VO²⁺ and X-Ray Produced V²⁺ in Tutton Salt*

Robert H. Borcherts† and Chihiro Kikuchi

University of Michigan, Ann Arbor, Michigan

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The electron spin resonance spectrum of the vanadyl ion (VO²⁺) in single crystals of $Zn(NH_4)_2(SO_4)_2 \cdot 6H_2O$ is studied and the properties of x-ray produced V²⁺ are compared to those of the V²⁺ grown directly into the same host lattice. In the unirradiated samples the V–O axis is found to have three possible orientations with populations in the ratio 20:5:1. For the most populous position the spin Hamiltonian parameters at X band are $S=\frac{1}{2}$, $g_x=1.9813$, $g_y=1.9801$, $g_z=1.9331$, $A_x=0.007120$/cm, $A_y=0.007244$/cm, $A_z=0.018281$/cm, and $Q'=7\times10^{-5}$/cm with the x, y principal axes of the g and A tensor being displaced from each other by $23°20'$. Furthermore, the vanadyl hyperfine lines show an additional anisotropic structure of five lines, absent in deuterated samples. The parameters for V²⁺ at K band in both the as-grown and irradiated crystals are $S=3/2$, $g_z=1.9717$, $g_y=1.9733$, $D=-0.15613$/cm, $E=-0.02280$/cm, and $A=-0.00825$/cm. A study of the effect of x-ray dose upon the line intensity is made. An impurity model of a vanadyl pentahydrate complex associated with a water moleculy vacancy is proposed.

I. INTRODUCTION

ALTHOUGH Tutton salts containing paramagnetic impurities have been the subject of investigations from several points of view since the early days of electron spin resonance, we have recently found that it is also useful for the study of oriented VO²⁺ radicals and of the valence changes of vanadium produced by ionizing radiations, namely the change from V⁴⁺ in the vanadyl ion to the vanadous state, V²⁺.

One of the earlier investigations using the Tutton salt was on the vanadous ion, V²⁺, by Bleaney, Ingram, and Scovil.[1] Later Kikuchi, Sirvetz, and Cohen[2] used these results to measure the nuclear spin and magnetic moment of the rare vanadium isotope ⁵⁰V. For tetravalent vanadium, Hutchison and Singer[3] noted a broad resonance at $g=1.96$. More recently Gager[4] made some studies of oriented VO²⁺ ions but the results have not been published. Randomly oriented VO²⁺ ions have been studied by a number of investigators.[5-10] A part of this interest was stimulated by the relatively high concentration of vanadium in crude oil.

Our interest in vanadium Tutton salts stemmed from the observation that both VO²⁺ and V²⁺ can be grown directly into the crystal lattice and that VO²⁺ ions so introduced can be readily converted to V²⁺ ions under ionizing radiations, such as x rays.[11] These facts then suggested the possibility of obtaining structural information about VO²⁺ in Tutton salts and also of determining the relation of the x ray produced to the as-grown vanadous ion. Our studies indicate that the complex formed by the vanadyl ion in Tutton salt is very much like that found in vanadyl sulfate pentahydrate.

The purpose of this paper is to present the experimental evidence leading to the model stated above and to add to the growing body of information on what might be called vanadium solid-state chemistry. The electron spin resonance properties of V³⁺ in corundum and the effects of x irradiation were reported earlier.[12] The results of our studies concerning the oxidation–reduction mechanisms on vanadium in MgO and on the nature of the bonding of vanadium in tin oxide will be reported later.

II. EXPERIMENTAL PROCEDURES

Single crystals of the vanadyl ion in the Tutton salt were grown by evaporation from a water solution of zinc ammonium sulfate with a VO/Zn concentration of 0.5%. Thermal neutron activation analysis of the single crystals grown from this solution were shown to have a VO/Zn concentration of 0.03%. For the preparation of the as-grown vanadous Tutton salt, the VO²⁺ ions in the 0.5% solutions were cathodically reduced with subsequent crystallization carried out in a carbon dioxide atmosphere.

The Tutton salts grow with well-recognized faces so that orientation becomes a task accomplished with relative ease.[13] The unit cell of the typical Tutton salt

[1] B. Bleaney, D. J. E. Ingram, and H. E. D. Scovil, Proc. Phys. Soc. (London) A64, 601 (1951).

[2] C. Kikuchi, M. Sirvetz, and V. W. Cohen, Phys. Rev. 88, 142 (1952).

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[5] B. M. Kozyrev, Discussions Faraday Soc. 19, 135 (1955).

[6] R. H. Sands, Phys. Rev. 99, 1222 (1955).

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[11] R. Borcherts, G. Wepfer, and C. Kikuchi, Bull. Am. Phys. Soc. 7, 118 (1962).

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[13] A. E. H. Tutton, *Crystalline Structure and Chemical Constitution* (Macmillan and Company, London, 1910).

contains two molecules and the six water molecules surrounding the divalent metal site of the $(0, \frac{1}{2}, \frac{1}{2})$ position are derived from the $(0, 0, 0)$ position by a translation to $(0, \frac{1}{2}, \frac{1}{2})$ followed by a reflection in the ac plane. An x-ray determination of the Tutton salt structure was done by Hoffman[14] in 1931. Recently Montgomery[15] has made a redetermination of the structure and has shown that the water octahedron is quite regular as compared with that reported by Hoffman.

The VO²⁺ ESR measurements were carried out at room temperature at about 9.3 kMc/sec with a Varian V-4500 EPR spectrometer and a 12-in. rotating electromagnet using 100-kc/sec field modulation while the V²⁺ EPR measurements were obtained at about 24 kMc/sec. Frequency measurements at X band were made with a Beckman transfer oscillator and a Universal EPUT and timer, while at K band a Hewlett-

TABLE I. Spin Hamiltonian constants for the three orientations of VO²⁺ in Zn(NH₄)₂(SO₄)·6H₂O.

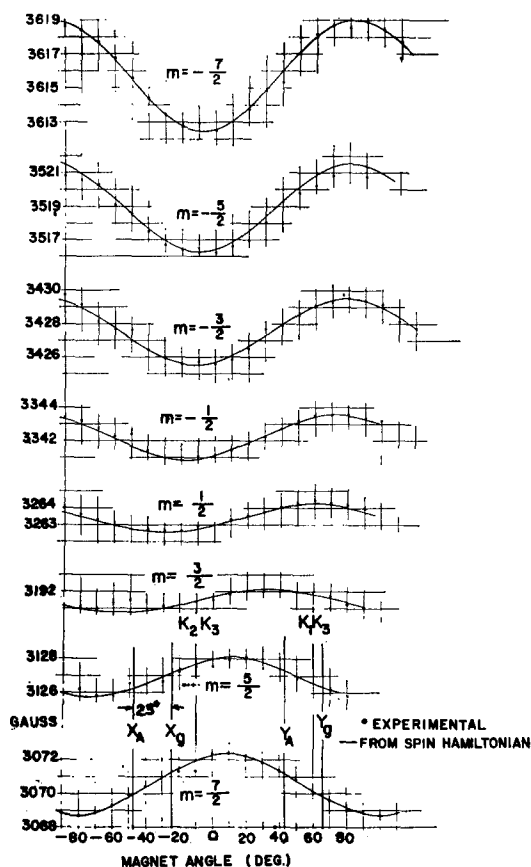|	Relative intensity		
	20	5	1
g_z	1.9331	1.9316	1.9299
g_x	1.9813	1.9808	1.981
g_y	1.9801	1.9797	...
A/cm	0.018280	0.018275	0.01844
B_x/cm	0.007137	0.007104	0.00725
B_y/cm	0.007256	0.007255	...
$\mathfrak{F}_{xy}$/cm	−0.00046	...	...
Q'/cm	0.00007	...	...

FIG. 1. Angular variation of magnetic field at resonance in the xy plane for VO²⁺ in deuterated zinc ammonium sulfate. This figure is for the most populous of the three VO²⁺ orientations in the Tutton salt. X_A and X_g refer to the x axes of the A and g tensors, respectively.

Packard absorption wavemeter was employed. The magnetic field at resonance was monitored with a Varian fluxmeter connected to the Beckman transfer oscillator and the Universal EPUT and timer. The x-ray irradiations were carried out in the white beam of a tungsten target x-ray tube at 50 KVP 50 mA. Cerous-ceric dosimetry, as described by Weiss,[16] was used to measure the beam intensity. The value of Q' in the vanadyl crystals was obtained by using ENDOR techniques at liquid helium temperatures at X-band.

III. HAMILTONIAN

For the usual ESR results of paramagnetic ions in crystalline solids the principal axes of the tensors in each of the terms of the spin Hamiltonian

$$\mathcal{H} = \beta \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S} + \mathbf{I} \cdot \mathbf{A} \cdot \mathbf{S} + \mathbf{I} \cdot \mathbf{Q} \cdot \mathbf{I} - \beta_N \mathbf{H} \cdot \mathbf{g}_N \cdot \mathbf{I}$$

are assumed to coincide so that the Hamiltonian can be written in the diagonal form

$$\mathcal{H}_{\text{rhombic}} = \beta [b_z H_z S_z + g_x H_x S_x + g_y H_y S_y]$$
$$+ D[S_z^2 - \tfrac{1}{3}S(S+1)] + E(S_x^2 - S_y^2) + A I_z S_z$$
$$+ B_x I_x S_x + B_y I_y S_y + Q'[I_z^2 - \tfrac{1}{3}I(I+1)] + Q''[I_x^2 - I_y^2]$$
$$- \beta_N [g_{Nz} H_z I_z + g_{Nx} H_x I_x + g_{Ny} H_y I_y].$$

When the principal axes of the g and A tensors do not coincide, additional terms of the form

$$\sum_{i,j}' F_{ij}[S_i I_j + I_i S_j]$$

need to be included. If the z axes coincide and the x, y principal axes do not, the off-diagonal terms then contain only the products $S_x I_y$ and $S_y I_x$. In this case, the observed hyperfine constants A, B_x, B_y, $F_{xy}(F_{xy}=F_{yx}$ since the tensor is symmetric) are related to the

[14] W. Hoffman, Z. Krist. **78**, 279 (1931).
[15] H. Montgomery, thesis, University of Washington, 1961, available from University Microfilms, Ann Arbor, London.

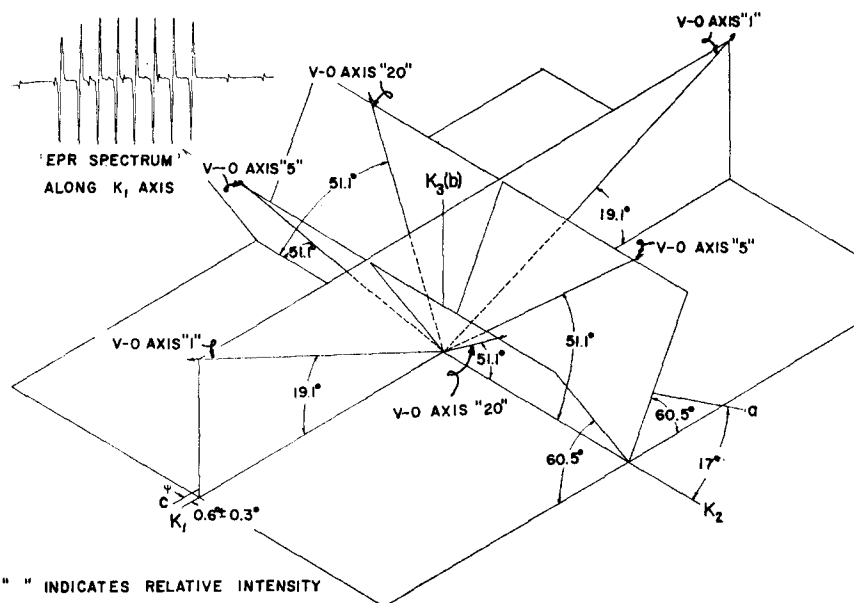[16] J. Weiss, Nucleonics **10**, 28 (1952); see also *ibid.* **17**, 73 (1959).

Fig. 2. Position of V–O axes in zinc ammonium sulfate as found by ESR. The V–O axis is the z axis of the spin Hamiltonian.

diagonal values of the hyperfine tensor A_z, A_x, A_y by

$$A = A_z,$$

$$B_x = A_x \cos^2\theta + A_y \sin^2\theta,$$

$$B_y = A_x \sin^2\theta + A_y \cos^2\theta,$$

$$F_{xy} = F_{yx} = \tfrac{1}{2}(A_y - A_x) \sin\theta \cos\theta,$$

where θ is the angle between the principal axes of the two tensors.

Evaluating the energy levels of the rhombic spin Hamiltonian for the case under consideration ($S=\tfrac{1}{2}$; selection rules $\Delta M = \pm 1$, $\Delta m = 0$; neglect quadrupole terms) we obtain for the resonant magnetic field in the xy plane

$$H_m(\delta) = \frac{h\nu}{g_{\perp}\beta} - \frac{m}{g_{\perp}\beta}\left[\frac{B_x+B_y}{2} + \frac{B_x-B_y}{2}\right.$$

$$\times\frac{(g_x^2\cos^2\delta - g_y^2\sin^2\delta)}{g_{\perp}^2} + 2\mathfrak{F}_{xy}\frac{g_xg_y}{g_{\perp}^2}\sin\delta\cos\delta\left.\right] - \frac{m^2}{2g_{\perp}^2\beta^2H}$$

$$\times\left[\mathfrak{F}_{xy}\frac{(g_x^2\cos^2\delta - g_y^2\sin^2\delta)}{g_{\perp}^2} - \frac{(B_x-B_y)}{g_{\perp}^2}g_xg_y\sin\delta\cos\delta\right]^2$$

$$- \frac{I(I+1)-m^2}{8g_{\perp}^2\beta^2H}\left[A + \frac{B_x+B_y}{2} - \frac{B_x-B_y}{2}\right.$$

$$\times\frac{(g_x^2\cos^2\delta - g_y^2\sin^2\delta)}{g_{\perp}^2} - 2\mathfrak{F}_{xy}\frac{g_xg_y}{g_{\perp}^2}\sin\delta\cos\delta\left.\right]^2$$

$$- \frac{I(I+1)-m^2}{8g_{\perp}^2\beta^2H}\left[A - \frac{B_x+B_y}{2} + \frac{B_x-B_y}{2}\right.$$

$$\times\frac{(g_x^2\cos^2\delta - g_y^2\sin^2\delta)}{g_{\perp}^2} + 2\mathfrak{F}_{xy}\frac{g_xg_y}{g_{\perp}^2}\sin\delta\cos\delta\left.\right]^2,$$

where $g_{\perp}^2 = g_x^2\cos^2\delta + g_y^2\sin^2\delta$ and $\mathfrak{F}_{xy} = F_{xy} + F_{yx}$.

If we assume that the three second-order terms make negligible contributions to the angular variation of $H_m(\delta)$, then the maxima and minima of the magnetic field for each value of m occur at

$$\tan 2\delta \approx \frac{4g_xg_y\mathfrak{F}_{xy}}{(g_x^2+g_y^2)(B_x-B_y)+(h\nu/m)(g_x^2-g_y^2)}.$$

Thus, one notices that if the principal axes of the g and A tensors coincide, then $\mathfrak{F}_{xy}=0$ and the extrema occur at $\delta=0$ and $90°$ for all values of m. Alternatively if $\mathfrak{F}_{xy}\neq0$, the maxima and minima occur at different values of δ.

IV. EXPERIMENTAL RESULTS

Figure 1 shows the resonant magnetic field in the xy plane for the larger population position of the vanadyl

Table II. Spin Hamiltonian constants for V^{2+} in $Zn(NH_4)_2(SO_4)\cdot6H_2O$.

	V^{2+} (grown)	V^{2+} (irradiated VO^{2+})	V^{2+} (Bleaney et al.[1])
g_x	1.9717 ± 5	1.9718 ± 5	1.951
g_y	1.9733 ± 5	1.9733 ± 5	$\cdots$
D/cm	-0.15613 ± 3	-0.15609 ± 3	0.158
E/cm	-0.02290 ± 3	-0.02297 ± 3	0.049
A/cm	-0.008263 ± 5	-0.008267 ± 5	0.0088
B/cm	-0.008246 ± 5	-0.008249 ± 5	$\cdots$
Θ[a]	$69.5°\pm0.5°$	$69.5°\pm0.5°$	$68°$
ϕ	$2°\pm5°$	$3°\pm1°$	$2°$

[a] The angles Θ and ϕ locate the z axis of the spin Hamiltonian in the crystal. Θ is the polar angle from the b axis and ϕ is the azimuthal angle from the c axis in the ac plane.
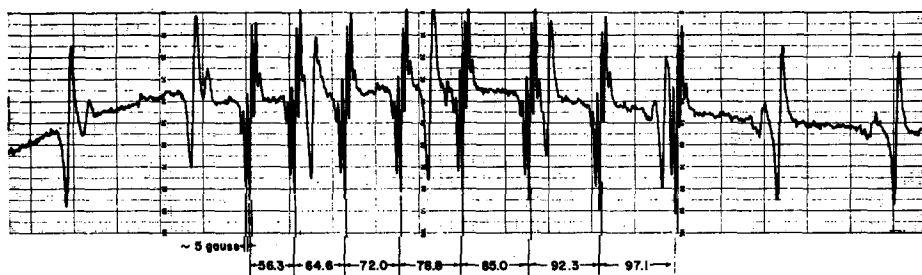
FIG. 3. Superhyperfine structure for the most populous position of VO²⁺ in Tutton salt. The magnetic field lies in the xy plane at the K_1K_2 plane shown in Fig. 1. The other signals are from the other orientations of the VO²⁺ ions.

Tutton salt grown from a heavy water solution.[17] Since the observed maxima (minima) of the hyperfine resonances do not all occur at the same angle the previous discussion shows that the principal axes for the g and A tensors are different. The curves in this figure are calculated from the rhombic spin Hamiltonian constants listed in Table I, Column 1. The planes K_1K_2 and K_2K_3 in Fig. 1 refer to the orientation of the vanadyl ion with respect to the magnetic susceptibility axes, K_1, K_2, K_3, of the crystal. These axes are shown in relation to the crystallographic axes in Fig. 2. Also shown in the figure are the three observed locations of the V–O axes for the two divalent sites.

As Table I indicates, the spin Hamiltonian constants vary slightly for each of the three positions and have a population ratio of 20:5:1.
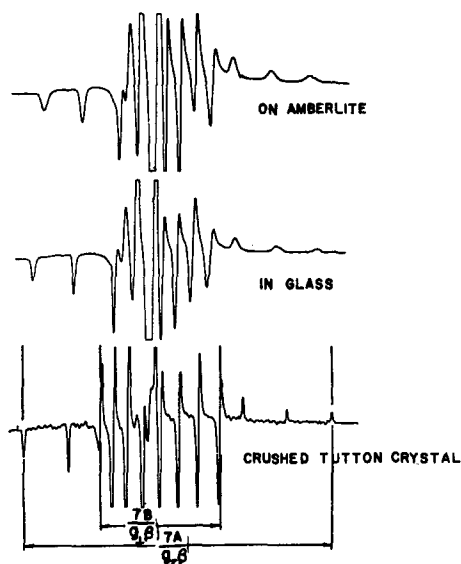

FIG. 4. EPR spectrum of randomly oriented VO²⁺ ions. The "noise" appearing between the "resonances" in the crushed crystal spectrum is actually EPR signals due to the finite size of the particles. This is evidenced by the lack of "noise" to the extreme right or left of the spectrum. Note also that the narrow signals in this spectrum compared to the other two is due to the regular crystalline field expected.

Another result, shown in Fig. 3, is the five-line super-hyperfine structure apparently due to some of the protons of the surrounding water molecules. This shf structure could not be resolved in crystals grown from a heavy water solution. By crushing one of the Tutton crystals containing the VO²⁺ ions one can obtain the ESR spectrum of randomly oriented VO²⁺. Such a spectrum is instructive since it enables one to compare similar "powder" spectra in different samples (see Fig. 4) and will point out the salient features of the spectra pertinent to the calculation of the spin Hamiltonian constants.

V. COMPARISON OF X-RAY PRODUCED AND AS-GROWN V²⁺

As mentioned earlier, the ESR investigation of V²⁺ in Tutton salt was made by Bleaney, Ingram, and Scovil.[1] These earlier measurements were checked for possible differences between the x-ray produced and as-grown V²⁺. The results are summarized in Table II and show that within experimental error the spin Hamiltonian parameters are identical[18] as illustrated

TABLE III. Spin Hamiltonian constants for V²⁺ (irradiated VO²⁺) in several Tutton salts.

	Zn(NH₄)₂(SO₄)·6H₂O	Mg(NH₄)₂(SO₄)₂·6H₂O	ZnK₂(SO₄)₂·6H₂O
g_x	1.9718	1.9720	1.9722
g_y	1.9733	1.9723	1.9741
D/cm	0.15609	0.15793	0.15244
E/cm	0.02297	0.02452	0.02742
A/cm	0.008267	0.008262	0.008253
B/cm	0.008249	0.008253	0.008212
θ	69.5°±0.5°	70.0°±0.5°	75.3°±0.5°
ϕ	3°±1°	1°±1°	11°±2°

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[17] Other than reducing the width of the vanadyl resonances by a factor of 3, the heavy water did not alter the spin Hamiltonian constants or the orientation of the crystalline field.

[18] As a further check a VO²⁺ crystal with a V₄⁺ seed crystal was x-irradiated and shown to have the same spin Hamiltonian constants before and after irradiation.
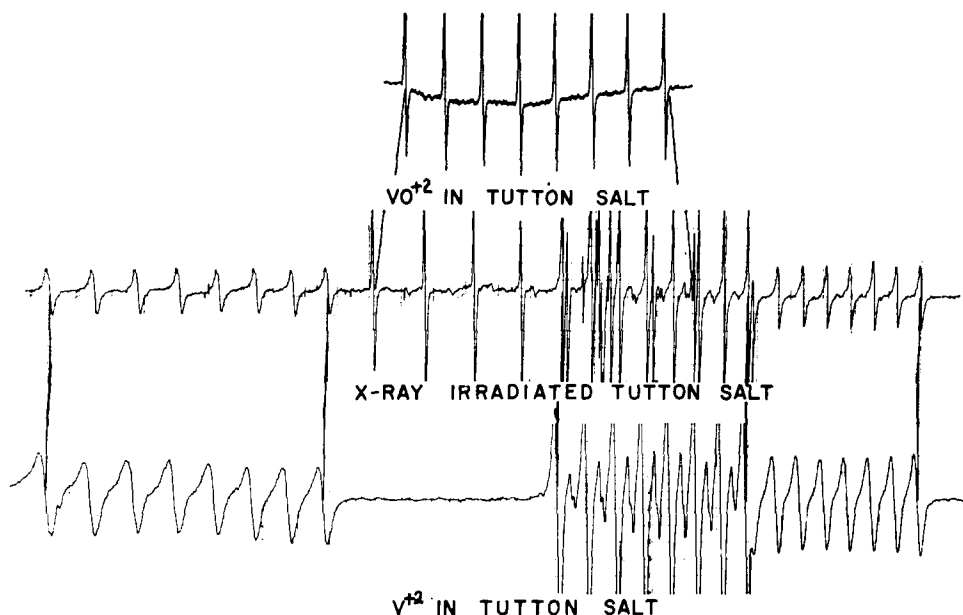
FIG. 5. ESR spectra of VO^{2+}, VO^{2+} (irradiated), and V^{2+} in $Zn(NH_4)_2(SO_4) \cdot 6H_2O$. The magnetic field is parallel to the K_2 axis.

by Fig. 5. The spin Hamiltonian constants and z axis orientation of the crystal field for V^{2+} (irradiated VO^{2+}) in two other Tutton salts are shown in Table III. These results indicate that substitution of different host ions into the crystal distort the octahedron by an amount that is measured by the changes in D, E, Θ, and ϕ.

An incongruity in the irradiation experiments is that only 80%–90% of the vanadyl signals are eliminated after approximately 10^8 rad and that further irradiation fails to convert additional VO^{2+} to V^{2+}. Of the 80%–90% of the vanadyl signals that are reduced only 15%–20% appears in the form of V^{2+}. In this respect, these results are similar to those reported by Lambe and Kikuchi.[12] An experiment carried out at 4.2°K failed to show any V^{3+} EPR signals.

VI. DISCUSSION

A model that is proposed for the above results is a vanadyl pentahydrate complex associated with a water

molecule vacancy. The Zn^{2+} ion is normally surrounded by six water molecules of hydration forming a distorted octahedron. When a VO^{2+} radical substitutes for Zn^{2+} ions, the axis of the vanadyl ion appears to be very nearly in the direction of the Zn–O bond directions. Table IV gives the bond distances and angles taken from Montgomery's[15] data, where the water molecule oxygens are numbered as shown in Fig. 6(a). Figure 6(b) shows the model proposed for the vanadyl ion in the Tutton salt for the most populous position. For each of the lower concentration positions the oxygen atom of the vanadyl ion lies in either the O_7 or O_8 directions. Comparison of the Zn–O bond directions and the V–O axes determined from the electron spin resonance measurements is given in Table V. The angle Θ is the
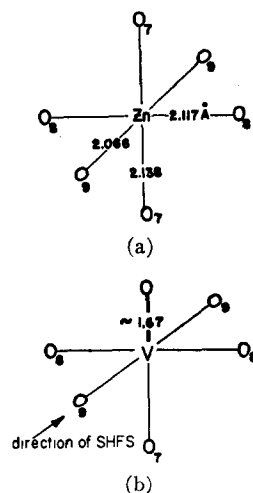
TABLE IV. X-ray data[15] of $Zn(NH_4)_2(SO_4)_2 \cdot 6H_2O$.

Distance[a] (Å)	
Zn–H$_2$O (O$_7$)	2.138
Zn–H$_2$O (O$_8$)	2.117
Zn–H$_2$O (O$_9$)	2.066

Angle	
O$_9$–Zn–O$_7$	90.8°
O$_8$–Zn–O$_7$	88.7°
O$_8$–Zn–O$_9$	99.4°

[a] Error associated with the above distances and angles are reported as ±0.015 Å and ±0.6°, respectively.

(a)

(b)

FIG. 6. (a) The octahedron of water molecules as found by Montgomery.[15] The O–Zn–O angles are listed in Table IV. (b) The model proposed for VO^{2+} in Tutton salt. Note that this figure is for the most populous position. The other two positions are with the VO bond in the Zn–O$_8$ and Zn–O$_9$ direction. The arrow indicates direction along which superhyperfine structure (shfs) is observed.

TABLE V. Comparison of Zn–H₂O directions with ESR determination of V–O axes.

	x-ray data[16]			EPR VO²⁺ data		
	Zn–H₂O Distance (Å)	Θ^a (deg)	ϕ (deg)	Θ (deg)	ϕ (deg)	Relative intensity
Zn–O₇	2.138	50.2	79.5	57	59	20
Zn–O₈	2.117	49	−71.5	57	−58	5
Zn–O₉	2.066	65	4	70.9	0.6	1

ª The angle Θ is the polar angle from the b axis and the angle ϕ is the azimuthal angle from the c axis in the ac plane.

polar angle from the b axis, and ϕ is the azimuthal angle from the c axis in the ac plane. The vanadyl pentahydrate complex suggested by the structure of vanadyl sulfate was used by Ballhausen and Gray[19] for the molecular orbital calculation, resulting in the following g values: $g_z = 1.940$, $g_\perp = 1.983$, $\langle g \rangle_{\text{Av}} = 1.969$. These values are close to the present experimental ones given in Table I. Interesting, also, is the fact that the population of the different orientations are in the order of the bond distances. For example, the Zn–O₇ direction is the most distant water molecule, hence

weakly bound, and also shows the most intense signals. The effect of x rays is possibly to break the vanadium-oxygen bond, causing the latter to move out to a site normally occupied by the oxygen of the missing water molecule. ENDOR investigation of the proton shfs is currently in progress, to see what additional information about the vanadyl complex can be obtained.

ACKNOWLEDGMENTS

[19] C. J. Ballhausen and H. B. Gray, J. Inorg. Chem. 1, 111 (1962).