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Technical Report

VANADIUM SOLID-STATE CHEMISTRY BY PARAMAGNETIC RESONANCE

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ABSTRACT

A brief review of the electron spin resonance properties of vanadium in crystalline solids, such as in sapphire, Tutton salt, and magnesium oxide, is given.

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I. INTRODUCTION

In an earlier report,¹ it was suggested that the electron spin resonance (ESR) technique can be developed into an analytical tool for the study of the changes in oxidation states brought about by high energy radiations. As the ionizing radiations proceed through the crystalline lattice, some of the energy is inevitably absorbed, resulting in the release of electrons through the photoelectric and Compton processes, or even by the pair production process, if the incident gamma radiation is sufficiently energetic. The electrons thus freed will for a short period of time move about in the solid and may eventually become trapped at metastable centers, resulting in ions with rather unusual valence states. Or possibly, the incident radiation may result in the breaking of electron bonds, again leading valence states not ordinarily found. Such changes in solids, however, can be expected to be small, so that the detection of the effects may fall outside range of standard chemical techniques. The purpose of this report is to indicate how ESR can be used to identify traces of chemical species produced by high energy radiations, and to indicate the progress that has been made in our laboratory subsequent to the suggestion.

Also, as indicated in our earlier report, vanadium is particularly well suited for the study of electron transfer and trapping processes in solids. The reason for this stems from the fact that vanadium is essentially isotopically pure V^{51} (V^{51} , 99.7%; V^{50} , 0.25%) whose nuclear spin is $7/2$ so that the ESR spectrum will have the characteristic 8 line structure. This hfs can then be used to identify vanadium. Furthermore, as the valence changes, the electron spin of the ion will change, and the electron spin of the vanadium in question can be ascertained from the angular dependence of the fine structure spectra. Combined with the ease of identification, there is the additional property that the valence state of vanadium can be changed easily. Thus it becomes possible to study the properties of the different valence states in the same host lattice.

In undertaking the present report, we wish to thank Dr. R. Borcherts and Mr. H. Azarbayejani for technical assistance, and for the financial support provided by the Reynolds Aluminum Company through the Michigan Memorial Phoenix Project.

II. GENERAL PRINCIPLES

We shall first discuss vanadium sapphire in order to illustrate the general principles. As indicated above, the nuclear spin of V^{51} is so that the ESR spectrum, regardless of the valence state will consist of 8 lines, of about equal intensity and spacings. The spacing between the components, known as the hyperfine coupling constant will vary from crystal to crystal, and from one valence state to another. In general, however, the separations fall in the range from about 70 to 150 gauss. What distinguishes one vanadium valence state from another is the number of such groups of 8 lines and the angular dependence of the groups. The electron configuration and the associated electron spin of the vanadium paramagnetic species that have been observed in sapphire are as follows:

Ion	Electron Configuration	Electron Spin
V^{4+}	3d	1/2
V^{3+}	3d ²	1
V^{2+}	3d ³	3/2

Consider first V^{4+} . The electron spin is 1/2, so that ESR absorption spectrums should consist of a single group of 8 lines. The ESR spectrum of this vanadium state in sapphire is shown in Figure 1. The lines are very weak. The spectrum seems to be isotropic with $g = 1.97$ and $A = B = 1.32 \times 10^{-4} \text{ cm}^{-1}$. This spectrum is observed in vanadium sapphire, prepared from a powder mixture containing 0.1% vanadium pentoxide.

Consider next V^{3+} . Vanadium in sapphire is considered to be in Al^{3+} substitutional sites, so that V^{3+} in corundum was first observed by Zverev and Prokhorov,² and their ESR results constitute a confirmation of the deductions from magnetic susceptibility measurements by Siegert³ and by van der Handel and Siegert.⁴ Subsequently, further confirmatory optical investigations have been reported by Pryce and Runciman.⁵

Theory and experiment indicate that the V^{3+} ground state, whose spin is 1, consists of two levels, one for $M = 0$ and the other for $M = \pm 1$ is studied. The ESR spectrum at X—consists of a single group of 8 lines, with lines very nearly equally spaced, with separation of about 114 gauss when the magnetic field is along the crystal C-axis. The spectrum, furthermore, is observed at 4.2°K, but not at 78°K. Also at liquid helium II temperatures, the intensities of lines are reduced, stemming from the depopulation of the magnetic $M = \pm 1$ state. A typical spectrum and its angular dependence are shown in Figures 2 and 3. An interesting fact is that the hfs. components are about 110 gauss apart, or about $1.02 \times 10^{-4} \text{ cm}^{-1}$. This value is smaller than that for V^{4+} . Information on g- and B are still lacking.

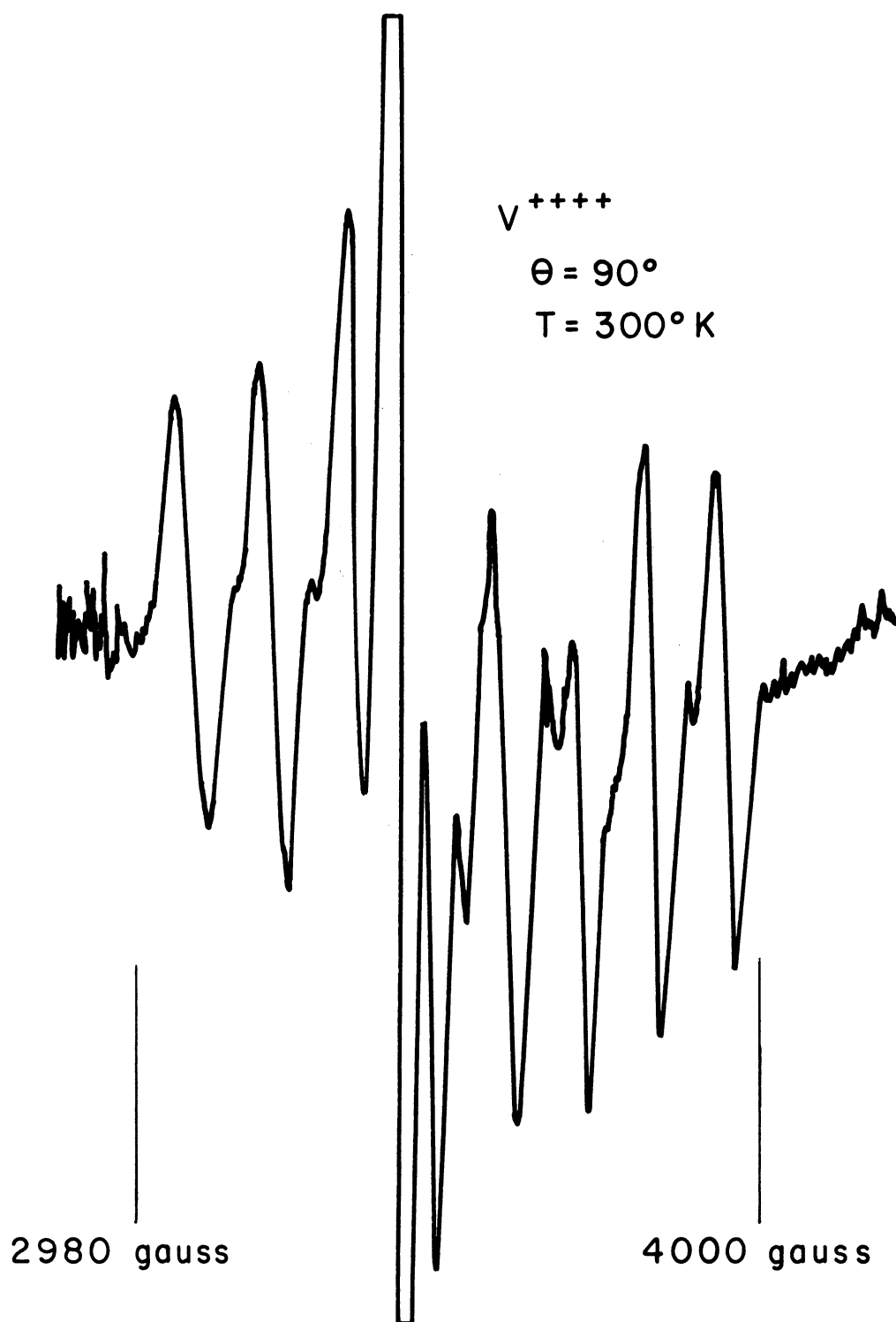


Figure 1. ESR spectrum of V^{4+} in sapphire.

V^{+++} $\theta = 0^\circ$
 $T = 4.2^\circ K$

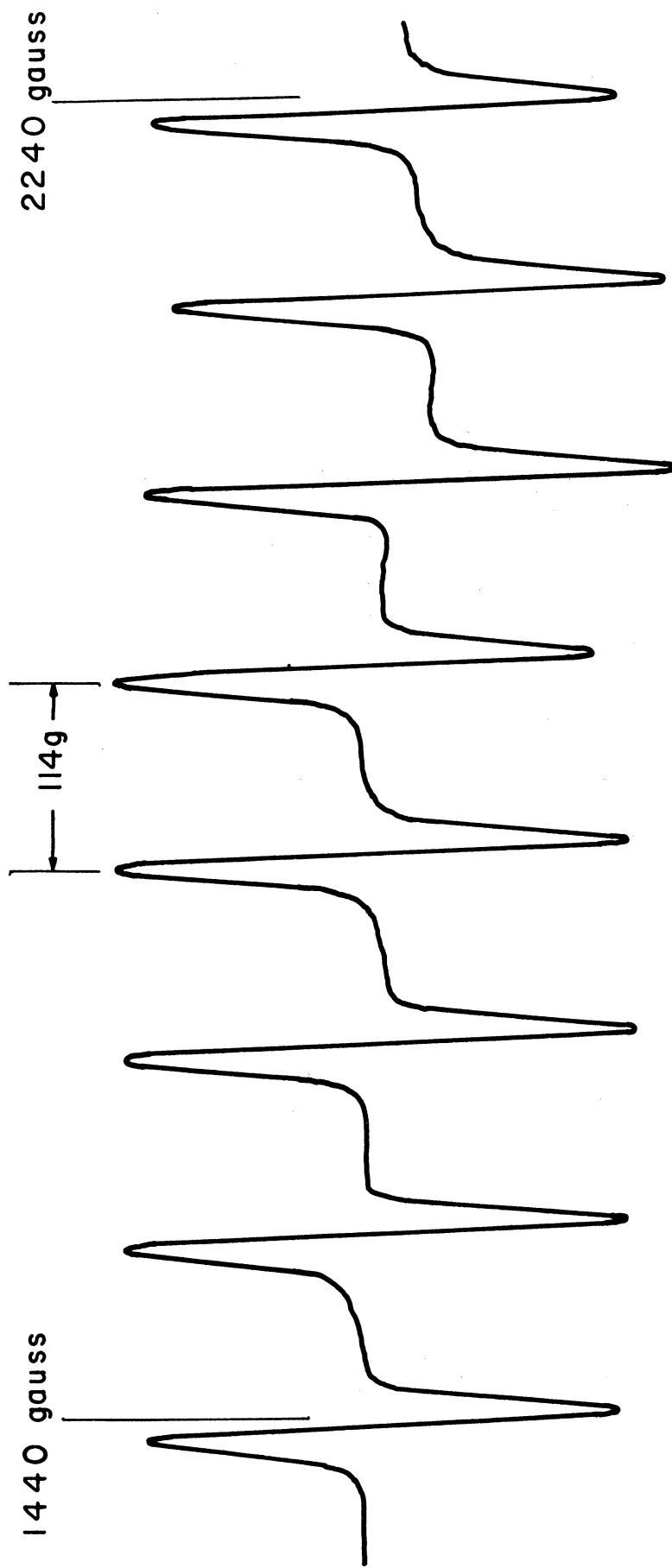


Figure 2. ESR spectrum of V^{+++} in sapphire.

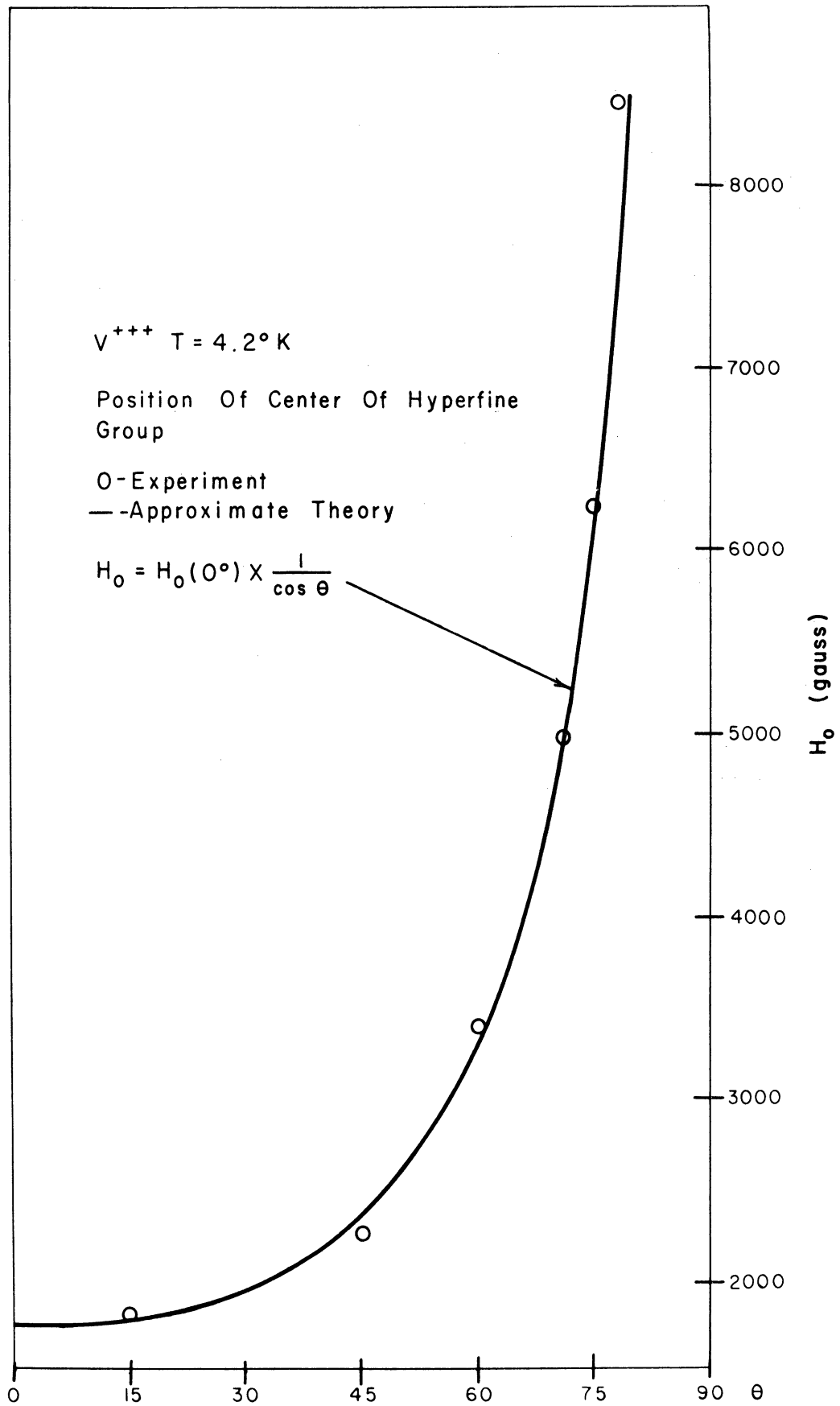


Figure 3. Angular dependence of ESR spectrum of V^{3+} in sapphire.

The ESR spectrum for V^{2+} can be produced by subjecting sapphires containing vanadium to ionizing radiations. Figure 4 gives the spectrum obtained from the so-called green sapphire, which contains a small amount of vanadium and cobalt. This spectrum was taken at K-band frequencies. There are three groups of 8 lines, indicating that the electron spin of the center is $3/2$, and the characteristic 8 line structure shows that it is due to vanadium. The strong lines accompanying the vanadium lines are due to Cr^{3+} which is isoelectronic with V^{2+} . The relative positions of the V^{2+} and Cr^{3+} lines indicate that the zero-field splitting, $2D$, for V^{2+} is somewhat smaller than that of Cr^{3+} . Our measurements indicate that $2D(V^{2+}) = 9.8$ Kmc/sec., and is to be compared to $2D(Cr^{3+}) = 11.5$ Kmc/sec. Also $g = 1.98$. For Cr^{3+} , $g = 1.97$.

A question raised by this study is the origin of the electrons responsible for the conversion of V^{3+} to V^{2+} . A study of the growth of the intensity of V^{2+} lines relative to V^{4+} seem to preclude the possibility that an electron is transferred from one vanadium ion to another. Furthermore, the saturation intensity of the V^{2+} spectrum seems to vary from sample to sample. However, to date, we have not been able to determine the factors that contribute to the stability of the V^{2+} and/or V^{4+} ion.

The practical reason motivating our investigations is that the stabilization of specific valence state is important in a program for the development of new materials for solid-state devices. For vanadium sapphire, V^{2+} is isoelectronic with Cr^{3+} , so that a properly prepared vanadium sapphire could be a material useful for masers and lasers, particularly in the presence of ionizing radiations. Figure 5 summarizes the present known information^{6,7} about isoelectronic ions V^{2+} , Cr^{3+} and Mn^{4+} in Al_2O_3 .

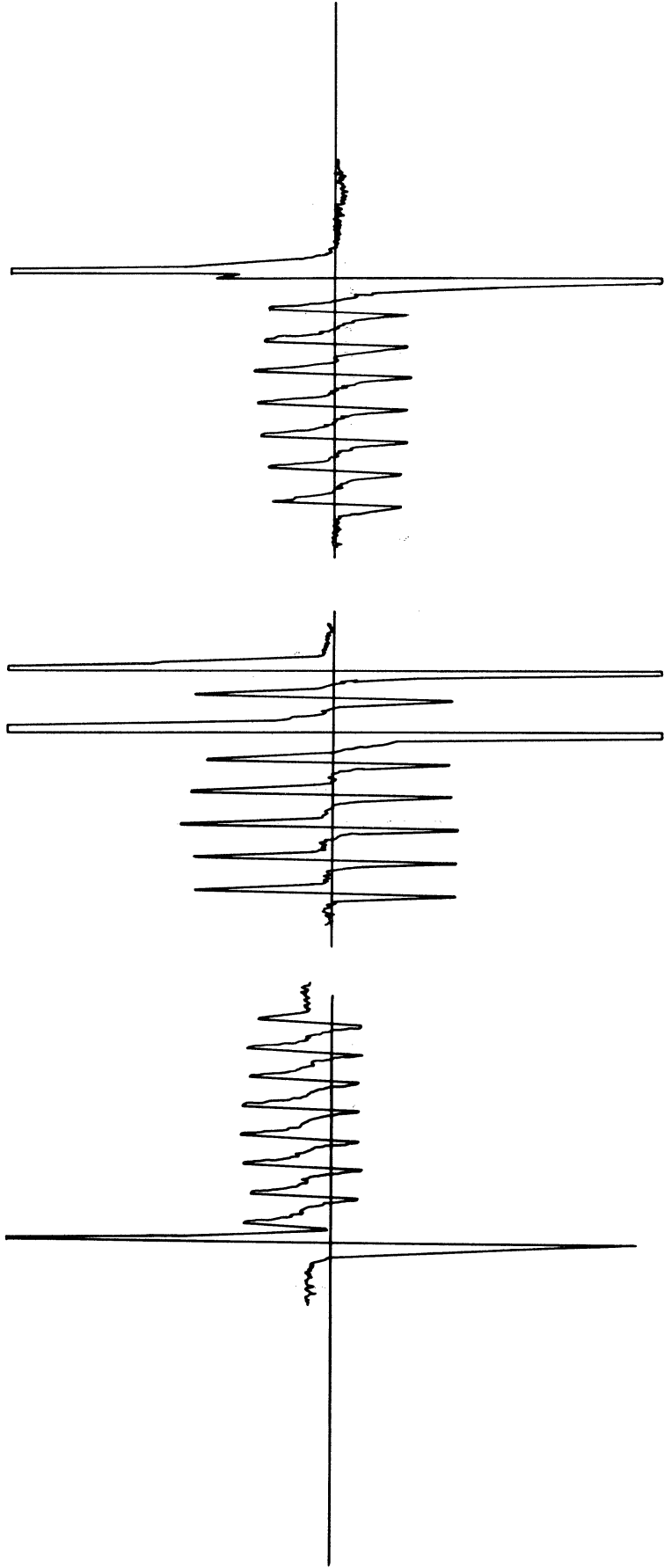


Figure 4. ESR spectrum for V^{2+} , in green sapphire at k-band.

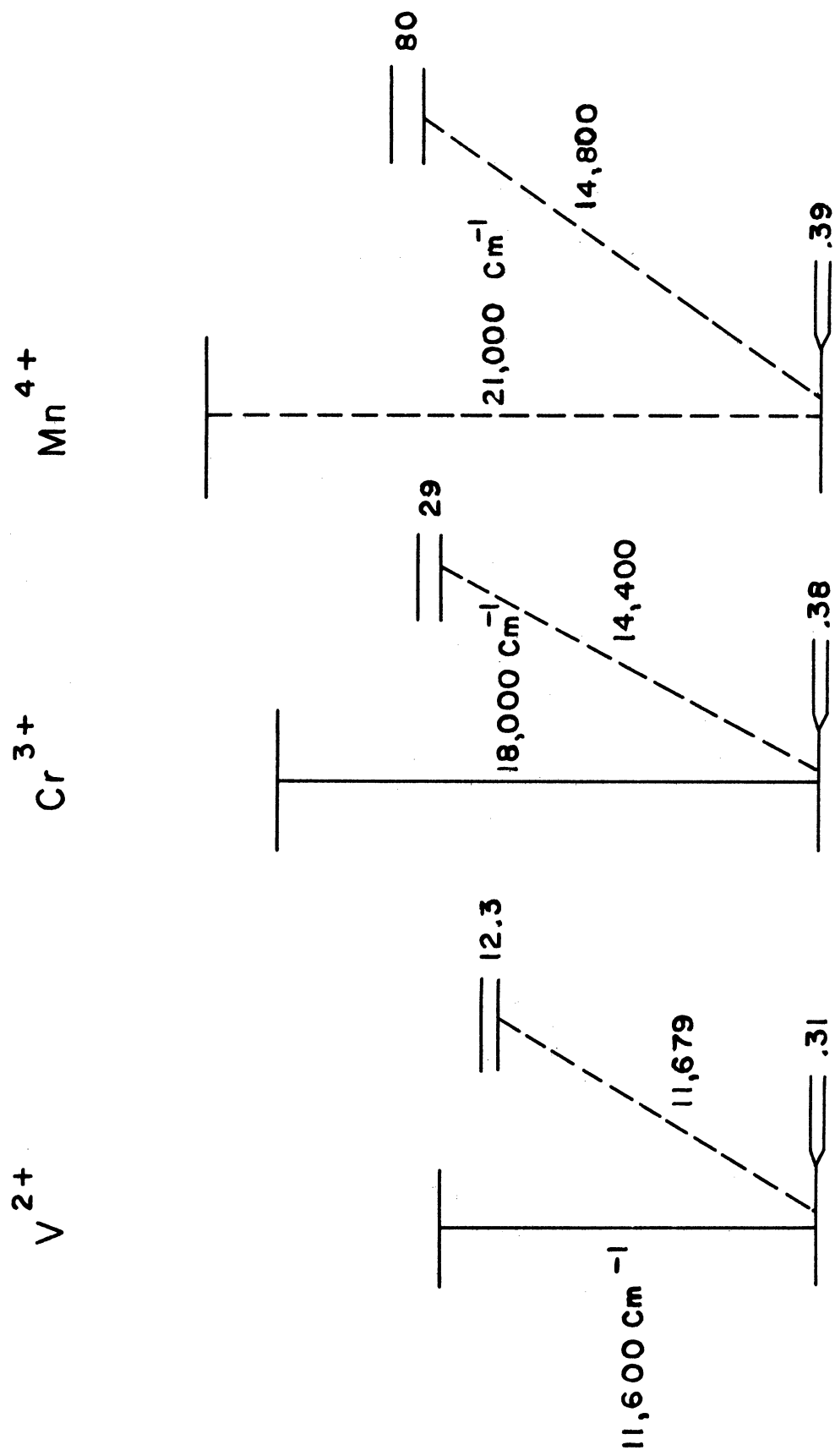


Figure 5. Energy levels of V^{2+} , Cr^{3+} , and Mn^{4+} .

III. VANADIUM IN TUTTON SALTS

After a few attempts to study vanadium chemistry in sapphire by purchasing single crystals of sapphires...at considerable cost... it became apparent that a direct attack on the problem would not yield useful results. Consequently, our attention was turned to vanadium in Tutton salts, because such crystals can be grown in our laboratory without difficulty. The vanadyl ion, VO^{++} , can be readily introduced into the zinc ammonium Tutton salt, and furthermore, our preliminary studies showed that the vanadyl vanadium can be converted to vanadous vanadium.

It should be noted that randomly oriented VO^{++} has been studied by a number of investigators. Among the first to make a study of VO^{++} in frozen aqueous solution was Kozyrev.⁸ Investigation of VO^{++} radicals on various absorbers was carried out by Faber and Rogers;⁹ vanadyl porphyrins by Roberts and Koski;¹⁰ vanadyl etioporphyrins dissolved in benzene and high viscosity oil by O'Reilly;¹¹ and vanadyl ions in aqueous, acetone, and ether solutions by Pake and Sands.^{12,13} Much of the interest in the vanadyl ion appears to have been stimulated by oil companies who are concerned with the relatively high concentration of vanadyl vanadium in crude oil. Aside from being important from the standpoint of the technology of refinery operation, there appears to be some geologic interest, because the presence of vanadium in oil casts some light on the nature of organisms involved in the production of petroleum.¹⁴

Despite this relative wealth of studies of randomly oriented VO^{++} in solutions, it appears that very little study has been made of oriented VO^{++} . Brief comments on tetravalent vanadium occur in the paper by Hutchison and Singer,¹⁵ and some unpublished investigations by W. B. Gager¹⁶ exist. Consequently, we have undertaken a systematic study of VO^{++} radicals in the Tutton salts, to determine whether vanadium occurs as VO^{++} or V^{4+} in these crystals, and to study the relation of V^{++} produced by ionizing radiation to that grown directly into the crystal. Our studies reveal that VO^{++} maintain its identity in these crystals, and that following irradiation, the vanadyl vanadium is converted to V^{++} that is indistinguishable from those grown directly into the crystal lattice. The basis for this remark is that the vanadous vanadium, V^{2+} produced by irradiation from VO^{++} in the Tutton salt, has within experimental error the same spin - Hamiltonian parameters and the same orientation of crystalline electric field as those of V^{++} Tutton salt grown from aqueous solution. While our investigations were in progress, the paper by Ballhausen and Gray¹⁷ appeared. We feel that our experimental results constitute a confirmation of the validity of their theoretical calculations.

The top two traces in Figure 6 give the ESR spectra of a single Tutton salt crystal containing a small concentration of VO^{2+} radical before and after x-irradiation. The VO^{2+} spectrum before irradiation is actually quite complex, due to the fact that there are two non-equivalent sites in the unit cell and to the observed three orientations of the VO^{2+} axis. However, if the crystal is properly oriented, the spectrum simplifies to the 8 lines shown at the top. The second trace shows the effect of x-irradiation. New groups of 8 lines occur, characteristic of vanadium, and by inspection it is seen that there are three such groups, suggesting that V^{2+} is produced by X-rays. The bottom trace is included to show that the V^{2+} ions produced by X-rays are identical to those obtained from the VO^{2+} doped Tutton salt by electrolytic reduction. A further check is obtained by growing a VO^{2+} crystal using as a seed a Tutton salt crystal containing V^{2+} . The V^{2+} spectrum produced by X-rays is found to coincide exactly with the V^{2+} spectrum present before x-irradiation.

To interpret these experimental results, let us consider the structure of the site occupied by VO^{2+} or V^{2+} . The crystal structure of Tutton salt is quite complex. However, for our purposes, we need to consider only the water molecules surrounding the Zn^{++} sites. X-ray diffraction studies indicate that each Zn^{++} site is surrounded by 6 ligand water molecules, with the oxygens lying closest to the Zn^{++} ions, as shown in Figure 7.

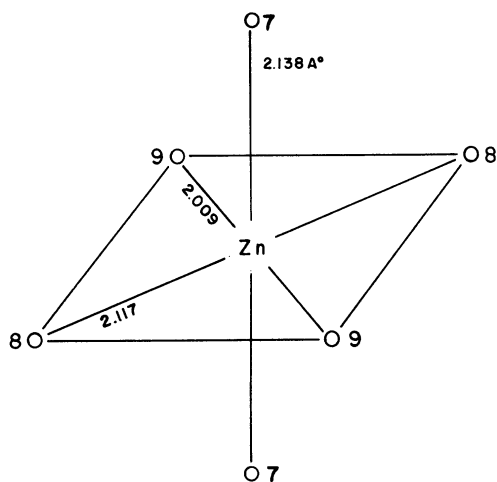


Figure 7. Simplified schematic of the Zn^{++} site in Tutton salt.

According to the recent X-ray diffraction analysis by H. Montgomery, the bond distances and angles are as given in Table I.

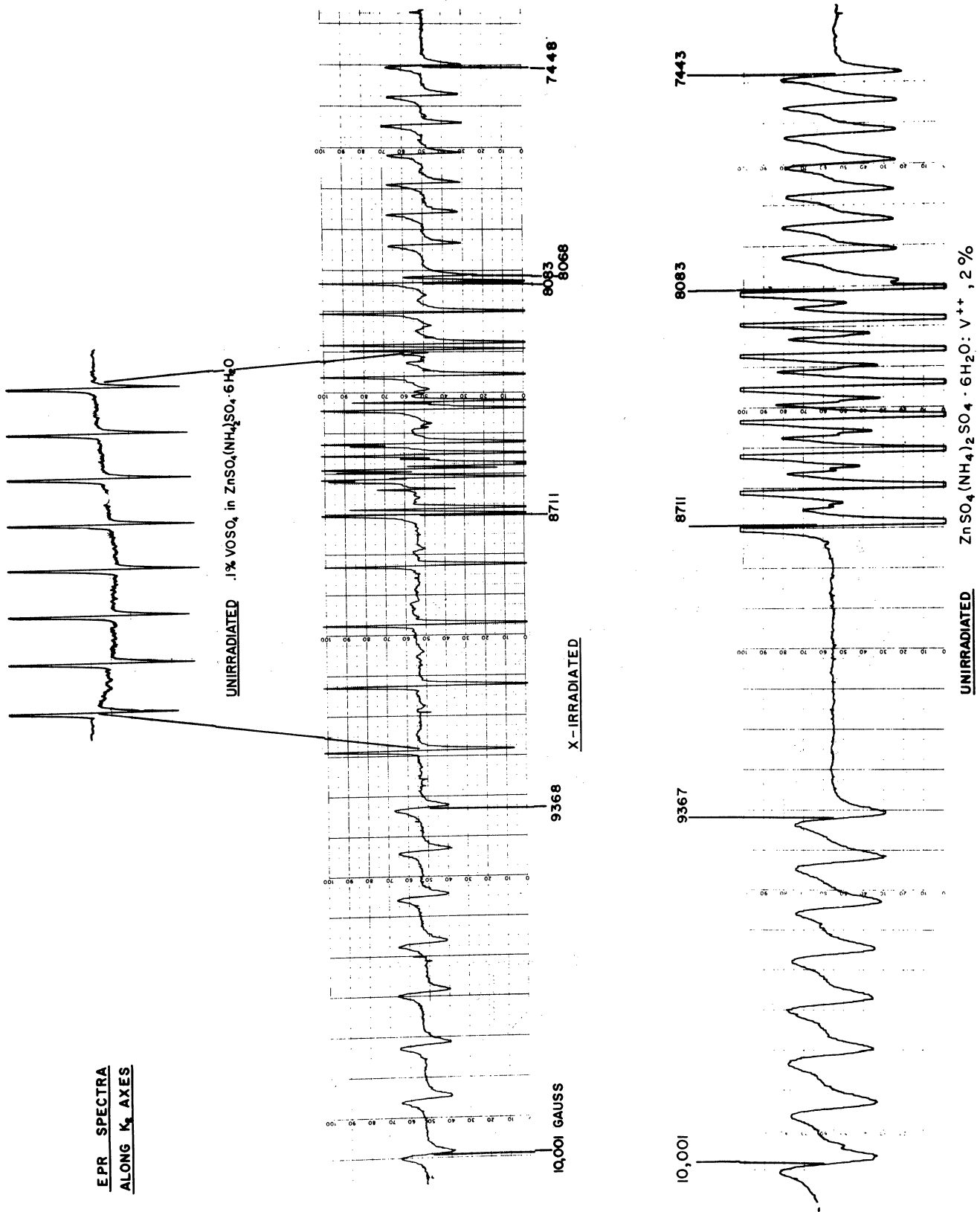


Figure 6. ESR spectra of VO_2^+ and V^{2+} in Tutton salt.

TABLE I

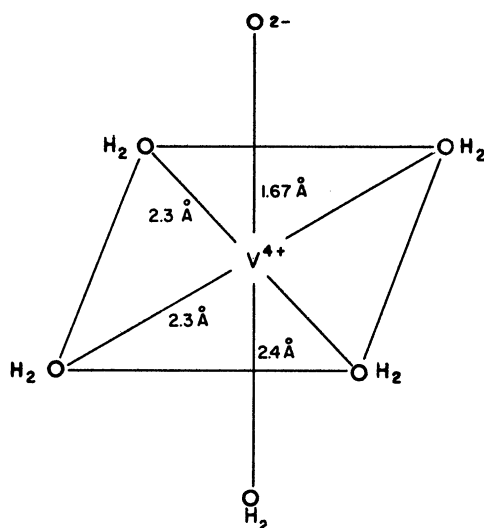
Zn⁺⁺ - O⁻⁻ BOND DISTANCES IN TUTTON SALT

	<u>Bond Distance</u>	<u>θ</u>	<u>ϕ</u>
Zn-O ₇	2.138	50.2	79.5
Zn-O ₈	2.117	49	-71.5
Zn-O ₉	2.066	65	4

The angle θ is the polar angle measured from the crystal b-axis, and ϕ is the azimuthal angle measured in the crystal ac-plane from the a-axis.

Suppose now that a V²⁺ ion is substituted for Zn²⁺ ion, without any distortion. The V²⁺ ion will be subjected to the crystalline electric field due to the 6 ligand water molecules. Both the hydrogens and oxygens will contribute to this field, but clearly the major contribution will come from the oxygens, because they lie closest to the V²⁺ ion. And furthermore, of oxygens, we can expect the nearest oxygen, which is O₉, to make the greatest contribution. Consequently, it is reasonable to suppose that the direction of the crystalline electric field to be more or less along O₉. In fact measurements show that the angles for the V²⁺ crystalline electric field are (69°, 0.6°), very nearly equal to the polar angles for O₉ (65°, 4°).

Consider next the effects of VO²⁺ radical substitution. Here it seems most appropriate to suppose that the structure is similar to that found in vanadyl pentahydrate, Figure 8. The vanadyl vanadium is assumed to occupy

Figure 8. Vanadyl pentahydrate.¹⁷

the Zn^{2+} site, and the vanadyl oxygen is assumed to lie along the directions of one of the water oxygens. This then suggests that three directions for the VO^{2+} axis are possible, in agreement with the observed experimental results. Furthermore, it is reasonable to suppose that the VO^{2+} axis will be in the direction of water molecule vacancy. Thus we can expect the most preferred direction to be along the most loosely bound water molecule, associated with O_7 . Since the bond distances to O_7 , O_8 , and O_9 are 2.138, 2.117, and 2.066 Å, so that the O_7 water molecule most weakly bound and the O_9 water molecule is most strongly bound. We can then infer that the O_7 direction is the most preferred orientation for the VO^{2+} axis, whereas the O_9 direction is the least preferred. Measurement of the relative intensities indicate that the probabilities for the three orientations are in the ratio of 20:5:1. Another evidence supporting this model is provided by the close agreement between the experimental g-values and the values calculated by Ballhausen and Gray, as shown in Figure 9.

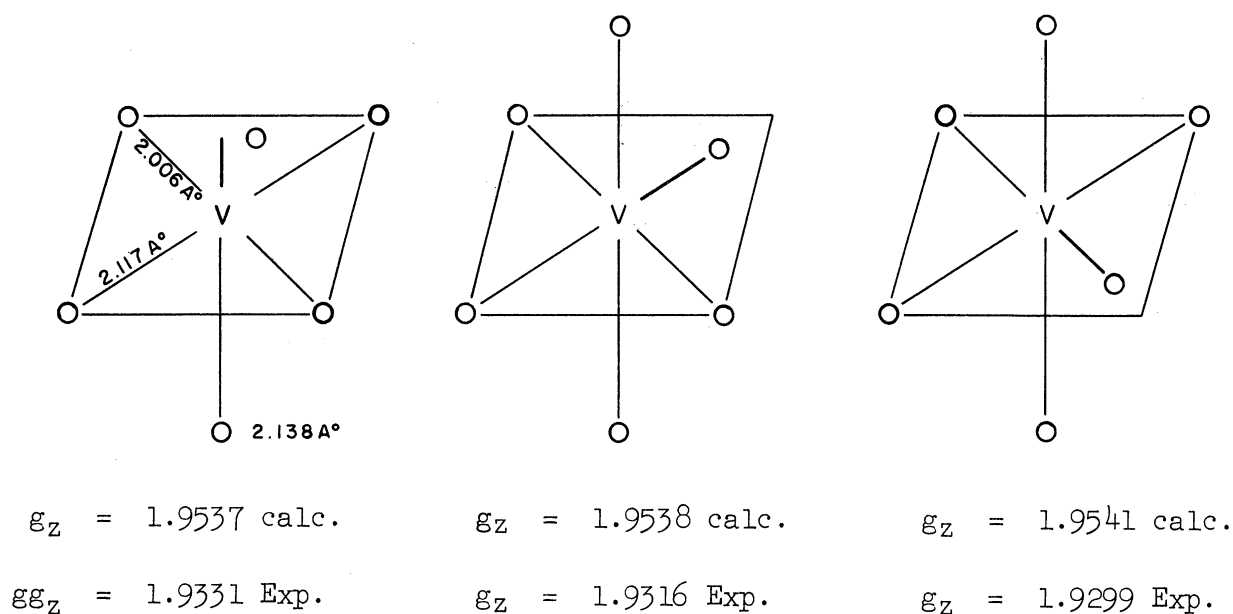


Figure 9. Vanadyl ion in substitutional site in Tutton salt.

Another fact is the excellent agreement of the single crystal and powder measurements. Thus, for the VO^{++} radical, sufficiently reliable results can be obtained from powder measurements. In Figure 10-a, we give the spectrum VO^{++} absorbed on Amberlite IR-4B, vanadium in glass is given in Figure 10-b, and vanadium in crushed Tutton salt in Figure 10-c. The spectrum shown in Figure 10-b indicates that vanadium is present as vanadyl vanadium in glass. The spectrum of VO^{++} in aluminum oxide powder is quite similar to those indicated above.

A partial summary of our results is presented in Table II.

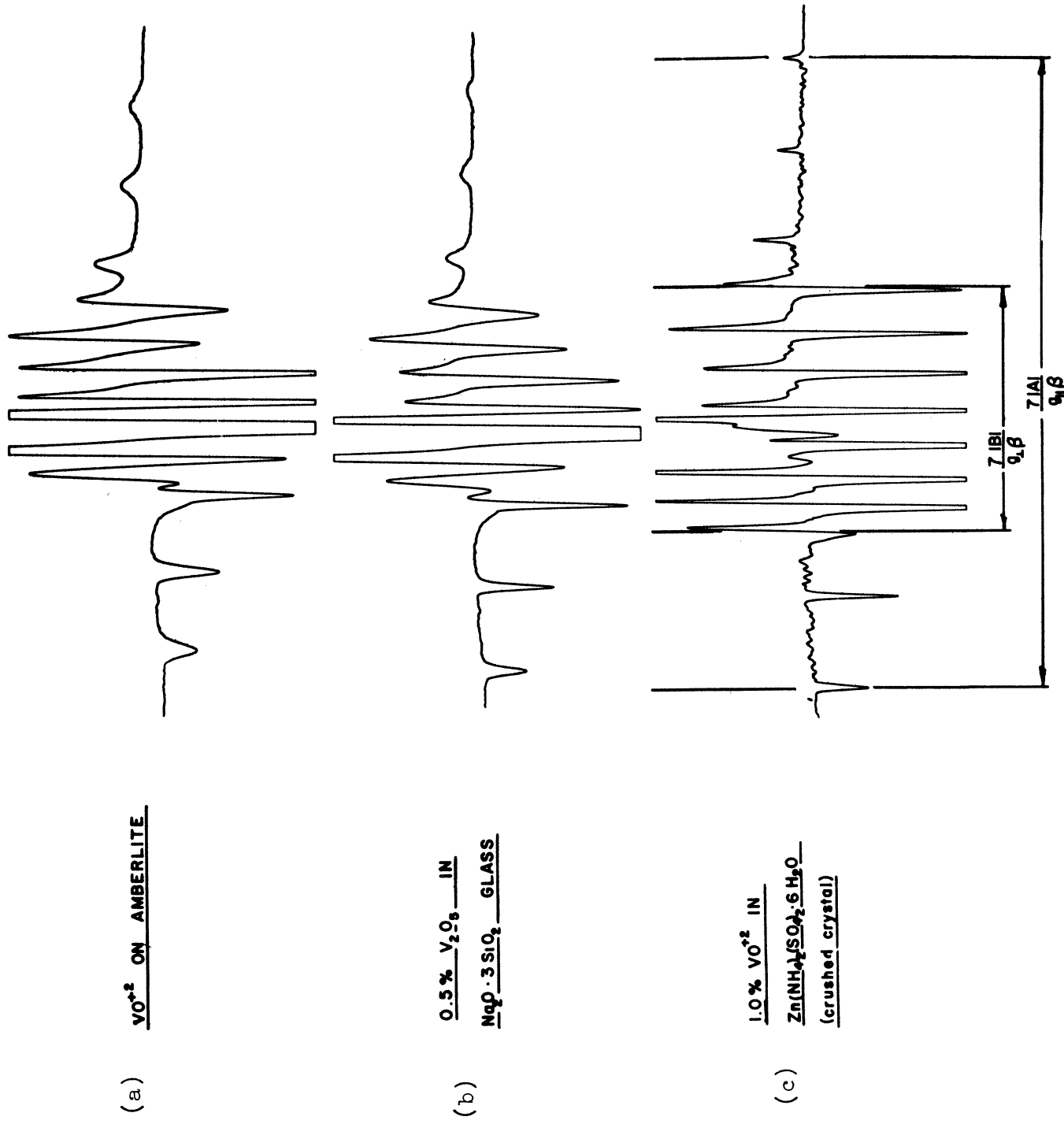


Figure 10. ESR spectra of randomly oriented VO²⁺ (x-band).

TABLE II

COMPARISON BETWEEN THE CRYSTAL AND THE POWDER DATA.

	<u>Orientation</u>		<u>Powder</u>	<u>Calculated</u> <u>(Ballhausen and Gray)</u>
g_{11}	1.9238 ± 2	1.9314 ± 2	1.935	1.940
g_1	1.9802 ± 3	1.9812 ± 3	1.980	1.983
g	1.9644 ± 3	1.9646 ± 2	1.965	1.969
(A)	0.01824 ± 2		0.182	
(B)	0.007162 ± 5		.00729	

Several interesting facts stand out. One is that for the two orientations, the individual g -values differ appreciably. Yet, the average g -values are equal, within experimental error. This perhaps is to be expected if the crystalline field provides the major contribution of Δg . For the two sites, the crystalline fields have different orientations with respect to the VO^{++} , but the trace of the g -tensor should be the same, if the ligand bonding effects do not change.

IV. ANGULAR DEPENDENCE OF $\text{CaO}:\text{V}^{2+}$ AND $\text{MgO}:\text{V}^{2+}$ FINE STRUCTURE

Recently we have observed another interesting characteristic of V^{2+} in CaO and in MgO . The spectra at four different angles for $\text{CaO}:\text{V}^{2+}$ are presented in Figure 11. We note that the V^{2+} spectra show an angular dependence very much like that of Mn^{4+} . At 0° , where the Mn^{4+} fine structure splitting is maximum, that of the V^{2+} is also the largest. This angular dependence of the V^{2+} spectrum is very surprising, because ions with $S = 3/2$ in a cubic field should show only an isotropic splitting coming from the second order terms in the electron-nuclear interaction.

A similar anomalous angular dependence was observed during the course of our investigation of vanadium in MgO single crystals. The small angular dependence of the vanadous vanadium ESR spectrum in MgO appears to have been first noticed by Low, who attributed the effect to a small rhombohedral distortion. Ham et al¹⁸ have observed a similar angular dependence in the spectrum of Co^{++} in CdTe .

The spin Hamiltonian for $s = 3/2$ ions in a cubic crystalline site is usually written as

$$\mathcal{H} = g\beta \underline{S} \cdot \underline{H} + A \underline{S} \cdot \underline{I} - g_N \beta_N \underline{I} \cdot \underline{H} \quad (1)$$

Bleaney¹⁹ and Koster and Statz²⁰ have indicated that the observed unexpected angular dependence can be explained in some cases by adding to the above spin Hamiltonian a correction term $\Delta\mathcal{H}$, Eq. (2) which accounts for higher order interactions of the Zeeman term $\beta(\underline{L} \cdot \underline{H} + 2\underline{S} \cdot \underline{H})$, the spin-orbit coupling term $\lambda \underline{L} \cdot \underline{S}$, and the hyperfine interaction term $\underline{P} \cdot \underline{I}$ with the energy levels of the ion in the crystalline field.

$$\begin{aligned} \Delta\mathcal{H} = & u\beta \left\{ S_x^3 H_x + S_y^3 H_y + S_z^3 H_z - \frac{1}{5} (\underline{S} \cdot \underline{H}) [3S(S+1) - 1] \right\} \\ & + U \left\{ S_x^3 I_x + S_y^3 I_y + S_z^3 I_z - \frac{1}{5} (\underline{S} \cdot \underline{I}) [3S(S+1) - 1] \right\} \end{aligned} \quad (2)$$

where x , y , and z are the cubic axes of the crystal and u and U are constants depending on g .

Using the corrected spin Hamiltonian $\mathcal{H} + \Delta\mathcal{H}$, we find energy levels of the ion to second order in A and first order in u and U to be

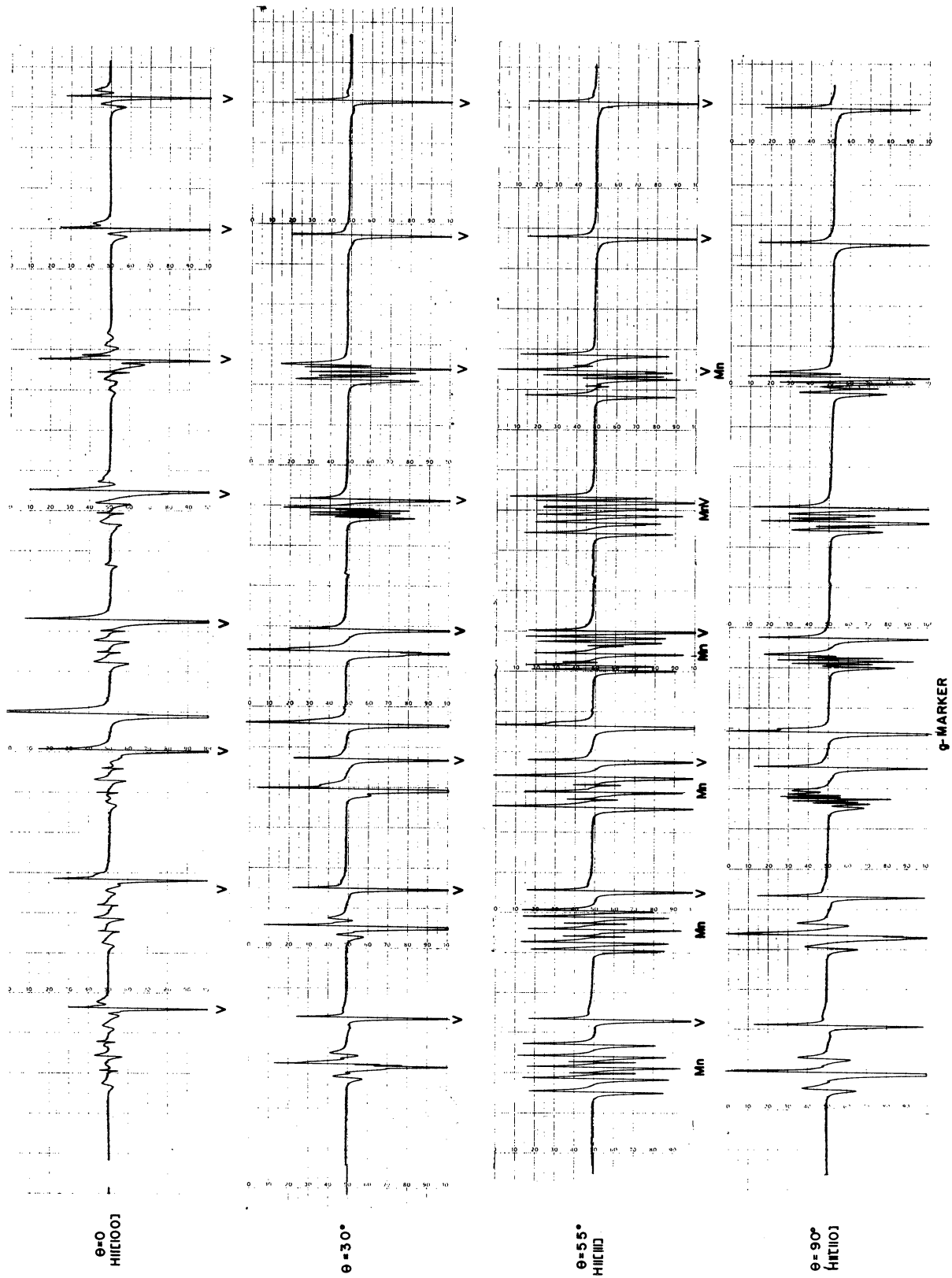


Figure 11. ESR spectra of V^{2+} in CaO .

$$\begin{aligned}
E_{M,m} &= g\beta HM + AmM + \frac{A^2}{2g\beta H_0} [mM^2 - m^2M + MI(I+1) - mS(S+1)] \\
&+ (u\beta H + Um) \left\{ M^3 - \frac{1}{5} [3S(S+1) - 1]M \right\} p
\end{aligned} \tag{3}$$

where

A = hyperfine coupling constant, m , M = eigenvalues of \underline{I} and \underline{S} along the applied magnetic field \underline{H} respectively,

\underline{I} = nuclear angular momentum of the ion,

\underline{S} = spin angular momentum of the ion,

H_0 = $h\nu/g\beta$,

and

$$p = 1 - 5(n_1^2 n_2^2 + n_2^2 n_3^2 + n_3^2 n_1^2)$$

with n_1 , n_2 , and n_3 being the direction cosines of the magnetic field with respect to the three cubic axes of the crystal.

In the case of the V^{2+} ion $I = 7/2$ and $S = 3/2$ and positions of the resonance lines in gauss are found from Eq. (3).

For $(m, M = 3/2) \rightarrow (m, M = 1/2)$ transitions,

$$H_\alpha = K \left[H_0 - \frac{A}{g\beta} m - \frac{A^2}{2(g\beta)^2 H_0} \left(\frac{63}{4} - m^2 \right) - \frac{A^2 m}{(g\beta)^2 H_0} - \frac{6}{5} \frac{Upm}{g\beta} \right] \tag{4}$$

For $(m, M = 1/2) \rightarrow (m, M = -1/2)$ transitions,

$$H_\beta = K \left[H_0 - \frac{A}{g\beta} m - \frac{A^2}{2(g\beta)^2 H_0} \left(\frac{63}{4} - m^2 \right) - \frac{6}{5} \frac{Upm}{g\beta} \right] \tag{5}$$

and for $(m, M = -1/2) \rightarrow (m, M = -3/2)$ transitions

$$H_\gamma = K \left[H_0 - \frac{A}{g\beta} m - \frac{A^2}{2(g\beta)^2 H_0} \left(\frac{63}{4} - m^2 \right) + \frac{A^2 m}{(g\beta)^2 H_0} - \frac{6}{5} \frac{Upm}{g\beta} \right] \tag{6}$$

where

$$k = (1 + 5/6 up/g)^{-1}$$

As we observe, the effect of $\Delta\mathcal{H}$ on position of the absorption lines depend on magnitude of u and U . In our case u and U were experimentally determined to be

$$u \approx 3 \times 10^{-5}$$

$$U \approx 10^{-6} \text{ cm}^{-1}$$

we found that these values can account only for a small part of the observed angular dependence of the ESR spectrum of the V^{2+} ion in MgO and in CaO. In the case of Co^{+2} ion in CdTe, investigated by Ham¹⁸ and coworkers, the constants u and U are much larger than those in our case and hence the observed anomalous angular dependence could be explained adequately by the correction term $\Delta\mathcal{H}$.

A theoretical estimate to the values of u and U can be made using 4th order perturbation calculations, to include interactions of the Zeeman, the spin-orbit coupling, and the hyperfine interaction term with the energy levels of the ion, Figure 12.

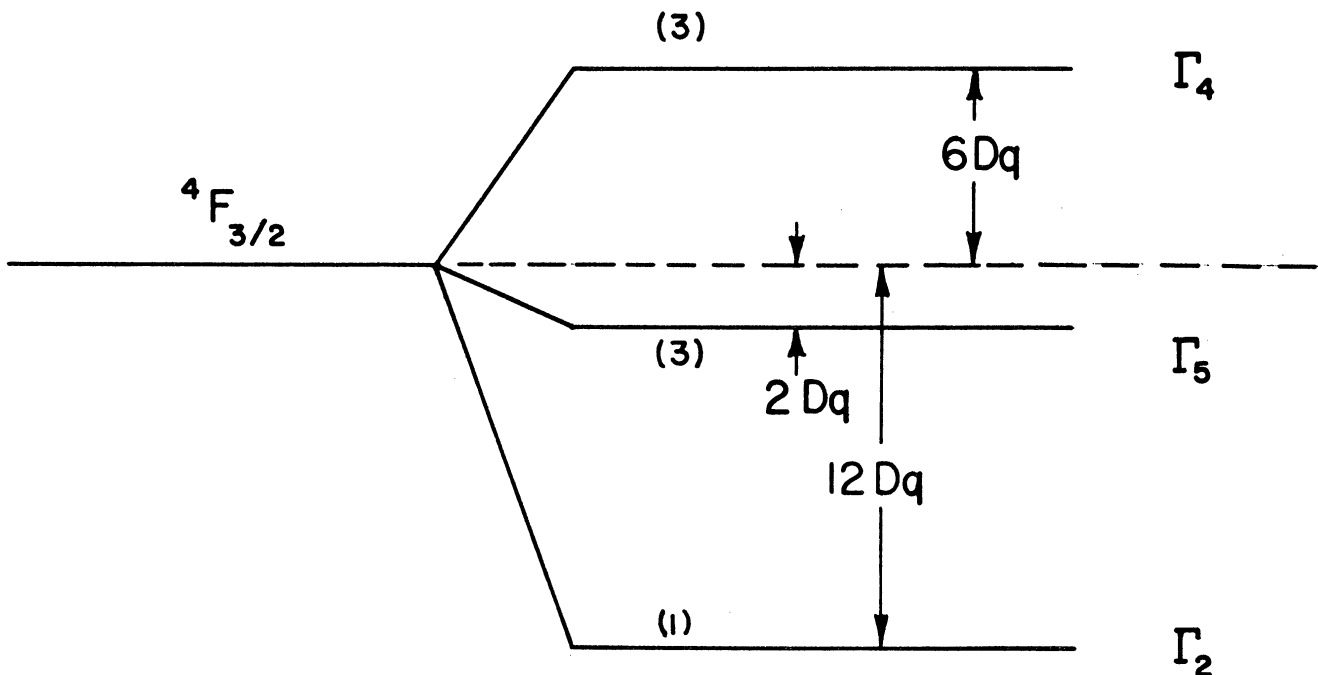


Figure 12. Energy levels of V^{2+} in MgO.

The result is

$$u_1 = \frac{120\lambda^3}{E_{52}^2 E_{42}} \quad (7)$$

$$U_1 = Pu_1 \quad (8)$$

where u_1 and U_1 are a part of contributions to u and U respectively $E_{42} \equiv (E)_{\Gamma_4} - (E)_{\Gamma_2}$, and $E_{52} \equiv (E)_{\Gamma_5} - (E)_{\Gamma_2}$ and $P \approx 0.0225$.

The values of E_{42} and E_{52} as given by Sturge⁷ are

$$E_{42} = 19,900 \text{ cm}^{-1}$$

$$E_{52} = 13,200 \text{ cm}^{-1}$$

and the value of λ can be approximately taken equal to that of the hexahydrated vanadous ion,²¹

$$\lambda = 44 \text{ cm}^{-1}$$

Substituting λ , E_{52} and E_{42} with their values, we find from Eqs. (7) and (8),

$$u_1 \approx 3 \times 10^{-6}$$

$$U_1 \approx 0.7 \times 10^{-7} \text{ cm}^{-1}$$

which are a lower limit estimate to the experimental values cited earlier.

V. VANADIUM IN MgO POWDER

Next a study of vanadium in MgO powder samples was undertaken with the hope that a recipe for the stabilization of vanadous vanadium could be worked out. The second objective to this program was to develop the necessary chemical techniques to measure the nuclear spin and magnetic moment of V^{49} . The nuclear parameters for this nuclide, which decays to Ti^{49} under electron capture 330 day half-life, were first reported by Weiss, Walter, Gilliam, and Cohen.²² However, the observations were made in a xylene solution of a vanadium (IV)-Cupferron Chelate, the individual vanadium Hfs. lines were quite broad, so that there is still some doubt on the reported values. On the other hand in MgO powder, the hfs lines are sharp, so that a precision value for the nuclear magnetic moment can be expected.

The MgO powder samples containing vanadium are prepared by wetting MgO powder with a solution of $VOSO_4$ so as to obtain about 0.1% for the V/Mg ratio. The samples are then dried, fired at a suitable temperature, and then irradiated with 50 Kvp X-rays. The dried samples often exhibit a spectrum suggestive of VO^{++} , but this disappears completely upon firing at $900^\circ C$ or higher. If, however, the sample is irradiated subsequently with X-rays, a spectrum is observed suggesting that vanadium is present as V^{2+} and/or V^{4+} , as shown in Figure 13a.

A typical spectrum obtained from a sample heated at temperatures of about $1200^\circ C$ and then X-rayed as shown in Figure 13b. There are the characteristic 8 lines corresponding to $I = 7/2$ for the nuclear spin of V^{51} . In addition, the principal hfs lines are flanked by two satellites, suggesting that the electron spin of the paramagnetic center is $3/2$. In fact, very good agreement between theory and experiment is obtained by assuming that the satellite splitting is due to second order effects in the electron-nuclear interaction term. Thus, there is every reason to believe that the spectrum presented here is due to vanadous vanadium, V^{2+} .

The presence of satellites in the spectrum of the powder samples is not readily expected because, as we have seen earlier, both the intensity and position of satellites in ESR of V^{2+} in a single MgO crystal are angular dependent. In fact it can be shown that we can have powder samples containing vanadous vanadium with an ESR spectra showing no distinguishable satellites. In order to show this, a relatively large $MgO:V^{2+}$ crystal was cut in small and average size crystals and following observations were made at x-band.

- (a) Each small crystal showed a weak V^{2+} spectrum.
- (b) Two small crystals, oriented in the same direction and glued

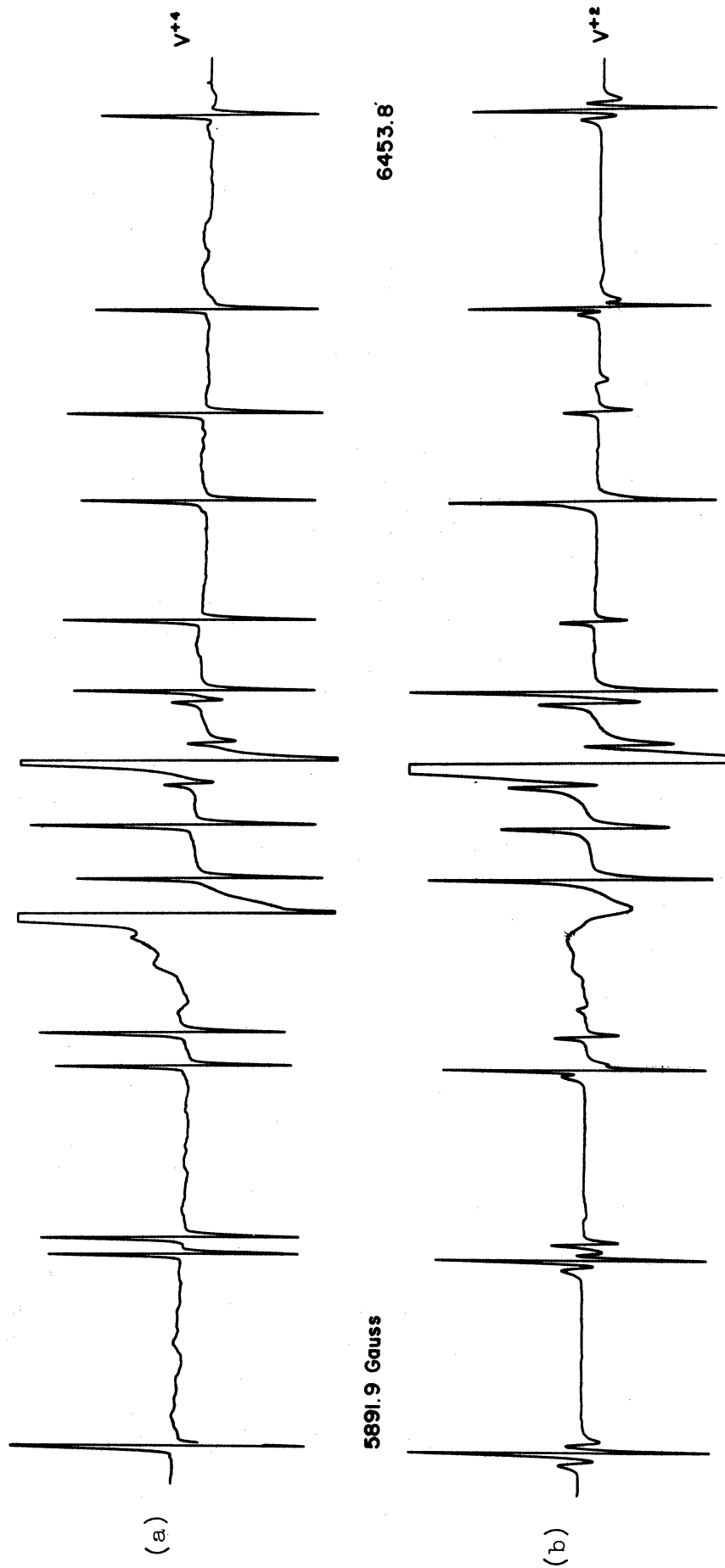


Figure 13. ESR spectra of vanadium in MgO powder samples.

together, produced stronger ESR signal with more distinguishable satellites.

- (c) Ten small crystals, including the ones used in (a) and (b), were placed randomly in a quartz probe. The ESR spectrum of this sample consists of a set of 8 main lines without any satellites.

The observations (a), (b), and (c) demonstrate clearly that the ESR spectra of the MgO:Vanadium powder samples which produce no satellites cannot be necessarily attributed to V^{4+} ion. In fact they may result from randomly oriented crystallites of $MgO:V^{2+}$.

Unlike the samples prepared at $900^{\circ}C$, the powder samples fired at $1200^{\circ}C$ are coarse and "lumpy". Thus, it is assumed that among the factors that contribute to the appearance of the satellites in powder samples, the degree of coarseness of the powder may be playing an important part. In order to show the connection between the size of the powder grains and the observed satellites, the powder samples and a small steel rod were placed in a quartz probe. The probe was then flushed with helium gas and sealed. By shaking the probe we were able to crush the powder grains, in an oxygen-free atmosphere. We observed that as the coarse grains were gradually ground to finer powder, the satellites became smaller until they finally disappeared.

The ultra-violet excitation techniques were used as an alternative method of identify the vanadium ions in the powder samples. From our preliminary work it was found that U-V emission spectrum of the powder samples, heat-treated at $1200^{\circ}C$ (whether they produce satellites or not) are somehow similar to that of the single $MgO:V^{2+}$ crystal. More works in this area are scheduled.

The direct chemical preparation of $MgO:V^{2+}$ powder samples were intended to remove some of the existing ambiguity in associating the observed spectra with V^{2+} and V^{4+} . It was found that samples heated at $1250^{\circ}C$ in a stream of carbon monoxide or hydrogen for about 10 hours and cooled to room temperature under a steady stream of these gases show strong ESR spectra before x-irradiation. These spectra, which remain qualitatively unaffected by a subsequent x-irradiation, are identical with the ones obtained by x-irradiation.

It is known^{7,23} that heating at elevated temperatures in a reducing atmosphere converts higher valancies of vanadium to V^{2+} and V^{3+} states. Since the latter has no ESR spectrum at room temperature, the observed spectrum of these powder samples is attributed to V^{2+} ions.

VI. VANADIUM IN Al_2O_3 POWDER

Although our investigations on Al_2O_3 powder samples are not complete yet, we shall present some of our preliminary results. The preparation of powder samples here is similar to that of MgO :Vanadium samples. We have observed that unheated unirradiated samples of aluminum oxide powder with vanadyl sulfate, VOSO_4 , produces the characteristic spectrum of VO^{++} ion similar to those shown in Figure 10a, b, and c. Upon heating the sample at about 1000°C , the vanadyl spectrum disappears. The heated samples upon x-irradiation in an oxygen-free atmosphere such as CO_2 , N_2 , or He_2 show a spectrum somewhat different from that of VO^{++} . It is tentatively held that this spectrum belongs to V^{++} .

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