may now be satisfied by (3.2) by choosing $b=S_A/\beta$ and

$$c=\frac{S_B}{\beta}\left[1-\left(\frac{3}{4y}\right)^2\right]; \tag{3.4}$$

then

$$S_B^x=S_B[1-(\tfrac{3}{4}y)^2]^{\frac{1}{2}}, \quad (y\geqslant\tfrac{3}{4}), \tag{3.5}$$

in agreement with the Yafet-Kittel result.

If, with the value of β given by (3.3), the eigenvalue (3.1) were the lowest of all the eigenvalues of (2.1), (for all $\mathbf{k}$), then C_1 would have been shown to be the ground state. This is not the case, for any y, giving consistency with the small deviations result.[6,10] For distorted spinels,[12] however, the same procedure yields a proof of the fact that the appropriate Yafet-Kittel configuration is the ground state whenever it is locally stable.[17]

[17] *Note added in proof*. This result, as well as that of Example 2 and the result discussed in reference 9, is easily generalized: In any lattice, local stability of a configuration of *coplanar* spins implies that the configuration is the ground state. However, we have found that metastable configurations of noncoplanar spins exist for some interactions in spinels.

SUMMARY AND DISCUSSION

We have shown that a straightforward generalization of the method of Luttinger and Tisza[1] allows the sloution of the ground spin-state problem in some new and physically interesting cases. The extended method has been applied elsewhere[12] to spinels for which neither the Néel nor the Yafet-Kittel configurations is the ground state. Using the device of "forced degeneracy" discussed in Example 3, it has been shown[12] that the ground state for an interesting class of such spinels is a new type of spiral which is ferrimagnetic.

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Pulsed Field Measurements of Large Zero-Field Splittings: V^{3+} in Al_2O_3

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Use of pulsed magnetic fields for determining large zero-field splittings of paramagnetic ions is considered. Measurements of zero-field splittings of over 50 cm^{-1} are feasible; a numerical example for $S=1$ is discussed in order to indicate the present range and limitations of the method. The method is applied to measurements of the zero-field splitting of V^{3+} in Al_2O_3 at 4.2°K and 1.5°K. Assuming $g_{||}=1.92$, $D=7.85$ cm^{-1} was determined from experiments with 4 mm and 8 mm wavelength radiation and pulsed magnetic fields of the order of 100 kilogauss. The magnitude and sign of D are in good agreement with earlier estimates from optical and microwave measurements.

INTRODUCTION

Energy level separations of paramagnetic ions of the order of 10 cm^{-1} cannot in general be readily observed with conventional paramagnetic resonance techniques. The present technology of millimeter wave generation and detection permits only a limited coverage of the frequency range of 10 cm^{-1} and above.[1] If, however, a very large external magnetic field is applied along preferred directions it is possible in many cases to "tune" one or more of the Zeeman levels of higher states so that transitions can be observed at a convenient frequency ν which is much less than the zero-field splitting.[2] Such large magnetic fields can easily be obtained for short times. In this note we indicate some of the possibilities as well as the limitations of pulsed magnetic field techniques as applied to such measurements. In particular we shall discuss the zero-field splitting of V^{3+} in corundum which we have measured using this technique.

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† Operated with support from the U. S. Army, Navy, and Air Force.
[1] G. S. Heller (private communication).
[2] S. Foner, J. phys. radium **20**, 336 (1959).

PARAMAGNETIC IONS WITH LARGE ZERO-FIELD SPLITTINGS

A large number of paramagnetic ions show Stark splittings between 1 and 50 cm^{-1}. The ions fall into three classes.

(a) Ions with an orbital singlet as the lowest Stark level, and with an odd number of electrons. These ions have long relaxation times in octahedral symmetries but usually show small zero-field splittings. In the few cases where the zero-field splitting is larger than 1 cm^{-1}, the separation among the various Kramers doublets can be inferred from a careful study of the angular dependence of the resonance spectra. This method is, however, not very accurate for $D\gg h\nu$. Zeeman levels of different Kramers doublets can be brought together by the

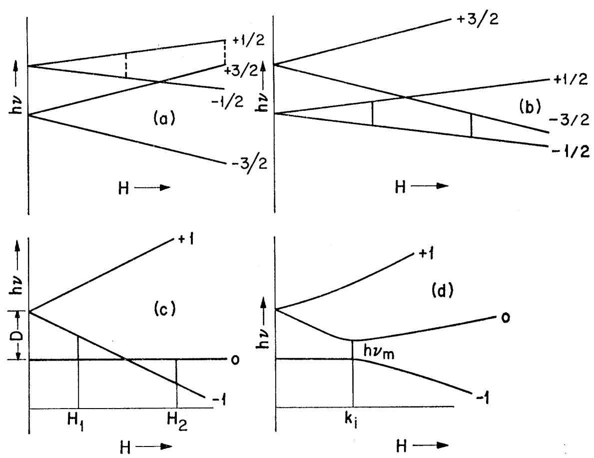

FIG. 1. Energy level diagrams illustrating possible transitions with pulsed fields when $|D|kT \gg 1$ and $E=0$. The dashed lines indicate possible transitions when the spin-lattice relaxation time, T_1, is sufficiently long, and the solid lines indicate expected transitions for $T_1^{-1} > \nu$. The energy levels are labelled according to their high field limiting M_s values. (a) $S=\frac{3}{2}$, $D<0$ and H parallel to the axis field direction. (b) Same as (a), but $D>0$. (c) Same as (a), but $S=1$, $D>0$. (d) Same as (c), but H not along the axial field direction. The minimum $|\Delta M_z|=1$ transition, $h\nu_m$, and the corresponding field $k_i = g\beta H_0/D$, are indicated.

application of a large magnetic field. Transitions among these doublets can then be observed if not forbidden by selection rules. Examples for $S=\frac{3}{2}$ and $D<0$ or $D>0$ are shown in Figs. 1(a) and 1(b).

For ions with an even number of electrons, the spin levels are usually split into a number of singlets in crystal fields of low symmetry. In this case high magnetic fields may also be used to great advantage.

(b) Ions of the iron group with orbitally degenerate levels as the lowest Stark level. These ions, which have a partially quenched orbital angular momentum, are strongly coupled with the lattice and have, therefore, short relaxation times. For ions with an odd number of electrons, resonance can only be observed for the lowest Kramers doublet at very low temperatures. For ions with an even number of electrons, the individual spin levels are usually separated in energy by more than $h\nu$ or kT and no transitions among these levels can be observed except possibly with high magnetic fields. Examples are V^{3+} and Fe^{2+}, or Cr^{2+} and Ni^{2+} in octahedral symmetry. Similar considerations prevail for the iron group elements in tetrahedral symmetry.

(c) Rare earth and actinide elements. For these ions pulsed magnetic field techniques will find many interesting applications. In these groups the crystal field is relatively weak for most symmetries. Many ions have Stark level separations less than 50 cm^{-1}. Examples of such ions are Ce^{3+}, Dy^{3+}, Tb^{3+}, and Yb^{3+}. The separations of these Stark levels has been inferred from fluorescent and optical absorption spectra in concentrated crystals. Since the g factors of the lowest levels are not strongly dependent on the separation of the other levels, it is difficult to estimate these separations from paramagnetic resonance in dilute crystals.

Pulsed fields of 750 kilogauss[3] have been achieved by discharge of a 2000-μf, 3000-v capacitor bank through suitably designed beryllium-copper solenoids. In this case the usable working volume was just sufficient to accommodate a 4-mm waveguide for room temperature measurements. Pulsed fields of 500 kilogauss can readily be produced over a volume sufficient for 4-mm resonance measurements at 4.2°K with a Dewar flask inserted into the working volume. Thus, pulsed field techniques can be used to measure zero-field splittings corresponding to wavelengths of 100 to 200 μ. Measurements at wavelengths of less than about 10 to 20 μ are readily made with conventional infrared techniques. The gap between 20 and 200 μ will also require infrared techniques since fields of 10^7 gauss are not readily produced. Of course, a large g value would effectively extend the present range of magnetic fields.

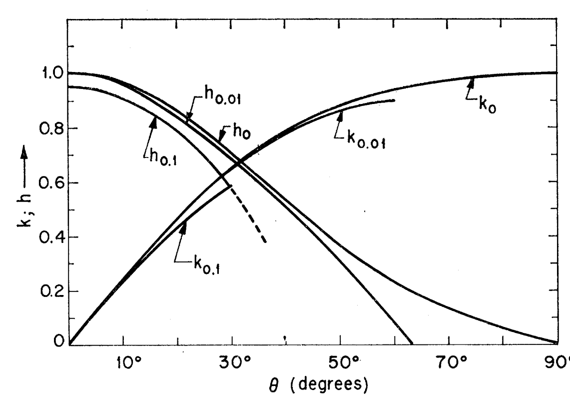

FIG. 2. Normalized plots of $h_i = h\nu_m/D$ versus angle, θ, between H and c axis, where ν_m is the minimum frequency of an observed $|\Delta M_z|=1$ transition, and normalized plots of $k_i = g\beta H_0/D$ versus angle where H_0 is the field corresponding to ν_m [see also Fig. 1(d)]. The subscripts of h_i and k_i correspond to values of $(E/D)^2 = 0$, 0.01, and 0.1, respectively.

PARAMAGNETIC RESONANCE OF IONS WITH $S=1$

As a particular example we shall consider ions with a ground state which can be described by a spin Hamiltonian with $S=1$. This occurs for example for Fe^{2+}, V^{3+}, and Ni^{2+} in octahedral and axial fields. Fe^{2+} in fluosilicate and in the ammonium sulfate shows splittings of the order of 10 cm^{-1}. V^{3+} in alums and in corundum also shows splittings of the same order of magnitude. Another class of systems, exchange coupled pairs of paramagnetic ions with relatively small exchange constants, is currently being investigated.

The energy levels are given by solutions W_i of

$$W^3 - 2DW^2 + [D^2 - (g\beta H)^2]W + (g\beta H)^2 D \sin^2\theta = 0, \quad (1)$$

where H is the applied field and θ is the angle between H and the principal axis. The solutions for $\theta = 0$ are

[3] S. Foner and H. H. Kolm, Rev. Sci. Instr. **27**, 547 (1956); **28**, 799 (1957).

shown in Fig. 1(c). Approximate solutions of interest can be obtained for small θ when $(g\beta H)^2 \gg D^2$ or $(g\beta H)^2 \ll D^2$, or for $(g\beta H)^2 \simeq D^2$. For small θ, transitions from the $M_z=0$ to $M_z=-1$ levels are given by

$$h\nu = D - g\beta H + \frac{\sin^2\theta}{2}\left[\frac{D^2 g\beta H + 3(g\beta H)^2 D}{D^2-(g\beta H)^2}\right] + O(\sin^4\theta) \quad (2)$$

for $(g\beta H)^2 \gg D^2$ or $(g\beta H)^2 \ll D^2$, and

$$h\nu = D\left[\pm\epsilon + \epsilon^2 \pm \frac{\sin^2\theta}{\epsilon}\right] + \cdots, \quad (3)$$

when it is assumed that $D \approx g\beta H$ and $\sin^2\theta \ll [1-(g\beta H/D)]^2 \equiv \epsilon^2$.

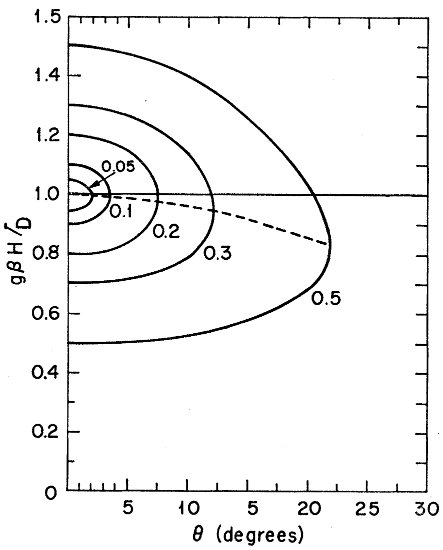

FIG. 3. Normalized values of $g\beta H/D$ versus angle for the case of $(E/D)^2=0$, and $h\nu/D=0.05$, 0.1, 0.2, 0.3, and 0.5. The resonance values $g\beta H/D$ below "cross over" and above "cross over" are plotted. The average between these two resonances, shown by the dashed curve for $h\nu/D=0.5$ cannot be distinguished from that for small values of $h\nu/D$ on the present scale.

When $h\nu \ll D$, two problems arise with high field resonance observations of the $|\Delta M_z|=1$ transitions. First, a minimum value of $h\nu_m$ is required when $\theta>0$ [see Fig. 1(d)], and second, estimates of the error in determining D require that θ be determined. In order to treat a specific case, interactions between the paramagnetic ions and nuclear magnetic moments were neglected, and the numerical solutions of Eq. (1) have been obtained as a function of θ. The values of $h\nu_m$ versus θ, plotted in Fig. 2 on a normalized scale, indicate the range of θ allowed for a given value of $h\nu/D$. The resonance fields before "crossover," H_1, and after "crossover," H_2, for a fixed $h\nu_1$, permit evaluation of θ and D if g is known; otherwise an additional experiment at a second frequency ν_2 is required to determine g. Normalized values of H_1 and H_2 versus θ are shown in Figs.

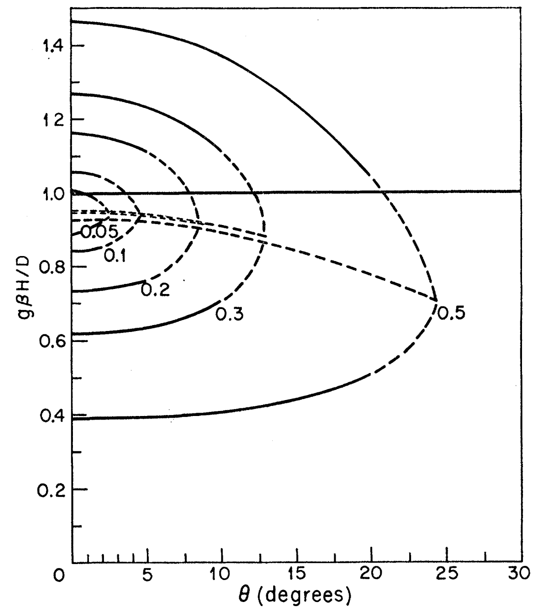

FIG. 4. Normalized values of $g\beta H/D$ versus angle similar to those in Fig. 3, but for $(E/D)^2=0.1$. In this case the averages for different values of $h\nu/D$ are distinguishable.

3 and 4 for various values of $h\nu/D$ when $g=2$. These are also compared with the approximate solution $D=[H_1+\Delta(H_1-H_2)/2]g\beta$ shown by the dashed curves, and the horizontal line $g\beta H/D=1$. The approximation is accurate to one percent when $\theta \leq 2$ degrees. Finally, the addition of a small rhombic term to the spin Hamiltonian is considered when H is applied in the plane at 45° to the x and y direction. The change in Eq. (1) is that a term E^2 is added to the coefficient of W. The numerical results are compared in Figs. 2 and 4 for $(E/D)^2=0.1$ and $(E/D)^2=0.01$. Figure 3 approximates closely the results for the case $(E/D)^2=0.01$. As indicated in Fig. 4, some care in evaluating D is necessary; a shift of the cross-over point may be caused by misalignment or an added E term. Assuming $g=2.0$ and $\omega/\gamma=25$ kilogauss (4-mm radiation), it follows from Fig. 2 that for $\theta<2°$, $h\nu/D>0.05$ can be observed with an applied field of about 500 kilogauss. Larger values of g or ω, or more accurate orientation of H would permit even larger values of D to be measured by this technique.

PARAMAGNETIC RESONANCE SPECTRUM OF V^{3+} IN Al_2O_3

The energy level scheme of V^{3+} in a cubic and trigonal field shows that the lowest cubic triplet, Γ_4, is split by the trigonal field into a doublet and a lower lying singlet with a separation δ of the order of 1000 cm^{-1}. Spin-orbit coupling and the trigonal field remove the threefold spin degeneracy of the orbital singlet and split this into a lower lying singlet ($M_z=0$) and higher lying doublet ($M_z=\pm1$). For the relatively small λ/δ of this case, this separation is given by $\alpha'^2\lambda^2/\delta-3\rho/2$ to first order. The first term is the second order contribution of the spin-orbit coupling, where α' is a constant, λ is the spin-orbit coupling constant in the crystal, and the second term $3\rho/2$ is the contribution from spin-spin interaction. The magnitude of ρ is known neither for gaseous ions nor for ions in crystals. It is estimated to be probably a fraction of a wave number.[4] The separation between the doublet and the singlet has been estimated from optical spectra to be (8 ± 1) cm^{-1}.[5,6] Zverev and Prokhorov[7] have measured the paramagnetic resonance spectrum of the higher lying doublet. Eight hyperfine lines, each 20 gauss wide and spaced 108 gauss apart, were observed. From the intensity variation of this spectrum with temperature they estimate this splitting to be about 10 cm^{-1}. No resonance could be seen below 2°K.

We have observed the direct transition from the $M_z=0$ to the $M_z=-1$ level at 4.2°K with 36 and 71 kMc/sec radiation. From the pulsed field measurements, the crossover of the $M_z=0$ and $M_z=-1$ transition is calculated to occur at 88 kilogauss within an accuracy of $\pm5\%$. Reference to Fig. 3 shows that, for the small values of $h\nu/D$ employed, errors due to misalignment were less than 2%. The measured value[7] of $g_{\parallel}=1.92$ leads to a zero-field splitting of 7.85 ± 0.4 cm^{-1} which is in good agreement with the optical data.[8] A line width of approximately 350 gauss was observed at high fields but no hyperfine structure could be resolved. Greater resolution has been limited by bandpass of the detectors and amplifiers used for the pulsed observations. No further resolution was noted for $T=1.5$°K although the intensity of the $|\Delta M_z|=1$ transition increased as expected for $D>0$.

Resolution of the hyperfine structure was limited for two reasons. The pulsed field period could not easily be increased, so that even when the resonance occurred at the field peak, a time interval of 20 μsec was required to sweep through the resonance. Sufficient gain was obtained with an amplifier of 350 kc/sec bandwidth, which limited resolution of the predicted lines. Furthermore, each hyperfine line was expected to be broader than the low field $|\Delta M_z|=2$ observation because $\partial\nu/\partial H$ was less for the $|\Delta M_z|=1$ transition. Additional broadening would result from the curvature of the energy levels even if other interactions were negligible, if θ were greater than zero.

We finally should like to remark that a determination of D, $g_\perp$ and δ would determine ρ as well as $\alpha'\lambda$ in the solid. These variables occur in the expressions for $g_\perp$, $g_\parallel$, and D, i.e.[9]

$$g_\perp \sim 2-2\alpha'^2\lambda^2/\delta^2,$$

$$g_\parallel \sim 2-(\alpha+2)\alpha'^2\lambda^2/\delta^2,$$

$$D\sim -\frac{3\rho}{2}+\frac{\alpha'^2\lambda^2}{\delta}\sim -\frac{3\rho}{2}+(2-g_\perp)\delta/2.$$

Runciman and Pryce[6] indicate that $\delta\sim1200$ cm^{-1}. We have looked for an absorption spectrum in this region but have not found any definite absorption line.[5] Using their values of δ and the value of D of 7.5 to 8 cm^{-1} we find that $g_\parallel\sim1.98$ cm^{-1}, which seems to be inconsistent with the measured value[7] of $g_\parallel$. However, there is some indication of weak absorption in the region of $810\rightarrow850$ cm^{-1}. Assuming $\delta=830$ cm^{-1} and $\alpha=1.5$, we find $g_\parallel\sim1.96$ in slightly better agreement with the measured $g_\parallel$ value. It seems, therefore, of great interest to determine $g_\perp$ with great accuracy.

ACKNOWLEDGMENTS

We are grateful to Mrs. Margaret G. Durgin for computing the normalized curves discussed in the text and to Mrs. Jane S. Coe for assistance with calculations.

[4] M. H. L. Pryce, Phys. Rev. **80**, 1032 (1950). Pryce infers the magnitude ρ from the deviation from the interval rule. This procedure is very suspect since these deviations can easily be explained as partial breakdown of Russel-Saunders coupling. It seems, therefore, that with the exception of helium, there are no reliable estimates of the magnitude of this coupling.

[5] W. Low (unpublished results).

[6] M. H. L. Pryce and W. A. Runciman, Discussions Faraday Soc. **26**, 35 (1958).

[7] K. M. Zverev and A. M. Prokhorov, J. Exptl. Theoret. Phys. (U.S.S.R.) **34**, 1023 (1958) [translation: Soviet Phys.-JETP **34(7)**, 707 (1959)].

[8] The value of 7.85 cm^{-1} measures the separation of the $M_z=0$ to $M_z=-1$ transition. The spin Hamiltonian probably contains a term $E(S_x^2-S_y^2)$ which would split the doublet by $2E$, and which would agree with the observations of a $|\Delta M_z|=2$ transition between the doublet. From the results of Zverev and Prokhorov[7] we infer that E must be less than 0.3 cm^{-1}.

[9] A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) **A206**, 173 (1957).