

Spin Resonance of  $V^{2+}$ ,  $V^{3+}$ ,  $V^{4+}$  in  $\alpha\text{-Al}_2\text{O}_3$ <sup>†</sup>

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The electron-spin resonance absorption properties of vanadium sapphire are reported. It is shown that normally vanadium is predominantly trivalent with a small amount in the tetravalent state. After x or gamma irradiation, vanadium is converted to the divalent state. The hfs component separations 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 to study ionization effects in certain solids.

## I. INTRODUCTION

ALTHOUGH maser action in ruby has by now been investigated by workers in different laboratories,<sup>1</sup> some of the important information concerning the nature of chromium in corundum is still lacking. The initial measurements on the spin resonance properties of ruby were reported by Manenkov and Prokhorov,<sup>2</sup> by Zaripov and Shamonin,<sup>3</sup> and by Geusic,<sup>4</sup> and more detailed studies have been made by Schulz-DuBois.<sup>5</sup> The temperature dependence of the zero-field splitting was made by Cross and Terhune.<sup>6</sup> These measurements 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.

The investigations reported in this paper were undertaken to see if it is possible to obtain indirectly the answer to some of these questions. A direct attack to obtain this information by means of spin resonance measurements is met with difficulties because chromium does not have a well-recognizable signature. Natural chromium consists largely of the isotope of masses 50, 52, 54, but only 9.5% of the odd isotope  $\text{Cr}^{53}$ . Rubies containing  $\text{Cr}^{53}$  can be prepared, but the hyperfine structure is comparable to the line width, and furthermore, nothing is known about the effect of the oxidation state upon the hfs. Consequently, it seemed 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 va-

niadium ( $V^{51}$ ,  $I=\frac{7}{2}$ , 99.75%) and manganese ( $Mn^{55}$ ,  $I=\frac{5}{2}$ , 100%) flanking chromium to the left and right, respectively, in the periodic table. Molybdenum, consisting of  $Mo^{95}$  ( $I=\frac{5}{2}$ , 15.7%) and  $Mo^{97}$  ( $I=\frac{5}{2}$ , 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  $\text{Cr}^{3+}$ .<sup>7</sup> Attempts by us to observe resonance in this material have so far been unsuccessful.

The purpose of this paper then will be to present some of the spin resonance properties of various oxidation states of vanadium reported briefly earlier.<sup>8,9</sup> 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  $V^{4+}$ . If this sample is subjected to ionizing radiation, some of the vanadium is converted to  $V^{2+}$ . 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.<sup>10</sup> The present paper is also intended to complement the optical measurements of vanadium sapphire reported by Low<sup>11</sup> and by Pryce and Runciman.<sup>12</sup>

Recently, Wertz and his collaborators<sup>13</sup> have made a systematic study of the spin resonance properties of various iron group elements in  $\text{MgO}$ . 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  $V^{4+}$ ,  $V^{3+}$ ,  $V^{2+}$ , are  $\frac{1}{2}$ , 1, and  $\frac{3}{2}$ , respectively, and in a crystalline field of trigonal symmetry,

<sup>†</sup> Supported by Project MICHIGAN and the Air Force Office of Scientific Research.

<sup>1</sup> See for example, C. Kikuchi, J. Lambe, G. Makhov, and R. W. Terhune, *J. Appl. Phys.* **30**, 1061 (1959).

<sup>2</sup> A. A. Manenkov and A. M. Prokhorov, *J. Exptl. Theoret. Phys. (U.S.S.R.)* **28**, 762 (1955) [translation: *Soviet Phys.-JETP* **1**, 611 (1955)].

<sup>3</sup> M. M. Zaripov and In. Ia. Shamonin, *J. Exptl. Theoret. Phys. (U.S.S.R.)* **30**, 291 (1956) [translation: *Soviet Phys.-JETP* **3**, 171 (1956)].

<sup>4</sup> J. E. Geusic, *Phys. Rev.* **102**, 1252 (1956).

<sup>5</sup> E. O. Schulz-DuBois, *Bell System Tech. J.* **38**, 271 (1959).

<sup>6</sup> L. Cross and R. W. Terhune, *Bull. Am. Phys. Soc.* **3**, 37 (1958).

<sup>7</sup> K. D. Bowers and J. Owen, *Reports on Progress in Physics* (The Physical Society, London, 1955), Vol. 18, p. 304.

<sup>8</sup> C. Kikuchi, *Bull. Am. Phys. Soc.* **3**, 369 (1958).

<sup>9</sup> J. Lambe, R. Ager, and C. Kikuchi, *Bull. Am. Phys. Soc.* **4**, 261 (1959).

<sup>10</sup> R. A. Fisher and S. Goudsmit, *Phys. Rev.* **37**, 1057 (1931); S. Tolansky, *Hyperfine Structure in Line Spectra and Nuclear Spin* (Methuen and Company, Ltd., London, 1948).

<sup>11</sup> W. Low, *Z. physik. Chem.* **13**, 107 (1957).

<sup>12</sup> M. H. L. Pryce and W. A. Runciman, *Discussions Faraday Soc.* **26**, 34 (1958).

<sup>13</sup> J. E. Wertz, P. Auzins, J. H. E. Griffiths, and J. W. Orten, *Discussions Faraday Soc.* **26**, 66 (1958).

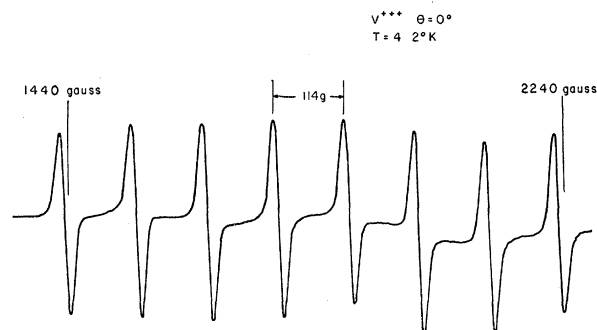


FIG. 1. Electron spin resonance spectrum of  $V^{+++}$  in  $\alpha\text{-Al}_2\text{O}_3$  at  $4.2^\circ\text{K}$  for magnetic field parallel to the  $c$  axis. The components are about 110 gauss apart.

each spin state can be distinguished from the others by the number and the angular dependence of the fine structure groups. On the other hand in  $\text{MgO}$ , the crystalline field is cubic, no fine structure splitting is produced, so that each of the three valence states is expected to give a single group of isotropic, or almost isotropic, 8 hfs lines. The three vanadium oxidation states can then be distinguished only by the differences, if any, of the hfs coupling constant.

## II. EXPERIMENTAL METHODS

The measurements were made with  $X$ - and  $K$ -band magnetic resonance spectrometers. The latter was used for some  $V^{++}$  measurements in order to avoid certain of the complications arising at  $X$ -band frequencies. However, the bulk of the measurements were carried out at 9400 Mc/sec. The  $X$ -band cavity was made of coated ceramic and the magnetic field was modulated at 5 kc/sec.<sup>14</sup>

The vanadium sapphire was irradiated either in the Co 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 is possible to transfer the sample into the magnetic resonance spectrometer without any appreciable warmup.

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  $\text{Cr}^{3+}$ . The  $T_1$  of  $\text{Cr}^{3+}$  according to our earlier measurements is known to be about 50 milliseconds at  $4.2^\circ\text{K}$ .

## III. EXPERIMENTAL RESULTS AND THEORETICAL ANALYSIS

### A. $V^{3+}$

The spin resonance of  $V^{3+}$  was observed in  $\alpha\text{-Al}_2\text{O}_3$  grown from a powder mixture of  $\text{Al}_2\text{O}_3$  and 0.1%  $\text{V}_2\text{O}_5$ .<sup>15</sup>

<sup>14</sup> J. Lambe and R. Ager, Rev. Sci. Instr. 30, 599 (1959).

<sup>15</sup> Prepared by Linde Company.

The results presented here are essentially the same as those of Zverev and Prokhorov,<sup>16</sup> but some points should be noted. They reported following the spectrum up to an angle of about  $60^\circ$  between the  $c$  axis and the magnetic field. Our measurements were made to  $80^\circ$ . For larger angles the spectrum fell beyond the magnetic field range of the Varian 12-inch magnet with  $5\frac{1}{4}$  inch gap. Figure 1 shows the spectra for  $0^\circ$ , 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 is observed at  $77^\circ\text{K}$  and  $300^\circ\text{K}$ . 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  $\Delta M = 2$ .

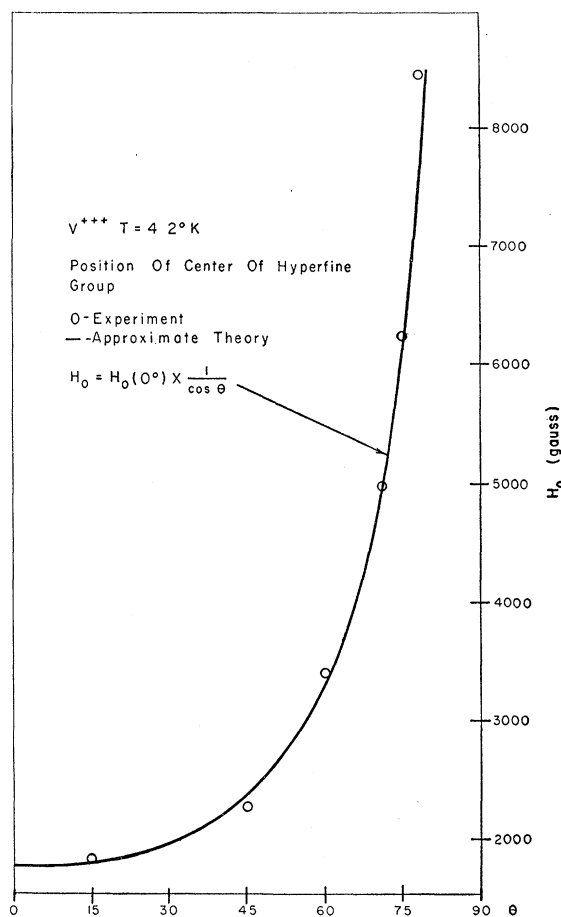


FIG. 2. Angular dependence of the center of hfs group of  $V^{+++}$ .

<sup>16</sup> G. M. Zverev and A. M. Prokhorov, J. Exptl. Theoret. Phys. (U.S.S.R.) 34, 1023 (1958) [translation: Soviet Phys.-JETP 7, 707 (1958)].

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

$$\mathcal{H} = g_{11}\beta H_z S_z + g_{\perp}(H_x S_x + H_y S_y) + D(S_z^2 - \frac{2}{3}) + E(S_x^2 - S_y^2) + AI_z S_z + B(I_x S_x + I_y S_y). \quad (1)$$

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

$$\mathcal{H} = g_{11}\beta H_z S_z + AS_z I_z, \quad (2)$$

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

$$h\nu = 2g_{11}\beta H \cos\theta + 2Am,$$

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

$$H_m = (\frac{1}{2}h\nu - Am) / (g_{11}\beta \cos\theta). \quad (3)$$

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

$$h\nu = (g_{11}\beta H \cos\theta + Am)$$

$$\times \left[ 2 - \frac{g_{\perp}^2 \beta^2 H^2 \sin^2\theta + B^2 \{I(I+1) - m^2\}}{D^2} + \frac{E^2}{(g_{11}\beta H \cos\theta + Am)^2} \right] - \frac{B^2 m}{D} \left[ 1 - \frac{E^2}{4g_{11}^2 \beta^2 H^2 \cos^2\theta} \right].$$

Another characteristic seen from Fig. 1 is the equal spacing of 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  $M = \pm 1$  are not connected to each other by the term  $B(I_x S_x + I_y S_y)$ .

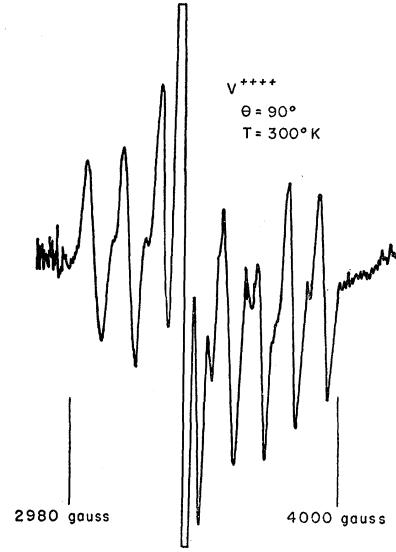


FIG. 3. Spin resonance spectrum of  $V^{4+}$  in  $\alpha\text{-Al}_2\text{O}_3$ , at room temperature for  $\theta = 90^\circ$ . The strong line near the center is due to a trace of iron impurity.

This term does connect the  $M = \pm 1$  levels with  $M = 0$ , but the latter is about  $8 \text{ cm}^{-1}$  away.<sup>12</sup>

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

In examining the spin resonance of our crystals at  $300^\circ\text{K}$ , a group of lines were noted in the region of  $g \approx 2$ . Closer study revealed that there are 8 such lines separated by  $140 \text{ gauss}$  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  $\text{Cr}^{3+}$ .

The spectrum of 8 lines is found in materials as received. The absorption strength is not increased by

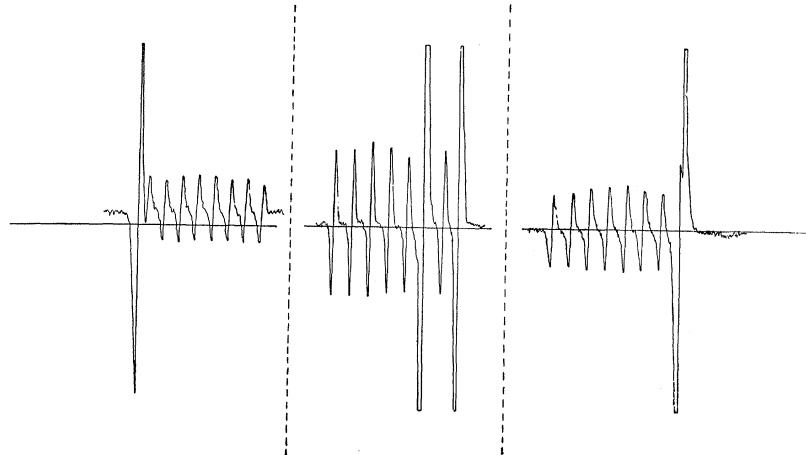


FIG. 4. Spin resonance spectrum of  $\gamma$ -irradiated green sapphire at  $K$ -band frequencies near  $0^\circ$ . The strong lines are due to chromium and iron impurities. At  $0^\circ$ , the low-field fine structure group comes at a field of about  $3500 \text{ gauss}$  below the main group.

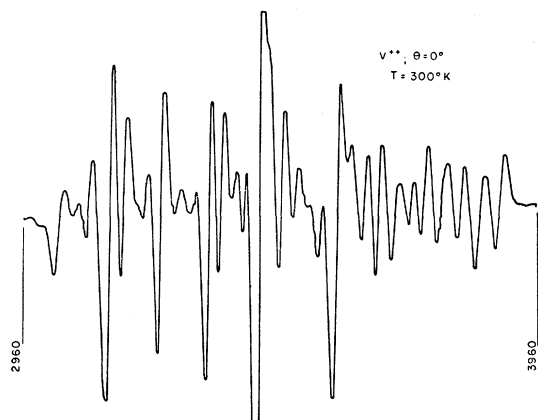


FIG. 5. Spin resonance spectrum of x-irradiated vanadium sapphire near the  $M = \frac{1}{2}$  and  $\frac{3}{2}$  cross-over. The trace was taken with an X-band spectrometer operating at 9400 Mc/sec.

x irradiation. The concentration is estimated to be about  $10^{16}/\text{cm}^3$ . Observations seem to show that both the  $g$ -value and the hfs constant are isotropic, having the values  $g_{11} = g_{\perp} \cong 1.97$  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<sup>17</sup> that the hfs constant  $A$  for  $V^{4+}$  is greater than that of  $V^{3+}$ .

### C. $V^{2+}$

This was first detected in green sapphire, subjected to gamma-irradiation, and brief comments have been made on previous occasions. Upon gamma or x irradiation, a spectrum consisting of three groups of 8 lines is produced as shown in Fig. 4. The presence of three groups shows that the electron spin is  $\frac{3}{2}$ , and the 8 lines of equal intensity, indicate that the nuclear spin

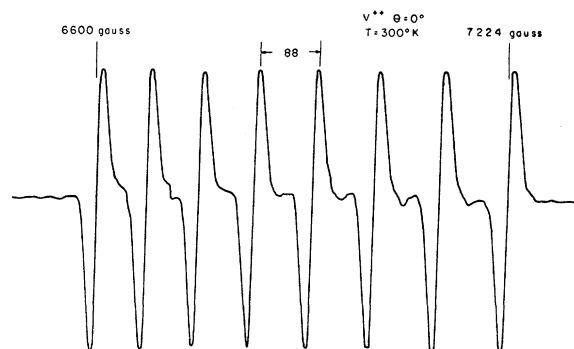


FIG. 6. Spin resonance spectrum of same sample as in Fig. 5 but at a higher magnetic field.

<sup>17</sup> N. M. McConnell, W. W. Porterfield, and R. E. Robertson, J. Chem. Phys. 30, 442 (1959).

of the paramagnetic center is  $\frac{7}{2}$ . Consequently, the spectrum is due to  $V^{4+}$  which is isoelectronic with  $\text{Cr}^{3+}$ . The nuclear spin of  $\text{Co}^{59}$ , another possible impurity in sapphire, is also  $\frac{7}{2}$ , but the  $\text{Co}^{4+}$  spectrum can be readily distinguished from that of  $V^{4+}$ . For according to Geusic,<sup>18</sup> the  $\text{Co}^{4+}$  spectrum in green sapphire is detected only near liquid helium temperatures and the hfs coupling constants  $A$  and  $B$  are 31.0 and 42.0 gauss, respectively. This is in contrast to the  $V^{4+}$  spectrum which is detected at room temperature and which has an isotropic coupling constant of 88 gauss. Furthermore,  $g = 1.98$  and the zero-field splitting is about 9.8 kMc/sec. Figures 5 and 6 show the typical spectra obtained at X-band frequencies for  $\theta = 0^\circ$ . The spectrum is complex near magnetic field of about 3300

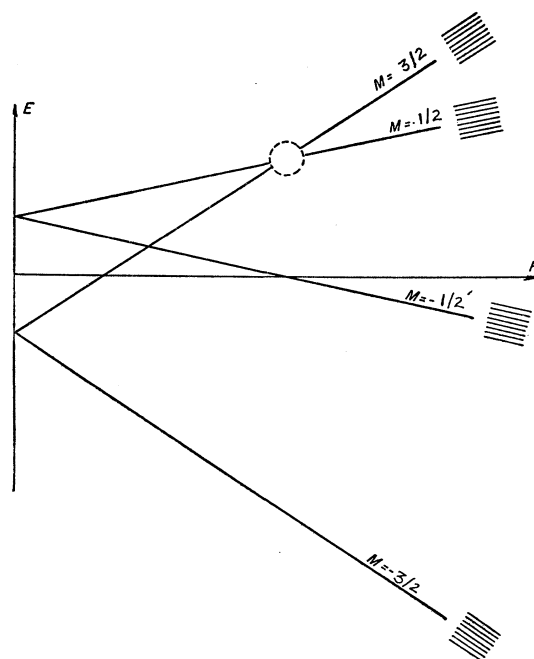


FIG. 7. Energy level diagram for  $\theta = 0^\circ$ ,  $S = \frac{3}{2}$  and  $I = \frac{7}{2}$ . The cross-over point for levels  $M = \frac{1}{2}$  and  $\frac{3}{2}$  is indicated by a circle.

gauss (see Fig. 5) because the levels  $M = \frac{1}{2}$  and  $\frac{3}{2}$  cross 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. 6.

The spin-Hamiltonian is given by

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

in which it is assumed that  $g$  and  $A$  are isotropic and that the sign of  $D$  is negative, as in  $\text{Cr}^{3+}$ . 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. 7. The energy level diagram is simple, except in the region

<sup>18</sup> J. E. Geusic, Bull. Am. Phys. Soc. 4, 261 (1959).

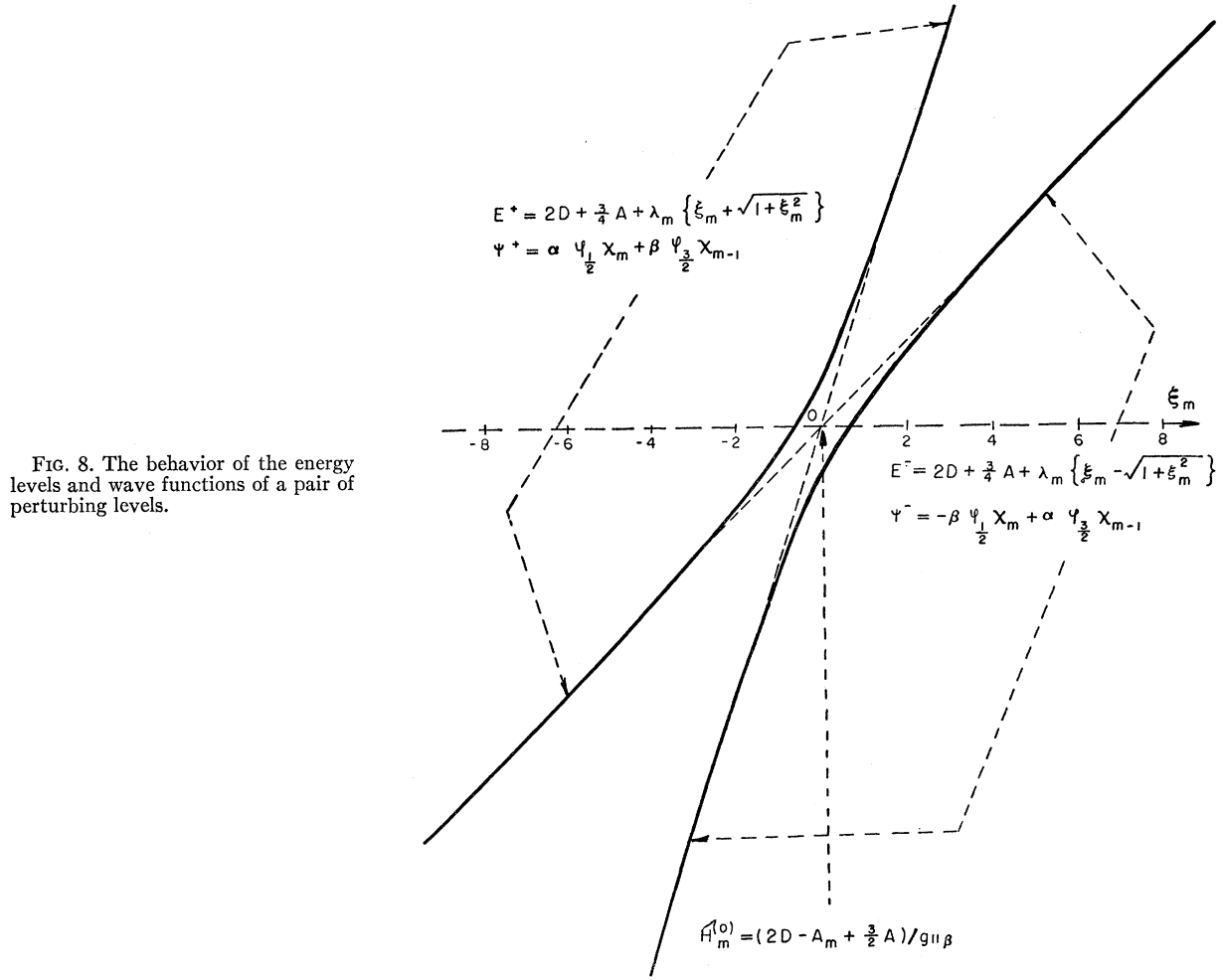


FIG. 8. The behavior of the energy levels and wave functions of a pair of perturbing levels.

of  $H \sim 0$  and  $2D/g\beta$ , the latter being marked by a circle. Figure 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

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

and

$$\xi_m = g_{||}\beta\Delta H_m/\lambda_m,$$

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,

$$N^2 \equiv 2[1 + \xi_m^2 + \xi_m(1 + \xi_m^2)^{1/2}],$$

$$\alpha \equiv 1/N,$$

and

$$\beta \equiv [\xi_m + (1 + \xi_m^2)^{1/2}]/N. \quad (6)$$

The effect of this admixing of wave functions at the cross-over point is to produce a spectrum consisting of more than 8 lines predicted by a simple theory. The

theoretically expected spectra for five different resonance frequencies are shown in Fig. 9. Note that the spectrum becomes progressively simpler as the resonance frequency is moved away from  $2D + \frac{3}{2}A$ . As indicated already the spectrum is also complex near zero magnetic field, because of the near degeneracy of the  $M = \pm \frac{1}{2}$  states. However, it should be noted that

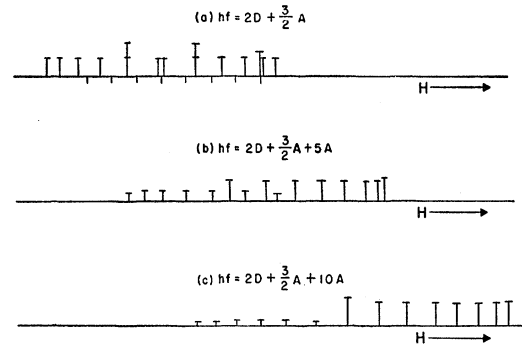


FIG. 9. Calculated spectrum for different resonance frequencies.

TABLE I. Experimentally observed hyperfine splittings of various vanadium ions.

Material	Valence	$A \times 10^4 \text{ cm}^{-1}$	State	References
$\text{V}(\text{NH}_4)_2 \cdot 6\text{H}_2\text{O}$	$\text{V}^{++}$	88	Crystal	a,b
$\text{K}_4\text{V}(\text{CH}_3)_2 \cdot 3\text{H}_2\text{O}$	$\text{V}^{++}$	56	Crystal	c
$\text{V}(\text{C}_5\text{H}_5)_2$	$\text{V}^{++}$	26	Benzene solution	d
$\text{VO}(\text{C}_5\text{H}_5)_2$	$\text{V}^{++}$	71	Benzene solution	d
$\text{VOSO}_4$	$\text{V}^{+++}$	114	Solution	e,f
Vanadium (IV)-cupferron chelate	$\text{V}^{++}$	...	Solution	g
$\text{MgO}:\text{V}$	$\text{V}^{++}$	76	Single crystal	h,i
Chelate vanadylacetyl-acetone	$\text{V}^{+++}$	107	Solution	j
Vanadyl eteoporphyrin I	$\text{V}^{+++}$	52	Benzene solution	k,l

(B = 159)

<sup>a</sup> B. Bleaney, D. J. E. Ingram, and H. E. D. Scovil, Proc. Phys. Soc. (London) **A64**, 39 (1951).<sup>b</sup> C. Kikuchi, M. H. Sirvetz, and V. W. Cohen, Phys. Rev. **92**, 109 (1953).<sup>c</sup> J. M. Baker and B. Bleaney, Proc. Phys. Soc. (London) **A65**, 952 (1952).<sup>d</sup> See reference 17.<sup>e</sup> G. E. Pake and R. H. Sands, Phys. Rev. **98**, 266 (1955).<sup>f</sup> G. E. Pake, I. Weissmann, and J. Townsend, Discussions Faraday Soc. **19**, 147 (1955).<sup>g</sup> M. M. Weiss, R. I. Walter, O. R. Gilliam, and V. W. Cohen, Bull. Am. Phys. Soc. **2**, 31 (1957).<sup>h</sup> See reference 13.<sup>i</sup> W. Low, Phys. Rev. **101**, 1827L (1956).<sup>j</sup> W. A. Anderson, and L. H. Piette, J. Chem. Phys. **30**, 591 (1959).<sup>k</sup> D. E. O'Reilly, J. Chem. Phys. **29**, 1188 (1958).<sup>l</sup> D. E. O'Reilly, J. Chem. Phys. **30**, 591 (1959).

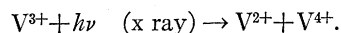
the energy levels are simple where the levels  $M = -\frac{1}{2}$  and  $\frac{3}{2}$  cross over ( $H \sim D/g\beta$ ) if both the crystalline field and hyperfine interaction have axial symmetry.

Some details of the x-ray process were noted. It is seen that the x-ray production of  $\text{V}^{2+}$  saturated quite rapidly. After about 3 hours of irradiation, no significant increase of  $\text{V}^{2+}$  was observed. There was a slight relaxation of the  $\text{V}^{2+}$  concentration immediately after x-irradiation, but thereafter the concentration remained essentially constant at 300°K. The  $\text{V}^{2+}$  ions, however, can be bleached by heating to 700°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°K. It is found that  $\text{V}^{2+}$  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  $\text{V}^{2+}$  to  $\text{V}^{4+}$  increases as might be expected on the basis of the charge mismatch with the lattice. The  $\text{V}^{4+}$  should tend to pull in the electron charge cloud more strongly than  $\text{V}^{2+}$ .  $\text{V}^{3+}$  is then roughly in between. The hfs coupling constants, are a measure of the electron charge density at the  $\text{V}^{51}$  nucleus.

#### IV. RADIATION PROCESS

The production of  $\text{V}^{2+}$  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



However, this process is ruled out because there is no apparent increase in the  $\text{V}^{4+}$  signal upon irradiation and also the final  $\text{V}^{2+}$  signal is much larger than the  $\text{V}^{4+}$  signal. Furthermore, the resonance absorption

signals of the trace impurities,  $\text{Cr}^{3+}$  and  $\text{Fe}^{3+}$ , were carefully examined, but no observable effects due to x rays were detected. We are thus led to the assumption that some unknown center in the sapphire can yield an electron which can be trapped at  $\text{V}^{3+}$  to give  $\text{V}^{2+}$ . Since a fairly high concentration of  $\text{V}^{2+}$  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  $\text{Cr}^{3+}$  and  $\text{V}^{3+}$  to sapphire increases the sensitivity to x-ray coloration.<sup>19</sup> In the case of  $\text{V}^{3+}$ , it may be that by trapping out electrons, the  $\text{V}^{3+}$  tend 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.

#### V. DISCUSSION

In contrast to manganese, which has been studied in a variety of host materials, liquid or solid,<sup>20</sup> the spin resonance investigations of vanadium have been limited so 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 almost always divalent, whereas, with vanadium the oxidation state can be readily altered by ionizing radiation.

During the course of this investigation, it occurred to us that it might be possible to obtain information about the nature of atomic displacements produced by

<sup>19</sup> J. H. Mathews and J. Lambe, Bull. Am. Phys. Soc. **4**, 284 (1959).

<sup>20</sup> See for example, J. S. Van Wieringen, Discussions Faraday Soc. **19**, 118 (1955); and O. Matsumura, J. Phys. Soc. (Japan). **14**, 108 (1959).

nuclear radiation by examining the spin resonance spectrum of ruby near the first cross-over, 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 spin-Hamiltonian will contain a rhombic field term. This will have the effect of admixing the states  $S_z = -\frac{1}{2}$  and  $\frac{3}{2}$ . 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.

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### Surface Impedance of a Superconductor in a Magnetic Field\*

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Explicit expressions for the static magnetic field variation of the surface impedance in a superconductor are derived. Detailed consideration is given to the two limiting cases of the classical skin effect and of the extreme anomalous skin effect, with the static field either parallel or perpendicular to the rf current. The transport calculation is carried out for a two-fluid model with the supercurrent obeying the London equation and the normal current following a nonlocal relation. It is suggested that a comparison between theory and the experimental data yields information on the energy band structure of normal electrons in the superconducting state.

#### I. INTRODUCTION

EXPERIMENTAL investigations of the surface impedance of superconducting tin in a static magnetic field have been reported by Pippard at 9.4 kMc/sec<sup>1</sup> and by Spiewak at 1 kMc/sec.<sup>2</sup> In particular, the observation at 1 kMc/sec of a decrease in both the surface resistance,  $R$ , and the surface reactance,  $X$ , with increasing static magnetic field,  $H$ , has not been explained. Nor has it been understood why the relative signs of  $[R(H) - R(0)]$  and  $[X(H) - X(0)]$  are dependent on temperature, on the magnitude and orientation of  $H$  relative to the rf magnetic field, on crystal-line orientation, and on the rf frequency. In this paper, an attempt is made to achieve an understanding of these experimental results and to consider the type of information that can be obtained on the energy band structure of the superconducting metal from studies of the surface impedance in a static magnetic field.

Studies of the anomalous skin effect in a magnetic field have provided a powerful tool for the investigation of the band structure in normal metals.<sup>3</sup> Important information has been obtained by cyclotron resonance experiments on the effective masses of the electrons and

on the shape of the Fermi surface in Sn,<sup>4,5</sup> Cu,<sup>4,6</sup> and Bi.<sup>7</sup> Since the magnetic field dependence of the surface impedance differs as to whether the metal is in the normal or superconducting state, the information obtained through these studies is different for the two cases.

In this paper, the surface impedance of a superconductor in a magnetic field is calculated by extending the two-fluid model first introduced by Maxwell, Marcus, and Slater<sup>8</sup> to treat the zero field problem. Specular reflection boundary conditions are applied to the case of a superconductor in a magnetic field following the Serber treatment of the zero field superconducting surface impedance problem<sup>9</sup> and the Mattis and Dresselhaus treatment of the normal metal in a magnetic field.<sup>10</sup> There are two principal reasons for choosing this approach. Its relative simplicity permits an explicit determination of the field variation for both  $R$  and  $X$ . Since at frequencies,  $\nu < 10$  kMc/sec the electromagnetic propagation does not directly involve

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