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Crystalline Stark Splitting and Microwave Resonance Absorption in Paramagnetic Salts*

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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 approximately to certain magnetically dilute salts containing Fe^{+++}, Gd^{+++}, and Cr^{+++} ions, respectively, provided that exchange interactions do not play an important role and that the assumed symmetries are approximately correct. 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[1-4] 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 radiofrequency or microwave electromagnetic field. The salt is placed in an r-f circuit element situated 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:

$$f/H_0=\frac{e}{2\pi mc}=2.80\ \text{megacycles/oe}, \qquad (1)$$

where f = frequency, H_0 = static magnetic field, e = electronic charge in e.s.u., m = electronic mass, and 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.[7] Under this condition, the experiment is analogous to the nuclear magnetic resonance experiment. It may be noted that this equation also holds in the presence of strong exchange coupling between spins.

On the present picture of paramagnetic solids the energy levels of the paramagnetic ions are affected in an important way by the inhomogene-

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[1] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932).

[2] H. B. G. Casimir, *Magnetism and Very Low Temperatures* (Cambridge University Press, Teddington, England, 1940).

[3] Université de Strasbourg, *Le Magnétisme: Tome 3: Paramagnétisme* (Institut International de Coopération Intellectuelle, Paris, 1940).

[4] C. J. Gorter, *Paramagnetic Relaxation* (Elsevier Publishing Company, Inc., Amsterdam, 1947).

[5] W. G. Penney and G. J. Kynch, Proc. Roy. Soc. **A170**, 112 (1939); see also J. H. Van Vleck, J. Phys. Chem. **41**, 67 (1937); S. Freed, Rev. Mod. Phys. **14**, 105 (1942).

[6] E. Zavoisky, J. Phys. U.S.S.R. **9**, 211, 245, 447 (1945); **10**, 170, 197 (1946); see also R. L. Cummerow and D. Halliday, Phys. Rev. **70**, 433 (1946); R. L. Cummerow, D. Halliday, and G. E. Moore, Phys. Rev. **72**, 173 (1947).

[7] J. Frenkel, J. Phys. U.S.S.R. **9**, 299 (1945).

ous 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 absorption spectrum, in contrast to the single line found by Zavoisky.

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.* Various effects of exchange coupling are considered by J. H. Van Vleck, in a paper which is to appear in *The Physical Review.* It should also be emphasized that the angular dependence of the crystalline electric fields may be more complicated than assumed here.

Note added in proof: Measurements on Chrome Ammonium Alum at microwave frequencies have been reported very recently[7a] which show clearly the expected effect of the Stark splitting.

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 over-all splittings of the ground state:

$Gd_2(SO_4)_3\cdot 8\ H_2O$	$1.0\ \text{cm}^{-1}$,
$Gd_2(C_2O_4)_3\cdot 10\ H_2O$	$0.60\ \text{cm}^{-1}$,
$KCr(SO_4)_2\cdot 12\ H_2O$	$0.16\ \text{cm}^{-1}$,
$FeNH_4(SO_4)_2\cdot 12\ H_2O$	$0.13\ \text{cm}^{-1}$.

Splittings in the neighborhood of one cm^{-1} are in principle accessible to investigation 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 (atomic radius/wavelength)$^2\times$(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

$$p=(2\pi/\hbar^2)|\mu_{12}{}^x|^2 I, \qquad (2)$$

where $\mu_{12}{}^x$ is the matrix element of the magnetic-moment operator $\mu_x=g\mu_B J_x$ and I is the total energy in the incident radiation field per unit volume per unit frequency interval.

[7a] D. M. S. Bagguley and J. H. E. Griffiths, Nature **160**, 532 (1947); P. R. Weiss, C. A. Whitmer, H. C. Torrey, and Jen-Sen Hsiang, Phys. Rev. **72**, 975 (1947).

[8] H. C. Torrey, E. M. Purcell, and R. V. Pound, Phys. Rev. **69**, 680 (1946).

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

$$(N_1-N_2)=N_1(1-\exp[-\hbar\omega_0/kT])\cong\frac{N}{2}\frac{\hbar\omega_0}{kT} \tag{3}$$

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

$$\frac{1}{2}\frac{\hbar\omega_0}{kT}(\hbar\omega_0)Np. \tag{4}$$

Suppose that the band width of the incident electromagnetic wave is Δf and the width of the resonance line (resulting from 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 band width of the r-f radiation field. Let $U=I\Delta f$ be the total energy density in the incident radiation field; then

$$P=\frac{2\pi^2\omega_0^2|\mu_{12}^x|^2 n}{kT\Delta\omega_0}U \tag{5}$$

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

$$Q^{-1}=\frac{P}{\omega_0 U}\sim\frac{\omega_0}{\Delta\omega_0}\frac{\mu^2 n}{kT}\sim\frac{\hbar\omega_0}{kT} \tag{6}$$

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

From Eq. (6) one has, for $T=300°\text{K}$ 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 wave-length.

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, Γ_i, of the symmetry group of the crystalline field. The characters of the irreducible representations are given in the papers of Bethe,[9] Tisza,[10] and Jahn.[11] The character of the magnetic-moment operator under a rotation through an angle φ is given by $\chi(\varphi)=1+2\cos\varphi$, since the magnetic-moment transforms as an axial vector.

It is a fundamental result of group theory that magnetic dipole transitions are allowed between levels m and n only if $\Gamma_m^*\times\Gamma_n\times\Gamma_a$ contains the identical representation Γ_1; here Γ_a is the representation of an axial vector. The allowed transitions found from the character calculations are given below; the representations are labeled according to the notation of Bethe.[9] 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 $\Gamma_{a,b}\leftrightarrow\Gamma_c$ indicates that the energy level whose eigenfunctions belong to Γ_c has allowed magnetic-dipole transitions to and from the energy levels whose eigenfunctions belong to Γ_a and Γ_b.

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

$\Gamma_{1,3,4}\leftrightarrow\Gamma_4$; $\Gamma_{2,3,4,5}\leftrightarrow\Gamma_5$; $\Gamma_{6,8}\leftrightarrow\Gamma_6$; $\Gamma_{7,8}\leftrightarrow\Gamma_7$; $\Gamma_8\leftrightarrow\Gamma_8$.

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

Transitions for J_z: $\Gamma_1\leftrightarrow\Gamma_2$; $\Gamma_3\leftrightarrow\Gamma_4$; $\Gamma_5\leftrightarrow\Gamma_5$; $\Gamma_6\leftrightarrow\Gamma_6$; $\Gamma_7\leftrightarrow\Gamma_7$.

Transitions for J_x, J_y: $\Gamma_{1,2,3,4}\leftrightarrow\Gamma_5$; $\Gamma_{6,7}\leftrightarrow\Gamma_6$; $\Gamma_7\leftrightarrow\Gamma_7$.

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

Transitions for J_z: $\Gamma_1\leftrightarrow\Gamma_2$; $\Gamma_3\leftrightarrow\Gamma_3$; $\Gamma_4\leftrightarrow\Gamma_4$; $\Gamma_5\leftrightarrow\Gamma_5$.

Transitions for J_x, J_y: $\Gamma_1\leftrightarrow\Gamma_3$; $\Gamma_3\leftrightarrow\Gamma_3$; $\Gamma_4\leftrightarrow\Gamma_5$; $\Gamma_5\leftrightarrow\Gamma_5$.

Rhombic Group ($\Gamma_{\text{axial}}=\Gamma_2+\Gamma_3+\Gamma_4=\Gamma_{(x)}+\Gamma_{(y)}+\Gamma_{(z)}$)

Transitions for Γ_2: $\Gamma_1\leftrightarrow\Gamma_2$; $\Gamma_3\leftrightarrow\Gamma_4$; $\Gamma_5\leftrightarrow\Gamma_5$.

Transitions for Γ_3: $\Gamma_1\leftrightarrow\Gamma_3$; $\Gamma_2\leftrightarrow\Gamma_4$; $\Gamma_5\leftrightarrow\Gamma_5$.

Transitions for Γ_4: $\Gamma_1\leftrightarrow\Gamma_4$; $\Gamma_2\leftrightarrow\Gamma_3$; $\Gamma_5\leftrightarrow\Gamma_5$.

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

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[9] H. A. Bethe, Ann. d. Physik 3, 133 (1929); see also E. Wigner, Göttingen Nachrichten 133 (1930).

[10] L. Tisza, Zeits. f. Physik 82, 48 (1933).

[11] H. Jahn, Proc. Roy. Soc. A164, 117 (1938); see also W. Opechowski, Physica 7, 552 (1940).

[12] H. Bethe, Zeits. f. Physik 60, 218 (1930).

state of the ion splits in a cubic field into a twofold degenerate level belonging to Γ_6, a twofold degenerate level belonging to Γ_7, and a fourfold degenerate level belonging to Γ_8. The selection rules permit transitions between Γ_6 and Γ_8, and between Γ_7 and Γ_8, but not between Γ_6 and Γ_7.

If the over-all splitting of the ground state in $Gd_2(SO_4)_3 \cdot 8H_2O$ is 1.0 cm^{-1}, as given by Gorter,[4] the allowed transitions will correspond to wave-lengths of 1.6 cm and 2.7 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 fourfold level between the two twofold levels.

Intensity Factors

Equation (5) is a quite general expression for the power absorption when the band width Δf of the incident electromagnetic wave is small in comparison with the effective band width $\Delta\omega_0$ of the resonance, and for $kT \gg \hbar\omega_0$. 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 $\omega_0^2|\mu_{12}^x|^2$ in Eq. (5).

For convenience, we prefer to discuss the dimensionless quantity

$$\Theta_{mn}{}^i = (\hbar\omega_0/\delta)^2 |(m|J_i|n)/\hbar|^2. \quad (7)$$

This will be called the ***intensity factor***. Here **J** is the angular-momentum operator; δ 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

$$J_x = \tfrac{1}{2}(J_+ + J_-); \quad (8)$$

now from the reality of J_x and J_y,

$$(m|J_-|n)^* = (n|J_+|m), \quad (9)$$

so that

$$(m|J_x|n) = \tfrac{1}{2}\{(m|J_+|n) + (n|J_+|m)^*\}. \quad (10)$$

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.[14] 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[13] in their theoretical study of

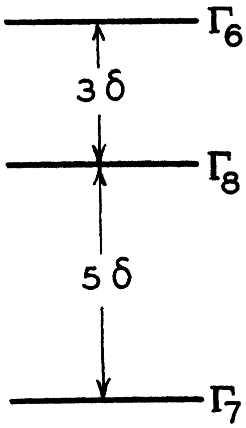

FIG. 1. Energy levels of ^8S state after splitting by cubic electrostatic potential of form $V = D(x^4+y^4+z^4)$; the overall separation is 8δ.

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[13] M. H. Hebb and E. M. Purcell, J. Chem. Phys. **5**, 338 (1937).

[14] J. H. Van Vleck and W. G. Penney, Phil. Mag. **17**, 961 (1934).

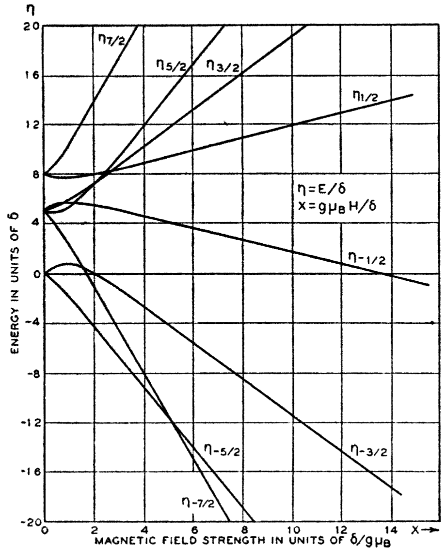

FIG. 2. Eigenvalues of ^8S state as a function of the strength of the static magnetic field in the [001] directions; a constant cubic electrostatic field is also present. The The subscripts on the η's indicate the value of the magnetic quantum number, M_J, characterizing the state for $x \gg 1$.

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 $^8S_{7/2}$, and in Fe^{+++} and Mn^{++} ($^6S_{5/2}$). Type (b) splitting is found, for example, in potassium chromic alum ($KCr(SO_4)_2 \cdot 12\,H_2O$), 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 twofold levels and one fourfold level. The validity of the cubic field assumption is uncertain. According to Bethe (cf. reference 9, p. 155), the twofold levels belong to Γ_6 and Γ_7, the fourfold level to Γ_8. We assume that the splitting* takes place as in Fig. 1, which is consistent with the work of Hebb and Purcell.[13] The zero-order wave functions belonging to these representations are listed below.

$$\left.\begin{aligned}\psi_a^{(1)}&=\tfrac{1}{2}[3^{\frac{1}{2}}\Phi_{5/2}-\Phi_{-3/2}]\\ \psi_a^{(2)}&=\tfrac{1}{2}[3^{\frac{1}{2}}\Phi_{-5/2}-\Phi_{3/2}]\end{aligned}\right\}\Gamma_7,$$
$$\left.\begin{aligned}\psi_b^{(1)}&=(7/12)^{\frac{1}{2}}[\Phi_{7/2}-(5/35^{\frac{1}{2}})\Phi_{-1/2}]\\ \psi_b^{(2)}&=(7/12)^{\frac{1}{2}}[\Phi_{-7/2}-(5/35^{\frac{1}{2}})\Phi_{1/2}]\\ \psi_b^{(3)}&=\tfrac{1}{2}[\Phi_{5/2}+3^{\frac{1}{2}}\Phi_{-3/2}]\\ \psi_b^{(4)}&=\tfrac{1}{2}[\Phi_{-5/2}+3^{\frac{1}{2}}\Phi_{3/2}]\end{aligned}\right\}\Gamma_8, \qquad (11)$$
$$\left.\begin{aligned}\psi_c^{(1)}&=(5/12)^{\frac{1}{2}}[\Phi_{7/2}+(7/35^{\frac{1}{2}})\Phi_{-1/2}]\\ \psi_c^{(2)}&=(5/12)^{\frac{1}{2}}[\Phi_{-7/2}+(7/35^{\frac{1}{2}})\Phi_{1/2}]\end{aligned}\right\}\Gamma_6.$$

Φ_m denotes a function with $J=7/2$, $M_J=M$. We obtain for the secular equation in the presence of an [001] directed magnetic field:

$$\begin{array}{c|c|c|c|c|} & \psi_c^{(1)} & \psi_b^{(1)} & \psi_b^{(3)} & \psi_a^{(1)} \\ \hline \psi_c^{(1)} & 8\delta+\frac{7}{6}a-E & \frac{1}{3}(35)^{\frac{1}{2}}a & 0 & 0 \\ \hline \psi_b^{(1)} & \frac{1}{3}(35)^{\frac{1}{2}}a & 5\delta+\frac{11}{6}a-E & 0 & 0 \\ \hline \psi_b^{(3)} & 0 & 0 & 5\delta-\frac{1}{2}a-E & \sqrt{3}a \\ \hline \psi_a^{(1)} & 0 & 0 & \sqrt{3}a & \frac{3}{2}a-E \\ \hline \end{array} = 0. \qquad (12)$$

Here $a=g\mu_BH$ ($g=2$ 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:

$$\left.\begin{aligned}\eta_{\pm 7/2}&=\pm\frac{3}{2}x+\frac{13}{2}\pm\frac{1}{2}\left(\left(3\mp\frac{2}{3}x\right)^2+\frac{140}{9}x^2\right)^{\frac{1}{2}},\\ \eta_{\pm 5/2}&=\pm\frac{1}{2}x+\frac{5}{2}\pm\frac{1}{2}((5\mp 2x)^2+12x^2)^{\frac{1}{2}},\\ \eta_{\pm 3/2}&=\mp\frac{1}{2}x+\frac{5}{2}\pm\frac{1}{2}((5\pm 2x)^2+12x^2)^{\frac{1}{2}},\\ \eta_{\pm 1/2}&=\mp\frac{3}{2}x+\frac{13}{2}\pm\frac{1}{2}\left(\left(3\pm\frac{2}{3}x\right)^2+\frac{140}{9}x^2\right)^{\frac{1}{2}},\end{aligned}\right\} \qquad (13)$$

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* 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.

Table I. Frequencies and intensity factors for transitions in $J=7/2$ case; cubic field. Table is labeled in terms of dimensionless quantities $\eta=E/\delta$ and $x=g\mu_B H/\delta$, where δ is as shown in Fig. 1. The intensity factor is defined by Eq. (7) and is given in this case by $\Theta_x=\frac{1}{4}|(m|J_+|n)|^2(\Delta\eta)^2$ and $\Theta_z=|(m|J_z|n)|^2(\Delta\eta)^2$. The static magnetic field is in the Z direction; this is also the [001] direction.

Transitions	Quantity	0.1	0.3	0.5	0.7	1.0	1.5	$\leftarrow x \rightarrow$ 2.0	3.0	5.0	7.5	10.0	15.0
$7/2 \longleftrightarrow 1/2$	$\Delta\eta$	0.23	0.71	1.22	1.76	2.60	4.05	5.53	8.51	14.51	22.00	29.50	44.50
	Θ_x	0.07	0.59	1.35	2.08	2.93	3.74	4.15	4.51	4.73	4.82	4.86	4.88
$7/2 \longleftrightarrow -7/2$	$\Delta\eta$	3.33	4.13	5.09	6.19	7.98	11.19	14.53	21.36	35.22	52.65	70.11	105.07
	Θ_x	8.10	6.57	5.04	3.78	2.47	1.34	0.82	0.39	0.14	0.09	0.04	0.02
$1/2 \longleftrightarrow -1/2$	$\Delta\eta$	2.73	2.33	2.09	1.99	1.98	2.19	2.53	3.36	5.22	7.65	10.11	15.07
	Θ_x	9.27	9.97	10.49	11.14	12.74	17.28	24.04	43.85	107.71	232.68	407.68	907.61
$-1/2 \longleftrightarrow -7/2$	$\Delta\eta$	0.37	1.09	1.78	2.44	3.40	4.95	6.47	9.49	15.49	23.00	30.50	45.50
	Θ_x	0.09	0.73	1.63	2.46	3.35	4.14	4.49	4.76	4.89	4.93	4.93	4.92
$7/2 \longleftrightarrow 5/2$	$\Delta\eta$	3.17	3.56	3.98	4.40	5.00	5.84	6.53	7.72	9.85	12.40	14.93	19.96
	Θ_x	28.02	31.75	35.13	40.73	48.86	63.20	77.32	105.98	170.79	270.04	390.78	697.32
$5/2 \longleftrightarrow -1/2$	$\Delta\eta$	0.21	0.52	0.66	0.66	0.42	0.41	1.53	4.16	9.88	17.24	24.68	39.62
	Θ_x	0.02	0.14	0.26	0.25	0.08	0.04	0.36	1.04	1.77	2.15	2.33	2.50
$7/2 \longleftrightarrow -3/2$	$\Delta\eta$	7.99	8.08	8.34	8.74	9.58	11.41	13.53	18.16	27.88	40.24	52.68	77.62
	Θ_x	0.10	0.87	1.95	2.72	2.92	2.07	1.28	0.55	0.18	0.07	0.04	0.02
$-1/2 \longleftrightarrow -3/2$	$\Delta\eta$	5.03	5.04	5.02	5.00	5.00	5.16	5.47	6.28	8.15	10.60	13.07	18.04
	Θ_x	58.41	62.23	66.32	69.50	76.14	89.59	105.55	144.42	247.28	419.62	639.47	1220.2
$5/2 \longleftrightarrow 3/2$	$\Delta\eta$	0.10	0.29	0.44	0.55	0.61	0.49	0.18	0.65	2.56	5.03	7.51	12.51
	Θ_x	0.02	0.19	0.47	0.77	2.02	0.67	0.09	1.28	19.61	75.75	169.42	469.24
$3/2 \longleftrightarrow -3/2$	$\Delta\eta$	4.91	4.81	4.80	4.89	5.20	6.05	7.18	9.79	15.47	22.81	30.23	45.16
	Θ_x	17.94	15.90	13.62	11.32	8.25	4.77	2.92	1.36	0.49	0.22	0.12	0.05
$5/2 \longleftrightarrow -5/2$	$\Delta\eta$	5.11	5.41	5.80	6.29	7.20	9.05	11.18	15.79	25.47	37.81	50.23	75.16
	Θ_x	19.43	20.13	19.88	18.72	15.83	10.68	7.08	3.53	1.34	0.60	0.34	0.15
$-3/2 \longleftrightarrow -5/2$	$\Delta\eta$	0.30	0.89	1.44	1.95	2.61	3.49	4.18	5.35	7.44	9.97	12.49	17.49
	Θ_x	0.20	1.82	5.02	9.63	18.41	34.87	51.40	85.33	166.07	298.44	467.63	918.01
$3/2 \longleftrightarrow 1/2$	$\Delta\eta$	2.84	2.56	2.31	2.09	1.79	1.30	0.82	0.14	2.10	4.57	7.06	12.04
	Θ_x	24.52	21.19	18.08	15.21	11.36	6.15	2.47	0.08	16.46	78.19	186.47	543.19
$1/2 \longleftrightarrow -5/2$	$\Delta\eta$	8.05	8.25	8.56	8.94	9.60	10.84	12.18	14.99	20.81	28.22	35.66	50.61
	Θ_x	0.09	0.68	1.44	2.10	2.80	3.35	3.55	3.62	3.43	3.29	3.18	3.07
$3/2 \longleftrightarrow -7/2$	$\Delta\eta$	0.25	0.85	1.56	2.34	3.60	5.84	8.18	12.99	22.81	35.22	47.66	72.61
	Θ_x	0.02	0.12	0.23	0.31	0.35	0.32	0.27	0.17	0.08	0.04	0.02	0.01
$-5/2 \longleftrightarrow -7/2$	$\Delta\eta$	4.96	4.84	4.69	4.51	4.21	3.70	3.18	2.14	0.10	2.43	4.94	9.96
	Θ_x	53.93	49.01	44.13	39.58	33.49	25.04	18.21	8.16	0.02	10.34	42.84	173.77
$7/2 \longleftrightarrow -1/2$	$\Delta\eta$	2.96	3.04	3.32	3.75	4.58	6.24	8.06	11.87	19.72	29.65	39.61	59.57
	Θ_z	35.0	35.0	35.0	35.0	35.0	35.0	35.0	35.0	35.0	35.0	35.0	35.0
$1/2 \longleftrightarrow -7/2$	$\Delta\eta$	3.09	3.41	3.87	4.43	5.39	7.14	9.00	12.85	20.71	30.64	40.61	60.57
	Θ_z	35.0	35.00	35.00	35.00	35.00	35.00	35.0	35.0	35.0	35.0	35.0	35.0
$5/2 \longleftrightarrow -3/2$	$\Delta\eta$	4.81	4.52	4.36	4.34	4.58	5.57	7.00	10.44	18.03	27.84	37.75	57.66
	Θ_z	75.0	75.0	75.0	75.0	75.0	75.0	75.0	75.0	75.0	75.0	75.0	75.0
$-5/2 \longleftrightarrow 3/2$	$\Delta\eta$	5.21	5.70	6.24	6.84	7.81	9.54	11.36	15.13	22.91	32.79	42.72	62.65
	Θ_z	75.0	75.0	75.0	75.0	75.0	75.0	75.0	75.0	75.0	75.0	75.0	75.0

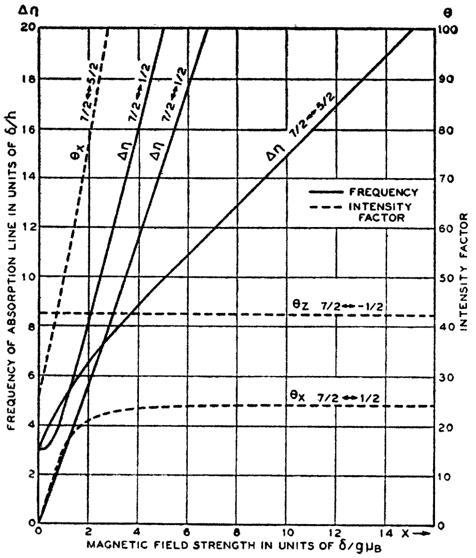

FIG. 3. Frequency and intensity factor for some typical absorption lines resulting from an ^8S state; the intensity factor is proportional to the power absorption and is defined by Eq. (7). *Note added in proof:* Two frequency curves are labeled in the figure as $7/2\longleftrightarrow 1/2$; of these two curves the left hand one is incorrectly labeled and should read $7/2\longleftrightarrow -1/2$.

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

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 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 $\Delta M_J=\pm 1$, in agreement with the usual selection rule. An example of such a transition is $7/2\leftrightarrow 5/2$, for which the values of the frequency and intensity factor are shown in Fig. 3. A number of lines are weak for all x: an example is $3/2\leftrightarrow -7/2$. All of the Z-polarized lines have constant values of the intensity factor, independent of x; an example is the line $7/2\leftrightarrow 1/2$ shown in Fig. 3. The crossing points on the eigenvalue diagram (Fig. 2) correspond to lines of zero frequency.

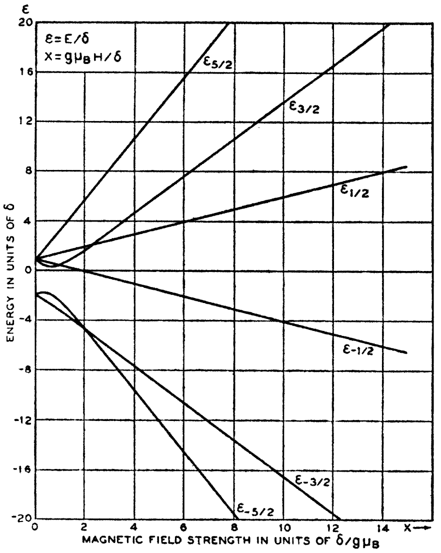

FIG. 4. Eigenvalues of ^6S state as a function of the static magnetic field in the [001] direction.

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

The case of $J=5/2$ is very similar to that of $J=7/2$. 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

$$\left.\begin{aligned}\epsilon_{\pm 1/2}&=1\pm\frac{1}{2}x,\\ \epsilon_{\pm 5/2}&=\pm\frac{x}{2}-\frac{1}{2}\pm 2[x^2\pm x+(3/4)^2]^{\frac{1}{2}},\\ \epsilon_{\pm 3/2}&=\mp\frac{x}{2}-\frac{1}{2}\pm 2[x^2\mp x+(3/4)^2]^{\frac{1}{2}},\end{aligned}\right\}\qquad(14)$$

where, as before, $x=g\mu_BH/\delta$, $\epsilon=E/\delta$ (3δ being

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** 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.

[15] P. Debye, Ann. d. Physik **32**, 85 (1938).

[16] R. de L. Kronig and C. J. Bouwkamp, Physica **6**, 290 (1939).

the over-all splitting in the crystalline electric field alone). In the case under consideration, just as in the 7/2 case, one has $L=0$ so that $g=2$. In Fig. 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. ($KCr(SO_4)_2 \cdot 12H_2O$)

According to Hebb and Purcell the Cr^{+++} ion in this salt is in a $^4F\Gamma_8$ 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 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 system independently.***

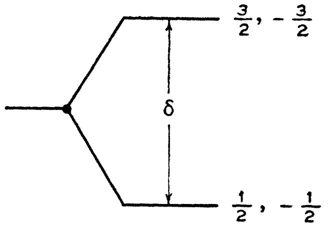

FIG. 5. Energy levels for $KCr(SO_4)_2 \cdot 12\,H_2O$ in presence of axial electrostatic field.

Taking for the crystalline potential only the

TABLE II. Frequencies and intensity factors for transitions in $J=5/2$ case; cubic field. Table is labelled in terms of dimensionless quantities $\epsilon=E/\delta$ and $x=g\mu_BH/\delta$, where δ is the over-all splitting in the electric field alone. The intensity factor is defined by Eq. (7) and is given in this case by $\Theta_x=\frac{1}{4}|(m|J_+|n)|^2(\Delta\epsilon)^2$ and $\Theta_z=|(m|J_z|n)|^2(\Delta\epsilon)^2$. The static magnetic field is in the Z direction; this is also the [001] direction.

Transitions	Quantity	$\leftarrow x \rightarrow$ 0.1	0.3	0.5	0.7	1.0	1.5	2.0	3.0	5.0	7.5	10.0	15.0
$3/2 \longleftrightarrow 1/2$	$\Delta\epsilon$	0.23	0.61	0.88	1.01	1.00	0.71	0.30	0.62	2.57	5.04	7.53	12.52
	Θ_x	0.02	0.25	0.78	1.37	1.67	0.94	0.17	0.77	13.15	50.82	113.40	313.44
$5/2 \longleftrightarrow -1/2$	$\Delta\epsilon$	0.24	0.75	1.29	1.85	2.70	4.15	5.62	8.59	14.56	22.04	29.53	44.52
	Θ_x	0.02	0.10	0.21	0.32	0.46	0.64	0.76	0.92	1.09	1.18	1.23	1.29
$-3/2 \longleftrightarrow -1/2$	$\Delta\epsilon$	3.04	3.15	3.29	3.45	3.70	4.25	4.62	5.59	7.56	10.03	12.53	17.52
	Θ_x	16.00	18.08	20.29	22.66	26.54	35.52	42.24	62.08	113.92	201.32	313.76	613.55
$-5/2 \longleftrightarrow 1/2$	$\Delta\epsilon$	2.97	2.99	3.12	3.39	4.00	5.29	6.70	9.62	15.57	23.04	30.53	45.52
	Θ_x	14.00	11.93	9.72	7.61	5.33	3.56	2.83	2.23	1.85	1.69	1.61	1.54
$5/2 \longleftrightarrow -5/2$	$\Delta\epsilon$	3.11	3.44	3.91	4.54	5.70	7.94	10.33	15.21	25.13	37.58	50.06	75.04
	Θ_x	5.28	5.45	4.89	3.82	2.34	1.10	0.62	0.27	0.10	0.04	0.02	0.01
$5/2 \longleftrightarrow 3/2$	$\Delta\epsilon$	0.37	1.06	1.67	2.16	2.70	3.36	3.92	4.97	6.99	9.49	12.00	17.00
	Θ_x	0.09	0.89	2.60	4.97	8.60	13.93	19.14	30.79	61.02	112.68	179.91	361.10
$3/2 \longleftrightarrow -3/2$	$\Delta\epsilon$	2.91	2.84	2.91	3.14	3.70	4.94	6.33	9.21	15.13	22.58	30.06	45.04
	Θ_x	4.63	3.71	2.71	1.82	0.98	0.43	0.23	0.10	0.04	0.02	0.01	0.00
$-5/2 \longleftrightarrow -3/2$	$\Delta\epsilon$	0.17	0.46	0.67	0.76	0.70	0.36	0.08	1.03	3.01	5.51	8.00	13.00
	Θ_x	0.02	0.17	0.42	0.62	0.58	0.16	0.01	1.34	11.34	37.89	80.07	211.38
$5/2 \longleftrightarrow -3/2$	$\Delta\epsilon$	3.28	3.90	4.58	5.30	6.40	8.31	10.25	14.18	22.11	32.08	42.06	62.04
	Θ_z	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00
$-5/2 \longleftrightarrow 3/2$	$\Delta\epsilon$	2.75	2.37	2.24	2.37	3.00	4.58	6.40	10.25	18.14	28.09	38.07	58.00
	Θ_z	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00

*** Part of this calculation was performed previously for another purpose by L. J. F. Broer, Physica 9, 547 (1942).

TABLE III. Frequencies $\Delta\epsilon$ for transitions in case of $KCr(SO_4)_2\cdot 12H_2O$; H_z Parallel [001].*

Transition	$\leftarrow x \rightarrow$									
	.1	.2	.3	.4	.6	1.0	2.0	5.0	10.0	15.0
$3/2\longleftrightarrow 1/2$	.30	.57	.80	.99	1.29	1.91	3.56	8.70	17.34	25.99
$3/2\longleftrightarrow -1/2$	1.03	1.13	1.31	1.56	2.17	3.52	6.95	17.33	34.65	51.96
$-3/2\longleftrightarrow 3/2$	1.33	1.70	2.11	2.54	3.47	5.42	10.51	26.03	51.98	77.96
$-1/2\longleftrightarrow 1/2$	.73	.55	.50	.57	.88	1.61	3.39	8.63	17.31	25.97
$-3/2\longleftrightarrow 1/2$	1.03	1.13	1.31	1.56	2.17	3.52	6.95	17.33	34.65	51.96
$-3/2\longleftrightarrow -1/2$	.30	.57	.80	.99	1.29	1.91	3.56	8.70	17.34	25.99

* Table is labeled in terms of dimensionless quantities $\epsilon = E/\delta$ and $x = g\mu BH/\delta\sqrt{3}$, where δ is as shown in Fig. 5.

second-order terms, we find

$$V_{\mathrm{trig}} = D(x^2+y^2-2z^2), \tag{15}$$

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

$$\begin{aligned} H &= V_{\mathrm{trig}} + H_{\mathrm{mag}} \\ &= V_{\mathrm{trig}} + g\mu_B(\mathbf{H}\cdot\mathbf{J}). \end{aligned} \tag{16}$$

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

$$\mathbf{H}\cdot\mathbf{J} = \frac{H}{\sqrt{3}}(J_x+J_y+J_z) \tag{17}$$

or

$$H_{\mathrm{mag}} = \alpha(\tfrac{1}{2}(1-i)J_+ + \tfrac{1}{2}(1+i)J_- + J_z), \tag{18}$$

where

$$\alpha = g\mu_B H/3^{\frac{1}{2}}.$$

The level scheme in the absence of H_{mag} is as shown in Fig. 5. Here the levels are labeled by their *weak field* quantum numbers. Introducing now H_{mag}, we get as our secular equation:

$$\begin{array}{c|c|c|c|c|} & \frac{3}{2} & \frac{1}{2} & -\frac{1}{2} & -\frac{3}{2} \\ \hline \frac{3}{2} & \frac{1}{2}+\frac{3}{2}x-\epsilon & \frac{1-i}{2}3^{\frac{1}{2}}x & 0 & 0 \\ \hline \frac{1}{2} & \frac{1+i}{2}3^{\frac{1}{2}}x & -\frac{1}{2}+\frac{1}{2}x-\epsilon & (1-i)x & 0 \\ \hline -\frac{1}{2} & 0 & (1+i)x & -\frac{1}{2}-\frac{1}{2}x-\epsilon & \frac{1}{2}(1-i)3^{\frac{1}{2}}x \\ \hline -\frac{3}{2} & 0 & 0 & \frac{1+i}{2}3^{\frac{1}{2}}x & \frac{1}{2}-\frac{3}{2}x-\epsilon \\ \hline \end{array} = 0, \tag{19}$$

where $\epsilon \equiv E/\delta$, $x \equiv \alpha/\delta$. Expanding gives

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

the roots of which are

$$\left.\begin{aligned} \epsilon(\tfrac{3}{2}) &= \tfrac{1}{2}(1+15x^2+6x(1+4x^2)^{\frac{1}{2}})^{\frac{1}{2}}, \\ \epsilon(\tfrac{1}{2}) &= \tfrac{1}{2}(1+15x^2-6x(1+4x^2)^{\frac{1}{2}})^{\frac{1}{2}}, \\ \epsilon(-\tfrac{1}{2}) &= -\tfrac{1}{2}(1+15x^2-6x(1+4x^2)^{\frac{1}{2}})^{\frac{1}{2}}, \\ \epsilon(-\tfrac{3}{2}) &= -\tfrac{1}{2}(1+15x^2+6x(1+4x^2)^{\frac{1}{2}})^{\frac{1}{2}}, \end{aligned}\right\} \tag{21}$$

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 $\psi(M)$ belonging to $\epsilon(M)$ and also the matrix elements of J_+, J_z. It should be remembered that these are J_z 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 matric 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

$$\begin{aligned}|(M|T|M')|^2=&\tfrac{1}{2}|(M|J_+|M')|^2\\&+\tfrac{1}{2}|(M'|J_+|M)|^2+|(M|J_z|M')|^2\\&+Im(M|J_+|M')(M'|J_+|M)\\&+Re((M|J_+|M')(M|J_z|M')^*\\&+(M'|J_+|M)(M|J_z|M'))\\&+Im((M|J_+|M')(M|J_z|M')^*\\&\qquad+(M'|J_+|M)(M|J_z|M')).\end{aligned}\tag{22}$$

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 Fig. 6; and the associated frequencies are tabulated in Table III.

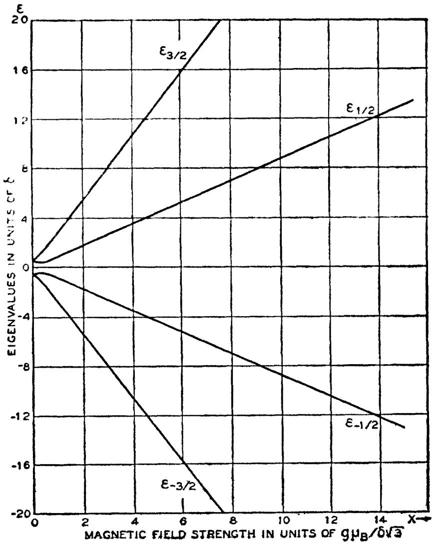

FIG. 6. Eigenvalues for $KCr(SO_4)_2\cdot 12\ H_2O$ as a function of the strength of the static magnetic field in the (001) direction.

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 Cummerow 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[11])

	E	R	$2C_1'$	$2C_1''$	$3C_2'$	$3C_2''$
Γ_1	1	1	1	1	1	1
Γ_2	1	1	1	1	−1	−1
Γ_3	2	2	−1	−1	0	0
Γ_4	2	−2	−2	2	0	0
Γ_5	2	−2	1	−1	0	0

Note—Γ_4 is used to denote two conjugate-complex one-dimensional representations.

Character Table—Rhombic Double Group (after Bethe[9])

	E	R	$2C_1$	$2C_2$	$2C_3$
Γ_1	1	1	1	1	1
Γ_2	1	1	−1	1	−1
Γ_3	1	1	−1	−1	1
Γ_4	1	1	1	−1	−1
Γ_5	2	−2	0	0	0

APPENDIX B

Center of Gravity Sum Rule for Crystalline Fields

Consider an unperturbed system which has a definite angular momentum J. It undergoes a perturbation resulting from 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, except by the amount of the Madelung potential.

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

$$\bar{W}=\frac{1}{2J+1}\sum_i \int \psi_i^* V\psi_i d\tau,$$

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

$$\bar{W}=\frac{1}{2J+1}\sum_M \int \psi_M^* V\psi_M d\tau$$

$$=\frac{1}{2J+1}\int d\tau\, V(\sum_M \psi_M^*\psi_M).$$

Now $\sum_M \psi_M^*\psi_M$ is rotationally invariant, since the ψ_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 see 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 by the Madelung potential 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 identity representation. Therefore, according to the usual group theoretical argument the integral in $\bar{W}$ vanishes, and the required result has been established. A weaker form of this theorem has been given previously by Kynch.[17]

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

$$\psi(M)=[\Phi_{3/2}+a_M\Phi_{1/2}+b_M\Phi_{-1/2}+c_M\Phi_{-3/2}]/[1+|a_M|^2+|b_M|^2+|c_M|^2]^{\frac{1}{2}}$$

where

$$a_M=-\frac{(\frac{1}{2}+\frac{3}{2}x-\epsilon(M))}{\sqrt{3}x}(1+i),$$

$$b_M=-i(3^{\frac{1}{2}}/2)-(1+i)\frac{(-\frac{1}{2}+\frac{1}{2}x-\epsilon(M))}{2x}a_M,$$

$$c_M=-\frac{(1+i)(3^{\frac{1}{2}}/2)xb_M}{(\frac{1}{2}-\frac{3}{2}x-\epsilon(M))}.$$

The matrix elements of J_+ and J_z are now

$$(M'|J_z|M)=\frac{\frac{3}{2}+\frac{1}{2}(a_{M'}^*a_M-b_{M'}^*b_M)-\frac{3}{2}c_{M'}^*c_M}{[(1+|a_M|^2+|b_M|^2+|c_M|^2)\times(1+|a_{M'}|^2+|b_{M'}|^2+|c_{M'}|^2]^{\frac{1}{2}}}$$

$$(M'|J_+|M)=\frac{3^{\frac{1}{2}}a_M+2a_{M'}^*b_M+3^{\frac{1}{2}}b_{M'}^*c_M}{[(1+|a_M|^2+|b_M|^2+|c_M|^2)\times(1+|a_{M'}|^2+|b_{M'}|^2+|c_{M'}|^2)]^{\frac{1}{2}}}.$$

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[17] G. J. Kynch, Trans. Faraday Soc. **33**, 1402 (1937).