The general Hamiltonian for a free ion is,

$$H = H_F + H_{LS} + H_{SS} + H_B + H_N + H_Q + H_h$$

where $H_F$ represents the interaction of the electrons with the nuclear charge and the mutual repulsion of the electrons and is usually of the order of $10^5 \text{cm}^{-1}$. $H_{LS}$ represents the interaction between the electron spin with the orbital moment and is of the order of $10^2 \text{cm}^{-1}$ for the iron group and $10^3 \text{cm}^{-1}$ for the rare earths and uranium groups. $H_{SS}$ represents the mutual interaction between the magnetic dipoles and is of the order of $1 \text{cm}^{-1}$. The term $H_B$ represents the interaction of electrons with the external magnetic field and is of the order of $1 \text{cm}^{-1}$. The term $H_N$ describes the dipole and dipole interaction between the nuclear moment and the magnetic moment of the electron and also the anomalous interaction of the electrons with the nuclear spin and is of the order of $10^{-1} - 10^{-3} \text{cm}^{-1}$. The term $H_h$ represents the direct effect of the applied magnetic field on the nuclear magnetic moment and is of the order of $10^{-3} \text{cm}^{-1}$.
CRYSTAL FIELD

When the paramagnetic ion is incorporated in a solid, there are interactions between it and its surroundings. These interactions are mainly of two types: (i) interaction between the paramagnetic ions, and (ii) those between the paramagnetic ion and the diamagnetic neighbours. The former type of interaction can be reduced effectively to a small value by diluting the paramagnetic substances with an isomorphous diamagnetic salt. The ions (ligands) surrounding the paramagnetic ion produce a strong electrostatic field (the ligand field) at the paramagnetic ion site. (The ions are regarded as point charges.\textsuperscript{1-3} However, when the overlap of wave functions of the surrounding ions and the paramagnetic ion is considerable, e.g. when a superhyperfine structure is observed, the ions cannot be regarded as point charges and one has to apply molecular orbital calculations). The electrostatic field reflects the symmetry of the site of the paramagnetic ion. The electrons, localized on the ions and moving in this field, experience a Stark splitting of their orbital levels, and there degeneracies are partly lifted depending on the symmetry at the site, and thus can be predicted by group theory. In the case of local cubic symmetry group 1,2,3, or 4 fold degenerate levels are found, but in case of lower symmetry, levels very often are either singlets or degenerate in pairs only. An important theorem concerning the residual degeneracy is due to Kramers', in a
system containing an odd number of electrons, at least two fold degeneracy must remain in the absence of a magnetic field. The pair of states (Kramers' doublets) involved are time conjugate, one being obtained from the other by use of time reversal operator, they can be split by a magnetic perturbation (a time odd operator), but not by an electrostatic perturbation, which is even under time reversal.

The crystal field interaction is affected by the electrostatic screening of the unpaired electrons if the outer shells are occupied. Depending upon its magnitudes relative to other interactions, the crystalline field interaction is generally classified into three categories.

(1) Weak crystal field

The crystal field interaction is small in comparison with the spin-orbit interaction. Here the crystal field splitting is small in comparison with the splitting between multiplets. This applies to rare earth and actinide groups.

<table>
<thead>
<tr>
<th>Name of group</th>
<th>Atomic number</th>
<th>Incomplete shell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rare Earth</td>
<td>58(Ce) to 70(Yb)</td>
<td>4f</td>
</tr>
<tr>
<td>Actinide</td>
<td>&gt; 90(Th)</td>
<td>5f-6d</td>
</tr>
</tbody>
</table>

e.g. in case of rare earth the unfilled 4f shell is an inner shell screened by the 5s and 5p shells
crystal field splitting because of the screening electrons is less than \(1000\text{cm}^{-1}\) in most cases, on the other hand, the spin orbit coupling energy is greater (600-3000\text{cm}^{-1} \text{Ce to Yb}) than in the 3d ions.

(2) Intermediate crystal field

The crystal field interaction is small in comparison with the electrostatic interaction but large in comparison with spin-orbit interaction. Here the crystal field splitting is large in comparison with the separation of the different multiplets. The applies to salts of the iron group.

<table>
<thead>
<tr>
<th>Name of group</th>
<th>Atomic number</th>
<th>Incomplete shell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>21(Sc) to 29(Cu)</td>
<td>3d</td>
</tr>
</tbody>
</table>

e.g. In case of iron group in which 3d shell is the outermost shell orbital motion of the 3d electrons are strongly perturbed by the crystalline field.

(3) Strong crystal field

The crystal field interaction is large in comparison with the electrostatic interactions. Here the crystal field splitting is large in comparison with separation of different multiplets. This occurs in the ions of the platinum and palladium groups.
Name of group | Atomic number | Incomplete shell
--- | --- | ---
Palladium | 40(Zr) to 47(Ag) | 4d
Platinum | 72(Hf) to 79(Au) | 5d

In addition to 4d and 5d electrons, sometimes it occurs in iron group ions, particularly in strongly covalent compounds such as the cyanides and other examples are known as Co$^{2+}$ in rutile (TiO$_2$) and in Alumina (Al$_2$O$_3$).

**THE SPIN-HAMILTONIAN**

Unpaired electrons in a solid are subject to many interactions: those of the orbital motion and spin with each other, with the applied magnetic field, and with magnetic moments of nearby nuclei. There are also electrostatic and covalent interactions with the crystalline environment. Generally the theoretical description of a paramagnetic entity is so complex that a complete solution for the energy levels and wavefunctions is impractical. Commonly electron spin resonance is limited to a set of low-lying energy levels whose magnetic behaviour is described by an expression called the "Spin-Hamiltonian".

The lowest group of electronic states is characterized by a single quantum number $S'$, even though each state is really a complicated mixture of the spin and orbital wave functions of the free ion. $S'$ is called the effective or
fictitious spin of the system, and is defined simply by equating $2S + 1$ to the number of electronic levels in the lowest group. For some cases $S'$ equals the spin value $S$ e.g. $\text{Cr}^{3+}(d^3)$ has a $^4F$ ground state. In an octahedral field, the lowest level is an orbital singlet. The next highest state, an orbital triplet, is about 18,000 cm$^{-1}$ higher. The low-lying singlet has a four-fold spin degeneracy. An external magnetic field removes the four-fold spin degeneracy and transitions between the levels can be induced according to the selection rule $\Delta M = \pm 1$. The real spin $S$ therefore equals $S' = 3/2$. For other cases $S' \neq S$ e.g. in case of $\text{Co}^{2+}(d^7)$ the ground state is also $^4F$. In an octahedral field the ground state is an orbital triplet, spin orbit coupling removes part of the orbital degeneracy and the four-fold spin degeneracy. The levels are split into a lowest doublet and higher lying four-fold and six-fold degenerate levels. These levels are separated by about 600 and 1000 cm$^{-1}$. In this case $S = 3/2$, however $2S + 1 = 2$ or $S' = 1/2$, since only transitions between the lowest doublet can be observed. The higher lying levels are not sufficiently populated at liquid helium temperatures. This use of an effective spin means that for temperatures where only $2S' + 1$ lowest electronic levels are appreciably populated the paramagnetic ion is treated like a magnetic dipole which has $2S' + 1$ allowed orientations in an applied magnetic field, and each energy level is associated with one
orientation. But the effective magnetic moment of this dipole (and hence the splitting produced by the applied field) does not correspond to a 'spin only' value; it is different by the factor $g/g_0$, where $g$ is called the spectroscopic splitting factor.

The energy level, however, often have initial splitting in zero magnetic field. This means that the dipole cannot be treated as free but that, in addition to the interaction with the applied magnetic field, energy terms must also be added representing electrostatic interaction between magnetic electrons and the crystal field (which may give stark splitting if $S > 1/2$) and magnetic interaction between electrons and nucleus (which may give hyperfine splitting).

The sum of all the terms, written as a sum of energy operators to be applied to the effective spin states, constitutes the spin-Hamiltonian for the system. The advantage of using a spin-Hamiltonian is that the rather complicated behaviour of the lowest energy levels of the paramagnetic ion in a magnetic field can be described by specifying the effective spin, together with a small number of parameters which measures the magnitude of the various terms in the spin-Hamiltonian.
(i) The spectroscopic splitting factor $g$

The parameter which may be associated with a single absorption line is its actual resonance position. If the microwave frequency is held constant then the Eq. (1.11) shows that the only two parameters that can vary are the values of the externally applied magnetic field and the value of $g$-factor. Hence, a measurement of the value of the field at which resonance occurs determine the value of the $g$-factor associated with particular unpaired electron in the atom or molecule in which it is residing.

An electron with no orbital angular momentum has a $g$ value equal to that of the free electron spin, i.e. equal to 2.0023. If on the other hand, the electron is moving in an atomic orbital associated with a single atom, it may possess considerable orbital angular momentum and this will shift the $g$-value away from that appropriate to the free spin. The reason for this shift in $g$ value is that the relationship between magnetic moment and angular momentum is different for spin motion and for orbital motion.

In the case of an electron associated with a free atom, which has no external magnetic or electric fields acting on it, the resultant $g$-value can be derived directly in terms of quantum numbers defining the total spin and orbital magnetic moments, $\vec{S}, \vec{L}$, and $\vec{J}$. The $g$ value is infact,
then identical with Lande's splitting factor and is given by the Eq. (1.4). If the unpaired electron is associated with an atom contained within a solid crystalline lattice then quite strongly internal electric field, which arises from the interaction between atom and its surroundings will also be acting on it. These electric fields act on the orbital states of the atom and can vary radically alter their energies, and, as a result, the simple Lande factor can no longer be applied. Here the position of the resonance for a fixed frequency is determined by the competitive effects of the environment, which field tends to 'quench' (the electronic orbital motion interacts strongly with the crystalline fields and become decoupled from the spin, a process called 'quenching') the orbital angular momentum.

The more complete the quenching, the closer the g-factor approaches the free electron value. For example, \( g = 2.0036 \) in the free radical \( \alpha, \alpha'-\text{diphenyl}-\beta-\text{picryl hydrazyl} \) which is very close to the free electron value of 2.0023. It equals 1.98 in many chromium compounds, and it sometimes exceeds 6 for \( \text{Co}^{2+} \). Thus the amount of quenching varies with the spin systems.

In the general case therefore the quantitative field frequency relation is not known a priori and we write
the generalized resonance condition as

\[ h\nu = g\beta B \]

where \( g \) is the \( g \)-factor, and is determined from the spectrum. The above equation can be regarded as giving the separation between the eigen values of a spin Hamiltonian

\[ H = g\beta \vec{S}.\vec{B} \]

so that \( g \) is a measure of the effective magnetic moment associated with an angular momentum \( \vec{S} \) such that there are \((2S+1)\) energy levels in an applied magnetic field.

Since the magnitude of the orbital part of the magnetic moment depends on the crystal field its magnitude is usually different for different directions of \( B \), and shows an angular variation which follows the symmetry of the crystal field. The total \( g \) value (spin plus orbit) may then be anisotropic by an amount which depends on the magnitude of the orbital contribution to the moment, and on the asymmetry in the crystal field.

The spin-Hamiltonian for the interaction of \( \vec{S} \) with the applied field \( \vec{B} \) is expressed as

\[ H = \beta \vec{S}.g.\vec{B} \]
(ii) Fine structure

The spectra of oriented system of total spin greater than one half often show \((2S)\) features, indicating unequal separation between the \((2S+1)\) Zeeman levels. This structure is called fine structure by analogy with the appearance of structure in atomic optical spectra when the degeneracy of the levels in a term is lifted through spin orbit coupling. The fine structure reflects a splitting of the \((2S+1)\) levels even in the absence of a magnetic field, a phenomenon called zero field splitting. If magnesium ions existed in free state and were not subjected to the electrostatic fields inside the crystal or molecule, then all possible orientations of \(S = 5/2\) total spin vector would have same energy, and hence all would be degenerate on an energy-level diagram, as shown in Figure 2.1. The application of an external magnetic field would then cause the spins to take up different quantized orientations with respect to this field. The possible orientations varying from those with a component of \(M_s = + 5/2\) in the direction of the field through those with orientations corresponding to \(M_s = + 3/2\); \(+ 1/2\); \(- 1/2\); \(- 3/2\) to the other extreme of \(- 5/2\). Moreover the energies of those different orientations will diverge with the application of the applied magnetic field, by amounts proportional to the resolved spin quantum number. Transition from one state to another must again obey the
FIG. 2.1 DIVERGENCE OF DIFFERENT COMPONENT LEVELS WITH APPLIED MAGNETIC FIELD. IF THERE IS NO INTERNAL FIELD, ALL OF THE SIX $M_s$ LEVELS OF Mn$^{2+}$ ION HAVE THE SAME ENERGY IN ZERO FIELD.
normal selection rule $\Delta M_s = \pm 1$ so that only those indicated by the arrows are allowed, and it is evident that for a given incoming microwave frequency all the possible transitions will take place at the same value of the externally applied field, and hence a single absorption line will be produced from the overlapping transitions.

If the manganese ion is present in a crystal, it will be acted on by the internal electrostatic field and the effect of latter on the energy levels of the ion is profound. First of all they split the ground state into a number of components. The number of such components and the extent of the splitting depends critically on the symmetry of the electric field and on its strength but electric field itself cannot remove the two fold degeneracy associated with states of the same resolved quantum numbers. The action of the internal field will therefore be as indicated on the left hand side of Fig. 2.2, and zero-field electronic splitting will be produced between $\pm 1/2$, the $\pm 3/2$, and the $\pm 5/2$ levels, as indicated. Application of the external magnetic field will now remove the two-fold degeneracy of these spin levels will diverse in the way shown in Fig. 2.2. At high enough values of the external magnetic field they will be arranged in an energy order from $+5/2$ to $-5/2$ as indicated. The allowed transitions between them no
Figure 2.2

Divergence of different component levels of Mn$^{2+}$ ion from zero field splittings produced by the internal fields.
longer occur at the same value of the external magnetic field, however, five separate absorption will now be obtained. The separation between these is a direct reflection of the separation produced in zero magnetic field by the electrostatic internal fields, and can therefore be used as a measure of this quantity.

In the spin-Hamiltonian this term is represented by:

\[ H = \vec{S} \cdot \vec{D} \cdot \vec{S} \]

where \( \vec{D} \) is a tensor quantity.

(iii) Magnetic hyperfine structure

Hyperfine structure in the ESR spectra arises from the interaction of unpaired electron spin with nuclear magnetic moment. An unpaired electron will not only experience the externally applied magnetic field, but also interact with the field produced by the magnetic moment of the nucleus itself. Although the magnetic moments of nuclei are very small, the magnetic field which they produce at the site of their own electrons can be \(~10\) mT for an electron moving around a nucleus which has magnetic moment of about one nuclear magnetone.

Thus an electron experiences the magnetic field which is applied externally as well as the magnetic field
due to the nuclear magnetic moment. The nuclear moment is space quantized in the direction of internal magnetic field (which is largely due to electrons) and can take up \((2I+1)\) positions, \(I\) being the nuclear spin quantum number. The \((2I+1)\) different orientations in turn produce \((2I+1)\) incremental fields at the site of electron spin. These \((2I+1)\) incremental fields will all have different components resolved along the direction of the external magnetic field, and as a result, the total magnetic field, experienced by the electron spin will have one of \((2I+1)\) different possible values, the particular value depending on the orientation of the particular nucleus around which the electron is orbiting. The energy difference between each electronic state is therefore different for \((2I+1)\) nuclear orientations and this gives rise to \((2I+1)\) lines. Since the energies associated with these \((2I+1)\) different nuclear orientations differ only by a very small amount, there will be an equal number of nuclei in all of the \((2I+1)\) orientations at normal temperature and hence there will be an equal number of unpaired electrons experiencing the \((2I+1)\) different values of the total magnetic field. Thus the hyperfine lines in each electronic transition have equal intensity. This make it readily possible to distinguish a hyperfine splitting from an electronic fine splitting where the lines have unequal intensities.

The electron spin-nuclear spin Hamiltonian can be
expressed in the form
\[ H = S \cdot A \cdot I \]
where \( A \) is the nuclear coupling tensor.

(iv) Quadrupole interaction

When the nucleus has a spin \( I \geq 1 \), and there is also an electric field gradient at the nucleus, an interaction with the nuclear electric quadrupole moment may arise. The electric field gradient is set up by the anisotropic distribution of electric charges on the paramagnetic ion and its immediate neighbours.

The Hamiltonian corresponding to quadrupole interaction can be expressed in the most convenient form
\[ H_Q = I \cdot Q \cdot I \]
here \( Q \) is the quadrupole coupling tensor.

The effect of quadrupole interaction on the resonance spectrum is usually complicated because it is accompanied by a large magnetic hyperfine structure interaction, so that there is a competition between the electric field gradient, and the magnetic field from the unpaired electrons, in fixing the orientations of the nucleus, the result is that, for a general direction of \( B \), the intensities and spacing of the usual \((2I+1)\) hyperfine lines corresponding to transition with \( \Delta m = 0 \) are modified by \( Q \), and there are
also additional lines corresponding to the normally
forbidden transitions $\Delta m = \pm 1, \pm 2$.

(v) The direct effect of $B$ on nucleus.

The nuclear magnetic moment interacts directly with
the applied field $B$. This interaction cannot effect the
ESR spectrum, unless the paramagnetic electrons are coupled
to the nucleus by the magnetic or electrostatic interaction.
If there is such coupling, there may be a measurable effect
on the spectrum, but this is usually very small, or negligible,
compared with all other terms. In any case, it will not
effect the spacing of $\Delta m = 0$ transitions, which are the
ones normally observed. The Hamiltonian can be written as

$$H_N = - g_N \mu_N B \cdot I$$

where $\mu_N$ is nuclear magneton, and $g_N$ is nuclear $g$-factor.

The various terms discussed above are in most cases
sufficient to describe the lowest energy levels of a paramagnetic
ion in a crystal. Collecting together they give the complete
spin-Hamiltonian

$$H = g \vec{S} \cdot \vec{g} \cdot B + D \cdot S + A \cdot I + Q \cdot I - g_N \mu_N B \cdot I$$

The tensors $\vec{g}$ and $\vec{D}$ are symmetrical but $\vec{A}$ is not
necessarily so. For rhombic and higher symmetries where
the environment possesses three orthogonal symmetry axes,
the off diagonal elements of $D, g$ and $A$ vanish and all
tensors have three symmetry axes are the principal axes (x, y, z).

The spin-Hamiltonian with respect to three axes is usually written as

\[ H = \beta (g_z B_z S_z + g_x B_x S_x + g_y B_y S_y) + D \left[ S_z^2 - \frac{1}{3} S(S+1) \right] \]
\[ + \epsilon (S_x^2 - S_y^2) + A_z I_z + A_x I_x + A_y I_y \]
\[ + Q' \left[ I_z^2 - \frac{1}{3} I(I+1) \right] + Q'' (I_x^2 - I_y^2) \]
\[ - \frac{B}{N} \vec{B} \cdot \vec{I} \]  

(2.00)

The form of the Hamiltonian for particular case depends largely on the symmetry of the crystal field, or of the surrounding of the paramagnetic ion. The expression is however not the most general expression for the spin-Hamiltonian permitted by symmetry consideration. For instance in cubic symmetry terms of the form \( S_x^4 + S_y^4 + S_z^4 \) have to be added.

For cubic symmetry

\[ g_x = g_y = g_z, \ A_x = A_y = A_z, \ D = E = Q' = Q'' = 0 \]

For tetragonal or trigonal symmetry

\[ g_z = g_y, \ g_x = g_x = g_\perp, \ A_z = A_\perp, \ A_x = A_y = A_\perp \]

and \( E = Q'' = 0 \).
The spin-Hamiltonian can also be written in the form

\[ H = \beta \vec{S} \cdot \vec{g} \cdot \vec{B} + \sum_{k=0}^{2} \sum_{l=0}^{\infty} B_k^l \hat{O}_k(s) + \hat{S} \cdot \hat{A} \cdot \hat{I} \]

\[ + \sum_{n=0}^{m} \sum_{m=-n}^{n} C_n^m \hat{O}_n^m(\vec{I}) - g_N \beta_N \vec{B} \cdot \vec{I} \]

(2.1)

The \( \hat{O}_k^l \) operators are referred to as equivalent operators and their form tabulated by Abragam & Bleaney. For \( \hat{O}_k^l(s) \) the operators \( \hat{J}_1 \) are replaced by \( \hat{S}_1 \), and for \( \hat{O}_n^m(\vec{I}) \) operators, \( \hat{J}_1 \) are replaced by \( \hat{I}_1 \). The coefficients \( k \) and \( n \) must be non zero even integers, where \( q \) and \( m \) are any positive or negative integers within the range \( -k \leq q \leq k \), \( -n \leq m \leq n \). The coefficients \( B_k^l \) and \( C_n^m \) assume definite values for specific interactions.

The relationship of the \( B_k^l \) coefficients with parameters \( b_k^l \), which is also frequently used in ESR, and with the other traditional parameters are given below.

\[ D = 3B_2^0 = b_2^0 \]
\[ E = B_2^0 = (1/3)b_2^2 \] (for orthorhombic zero field interaction)
\[ a = 120B_4^0 = 24b_4^4 \] (for fourfold axis coordinate system)
\[ a = -80B_4^0 = -1600\sqrt{2}b_4^3 = -(80/3)b_4^3 \] (for the three fold axis coordinate system).

Spin lattice relaxation

Exchange of energy between the thermal motions of the solid and the magnetic spin states, usually reffered to as spin lattice relaxation, is essential to the observation of
magnetic resonance. Without such an exchange, a continuous absorption of microwave resonant energy would not be possible.

The spin lattice relaxation time measures the energy transfer from the paramagnetic ions to the surroundings, that is to say, to the crystal lattice. This relaxation time $T_1$, often called the longitudinal relaxation time, is defined for two energy levels by

$$\frac{d}{dt} (\Delta N - \Delta N_0) = - \frac{(\Delta N - \Delta N_0)}{T_1}$$

where $\Delta N$ is the population difference between the two levels, $\Delta N_0$ is this difference at equilibrium. The differential equation expresses the rate at which the system approaches the equilibrium often having been disturbed by the absorption of energy.

As a rough rule long spin lattice times are to be expected when the $g$-value is closer to free spin value 2.0023 and short relaxation times when $g$ departs markedly from this value. Examples of the former type are isolated spins attached to defects, and transition group ions that have half-filled shells, whose ground states are $S$-states: on the other hand, short relaxation times are found for all ions of the $4f,5f$ groups (except those with the half-field shells $f^7$), and those ions of the $d$-groups for which the ligand field leaves orbitally degenerate ground state. The relaxation proceeds by three main processes discussed below:
(i) Direct process

A phonon of the same energy as the spin quantum required for a resonance transition is absorbed by the spin system, resulting in 'up' transition or a phonon is emitted, accompanied by a 'down' transition within the spin system. It becomes relatively more important at low temperature. The temperature dependence of $T_1$ in this process is expressed by

$$\frac{1}{T_1} \propto T$$

where $T$ is the absolute temperature.

(ii) Raman process

A phonon of any frequency ($\omega / 2\pi$) may interact with a spin, causing a transition (up or down) within the system. The phonon being scattered with a different frequency ($\omega' / 2\pi$) respectively, where $\nu$ is the ESR frequency. For this method to be effective, there must be lattice modes having difference frequencies equal to the ESR frequency. Such vibrations, however, can be in the higher frequency region more densely populated at ordinary temperatures. Furthermore, many modes pairs can participate in the process since the only requirement is that their difference frequency be equal to the ESR frequency. The effectiveness of this process would decrease rapidly with decrease of temperature.
since vibrations at frequencies would be frozen out as the temperature is lowered. The relaxation time $T_1$ depends on the temperature in the following manner.

\[ \frac{1}{T_1} \propto T^5 \quad \text{for multiplet with small splitting} \]

\[ \propto T^7 \quad \text{for non-Kramers doublet} \]

\[ \propto T^9 \quad \text{for Kramers doublet.} \]

(iii) Orbach process

This involves absorption of a phonon by a direct process to excite the spin system to a much higher level, at an energy $\Delta$ above the ground doublet, followed by the emission of another phonon of slightly different energy so that the magnetic ion is indirectly transferred from one level to the other of the ground doublet. This process is also strongly temperature dependent, being determined by the number of phonons of energy $\Delta$ available to excite the ion to the upper state at $\Delta$. It is more restricted than the Raman process because two specific transitions are involved. The relaxation rate is given by

\[ \frac{1}{T_1} \propto \exp(-\Delta/kT) \]

where $k$ is Boltzmann constant.

At liquid helium temperature, only the direct process
is usually significant, whereas the Raman and Orbach terms become dominant at higher temperature.

Spin spin relaxation

It contains all the mechanisms where by the spins can exchange energy amongst themselves, rather than giving it back to the lattice, or molecular system as a whole.

(1) Dipole interaction

It arises from the influence of the magnetic field of one paramagnetic ion on the dipole moments of neighbouring ions. The actual local field at any given site will depend on the arrangement of the neighbours and the directions of their dipole moments. If the external magnetic field acts on the paramagnetic compound, the local field at each ion must be added vectorially to it. If the local field is small compared with the external field (which might be ~Tesla), only the component of the former parallel to the latter is important. The size of this component varies from site to site, giving a random displacement to the resonance frequency of each ion. If the paramagnetic ions are identical, so that they process at the same frequency in the external magnetic field, there is an additional resonance interaction. The precessing components of one magnetic dipole set-up an oscillatory field at another dipole which is just at right frequency to cause magnetic resonance transitions and vice
versa. The mutual interaction produces resonance transitions that are equivalent to the exchange of quanta between neighbouring ions.

Thus the quanta are exchanged among neighbouring ions by mutual spin flip and spins are in thermal equilibrium amongst themselves. If this equilibrium is disturbed, it is reestablished exponentially with time constant $T_2$ which is called spin-spin relaxation time.

(ii) Exchange coupling

This is important only in undiluted crystals where the paramagnetic sites are so close together that the orbitals of the unpaired electrons overlap. Here the spins interact electrostatically through a short range interaction which is called exchange interaction. This results in a change in width of absorption lines in the ESR spectrum.

ESR linewidth

Various sources of linewidths in the ordinary spectra of ions in diamagnetic hosts are

(i) Spin-lattice interaction

This interaction between the impurity and the vibrational modes of the lattice takes place through the orbital angular momentum of the impurity and is strongly temperature dependent at high temperatures. Since the S-state impurity ions have basically zero orbital angular momenta,
this interaction is negligible for them. For instance the ESR linewidths of Gd$^{3+}$ spectra in the diamagnet YVO$_4$ show negligible temperature dependence in the wide temperature range of $6 < T < 550$K. This source of line broadening can thus be safely ignored for S-state ions.

(ii) Fine, hyperfine and superhyperfine interactions

These are respectively the interactions of the electronic spins of the impurities with

(a) the crystal field, (b) the nuclear spins of their own atoms and (c) the nuclear spins of the ligands. The unresolved splittings due to these interactions are not negligible and should be determined in comparable diamagnets and subtracted from the linewidths of the impurities in the paramagnets under study.

(iii) Impurity-impurity interaction

This interaction which for paramagnetic impurities, is almost exclusively due to the long-range magnetic dipolar interactions, can be drastically reduced by going to highly dilute samples. The remnant magnetic dipolar interactions are negligible in moderately dilute cases.

In addition to these sources of line broadening in diamagnetic hosts, there are three major sources pecular
to paramagnetic hosts. These are

(iv) The static broadening due to the magnetic dipolar and exchange interactions of the impurity with the host ions.\textsuperscript{17,19,20,23}

(v) The life-time broadenings due to the fluctuating fields produced by the relaxation processes of the host ions.\textsuperscript{12,17,18,23,24}

(vi) The indirect superhyperfine interactions of the electronic states of the impurities with the nuclei of the paramagnetic host ions via the polarization of the host electronic states.\textsuperscript{16,25,26}

\textit{Mn}^{2+} \textit{ion}

In the case of a manganese ion there are five 3d electrons constituting a half-filled shell. According to Hund's rule (which states that (i) of all the terms allowed by the Pauli principle, the lowest will be one of maximum multiplicity and of these terms with maximum multiplicity that with greatest L value will be the lowest (ii) For configurations consisting of electrons in a less than half filled shell the spin-orbit splitting is usually normal, that is the multiplet with the smallest J is lowest, for configurations with a more than half filled
shell the multiplets are usually inverted), the ground state of the free ion is thus \( ^6S_{5/2} \) \((L = 0, S = 5/2)\) which is six-fold degenerate in spin. Bethe\(^{27}\) has shown that in a cubic field this six fold degenerate level will split into a four-fold degenerate and a two-fold degenerate level. A departure from the cubic symmetry would cause a further splitting of the four-fold level. In a trigonal field, the six-fold degenerate level is split into three doublets. The remaining degeneracy can be removed by applying an external magnetic field. In high field transitions, \( \Delta M = \pm 1 \), five fine structure lines are expected. Since \(^{55}\)Mn has nuclear spin \( I = 5/2 \) and the allowed transitions are those in which \( m \) the nuclear magnetic quantum number does not change, each of the fine structure lines will therefore split into six hyperfine lines shown in Figure 2.3. The spin-Hamiltonian for \(^{2+}\)Mn in a rhombic crystalline field is of the form\(^{28}\)

\[
H = \beta \left( g_x B_x S_x S_x + g_y B_y S_y S_y + g_z B_z S_z S_z \right) + D \left[ S_z^2 - \frac{1}{3} S(S+1) \right] \\
+ E(S_z^2 - S_y^2) + \left( a/6 \right) \left[ S_x^4 + S_y^4 + S_z^4 - \frac{1}{5} S(S+1)(3S^2+3S-1) \right] \\
+ A_x S_x I_z + A_y S_y I_x + A_z S_z I_y - g_N \beta_B I \\
+ Q' \left[ I_z^2 - \frac{1}{3} I(I+1) \right] + Q'' \left( I_x^2 - I_y^2 \right) 
\]

(2.2)

where \( Q' \) and \( Q'' \) are the axial and rhombic parts of the nuclear quadrupole interaction and \( 'a' \) is the cubic
FIG. 2.3 ESR SPECTRUM OF MANGANESE ENERGY LEVEL DIAGRAM SHOWING THE PRODUCTION OF THE FIVE GROUPS OF SIX HYPERFINE COMPONENTS.
component of the crystalline field.

Fine structure

The fine structure part of the spin-Hamiltonian is

\[ \beta (g_x B_x S_x + g_y B_y S_y + g_z B_z S_z) + D \left[ S_z^2 - \frac{1}{3} S(S+1) \right] + E \left( S_x^2 - S_y^2 \right) + \frac{a}{6} \left[ S_x^4 + S_y^4 + S_z^4 \right] - \frac{1}{5} \frac{(a/6)}{S(S+1)} (3S^2 + 3S - 1) \]

using the energy level expression, the magnetic field value \( B \) for the transition \( \Delta M \) to the second order of perturbation is given by \(^{29}\) (the small term 'a' is in the first order only)

\[ B_{\Delta M} = -\frac{B_0}{\Delta M} - f_1 (2M+\Delta M) - 5f_2 (2M+\Delta M) \]

\[ \left\{ 7 \left[ M^2 + (M+\Delta M)^2 \right] - 6S(S+1)+5 \right\} + \left( \frac{1}{2B_0} \right) \left[ f_2^2 + f_4^2 \right] \left[ 4S(S+1) - 24M^2 - 24M \Delta M - 8 \Delta M^2 - 1 \right] \]

\[ - \left( \frac{1}{8B_0} \right) \left[ f_2^2 + f_6^2 \right] \left[ 2S(S+1) - 6M^2 - 6M \Delta M - 2 \Delta M^2 - 1 \right] \]

(2.3)

where

\[ f_1 = (1/2) \left[ D(3\cos^2\alpha - 1) - 3E \sin^2\alpha \cos 2\beta \right] \]

\[ f_2 = \left( \frac{5}{8} \right) \left[ (a/120) \left( \sin^4\alpha \cos^4\beta + 7 \cos^4\alpha - 6 \cos^2\alpha + 3/5 \right) \right] \]

\[ f_3 = -(1/2) (D+E \cos 2\beta ) \sin 2\alpha \]
\[ f_4 = E \sin \alpha \sin 2\beta \]
\[ f_5 = D \sin^2 \alpha - E(\cos^2 \alpha + 1) \cos 2\beta \]
\[ f_6 = 2E \cos \alpha \sin 2\beta \]
\[ \sin \alpha = \frac{g \parallel}{g} \sin \theta \]
\[ \cos \alpha = \frac{g_z}{g} \cos \theta \]
\[ \sin \beta = \frac{g_x}{g \parallel} \cos \phi \]
\[ \cos \beta = \frac{g_y}{g \parallel} \sin \phi \]
\[ g_\parallel = g_x \sin^2 \beta + g_y \cos^2 \beta \]
\[ g^2 = g_\parallel \sin^2 \phi + g_z \cos^2 \phi \]

The transitions \( \Delta M = \pm 1 \), in zx and xy planes are obtained from the equation by keeping \( \phi = 0^\circ \) and \( \theta \) variable, and \( \theta = 90^\circ \) and \( \phi \) variable respectively.

Hyperfine structure

In an exial field the sub-Hamiltonian of the nuclear interaction is

\[ H_N = A_\parallel S_z I_z + A_\perp (S_x I_x + S_y I_y) + Q \left[ I_z^2 - \frac{1}{3} I(I+1) \right] - g_N \beta_N \overrightarrow{B} \cdot \overrightarrow{I} \]

The hyperfine contribution to \( \Delta M = \pm 1, \Delta m = 0 \) transitions is given by \(^3\) by neglecting the small
term - $g_N \overleftrightarrow{B}, I$).

\[
K_m + \frac{A_{\perp}^2}{4 g \beta B_0} \left( \frac{A_{\parallel}^2 + K^2}{K^2} \right) [I(I+1) - m^2] + \frac{A_{\perp}^2}{2 g \beta B_0} \left( \frac{A_{\parallel}^2}{K^2} \right) (2M-1)m
\]

\[
+ \frac{1}{2g \beta B_0} \left( \frac{A_{\parallel}^2 - A_{\perp}^2}{K^2} \right)^2 \left( \frac{g_{\|} g_{\perp}}{g^2} \right)^2 \sin^2 \theta \cos^2 \theta m^2
\]

\[
+ \frac{Q'^2}{2K^2(M-1)} \left( \frac{A_{\parallel}^2}{K^2} \right)^2 \left( \frac{A_{\parallel}^2}{K^2} \right)^2 \sin^2 \theta \cos^2 \theta in \sin^2 \theta m^2
\]

\[
- \frac{Q'^2}{8K^2(M-1)} \left( \frac{A_{\parallel}^2}{K^2} \right)^4 \sin^2 \theta \cos^2 \theta in \sin^2 \theta \sin^2 \theta m^2
\]

where

\[
K^2 = A_{\|}^2 g_{\parallel}^2 \cos^2 \theta + A_{\perp}^2 g_{\perp}^2 \sin^2 \theta
\]

\[
g^2 = g_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta
\]

The hyperfine correction to the fine structure transitions $M \rightarrow M-1$ in axial crystalline fields after neglecting the quadrupole correction is given by

For $\theta = 0^\circ$

\[
- K_m - \left( \frac{A_{\|}^2}{4B_0} \right) \left( \frac{A_{\parallel}^2 + A_{\perp}^2}{K^2} \right) [I(I+1) - m^2] - \frac{A_{\perp}^2}{2B_0} \left( \frac{A_{\parallel}^2}{K^2} \right) [m(2M-1)]
\]

(2.5)

if hyperfine splitting constant is assumed to be isotropic as is approximated in the case for S-state ions

\[
hfc = - A_{m} - \frac{A_{\perp}^2}{2B_0} [I(I+1) - m^2] - m(2M-1) \frac{A_{\perp}^2}{2B_0}
\]

(2.6)
FORBIDDEN HYPERFINE TRANSITIONS AND THEIR INTENSITIES

In the paramagnetic resonance spectrum of Mn$^{2+}$ ion, a number of extra hyperfine lines have often been observed which appear to correspond to transitions in which the nuclear magnetic number $m$ changes by $\pm 1$. These were first reported by Bleaney and Ingram in manganese ammonium sulfate and manganese fluosilicate (both diluted); these lines appeared when the external magnetic field was not either parallel or perpendicular to crystal axes. After the analysis of Friedman and Low, Bleaney and Rubins verified that the crystalline field and hyperfine interaction admix zero-order wave functions and make such transitions possible. They give a simple formula for the intensity and doublet separation of these lines based on the perturbation theory where the states $|M m\rangle$ quantized along the external magnetic field ($B$) direction were used as eigenfunctions. However their expressions are unsatisfactory to explain the various experiments qualitatively.

Bir has given improved expressions for the intensity but again using the perturbation theory. The basic idea of his work is that the direction (and the magnitude) of the effective magnetic field acting on the nuclear spin (the quantization axis) differs from the direction of external magnetic field in the presence of large hyperfine interaction and is also different in the different electronic
states.

The dependence of the direction of the quantization axis on the electron states of the ion leads to the non-orthogonality of the nuclear spin functions, pertaining to different electron states and corresponding to different projections of the nuclear spin. This results in the appearance of forbidden transitions and a corresponding reduction of the intensity of the allowed transitions.

Bir gives the expression for the transition probabilities of the allowed and forbidden lines in terms of the spin-Hamiltonian parameters $D$ and $E$, and the electronic $g$-factor which is assumed to be isotropic. The probability of a transition from the state $|M,m\rangle$ to the state $|M',m'\rangle$ under the action of r-f field is the square of the modulus of the matrix element $|W_{MM',mm'}|^2$ where

$$|W_{MM',mm'}|^2 = |W_{e,MM'}|^2 |P_{mm'}^{I} (\mu_{MM'})|^2$$

(2.7)

The first term on the right hand side of the equation gives the electronic transition probability, the second term gives the nuclear transition probability and $\mu_{MM'}$ is the cosine of the angle formed by the effective electron fields in initial and final states.

The function $W_{e,M,M-1}$ in the electronic transition
probability is proportional to

\[ 1 + \frac{\rho^2}{(g\beta B_0)^2} \left[ 3M(M-1) - S(S+1) + \frac{3}{2} \right] - \frac{\lambda^2}{4(g\beta B_0)^2} \left[ 4S(S+1) - 3 \right] + \frac{\rho(2M-1)}{g\beta B_0} - \frac{3\lambda^2(2M-1)^2}{4(g\beta B_0)^2} + \frac{\rho\sigma}{(g\beta B_0)^2} \left[ S(S+1) - M(M-1) - 1 \right] \]

where

\[ \sigma = \frac{1}{2} \left[ D(3\cos^2 \phi - 1) + 3E \sin^2 \phi \cos 2\phi \right] \]
\[ \rho = \frac{1}{4} \left[ D \sin^2 \phi + E(\cos^2 \phi \cos 2\phi - \sin^2 \phi) + 2iE \cos \phi \sin 2\phi \right] \]
\[ \lambda = \sin \phi \left[ \cos \phi (D - E \cos 2\phi) + iE \sin 2\phi \right] \]

The value of \(|W_{e,MM}^I|^2\) changes with change in angle but this change is slow. The functions \(P_{mm}^I\) are related to the Jacobi polynomials. The number of independent functions for \(I = 5/2\) is six and the functions are given below

\[ |P_{5/2,5/2}|^2 = \left( \frac{1+\mu}{2} \right)^5 \]
\[ |P_{3/2,3/2}|^2 = \left( \frac{1+\mu}{2} \right)^3 \left( \frac{3-5\mu}{2} \right)^2 \]
\[ |P_{1/2,1/2}|^2 = \left( \frac{1+\mu}{2} \right) \left( \frac{5\mu^2-2\mu-1}{2} \right)^2 \]
\[ |P_{5/2,3/2}|^2 = 5 \left( \frac{1-\mu}{2} \right) \left( \frac{1+\mu}{2} \right)^4 \]
\[ |P_{3/2,1/2}|^2 = \left( \frac{1+\mu}{2} \right)^2 \left( 1-\mu \right) \left( \frac{1-5\mu}{2} \right)^2 \]
\[ |P_{5/2,1/2}|^2 = 10 \left( \frac{1-\mu}{2} \right)^2 \left( \frac{1+\mu}{2} \right)^3 \]
\[ \mu = 1 - \left[ \frac{g^2}{2} (g B_0)^2 \right] (M-M')^2 \left[ 1 + \frac{3(S+1)}{3M} \right]^2 \] (2.8)

The functions \( |P_{mm}^\dagger (\mu)|^2 \) are symmetric about the polar angle \( \theta = 45^\circ \), having equal intensity at \( \theta = 0^\circ \) and \( 90^\circ \). For a non-vanishing value of \( E \) the electronic transition probability \( |W_{e,M,M-1}|^2 \) can change the symmetry pattern significantly. In this case, the total transition probability \( |W_{M,M',M-1}|^2 \) is greater for \( \theta = 0^\circ \) than for \( \theta = 90^\circ \). The function \( |P_{mm}^\dagger (\mu)|^2 \) changes very rapidly with change in \( \mu \).

**FORBIDDEN HYPERFINE DOUBLET SEPARATION**

The expressions for hyperfine forbidden doublet separation in various fine structure transitions have been obtained using the third order perturbation theory neglecting the small term in \( 'a' \) and \( 'F' \). The anisotropy in hyperfine constant and \( g \)-value are neglected and assuming \( gB \gg |D|, |E| \) and \( |A_z| \).

The expressions for doublet separation of hyperfine transitions in the various fine structure transitions are

\[ M = \pm 1/2 \rightarrow \pm 1/2 \]

\[ \Delta m = \pm 1 \text{ transitions} \]

\[ \Delta B = B |1/2, m+1\rangle \rightarrow |1/2, m-1\rangle, B |1/2, m\rangle \rightarrow |1/2, m+1\rangle \]
\[
\Delta m = \pm 2 \text{ transitions}
\]

\[
\Delta \mathcal{B} = B|1/2, m+1\rangle \rightarrow |1/2, m-1\rangle \quad \Delta \mathcal{B} = B|1/2, m-1\rangle \rightarrow |1/2, m+1\rangle
\]

\[
\Delta \mathcal{B} = \frac{17 A_z^2}{B_0} + 4 \left( \frac{\gamma R}{g \beta} \right) B_0 - 2m \left[ 4p - \frac{16 A_z^2 \sigma}{B_0^2} + \frac{25 A_z^3}{B_0^2} + 2 \left( \frac{\gamma R}{g \beta} \right) A_z \right]
\]

\[
M = +3/2 \rightarrow +1/2
\]

\[
\Delta m = \pm 1 \text{ transitions}
\]

\[
\Delta \mathcal{B} = B|3/2, m+1\rangle \rightarrow |1/2, m\rangle \quad \Delta \mathcal{B} = B|3/2, m\rangle \rightarrow |1/2, m+1\rangle
\]

\[
\Delta \mathcal{B} = -2A_z + 2 \left( \frac{\gamma R}{g \beta} \right) B_0 - 2p (2m+1) - \frac{|\mathcal{M}|^2}{B_0^2} \left( \frac{256}{3} \right) A_z + \frac{|\mathcal{M}|^2}{B_0^2} 52A_z
\]

\[
\frac{A_z^2}{B_0} (2m+ \frac{17}{2}) + \frac{A_z^2 \sigma}{B_0^2} (14m+9) - \frac{A_z^3}{B_0^2} \left( m^2 + 19m + \frac{51}{4} \right)
\]

\[
M = +5/2 \rightarrow +3/2
\]

\[
\Delta m = \pm 1 \text{ transitions}
\]

\[
\Delta \mathcal{B} = B|5/2, m+1\rangle \rightarrow |3/2, m\rangle \quad \Delta \mathcal{B} = B|5/2, m\rangle \rightarrow |3/2, m+1\rangle
\]

\[
\Delta \mathcal{B} = -4A_z + 2 \left( \frac{\gamma R}{g \beta} \right) B_0 - 2p (2m+1) - \frac{|\mathcal{M}|^2}{B_0^2} \left( \frac{40}{3} \right) A_z + \frac{|\mathcal{M}|^2}{B_0^2} 56A_z
\]
\[
\begin{align*}
\Delta m &= \pm 1 \text{ transitions} \\
\Delta B &= B|\pm\frac{1}{2}, m+1\rangle \rightarrow |\pm\frac{3}{2}, m\rangle \\
&\quad - B|\pm\frac{1}{2}, m\rangle \rightarrow |\pm\frac{3}{2}, m+1\rangle \\
&= -2A_z - 2\left(\frac{\gamma B}{g}\right)_N B_o + 2P(2m+1) - \frac{1 \hbar^2}{B_o} \left(\frac{\gamma B}{g}\right)_N A_z + \frac{1 \hbar^2}{B_o} 52A_z \\
&\quad + \frac{A_z^2}{B_o} (2m - \frac{13}{2}) - \frac{A_x^2}{B_o} (14m+5) - \frac{A_x^2}{B_o} (m^2+17m-\frac{123}{4}) \\
&= -4A_z - 2\left(\frac{\gamma B}{g}\right)_N B_o + 2P(2m+1) - \frac{1 \hbar^2}{B_o} \left(\frac{\gamma B}{g}\right)_N A_z + \frac{1 \hbar^2}{B_o} 56A_z \\
&\quad + \frac{A_z^2}{B_o} (4m - \frac{5}{2}) - \frac{A_x^2}{B_o} 18m - \frac{A_x^2}{B_o} (2m^2+5m-30) \\
&\quad + \frac{1 \hbar^2}{B_o} \left(\frac{\gamma B}{g}\right)_N A_z + \frac{1 \hbar^2}{B_o} 56A_z \\
&\quad + \frac{A_z^2}{B_o} (4m - \frac{5}{2}) - \frac{A_x^2}{B_o} 18m - \frac{A_x^2}{B_o} (2m^2+5m-30) \\
&= P = \frac{1}{2} \left[ Q'(3\cos^2\theta - 1) + 3Q'' \sin^2\theta \cos 2\phi \right] \\
\end{align*}
\]
Zero field splitting of S-state ions (Mn\(^{2+}\))

The S-state in principle will have no interaction with crystal field, to first order, hence no zero field splitting. However, small to very large zero field splitting for Mn\(^{2+}\), Fe\(^{3+}\) and Gd\(^{3+}\) has been observed in practice. Out of numerous theoretical attempts made to calculate zero field splitting Mn\(^{2+}\) ion, none is found entirely satisfactory and the problem still remains unsolved and challenging to the theoretical workers. We would not attempt any discussion on this point except citing references,\(^{37-45}\) in which attempts have been made towards theoretical explanation of zero field splitting in S-state ions.

Hyperfine structure

The ground state of 3d\(^5\) (Mn\(^{2+}\)) electronic configuration shows an anomalous hyperfine structure. The values of the hyperfine structure constants that have been measured for these ions are quite large. Abragam\(^{46}\) first suggested that this was due to an admixture of the 3s4s 3d\(^5\) configuration into 3s\(^2\)3d\(^5\) configuration. However, an estimate of the admixture by Abragam et al.\(^{47}\) showed it to be too small to account for the observed hyperfine structure. An explanation that is quantitatively able to explain the hyperfine structure has been given by Heine,\(^{48}\) Wood et al.\(^{49}\)
and Watson et al.\textsuperscript{50} According to this, in the paramagnetic ion 3d\textsuperscript{5}, in the state \(S_z = S = 5/2\), the spins of all five 3d electrons are up. The electrostatic repulsion between an s-electron of an inner shell with spin up say 1s\textsuperscript{+} and these 3d electrons will not be the same as that for an electron in the state 1s\textsuperscript{−}. This is a consequence of the exclusion principle that prevents two electrons with parallel spin from occupying the same position in space. This causes a polarization of the s\textsuperscript{2} configuration which can then produce a magnetic field at the nucleus. Detailed calculations of the polarizations of the 1s\textsuperscript{2}, 2s\textsuperscript{2}, 3s\textsuperscript{2} configuration had been made by Watson and Freeman.\textsuperscript{50} They were able to account for the observed hyperfine structure of the 3d\textsuperscript{5} ions in ionic crystals quantitatively.

Gd\textsuperscript{3+} ion

Gd\textsuperscript{3+} has 4f\textsuperscript{7} electronic configuration and accordingly the Hund's rule ground state is \(S_{7/2}\). The eight fold degeneracy of this state is partially removed by the crystalline electric field to which it is exposed when it is substituted into a host lattice. The group theoretical considerations of Bethe\textsuperscript{27} show that a crystalline electric field potential with cubic symmetry splits an eight-fold degenerate free-ion ground state into two doublets and one quartet and that axial symmetry splits this state into four
doublets. In general, the observed ground state splitting of Gd$^{3+}$ in crystalline electric potentials of various symmetries are $0.2 \text{cm}^{-1}$. Consequently they are readily accessible to direct measurement using ESR technique at microwave frequencies with commonly available laboratory magnetic fields. It is challenging to study the ground state splitting of an $S$-state ion like Gd$^{3+}$ because no satisfactory theoretical explanation has been found for the magnitude of there splitting. A theoretical explanation of the splitting of the ground state of Gd$^{3+}$ ion in a crystalline electric potential is not yet possible despite the extensive literature available describing the results of experimental studies on this ion.$^{51}$

The spin-Hamiltonian for Gd$^{3+}$ ion in crystals with orthorhombic site symmetry is $^{51}$

$$H = \beta \vec{S} \cdot \vec{g} \cdot \vec{B} + (1/3) b_2^0 O_2^0 + (1/60) b_4^0 O_4^0 + (1/1260) b_6^0 O_6^0$$
$$+ (1/3) b_2^2 O_2^2 + (1/60) b_4^2 O_4^2 + (1/1260) b_6^2 O_6^2$$
$$+ (1/60) b_4^4 O_4^4 + (1/1260) b_6^4 O_6^4 + (1/1260) b_6^6 O_6^6 + \vec{S} \cdot \vec{A} \cdot \vec{I}$$

(2.15)

and spin-Hamiltonian for trigonal symmetry is given by

$$H = \beta \vec{S} \cdot \vec{g} \cdot \vec{B} + (1/3) b_2^0 O_2^0 + (1/60) b_4^0 O_4^0 + (1/1260) b_6^0 O_6^0$$
$$+ (1/3) b_4^3 O_4^3 + (1/36) b_6^3 O_6^3 + (1/1260) b_6^6 O_6^6 + \vec{S} \cdot \vec{A} \cdot \vec{I}$$

(2.16)
where the symbols have their usual meaning and $S = 7/2$.
The hyperfine structure in the ESR spectrum of Gd$^{3+}$ is not normally observed since the linewidth usually obscures this structure.

**VO$^{2+}$ ion**

The V$^{4+}$ belongs to the iron group ions. The ground state of free ion is $^2D$. It has a $3d^1$ ground state configuration with an electronic spin $S = 1/2$. The total degeneracy of the ground state of the free ion is $(2L+1)(2S+1) = 10$. The action of tetragonal crystal field along with spin-orbit interaction can remove the orbital degeneracy. The splitting between the orbital level is very large and therefore one expect all V$^{4+}$ ions to be in the lowest state which is still two-fold degenerate in spin. Most studies of tetravalent vanadium have been made with vanadyl ion VO$^{2+}$ is believed to exist in a sort of octahedral coordination with its surroundings. The local crystal field symmetry of the VO$^{2+}$ ion is usually tetragonal in different crystal hosts. In vanadyl ion complexes the unpaired electron is in the orbitally singlet state which is still two-fold degenerate in spin. Thus for VO$^{2+}$ the effective spin is $S = 1/2$. On application of a magnetic field, the spin-doublet splits into two and one expects a single electronic transition between these two levels. The VO$^{2+}$ ($^5I_1$) has
nuclear spin $I = 7/2$. Hence the fine structure line will be split into eight hyperfine lines. The spin-Hamiltonian which describes the energy levels of $\text{VO}^{2+}$ ion is

$$H = \beta S \cdot B + S \cdot A I + S \cdot Q I - g_N \beta_N I,$$

assuming the $g$, $A$ and $Q$ tensors to have identical principal axes, the energies of $\Delta M = \pm 1, \Delta m = 0$ allowed transitions to second-order from equation (neglecting the last two terms in equation) are\(^5\)

\[
\hbar \nu = g \beta B + K m + \frac{\hbar^2}{2 \gamma \cdot \beta B} \left( \frac{1}{2} \sum \frac{g_x^2}{g^2} \right) \sin^2 \phi \cos^2 \phi \\
+ \frac{g_x g_y (A_x^2 - A_y^2)}{g_x g_z} \sin^2 \phi \sin^2 \phi \cos^2 \phi \left( \frac{1}{2} \sum \frac{g_k}{g_z} \right) \\
+ \frac{g_x^2 g_y^2 A_z^2}{g_x^2} \frac{g_k}{g_z} (A_x^2 - A_y^2) \sin^2 \phi \cos^2 \phi \left( \frac{1}{2} \sum \frac{g_k}{g_z} \right) \\
\times \cos^2 \phi \sin^2 \phi \cos^2 \phi \left( \frac{1}{2} \sum \frac{g_k}{g_z} \right) \\
\frac{\hbar^2 (I(I+1) - m^2)}{4 g \beta B} \tag{2.17}
\]

where

- $g = (g_x^2 \sin^2 \phi + g_z^2 \cos^2 \phi)^{1/2}$
- $g_x = (g_x^2 \cos^2 \phi + g_y^2 \sin^2 \phi)^{1/2}$
- $g_k = (g_x^2 \sin^2 \phi + g_z^2 A_z^2 \cos^2 \phi)^{1/2}$
$g_K = (g_x^2 \cos^2 \phi + g_y^2 \sin^2 \phi)^{1/2}$

For axial symmetry

$A_z = A_{||}, \quad A_x = A_y = A_{\perp}, \quad A = g_A A_{||}/g$

$g_z = g_{||}, \quad g_x = g_y = g_{\perp}$

Experimental details

The experiments were carried out on a JEOL JES-FE3X homodyne X-band spectrometer (operating in the frequency range $8.8 \text{ to } 9.6 \text{ GHz}$) and using an electromagnet of 12-inch pole diameter. The Gunn oscillator is used as a source of microwaves. The magnetic field set by different knobs ($1.0 \text{ mT}, 10.0 \text{ mT}, 100.0 \text{ mT}$ steps and $1.0 \text{ mT}$ continuously variable), the magnetic field sweeps by different sweep widths ($\pm 0.025, \pm 0.05, \pm 0.1, \pm 0.25, \pm 0.5, \pm 1.0, \pm 2.5, \pm 5.0, \pm 10.0, \pm 25.0, \pm 50.0, \pm 100.0, \pm 250.0, \pm 500.0 \text{ mT}$) using sweep time of various range ($0.5, 1, 2, 4, 8, 16, 32, 64, 128 \text{ min}$). The magnetic field setting accuracy is $0.5\%$ and homogeneity is $1 \times 10^{-5}$. The spectrometer has $200 \text{ mW}$ microwave power output with $1 \times 10^{-6}$ frequency stability. The resolution is better than $1 \times 10^{-5}$. The ESR spectra were studied by using a JES-MCX-1A multimode cylindrical cavity operating in the $\text{TE}_{011}$ mode and $100 \text{ kHz}$ field modulation ($0.0002 \sim 2.0 \text{ mT}$). As a reference for magnetic field strength the resonance line of DPPH with
g = 2.0036 is used. The set magnetic field is read directly from the light emitting diodes. It is assumed that the magnetic field changes linearly with time during the sweeping of the magnetic field. The crystals were mounted on quartz rod of diameter 5mm. The angular variation studies were done using a JES-UCR-2X sample angular rotating device. Temperature variations experiments have been performed using a JES-VT-3A variable temperature controller with JES-UCT-2AX variable temperature adapter. For low temperature measurements, nitrogen gas evaporated from liquid nitrogen in metal dewar is used. Liquid nitrogen measurements have been made using a JES-UCD-2X insertion type dewar vessel. Temperature was measured using a copper constantan thermocouple. The e.m.f. of the thermocouple was measured using a Toshniwal PL52N portable potentiometer. The ESR spectra were observed on spectrometer oscilloscope having 133mm diameter, recorded on chart having size 250(W) x 360(L)mm. by using a DY-T recorder with different chart speed.

Crystal growth

Doped single crystals of Tutton salts, di barium zinc formate tetrahydrate, double nitrates and zinc selenate hexahydrate were grown from saturated solutions by slow evaporation.
The crystals of di barium zinc formate tetrahydrate were synthesised from aqueous solution of formic acid and corresponding metal carbonates mixed in stoichiometric ratio. The manganese and vanadyl salts were added in the form of sulfates over a wide range of concentrations (0.005% to 5%).

The crystals of Tutton salts and zinc selenate hexahydrate were synthesised from aqueous solution of selenic acid and corresponding metal carbonates mixed in stoichiometric ratio. The manganese and vanadyl salts were added in the form of sulfates over a wide range of concentrations.

The crystals of double nitrates were synthesised from aqueous solution of corresponding metal nitrates mixed in stoichiometric ratio to which a few drops of nitric acid are added. The gadolinium salt was added in the form of nitrate. The crystal grew in the form of hexagonal plates the plane of which is perpendicular to the trigonal axis.

The dimensions of the crystals used in the present study are of a few mm³.
REFERENCES


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GENERAL REFERENCES


