PHYSICAL REVIEW B VOLUME 42, NUMBER 13 1 NOVEMBER 1990

Brief Reports

EPR of a VO^{2+}-doped Zn(NH$_4$)$_2$(SO$_4$)$_2$·6H$_2$O single crystal: Ligand superhyperfine interaction

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(Received 27 December 1989; revised manuscript received 12 June 1990)

Detailed X-band electron-paramagnetic-resonance (EPR) studies of the VO^{2+} ion have been carried out on a single crystal of the Tutton salt Zn(NH$_4$)$_2$(SO$_4$)$_2$·6H$_2$O at 295, 80, and 4.2 K. The data are indicative of the presence of two physically equivalent VO^{2+} sites in the unit cell, each consisting of three magnetically inequivalent VO^{2+} ions, one of them being present with a much smaller probability. Each vanadyl hyperfine line is characterized by an anisotropic temperature-independent quintet superhyperfine (SHF) splitting, with the intensity ratios 1:4:6:4:1. The origin of the SHF splittings has been explained. The principal values and the orientations of the principal axes of the SHF-interaction tensor, as well as the density of the unpaired electron at the site of ligand protons, have been estimated. The "in-plane anisotropy" controversy has been resolved.

I. INTRODUCTION

Room-temperature (RT) EPR of VO^{2+}-doped Zn(NH$_4$)$_2$·6H$_2$O (ZASH, hereafter) single crystal has been previously reported by Borcherts *et al.*,[1] observing superhyperfine (SHF) structure for only one out of the three possible magnetically inequivalent VO^{2+} ions; no studies regarding the principal values and principal axes of the SHF-interaction tensor ($\tilde{\mathbf{A}}^L$) were reported. Strach *et al.*,[2] from their zero-field EPR measurements, reported RT VO^{2+} hyperfine-interaction studies on ZASH. Thus far, no EPR study on VO^{2+}-doped ZASH single crystal has been reported below RT. Further, there exists the so-called "in-plane anisotropy" controversy, i.e., according to Borcherts *et al.*,[1] although the principal Z axes of the $\tilde{\mathbf{g}}^2$ and $\tilde{\mathbf{A}}^2$ tensors are coincident, their principal X,Y axes are not coincident,[1] which is contrary to the findings of Strach *et al.*[2] The present paper reports extensive X-band EPR study on VO^{2+}-doped ZASH single crystal at 295, 80, and 4.2 K, with particular emphasis on (i) the interpretation of the SHF splitting for the three magnetically inequivalent VO^{2+} ions in the unit cell of ZASH, (ii) resolution of the "in-plane anisotropy" controversy, and (iii) estimation of the density of the unpaired electron of VO^{2+} at the site of ligand protons.

II. SAMPLE PREPARATION AND CRYSTAL STRUCTURE

Single crystals of ZASH, doped with VO^{2+} (0.5 at. %), were grown at room temperature by slow evaporation of a saturated aqueous solution, containing stoichiometric amounts of ZnSO$_4$·7H$_2$O and (NH$_4$)$_2$SO$_4$, to which an appropriate amount of VOSO$_4$·2H$_2$O powder was added.

A ZASH crystal is characterized by monoclinic symmetry (space group $P2_1/a$).[3–5] The dimensions of the unit cell are $a=9.28$ Å, $b=12.57$ Å, $c=6.25$ Å, and $\beta=106.8°$; it contains two divalent metal ions, each of which is surrounded by six water molecules, labeled as H$_2$O(7), H$_2$O(8), and H$_2$O(9) in pairs, forming closely an octahedron with distances $d_{\text{Zn-O}(7)}=2.138$ Å, $d_{\text{Zn-O}(8)}=2.117$ Å, and $d_{\text{Zn-O}(9)}=2.066$ Å. A ZASH crystal has similar growth habits as that of the other Tutton salts;[6] the b axis is easy to identify, being perpendicular to the (010) plane, which is well developed in the form of a rectangular flat surface, containing the a^* ($=a\sin\beta$) and c axes.

III. EPR SPECTRA

EPR spectra were recorded at 295, 80, and 4.2 K for the orientation of the external Zeeman field ($\mathbf{B}$), in three mutually perpendicular planes, defined by the X, Y, and Z axes (laboratory frame): The X axis was chosen to be parallel to the crystallographic $\hat{\mathbf{b}}$ axis, axis, while the Y and Z axes were chosen to lie in the (010) plane, of the crystal, with the Z axis being perpendicular to the largest flat face of the crystal.[6] For an arbitrary orientation of $\mathbf{B}$ and at any temperature, there were observed four sets of typical VO^{2+} spectra with strong intensity and two sets with much weaker intensity, characterized by eight VO^{2+} allowed hyperfine (HF) lines each. Figure 1 depicts a typical spectrum for VO^{2+} for $\mathbf{B}$ in the a^*-c plane at 30° from the Z axis. The six sets of HF lines can be divided

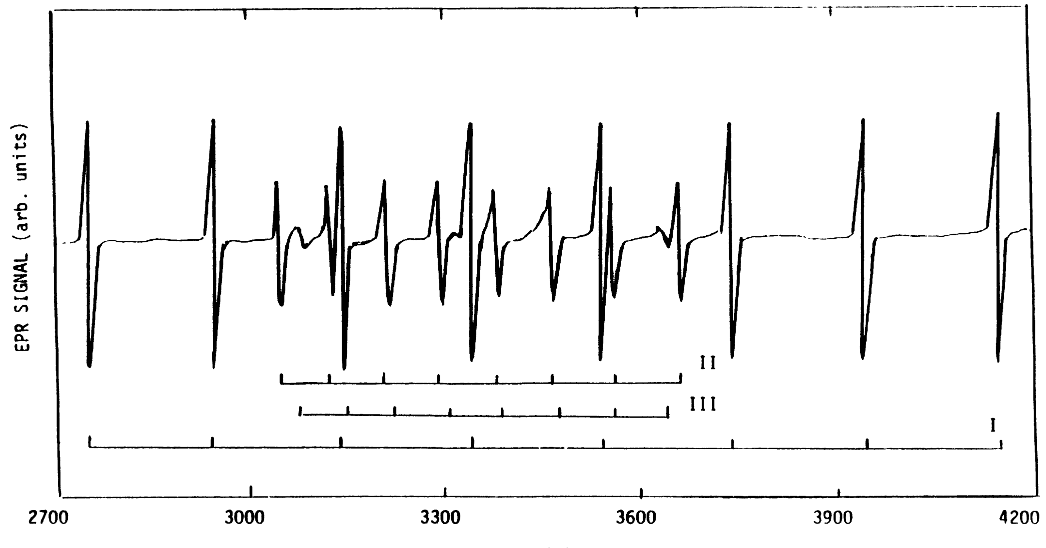

FIG. 1. First-derivative RT EPR spectrum, obtained for **B** in the Z-Y (a^*-c) plane, 30° from the Z axis. Due to the inversion symmetry, only three sets of VO^{2+} HF lines were observed in this plane (the lines for the three groups of two physically equivalent VO^{2+} ions merged), although there were six sets of lines at an arbitrary orientation of **B** (Sec. III). The line positions for the three ions I, II, and III are clearly marked. For the ion III, three lines were seen; the other five lines were overlapped by the lines corresponding to ions I and II, having much larger intensities.

into three groups of two physically equivalent ions each (I, II with strong intensity, and III with much weaker intensity) which are obtained from each other by symmetry, conforming to the fact that the three VO^{2+} ions, which are located at each of the two Zn^{2+} sites, are physically equivalent, being situated symmetrically about the a^*-c plane. The lines corresponding to the ions III were only studied, insofar as their SHF splitting is concerned, due to their much weaker intensities. The ratios of the intensities of the VO^{2+} EPR lines corresponding to the ions I, II, and III were found to be about 10:5:1; these are different from those reported by Borcherts *et al.*,[1] which are 20:5:1.

A. SHF structures at room temperature

Figure 2 exhibits the SHF structure of VO^{2+} for ions I, II, and III for the orientation of **B** for which the respective maximum SHF splittings were observed. Anisotropic quintet SHF splittings, with the relative-intensity ratios 1:4:6:4:1, for ions I and II were observed for **B** in the Z-X and X-Y planes; no significant SHF splitting was observed for **B** in the Z-Y plane. The maximum SHF splitting for ion I was found to occur for **B** in the X-Y plane, at an angle of 50° with the X axis (referred to as the X_A axis); this direction is very close to the Zn^{2+}-$H_2O(7)$ direction. The SHF splitting for ion I was symmetric about the X_A axis for **B** in the X-Y plane. When **B** deviated by more than 35° from the X_A axis, the SHF splitting for ion I was no longer resolved and the five SHF lines merged to form a single HF line. For **B** in the ZX plane, the SHF splitting for ion I was the largest for $\mathbf{B}\|\hat{\mathbf{X}}$; it decreases as **B** deviated from the X axis, becoming unresolved for $\mathbf{B}\|\hat{\mathbf{Z}}$. For ion II, the maximum SHF splitting occurred for **B** in the XY plane, 90° away from X_A, and very close to the Zn^{2+}-$H_2O(8)$ direction (X_B axis). The features of the SHF splitting for **B** in the XY plane for ion II were found to be the same as those for ion I, except that there the symmetry occurred about the X_B axis, which lies at 90° from the X_A axis. Although, for ion III, the EPR lines had the smallest intensity, their SHF splitting was still clearly observed. The direction of **B** for which the maximum SHF splitting for ion III occurred was found to be perpendicular to those for the ions I and II, i.e., the laboratory Z axis, which is the Zn^{2+}-$H_2O(9)$ direction.

B. Temperature dependence of SHF splitting

The crystal was orientated at RT for studying the temperature dependence of the SHF splitting in such a way that B was successively along the three directions for which the maxima of SHF splittings of lines occurred for one of the three physically equivalent VO^{2+} ions. The SHF splitting was observed to be independent of temperature in the 123–398 K range for any ion. (Below 123 K a cavity of small Q was used, which did not yield sufficient resolution of the EPR spectrum to exhibit SHF splitting. Above 398 K the crystal deteriorated.)

IV. SPIN HAMILTONIAN AND EVALUATION OF $\tilde{g}^2$ AND $\tilde{A}^2$ TENSORS

A. Spin Hamiltonian

The spin Hamiltonian describing the interactions of the VO^{2+} ion can be expressed as[7]

$$\mathcal{H}=\mu_B\mathbf{S}\cdot\tilde{g}\cdot\mathbf{B}+\mathbf{S}\cdot\tilde{A}\cdot\mathbf{I}+\mathbf{S}\cdot\tilde{A}^{L}\cdot\mathbf{I}_L \ . \qquad (4.1)$$

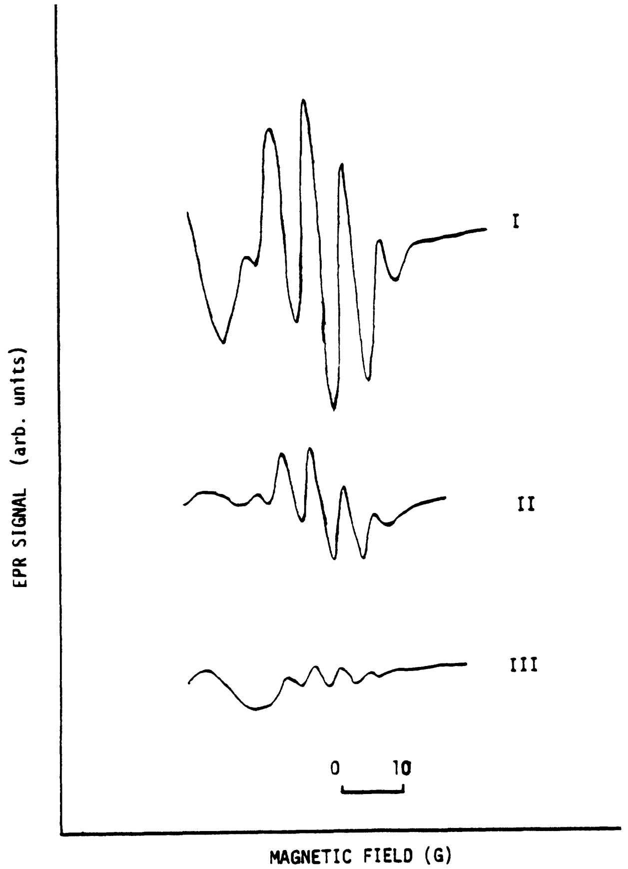

FIG. 2. X-band (klystron frequency $\approx$9.5 GHz) first-derivative RT EPR absorption spectra, exhibiting the SHF structure for the ions I, II, and III of VO^{2+}-doped ZASH single crystal, for the orientation of **B** for which the respective maximum SHF splittings were observed (Sec. III). The intensity ratios of the five SHF lines are 1:4:6:4:1 for any ion. It is seen that the SHF splitting for ion III is a bit smaller. The intensities of the lines for ion III are much weaker than those for ions I and II.

In Eq. (4.1), the successive terms represent the electronic Zeeman, the HF interaction, and the SHF interaction with the ligand protons, respectively.

B. Evaluation of the $\tilde{\mathbf{g}}^2$ and $\tilde{\mathbf{A}}^2$ tensors

The principal values and direction cosines of the $\tilde{\mathbf{g}}^2$ ($\equiv \tilde{\mathbf{g}}^T \cdot \tilde{\mathbf{g}}$) and $\tilde{\mathbf{A}}^2$ ($\equiv \tilde{\mathbf{A}}^T \cdot \tilde{\mathbf{A}}$) tensors at 295, 80, and 4.2 K were evaluated by the use of a least-squares fitting (LSF) procedure,[8-10] applicable to noncoincident principal axes of the $\tilde{\mathbf{g}}^2$ and $\tilde{\mathbf{A}}^2$ tensors. In this procedure all HF line positions observed for **B** in the Z-X, Z-Y, and X-Y planes are simultaneously fitted and the eigenvalues are calculated to second order in perturbation. The values so obtained for the VO^{2+} ions I and II at RT are listed in Table I. The absolute signs of the principal values of the matrix $\tilde{\mathbf{A}}$ have been assumed to be negative in accordance with those determined by Muncaster and Parke.[11] The present values of the spin-Hamiltonian parameters are temperature independent to within 1% for $\tilde{\mathbf{g}}$ principal values and to within 3% for $\tilde{\mathbf{A}}$ principal values. This temperature independence is typical of vanadyl complexes, whose EPR spectra are characterized by an axial symmetry of the ligand field with small distortion, as revealed by the slightly unequal principal values $A_{x''}$ and $A_{y''}$ of the hyperfine-interaction matrix, $\tilde{\mathbf{A}}$ (Table I).

C. The "in-plane anisotropy" controversy

It is seen from Table I that the principal axes of the $\tilde{\mathbf{g}}^2$ and $\tilde{\mathbf{A}}^2$ tensors are almost coincident; in particular, no significant "in-plane anisotropy" exists. This is consistent with the results of Strach *et al.*,[2] and in disagreement with those of Borcherts *et al.*[1]

V. SUPERHYPERFINE INTERACTION

The maxima of the principal values of the SHF coupling tensor, $\tilde{\mathbf{A}}^L$, for the interaction of the VO^{2+} ion

TABLE I. Principal values and direction cosines of the $\tilde{\mathbf{g}}$ and $\tilde{\mathbf{A}}$ matrices of VO^{2+}-doped ZASH single crystal for ions I and II at room temperature. (The corresponding values at 80 and 4.2 K differ only within 1% and 3% for the principal values of $\tilde{\mathbf{g}}$ and $\tilde{\mathbf{A}}$ matrices, respectively.) The principal values of $\tilde{\mathbf{g}}$ are dimensionless, while those of $\tilde{\mathbf{A}}$ are expressed in GHz. The direction cosines of the $\tilde{\mathbf{g}}^2$ tensor (X',Y',Z') are given with respect to the X, Y, and Z axes (laboratory frame), defined in Sec. III, while those of the $\tilde{\mathbf{A}}^2$ tensor (X'',Y'',Z'') are expressed relative to (X',Y',Z'), the principal axes of the $\tilde{\mathbf{g}}^2$ tensor.

		Direction cosines		
Ion	Principal values	Z/Z'	X/X'	Y/Y'
I	$g_{z'}=1.9384\pm0.0020$	0.4582	0.8011	0.3852
	$g_{x'}=1.9854\pm0.0020$	-0.8107	0.5543	0.1884
	$g_{y'}=1.9742\pm0.0020$	0.3644	0.2260	0.9034
	$A_{z''}=-0.5648\pm0.0050$	-0.9974	0.0248	0.0677
	$A_{x''}=-0.2881\pm0.0050$	-0.0406	0.9692	0.2429
	$A_{y''}=-0.1724\pm0.0050$	0.0596	-0.2450	0.9677
II	$g_{z'}=1.9315\pm0.0020$	0.5299	0.2297	0.8164
	$g_{x'}=1.9821\pm0.0020$	-0.7609	-0.2964	0.5773
	$g_{y'}=1.9884\pm0.0020$	0.3745	-0.9271	0.0177
	$A_{z''}=-0.5343\pm0.0050$	0.9948	0.1234	0.1221
	$A_{x''}=-0.2588\pm0.0050$	-0.1423	0.9767	0.1608
	$A_{y''}=-0.1676\pm0.0050$	0.0993	0.1758	-0.9794

with the protons of the nearest-neighbor water molecules in the ZASH lattice, for the VO^{2+} ions I, II, and III, were evaluated, from the respective maximum SHF splittings, to be 14.6, 14.6, and 12.9 MHz, using the following expression:[7]

$$A_{\parallel}^{L}=(\tfrac{1}{4})\mu_B g_{\perp}(B^{-}-B^{+}) , \qquad (5.1)$$

where $(B^{-}-B^{+})$ is the overall SHF splitting. For ion I of ZASH, since the SHF splittings of the lines for **B** along the two principal directions of the SHF tensor $\tilde{\mathbf{A}}^{L}$, other than that along which the maximum VO^{2+} SHF splitting occurred, were not clearly observed, it was concluded that the two other principal values of $\tilde{\mathbf{A}}^{L}$ for ion I were almost zero. Similar considerations are applicable to ions II and III.

It is noted here that the nearest-neighbor ligands of VO^{2+} ions I and II, for the two physically equivalent sites, responsible predominantly for the SHF splittings, are the four protons of the two $H_2O(9)$ molecules, which are the closest to the VO^{2+} sites. The resulting EPR spectra should, thus, consist of five SHF lines, due to the combined spin $I_L=2$ of the four protons of nuclear spins $\frac{1}{2}$ each, with the intensity ratios 1:4:6:4:1;[1] this is in agreement with the present observations. Further, the SHF splitting is expected to possess axial symmetry about the bond axis,[12] i.e., the straight line drawn though the position of the magnetic electron of the VO^{2+} ion (I or II) and the center of the four protons of the two $H_2O(9)$ molecules (a Zn^{2+} site), for the two sites. Accordingly, the combined effect of the four protons results in the experimental maximum SHF splitting to occur along the Zn^{2+}-$H_2O(7)$ direction for ion I, and along the Zn^{2+}-$H_2O(8)$ direction for ion II, as deduced using the crystallographic data. There is a similar mechanism responsible for the SHF splitting of ion III, except that here the four protons responsible for this splitting belong either to the two $H_2O(7)$, or the two $H_2O(8)$, molecules. Since the distances between the VO^{2+} ion and the ligand protons of the two $H_2O(7)$, or the two $H_2O(8)$, molecules are a little longer than that of $H_2O(9)$ molecules from the VO^{2+} ion, the resulting SHF interaction is a bit weaker than that of ions I and II, as confirmed presently. (For more details, see Misra and Sun.[13])

VI. DENSITY OF THE UNPAIRED ELECTRON OF VO^{2+}

The density of the unpaired electron, f_s, at the site of ligand protons can be estimated from the values of the SHF interaction,[14] determined in Sec. V. The final expression, applicable presently, is

$$f_s=A_{\parallel}^{L}/(3A_s^{0}) , \qquad (6.1)$$

where A_s^0 is the Fermi-contact interaction (reported to be 1420 MHz for Tutton salts[15]) and $A_{\parallel}^{L}$ is the largest SHF principal value. In deducing Eq. (6.1), the fact that two principal values of $\tilde{\mathbf{A}}^{L}$ are zero has been taken into account. Finally, f_s is estimated to be 0.34% for each of the ions I and II, and 0.30% for ion III.

VII. CONCLUDING REMARKS

The salient features of the present study are as follows.

(i) The principal values and orientations of the principal axes of the $\tilde{\mathbf{g}}$ and $\tilde{\mathbf{A}}$ matrices for VO^{2+} in ZASH have been determined at 295, 80, and 4.2 K. In particular, low temperature values have been determined for the first time; these indicate that there is *no* significant variation in the $\tilde{\mathbf{g}}$ and $\tilde{\mathbf{A}}$ matrices at low temperatures.

(ii) The SHF splitting for the three magnetically inequivalent VO^{2+} ions have been clearly observed, and interpreted. The principal values and orientations of the SHF tensors for the three VO^{2+} ions have been determined. The SHF interaction constants have been found to be temperature independent.

(iii) The densities of the unpaired electron of VO^{2+} at ligand protons have been estimated for the three magnetically inequivalent VO^{2+} ions.

(iv) The present study has resolved the "in-plane anisotropy" controversy, in that the principal axes of the $\tilde{\mathbf{g}}$ and $\tilde{\mathbf{A}}$ matrices in the X-Y plane are determined to be coincident.

ACKNOWLEDGMENTS

The authors are grateful to the Natural Sciences and Engineering Research Council (NSERC) of Canada for financial support (Grant No. OGP0004485), and to the Concordia University Computer Center for providing access to their facilities to analyze the data.

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