*) in which the copper ions are assumed to be subjected to a normal type of crystal field, together with an exchange interaction $\mathcal{J}(\mathbf{S}_i \cdot \mathbf{S}_j)$ which is isotropic in the true spins. If the same tetragonal crystal field is assumed for each ion, then an anisotropic exchange interaction between the effective spins results when the spin-orbit interaction is introduced into the theory. Its size can be linked to the g -values:

$$D_{\text{ex}} = 3\mathcal{J}'_z/4 = \frac{1}{8}\mathcal{J}\{\frac{1}{4}(g_z-2)^2 - (g_{\perp}-2)^2\}. \quad (9.37)$$

If we take $\mathcal{J} = 310 \text{ cm}^{-1}$, $g_z = 2.344$ and $g_{\perp} = 2.073$ (the mean of g_x, g_y) we find $D_{\text{ex}} = +0.95 \text{ cm}^{-1}$ and, on the assumption of tetragonal symmetry, $E = 0$.

An additional contribution to D comes from magnetic dipole-dipole interaction between the two copper ions, which on a point dipole model gives

$$D_{\text{dip}} = -(2g_z^2 + g_{\perp}^2)\beta^2/2r^3. \quad (9.38)$$

With the interionic distance $r = 0.264 \text{ nm}$, and the measured values of g_z, g_{\perp} this gives $D_{\text{dip}} = -0.19 \text{ cm}^{-1}$, so that the net calculated value of D is $D_{\text{ex}} + D_{\text{dip}} = +0.76 \text{ cm}^{-1}$. This is over twice the measured value. The discrepancy is most likely due to use of the value $\mathcal{J} = 310 \text{ cm}^{-1}$ in eqn (9.37). This value, obtained from the singlet-triplet splitting, represents the exchange interaction between two cupric ions in the ground orbital states produced by the splitting due to the tetragonal crystal field. However it is easily shown (see Bleaney and Bowers 1952*b*) that the splitting of the triplet depends on the exchange interaction between one cupric ion in the ground state and the other cupric ion in an excited orbital; there are in fact two such excited orbitals involved, which have matrix elements to the ground orbital through the spin-orbit coupling. If we allow for different values of the exchange interaction when an excited orbital is involved, we should write

$$D_{\text{ex}} = \frac{1}{8}\{\frac{1}{4}\mathcal{J}_1(g_z-2)^2 - \mathcal{J}_2(g_{\perp}-2)^2\}. \quad (9.39)$$

There is no evidence as to the values of $\mathcal{J}_1, \mathcal{J}_2$ and a meaningful comparison with experiment (where the sign of D has not been determined) is impossible.

A partially resolved hyperfine structure is observed (see Fig. 9.4) when the external magnetic field is along the z -axis. The electronic transition is split into components displaced from the centre by an

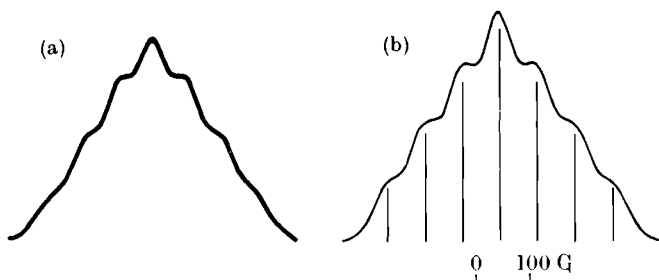


FIG. 9.4. Hyperfine structure due to coupled pairs of Cu^{2+} ions in cupric acetate, $\text{Cu}_2\text{Ac}_4 \cdot 2\text{H}_2\text{O}$. (a) Oscillogram showing hyperfine structure with magnetic field parallel to z -axis. (b) Calculated hyperfine structure, assuming Gaussian line shape and half width at half intensity of 35 G. (Bleaney and Bowers 1952b.)

amount $\frac{1}{2}A(m_i + m_j)$, where A is the hyperfine parameter for an isolated copper ion, and m_i, m_j the nuclear magnetic quantum numbers for the two copper ions of the pair. Since $I_i, I_j = \frac{3}{2}$, the sum $m_i + m_j$ can take all integral values from $+3$ to -3 , but the intermediate values can be obtained in more than one way, giving a set of 7 equally spaced lines with relative intensity 1:2:3:4:3:2:1. The experimental line shape is compared with its reconstructed shape in Fig. 9.4. The values of A_x, A_y, A_z given in the first column of Table 9.2 for the triplet spectrum refer to the separation of successive lines, and are close to half the values in column three for the isolated ion. The factor $\frac{1}{2}$ occurs because we are dealing with two identical ions for which the hyperfine interaction is much smaller than the strong exchange interaction, so that we must project the spin vector of each ion onto the total spin \mathbf{T} . The factor is only $\frac{1}{2}$ if each ion has the same value of S , as can be immediately understood from a vector coupling model in which $\mathbf{S}_i, \mathbf{S}_j$ precess about the total spin \mathbf{T} .

9.6. Interaction between a pair of dissimilar ions

The discussion in the last section of the energy levels and spectrum of a pair of interacting ions with effective spin $S = \frac{1}{2}$ was confined to the case of a pair of similar ions. We now consider the case of a pair of dissimilar ions, again each with $S = \frac{1}{2}$. For the sake of simplicity we assume that the principal axes of the two g -tensors are identical but the principal g -factors themselves are not. Initially we allow the spin-spin interaction to be anisotropic, with the same form as in eqn (9.24). If an external magnetic field H_z is applied along the z -axis (a principal axis for both the g -tensor and the interaction tensor), the

Hamiltonian is

$$\mathcal{H} = \beta H_z(g_{iz}S_{iz} + g_{jz}S_{jz}) + \mathcal{J}_x S_{ix}S_{jx} + \mathcal{J}_y S_{iy}S_{jy} + \mathcal{J}_z S_{iz}S_{jz}. \quad (9.40)$$

The energy matrix is similar to (9.25); writing

$$g_z = \frac{1}{2}(g_{iz} + g_{jz}), \quad \delta g_z = \frac{1}{2}(g_{iz} - g_{jz}),$$

we obtain

$$\begin{vmatrix} |++\rangle & +g_z\beta H_z + \frac{1}{4}\mathcal{J}_z, & 0 & 0 & \frac{1}{4}(\mathcal{J}_x - \mathcal{J}_y) \\ |+-\rangle & 0 & +\delta g_z\beta H_z - \frac{1}{4}\mathcal{J}_z, & \frac{1}{4}(\mathcal{J}_x + \mathcal{J}_y) & 0 \\ |-+\rangle & 0 & \frac{1}{4}(\mathcal{J}_x + \mathcal{J}_y) & -\delta g_z\beta H_z - \frac{1}{4}\mathcal{J}_z, & 0 \\ |--\rangle & \frac{1}{4}(\mathcal{J}_x - \mathcal{J}_y) & 0 & 0 & -g_z\beta H_z + \frac{1}{4}\mathcal{J}_z \end{vmatrix} \quad (9.41)$$

in which the labelling of the states $|+-\rangle$, etc. is the same as in (9.25). The important difference between (9.41) and (9.25) is that the diagonal matrix elements for the states $|+-\rangle$ and $|-+\rangle$ are no longer identical, and this is most significant when the difference in Zeeman energy $\delta g_z\beta H_z$ is large compared with the interaction between the two ions, which appears in the off-diagonal matrix elements between these two states. For simplicity we consider first the case where this inequality is so well satisfied that we can use first-order perturbation theory and neglect the off-diagonal terms. In this approximation the states and energy levels are as shown in Fig. 9.5; the allowed transitions are just those in which the z -component of the spin of one ion is reversed, and occur at

$$h\nu = g_{iz}\beta H_z \pm \frac{1}{2}\mathcal{J}_z, \quad h\nu = g_{jz}\beta H_z \pm \frac{1}{2}\mathcal{J}_z. \quad (9.42)$$

This spectrum consists of two pairs of lines, one pair centred on the point at which the transition for ion i would occur in the absence of any interaction, the other similarly centred for ion j . The separation of the lines in each pair is just \mathcal{J}_z , and the important difference between this and the separation in eqn (9.35) is that whereas the separation for similar ions depends only on the anisotropic part \mathcal{J}' of the exchange interaction, the separation for dissimilar ions (eqn (9.42)) gives the component \mathcal{J}_z of the entire interaction. Obviously similar measurements with the magnetic field along the x , y axes will yield the quantities \mathcal{J}_x , \mathcal{J}_y .

We now relax the restriction that the spin-spin interaction be small compared with the difference in Zeeman energy and consider a general case. However we reduce the number of parameters involved by assuming that the interaction is a simple isotropic interaction, so that $\mathcal{J}_x = \mathcal{J}_y = \mathcal{J}_z = \mathcal{J}$. This enables us to express the energy

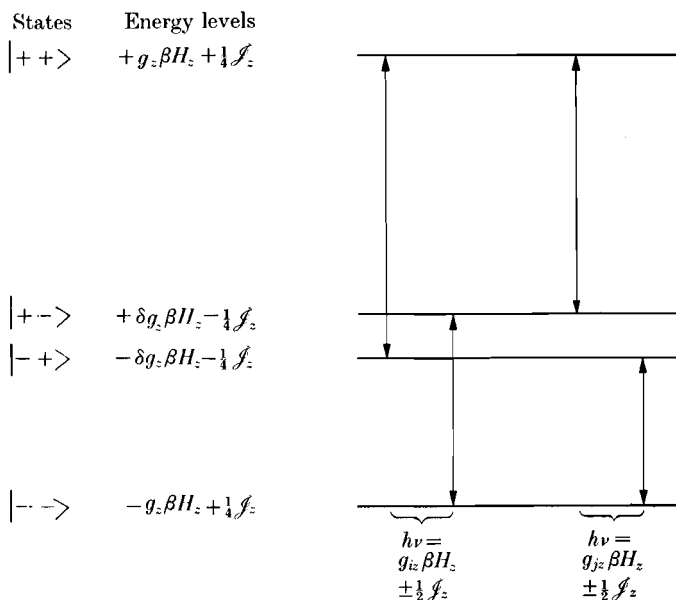


FIG. 9.5. Approximate states and energy levels for a pair of dissimilar ions for which the difference in Zeeman energy $(g_{iz} - g_{jz})\beta H_z = 2\delta g_z\beta H_z$ is large compared with the spin-spin interaction energy $\frac{1}{4}(\mathcal{J}_x + \mathcal{J}_y)$. The allowed transitions (in first approximation) correspond to the z -component of one spin being reversed under the combined effect of the external field plus the steady component \mathcal{J}_z of the interaction due to the other spin.

levels in terms of a parameter $x = \frac{1}{4}\mathcal{J}/(\delta g_z\beta H_z)$, and the spectrum can be studied as x is allowed to increase from zero (no interaction) to very large values (strong interaction). The states and energy levels are given in Table 9.3.

When $x = 0$ (no interaction), the allowed transitions are $a \leftrightarrow c$, $b \leftrightarrow d$, which both occur at $h\nu = g_{iz}\beta H_z$; and $a \leftrightarrow b$, $c \leftrightarrow d$, which both occur at $h\nu = g_{jz}\beta H_z$; this is, of course, just the case of two

TABLE 9.3

States and energy levels for a pair of ions of spin $S = \frac{1}{2}$, which are dissimilar (different g -values), subject to isotropic exchange interaction. Here $\tan 2\alpha = 2x = \frac{1}{2}\mathcal{J}/(\delta g_z\beta H_z)$

States	Energy levels
(a) $ ++\rangle$	$+g_z\beta H_z + (\delta g_z\beta H_z)x$
(b) $\cos \alpha +-\rangle + \sin \alpha --\rangle$	$(\delta g_z\beta H_z)\{-x + (1 + 4x^2)^{\frac{1}{2}}\}$
(c) $\sin \alpha +-\rangle - \cos \alpha --\rangle$	$(\delta g_z\beta H_z)\{-x - (1 + 4x^2)^{\frac{1}{2}}\}$
(d) $ --\rangle$	$-g_z\beta H_z + (\delta g_z\beta H_z)x$

isolated ions with different values of g_z . When x is small, these transitions split into two doublets, the components of each doublet being separated by an amount \mathcal{J} in first approximation; this is the case treated earlier in this section, where it was shown more generally that if the interaction is anisotropic, the doublet separation is \mathcal{J}_z ($=\mathcal{J}$ in this case) when the external field is applied along the z -axis.

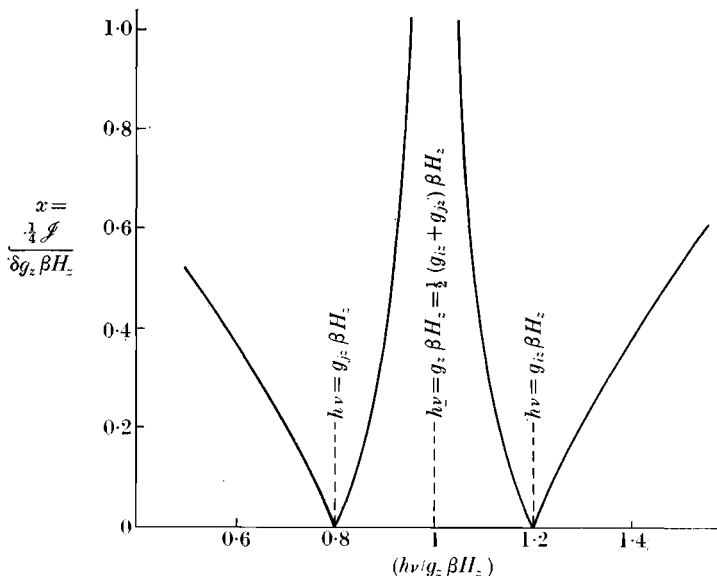


FIG. 9.6. Spectrum of a pair of dissimilar ions with isotropic exchange interaction corresponding to the Hamiltonian ($S_i = S_j = \frac{1}{2}$),

$$\mathcal{H} = \beta H_z (g_{iz} S_{iz} + g_{jz} S_{jz}) + \mathcal{J} (\mathbf{S}_i \cdot \mathbf{S}_j).$$

The states and energy levels are given in Table 9.3 in terms of the parameter $x = \frac{1}{4}\mathcal{J}/(\delta g_z \beta H_z)$. At $x = 0$ (no interaction), the transitions occur at $h\nu = g_{iz}\beta H_z$, $g_{jz}\beta H_z$ appropriate to the isolated ions. As x increases the outer transitions diverge (and become steadily weaker); the inner transitions converge on the mean frequency $h\nu = g_z \beta H_z = \frac{1}{2}(g_{iz} + g_{jz})\beta H_z$ (and become stronger). The diagram is drawn for

$$\delta g_z/g_z = 0.2.$$

As x increases, the two transitions $a \leftrightarrow c$, $c \leftrightarrow d$, which are diverging in frequency (see Fig. 9.6), gradually lose intensity, while the transitions $a \leftrightarrow b$, $b \leftrightarrow d$, which are converging towards the point

$$h\nu = g_z \beta H_z = \frac{1}{2}(g_{iz} + g_{jz})\beta H_z,$$

become rather stronger. When x is extremely large, only these two latter have appreciable intensity, and they lie close to a frequency which is midway between the frequencies appropriate to the isolated ions. When x approaches infinity, the value of α approaches $\pi/4$ and the energy levels can be divided into a triplet a , b , d whose states are

symmetric, and a singlet c whose state is antisymmetric. This is similar to the position considered in § 9.4, where transitions within the triplet only are allowed, but here transitions between the triplet and singlet are also allowed when x is small but become increasingly forbidden as $x \rightarrow \infty$.

The essential difference between the energy matrices (9.25) and (9.41) is that in the former the diagonal elements for the states $|+-\rangle$ and $| - + \rangle$ are the same, whereas in the latter they are different. In the former case the off-diagonal elements produce a splitting of the two states in first order, while in the latter the off-diagonal elements produce a first-order effect only when they are of the same order as the difference between the diagonal elements. Physically the situation can be interpreted as follows. When the ions are identical, they precess at the same rate in the external magnetic field. When spin-spin interaction is present, each ion experiences also a field set up by the other ion which has both steady and oscillatory components. (In the simple case of magnetic dipole interaction this is just the local magnetic field of the other ion.) For identical ions this oscillatory component is just at the right frequency to cause a spin 'flip', thus giving an additional interaction because of the resonance effect whereby ion ' i ' moves from the 'up' to the down position while ion ' j ' moves from 'down' to 'up'. This corresponds to the exchange of a quantum of energy and does not change the total Zeeman energy of the pair in the external field.

When the ions are not identical they precess at different velocities in the external magnetic field and there is no resonance effect if the interaction between them is small compared with the difference in velocities of precession. If this inequality is reversed, and the interaction is large, there is a high rate of mutual spin 'flipping' whose frequency is of order $\frac{1}{4}(\mathcal{J}_x + \mathcal{J}_y)/\hbar$, which is rapid compared with the difference of precession frequencies in the external field. This field therefore sees only an average of the two ions, and the spectral line is observed at $\frac{1}{2}(g_{iz} + g_{jz})\beta H_z = g_z\beta H_z$ instead of at or near the individual frequencies $g_{iz}\beta H_z$, $g_{jz}\beta H_z$.

Figure 9.6 shows how the line positions vary as the relative sizes of the spin-spin interaction and $\delta g_z\beta H_z$ vary from one extreme to the other. In practice the spin-spin interaction for a given system is fixed in size but we can achieve a variation in $x = \frac{1}{4}\mathcal{J}/(\delta g_z\beta H_z)$ by measuring at different magnetic fields, i.e. at different frequencies. In copper sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, an effect of this kind for the two types of Cu^{2+}

ion was reported by Bagguley and Griffiths (1948) and Pryce (1948); this was the first direct observation of exchange effects in paramagnetic resonance. At lower frequencies (~ 10 GHz) only a single resonance line is observed, but at higher frequencies (40 to 60 GHz) two lines are resolved (Bagguley and Griffiths 1950, Ono and Ohtsuka 1958). The g -tensors of the two Cu^{2+} ions are similar but the principal axes are differently oriented, so that the phenomenon can also be studied as a function of δg by varying the orientation of the magnetic field with respect to the crystal axes.

Although we have treated above only the case of a pair of ions that are dissimilar in the principal values of their g -factors, the distinction between 'similar' and 'dissimilar' ions is more general. A pair of ions may be identical except that their nuclei are isotopes of the same element with different hyperfine structures (see, for example, Baker (1964a)). If the ions have effective spins greater than $S = \frac{1}{2}$ they may have 'fine structures' with differently oriented principal axes, as in a chromic alum. The essential distinction is: in the energy matrix of a pair of ions do two states have the same energy in the absence of spin-spin interaction, or do their energies differ by an amount large compared with the spin-spin interaction? In the latter case we need include only the diagonal components of their mutual interaction; in the former the off-diagonal components will be equally important. For the simple examples treated in this and the previous section, the interaction splits each spectrum line into a doublet; for dissimilar ions with a weak interaction, the doublet splitting (for a magnetic field along the z -axis) is \mathcal{J}_z , whereas for similar ions the corresponding splitting is

$$\mathcal{J}_z - \frac{1}{2}(\mathcal{J}_x + \mathcal{J}_y) = \mathcal{J}'_z - \frac{1}{2}(\mathcal{J}'_x + \mathcal{J}'_y) = \frac{3}{2}\mathcal{J}'_z, \quad (9.43)$$

where we have used the fact that $\mathcal{J}'_x + \mathcal{J}'_y + \mathcal{J}'_z = 0$ for the components of the anisotropic interaction. We shall meet these two quantities again in the following sections on line broadening.

In conclusion it should be noted that when the interaction tensor contains off-diagonal terms such as $S_{ix}S_{jz}$, etc. (and these are generally present in magnetic dipole interaction), transitions between the 'triplet' and 'singlet' states are no longer forbidden either for pairs of similar or dissimilar ions.

9.7. Line broadening by spin-spin interaction

In the previous sections we have considered only isolated pairs of magnetic ions; but in a paramagnetic salt each ion is surrounded by a number of other ions at varying distances. The interaction between each pair is a function of the distance between them and the angle

which the line joining their centres makes with the crystal axes; with indirect exchange it may also depend on the arrangement of diamagnetic ions in between. The effect of this interaction is to displace the resonance line from that of a single ion by an amount dependent on the strength of the interaction, and the intensity at a given displacement depends on the number of pairs with a given size of interaction. If we consider in turn pairs of ions in a crystal with increasing separation we may expect their interaction to diminish in size but the number of such pairs increases. Hence lines that are displaced by a small amount will have greater intensity, while lines displaced by a larger amount will have a smaller intensity. With only a small number of ions, the absorption curve may show some structure, but with a crystal of ordinary size the number of interacting ions is so large that a broad absorption curve with no structure is to be expected. Exceptions to this occur if the interaction of one ion with two of three of its neighbours is much greater than its interaction with other neighbours. One such example, cupric acetate, has already been described in § 9.5, where given pairs of ions are strongly coupled by exchange interaction; a less dramatic example is neodymium ethylsulphate (see Fig. 9.9) where interaction (mainly magnetic dipole in origin) with two nearest neighbours predominates sufficiently to give a structure to the absorption curve, while more distant neighbours give only an unresolved broadening.

The complete Hamiltonian for a set of interacting ions consists of (a) a set of terms \mathcal{H}_i , the separate spin Hamiltonian for each ion, summed over all ions; and (b) a set of terms \mathcal{H}_{ij} , the interaction Hamiltonian for each pair of ions, summed over all pairs. Formally we may write this as

$$\mathcal{H} = \sum_i \mathcal{H}_i + \sum_{i>j} \mathcal{H}_{ij}, \quad (9.44)$$

where the summation nomenclature $j > i$ reminds us that each pair must be counted only once. Exact diagonalization of this Hamiltonian, which would yield all the eigenvalues and hence the details of the width and the shape of the absorption curve, is clearly impossible. An alternative approach, originally due to Waller (1932), is the method of 'moments'. The n th moment of an absorption line is defined by the relation

$$\begin{aligned} \langle \Delta \nu^n \rangle &= \frac{\int (\nu - \nu_0)^n f(\nu) \, d\nu}{\int f(\nu) \, d\nu} \\ &= \int (\nu - \nu_0)^n f(\nu) \, d\nu, \end{aligned} \quad (9.45)$$

where $f(\nu)$ is the value of the 'shape factor' at frequency ν , (see § 2.3), which is normalized so that $\int f(\nu) d\nu = 1$ when the integral is taken over all frequencies, and ν_0 is the frequency at which the line would occur in the absence of any interaction. If the absorption curve (more strictly, the shape factor) is symmetrical about this frequency ν_0 , then clearly all the odd moments (including the first, $n = 1$) will vanish, so that we need consider only the even moments. In principle these moments give information about the line shape in an indirect way, which is progressively more exact the higher the number of moments computed. Although these moments can be computed without having to diagonalize exactly the whole matrix corresponding to eqn (9.44), the labour is excessive for the higher moments. In practice only the second moment $\langle \Delta\nu^2 \rangle$ is easily found, and the fourth moment $\langle \Delta\nu^4 \rangle$ has been calculated only for a few special cases. This does not represent a serious drawback for comparison with experiment, because calculation of the higher moments from measured absorption curves is very inaccurate, the major contribution coming from the extreme wings of the curve where the absorption is small and difficult to measure exactly. In any case the theoretical computations can only be carried through if the way in which the interactions vary is known for all pairs of ions; this condition is fulfilled for a crystal of known structure if only magnetic dipole interactions are involved, but seldom holds if exchange or other interactions are present.

An extensive discussion of dipolar broadening (including the effect of isotropic exchange) can be found in Van Vleck (1948). In view of the limitations mentioned above, we give only a sketch of the method using the nomenclature adopted in this chapter. We begin by restricting the discussion to a set of identical spins, with no fine structure or hyperfine structure, subjected to an external magnetic field \mathbf{H} whose direction we take to be the z -axis of a system of Cartesian coordinates. Then the general Hamiltonian (9.44) will have the form

$$\mathcal{H} = g\beta H \sum_i S_{iz} + \sum_{j>i} (\mathbf{S}_i \cdot \mathcal{J}_{ij} \cdot \mathbf{S}_j), \quad (9.46)$$

where the interaction term embraces all interactions that are linear in the spin coordinates and expressible in tensor form. That is, each interaction term has the form (dropping the subscripts i, j on \mathcal{J} for convenience)

$$\begin{aligned} (\mathbf{S}_i \cdot \mathcal{J} \cdot \mathbf{S}_j) = & \mathcal{J}(\mathbf{S}_i \cdot \mathbf{S}_j) + \mathcal{J}'_{xx} S_{ix} S_{jx} + \mathcal{J}'_{yy} S_{iy} S_{jy} + \mathcal{J}'_{zz} S_{iz} S_{jz} + \\ & + \mathcal{J}'_{xy} S_{ix} S_{jy} + \mathcal{J}'_{yx} S_{iy} S_{jx} + \\ & + \mathcal{J}'_{yz} S_{iy} S_{jz} + \mathcal{J}'_{zy} S_{iz} S_{jy} + \\ & + \mathcal{J}'_{zx} S_{iz} S_{jx} + \mathcal{J}'_{xz} S_{ix} S_{jz}. \end{aligned} \quad (9.47)$$

Here the form of the first term is that of an isotropic exchange interaction while the remainder is that of an 'anisotropic' exchange interaction, in which

$$\mathcal{J}'_{xx} + \mathcal{J}'_{yy} + \mathcal{J}'_{zz} = 0. \quad (9.48)$$

This distinction is similar to that made in § 9.5, though the assumption was made there that the interaction could be reduced to the simple form of eqn (9.24). Here the z -axis is chosen to be that of the external magnetic field, which is not necessarily a principal axis of the interaction tensor, nor is the latter necessarily a symmetrical tensor. Equation (9.48) is valid whatever system of axes is used; it makes the trace of the anisotropic tensor zero, while the coefficient \mathcal{J} of the term $\mathcal{J}(\mathbf{S}_i \cdot \mathbf{S}_j)$ is independent of the choice of axes.

Of the terms in (9.47) we now pick out those for which the total z -component of the spin ($S_{iz} + S_{jz}$) is constant. For any given pair these are

$$\begin{aligned} \mathcal{J}(\mathbf{S}_i \cdot \mathbf{S}_j) + \mathcal{J}'_{zz}S_{iz}S_{jz} + \frac{1}{2}(\mathcal{J}'_{xx} + \mathcal{J}'_{yy})(S_{ix}S_{jx} + S_{iy}S_{jy}) \\ = (\mathcal{J} - \frac{1}{2}\mathcal{J}'_{zz})(\mathbf{S}_i \cdot \mathbf{S}_j) + (3\mathcal{J}'_{zz}/2)S_{iz}S_{jz}, \end{aligned} \quad (9.49)$$

where we have used eqn (9.48). The reason why we select these terms can readily be seen by considering the energy matrix of a pair of similar ions. The Hamiltonian, including the Zeeman interaction and the 'truncated' Hamiltonian (9.49), is

$$\mathcal{H} = g\beta H(S_{iz} + S_{jz}) + (\mathcal{J} - \frac{1}{2}\mathcal{J}'_{zz})(\mathbf{S}_i \cdot \mathbf{S}_j) + (3\mathcal{J}'_{zz}/2)S_{iz}S_{jz} \quad (9.50)$$

and, if the basis states (cf. § 9.5) are taken as

$$|++\rangle, \quad \frac{1}{\sqrt{2}}(|+-\rangle \pm |-+\rangle), \quad |--\rangle,$$

the energy matrix is diagonal. The allowed transitions are all of the form $\Delta M = \pm 1$, where $M = (S_{iz} + S_{jz})$ is the total z -component of the spin, and occur near $h\nu = g\beta H$ provided that $\mathcal{J}'_{zz} \ll g\beta H$. The terms omitted are all off-diagonal terms, whose effect is to admix the basis states and allow other transitions of the type $\Delta M = 0, \pm 2$, which occur near $h\nu = 0, 2g\beta H$. Similar considerations hold when we consider a large number of interacting similar ions, for which the truncated Hamiltonian is

$$\mathcal{H} = g\beta H \sum_i S_{iz} + \sum_{j>i} \{(\mathcal{J} - \frac{1}{2}\mathcal{J}'_{zz})(\mathbf{S}_i \cdot \mathbf{S}_j) + (3\mathcal{J}'_{zz}/2)S_{iz}S_{jz}\}. \quad (9.51)$$

The z -component $M = \sum_i S_{iz}$ is a constant of the motion, and the

allowed transitions are all of the type $\Delta M = \pm 1$ and occur near $h\nu = g\beta H$. The interaction terms omitted from the truncated Hamiltonian (9.51) introduce matrix elements of the type $\Delta M = \pm 1, \pm 2$, and make transitions of the form $\Delta M = 0, \pm 2, \pm 3$ weakly allowed (higher values of ΔM also occur with rapidly decreasing intensity). The subsidiary line near $h\nu = 0$ corresponds to the non-resonant spin-spin relaxation phenomenon observed at radio-frequencies of order \mathcal{J}'/h ; the line at $h\nu = 2g\beta H$ has been observed experimentally (see Fig. 9.7) by Bleaney and Ingram (1951) in a cobaltous salt where

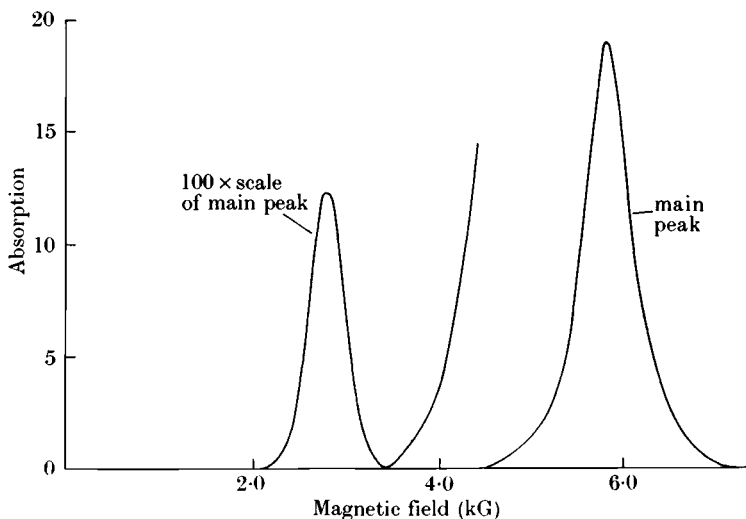


Fig. 9.7. Spectrum of concentrated cobalt ammonium sulphate along the K_2 axis at 20°K and $\bar{\nu} = 0.84 \text{ cm}^{-1}$. The line at half-field is shown on a scale $100 \times$ that of the main line (its height is 0.6 per cent of that of the main line). The line shape indicates that there is a considerable amount of exchange narrowing (Bleaney and Ingram 1951).

the effective spin of the Co^{2+} ion is $\tilde{S} = \frac{1}{2}$, and such a line cannot be a single ion transition.

We now consider the problem of calculating the second moment of an absorption line centred on frequency ν_0 , and for which the shape factor at frequency ν has the value $f(\nu)$. Since we can write

$$\nu = \nu_0 + (\nu - \nu_0),$$

we have

$$\nu^2 = \nu_0^2 + 2\nu_0(\nu - \nu_0) + (\nu - \nu_0)^2$$

and

$$\int \nu^2 f(\nu) d\nu = \int \nu_0^2 f(\nu) d\nu + \int 2\nu_0(\nu - \nu_0) f(\nu) d\nu + \int (\nu - \nu_0)^2 f(\nu) d\nu.$$

If the line shape is symmetrical about ν_0 , the second term on the right-hand side vanishes and, since ν_0 is a constant and $\int f(\nu) d\nu = 1$, we have

$$\langle \nu^2 \rangle = \nu_0^2 + \langle \Delta \nu^2 \rangle. \quad (9.52)$$

The conditions under which the assumption of a line shape symmetrical about ν_0 is valid will be discussed later (§ 9.11).

Equation (9.52) enables us to find $\langle \Delta \nu^2 \rangle$ using a quantum-mechanical formula for $\langle \nu^2 \rangle$. Suppose transitions are induced by an oscillatory magnetic field polarized along the x -axis. Then, if there is no anisotropy in g , the transition probabilities are found from the matrix elements of the operator $S_x = \sum_i S_{ix}$. Let $(S_x)_{nn'}$ be the matrix element between two eigenstates of (9.51) denoted by n and n' , for which the corresponding frequency is $\nu_{nn'} = (\mathcal{H}_n - \mathcal{H}_{n'})/h$. Then the mean square absorption frequency (in which each frequency is weighted with the square of the appropriate amplitude) is

$$\langle \nu^2 \rangle = \frac{\sum_{n,n'} \{ \nu_{nn'}^2 |(S_x)_{nn'}|^2 \}}{\sum_{n,n'} |(S_x)_{nn'}|^2}. \quad (9.53)$$

Both numerator and denominator can be expressed as diagonal sums, giving

$$h^2 \langle \nu^2 \rangle = - \frac{\text{Tr} [\mathcal{H} S_x - S_x \mathcal{H}]^2}{\text{Tr} [S_x]^2}, \quad (9.54)$$

which has the advantage that the spur or trace (Tr) is invariant and can be computed without having to diagonalize the Hamiltonian (9.51), and finding the individual eigenvalues. Evaluation of the traces (cf. Van Vleck 1948) gives

$$h^2 \langle \Delta \nu^2 \rangle = \frac{1}{3} S(S+1) \sum_{j>i} (3 \mathcal{J}_{zz}'/2)_{ij}^2. \quad (9.55)$$

The striking feature of this result is that it contains only the anisotropic part of the interaction, and is independent of the isotropic term ($S_i \cdot S_j$). This is in line with the result found in § 9.5 for the spectrum of a pair of similar ions, which consists of a single line at $h\nu = g\beta H$ if only an isotropic interaction is present, but otherwise contains several lines split by an amount dependent on the size of the anisotropic part of the interaction. For a system of many interacting ions we may picture the broadened line as consisting of a multiplicity of such split pair spectra, though this is, of course, an over-simplification since we have to picture each ion as being paired off with every other ion.

In many paramagnetic crystals there may be more than one set of paramagnetic ions, such as two sets of electronic spins with different g -values, or one set of electronic spins and one set of nuclear spins. We must therefore carry out a calculation similar to that above, but in which we treat the interactions between similar spins all belonging to the same set S separately from the interactions between a spin S of one set and a spin S' of the other set. We assume that the two sets of spins have different g -values g and g' , and give two distinct resonance lines at $h\nu = g\beta H$ and $g'\beta H$ respectively whose separation is large compared with their widths; this implies that the spin-spin interaction between spins of the different species is small compared with the difference $(g-g')\beta H$ in their Zeeman energies (cf. § 9.6). Suppose we wish to find the second moment of one of the lines (that of the first set of spins). For interactions with other spins of the same set we proceed exactly as above, but for interactions between dissimilar spins we retain in our truncated interaction Hamiltonian for each pair only the term

$$\mathcal{J}_{zz} S_{iz} S'_{iz}. \quad (9.56)$$

Comparison with (9.49) shows that we have excluded terms of the type $S_{i+} S'_{j-}$, $S_{i-} S'_{j+}$, which would correspond to mutual spin flips between the two sets of ions; these terms are associated with a subsidiary absorption line at $h\nu = (2g-g')\beta H$ which, under the condition given above, is distinct from the main line at $g\beta H$. The formula for the second moment then becomes

$$\hbar^2 \langle \Delta \nu^2 \rangle = \frac{1}{3} S(S+1) \sum_{j>i} (3 \mathcal{J}'_{zz}/2)_{ij}^2 + \frac{1}{3} S'(S'+1) \sum_{j',i} (\mathcal{J}_{zz}^2)_{ij'}, \quad (9.57)$$

where the first summation is over pairs of ion i with all similar ions of the first set only, while the second is over all pairs of ion i with dissimilar ions belonging to the second set only. An important difference between the two summations is that in the second case the quantity \mathcal{J}_{zz} is involved and not just the term \mathcal{J}'_{zz} belonging to the anisotropic part of the interaction. This means that the isotropic interaction contributes to the second moment for dissimilar ions, but not for similar ions, corresponding to the differences already found for single pairs of interacting ions in §§ 9.5 and 9.6. A further correspondence appears in the factor $(\frac{3}{2})$ in the term $(3 \mathcal{J}'_{zz}/2)$ for similar ions arising from the resonance effect that enhances the interaction between them. This factor is absent from the term \mathcal{J}_{zz} for dissimilar ions.

9.8. Line shape due to dipolar spin-spin interaction

As noted in the last section, computations of line width and moments can be carried out only if the interaction constants are known for all pairs of spins in a crystal. In general, this restricts the computations to cases where the interaction is entirely due to magnetic dipole interaction between the spins, a situation that is rather rare if the magnetic moments are electronic rather than nuclear in origin. For this reason the following discussion will in the main be qualitative rather than quantitative.

If the interaction is dipolar, and the g -factors of the two spins involved are each isotropic, the form of the interaction is given by eqn (9.3). This is a particular form of the more general tensor-type interaction assumed in eqn (9.46), and since (9.3) has zero trace the 'isotropic' part of the interaction as defined by eqns (9.47), (9.48) vanishes; that is, $\mathcal{J} = 0$, and the distinction between quantities \mathcal{J}_{xx} and \mathcal{J}'_{xx} , etc., is unnecessary. (This does not hold if the g -factors are anisotropic, since the sum $\mathcal{J}_{xx} + \mathcal{J}_{yy} + \mathcal{J}_{zz} = 0$ for eqn (9.3) but not for (9.5a) or (9.5b).) If there are two sets of spins, S and S' , with isotropic g -factors g, g' , the quantities needed for the calculation of the second moment given by (9.57) are

$$(\mathcal{J}'_{zz})_{ij} = g^2 \beta^2 r_{ij}^{-3} (1 - 3n_{ij}^2) \text{ for similar pairs,} \quad (9.58a)$$

and

$$(\mathcal{J}_{zz})_{ij'} = gg' \beta^2 r_{ij'}^{-3} (1 - 3n_{ij'}^2) \text{ for dissimilar pairs.} \quad (9.58b)$$

Here r_{ij} is the distance between the centres of spins i, j and $n_{ij} = \cos \theta_{ij}$ where θ_{ij} is the angle that the line joining the centres makes with the external magnetic field \mathbf{H} (i.e. with the z -axis). The value of \mathcal{J}_{zz} is just the interaction between the z -component of spin S_i and the z -component of the local field at its centre, that is produced by the z -component of spin S'_j . If mutual spin flips among the spins S' can be neglected, this component is a constant of the motion, and contributes just a static component to the local field, so that broadening of the line due to interaction with dissimilar spins is essentially similar to that which would be produced by inhomogeneities in the external magnetic field. If no other form of broadening is present the line is said to be 'inhomogeneously broadened'. In the extreme case the wave train emitted or absorbed by a spin is infinite in length, but is at a slightly different frequency from that of other spins subjected to different local fields (cf. § 2.6).

When the interacting spins are identical there is the additional

resonance interaction due to the precessing components of the spins, which in eqn (9.57) makes the relevant quantity ($3\mathcal{J}'_{zz}/2$) rather than \mathcal{J}_{zz} . Since in the present case there is no distinction between \mathcal{J}'_{zz} and \mathcal{J}_{zz} , the second moment for similar spins is just a factor ($\frac{3}{4}$) greater than that obtained simply by including only the static components of the interaction. (Obviously the factor ($\frac{3}{4}$) is correct only if the g -factor is isotropic, since otherwise $\mathcal{J}'_{zz} \neq \mathcal{J}_{zz}$.) This resonance interaction between identical spins shortens the lifetime of the individual spin states through mutual spin flips. In the over-simplified model discussed in Chapter 2 the average lifetime of a spin state is described by a parameter τ_2 , the spin-spin or transverse relaxation time. The line in such a case is said to be 'homogeneously broadened'; the spins emit or absorb wave trains of finite length whose mean duration in time is τ_2 , and whose probability distribution is of the form $\exp(-t/\tau_2)$. The line shape should be given by the Lorentz factor

$$\begin{aligned} f(\nu) &= \frac{2\tau_2}{1 + 4\pi^2(\nu - \nu_0)^2\tau_2^2} \\ &= \frac{1}{\pi} \frac{\Delta\nu}{(\Delta\nu)^2 + (\nu - \nu_0)^2}, \end{aligned} \quad (9.59)$$

where $\Delta\nu = 1/(2\pi\tau_2)$. For such a line shape, the intensity falls to one-half the maximum value when the frequency deviates by $\pm\Delta\nu$ from the central frequency ν_0 . If the second moment of such a line is computed by eqn (9.45), it is found to be infinite; since we know from eqn (9.55) that the second moment is finite, it follows that the line shape cannot be Lorentzian, and the absorption in the wings must fall more rapidly than predicted by eqn (9.59). Again, since the second moment given by (9.59) is infinite, there is no way of relating the line breadth parameter $\Delta\nu$ in (9.59) to the second moment computed from eqns (9.57) and (9.58).

In practice it is often useful to have a simple analytical form for the line shape, even if only approximately correct. An alternative assumption for the shape factor is that of a Gaussian error function

$$f(\nu) = \frac{1}{(2\pi\langle\Delta\nu^2\rangle)^{\frac{1}{2}}} \exp\left\{-\frac{(\nu - \nu_0)^2}{2\langle\Delta\nu^2\rangle}\right\}, \quad (9.60)$$

which is normalized, and contains no arbitrary parameter, since it gives a second moment just equal to $\langle\Delta\nu^2\rangle$. The higher moments can also be readily calculated, and (9.60) gives for the fourth moment

$$\langle \Delta \nu^4 \rangle = 3(\langle \Delta \nu^2 \rangle)^2, \text{ or}$$

$$(\langle \Delta \nu^4 \rangle)^{\frac{1}{2}} = 1.32(\langle \Delta \nu^2 \rangle)^{\frac{1}{2}}. \quad (9.61)$$

An explicit calculation of $\langle \Delta \nu^4 \rangle$ for a simple cubic lattice of spins by Van Vleck (1948, 1957) by the rigorous method of moments gives a check on the validity of the Gaussian assumption. For $S = \frac{1}{2}$, and an external field directed along an $\langle 001 \rangle$ axis, he finds the factor to be 1.25 rather than the 1.32 given in (9.61). For a field directed along a $\langle 111 \rangle$ axis, or if $S > \frac{1}{2}$, the factor is even nearer to 1.32.

An experimental determination of line shape is shown in Fig. 9.8; the experimental points agree well with the Gaussian shape whose second moment has been computed by the diagonal sum method (with

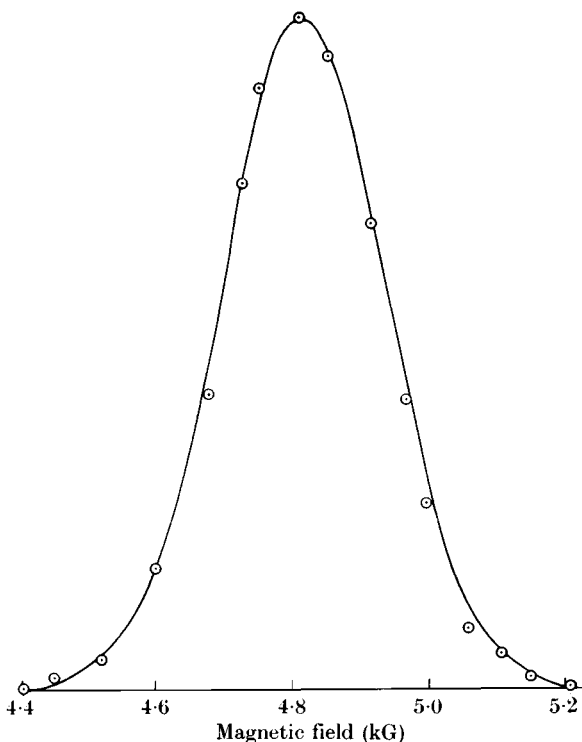


FIG. 9.8. The $-\frac{3}{2} \leftrightarrow -\frac{1}{2}$ transition in caesium chrome alum, $\text{CsCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, for which the single ion spin Hamiltonian is

$$\mathcal{H} = g\beta(\mathbf{H} \cdot \mathbf{S}) + D\{S_z^2 - \frac{1}{3}S(S+1)\}$$

with $S = \frac{3}{2}$. There are four ions in unit cell, and in the figure \mathbf{H} is along the z -axis (a $\langle 111 \rangle$ axis) for one ion only. The continuous line is computed using a Gaussian shape and a root mean square width of 118 G, the calculated value for dipolar interaction assuming that ions whose trigonal axes are differently oriented are to be counted as dissimilar ions.

This gives a good fit to the experimental points (Bleaney 1950).

one simplifying assumption—see legend to Fig. 9.8). In this substance (as in all the alums) the magnetic ions lie on a face-centred cubic lattice, and each ion is surrounded by twelve equidistant nearest neighbours. Although this substance is cubic, the line width is not isotropic because of the angular factors in eqns (9.58a), (9.58b). The variation in line width is most dramatic in cases where the dipolar contribution from all the nearest neighbours vanishes at certain orientations of the external field. If g is isotropic, this requires that $(1 - 3 \cos^2 \theta_{ij}) = 0$, or $\theta_{ij} = 54^\circ 44'$, where θ_{ij} is the angle between the external field and the lines joining nearest neighbours. This condition is fulfilled in two cases of cubic symmetry:

(a) If the magnetic ions lie on a simple cubic lattice, so that the six nearest neighbours lie in pairs along $[001]$, $[010]$, and $[100]$, and \mathbf{H} is directed along a $\langle 111 \rangle$ axis;

(b) in a lattice of the CaF_2 type, with nearest neighbour magnetic ions along the $\langle 111 \rangle$ axes, when \mathbf{H} is along an $\langle 001 \rangle$ axis.

These conditions, with isotropic g -factor and purely dipolar interaction, are more readily achieved with nuclear than with electronic dipoles. A special case of (b) is CaF_2 with an isolated electronic magnetic ion on a Ca site, when the first-order interaction with the eight nearest neighbour F^- nuclear moments vanishes for \mathbf{H} along an $\langle 001 \rangle$ axis provided the interaction is entirely dipolar in form.

The assumption of a Gaussian line shape is most likely to be a good approximation when the number of equidistant nearest neighbours is fairly large. In other cases, when the number of nearest neighbours is rather small, the Gaussian assumption may be seriously wrong. A notable example is neodymium ethylsulphate, in which the Nd^{3+} ion has two equidistant nearest neighbours at 0.7 nm along the c -axis, which give a partly resolved structure (see Fig. 9.9) when the external field is along the c -axis. In a first approximation the line consists of a triplet with a 1:2:1 intensity distribution, corresponding to the chances of neighbouring spins being both 'up'; one 'up' and one 'down' (which can arise in two ways); and both 'down' respectively. The six next-nearest neighbours are about 0.88 nm away in directions such that when the external field is along the c -axis they contribute only a rather small dipolar field. Since all ions have symmetry about the c -axis, it is readily found from eqn (9.5a) that when \mathbf{H} is along this axis

$$\mathcal{J}_{zz} = g_{iz}g_{jz}(1 - 3n_{ij}^2)\beta^2 r_{ij}^{-3} \quad (9.62)$$

and

$$\mathcal{J}'_{zz} = \frac{1}{3}(2g_{iz}g_{jz} + g_{i\perp}g_{j\perp})(1 - 3n_{ij}^2)\beta^2 r_{ij}^{-3}. \quad (9.63)$$

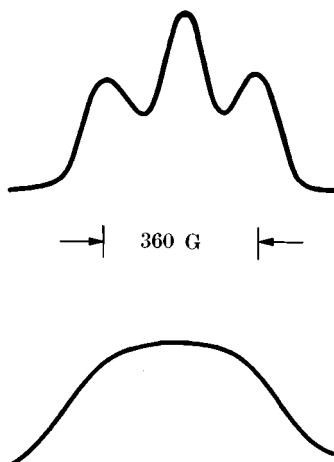


FIG. 9.9. Oscillogram of the spectrum of neodymium ethylsulphate. Above, triplet structure observed with magnetic field parallel to the crystal (hexagonal) axis; below, spectrum with magnetic field normal to crystal axis (Bleaney, Elliott, and Scovil 1951).

Thus the first-order dipolar contribution from neighbouring ions vanishes in this case if their directions are such that $(1 - 3n_{ij}^2) = 0$, irrespective of whether they are identical or not, and irrespective of the anisotropy in their g -tensors provided they have axial symmetry ($g_x = g_y = g_{\perp}$). In the ethylsulphates the directions of the next nearest neighbours are near to fulfilling the condition $(1 - 3n_{ij}^2) = 0$.

The angular dependence just derived applies to the case of \mathbf{H} along the unique axis and neighbouring ions not along this axis. The converse case, of a pair of ions along the c -axis (such as the nearest neighbours in the ethylsulphates) and \mathbf{H} at an angle to this axis, does not give the same angular dependence except when the g -values are isotropic. For such a pair of ions, if \mathbf{H} is at an angle θ to the z -axis, which is the symmetry axis and also the line joining the ions, we have

$$\mathcal{H}_i = \beta H (S_{iz} g_{i\parallel} \cos \theta + S_{ix} g_{i\perp} \sin \theta) \quad (9.64)$$

$$\mathcal{H}_j = \beta H (S_{jz} g_{j\parallel} \cos \theta + S_{jx} g_{j\perp} \sin \theta) \quad (9.65)$$

where, because of the axial symmetry, we can assume that \mathbf{H} lies in the xz -plane. The interaction Hamiltonian would be just (9.5b) if the interaction were purely dipolar, but we may take the rather more general form

$$\mathcal{H}_{\text{ss}} = \mathcal{J}_{\perp} (S_{ix} S_{jx} + S_{iy} S_{jy}) + \mathcal{J}_{\parallel} S_{iz} S_{jz}, \quad (9.66)$$

which includes other possible contributions axially symmetric in form. If the Zeeman interactions are much larger than the spin-spin

interaction, they must be diagonalized first; this can be achieved by a rotation of axes about the y -axis (as in § 3.2) through angles of ϕ_i and ϕ_j for spins S_i and S_j respectively, where $\tan \phi_i = (g_{i\perp}/g_{i\parallel})\tan \theta$ and $\tan \phi_j = (g_{j\perp}/g_{j\parallel})\tan \theta$. Then the interaction Hamiltonian becomes

$$\mathcal{H}'_{ss} = (\mathcal{J}_{\perp} \cos \phi_i \cos \phi_j + \mathcal{J}_{\parallel} \sin \phi_i \sin \phi_j) S'_{ix} S'_{jx} + \mathcal{J}_{\perp} S_{iv} S_{jv} + (\mathcal{J}_{\perp} \sin \phi_i \sin \phi_j + \mathcal{J}_{\parallel} \cos \phi_i \cos \phi_j) S'_{iz} S'_{jz} + \dots, \quad (9.67)$$

where we have retained only terms of the form

$$\mathcal{H}''_{ss} = \mathcal{J}_x S'_{ix} S'_{jx} + \mathcal{J}_y S'_{iy} S'_{jy} + \mathcal{J}_z S'_{iz} S'_{jz}. \quad (9.67a)$$

If the ions are dissimilar we need for the second moment calculation just the coefficient

$$\begin{aligned} \mathcal{J}_z &= \mathcal{J}_{\perp} \sin \phi_i \sin \phi_j + \mathcal{J}_{\parallel} \cos \phi_i \cos \phi_j \\ &= (g_{i\perp} g_{j\perp} / g_i g_j) \mathcal{J}_{\perp} \sin^2 \theta + (g_{i\parallel} g_{j\parallel} / g_i g_j) \mathcal{J}_{\parallel} \cos^2 \theta, \end{aligned} \quad (9.68)$$

in which we have, as usual,

$$\begin{aligned} g_i^2 &= g_{i\perp}^2 \sin^2 \theta + g_{i\parallel}^2 \cos^2 \theta, \\ g_j^2 &= g_{j\perp}^2 \sin^2 \theta + g_{j\parallel}^2 \cos^2 \theta. \end{aligned} \quad (9.69)$$

If the ions are similar, their g -factors are the same and $\phi_i = \phi_j = \phi$. Then in (9.67a) we have

$$\left. \begin{aligned} \mathcal{J}_x &= \mathcal{J} + \mathcal{J}'_x = \mathcal{J}_{\perp} \cos^2 \phi + \mathcal{J}_{\parallel} \sin^2 \phi, \\ \mathcal{J}_y &= \mathcal{J} + \mathcal{J}'_y = \mathcal{J}_{\perp}, \\ \mathcal{J}_z &= \mathcal{J} + \mathcal{J}'_z = \mathcal{J}_{\perp} \sin^2 \phi + \mathcal{J}_{\parallel} \cos^2 \phi, \end{aligned} \right\} \quad (9.70)$$

in which we have made the usual separation into an interaction with trace $\mathcal{J}'_x + \mathcal{J}'_y + \mathcal{J}'_z = 0$, and an 'isotropic' part whose coefficient is

$$\mathcal{J} = \frac{1}{3}(\mathcal{J}_x + \mathcal{J}_y + \mathcal{J}_z) = \frac{1}{3}(\mathcal{J}_{\parallel} + 2\mathcal{J}_{\perp}). \quad (9.71)$$

In computing the second moment (cf. eqn (9.57)) we need the quantity

$$\begin{aligned} \frac{3}{2} \mathcal{J}'_z &= \frac{1}{2}(\mathcal{J}_{\parallel} - \mathcal{J}_{\perp})(3 \cos^2 \phi - 1) \\ &= \frac{1}{2}(\mathcal{J}_{\parallel} - \mathcal{J}_{\perp}) \left(3 \frac{g_{\parallel}^2}{g^2} \cos^2 \theta - 1 \right). \end{aligned} \quad (9.72)$$

If the interaction is purely dipolar in origin, we have from (9.5b),

$$\left. \begin{aligned} \mathcal{J}_{\parallel} + 2\mathcal{J}_{\perp} &= -2(g_{\parallel}^2 - g_{\perp}^2)\beta^2 r_{ij}^{-3}, \\ \mathcal{J}_{\parallel} - \mathcal{J}_{\perp} &= -(2g_{\parallel}^2 + g_{\perp}^2)\beta^2 r_{ij}^{-3}, \end{aligned} \right\} \quad (9.73)$$

from which we see that the tensor interaction (9.67a) is traceless ($\mathcal{J} = 0$) only if g is isotropic.

A perhaps surprising feature of (9.72) is that whatever values the coefficients \mathcal{J}_{\parallel} , \mathcal{J}_{\perp} may have, the angular variation of \mathcal{J}'_z given by the last bracket in (9.72) is from a maximum of $+2$ when \mathbf{H} is parallel to the symmetry axis ($\theta = 0$) to -1 when \mathbf{H} is perpendicular ($\theta = \pi/2$). The anisotropy in g affects only the angular variation at intermediate values of θ ; in particular, \mathcal{J}'_z passes through zero at $\tan^2\theta = (2g_{\parallel}^2/g_{\perp}^2)$. In the case of neodymium ethylsulphate referred to earlier in this section, the triplet separation is proportional to \mathcal{J}'_z and is only well resolved (cf. Fig. 9.9) when \mathcal{J}'_z has its maximum value, i.e. when \mathbf{H} is along the symmetry axis.

9.9. Effect of exchange interaction on line shape

In the previous section we considered the width and shape of a line when the spin-spin interaction is wholly dipolar in origin. This is seldom the case for a system of electronic dipoles, and in many paramagnetic substances exchange interaction may be more important than the dipolar interaction.

Initially we consider again the simple case of a set of identical ions with isotropic g -factors and no 'fine' or hyperfine splittings, coupled together by dipolar interaction and isotropic exchange interaction. As we have seen already from § 9.7, eqn (9.55), the second moment is unaltered by an isotropic exchange term. However Van Vleck (1948) has shown that the formula for the fourth moment contains the isotropic exchange energy, so that the fourth moment is larger than it would be in the absence of such exchange interaction. This information is obviously insufficient to determine the line shape, but it is readily seen that the behaviour of the two moments implies that the line must be narrowed in the centre and extended in the wings in order to increase the fourth moment while keeping the second moment constant. This is the phenomenon of 'exchange narrowing', first predicted by Gorter and Van Vleck (1947). Physically it can be regarded as an effect akin to motional narrowing of a magnetic resonance line in a liquid. In order that the local field experienced by a given ion shall shift its precession frequency, and hence broaden the resonance for an assembly of ions, the local field must persist for a time long compared with the duration of the 'wave train' absorbed by the ion. If the local field fluctuates rapidly during this time, its effect tends to be averaged out. When the exchange energy is large, the orientation of neighbouring spins is being changed at a rate of order $|(\mathcal{J}/\hbar)|$ through mutual spin flips, so that the local dipolar field fluctuates at a similar rate and

tends to be averaged out. For this to be effective, we require

$$|(\mathcal{J}/h)| \gg (\langle \Delta\nu^2 \rangle)^{\frac{1}{2}},$$

where $\langle \Delta\nu^2 \rangle$ is the second moment due to dipolar interaction.

The problem of the shape of an exchange-narrowed line has been considered in more detail by Anderson and Weiss (1953), using a mathematical model in which the dipolar interaction is assumed to produce a Gaussian distribution of internal fields and, in addition, this field is time-modulated in a random way. If the above inequality is satisfied, this theory gives a line shape where the wings of the line fall away exponentially as for a Gaussian shape, but near the centre the line is Lorentzian in shape, with a half-width

$$(\Delta\nu)_{\frac{1}{2}} \approx (\langle \Delta\nu^2 \rangle)/(\mathcal{J}/h). \quad (9.74)$$

Here $\langle \Delta\nu^2 \rangle$ is the second moment due to dipolar interaction, and (\mathcal{J}/h) is the exchange energy in frequency units. However, when this frequency exceeds the resonance frequency, the truncated Hamiltonian (9.55) should not be used in computing $\langle \Delta\nu^2 \rangle$, but all the \mathcal{J}' terms in (9.47). For a set of identical spins with isotropic g -factors, this gives a value for $\langle \Delta\nu^2 \rangle$ which is larger by a factor $\frac{1}{2}$ than that obtained from (9.55) and (9.58a) (see, for instance, Abragam (1961)). The increase in line width at lower resonance frequencies, and its reduction at higher frequencies, has been measured for $\text{K}_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}$ (see, for example, Henderson and Rogers (1966)), and for $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$ by Rogers, Carboni, and Richards (1967).

Equation (9.74) is only valid and exchange narrowing will only be appreciable provided that $|\mathcal{J}/h| \gg (\langle \Delta\nu^2 \rangle)^{\frac{1}{2}}$. Here \mathcal{J} must be the value of the isotropic exchange interaction expressed in terms of the *effective spins*. We have seen (§ 9.3) that when there is considerable magnetic anisotropy, the exchange interaction expressed in terms of effective spins may be quite anisotropic, even if we start from an exchange interaction that is isotropic when expressed in terms of the *real spins*. In this case the appropriate value for $\langle \Delta\nu^2 \rangle$ is given by eqn (9.55), which includes all contributions to the anisotropic part of the spin-spin interaction; clearly, when \mathcal{J}' is of the same order as \mathcal{J} , there is no appreciable narrowing, and if \mathcal{J}' is mainly due to exchange its effect is to broaden rather than to narrow the line. Thus the narrowing of resonance lines by exchange interaction is most likely to be effective when the dipole moments are almost wholly due to electron spin, as in a half-filled shell such as $3d^5$, Mn^{++} , Fe^{3+} in a weak crystal field.

The phenomenon of exchange narrowing depends on the property that isotropic exchange interaction does not contribute to the second moment when we have a system of identical ions. This is no longer true when the ions are not identical, and isotropic exchange then makes a contribution to the second moment. Apart from the obvious case of ions of different species, ions of the same species are essentially not identical under conditions such as the following:

- (a) the axes of their g -tensors are differently oriented, e.g. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$; see § 9.6;
- (b) they possess a hyperfine structure, e.g. neodymium ethylsulphate; see Baker (1964a);
- (c) they possess a 'fine structure', e.g. nickel salts; see Ishiguro, Kambe, and Usui (1951), Stevens (1952b).

Basically the essential criterion is that ions are counted as dissimilar if they give resolved resonance lines; then in calculating the second moment we take as the centre point the position of the unbroadened line. When the exchange interaction becomes comparable with the separations between the lines the situation becomes complicated, and if the exchange interaction is still larger the lines become merged. Exchange narrowing then sets in, with half-width given by eqn (9.74), provided that we include in $\langle \Delta\nu^2 \rangle$ the contributions from the line splittings.

The general question of methods of calculating moments when fine structure is present is discussed by Pryce and Stevens (1950), Kambe and Usui (1952), and McMillan and Opechowski (1960, 1961). The last authors also treat particularly the changes in moments which occur at low temperatures where departures from random orientation in the spin system cannot be neglected, a subject that is briefly discussed in § 9.11.

9.10. Magnetic dilution, and the spectra of pairs

In most salts that are paramagnetic down to fairly low temperatures the distances between the nearest paramagnetic ions lie in the range 0.5–0.8 nm, and the line widths due to magnetic dipolar interaction between the ions are of order 10^2 – 10^3 G. This is sufficient to obscure many details of the resonance line, such as hyperfine structure. In more concentrated salts the lines may be narrowed by exchange interaction, but at the same time small splittings due to fine or hyperfine effects tend to be averaged out. Since spin-spin interaction falls off rapidly with increasing inter-ionic distance, considerable reductions

in line width can be achieved by the use of 'magnetically dilute' salts, in which the majority of the paramagnetic ions are replaced by suitable diamagnetic ions in an isomorphic crystal. For hydrated salts where the waters of hydration are the immediate neighbours of the paramagnetic ion, a residual width of order 10 G is attained at a relative concentration of paramagnetic ions in the range 0.1 to 1 per cent. This residual width is due to the nuclear magnetic moments of the protons, which are typically at a distance of a little over 0.2 nm; an $M(6H_2O)$ complex characteristic of the iron group contains twelve such protons, while a lanthanide ethylsulphate group contains eighteen. This residual width can be reduced by a factor of about one-third by deuteration, because of the smaller nuclear moment of the deuteron.

Considerable narrower lines, with widths less than 1 G in favourable circumstances, can be achieved by the use of oxides such as MgO , ThO_2 where the only isotopes with nuclear moments (^{25}Mg , ^{17}O) are in low abundance. Clearly such narrow lines can only be attained if the concentration of paramagnetic ions is made sufficiently small. Paradoxically, quite 'narrow' lines can also be observed in substances such as fluorides (ZnF_2 , CaF_2) where the ^{19}F ions with their large nuclear moments are the immediate neighbours of the paramagnetic ion; this occurs when electron transfer between the paramagnetic ion and the nearest F^- ions is sufficient to give a resolved fluorine hyperfine structure. The width of the individual lines then arises only from interaction with more distant magnetic moments.

If the replacement of paramagnetic by diamagnetic ions is a purely random process, the chance of a paramagnetic ion occupying a given site is just equal to the fractional concentration c . In the calculation of the second moment $\langle \Delta \nu^2 \rangle$, the sums involved in, for example, eqn (9.57), are each proportional to c since, for any given paramagnetic ion, the chance of any given neighbouring site being occupied by another paramagnetic ion is just proportional to c . At first sight this would suggest that the line width would fall on dilution only as $c^{\frac{1}{2}}$, but in practice the line width falls faster than this. The reason for this is that dilution does not reduce the magnitude of the interaction between any given pair of ions, but only the chance that such a pair will occur. Thus a pair of near-by ions with (presumably) a large spin-spin interaction will give rise to lines well out in the wings of the main line, and as the line width is reduced these appear as satellites to the main line. In the sums involved in computing the second (and higher) moments the furthest out satellites make a more than average contribution;

such contributions keep the second moment proportional to the concentration, but the fallacy in using the root mean second moment $(\langle \Delta\nu^2 \rangle)^{\frac{1}{2}}$ as a measure of line width is that this incorrectly assumes that the line shape remains unaltered. At sufficiently low concentrations the dominant contribution to all moments $\langle \Delta\nu^{2n} \rangle$ comes from sums over pairs of ions, and is thus proportional to c , showing that the line shape must change (Kittel and Abrahams 1953). The arguments using the method of moments set out by these authors agree with the analysis of Anderson (1951) that at concentrations below about 0.1 the centre of the line is Lorentzian in shape, with a half-width roughly proportional to the concentration.

At relative concentrations of order $c = 10^{-2}$ – 10^{-1} the satellite lines are sufficiently intense and well resolved that their spectrum can be observed and fitted to a spin Hamiltonian with fair accuracy. The centre portion of the spectrum is obscured by the main line due to 'isolated' ions, which at low concentrations are relatively more abundant than 'pairs' of ions, and a rather careful and painstaking analysis is needed to identify with what type of pair a given set of satellites is associated. When the effective spin of the ions is $S = \frac{1}{2}$, the energy levels split into singlet and triplet as discussed in §§ 9.5–9.6. When the ions are identical, the 'isotropic' part of the interaction determines the singlet-triplet splitting whose size can be found from intensity measurements as a function of temperature, while the 'anisotropic' part is found from the splitting of the triplet as measured by the separation of the satellites as a function of orientation of the external magnetic field. An example of an extensive analysis of this type is the work on $K_2(\text{Ir}, \text{Pt})\text{Cl}_6$ and related compounds by Griffiths, Owen, Park, and Partridge (1959). Here the Ir^{4+} , $5d^5$, ions are subject to a strong ligand field (see Chapter 8) of exact octahedral symmetry, with effective spin $S = \frac{1}{2}$ and $g = 1.79$ (isotropic); the Pt^{4+} , $5d^6$, ions with a closed $d\epsilon$ shell act as diluent. The spin-spin interaction is assumed to have the form

$$\mathcal{H}_{\text{ss}} = \mathcal{J}(\mathbf{S}_i \cdot \mathbf{S}_j) + \mathcal{J}'_x S_{ix} S_{jx} + \mathcal{J}'_y S_{iy} S_{jy} + \mathcal{J}'_z S_{iz} S_{jz}, \quad (9.75)$$

where the anisotropic terms can also be written in the form

$$D_e \{ 2S_{iz} S_{jz} - S_{ix} S_{jx} - S_{iy} S_{jy} \} + E_e (S_{ix} S_{jx} - S_{iy} S_{jy}) \quad (9.76)$$

$$= D_e \{ 3S_{iz} S_{jz} - (\mathbf{S}_i \cdot \mathbf{S}_j) \} + E_e (S_{ix} S_{jx} - S_{iy} S_{jy}) \quad (9.77)$$

with (since $\mathcal{J}'_x + \mathcal{J}'_y + \mathcal{J}'_z = 0$)

$$D_e = \frac{1}{2} \mathcal{J}'_z, \quad E_e = \frac{1}{2} (\mathcal{J}'_x - \mathcal{J}'_y). \quad (9.78)$$

The crystal structure is face-centred cubic, so that each Ir^{4+} ion has twelve nearest neighbours (nn) and six next nearest neighbours (nnn). The interaction parameters are given in Table 9.4.

TABLE 9.4

Interaction parameters between Ir^{4+} ions in two salts. After Table 1 (see also Table 8) of Harris and Owen (1965)

		$\text{K}_2(\text{Ir}, \text{Pt})\text{Cl}_6$	$(\text{NH}_4)_2(\text{Ir}, \text{Pt})\text{Cl}_6$
Nearest neighbours	\mathcal{J} (cm^{-1})	$+8.0 \pm 0.8$	$+5.2 \pm 0.8$
	\mathcal{J} ($^\circ\text{K}$)	$+11.5 \pm 1$	$+7.5 \pm 1$
	D_e (cm^{-1})	$+0.45 \pm 0.01$	$+0.42 \pm 0.01$
	E_e (cm^{-1})	-0.18 ± 0.01	-0.22 ± 0.01
Next-nearest neighbours	\mathcal{J} (cm^{-1})	$+0.38 \pm 0.03$	$+0.27 \pm 0.03$

The interactions are antiferromagnetic (\mathcal{J} positive) in character, the triplet level lying above the singlet. Comparisons have been made with the magnetic behaviour (Cooke, Lazenby, *et al.* 1959) of the undiluted salts, which become antiferromagnetic below 3.05 and 2.15°K respectively. These transition temperatures are smaller than the Curie-Weiss constants by a factor of about $\frac{1}{10}$; this is related to the small size of the isotropic interaction between next nearest neighbours, which has been measured indirectly from the spectra of triads of three coupled ions (Harris and Owen 1965). The magnitude of the exchange interaction and its dependence on the inter-ionic distance has been discussed using a simple model by Griffiths *et al.* (1959), and in more detail by Judd (1959c). The problem of magnetic order in the co-operative state is considered in the papers quoted, and is discussed using spin-wave theory by Lines (1963).

The observation of pair spectra is considerably more difficult for ions whose effective spins are greater than $\frac{1}{2}$ because the spectrum of each single ion may be complicated through the presence of fine and hyperfine structure. A brief survey of some experiments is given by Owen (1961). Suppose the spectrum of a single ion i is given by the Hamiltonian

$$\mathcal{H}_i = g\beta(\mathbf{H} \cdot \mathbf{S}_i) + D_c\{S_{iz}^2 - \tfrac{1}{3}S_i(S_i+1)\} + E_c(S_{ix}^2 - S_{iy}^2) + A(\mathbf{S}_i \cdot \mathbf{I}_i) \quad (9.79)$$

with an identical Hamiltonian for ion j . The fine structure terms in D_c , E_c are labelled with subscript c , and have their origin in higher-order effects of the crystal field. Two similar ions are then coupled by

an interaction of the type given by eqns (9.75), (9.77). We assume that the axes (x, y, z) for D_e, E_e are the same as those for D_o, E_o ; usually this requires that the z -axis is not only the line joining the ions but also a principal axis of the ligand interaction (in other cases this assumption is equivalent to neglect of terms of the form $S_{ix}S_{iz}$, etc. in (9.79) or terms of the form $S_{ix}S_{jz}$, etc. in (9.75)).

If g, A are isotropic, and the term in \mathcal{J} is much larger than any of the others, the spins $\mathbf{S}_i, \mathbf{S}_j$ couple to form states of total spin \mathbf{S} whose values are $(S_i+S_j), (S_i+S_j-1), \dots, 0$, in terms of which the spin Hamiltonian may be written

$$\mathcal{H} = g\beta(\mathbf{H} \cdot \mathbf{S}) + \frac{1}{2}\mathcal{J}\{S(S+1) - S_i(S_i+1) - S_j(S_j+1)\} + \quad (9.80)$$

$$+ D_S\{S_z^2 - \frac{1}{3}S(S+1)\} + E_S(S_x^2 - S_y^2) + \quad (9.81)$$

$$+ \frac{1}{2}A\{\mathbf{S} \cdot (\mathbf{I}_i + \mathbf{I}_j)\}. \quad (9.82)$$

Here (9.81) is the reduced value of the 'fine' structure for the state of total spin \mathbf{S} . The values of D_S, E_S are given by

$$D_S = (3\alpha_S D_e + \beta_S D_o); \quad E_S = (\alpha_S E_e + \beta_S E_o) \quad (9.83)$$

where

$$\left. \begin{aligned} \alpha_S &= \frac{1}{2} \left\{ \frac{S(S+1) + 4S_i(S_i+1)}{(2S-1)(2S+3)} \right\}, \\ \beta_S &= \frac{3S(S+1) - 3 - 4S_i(S_i+1)}{(2S-1)(2S+3)}. \end{aligned} \right\} \quad (9.84)$$

The hyperfine constant in eqn (9.82) is halved because each ion is identical (see end of § 9.5). The overall width of the hyperfine structure is unaltered, but the components have maximum intensity in the middle and minimum at the ends of the hyperfine structure as in Fig. 9.4.

The major term (9.80) represents a set of states of total spin S whose energies follow the Landé interval rule. If \mathcal{J} is positive (antiferromagnetic), the state $S = 0$ is lowest, with $S = 1$ higher in energy by \mathcal{J} , and $S = 2$ higher than the latter by energy $2\mathcal{J}$, etc. The Zeeman interaction splits each state of total spin S into $2S+1$ substates, the separation of consecutive substates being just $g\beta H$, independent of S . However the spectrum of a state of total spin S may be identified (a) by its fine structure (resulting from (9.81)) of $2S$ transitions allowed by the selection rule $\Delta S_z = \pm 1$, which is valid so long as $g\beta H \gg D_S, E_S$; (b) by the variation of intensity with temperature. If \mathcal{J} is positive, a state of total spin S is higher in energy than the ground state $S = 0$

by an amount $W_S = \frac{1}{2} \mathcal{J} S(S+1)$, and the population of each of its substates is proportional to the quantity

$$I_S = \frac{\exp(-W_S/kT)}{\sum_S (2S+1) \exp(-W_S/kT)} \quad (9.85)$$

which (apart from temperature-independent factors) gives the temperature variation of the intensity of a transition within a given manifold S relative to that for a normal paramagnetic ion with no excited states. The form of the function I_S is shown in Fig. 9.10 for the case

$$S_i = S_j = \frac{5}{2}$$

and a simple isotropic exchange interaction for which $W_S = \frac{1}{2} \mathcal{J} S(S+1)$.

As mentioned in § 9.3, extra terms may occur in the exchange interaction for values of S_i, S_j greater than $\frac{1}{2}$. If we include a simple biquadratic term, making the exchange Hamiltonian

$$\mathcal{H}_{\text{ex}} = \mathcal{J}(\mathbf{S}_i \cdot \mathbf{S}_j) + \mathcal{J}^{(2)}(\mathbf{S}_i \cdot \mathbf{S}_j)^2, \quad (9.86)$$

the separation between successive manifolds of total spin $S, S-1$ becomes

$$W_S - W_{S-1} = \mathcal{J}S + \mathcal{J}^{(2)}S\{S^2 - S_i(S_i+1) - S_j(S_j+1)\}, \quad (9.87)$$

showing that the Landé interval rule is no longer obeyed. If the energy

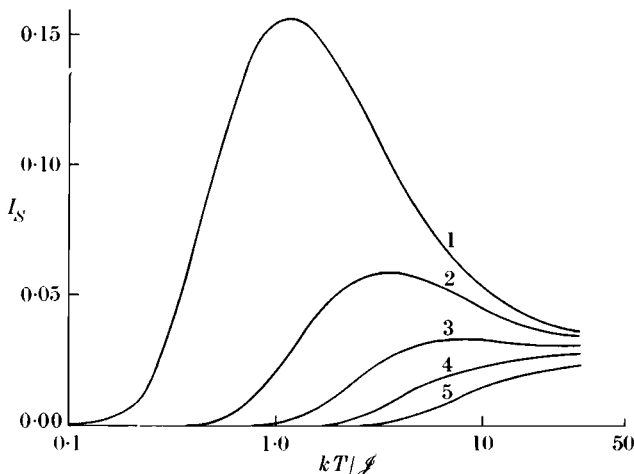


FIG. 9.10. The relative intensity, as measured by the function I_S (eqn (9.85)), of transitions for a pair of spins $S_i = S_j = \frac{5}{2}$, coupled by an exchange interaction $\mathcal{J}(\mathbf{S}_i \cdot \mathbf{S}_j)$. The numbered curves give the intensity for the different manifolds of total spin $S = 1, 2, 3, 4$, and 5 , whose energy is $W_S = \frac{1}{2} \mathcal{J} S(S+1)$ above the ground state $S = 0$, plotted against the reduced temperature (kT/\mathcal{J}) . (After Owen 1961.)

of more than one excited state can be found experimentally, the values of both \mathcal{J} and $\mathcal{J}^{(2)}$ are determined. Work on Mn^{2+} pairs in MgO suggests that $\mathcal{J}^{(2)}$ is about a few per cent of \mathcal{J} , though the biquadratic term may be partly due to exchange-induced distortion of the lattice (Harris and Owen 1963; Rodbell, Jacobs, Owen, and Harris 1963).

9.11. Temperature-dependent effects

Apart from the excited states in pair spectra, the possibility of temperature-dependent effects in spin-spin interaction has not so far been considered. The Hamiltonian for spin-spin interaction does not in itself contain any explicit temperature-dependence, and the width and shape of lines resulting from spin-spin interaction might therefore be expected to be constant. This is true over a wide temperature range in most substances, but in this section we discuss two effects that modify this result, one at high temperatures, the other at low temperatures.

As pointed out in § 9.9, the full effects of spin-spin interaction in line broadening appear only if the local field due to neighbouring ions persists for a time long compared with a characteristic time τ_2 whose reciprocal is immediately related to the line width due to spin-spin interaction only when the resonance line is 'homogeneously broadened'. If the line width is predominantly due to 'inhomogeneous broadening', it is better to regard τ_2 as representing the average duration of the wave train emitted or absorbed by the spin system. If the local field is due to another species of ions whose spin-lattice relaxation time is τ_1 , the local field will persist only for a time of order τ_1 , and over longer periods the local field will be 'averaged out'. This is a form of motional narrowing which can be observed in a compound that contains two paramagnetic species, one with an abnormally short value of τ_1 , the other with a long value of τ_2 (and hence also of τ_1), such as neodymium ethylsulphate containing a small fraction of gadolinium ions (Bleaney, Elliott, and Scovil 1951). At a temperature of 90°K , no resonance due to the Nd^{3+} ions was observed because of broadening due to the very small value of τ_1 ($< 10^{-11}$ s), while the Gd^{3+} resonance was observed with a line width substantially the same as in a diamagnetic host lattice such as lanthanum ethylsulphate. At 20°K , where the value of τ_1 for the Nd^{3+} ions is at least 10^{-8} s, the full effect of their magnetic dipolar field is observed in the Gd^{3+} spectrum. The contrast in resolution is shown in Fig. 9.11. The effective spin-lattice relaxation time for the Gd^{3+} ions was found to be much shorter than in a diamagnetic host owing to coupling with the rapidly fluctuating

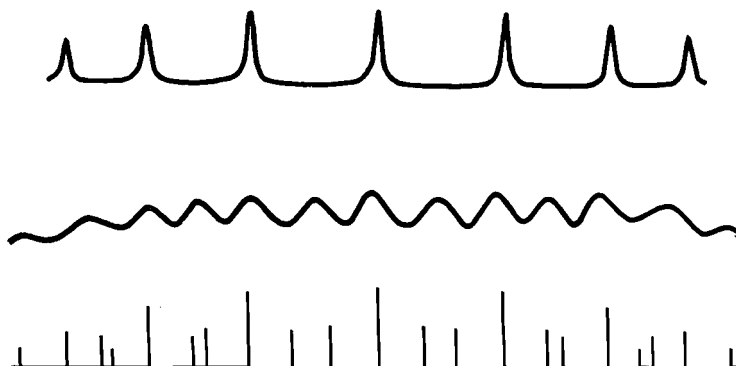


FIG. 9.11. The spectrum of Gd^{3+} , $4f^7$, $^8S_{7/2}$ present in low concentration in a single crystal of neodymium ethylsulphate. Above, spectrum at 90°K , showing absence of broadening, owing to rapid relaxation of the Nd^{3+} ions. Centre, spectrum at 20°K , broadened by dipolar field of Nd^{3+} ions. Below, triplet structure on each Gd^{3+} line, calculated assuming dipolar interaction with nearest pair of Nd^{3+} ions (cf. Fig. 9.9). The external magnetic field is parallel to the c -axis of the crystal, and the two nearest Nd^{3+} ions lie along this axis. (After Bleaney, Elliott, and Scovil 1951.)

fields produced by the Nd^{3+} ions, which provides a path by which energy can be rapidly transferred to the lattice. As in the case of nuclear magnetic resonance in a liquid, the narrowing effect for the Gd^{3+} ions is most pronounced the shorter the spin-lattice relaxation time of the neodymium ions, while the reduction of τ_1 for the Gd^{3+} ions should be most pronounced when τ_1^{-1} for the Nd^{3+} ions is of the same order as the resonant frequency of the Gd^{3+} ions (i.e. when the Fourier components at the Gd^{3+} resonance frequency of the fluctuating local field due to the Nd^{3+} ions have their maximum amplitude).

True motional narrowing requires much shorter correlation times for electron than for nuclear magnetic resonance, and (apart from conduction electron spin resonance) is correspondingly less important. In liquids it is associated with some unusual effects on the hyperfine structure (see, for example, McConnell (1956); McGarvey (1956)); in ionic solids it occurs only at temperatures where rapid ionic diffusion becomes possible.

The second (low temperature) effect that we now discuss does not depend on the intervention of another phenomenon such as spin-lattice relaxation, but is a consequence simply of the changing Boltzmann population of the different magnetic levels. In considering broadening due to spin-spin interaction we have so far assumed that all orientations of neighbouring dipoles are equally probable. This is of course an approximation that is not seriously in error at high

temperatures such that $kT \gg g\beta H$, but as the temperature falls and we approach the region where kT is of the same order as $g\beta H$ the population of the spin-orientation states of higher energy becomes substantially less than that of the low-energy spin orientations. If (as we are assuming) the energy difference is mainly due to the Zeeman energy in an external field, the population shift is from the orientations where the magnetic dipoles are antiparallel to the field (if the gyro-magnetic ratio is negative, as for free electrons, this means the spin orientations parallel to the field) into the dipole parallel (spin antiparallel) positions. For convenience we refer to this as a shift from the 'up' positions to the 'down' positions. When $kT \ll g\beta H$, the spins are almost entirely in the 'down' position and the static magnetization of the sample approaches its saturation value.

We now consider the local field at a given ion. If the neighbouring spins are predominantly in the 'up' position, the local field that they set up at the given ion will be (say) positive, while if they are predominantly 'down' the local field will be negative. The line broadening arises from the random statistical variation in the chances of any given neighbour being 'up' or 'down', but if on average these chances are equal the centre of gravity of the line will not be shifted from the resonance position for a single ion. If the chances are unequal, one wing of the broadened line will have higher intensity and the other lower intensity (see Fig. 9.12), so that the centre of gravity will be shifted. The effect becomes progressively greater in proportion to the amount by which the mean expectation value of 'down' spin predominates over 'up' spin. The size of the shift is determined by the mean value of the local field, which is proportional to the mean magnetization of the spin system(s) responsible for the local field.

As the temperature is reduced so that kT becomes much smaller than $g\beta H$, the spins fall more and more into the 'down' state and the local field approaches its maximum value corresponding to the saturation magnetization of the paramagnetic system. At the same time the shift in the centre of gravity of the resonance line approaches its maximum value. This is accompanied by a decrease in the randomness of spin orientation (decrease in entropy) so that the resonance line becomes less broad and, ideally, when all spins are completely aligned, the width should approach zero. However this assumes that the local field (and hence the line shift) is the same in all parts of the sample, and, because of demagnetizing fields, this is true only for certain sample shapes such as a sphere or ellipsoid.

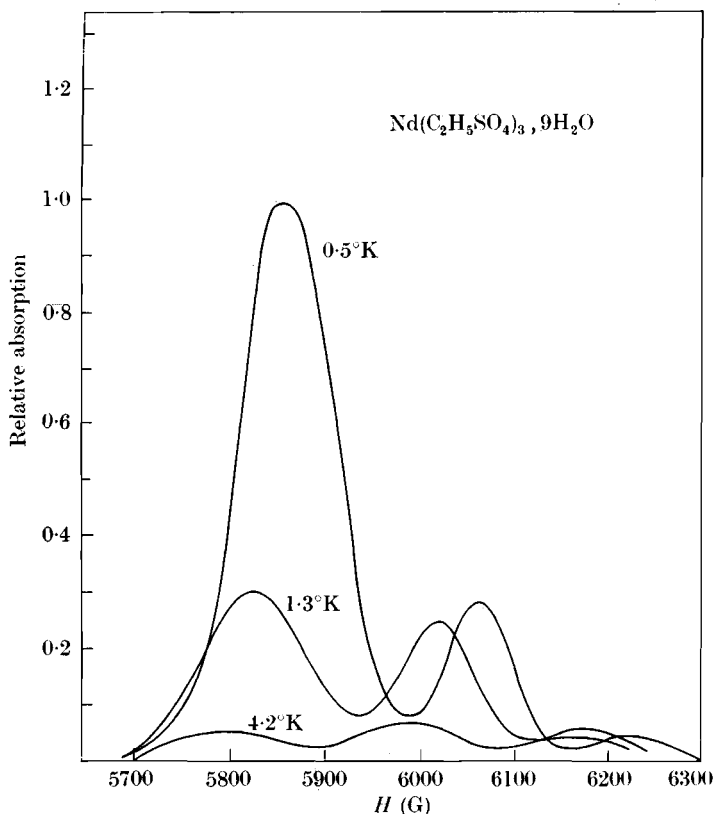


FIG. 9.12. Resonance absorption at 30 GHz in neodymium ethylsulphate at very low temperatures (magnetic field parallel to hexagonal axis). As the temperature is lowered the absorption strength increases and shifts progressively to one side. The spin-spin interaction is mainly due to the dipolar field of nearest neighbours along the hexagonal axis; when these dipoles are aligned in the external field their local field adds to the external field, so that at very low temperatures the intensity is concentrated in the line on the low field side when observed at constant frequency. (After Svare and Seidel 1964.)

For a system of spins $S = \frac{1}{2}$ the nature of the temperature dependence proves to be rather simple. If the Zeeman Hamiltonian for a magnetic field parallel to the z -axis is

$$\mathcal{H} = g\beta HS_z$$

the mean expectation value of S_z is

$$\langle S_z \rangle = -\frac{1}{2} \tanh(g\beta H/2kT). \quad (9.88)$$

The shift in the centre of gravity of the resonance line with temperature is measured by the first moment

$$\langle \Delta\nu \rangle = \langle \nu \rangle - \nu_0, \quad (9.89)$$

where ν_0 is the centre frequency of the unshifted line. At any given temperature we should expect the shift $\langle \Delta\nu \rangle$ to be proportional to the value of $\langle S_z \rangle$. From the method of moments the actual relations are found to be

$$\hbar \langle \Delta\nu \rangle = -\frac{1}{2} \tanh\left(\frac{g\beta H}{2kT}\right) \sum_j (3\mathcal{J}'_{zz}/2)_{ij} \quad (9.90)$$

if all the spins are identical, and

$$\hbar \langle \Delta\nu \rangle = -\frac{1}{2} \tanh\left(\frac{g'\beta H}{2kT}\right) \sum_j (\mathcal{J}_{zz})_{ij'} \quad (9.91)$$

for interaction with a system of non-identical spins $S' = \frac{1}{2}$ denoted by j' , whose g -factor for a field along the z -axis is g' .

In calculating the second moment we are interested in its value relative to the centre of gravity ($\nu_0 + \langle \Delta\nu \rangle$) of the shifted line, i.e. in the quantity

$$\begin{aligned} \langle \Delta\nu^2 \rangle_c &= \langle \{\nu - (\nu_0 + \langle \Delta\nu \rangle)\}^2 \rangle \\ &= \langle \Delta\nu^2 \rangle - (\langle \Delta\nu \rangle)^2 \end{aligned} \quad (9.92)$$

rather than the second moment $\langle \Delta\nu^2 \rangle$ measured relative to the frequency ν_0 of the unshifted line. In the high temperature limit assumed in §§ 9.7–9.10 the value of $\langle \Delta\nu \rangle$ goes to zero, and the distinction between $\langle \Delta\nu^2 \rangle_c$ and $\langle \Delta\nu^2 \rangle$ is unnecessary. This is no longer true at low temperatures. It turns out that for a set of identical spins $S = \frac{1}{2}$ the formula for the second moment measured from the centre of the shifted line is

$$\hbar^2 \langle \Delta\nu^2 \rangle_c = \frac{1}{4} \left\{ 1 - \tanh^2\left(\frac{g\beta H}{2kT}\right) \right\} \sum_j (3\mathcal{J}'_{zz}/2)_{ij}^2, \quad (9.93)$$

while for a spin i surrounded by a set of non-identical spins j' , also with $S' = \frac{1}{2}$, we have

$$\hbar^2 \langle \Delta\nu^2 \rangle_c = \frac{1}{4} \left\{ 1 - \tanh^2\left(\frac{g'\beta H}{2kT}\right) \right\} \sum_{j'} (\mathcal{J}_{zz})_{ij'}^2. \quad (9.94)$$

The temperature-dependent factors in curly brackets in (9.93), (9.94) reduce to unity in the high temperature limit (in agreement with eqn (9.57), specialized to $S = S' = \frac{1}{2}$) and vanish as $T \rightarrow 0$.

Experimental determinations of line shift and shape at very low temperatures have been made by Svare and Seidel (1964), who also discuss the effects of demagnetizing fields and non-uniform precession within the sample (magnetostatic modes). The classification into 'identical' and 'non-identical' spins is not straightforward when the

resonance frequencies are shifted by appreciably different amounts through interaction with neighbouring spins, as in Fig. 9.12. When $S > \frac{1}{2}$, there may be the additional complication of crystal field splittings. The theory is discussed in some detail by McMillan and Opechowski (1960, 1961), and compared with experiment by Svare and Seidel (1964).