CRYSTALLINE STARK SPLITTING
AND MICROWAVE RESONANCE ABSORPTION
IN PARAMAGNETIC SALTS

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by

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Abstract

A theoretical discussion is given of the application of microwave absorption measurements to the determination of energy levels in single crystals of paramagnetic salts. Selection rules are given for magnetic dipole transitions between sublevels in the presence of crystalline electric fields of cubic, tetragonal, trigonal and rhombic symmetry. The Zeeman effect in the presence of crystalline electric fields is discussed in some detail for three special cases: a) $J = 5/2$, cubic field; b) $J = 7/2$, cubic field; c) $J = 3/2$, trigonal field. These examples may correspond to certain magnetically dilute salts containing Fe$^{+++}$, Gd$^{+++}$ and Cr$^{+++}$ ions, respectively, provided that exchange interactions do not play an important role. Numerical values are tabulated for the relative frequencies and line strengths associated with magnetic dipole transitions in the cases discussed. The character of the spectra may change radically between the limit where the Zeeman splitting is small in comparison with the Stark splitting, and the opposite limit where the Stark splitting may be neglected.
I. INTRODUCTION

The present knowledge\(^1\) of the quantum states of paramagnetic salts is largely derived from the interpretation of measurements of magnetic susceptibilities, specific heats, and optical absorption spectra. The difficulties in giving a consistent account of the various phenomena have been emphasized by Van Vleck at the 1939 Strasbourg conference\(^3\), and by Penney and Kynch\(^5\).

The recent experimental discovery by Zavoisky\(^6\) of paramagnetic resonance absorption provides a new and direct method for the investigation of closely spaced energy levels in paramagnetic materials. The method consists of observing by means of electrical measurements the quantum transitions induced by a radio frequency or microwave electromagnetic field. The salt is placed in an r-f circuit element situated

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(2) M.B.C. Casimir, Magnetism and Very Low Temperatures (Cambridge University Press, 1940)
(3) Université de Strasbourg, LeMagnetisme: Tome 3; Paramagnetisme (Institut International de Coopération Intellec-
     tuelle, Paris, 1940)
(4) C.J. Gorter, Paramagnetic Relaxation (Elsevier, Amsterdam, 1947)
     Freed, Rev. Mod. Phys. 14, 105 (1942)
(6) E. Zavoisky, J. Phys. U.R.S.S. R. 2, 211, 245, 447 (1945); 12, 170, 157 (1945); see also R.L. Cunnison and D. Halliday,
between the pole pieces of an electromagnet. As the strength of the static field is varied the power absorption in the salt is found to pass through a well-defined maximum.

In the measurements reported by Zavoisky the position of the resonance satisfies closely the Larmor equation for electron spins:

$$f/H_0 = \frac{e}{2\mu n c} = 2.30 \text{ mc/0e}$$

where $f$ = frequency; $H_0$ = d.c. magnetic field; $e$ = electronic charge in c.s.u.; $\mu$ = electronic mass; $c$ = velocity of light.

The applicability of Eq. (1) to electron states in solids in which the spin is free was pointed out by Frenkel. Under this condition, the experiment is analogous to the nuclear magnetic resonance experiment.

On the present picture of paramagnetic solids the energy levels of the paramagnetic ions are affected in an important way by the inhomogeneous crystalline electric fields, which are caused largely by the dipole moments of the water of hydration. The crystalline Stark effect splits the degenerate energy levels of the free ions. This splitting of a single level into several components makes possible the occurrence in an r-f field of magnetic dipole transitions between the split components, even in the absence of a static magnetic field. A second effect of the splitting is to change the character of the Zeeman effect in a static magnetic field: under certain conditions we might expect to find several lines in the absorp-

tion spectrum, in contrast to the single line found by Zevoi-
sky.

In Section II of this paper we discuss some aspects of microwave absorption spectra in the absence of the Zeeman effect \( (H_0=0) \). In Section III the combined Zeeman and crystalline Stark effects are considered for three particular situations of interest in the microwave range. All of our calculations refer to single crystals, with the static and r-f magnetic fields along crystal axes of high symmetry. The situation for powdered specimens of these salts is extremely complicated, and would probably not give as much information as the single crystals.

It is possible that in a large number of salts the effect of the Stark splitting will be erased by strong exchange coupling between ions. The prevalence of such coupling is perhaps one of the more important things which might be determined by paramagnetic resonance experiments. The specific cases of crystalline splitting considered in this paper are presented only as illustrations of the kind of behavior to be expected in the absence of exchange interactions; our calculations are not applicable in the presence of strong exchange coupling, although this may turn out to be the most common situation. Various effects of exchange coupling are considered by J. H. Van Vleck, in a paper which is to appear in the Physical Review.
II. MICROWAVE ABSORPTION CAUSED BY CRYSTALLINE STARK SPLITTING

The usual Stark splittings in crystals are of the order of some hundred or thousand cm\(^{-1}\); in certain circumstances, however, the splittings are of the order of one cm\(^{-1}\). This is the case with some of the salts studied in magnetic cooling experiments. For example, Gorter\(^4\) gives the following overall splittings of the ground state:

\[
\begin{align*}
\text{Gd}_2(\text{SO}_4)_3 & \cdot 8\text{H}_2\text{O} & 1.0 \text{ cm}\;^1 \\
\text{Gd}_2(\text{C}_2\text{O}_4)_3 & \cdot 10\text{H}_2\text{O} & 0.60 \text{ cm}\;^1 \\
\text{CrK}(\text{SO}_4) & \cdot 12\text{H}_2\text{O} & 0.16 \text{ cm}\;^1 \\
\text{FeNH}_4(\text{SO}_4)_2 & \cdot 12\text{H}_2\text{O} & 0.13 \text{ cm}\;^1
\end{align*}
\]

Splittings in the neighborhood of one cm\(^{-1}\) are in principle accessible to investigations by means of microwave methods. The selection rules in general permit a number of magnetic dipole transitions. Electric dipole transitions are forbidden by the parity rule, since the parity of initial and final states are identical when these states originate from the same degenerate level of the free ion. Electric quadrupole transitions are less probable than magnetic dipole transitions by a factor of the order of \((\text{atomic radius/wavelength})^2 \times (\text{Debye unit/Bohr magneton})^2\), which is of the order of \(10^{-12}\) for \(\lambda = 1\) cm.

**Magnitude of the Effect**

The magnitude and detectability of the resonance absorption effect may be estimated by reasoning similar to
that given by Torrey, Purcell and Pound\(^8\) for the case of nuclear resonance. We shall consider the power absorbed by a system which has two eigenstates 1 and 2 with eigenvalues differing by the energy \(\hbar \omega_0\). The transition probability between states 1 and 2 for a single system per unit time for \(x\)-polarized radiation is

\[
p = (2\pi/\hbar^2) |u_{12}^x|^2 I,
\]

where \(u_{12}^x\) is the matrix element of the magnetic moment operator \(\mu^x = \hbar \mu_B j^x\) and \(I\) is the total energy in the incident radiation field per unit volume per unit frequency interval.

In thermal equilibrium the number of systems in the ground state is greater than the number of systems in the excited state; the excess is

\[
(N_1 - N_2) = N_1 (1 - e^{-\hbar \omega_0 / kT}) \approx \hbar \omega_0 / kT
\]

for \(\hbar \omega_0 / kT \ll 1\); here \(N\) is the total number of systems. The power absorption is given by

\[
\frac{1}{2} \left( \frac{\hbar \omega_0}{kT} \right) (\hbar \omega_0) N p
\]

Suppose that the bandwidth of the incident electromagnetic wave is \(\Delta f\) and the width of the resonance line (due to magnetic moment interactions) is \(\Delta \omega_0\) (\(\gg \Delta f\)); then only the fraction \(2\pi \Delta f / \Delta \omega_0\) of the total number of systems have their resonances within the bandwidth of the r-f radiation field. Let \(U = I \Delta f\) be the total energy density in the incident radiation field; then-

\[(3)\ H.C. Torrey, E.M. Purcell and R.V. Pound, Phys. Rev. 52, 630 (1946)\]
\[ p = \frac{2n^2 \omega_0^2 |\mu_{12}|^2}{kT \Delta \omega_0} \]  

is the integrated power absorption per unit volume, where \( n \) is the number of paramagnetic ions per unit volume.

Now the \( Q \) of the system is given by

\[ Q^{-1} = \frac{p}{\omega_0 U} \sim \frac{\omega_0}{\Delta \omega_0} \frac{\mu_n^2}{kT} \frac{\gamma \omega_0}{kT} \]  

(6)

if the line width is considered as caused by magnetic dipole interactions, so that \( \gamma / \Delta \omega_0 \sim \mu^2/a^3 \sim n \mu^2 \).

From Eq. (6) one has, for \( T = 300^\circ K \) and \( \lambda = 1 \) cm, \( Q \sim 200 \), which is easily detectable in the presence of empty cavity \( Q \)'s which may be of the order of 1000 or more at this wavelength.

**Selection Rules**

We have pointed out that the allowed transitions are magnetic dipole transitions. One can proceed to calculate the selection rules by group theoretical methods. The eigenfunctions corresponding to the energy levels in the crystalline electric fields transform according to the irreducible representations \( \Gamma_i \) of the symmetry group of the crystalline field. The characters of the irreducible representations are given in the papers of Bethe, Tisza, and Jahn. The character of the magnetic moment operator under a rotation through an angle \( \phi \) is given by \( \chi(\phi) = 1 + 2 \cos \phi \), since the magnetic

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(10) L. Tisza, Zeits. f. Physik 32, 48 (1933)
moment transforms as an axial vector.

It is a fundamental result of group theory that transitions are allowed between levels \( m \) and \( n \) only if \( \Gamma_m^x \Gamma_n \Gamma_a \) contains the identical representation \( \Gamma_1 \); here \( \Gamma_a \) is the representation of an axial vector. The allowed transitions found from the character calculations are given below; the representations are labelled according to the notation of Bethe. In the cases of the one and two-valued rhombic and trigonal groups, which were not given in detail by Bethe, the character tables are given in Appendix A.

The notation \( \Gamma_a, b \rightarrow \Gamma_c \) indicates that the energy level whose eigenfunctions belong to \( \Gamma_c \) has allowed magnetic dipole transitions to and from the energy levels whose eigenfunctions belong to \( \Gamma_a \) and \( \Gamma_b \).

**Cubic Group** (\( \Gamma_{\text{axial}} = \Gamma_4 \))

\( \Gamma_{1,3,4} \rightarrow \Gamma_4; \Gamma_{2,3,4,5} \rightarrow \Gamma_5; \Gamma_{6,8} \rightarrow \Gamma_8; \Gamma_{7,8} \rightarrow \Gamma_7; \Gamma_3 \rightarrow \Gamma_8. \)

**Tetragonal Group** (\( \Gamma_{\text{axial}} = \Gamma_2 + \Gamma_5 = \Gamma(z) + \Gamma(x,y) \))

Transitions for \( J_z: \Gamma_1, \Gamma_2, \Gamma_3, \Gamma_4, \Gamma_5 \rightarrow \Gamma_5; \Gamma_6, \Gamma_7 \rightarrow \Gamma_7. \)

Transitions for \( J_x, J_y: \Gamma_{1,2,3,4} \rightarrow \Gamma_5; \Gamma_6 \rightarrow \Gamma_6; \Gamma_7 \rightarrow \Gamma_7. \)

**Trigonal Group** (\( \Gamma_{\text{axial}} = \Gamma_2 + \Gamma_3 = \Gamma(z) + \Gamma(x,y) \))

Transitions for \( J_z: \Gamma_1 \rightarrow \Gamma_2; \Gamma_3 \rightarrow \Gamma_3; \Gamma_4, \Gamma_5 \rightarrow \Gamma_5. \)

Transitions for \( J_x, J_y: \Gamma_1 \rightarrow \Gamma_3; \Gamma_3 \rightarrow \Gamma_3; \Gamma_4 \rightarrow \Gamma_5; \Gamma_5 \rightarrow \Gamma_5. \)
Rhombic Group \( \Gamma_{\text{axial}} = \Gamma_2 + \Gamma_3 + \Gamma_4 = \Gamma(x) + \Gamma(y) + \Gamma(z) \)

Transitions for \( \Gamma_2 \): \( \Gamma_1 \rightarrow \Gamma_2 \); \( \Gamma_3 \rightarrow \Gamma_4 \); \( \Gamma_5 \rightarrow \Gamma_5 \).

Transitions for \( \Gamma_3 \): \( \Gamma_1 \rightarrow \Gamma_3 \); \( \Gamma_2 \rightarrow \Gamma_4 \); \( \Gamma_5 \rightarrow \Gamma_5 \).

Transitions for \( \Gamma_4 \): \( \Gamma_1 \rightarrow \Gamma_4 \); \( \Gamma_2 \rightarrow \Gamma_3 \); \( \Gamma_5 \rightarrow \Gamma_5 \).

The selection rules for the tetragonal case have been given previously by Bethe\(^{12}\).

The application of these selection rules may be illustrated by the case of the Gd\(^{+++}\) ion, for which \( J = 7/2 \). According to Bethe\(^{9}\) the ground state of the ion splits in a cubic field into a two-fold degenerate level belonging to \( \Gamma_6 \); a two-fold degenerate level belonging to \( \Gamma_7 \); and a four-fold degenerate level belonging to \( \Gamma_8 \). The selection rules permit transitions between \( \Gamma_6 \) and \( \Gamma_8 \), and between \( \Gamma_7 \) and \( \Gamma_8 \), but not between \( \Gamma_6 \) and \( \Gamma_7 \).

If the overall splitting of the ground state in Gd\(_2\)(SO\(_4\))\(_3\) . 8H\(_2\)O is 1.0 \( \text{cm}^{-1} \), as given by Gorter\(^{4}\), the allowed transitions will correspond to wavelengths of 1.6 \( \text{cm} \) and 2.7 \( \text{cm} \). This follows from the fact that, if only the cubic term of the fourth degree in the crystalline potential is considered\(^{13}\), the splitting is in the ratio of 5 to 3, with the four-fold level between the two two-fold levels.

Intensity Factors

Eq. (5) is a quite general expression for the power absorption when the bandwidth \( \Delta f \) of the incident electromagnetic

\(^{12}\) H. Bethe, Zeit. f. Physik 60, 213 (1930)
\(^{13}\) H. H. Hebb and E. H. Purcell, J. Chem. Phys. 5, 338 (1937)
tic wave is small in comparison with the effective bandwidth \( \Delta \omega_0 \) of the resonance, and for \( kT \gg \gamma \omega_0 \). In the absence of detailed knowledge regarding the dependence of \( \Delta \omega_0 \) on the crystalline and applied magnetic fields, we shall suppose for the sake of discussion that \( \Delta \omega_0 \) is a constant for any specific salt. Under this assumption the dependence of the power absorption on frequency and magnetic field intensity is determined by the factor \( \omega_0^2 |\chi_{12}^x|^2 \) in Eq. (5).

For convenience we prefer to discuss the dimensionless quantity:

\[
\frac{\Omega_{\text{int}}}{\text{man}} = \left( \frac{\gamma \omega_0}{\delta} \right)^2 \left| (m|J_y|n) / \gamma \right|^2
\]

This will be called the intensity factor. Here \( J \) is the angular momentum operator; \( \delta \) is an energy which must be defined for each specific problem - it is closely related to the purely crystalline splitting.

In general it is more convenient to work with the operators \( J_+ = J_x + iJ_y \) and \( J_- = J_x - iJ_y \), than with \( J_x \) or \( J_y \) separately. One has

\[
J_x = \frac{1}{2} (J_+ + J_-);
\]

now from the reality of \( J_x \) and \( J_y \),

\[
(i|J_-|n)^* = (m|J_+|n),
\]

so that

\[
(m|J_x|n) = \frac{1}{2} \left( (m|J_+|n) + (n|J_+|m)^* \right)
\]

This relation is used to calculate the matrix elements of \( J_x \) from those of \( J_+ \).

Tables of numerical values of the intensity factor are given in the following sections along with the energy
differences associated with the various transitions.

III. COMBINED CRYSTALLINE AND ZEEMAN SPLITTING

It is not possible to discuss in a general fashion the behavior of energy levels in the presence of combined crystalline electric fields and external static magnetic fields. Rather, it is necessary to find in detail for each individual case the solution to the quantum mechanical perturbation problem.

Level splittings corresponding to microwave frequencies are believed to arise only in somewhat special situations, including:

(a) When the ground state of the free ion is an $S$ state, the crystalline field causes splitting only in conjunction with spin-orbit coupling. The resultant splitting is small.

(b) A small crystalline field of low symmetry may remove the degeneracy left by a larger crystalline field of higher symmetry. For example, a predominantly cubic field may have a small trigonal component which gives rise to a further splitting.

Hebb and Purcell in their theoretical study of magnetic cooling experiments discuss examples where the splitting is of the order of magnitude of one cm$^{-1}$. Type (a) splitting is found, for example, in salts of trivalent gadolinium, where the ground level is $^3S_7/2$; and in Fe$^{+++}$ and In$^{++}$ ($^6S_5/2$). Type (b) splitting is found for example in potassium (14) J. H. Van Vleck and V. G. Foner, Phil. Mag. 17, 961 (1934)
chronic alum \( \text{KCr(SO}_4\text{)}_2 \cdot 12 \text{H}_2\text{O} \), where there is thought to be a small trigonal field superposed on the predominant cubic field. The possible transitions and corresponding intensity factors for the cases just cited are discussed in detail below.

Case I. \( J = 7/2 \) (Gd\( ^{+++} \))

In the absence of external magnetic fields this state is split by a cubic electric field into two two-fold levels and one four-fold level. According to Bethe (cf reference 9, p. 155) the two-fold levels belong to \( \Gamma_6 \) and \( \Gamma_7 \), the four-fold level to \( \Gamma_8 \). We assume that the splitting\(^{15}\) takes place as in Figure I, which is consistent with the work of Hobbs and Purcell\(^{13}\). The zero order wave functions belonging to these representations are listed below.

\(^{15}\) However, the situation in the Gd\( ^{+++} \) salts may not be so simple. We are indebted to Professor F. J. Belinfante for correspondence regarding a detailed treatment of the energy level scheme in preparation by Van Dyk and himself.
\[\psi_a^{(1)} = \frac{1}{2} \left[ \frac{1}{3} \phi_{5/2} - \phi_{-3/2} \right] \]  \hspace{1cm} \Gamma_7

\[\psi_a^{(2)} = \frac{1}{2} \left[ \phi_{-5/2} - \phi_{3/2} \right] \]

\[\psi_b^{(1)} = \left(\frac{7}{12}\right)^{1/2} \left[ \phi_{7/2} - \left(\frac{5}{3}\right)^{1/2} \phi_{-1/2} \right] \]  \hspace{1cm} \Gamma_8

\[\psi_b^{(2)} = \left(\frac{7}{12}\right)^{1/2} \left[ \phi_{-7/2} - \left(\frac{5}{3}\right)^{1/2} \phi_{1/2} \right] \]

\[\psi_b^{(3)} = \frac{1}{2} \left[ \phi_{5/2} + \frac{3}{2} \phi_{-3/2} \right] \]

\[\psi_b^{(4)} = \frac{1}{2} \left[ \phi_{-5/2} + \frac{3}{2} \phi_{3/2} \right] \]

\[\psi_c^{(1)} = \left(\frac{5}{12}\right)^{1/2} \left[ \phi_{7/2} + \left(\frac{7}{3}\right)^{1/2} \phi_{-1/2} \right] \]  \hspace{1cm} \Gamma_6

\[\psi_c^{(2)} = \left(\frac{5}{12}\right)^{1/2} \left[ \phi_{-7/2} + \left(\frac{7}{3}\right)^{1/2} \phi_{1/2} \right] \]

\(\phi_m\) denotes a function with \(J = 7/2, \Pi_J = M\). We obtain for the secular equation in the presence of an (001) directed magnetic field.
Here \( a = g \nu \mu_B (g=2 \text{ since } L = 0) \), and there is a similar block involving \((-a)\) for \((a)\) and the remaining functions. This result has been essentially given by Hebb and Purcell in another connection. Introducing dimensionless quantities 
\( \eta = E/\delta, x = a/\delta \) one finds for the eigenvalues

<table>
<thead>
<tr>
<th>( \psi_c^{(1)} )</th>
<th>( \psi_b^{(1)} )</th>
<th>( \psi_b^{(3)} )</th>
<th>( \psi_a^{(1)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{5}{2} a )</td>
<td>( \frac{1}{3} \sqrt{3} a )</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>( \frac{5}{2} a )</td>
<td>( \frac{1}{3} \sqrt{3} a )</td>
<td>( \frac{3}{2} a - E )</td>
</tr>
<tr>
<td>( \psi_c^{(1)} )</td>
<td>( \psi_b^{(1)} )</td>
<td>( \psi_b^{(3)} )</td>
<td>( \psi_a^{(1)} )</td>
</tr>
<tr>
<td>( \frac{1}{3} \sqrt{3} a )</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

(12)
\( \eta_{7/2} = \frac{3}{2} x + \frac{13}{2} + \frac{1}{2} \sqrt{(3 - \frac{2}{3} x)^2 + \frac{140}{9} x^2} \)

\( \eta_{5/2} = \frac{1}{2} x + \frac{5}{2} + \frac{1}{2} \sqrt{(5 - 2x)^2 + 12 x^2} \)

\( \eta_{3/2} = -\frac{1}{2} x + \frac{5}{2} + \frac{1}{2} \sqrt{(5 + 2x)^2 + 12 x^2} \)

\( \eta_{1/2} = -\frac{3}{2} x + \frac{13}{2} + \frac{1}{2} \sqrt{(3 + \frac{2}{3} x)^2 + \frac{140}{9} x^2} \)

\( \eta_{-1/2} = \frac{3}{2} x + \frac{13}{2} - \frac{1}{2} \sqrt{(3 - \frac{2}{3} x)^2 + \frac{140}{9} x^2} \)

\( \eta_{-3/2} = \frac{1}{2} x + \frac{5}{2} - \frac{1}{2} \sqrt{(5 - 2x)^2 + 12 x^2} \)

\( \eta_{-5/2} = -\frac{1}{2} x + \frac{5}{2} - \frac{1}{2} \sqrt{(5 + 2x)^2 + 12 x^2} \)

\( \eta_{-7/2} = -\frac{3}{2} x + \frac{13}{2} - \frac{1}{2} \sqrt{(3 + \frac{2}{3} x)^2 + \frac{140}{9} x^2} \)

The authors have available copies of the analytical expressions for the wave functions and matrix elements as functions of \( x \) for distribution to anyone who may require them.

The sum of the squares of all the matrix elements of \( J_+ \) is exactly 84 for \( J = 7/2 \), independent of the value of \( x \). This result follows from the principle of spectroscopic stability (cf. reference 1, p. 139), and provides a very useful

The \( \eta \)'s being labeled according to the levels they represent in very large fields. These are plotted in Figure 2. The numerical values of the frequencies and intensity factors corresponding to non-vanishing matrix elements are to be found* in Table I, while Figure 3 gives plots of intensity factors and frequencies of typical lines vs. applied magnetic field.
check on the numerical calculations.

For strong magnetic fields the eigenvalues and matrix elements approach the values characteristic of free ions. From Table I we see, for example, that for large $x$ the largest values of the intensity factors belong to those $x$-polarized transitions for which $|\Delta n| = \pm 1$, in agreement with the usual selection rule. An example of such a transition is \( \frac{7}{2} \leftrightarrow \frac{5}{2} \), for which the values of the frequency and intensity factor are shown in Figure 3. A number of lines are weak for all $x$: an example is $\frac{3}{2} \leftrightarrow -\frac{7}{2}$. All of the $z$-polarized lines have constant values of the intensity factor, independent of $x$; an example is the line $\frac{7}{2} \leftrightarrow -\frac{3}{2}$ shown in Figure 3. The crossing points on the eigenvalue diagram (Figure 2) correspond to lines of zero frequency.

Case II \( J = \frac{5}{2} \) (Fe$^{++}$, Mn$^{++}$).

The case of $J = \frac{5}{2}$ is very similar to that of $J = \frac{7}{2}$. The roots of the secular equation for an (001) magnetic field and a cubic electric field have been given by Debye$^{15}$ and also by Kronig and Bouwkamp$^{16}$.

We shall not discuss this state in any detail, but merely give results. The energy levels are

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(16) R. de L. Kronig and C. J. Bouwkamp, Physica 6, 290 (1939)
\[
\begin{align*}
\epsilon_{1/2} &= 1 + \frac{1}{2} x \\
\epsilon_{-1/2} &= 1 - \frac{1}{2} x \\
\epsilon_{5/2} &= \frac{x}{2} - \frac{1}{2} + 2 \left[ x^2 + x + (3/4)^2 \right]^{1/2} \\
\epsilon_{3/2} &= -\frac{x}{2} - \frac{1}{2} + 2 \left[ x^2 - x + (3/4)^2 \right]^{1/2} \\
\epsilon_{-3/2} &= \frac{x}{2} - \frac{1}{2} - 2 \left[ x^2 + x + (3/4)^2 \right]^{1/2} \\
\epsilon_{-5/2} &= -\frac{x}{2} - \frac{1}{2} - 2 \left[ x^2 - x + (3/4)^2 \right]^{1/2}
\end{align*}
\]  

(14)

where as before \( x = \frac{g \mu_B H}{\Delta} \), \( \epsilon = E/\delta \) (\( \delta \) being the overall splitting in the crystalline electric field alone). In the case under consideration, just as in the 7/2 case, \( L = 0 \) so that \( g = 2 \). In Figure 4 one finds these energies plotted as a function of external field. Table II gives the numerical values of the frequencies and intensity factors.

The principle of spectroscopic stability applied to the \( J = 5/2 \) case tells us that the sum of the squares of all the matrix elements of \( J_+ \) is 35, independent of \( x \).

Case III \((\text{KCr (SO}_4)_2 \cdot 12 \text{H}_2\text{O})\)

According to Hobb and Purcell the \( \text{Cr}^{+++} \) ion in this salt is in a \( 4\text{F}_{3/2} \) state, which is not split by the cubic crystalline field. If one assumes that there is also present a small field of trigonal symmetry the axis of which coincides with one of the body diagonals of the cubic lattice (this is to be expected from X-ray studies of the salt), then the \( J = 3/2 \) state does split and give rise to possibilities for microwave absorption. Now in this alum the \( \text{Cr}^{+++} \) ions lie on
a face centered cubic lattice, i.e., on interpenetrating simple cubic lattices. If one resolves the face-centered lattice into the four simple cubic lattices then one finds that the trigonal axis of the electric field is in each case along a different body diagonal of the unit cube. We shall treat these four simple cubic systems independently.

Taking for the crystalline potential only the second order terms we find

\[ V_{\text{trig}} = D (x^2 + y^2 - 2z^2), \quad (15) \]

where the \( z \) axis is here taken as the body diagonal. This potential has more than trigonal (i.e., it has axial) symmetry as a result of our dropping higher terms. Just because of this apparent axial symmetry, however, a magnetic field placed in the (001) crystallographic direction will look the same to each component simple cubic array. That is, the properties of the states as functions of the field should depend only on the strength of the field and the angle between the field direction and the trigonal axis. We therefore need consider only one of the component arrays, say the one with trigonal axis in the (111) direction.

We now have to solve the problem of an atom with \( J = 3/2 \) perturbed by an interaction

\[ H = V_{\text{trig}} + H_{\text{mag}} \]
\[ = V_{\text{trig}} + g_p \mu_B (H \cdot J) \quad (16) \]

for a \( \frac{3}{2} \) state \( g = 2/5 \). Taking the direction of quantization to be along the (111) direction, and choosing the \( x \) and \( y \) axes
such that the component of $H$ perpendicular to the $z$ axis lies equally between them we have

$$\vec{H} \cdot \vec{J} = \frac{H}{\sqrt{3}} (J_x + J_y + J_z) \quad \text{or} \quad (17)$$

$$H_{\text{mag}} = a \left( \frac{1}{2} (1-i) J_+ + \frac{1}{2} (1+i) J_- + J_z \right) \quad (18)$$

where

$$a = g_\mu_B H/3\hbar$$

The level scheme in the absence of $H_{\text{mag}}$ is as shown in Figure 5. Here the levels are labelled by their weak field quantum numbers. Introducing now $H_{\text{mag}}$ we get as our secular equation:

$$\begin{array}{cccc}
3/2 & 1/2 & -1/2 & -3/2 \\
3/2 & \frac{1}{2} + \frac{3}{2} x & -\frac{1}{2} + \frac{1}{2} x - \epsilon & 0 & 0 \\
1/2 & \frac{1}{2} + \frac{3}{2} x & \frac{1}{2} + \frac{1}{2} x - \epsilon & (1-i) x & 0 \\
-1/2 & 0 & (1+i) x & -\frac{1}{2} - \frac{1}{2} x - \epsilon & \frac{1}{2} (1-i) 3^2 x \\
-3/2 & 0 & 0 & \frac{1}{2} + \frac{3}{2} x & \frac{1}{2} - \frac{3}{2} x - \epsilon \\
\end{array}$$

where $\epsilon \equiv E/\delta$, $x \equiv a/\delta$.

Expanding gives

$$\epsilon^4 - \frac{1}{2} (1 + 15x^2) \epsilon^2 + \frac{1}{16} (1 + 81x^2 - 6x^2) = 0 \quad (20)$$

the roots of which are
\[ \varepsilon(\frac{3}{2}) = \frac{1}{2} \left( 1 + 15x^2 + 6x \sqrt{1 + 4x^2} \right)^{1/2} \]
\[ \varepsilon(\frac{1}{2}) = \frac{1}{2} \left( 1 + 15x^2 - 6x \sqrt{1 + 4x^2} \right)^{1/2} \]
\[ \varepsilon(-\frac{1}{2}) = -\frac{1}{2} \left( 1 + 15x^2 - 6x \sqrt{1 + 4x^2} \right)^{1/2} \]
\[ \varepsilon(-\frac{3}{2}) = -\frac{1}{2} \left( 1 + 15x^2 + 6x \sqrt{1 + 4x^2} \right)^{1/2} \]

(21)

where we have labeled the energies with their appropriate
strong field quantum numbers. To find the selection and intensity rules it is necessary to find the wave functions \( \psi(\mathbf{r}) \)
belonging to \( \varepsilon(\mathbf{r}) \) and also the matrix elements of \( J_+ \), \( J_- \).
It should be remembered that these are \( J_+ \) and \( J_- \) relative to the system of quantization used in this problem. For an r-f field along the (001) axis for example we will not have only \( J_z \) elements present. The wave functions and the corresponding matrix elements are to be found in Appendix C.

In order to calculate the relative intensities of the different lines we must know the direction of the r-f field. If, for example, the r-f field is directed along the (001) axis then the relative intensities are given by calculating the matrix elements of \( J_x + J_y + J_z = T \). A simple calculation shows
\[
|\langle M | T | M' \rangle|^2 = \frac{1}{2} |\langle M | J_+ | M' \rangle|^2 + \frac{1}{2} |\langle M | J_+ | M' \rangle|^2 + |\langle M | J_z | M' \rangle|^2
\]
\[ + \text{Im} \left( \langle M | J_+ | M' \rangle \langle M' | J_+ | M \rangle \right) \]
\[ + \text{Re} \left( \langle M | J_+ | M' \rangle \langle M' | J_+ | M \rangle^* + \langle M' | J_+ | M \rangle \langle M | J_+ | M' \rangle^* \right) \]
\[ + \text{Im} \left( \langle M | J_+ | M' \rangle \langle M' | J_z | M' \rangle^* + \langle M' | J_+ | M \rangle \langle M | J_z | M' \rangle^* \right) \]
(22)
All of the intensity factors for this case are very small. This is partly the consequence of taking the r.f. field parallel to the static field. A plot of the eigenvalues as a function of $x$ is given in Figure 6.

IV. CONCLUSION

It is seen from the above treatment, which is based on the usual simplified model, that the microwave absorption spectrum of paramagnetic crystals is expected to be a rather complicated function of the external static magnetic field. We wish to emphasize again that the influence of exchange coupling between paramagnetic ions has been entirely neglected. This coupling in many salts may submerge the effects we have considered, and may result in a simpler spectrum. Indeed, it may well be that an effect of this sort occurs in the measurements of Zavoisky and of Summerow and Halliday, most of which were made on magnetically-concentrated salts. The type of situation which we have treated is most likely to be realized in salts which are magnetically very dilute. One should also note the importance of using single crystals with the static and r-f magnetic fields along crystal axes of high symmetry.

ACKNOWLEDGMENTS

We wish to thank Professors J. H. Van Vleck, C. J. Gorter and L. Tisza for several discussions, and Miss Ruth Krock for computational assistance. One of us (C.K.) is indebted to the John Simon Guggenheim Memorial Foundation for a Fellowship during the tenure of which this work was carried out.
Appendix A

Character Table - Trigonal Double Group (after Jahn\textsuperscript{11})

<table>
<thead>
<tr>
<th></th>
<th>E</th>
<th>R</th>
<th>2C\textsubscript{1}</th>
<th>2C\textsubscript{1}</th>
<th>3C\textsubscript{2}</th>
<th>3C\textsubscript{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Gamma_1)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>(\Gamma_2)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>(\Gamma_3)</td>
<td>2</td>
<td>2</td>
<td>-1</td>
<td>-1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(\Gamma_4)</td>
<td>2</td>
<td>-2</td>
<td>-2</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(\Gamma_5)</td>
<td>2</td>
<td>-2</td>
<td>1</td>
<td>-1</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Note - \(\Gamma_4\) is used to denote two conjugate-complex one-dimensional representations.

The splitting scheme for the trigonal group is as follows:

\[
\begin{align*}
\text{j} = 0 & \quad \Gamma_1 \\
\frac{1}{2} & \quad \Gamma_5 \\
1 & \quad \Gamma_2 + \Gamma_3 \\
\frac{3}{2} & \quad \Gamma_4 + \Gamma_5 \\
2 & \quad \Gamma_1 + 2\Gamma_3 \\
\frac{5}{2} & \quad \Gamma_4 + 2\Gamma_5 \\
3 & \quad \Gamma_1 + 2\Gamma_2 + 2\Gamma_3
\end{align*}
\]
Character Table - Rhombic Double Group (after Botho\textsuperscript{9})

<table>
<thead>
<tr>
<th></th>
<th>E</th>
<th>R</th>
<th>$2C_1$</th>
<th>$2C_2$</th>
<th>$2C_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$\Gamma_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$\Gamma_3$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$\Gamma_4$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$\Gamma_5$</td>
<td>2</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Consider an unperturbed system which has a definite angular momentum $J$. It undergoes a perturbation due to an external non-singular (electric) field satisfying Laplace's equation. We shall show that center of gravity of the $2J+1$ components of the originally degenerate energy level is not shifted, to the first order.

Let the eigenfunctions of the perturbed system be $\psi_i$ ($i=1;\ldots, 2J+1$). Then the center of gravity of the levels will be given by

$$\bar{\gamma} = \frac{1}{2J+1} \sum_i \int \psi_i^* V \psi_i \, dt$$

where $V$ is the perturbing potential. However this is simply the trace of $V$ in the representation $\psi_i$ and is invariant under choice of representation. We could therefore just as well use the eigenfunctions $\psi_{M}$ ($M=-J,\ldots, +J$) of the unperturbed system. That is,

$$\bar{\gamma} = \frac{1}{2J+1} \sum_{M} \int \psi_{M}^* V \psi_{M} \, dt$$

Now $\sum_{M} \psi_{M}^* \psi_{M}$ is rotationally invariant, since the $\psi_{M}$ form the basis vectors of a $(2J+1)$-dimensional irreducible representation of the rotation group, and in this "representation space" the sum indicated is just a scalar product. Now by the assumption that $V$ satisfies Laplace's equation (which is rotationally invariant) we have that $V$ must transform as one component of some representation of the rotation group. Since the only invariant solutions of Laplace's equation are a constant (which shifts all levels equally and just amounts to a change of the
energy zero point) and $1/r$ (which is singular) we can say that
the representation to which $V$ belongs does not contain the i-
dentity representation. Therefore according to the usual group
theoretical argument* the integral in $\Omega$ vanishes and the re-
quired result has been established. A weaker form of this
theorem has been given previously by Kynch**.

* Cf for example, H. Fyring, J. Walter and G. Kinball, Quantum

Appendix C

This appendix contains the wave functions and matrix element for K Cr Alum in an (001) static magnetic field. The wave functions are given by

\[ \Psi (II) = \frac{\delta^{3/2} + a_M \delta^{1/2} + b_M \delta^{-1/2} + c_M \delta^{-3/2}}{\left[ 1 + |a_M|^2 + |b_M|^2 + |c_M|^2 \right]^{1/2}} \]

where

\[ a_M = -\frac{1}{\sqrt{3}} \frac{\left( \frac{1}{2} + \frac{3}{2} x - \epsilon(II) \right)}{x} (1 + i) \]

\[ b_M = -i(3^{3/2}/2) - (1+i) \frac{\left( -\frac{1}{2} + \frac{1}{2} x - \epsilon(II) \right)}{2x} a_M \]

\[ c_M = -\frac{(1+i)(3^{3/2}/2) x b_M}{\left( \frac{1}{2} - \frac{3}{2} x - \epsilon(II) \right)} \]

The matrix elements of \( J_+ \) and \( J_z \) are now

\[ (II' | J_z | II) = \frac{\frac{3}{2} + \frac{1}{2} (a_{II'}, a_{II} - b_{II'} b_{II}) - \frac{3}{2} c_{II'} c_{II}}{\left[ (1+|a_{II}|^2 + |b_{II}|^2 + |c_{II}|^2)(1+|a_{II'}|^2 + |b_{II'}|^2 + |c_{II'}|^2) \right]^{1/2}} \]

\[ (II' | J_+ | II) = \frac{\frac{1}{2} a_M + 2a_{II'} b_M + 3\frac{1}{2} b_{II'} c_M}{\left[ (1+|a_{II}|^2 + |b_{II}|^2 + |c_{II}|^2)(1+|a_{II'}|^2 + |b_{II'}|^2 + |c_{II'}|^2) \right]^{1/2}} \]
Figure 1. Energy levels of $^8S$ state after splitting by electrostatic potential of form $V = D(x^4 + y^4 + z^4)$; the overall separation is $8\delta$. 
Figure 2. Eigenvalues of $^8S$ state as a function of the strength of the static magnetic field in the (001) direction; a constant cubic electrostatic field is also present. The subscripts on the $\eta$'s indicate the value of the magnetic quantum number $M_J$ characterizing the state for $x \gg 1$. 
Figure 3. Frequency and intensity factor for some typical absorption lines resulting from an S state; the intensity factor is proportional to the power absorption and is defined by Equation (7).
Figure 4. Eigenvalues of $^6S$ state as a function of the static magnetic field in the (001) direction.
Figure 5. Energy levels for KCr(SO$_4$)$_2$ $\cdot$ 12 H$_2$O in presence of axial electrostatic field.
Figure 6. Eigenvalues for $K \text{Cr(SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ as a function of the strength of the static magnetic field in the (001) direction.
### TABLE I

Frequencies and Intensity Factors for Transitions in $J = 7/2$ Case; Cubic Field

Table is labelled in terms of dimensionless quantities $\eta = E/\delta$ and $x = \sqrt{\eta} \delta/\delta$, where $\delta$ is as shown in Figure 1.

The intensity factor is defined by $\Theta_x^2 = \frac{1}{2} |(\eta|\delta|n)|^2 (\Delta \eta)^2$. The static magnetic field is in the $Z$ direction; this is also the (001) direction.

<table>
<thead>
<tr>
<th>Transitions Quantity</th>
<th>$1.0$</th>
<th>$2.0$</th>
<th>$3.0$</th>
<th>$5.0$</th>
<th>$10.0$</th>
<th>$15.0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1E \rightarrow ^3E$</td>
<td>2.26</td>
<td>2.50</td>
<td>2.75</td>
<td>3.00</td>
<td>3.50</td>
<td>4.00</td>
</tr>
<tr>
<td>$^1E \rightarrow ^1E$</td>
<td>2.14</td>
<td>2.36</td>
<td>2.58</td>
<td>2.80</td>
<td>3.20</td>
<td>3.60</td>
</tr>
<tr>
<td>$^3E \rightarrow ^3E$</td>
<td>3.80</td>
<td>4.00</td>
<td>4.20</td>
<td>4.40</td>
<td>5.00</td>
<td>6.00</td>
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<tr>
<td>$^3E \rightarrow ^1E$</td>
<td>3.60</td>
<td>3.80</td>
<td>4.00</td>
<td>4.20</td>
<td>4.80</td>
<td>5.80</td>
</tr>
</tbody>
</table>

*Note: Additional columns and rows may be present in the full table.*
Table II

Frequencies and Intensity Factors for Transitions in \( J = 5/2 \) Case: Cubic Field

Table is labelled in terms of dimensionless quantities \( \varepsilon = E/\delta \) and \( x = \gamma H/\delta \), where \( \delta \) is the overall splitting in the electric field alone. The intensity factor is defined by Eq. (7) and is given in this case by

\[
\Theta_x = \frac{1}{4} |\langle m|J_x|n\rangle|^2 (\Delta \varepsilon)^2 \text{ and } \Theta_z = |\langle m|J_z|n\rangle|^2 \mu_0. \]

The static magnetic field is in the \( z \) direction; this is also the \((001)\) direction.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Quantity</th>
<th>( \frac{1}{2} )</th>
<th>( 3 )</th>
<th>( 5 )</th>
<th>( 7 )</th>
<th>( 10 )</th>
<th>( 15 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{3}{2} \rightarrow \frac{1}{2} )</td>
<td>( \Delta \varepsilon )</td>
<td>0.23</td>
<td>0.61</td>
<td>0.88</td>
<td>1.01</td>
<td>1.00</td>
<td>0.71</td>
</tr>
<tr>
<td>( \frac{3}{2} \rightarrow \frac{1}{2} )</td>
<td>( \Theta_x )</td>
<td>0.02</td>
<td>0.25</td>
<td>0.78</td>
<td>1.37</td>
<td>1.67</td>
<td>0.94</td>
</tr>
<tr>
<td>( \frac{5}{2} \rightarrow \frac{3}{2} )</td>
<td>( \Delta \varepsilon )</td>
<td>0.24</td>
<td>0.75</td>
<td>1.29</td>
<td>1.85</td>
<td>2.70</td>
<td>4.15</td>
</tr>
<tr>
<td>( \frac{5}{2} \rightarrow \frac{3}{2} )</td>
<td>( \Theta_x )</td>
<td>0.02</td>
<td>0.10</td>
<td>0.21</td>
<td>0.32</td>
<td>0.46</td>
<td>0.64</td>
</tr>
<tr>
<td>( \frac{7}{2} \rightarrow \frac{3}{2} )</td>
<td>( \Delta \varepsilon )</td>
<td>3.04</td>
<td>3.15</td>
<td>3.29</td>
<td>3.45</td>
<td>3.70</td>
<td>4.25</td>
</tr>
<tr>
<td>( \frac{7}{2} \rightarrow \frac{3}{2} )</td>
<td>( \Theta_x )</td>
<td>16.00</td>
<td>18.08</td>
<td>20.29</td>
<td>22.66</td>
<td>26.54</td>
<td>35.52</td>
</tr>
<tr>
<td>( \frac{5}{2} \rightarrow \frac{7}{2} )</td>
<td>( \Delta \varepsilon )</td>
<td>2.97</td>
<td>2.99</td>
<td>3.12</td>
<td>3.39</td>
<td>4.00</td>
<td>5.29</td>
</tr>
<tr>
<td>( \frac{5}{2} \rightarrow \frac{7}{2} )</td>
<td>( \Theta_x )</td>
<td>14.00</td>
<td>11.93</td>
<td>9.72</td>
<td>7.61</td>
<td>5.33</td>
<td>3.56</td>
</tr>
<tr>
<td>( \frac{3}{2} \rightarrow \frac{5}{2} )</td>
<td>( \Delta \varepsilon )</td>
<td>3.11</td>
<td>3.44</td>
<td>3.91</td>
<td>4.54</td>
<td>5.70</td>
<td>7.94</td>
</tr>
<tr>
<td>( \frac{3}{2} \rightarrow \frac{5}{2} )</td>
<td>( \Theta_x )</td>
<td>5.28</td>
<td>5.45</td>
<td>4.89</td>
<td>4.82</td>
<td>2.34</td>
<td>1.10</td>
</tr>
<tr>
<td>( \frac{1}{2} \rightarrow \frac{5}{2} )</td>
<td>( \Delta \varepsilon )</td>
<td>3.97</td>
<td>1.06</td>
<td>1.67</td>
<td>2.16</td>
<td>2.70</td>
<td>3.36</td>
</tr>
<tr>
<td>( \frac{1}{2} \rightarrow \frac{5}{2} )</td>
<td>( \Theta_x )</td>
<td>0.09</td>
<td>0.89</td>
<td>2.60</td>
<td>4.97</td>
<td>8.60</td>
<td>13.93</td>
</tr>
<tr>
<td>( \frac{3}{2} \rightarrow \frac{5}{2} )</td>
<td>( \Delta \varepsilon )</td>
<td>2.91</td>
<td>2.84</td>
<td>2.91</td>
<td>3.14</td>
<td>3.70</td>
<td>4.94</td>
</tr>
<tr>
<td>( \frac{3}{2} \rightarrow \frac{5}{2} )</td>
<td>( \Theta_x )</td>
<td>4.63</td>
<td>3.71</td>
<td>2.71</td>
<td>1.82</td>
<td>0.98</td>
<td>0.43</td>
</tr>
<tr>
<td>( \frac{5}{2} \rightarrow \frac{3}{2} )</td>
<td>( \Delta \varepsilon )</td>
<td>1.74</td>
<td>0.46</td>
<td>0.67</td>
<td>0.76</td>
<td>0.70</td>
<td>0.36</td>
</tr>
<tr>
<td>( \frac{5}{2} \rightarrow \frac{3}{2} )</td>
<td>( \Theta_x )</td>
<td>0.02</td>
<td>0.17</td>
<td>0.12</td>
<td>0.62</td>
<td>0.58</td>
<td>0.16</td>
</tr>
</tbody>
</table>

\( E = \gamma H = \delta \quad \text{in the electric field alone.} \)