EPR of VO^{2+} in $ZnCs_2(SO_4)_2\cdot 6\,H_2O$ Single Crystals

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The EPR of VO^{2+} is studied in single crystals of $ZnCs_2(SO)_4)_2\cdot 6\,H_2O$ at X-band. The V-O axis is found to have two orientations. The spin-Hamiltonian parameters at 298 K are determined.

An EPR study of the vanadyl ion (VO^{2+}) in the Tutton salt $Zn(NH_4)_2(SO_4)_2\cdot 6\,H_2O$ (ZASH)[1] revealed some interesting features of the oriented vanadyl ion in the host lattice. The study suggested the possibility of obtaining structural information about the vanadyl ion and indicated that the complex formed in this case is very much like vanadyl sulfate pentahydrate. In this note we describe an EPR study of VO^{2+} in $ZnCs_2(SO_4)_2\cdot 6\,H_2O$ (ZCsSH) single crystals.

The crystal structure of Tutton salts is known to be monoclinic with space group $P2_1/a$[2]. The unit cell contains two formular units. The divalent metal sites at (0, 1/2, 1/2) and (0, 0, 0) are octahedrally coordinated by six water molecules.

Single crystals of ZCsSH containing vanadyl ions were grown by slow evaporation from a water solution of ZCsSH with a VO/Zn concentration ratio of 0.2%. The crystal grows with well defined faces[3] so that the orientation of the crystal becomes a relatively easy task. The experiments were performed on a Varian V-4502 EPR spectrometer, operating at X-band, provided with a 100 kHz field modulation.

The EPR spectrum was studied at 298 K. Two different sets of eight hyperfine lines characteristic of the splitting due to the ^{51}V ($I=7/2$) nucleus have been observed, indicating that VO^{2+} occupies two types of sites in the lattice. The intensities of the hyperfine lines of the spectra due to V-O at two sites are approximately in the ratio 5 : 1. The angular variation of the spectra was studied in the $a'b$ (where a' is perpendicular to the c axis in the ac plane), bc and ca' planes. Each of the eight hyperfine lines of a group splits into two as H is moved in the $a'b$ and bc planes (or in any general direction away from the crystal axes). However, the lines do not split in the $a'c$ plane. Figure 1 shows the angular variation of the hyperfine lines of the main VO^{2+} centre in the bc plane. The interesting feature of the experiment is the observation of a five-line superhyperfine structure at various orientations of the crystal in the magnetic field. This additional structure was also present in ZASH and was deduced to be caused by the protons of the surrounding water molecules[1].

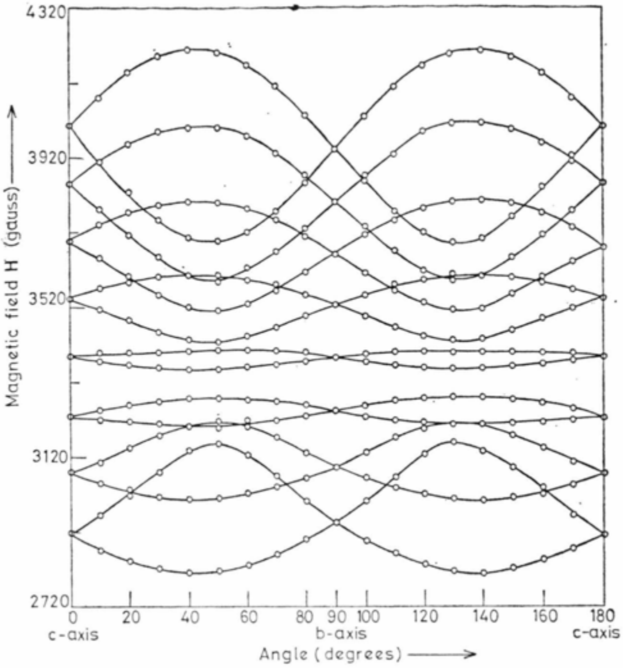

Fig. 1. Angular variation of the magnetic field at resonance in the bc plane for VO^{2+} in $ZnCs_2(SO_4)_2\cdot 6\,H_2O$. The solid lines are smooth curves that connect data points from the same transition. This figure is for the more populous of the two VO^{2+} orientations in the Tutton salt.

All the spectra are analysed using the spin-Hamiltonian corresponding to rhombic symmetry[4]. The spin-Hamiltonian parameters g and A (hyperfine

Table I. Spin-Hamiltonian parameters for two orientations of VO^{2+} in $ZnCs_2(SO_4)_2\cdot 6\,H_2O$ single crystals at 298 K. All the hyperfine parameters are in units of $10^{-4}\,cm^{-1}$.

	Relative intensity	
	5	1
g_z	1.936 ± 0.001	1.934 ± 0.001
g_x	1.985 ± 0.001	1.986 ± 0.001
g_y	1.983 ± 0.001	1.984 ± 0.001
A_z	181.0 ± 0.5	180.0 ± 0.5
A_x	71.60 ± 1	72.00 ± 1
A_y	70.00 ± 1	69.00 ± 1
Θ	$51°\pm1°$	$60°\pm1°$
Φ	$82°\pm2°$	$-58°\pm2°$

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coupling constant) along the orientation of the V-O axis are listed in Table I. Here Θ and Φ refer to the angles defining the direction of the z axis (V-O bond) relative to the crystal axes. Θ is the polar angle from the b axis and Φ is the azimuthal angle from the c axis in the ac plane. It can be seen from Table I that the principal values of $\vec{\mathbf{g}}$ and $\vec{\mathbf{A}}$ tensors for both species are approximately what one would except for a VO^{2+} centre. The results indicate that the $\vec{\mathbf{g}}$ and $\vec{\mathbf{A}}$ tensors are nearly axially symmetric. The axial spin-Hamiltonian parameters ($\parallel$, $\perp$) were determined from the spectrum of finely crushed ZCsSH:VO^{2+} crystals and are $g_{\parallel} = 1.935 \pm 0.001$, $g_{\perp} = 1.986 \pm 0.001$, $A_{\parallel} = 182 \pm 2 \times 10^{-4}\ \text{cm}^{-1}$, $A_{\perp} = 73 \pm 2 \times 10^{-4}\ \text{cm}^{-1}$. The accuracy of the constants determined from the powder spectrum is limited by the line widths. A calculation of the constants P and K using the equations given by Kivelson et al.[5] yielded $P = 119.1 \times 10^{-4}\ \text{cm}^{-1}$, $K = 0.86$ for VO^{2+} in ZCsSH.

The above results can be explained as follows. In ZCsSH, the Zn^{2+} is surrounded by an octahedron of water molecules. The two Zn^{2+} are situated at symmetry related sites. If VO^{2+} substitutes Zn^{2+} in the lattice, one should observe in general the spectra of two nonequivalent VO^{2+} ions which, however coincide in the mirror plane $a'c$. The observation of the splitting of the hyperfine lines in the $a'b$ and bc planes away from the crystallographic axes and the absence of splitting in the $a'c$ plane confirms that VO^{2+} substitutes Zn^{2+} in the lattice. When the VO^{2+} ion enters the Zn^{2+} site, V-O orients itself along any of the three mutually perpendicular metal-water directions within a given octahedron (possibly with different populations). Thus one excepts three VO^{2+} centres instead of two as observed in this experiment. Perhaps one of the Zn-H_2O directions is energetically unfavorable for the V-O bond. It is instructive to compare the orientations of different Zn-H_2O's with the orientation of the V-O axis. Although detailed structural studies are available only for crystals of ammonium Tutton salts[6–10], the isomorphism of the Tutton salts leads one to assume that the bond distances and angles in the hydration shell of Zn^{2+} in ZCsSH are not very different from those in ZASH. A comparison of the values of Θ and Φ obtained in this experiment with theoretical values of Θ and Φ for different Zn-H_2O bond lengths in ZASH as calculated by Borcherts et al.[1] suggests that the V-O bond is predomenantly nearly in the direction of the longest Zn-H_2O bond. This is expected because the farther a water molecule is away from the metal atom, the easier it is for the vanadyl ion to displace the water molecule in the direction to form the vanadyl pentahydrate complex.

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