

2900-116-R

Memorandum of Project MICHIGAN

**SPIN RESONANCE of  $V^{2+}$ ,  $V^{3+}$ ,  $V^{4+}$  in  $\alpha\text{-Al}_2\text{O}_3$**

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# WILLOW RUN LABORATORIES TECHNICAL MEMORANDUM

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Robert L. Hess  
Technical Director  
Project MICHIGAN

ABSTRACT

Divalent vanadium has properties similar to those of trivalent chromium in sapphire, which has wide application in masers. The electron-spin resonance absorption properties of vanadium sapphire are reported here. It is shown that vanadium normally is predominantly trivalent, with a small amount being in the tetravalent state. By x- or gamma-irradiation, vanadium is converted to the divalent state. The hyperfine-structure component separation for  $V^{2+}$ ,  $V^{3+}$ , and  $V^{4+}$  are about 88, 110, and 140 gauss, respectively. Because of its readily recognizable spin-resonance signature due to its nuclear spin, and because of the ease of producing different oxidation states, it is suggested that vanadium may be a suitable probe with which to study ionization effects in certain solids.

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INTRODUCTION<sup>1</sup>

The purpose of this memorandum is to present some of the spin-resonance properties of various oxidation states of vanadium which were reported earlier (Ref. 1 and 2) and to complement the optical measurements of vanadium sapphire reported by Low (Ref. 3) and by Pryce and Runciman (Ref. 4). Experiments were designed to provide further information concerning the nature of impurities in corundum in various oxidation states. The need for this further information became apparent following extensive preliminary investigation of maser action in ruby (Ref. 5).

The initial measurements on the spin-resonance properties of ruby were reported by Manenkov and Prokhorov (Ref. 6), by Zaripov and Schamonin (Ref. 7), and by Geusic (Ref. 8), and more detailed studies have been made by Schulz-DuBois (Ref. 9). The temperature dependence of the zero-field splitting was made by Cross and Terhune (Ref. 10). But these

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<sup>1</sup>It is a pleasure to acknowledge the technical assistance of R. Ager and J. Baker, who carried out many of the measurements during the progress of the present investigations.

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measurements merely indicate that some, if not all, of the chromium in corundum is in the form of  $\text{Cr}^{3+}$  and that the crystalline electric field about this ion has axial symmetry; these measurements do not reveal to what extent the chromium is present in other oxidation states, and, furthermore, do not show the degree of pairing and clustering.

An attempt to obtain this information directly by means of spin-resonance measurements has met with difficulties because chromium does not have an easily recognizable signature. Natural chromium consists largely of the isotope of masses 50, 52, 54, but only 9.5% of the odd isotope Cr-53. Rubies containing Cr-53 can be prepared, but the hyperfine structure (hfs) is comparable to the line width; furthermore, nothing is known about the effect of the oxidation state upon the hfs. Consequently, it appeared that a better approach would be to bracket the properties of chromium in corundum by substituting other paramagnetic ions in the lattice. The suitable candidates with well-recognizable signatures are vanadium (V-51,  $I = 7/2$ , 99.75%) and manganese (Mn-55,  $I = 5/2$ , 100%), flanking chromium to the left and right, respectively, in the periodic table. Molybdenum consisting of Mo-95 ( $I = 5/2$ , 15.7%) and Mo-97 ( $I = 5/2$ , 9.5%) offers another possibility. This element occurs directly beneath chromium in the periodic table, and spin-resonance studies in the paramagnetic salts have shown that it behaves somewhat like  $\text{Cr}^{3+}$  (Ref. 11). When vanadium sapphire is grown from a mixture of  $\text{Al}_2\text{O}_3$  and  $\text{V}_2\text{O}_5$  powder, spin-resonance measurements show that vanadium is predominantly trivalent with a small concentration of  $\text{V}^{4+}$ . If this sample is subjected to ionizing radiation, some of the vanadium is converted to  $\text{V}^{++}$ . Also, an interesting result is the monotonic increase of the hfs coupling constant with increasing degree of ionization. There is a similar effect in atomic hfs, but the resemblance appears to be only superficial (Ref. 12 and 13).

Recently, J. Wertz and his collaborators (Ref. 14) have made a systematic study of the spin-resonance properties of various iron-group elements in MgO. It should be noted, however, that  $\alpha\text{-Al}_2\text{O}_3$  has an advantage in that the various oxidation states of vanadium can be distinguished unambiguously. The reason for this is that the spin of the states  $\text{V}^{4+}$ ,  $\text{V}^{3+}$ , and  $\text{V}^{2+}$  are  $1/2$ ,  $1$ , and  $3/2$ , respectively; and in a crystalline field of trigonal symmetry, each spin state can be distinguished from the others by the number and the angular dependence of the fine-structure groups. Since the crystalline field in MgO is cubic, no fine-structure splitting is produced; thus each of the three valence states is expected to give a single group of 8 isotropic, or almost isotropic, hfs lines. The three vanadium oxidation states can then be distinguished only by the differences, if any, of the hfs coupling constant.

## EXPERIMENTAL METHODS

Measurements were made with X- and K-band magnetic resonance spectrometers. The latter was used for  $V^{++}$  measurements in order to avoid some of the complications arising at X-band frequencies. Most of the measurements, however, were carried out at 9400 mc/sec. The X-band cavity was made of coated ceramic so that 5-kc/sec magnetic-field modulation could be used (Ref. 15).

The vanadium sapphire was irradiated either in the Co-60 gamma-ray source or by means of 50-kv x-rays. For x-ray irradiation at liquid-nitrogen temperature, a styrofoam boat containing liquid nitrogen and the sample was placed adjacent to the exit port of the x-ray machine. With this arrangement it was possible to transfer the sample into the magnetic-resonance spectrometer without any appreciable warm-up.

The measurements of  $T_1$  of  $V^{2+}$  at liquid-helium temperature were made by comparing saturation of this resonance to that of trace impurities of  $Cr^{3+}$ . The  $T_1$  of  $Cr^{3+}$ , according to our earlier measurements, is known to be about 50 msec at 4.2°K.

## EXPERIMENTAL RESULTS

3.1.  $V^{3+}$ 

The spin resonance of  $V^{3+}$  was observed in  $\alpha$ - $Al_2O_3$  grown from a powder mixture of  $Al_2O_3$  and 0.1%  $V_2O_5$  prepared by The Linde Company. The results presented here are essentially the same as those of Zverev and Prokhorov (Ref. 16), but some points should be noted. These workers reported following the spectrum up to an angle of about 60° between the c-axis and the magnetic field. Our measurements were made to 80°. For larger angles the spectrum fell beyond the magnetic-field range of the Varian 12-in. magnet with 5 1/4-in. gap. Figure 1 shows the spectra for 0°, for which the hfs components, about 20 gauss wide, are 110 gauss apart, giving  $A = 1.02 \times 10^{-4} \text{ cm}^{-1}$ . As the angle is increased, the center of the spectrum shifts to higher fields and the separation between the components increases. As expected, the signal showed no sign of saturation up to power of 50 mw. No signal was observed at 77°K and 300°K. It was found that maximum absorption is obtained when the sample was placed in the cavity so that the rf field is parallel to the static magnetic field. This indicates that the transition under study is one for which  $\Delta M = 2$ .

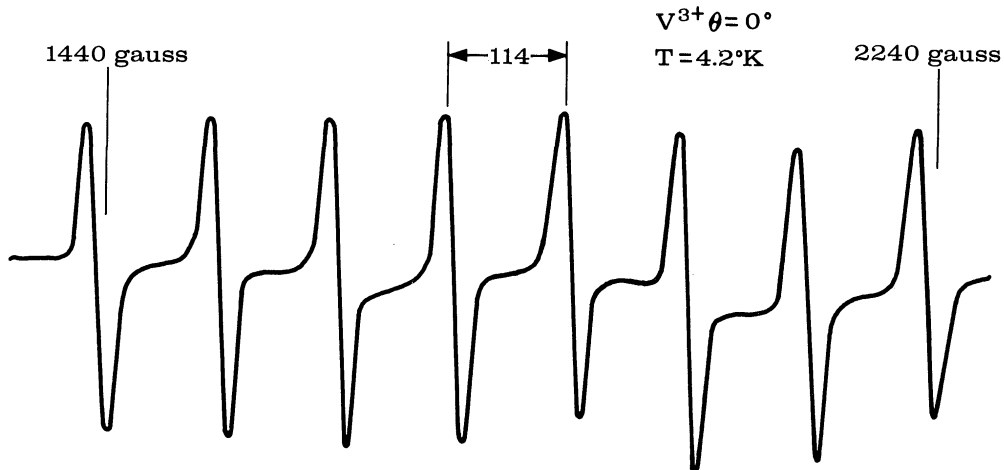


FIG. 1. SPECTRUM OF  $V^{3+}$  IN  $\alpha\text{-Al}_2\text{O}_3$  AT  $4.2^\circ\text{K}$  FOR  $\theta = 0^\circ$

The spin-Hamiltonian applicable to  $V^{3+}$  is given by

$$\mathcal{H} = g_{\parallel} \beta H_z S_z + g_{\perp} (H_x S_x + H_y S_y) + D S_z^2 + E(S_x^2 - S_y^2) + A I_z S_z + B(I_x S_x + I_y S_y). \quad (1)$$

The rhombic-field coefficient  $E$  causes the mixing of  $S_z = \pm 1$  states, resulting in the observed transitions. Since these levels are about  $10 \text{ cm}^{-1}$  above the  $S_z = 0$  level, the effective Hamiltonian can be written as

$$\mathcal{H} = g_{\parallel} \beta H_z S_z + A S_z I_z, \quad (2)$$

obtained by deleting from Eq. (1) those terms that give only off-diagonal elements and also by omitting the axial field term  $D S_z^2$ , which is the same for both  $S_z = \pm 1$ . From Eq. (2) it follows immediately that

$$h\nu = g_{\parallel} \beta H \cos \theta + 2 A m,$$

so that the position of the  $m$ -th hfs component is given by

$$H_m = \left( \frac{h\nu}{2} + A m \right) / (g_{\parallel} \beta \cos \theta). \quad (3)$$

The center of the spectrum then should vary as  $(\cos \theta)^{-1}$ , as shown in Fig. 2. A more detailed calculation (Appendix A) gives

$$h\nu = (g_{\parallel} \beta H \cos \theta + A m) \left\{ 2 - \frac{g_{\perp}^2 \beta^2 H^2 \sin^2 \theta + B^2 [I(I+1) - m^2]}{D^2} \right\}$$

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$$\left. + \frac{E^2}{(g_{\parallel} \beta H \cos \theta + Am)^2} \right\} + \frac{g_{\perp}^2 \beta H E \sin^2 \theta}{g_{\parallel} D \cos \theta} - \frac{B^2 m}{D} \left( 1 - \frac{E^2}{4g_{\parallel}^2 \beta^2 H^2 \cos^2 \theta} \right).$$

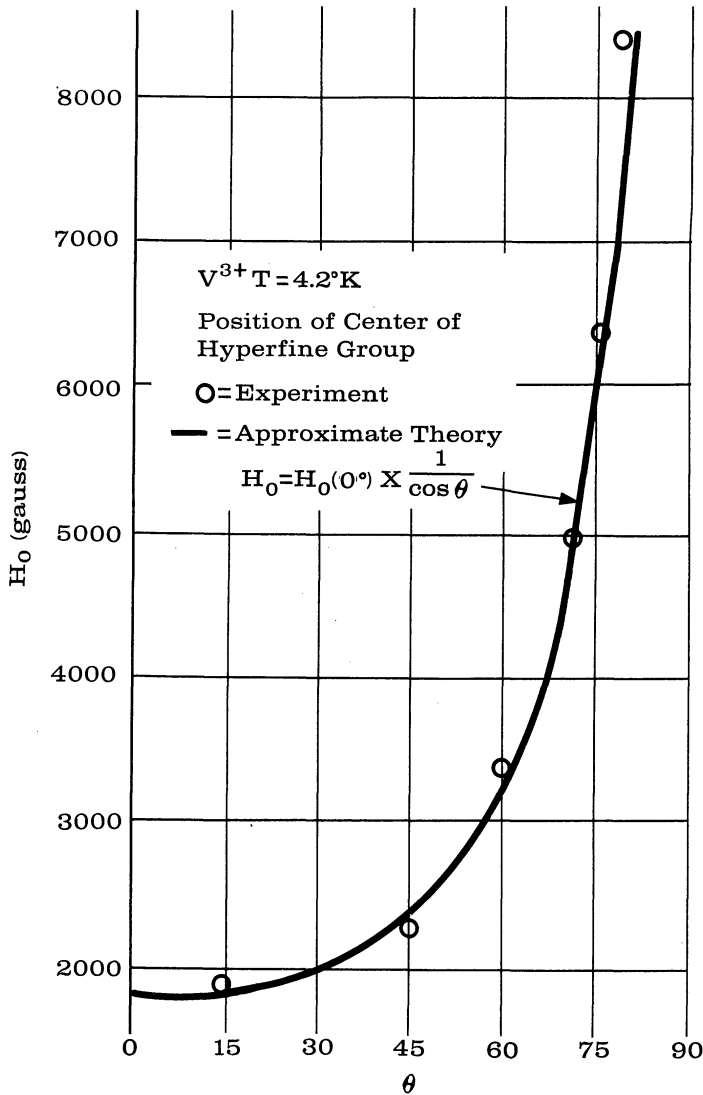


FIG. 2. ANGULAR DEPENDENCE OF POSITION OF CENTER OF HFS FOR  $V^{3+}$  AT  $4.2^{\circ}K$

Another characteristic seen from Fig. 1 is the equal-spacing hfs components. This is in contrast to the appreciable deviation from equal spacing for the  $V^{2+}$  hfs. The reason for the equal spacing of the  $V^{3+}$  hfs lines stems from the fact that the levels  $S_z = \pm 1$  are not connected to each other by the term  $B(I S_x + I S_y)$ . This term does connect the  $S_z = \pm 1$  levels with  $S_z = 0$ , but the latter is about  $10 \text{ cm}^{-1}$  away.

### 3.2. $V^{4+}$

In examining the spin resonance of our crystals at  $300^{\circ}K$ , a group of lines were noted in the region of  $g \cong 2$ . Closer study revealed that there are 8 such lines separated by 140 gauss and that the center of the group remained in the same position as the angle between the c-axis and the static magnetic field was varied. At  $\theta = 90^{\circ}$ , a fairly clean spectrum is obtained, as shown in Fig. 3. The strong line is due to a trace impurity of iron, which is usually found in sapphire. The spectrum at  $\theta = 0^{\circ}$  is complicated by the presence of a trace of  $Cr^{3+}$ .

The spectrum of 8 lines is found in materials as received. The absorption strength is not increased by x-irradiation. The concentration was estimated to be about  $10^{16}/\text{cm}^3$ . Observations suggest that both the g-value and the hfs constant are isotropic, having the values



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$$g_{\parallel} = g_{\perp} \cong 1.97 \text{ and } A = B = 1.32 \times 10^{-4} \text{ cm}^{-1}.$$

The fact that only one isotropic group of 8 lines is detected suggests that the spectrum is due to tetravalent vanadium. Furthermore, this assignment is consistent with the suggestion by McConnell, Porterfield, and Robertson (Ref. 17) that the hfs constant  $A$  for  $V^{4+}$  is greater than that of  $V^{2+}$ .

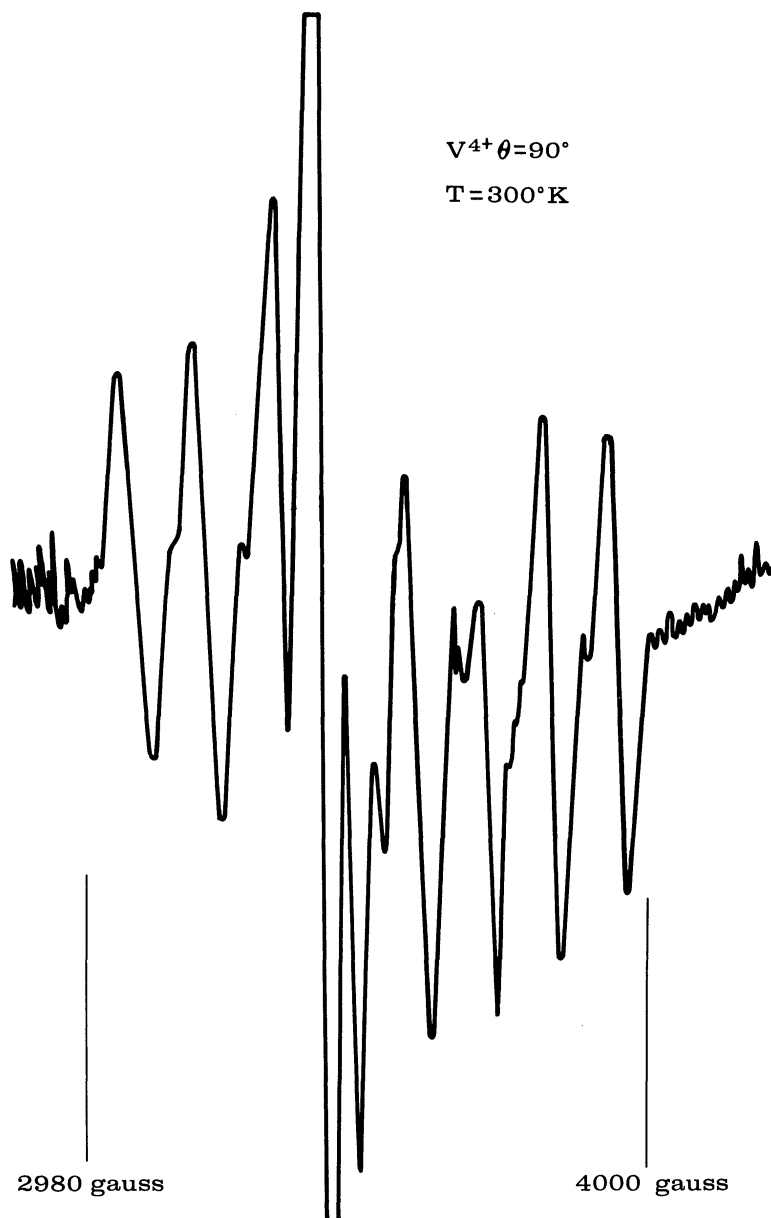


FIG. 3. SPECTRUM OF  $V^{4+}$  IN  $\alpha\text{-Al}_2\text{O}_3$  AT ROOM TEMPERATURE FOR  $\theta = 90^\circ$

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3.3.  $V^{2+}$ 

The  $V^{2+}$  spectrum was the first of vanadium sapphire detected in our laboratory. Brief comments have been made on two earlier occasions (Ref. 1 and 11). Upon gamma- or x-irradiation at room temperature, a spectrum consisting of three groups of 8 lines is produced. The presence of three groups shows that the electron spin of the paramagnetic center is  $3/2$ . Consequently, the spectrum is due to  $V^{2+}$ , which is isoelectronic with  $Cr^{3+}$ . The spectrum was examined at both X- and K-band frequencies. Figures 4 and 5 show the typical spectra obtained at X-band frequencies for  $\theta = 0^\circ$ . The spectrum is complex near the magnetic field of about 3300 gauss (Fig. 4) because the levels  $S_z = 1/2$  and  $3/2$  cross each other and the states become scrambled through the hyperfine interaction. At higher fields, the two levels become well separated so that the admixing decreases, resulting in a simple spectrum as shown in Fig. 5.

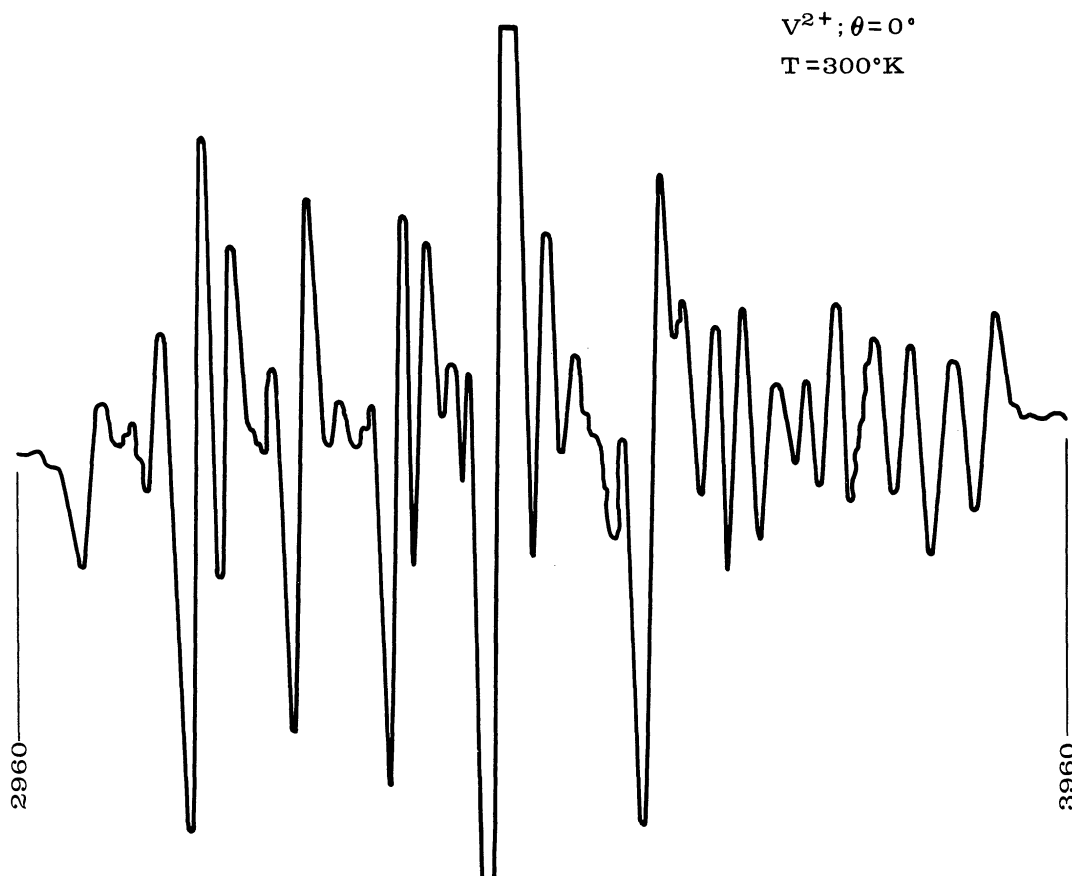


FIG. 4. SPECTRUM FOR  $V^{2+}$  IN  $\alpha\text{-Al}_2\text{O}_3$  AT  $300^\circ\text{K}$  FOR  $\theta = 0^\circ$  NEAR  $S_z = 1/2$  AND  $3/2$  CROSSOVER

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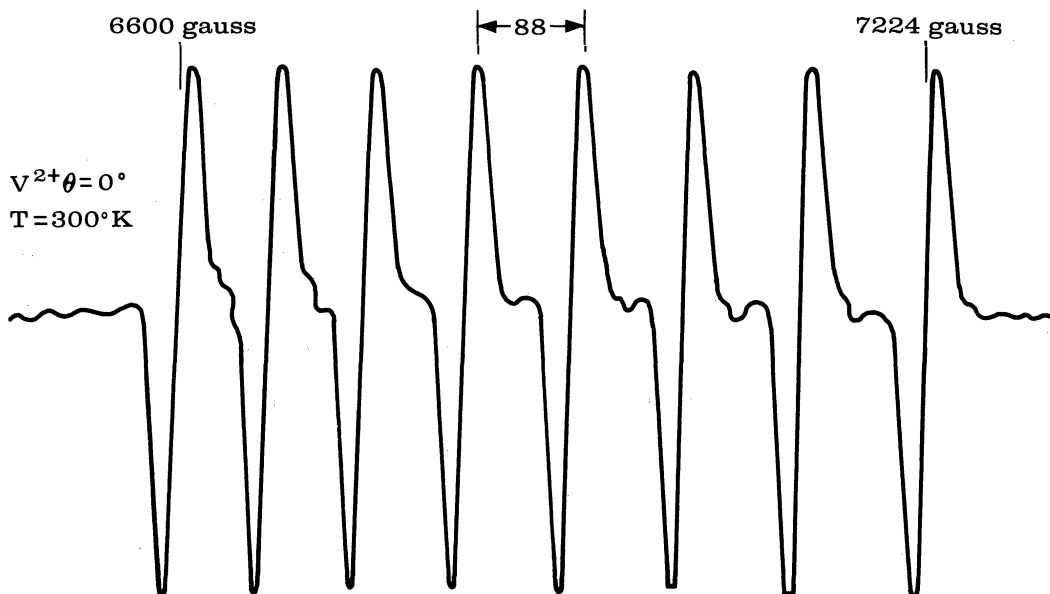


FIG. 5. SPECTRUM FOR V<sup>2+</sup> AT 300°K FOR θ = 0° WELL ABOVE THE CROSSOVER POINT

The spin-Hamiltonian is given by

$$\mathcal{H} = g\beta S \cdot H - D \left( S_z^2 - \frac{5}{4} \right) + AI \cdot S, \quad (4)$$

in which it is assumed that  $g$  and  $A$  are isotropic and that the sign of  $D$  is negative, as in Cr<sup>3+</sup>. If the magnetic field is along the  $c$ -axis ( $\theta = 0^\circ$ ), the energy-level diagram consists of four groups of 8 lines, depicted in Fig. 6. The energy-level diagram is simple, except in the region of  $H \sim 0$  and  $2D/g\beta$ , the latter being marked by a circle. Figure 7 shows the details of the crisscrossing of energy levels in this region; Fig. 8 gives the behavior of the wave functions and the energy levels of a pair of perturbing levels. The unperturbed electron and nuclear spin functions are represented by  $\phi_m$  and  $\chi_m$ , respectively, and  $\lambda_m$  and  $\xi_m$  are defined by

$$\lambda_m = \frac{\sqrt{3}}{2} A \sqrt{I(I+1) - m(m-1)}, \quad (5)$$

and

$$\xi_m = \frac{g_{\parallel} \beta \Delta H_m}{2\lambda_m},$$

in which  $\Delta H_m$  is measured from the point where the levels would cross were it not for the perturbing action of the hyperfine interaction. Furthermore,

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$$N^2 \equiv 2 \left( 1 + \xi_m^2 + \xi_m \sqrt{1 + \xi_m^2} \right),$$

$$\alpha \equiv \frac{1}{N},$$

and

$$\beta \equiv \frac{\xi_m + \sqrt{1 + \xi_m^2}}{N}. \tag{6}$$

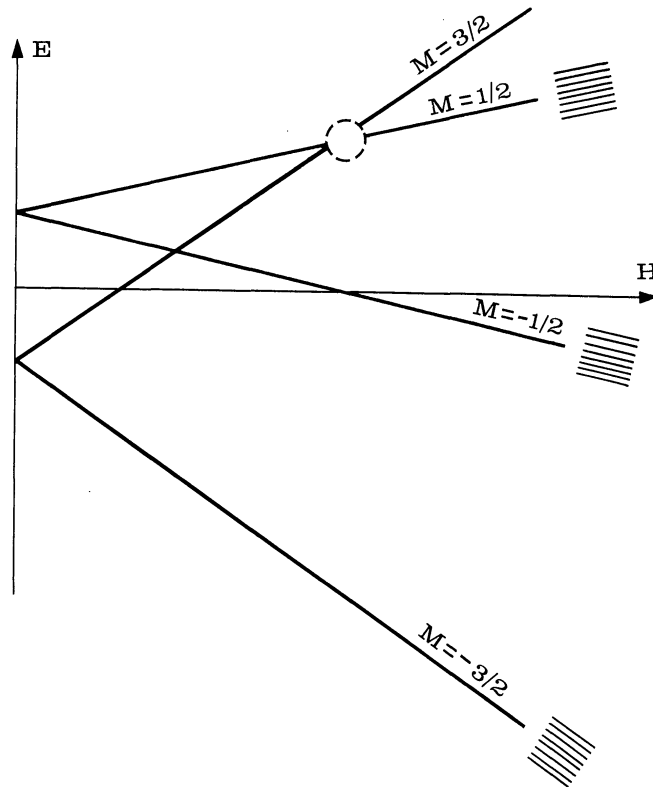


FIG. 6. ENERGY LEVEL DIAGRAM OF  $V^{2+}$  FOR  $\theta = 0^\circ$

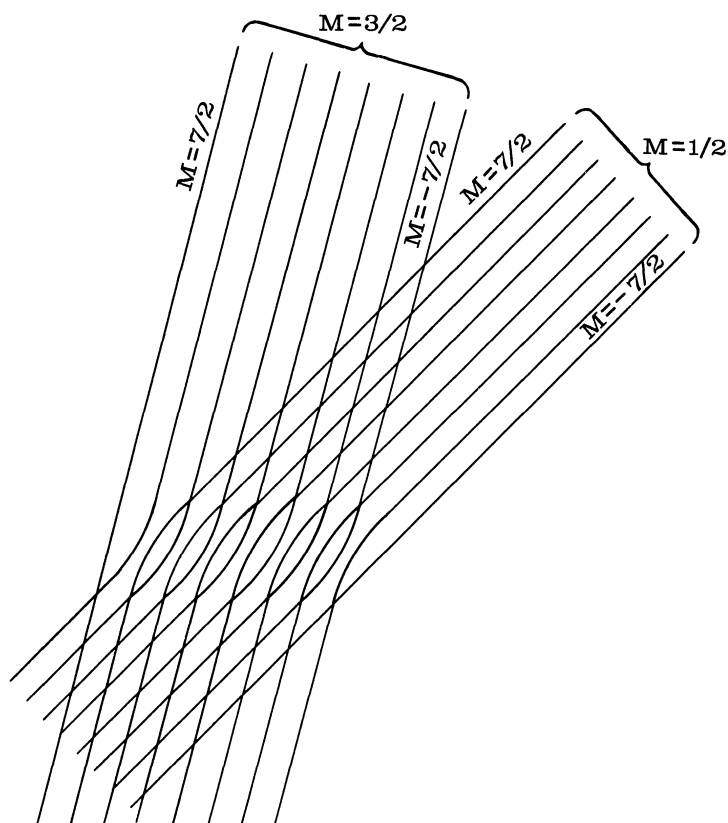


FIG. 7. DETAILS OF ENERGY LEVEL CRISSCROSSING NEAR CROSSOVER POINT

The effect of this admixing of wave functions at the crossover point is to produce a spectrum consisting of more than 8 lines predicted by a simple theory. The theoretically expected spectra for three different resonance frequencies are shown in Fig. 9. Note that the spectrum becomes progressively simpler as the resonance frequency is moved away from  $2D + 3/2A$ . As indicated already, the spectrum is also complex near zero magnetic field, because of the near-degeneracy of the  $S_z = \pm 1/2$  states. It should be noted, however, that the energy levels are simple where the levels  $S_z = -1/2$  and  $3/2$  cross over ( $H \sim D/g\beta$ ), if both the crystalline field and hyperfine interaction have axial symmetry. If such is not the case, the spectrum should again be complex. For this reason, a study of the region should reveal small deviations from the spin-Hamiltonian given by Eq. (4). This can be done by examining the transition  $-3/2 \leftrightarrow -1/2$  with resonance frequency

$$h\nu \sim g\beta H + 2D \sim 3D = 14,200 \text{ mc/sec,}$$

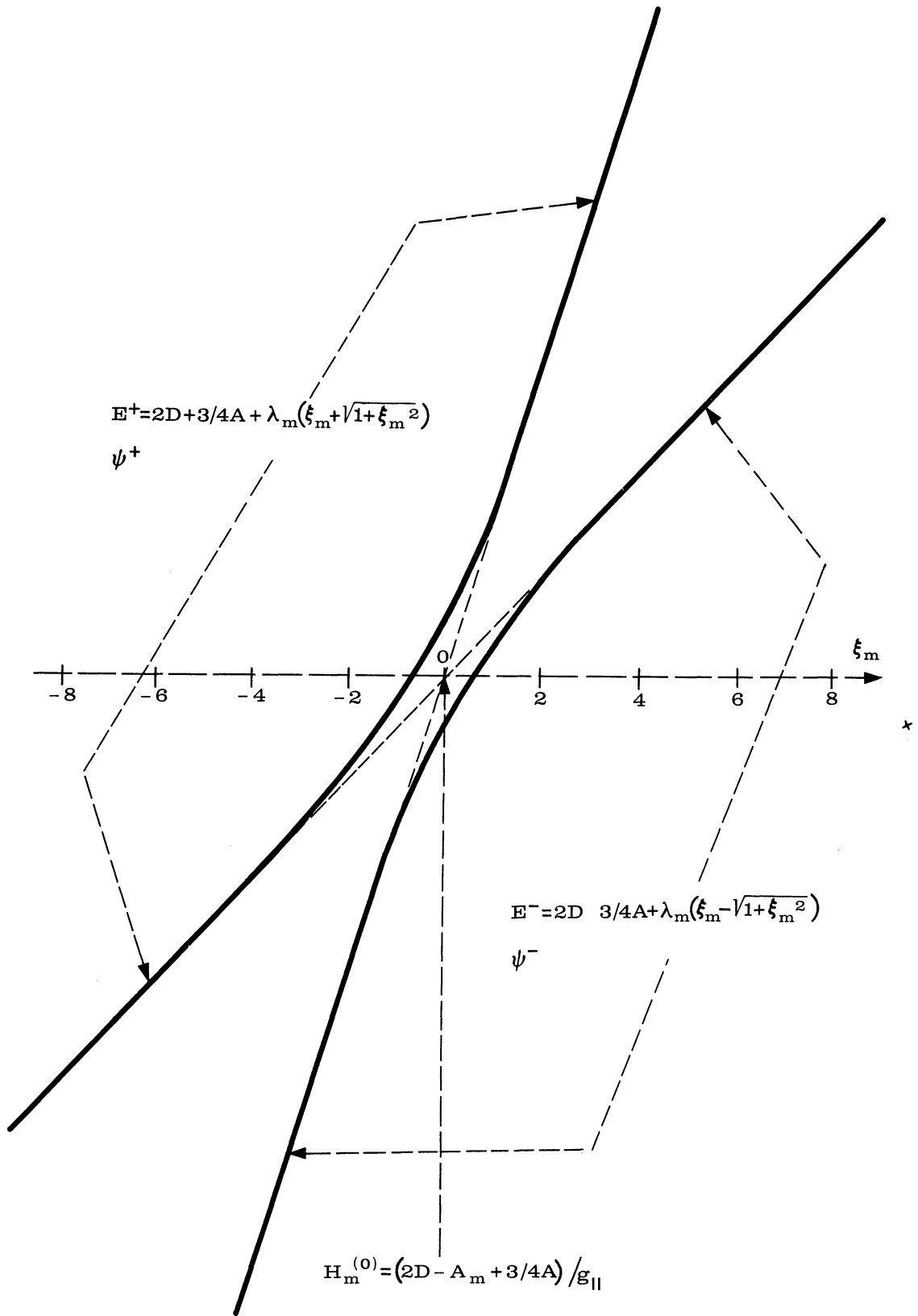


FIG. 8. ENERGY AND WAVE FUNCTIONS OF PERTURBING STATES

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or the transition (see Appendix B).

$$h\nu \sim g\beta H = 4700 \text{ mc/sec.}$$

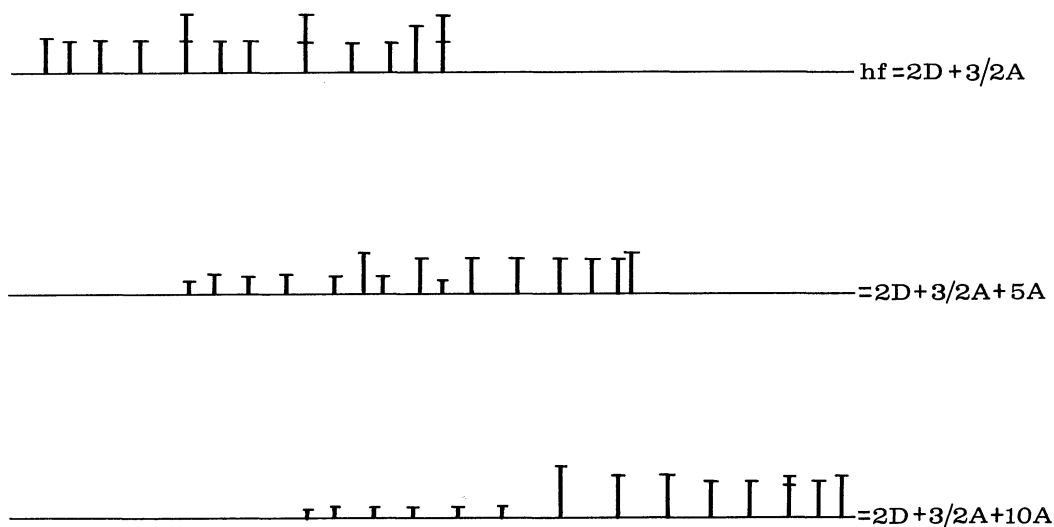


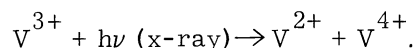
FIG. 9. CALCULATED SPECTRUM FOR DIFFERENT  
RESONANCE FREQUENCIES

Some details of the x-ray process were noted. It was seen that the x-ray production of  $V^{2+}$  saturated quite rapidly. After about 3 hr of irradiation, no significant increase of  $V^{2+}$  was observed. There was a slight relaxation of the  $V^{2+}$  concentration immediately after x-irradiation, but thereafter the concentration remained essentially constant at  $300^\circ\text{K}$ . The  $V^{2+}$  ions, however, can be bleached by heating to  $700^\circ\text{C}$ . X-irradiation did not appear to produce any new spin-resonance centers. Furthermore, the lines of  $\text{Cr}^{3+}$  and  $\text{Fe}^{3+}$  were not affected by the x-rays. Vanadium sapphire crystals were also irradiated and measured at  $77^\circ\text{K}$ . It was found that  $V^{2+}$  ions are produced, but the effects are similar to those of room-temperature irradiation.

It is of interest to note that the observed hyperfine splitting going from  $V^{2+}$  to  $V^{4+}$  increases as might be expected on the basis of the charge mismatch with the lattice. The  $V^{4+}$  should tend to pull in the electron charge cloud more strongly than  $V^{2+}$ .  $V^{3+}$  is then roughly in between. The hfs coupling constants are a measure of the electron charge density at the V-51 nucleus.

## IRRADIATION PROCESS

The production of  $V^{2+}$  by means of x-rays is of special interest in the study of electron-transfer processes in sapphire. The process that suggests itself immediately is



This process is ruled out, however, because there is no apparent increase in the  $V^{4+}$  signal upon irradiation and because the final  $V^{2+}$  signal is much larger than the  $V^{4+}$  signal. Furthermore, the resonance absorption signals of the trace impurities,  $Cr^{3+}$  and  $Fe^{3+}$ , were carefully examined, but no observable effects due to x-rays were detected. This suggests that some unknown center in the sapphire can yield an electron which can be trapped at  $V^{3+}$  to give  $V^{2+}$ . Since a fairly high concentration of  $V^{2+}$  is produced (about 0.01%), a substantial number of the electron-donor defects are likewise produced; these centers do not appear to show spin resonance.

It has been noted that the addition of  $Cr^{3+}$  and  $V^{3+}$  to sapphire increases the sensitivity to x-ray coloration (Ref. 18). In the case of  $V^{3+}$ , it may be that, by trapping out electrons, the  $V^{3+}$  tends to stabilize a color center which would then be a trapped hole. As yet, however, no definite statement can be made as to the nature of the electron donor.

## DISCUSSION

In contrast to those for manganese, which has been studied in a variety of host materials, liquid or solid (Ref. 19 and 20), the spin-resonance investigations of vanadium have been limited thus far to only a few materials. A list of some of the materials is given in Table I. It would be of interest to investigate the properties of vanadium in other materials such as ZnS, ZnO, CdS, etc., single crystals or powders. The advantage of using vanadium over manganese is that the latter appears to be always divalent, whereas with vanadium, the oxidation state can be readily altered by ionizing radiation.

During the course of this investigation, it appeared that it might be possible to obtain information about the nature of atomic displacements produced by nuclear radiation by examining the spin-resonance spectrum of ruby near the first crossover, occurring near 2000 gauss. If lattice vacancies produced by nuclear radiations become associated with the chromium ions, the crystalline electric field will no longer have axial symmetry, so that the appropriate



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spin-Hamiltonian will contain a rhombic-field term. This will have the effect of admixing the states  $S_z = -1/2$  and  $3/2$ . This particular region of the energy level diagrams can be explored with frequencies near 5.75 kmc/sec and/or 17.25 kmc/sec. The advantage of using chromium rather than vanadium is that the results will not be complicated by hyperfine interactions.

TABLE I. HYPERFINE STRUCTURE FOR VANADIUM IN VARIOUS MATERIALS

Material	Valence	$A \times 10^4 \text{ cm}^{-1}$	State	Ref.
$V(NH_4)_2 \cdot (SO_4)_2 \cdot 6H_2O$	$V^{++}$	88	Crystal	21, 22
$K_4V(CH)_6 \cdot 3H_2O$	$V^{++}$	-56	Crystal	23
$V(C_5H_5)_2$	$V^{++}$	26	Benzene solution	17
$VO(C_5H_5)_2$	$V^{++}$	71	Benzene solution	17
$VO SO_4$	$V^{++++}$	114	Solution	24, 25
Vanadium (IV)-Cupferron Chelate	$V^{++}$	---	Solution	26
MgO: V	$V^{++}$	76	Single crystal	14, 27
Chelate Vanadylacetyl- Acetone	$V^{++++}$	107	Solution	28
Vanadyl Eteoporphyrin I	$V^{++++}$	52	Benzene solution	29, 30

(B = 159)

APPENDIX A

Crystalline Field Calculations for  $V^{3+}$

The ground state of  $V^{3+}$  is  $(3d)^2 \ ^3F_3$ . In a cubic field, the orbital septuplet is split into an upper singlet and two triplets. The lowest triplet is split further by a trigonal field into a lower singlet and an upper doublet. When the spin is taken into account, with  $S = 1$ , the triplet becomes a ninefold level, which under the combined action of the trigonal field and the spin-orbit coupling is split with a singlet ( $M = 0$ ) lying lowest then, fairly close, a doublet ( $M = \pm 1$ ), and the remaining levels some hundreds of wave numbers higher. The magnetic susceptibility measurements indicate that the separation of the singlet and the doublet is of the order of  $5 \text{ cm}^{-1}$  (Fig. 10).

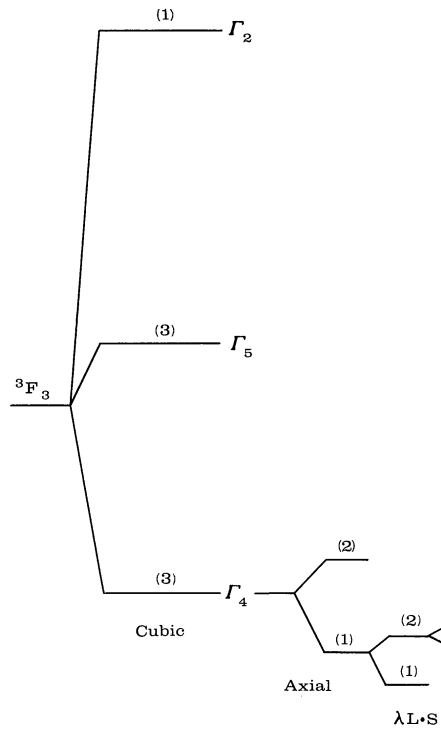


FIG. 10. CRYSTALLINE ELECTRIC FIELD SPLITTING OF THE GROUND STATE OF  $V^{3+}$

The Hamiltonian for the  $V^{3+}$  ion is given by

$$\mathcal{H} = \beta S \cdot g \cdot H + D \left( S_z^2 - \frac{2}{3} \right) + \frac{E}{2} \left( S_+^2 + S_-^2 \right) + A I_z S_z + \frac{B}{2} \left( I_+ S_- + I_- S_+ \right), \quad (7)$$

in which  $D$  and  $E$  are the axial and rhombic crystalline field lines, and  $A$  and  $B$  the parallel and perpendicular hfs coupling constants.

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Consider first the case in which the nuclear effects are neglected. The matrix elements of the Hamiltonian

$$\mathcal{H}' = \beta S \cdot g \cdot H + D \left( S_z^2 - \frac{2}{3} \right) + \frac{E}{2} \left( S_+^2 + S_-^2 \right) \quad (8)$$

are

$$\begin{aligned} \langle M | \mathcal{H}' | M \rangle &= \beta g_{\parallel} H_z M + D \left( M^2 - \frac{2}{3} \right) \\ \langle M + 1 | \mathcal{H}' | M \rangle &= \frac{1}{2} \beta g_{\perp} H_- \sqrt{2 - M(M + 1)} \\ \langle M - 1 | \mathcal{H}' | M \rangle &= \frac{1}{2} \beta g_{\perp} H_+ \sqrt{2 - M(M - 1)} \\ \langle M + 2 | \mathcal{H}' | M \rangle &= \frac{E}{2} \sqrt{[2 - M(M + 1)][2 - (M + 1)(M + 2)]} \\ \langle M - 2 | \mathcal{H}' | M \rangle &= \frac{E}{2} \sqrt{[2 - M(M - 1)][2 - (M - 1)(M - 2)]} . \end{aligned} \quad (9)$$

This gives rise to the matrix

	M = -1	0	1	
-1	$-g_{\parallel} \beta H_z + \frac{D}{3}$ $-\lambda$	$\frac{1}{\sqrt{2}} g_{\perp} \beta H_+$	E	(10)
0	$\frac{1}{\sqrt{2}} g_{\perp} \beta H_-$	$-\frac{2}{3} D$ $-\lambda$	$\frac{1}{\sqrt{2}} g_{\perp} \beta H_+$	
1	E	$\frac{1}{\sqrt{2}} g_{\perp} \beta H_-$	$g_{\parallel} \beta H_z + \frac{D}{3}$ $-\lambda$	

This leads to the characteristic equation

$$\begin{aligned} -\left(\frac{2}{3}D + \lambda\right) \left(\frac{1}{3}D - \lambda\right)^2 + \left(\lambda + \frac{2}{3}D\right) g_{\parallel}^2 \beta^2 H_z^2 \\ - g_{\parallel}^2 \beta^2 H_- H_+ \left(\frac{D}{3} - \lambda\right) + \frac{E}{2} g_{\perp}^2 \beta^2 \left(H_+^2 + H_-^2\right) + E^2 \left(\frac{2}{3}D + \lambda\right) = 0. \end{aligned} \quad (11)$$

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If the magnetic field is along the z-axis,  $H_+ = H_- = 0$ ,  $H_z = H$ , and the roots of Eq. (11) are

$$\lambda = -\frac{2}{3}D$$

and

$$\lambda = \frac{1}{3}D \pm \sqrt{E^2 + g_{\parallel}^2 \beta^2 H^2}. \quad (12)$$

The associated wave functions are

$$\begin{aligned} \lambda = -\frac{2}{3}D : \psi_0 &= \phi_0 \\ \lambda^+ = \frac{1}{3}D + \sqrt{E^2 + g_{\parallel}^2 \beta^2 H^2} : \psi^+ &= \frac{1}{N}(c_1 \phi_{-1} + c_2 \phi_1) \\ \lambda^- = \frac{1}{3}D - \sqrt{E^2 + g_{\parallel}^2 \beta^2 H^2} : \psi^- &= \frac{1}{N}(c_2 \phi_{-1} + c_1 \phi_1) \end{aligned} \quad (13)$$

with

$$c_1 \equiv \frac{E}{N}, \quad c_2 \equiv \frac{g_{\parallel} \beta H_z + \sqrt{E^2 + g_{\parallel}^2 \beta^2 H^2}}{N}$$

and

$$N^2 = 2E^2 + 2g_{\parallel}^2 \beta^2 H_z^2 + 2g_{\parallel} \beta H_z E^2 + g_{\parallel}^2 \beta^2 H^2.$$

These functions can be used to obtain the approximate angular dependence of the eigenvalues, and hence of the absorption spectrum. The Hamiltonian of Eq. (8) can be written in the form

$$\mathcal{H}' = \mathcal{H}^{(0)} + \mathcal{H}'' \quad (14)$$

with

$$\mathcal{H}^{(0)} = g_{\parallel} \beta S_z H_z + D \left( S_z^2 - \frac{2}{3} \right) + \frac{E}{2} \left( S_+^2 + S_-^2 \right)$$

and

$$\mathcal{H}'' = \frac{g_{\perp} \beta}{2} (H_- S_+ + H_+ S_-).$$

The Hamiltonian  $\mathcal{H}^{(0)}$  is diagonal in the wave functions of Eq. (13). If  $\mathcal{H}''$  be taken as the perturbation Hamiltonian, its matrix elements with respect to the wave functions of Eq. (13) are

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$$\langle 0 | \hat{H}'' | + \rangle = \frac{g_{\perp} \beta}{2N} (c_1 H_- + c_2 H_+) \sqrt{2}$$

and

$$\langle 0 | \hat{H}'' | - \rangle = \frac{g_{\perp} \beta}{2N} (-c_2 H_- + c_1 H_+) \sqrt{2},$$

(15)

so that

$$\lambda^+(\theta) = \frac{1}{3}D + \sqrt{E^2 + g_{\parallel}^2 \beta^2 H_z^2} + \frac{g_{\perp}^2 \beta^2 (c_1 H_- + c_2 H_+) (c_1 H_+ + c_2 H_-)}{2N^2 (D + \sqrt{E^2 + g_{\parallel}^2 \beta^2 H_z^2})} \quad (16)$$

and

$$\lambda^-(\theta) = \frac{1}{3}D - \sqrt{E^2 + g_{\parallel}^2 \beta^2 H_z^2} + \frac{g_{\perp}^2 \beta^2 |-c_2 H_- + c_1 H_+|^2}{2N^2 (D - \sqrt{E^2 + g_{\parallel}^2 \beta^2 H_z^2})}. \quad (17)$$

Therefore,

$$\begin{aligned} h\nu &= \lambda^+(\theta) - \lambda^-(\theta) \\ &= 2\sqrt{E^2 + g_{\parallel}^2 \beta^2 H_z^2} = \frac{g_{\perp}^2 \beta^2 H_+ H_- + \sqrt{E^2 + g_{\parallel}^2 \beta^2 H_z^2}}{D^2 - E^2 - g_{\parallel}^2 \beta^2 H_z^2} + \frac{g_{\perp}^2 \beta^2 (H_+^2 + H_-^2) c_1 c_2}{N^2 (D^2 - E^2 - g_{\parallel}^2 \beta^2 H_z^2)} \\ &\cong 2\sqrt{E^2 + g_{\parallel}^2 \beta^2 H_z^2} - \frac{g_{\perp}^2 \beta^2 \sqrt{E^2 + g_{\parallel}^2 \beta^2 H_z^2}}{D^2} H_+ H_- + \frac{g_{\perp}^2 \beta^2 c_1 c_2}{N^2 D^2} (H_+^2 + H_-^2), \end{aligned} \quad (18)$$

if  $g_{\parallel} \beta H_z \gg E$ .

Assume E small.

$$\begin{aligned} \psi^+ &= \phi_1 + \frac{E}{2g_{\parallel} \beta H_z} \phi_{-1} & \lambda^+(\theta) &= \frac{D}{3} + g_{\parallel} \beta H_z + \frac{E^2}{2g_{\parallel} \beta H_z} \\ \psi^- &= \phi_{-1} - \frac{E}{2g_{\parallel} \beta H_z} \phi_1 & \lambda^-(\theta) &= \frac{D}{3} - g_{\parallel} \beta H_z - \frac{E^2}{2g_{\parallel} \beta H_z} \end{aligned} \quad (19)$$

The above expression becomes

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$$h\nu = 2g_{\parallel}\beta H \cos \theta + \frac{E^2}{g_{\parallel}\beta H \cos \theta} - \frac{g_{\parallel}g_{\perp}^2\beta^3 H^3}{D^2} \sin^2 \theta \cos \theta + \frac{g_{\perp}^2\beta E \sin^2 \theta}{g_{\parallel} D \cos \theta}. \quad (20)$$

Return now to the original problem.

$$\mathcal{H}^{(0)} \equiv g_{\parallel}\beta S_z H_z + D \left( S_z^2 - \frac{2}{3} \right) + \frac{E}{2} (S_+^2 + S_-^2) + A I_z S_z, \quad (21)$$

$$\mathcal{H}'' = \frac{g_{\perp}\beta}{2} (H_- S_+ + H_+ S_-) + \frac{B}{2} (I_- S_+ + I_+ S_-).$$

The wave functions that diagonalize  $\mathcal{H}^{(0)}$  are obtained from the solution of

	-1	1
-1	$\frac{D}{3} - g_{\parallel}\beta H_z - Am$  $-\lambda$	  $E$
1	  $E$	$\frac{D}{3} + g_{\parallel}\beta H_z + Am$  $-\lambda$

The eigenvalues and the corresponding wave functions are

$$\lambda^+ = \frac{D}{3} + \sqrt{E^2 + (g_{\parallel}\beta H_z + Am)^2}, \quad (22)$$

$$\psi^+ = \frac{1}{N} (c_1 \phi_{-1} + c_2 \phi_1),$$

and

$$\lambda^- = \frac{D}{3} - \sqrt{E^2 + (g_{\parallel}\beta H_z + Am)^2}, \quad (23)$$

$$\psi^- = \frac{1}{N} (-c_2 \phi_{-1} + c_1 \phi_1),$$

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with

$$c_1 \equiv E, \tag{24}$$

$$c_2 \equiv g_{\parallel} \beta H_z + Am + \sqrt{E^2 + (g_{\parallel} \beta H_z + Am)^2},$$

and

$$N^2 = c_1^2 + c_2^2.$$

The off-diagonal elements corresponding to Eq. (15) are now

$$\langle 0, m | \mathcal{H}'' | +, m \rangle = \frac{g_{\perp} \beta}{\sqrt{2N}} (c_1 H_- + c_2 H_+)$$

and

$$\langle 0, m | \mathcal{H}'' | -, m \rangle = \frac{g_{\perp} \beta}{N\sqrt{2}} (-c_2 H_- + c_1 H_+), \tag{25}$$

and the additional elements are:

$$\langle 0, m+1 | \mathcal{H}'' | +, m \rangle = \frac{Bc_2}{N\sqrt{2}} \sqrt{I(I+1) - m(m+1)}$$

$$\langle 0, m-1 | \mathcal{H}'' | +, m \rangle = \frac{Bc_1}{N\sqrt{2}} \sqrt{I(I+1) - m(m-1)}$$

$$\langle 0, m+1 | \mathcal{H}'' | -, m \rangle = \frac{Bc_1}{N\sqrt{2}} \sqrt{I(I+1) - m(m+1)}$$

$$\langle 0, m-1 | \mathcal{H}'' | -, m \rangle = -\frac{Bc_2}{N\sqrt{2}} \sqrt{I(I+1) - m(m-1)}.$$

Therefore,

$$\lambda^+(\theta) = \frac{D}{3} + \sqrt{E^2 + (g_{\parallel} \beta H_z + Am)^2} + \frac{g_{\perp}^2 \beta^2}{2N^2} \frac{|c_1 H_- + c_2 H_+|^2}{D + \sqrt{E^2 + (g_{\parallel} \beta H_z + Am)^2}}$$

$$+ \frac{B^2}{2N^2} \frac{c_2^2}{D + \sqrt{E^2 + (g_{\parallel} \beta H_z + Am)^2}} [I(I+1) - m(m+1)]$$

$$+ \frac{B^2}{2N^2} \frac{c_1^2}{D + \sqrt{E^2 + (g_{\parallel}\beta H_z + Am)^2}} [I(I+1) - m(m-1)] . \quad (26)$$

$$\lambda^-(\theta) = \frac{D}{3} - \sqrt{E^2 + (g_{\parallel}\beta H_z + Am)^2} + \frac{g_{\perp}^2 \beta^2}{2N^2} \frac{|-c_2 H_- + c_1 H_+|^2}{D - \sqrt{E^2 + (g_{\parallel}\beta H_z + Am)^2}} \quad (27)$$

$$+ \frac{B^2 c_1^2}{2N^2} \frac{I(I+1) - m(m+1)}{D - \sqrt{E^2 + (g_{\parallel}\beta H_z + Am)^2}} + \frac{B^2 c_2^2}{2N^2} \frac{I(I+1) - m(m-1)}{D - \sqrt{E^2 + (g_{\parallel}\beta H_z + Am)^2}} .$$

Consequently,

$$h\nu = \lambda^+(\theta) - \lambda^-(\theta)$$

$$= 2\sqrt{E^2 + (g_{\parallel}\beta H_z + Am)^2} + \frac{g_{\perp}^2 \beta^2}{N^2} \frac{Dc_1 c_2 (H_-^2 + H_+^2)}{D^2 - E^2 - (g_{\parallel}\beta H_z + Am)^2} - \frac{g_{\perp}^2 \beta^2 \sqrt{E^2 + (g_{\parallel}\beta H_z + Am)^2}}{D^2 - E^2 - (g_{\parallel}\beta H_z + Am)^2} H_- H_+ \\ - [I(I+1) - m^2] \frac{B^2 \sqrt{E^2 + (g_{\parallel}\beta H_z + Am)^2}}{D^2 - E^2 - (g_{\parallel}\beta H_z + Am)^2} + \frac{B^2 (c_1^2 - c_2^2)}{N^2} \frac{Dm}{D^2 - E^2 - (g_{\parallel}\beta H_z + Am)^2} . \quad (28)$$

If  $g_{\parallel}\beta H_z + Am \gg E$ , the above result becomes

$$h\nu = 2(g_{\parallel}\beta H_z + Am) + \frac{E^2}{g_{\parallel}\beta H_z + Am} + \frac{g_{\perp}^2 \beta^2 DE (H_-^2 + H_+^2)}{2g_{\parallel}\beta H_z D^2} - \frac{g_{\perp}^2 \beta^2 (g_{\parallel}\beta H_z + Am)}{D^2} H_+ H_- \\ - \frac{B^2 (g_{\parallel}\beta H_z + Am)}{D^2} [I(I+1) - m^2] - \frac{B^2 m}{D} \left( 1 - \frac{E^2}{4g_{\parallel}^2 \beta^2 H_z^2} \right) , \quad (29)$$

or

$$h\nu = 2(g_{\parallel}\beta H \cos \theta + Am) + \frac{E^2}{g_{\parallel}\beta H \cos \theta + Am} + \frac{g_{\perp}^2 \beta H E \sin^2 \theta}{g_{\parallel} D \cos \theta} - \frac{g_{\perp}^2 \beta^2 H^2 (g_{\parallel}\beta H \cos \theta + Am) \sin^2 \theta}{D^2} \\ - \frac{B}{D} (g_{\parallel}\beta H \cos \theta + Am) [I(I+1) - m^2] - \frac{B^2 m}{D} \left( 1 - \frac{E^2}{4g_{\parallel}^2 \beta^2 H^2 \cos^2 \theta} \right) . \quad (30)$$



APPENDIX B

Crystalline Field Calculations for  $V^{2+}$

The ground state of the  $V^{2+}$  ion, like  $Cr^{3+}$ , is  ${}^4F_{3/2}$ , and its splitting in a crystalline field is as shown in Fig. 11. The spin-Hamiltonian of the  $V^{2+}$  ion is given by

$$\mathcal{H} = \beta S \cdot g \cdot H - D \left( S_z^2 - \frac{5}{4} \right) + A I_{z z} S_z + \frac{B}{2} (I_+ S_- + I_- S_+), \quad (31)$$

with  $S = 3/2$ , and  $I = 7/2$ . The sign of the crystalline field term,  $D$ , was taken to be negative, as in  $Cr^{3+}$ .

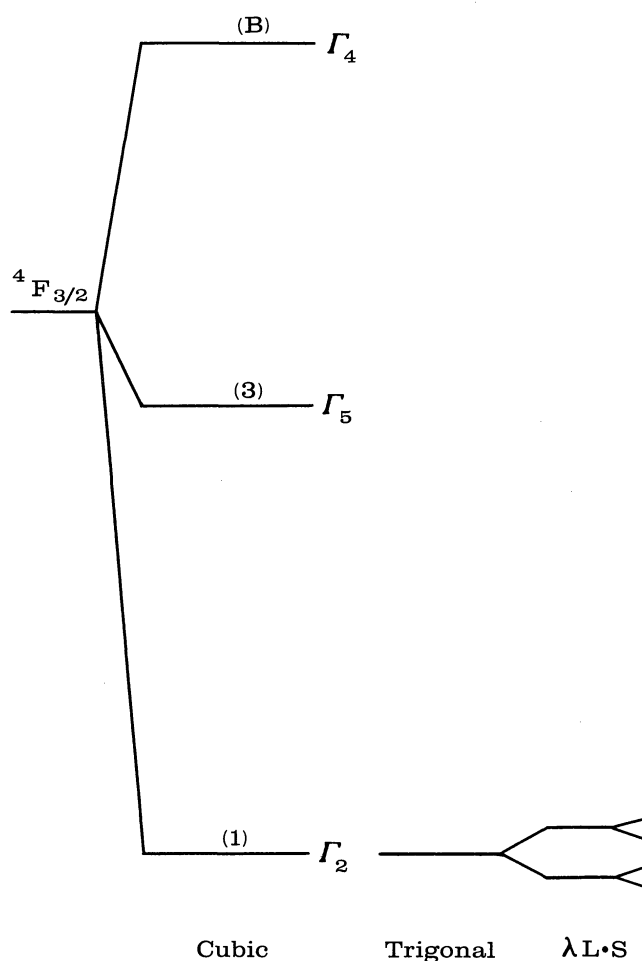


FIG. 11. CRYSTALLINE ELECTRIC FIELD SPLITTING OF THE GROUND STATE OF  $V^{2+}$

Of primary concern here will be the case in which the magnetic field is parallel to the  $c$ -axis. The Zeeman term then becomes  $g_{\parallel} \beta S_z H$ , so that the matrix elements are given by:

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$$\begin{aligned}
 \langle \pm \frac{3}{2}, m | \mathcal{H} | \pm \frac{3}{2}, m \rangle &= \pm \frac{3}{2} g_{\parallel} \beta H - D \pm \frac{3}{2} A m \\
 \langle \pm \frac{1}{2}, m | \mathcal{H} | \pm \frac{1}{2}, m \rangle &= \pm \frac{1}{2} g_{\parallel} \beta H + D \pm \frac{1}{2} A m \\
 \langle \frac{1}{2}, m+1 | \mathcal{H} | \frac{3}{2}, m \rangle &= \frac{\sqrt{3}}{2} B \sqrt{I(I+1) - m(m+1)} \\
 \langle -\frac{1}{2}, m+1 | \mathcal{H} | \frac{1}{2}, m \rangle &= B \sqrt{I(I+1) - m(m+1)} \\
 \langle -\frac{3}{2}, m-1 | \mathcal{H} | -\frac{1}{2}, m \rangle &= -\frac{\sqrt{3}}{2} B \sqrt{I(I+1) - m(m+1)}.
 \end{aligned} \tag{32}$$

The term values are then given by:

$$\begin{aligned}
 E\left(\frac{3}{2}, m\right) &= \frac{3}{2} g_{\parallel} \beta H - D + \frac{3}{2} A m + \frac{3B^2}{4} \frac{I(I+1) - m(m+1)}{g\beta H - 2D + A \left(m - \frac{1}{2}\right)} \\
 E\left(\frac{1}{2}, m\right) &= \frac{1}{2} g_{\parallel} \beta H + D + \frac{1}{2} A m + \frac{B^2 [I(I+1) - m(m+1)]}{g_{\parallel} \beta H + A \left(m + \frac{1}{2}\right)} - \frac{3B^2}{4} \frac{I(I+1) - m(m-1)}{g_{\parallel} \beta H - 2D + A \left(m - \frac{3}{2}\right)} \\
 E\left(-\frac{1}{2}, m\right) &= -\frac{1}{2} g_{\parallel} \beta H + D - \frac{1}{2} A m + \frac{3B^2}{4} \frac{I(I+1) - m(m+1)}{g_{\parallel} \beta H + 2D + A \left(m + \frac{3}{2}\right)} - B \frac{2I(I+1) - m(m-1)}{g_{\parallel} \beta H + A \left(m - \frac{1}{2}\right)} \\
 E\left(-\frac{3}{2}, m\right) &= -\frac{3}{2} g_{\parallel} \beta H - D - \frac{3}{2} A m - \frac{3B^2}{4} \frac{I(I+1) - m(m-1)}{g\beta H + 2D + A \left(m + \frac{1}{2}\right)}.
 \end{aligned} \tag{33}$$

If the second-order terms are neglected, the term values are linear in H. The dependence of the energy levels upon the magnetic field is then as shown in Fig. 6. The resonance conditions of the transition  $\frac{3}{2} \leftrightarrow \frac{1}{2}$  is given by

$$\begin{aligned}
 h\nu = E\left(\frac{3}{2}, m\right) - E\left(\frac{1}{2}, m\right) &= g\beta H - 2D + Am + \frac{3B^2}{4} \frac{I(I+1) - m(m+1)}{h\nu - \frac{A}{2}} \\
 &\quad - \frac{B^2 [I(I+1) - m(m+1)]}{h\nu + 2D + \frac{A}{2}} + \frac{3B^2}{4} \frac{I(I+1) - m(m-1)}{h\nu - \frac{3}{2}A}.
 \end{aligned} \tag{34}$$

For the  $-\frac{1}{2} \leftrightarrow \frac{1}{2}$  transition,

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$$\begin{aligned}
 h\nu = E\left(\frac{1}{2}, m\right) - E\left(-\frac{1}{2}, m\right) &= g\beta H + Am + \frac{B^2 [I(I+1) - m(m+1)]}{h\nu + \frac{A}{2}} \\
 &- \frac{3B^2}{4} \frac{I(I+1) - m(m-1)}{h\nu - 2D - \frac{3}{2}A} - \frac{3B^2}{4} \frac{I(I+1) - m(m+1)}{h\nu + 2D + \frac{3}{2}A} + \frac{B^2 [I(I+1) - m(m-1)]}{h\nu - \frac{A}{2}}.
 \end{aligned}
 \tag{35}$$

In the analysis given thus far, it has been assumed that all energy levels are distinct. However, in the region indicated by a circle in Fig. 6, the levels  $M = 1/2$  and  $3/2$  cross, so that  $E\left(\frac{3}{2}, m\right) = E\left(\frac{1}{2}, m+1\right)$ . Consequently, it is necessary to revamp the perturbation calculation.

For the degenerate or almost degenerate case, the submatrix for  $M = 1/2$  and  $3/2$  partitions into two  $1 \times 1$  matrixes and seven  $2 \times 2$  matrixes. The  $1 \times 1$  matrixes correspond to the states with the following wave functions and eigenvalues

$$\begin{aligned}
 \phi_{3/2} \chi_{7/2} \quad E\left(\frac{3}{2}, \frac{7}{2}\right) &= \frac{3}{2}g\beta H - D + \frac{21}{4}A \\
 \phi_{1/2} \chi_{-7/2} \quad E\left(\frac{1}{2}, -\frac{7}{2}\right) &= \frac{1}{2}g\beta H + D - \frac{7}{4}A.
 \end{aligned}
 \tag{36}$$

The remaining  $2 \times 2$  matrixes are of the form

	$\phi_{1/2} \chi_m$	$\phi_{3/2} \chi_{m-1}$
$\phi_{1/2} \chi_m$	$\frac{1}{2}g_{\parallel}\beta H + D$ $+\frac{1}{2}Am$	$\frac{\sqrt{3}}{2}B\sqrt{I(I+1) - m(m-1)}$
$\phi_{3/2} \chi_{m-1}$	$\frac{\sqrt{3}}{2}B\sqrt{I(I+1) - m(m-1)}$	$\frac{3}{2}g_{\parallel}\beta H - D$ $+\frac{3}{2}A(m-1)$

(37)

which gives for the eigenvalues

$$E = E_0 \pm \sqrt{\lambda_m^2 + \left(\frac{1}{2}g_{\parallel}\beta H - D + \frac{1}{2}Am - \frac{3}{4}A\right)^2}, \quad (38)$$

with

$$E^0 = g_{\parallel}\beta H + Am - \frac{3}{4}A \quad (39)$$

and

$$\lambda_m = \frac{\sqrt{3}}{2}B \sqrt{I(I+1) - m(m-1)}.$$

The above expressions can be written in a little more convenient form. Were it not for the off-diagonal elements, the levels for  $\phi_{1/2}\chi_m$  and  $\phi_{3/2}\chi_{m-1}$  would cross when

$$\frac{1}{2}g_{\parallel}\beta H + D + \frac{1}{2}Am = \frac{3}{2}g_{\parallel}\beta H - D + \frac{3}{2}A(m-1). \quad (40)$$

The magnetic field at which the levels cross then is given by

$$g_{\parallel}\beta H_m^{(0)} = 2D - Am + \frac{3}{2}A.$$

Writing then,

$$H = H_m^{(0)} + \Delta H_m,$$

from Eq. (38)

$$E = E_0 \pm \sqrt{\lambda_m^2 + \frac{1}{4}g_{\parallel}^2\beta^2\Delta H_m^2}, \quad (41)$$

and the 2 x 2 matrix can be written in the form

	$\phi_{1/2}\chi_m$	$\phi_{3/2}\chi_{m-1}$	
$\phi_{1/2}\chi_m$	$E_0 - \frac{1}{2}g_{\parallel}\beta\Delta H_m$	$\lambda_m$	(42)
$\phi_{3/2}\chi_{m-1}$	$\lambda_m$	$E^0 + \frac{1}{2}g_{\parallel}\beta\Delta H_m$	

The eigenvalues and the corresponding wave functions are

$$E^+ = E_0 + \lambda_m \sqrt{1 + \xi_m^2}, \quad (43)$$

$$\psi^+ = \frac{1}{N} \left[ \phi_{1/2} \chi_m + \left( \sqrt{1 + \xi_m^2} + \xi_m \right) \phi_{3/2} \chi_{m-1} \right],$$

and

$$E^- = E_0 - \lambda_m \sqrt{1 + \xi_m^2}, \quad (44)$$

$$\psi^- = \frac{1}{N} \left[ - \left( \xi_m + \sqrt{1 + \xi_m^2} \right) \phi_{1/2} \chi_m + \phi_{3/2} \chi_{m-1} \right],$$

where  $\xi_m = g_{||} \beta \Delta H_m / 2\lambda_m$ .

$$N^2 = 2 \left( 1 + \xi_m^2 + \xi_m \sqrt{1 + \xi_m^2} \right).$$

The dependence of the energies and wave functions are shown in Fig. 7 and 8.

The resonance condition for the transition between levels  $-1/2$  and  $\psi^\pm$  is then given by

$$\begin{aligned} h\nu &= E^\pm - E \left( -\frac{1}{2}, m \right) \\ &= 2D + \frac{3}{2} g_{||} \beta \Delta H_m \pm \lambda_m \sqrt{1 + \xi_m^2}. \end{aligned} \quad (45)$$

Physically, this means that each of the hfs components will be split into two, with intensities in the ratio  $(\alpha)^2 / (\beta)^2$ , where

$$\alpha \equiv \frac{1}{N} \quad (46)$$

and

$$\beta \equiv \frac{\xi_m + \sqrt{1 + \xi_m^2}}{N}.$$

Consider then

$$h\nu = 2D + \frac{3}{2} A + h\Delta\nu.$$

Equation (45) gives

$$\frac{h\Delta\nu}{\lambda_m} = 3\xi_m \pm \sqrt{1 + \xi_m^2}. \quad (47)$$

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The resonance magnetic fields can be obtained by solving this equation. Suppose first, that  $\Delta\nu = 0$ , i. e. ,

$$\begin{aligned}h\nu &= 2D + \frac{3}{2}A \\ \xi_m &= \pm \frac{1}{\sqrt{8}} \\ \Delta H_m &= \frac{2\lambda_m}{g_{\parallel}\beta} \xi_m = \pm \frac{\lambda_m}{\sqrt{2}g_{\parallel}\beta} \\ &= \sqrt{\frac{3}{8}} \frac{B}{g_{\parallel}\beta} \sqrt{I(I+1) - m(m-1)} .\end{aligned}$$

The calculated spectra for several resonance frequencies are shown in Fig. 9.

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Electron-spin  
Resonance  
Oxidation  
Ionization  
Irradiation

UNCLASSIFIED

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