EPR Study of VO^{2+} and Cr^{3+} in $Li_2SO_4 \cdot H_2O$ Single Crystal

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A single crystal X-band EPR study of VO^{2+} and Cr^{3+} in $Li_2SO_4 \cdot H_2O$ was carried out at room temperature. Analysis of the spectra indicates that VO^{2+} substitutes for Li^+ and that there are two magnetically inequivalent Li^+ sites. The charge compensation occurs by removal of a neighboring Li^+. The principal values of the **g** and **A** tensors of the spin Hamiltonian for the two sites were determined. Superhyperfine interaction of the $3d^1$ electron of VO^{2+} with the neighboring water protons in the unit cell was observed and found to be between 0 and 0.5 mT, depending on the orientation of the magnetic field. Two magnetically different sites were also observed for Cr^{3+}, and the results were explained by a rhombic spin Hamiltonian. The Hamiltonian parameters g, D, and E were determined. It is concluded that VO^{2+} and Cr^{3+} enter into the Li^+ places and the charge is compensated by a Li^+ vacancy in the VO^{2+} case and proton vacancies in the Cr^{3+} case.

Key words: EPR, VO^{2+}, Cr^{3+}, $Li_2SO_4 \cdot H_2O$.

Introduction

The electron paramagnetic resonance (EPR) method provides a detailed description of the nature of the electric field symmetry produced by the ligands around the paramagnetic ions [1–4]. The vanadyl ion, VO^{2+}, and the chromium ion, Cr^{3+}, have extensively been used as probes to study the symmetries of the crystalline electric fields. In most of the complexes, VO^{2+} and Cr^{3+} posses axial symmetry, both the **g** and **A** tensors indicating this. A further interest is the compensation of the charge imbalance when divalent or trivalent impurities are introduced in place of monovalent cations. In these cases positive ion vacancies are assumed to fulfill the charge compensation, and in some cases the principal directions of the magnetic tensors of the divalent impurities agree with the impurity-positive ion vacancy directions. In this paper we report the results on VO^{2+} and Cr^{3+} in $Li_2SO_4 \cdot H_2O$. No previous study could be found on single crystals of this compound doped with these ions.

$Li_2SO_4 \cdot H_2O$ is a monoclinic crystal, space group P_{2_1}. Its unit cell dimensions are $a = 0.5435$ nm, $b = 0.4836$ nm, $c = 0.8140$ nm, and $\beta = 107.23°$, where β is the angle between the a and c axes [5, 6]. The positions of the atoms are shown in Fig. 1 by the projection of the unit cell on its ac plane [6–9]. The compound contains the two Li atoms Li_1 and Li_2, Li_1 being coordinated only to the oxygen atoms of the SO_4 groups, while one of the O atoms around Li_2 is the oxygen of the water molecule.

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Experimental

The single crystals were grown by slow evaporation of a concentrated aqueous solution of $Li_2SO_4 \cdot H_2O$

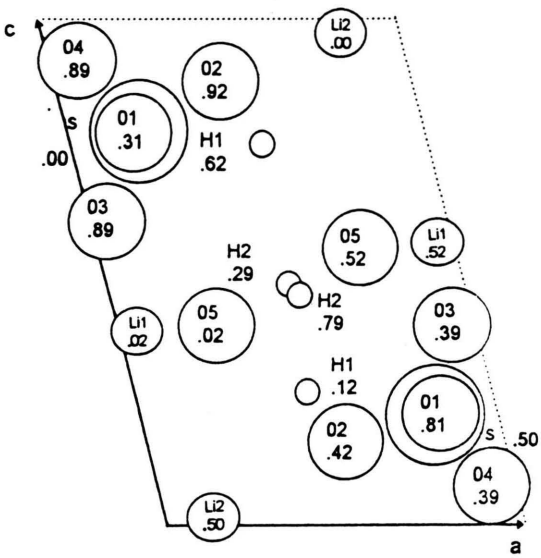

Fig. 1. Projection of the $Li_2SO_4 \cdot H_2O$ crystal unit cell on its a^*c plane. Atoms are drawn with a radius proportional to the square root of their atomic mass. The numbers correspond to the atom's height along a perpendicular projection to the plane (in percentage of the unit cell length).

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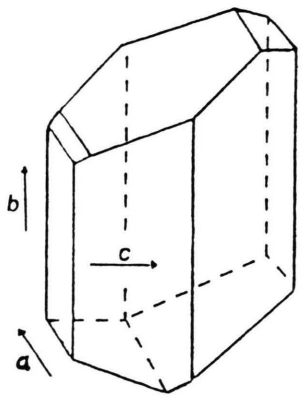

Fig. 2. Crystal habit and orientation of the crystalline axes of $Li_2SO_4 \cdot H_2O$.

containing 0.1 weight per cent of $VOSO_4$ and $Cr_2(SO_4)_3$ for doping. Well shaped single crystals were obtained. The crystal habit and crystalline axes are shown in Figure 2. The EPR spectra were recorded with a Varian X-band E-109C model EPR spectrometer at room temperature. The single crystals were mounted on a goniometer and rotated around the a^*, b, c crystal axes in the magnetic field to explore the bc, a^*c, and a^*b planes. The spectra were recorded at 10° intervals. The magnetic field modulation frequency was 100 kHz. The g values were measured by comparison with a diphenylpicrylhydrazyl sample of $g = 2.0036$.

Results and Discussions

A) VO^{2+}

The VO^{2+} doped single crystals exhibit the characteristic spectrum of 8 lines shown in Figure 3. This is due to the hyperfine interaction of the $3d^1$ electron with the vanadium nucleus of $I = 7/2$ when the magnetic field is along the b axis. At any orientation in the a^*c plane a spectrum similar to this, consisting of 8 lines, appears. However, when the magnetic field departs form the b axis or is at any other orientation except in the a^*c plane, the number of hyperfine lines becomes 16. These are consistent with the properties of monoclinic symmetry and indicate the existence of two magnetically inequivalent sites of VO^{2+} in the crystal. The variations of the EPR line positions against the orientations of the magnetic field are shown in Figure 4. The g and A parameters were calculated from the observed spectra for all orientations of the magnetic field in the three planes. The principal values of the **g** and **A** tensors and direction cosines with respect to the b, c, a^* axes were determined using

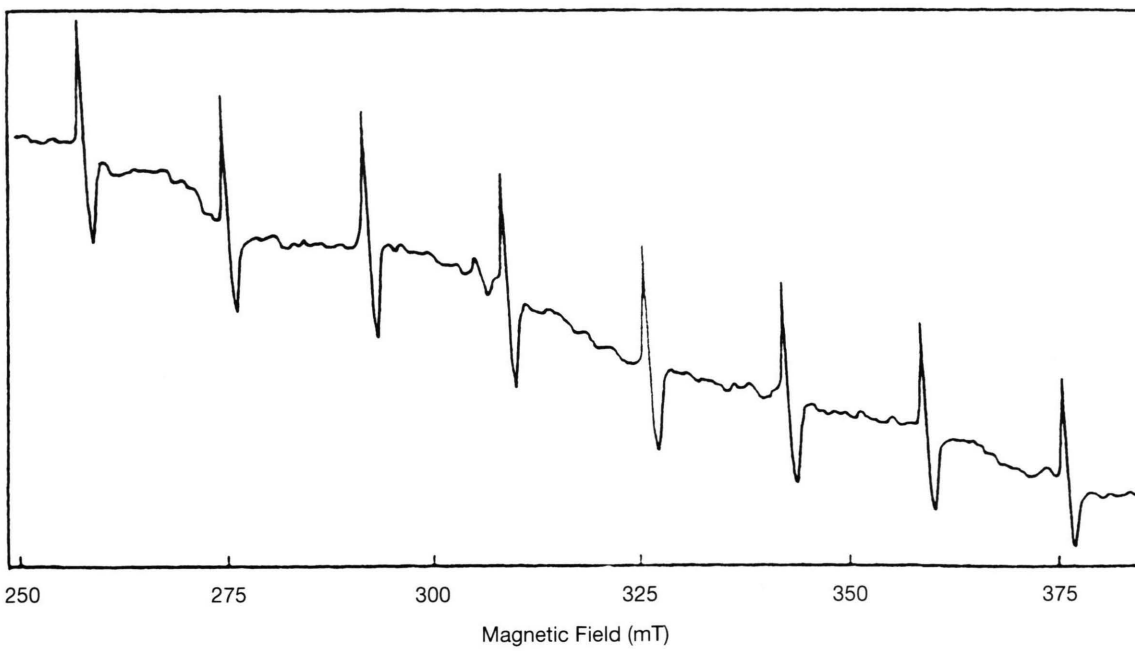

Fig. 3. EPR spectrum of VO^{2+} doped in $Li_2SO_4 \cdot H_2O$ single crystal. The magnetic field is along the crystalline b-axis.

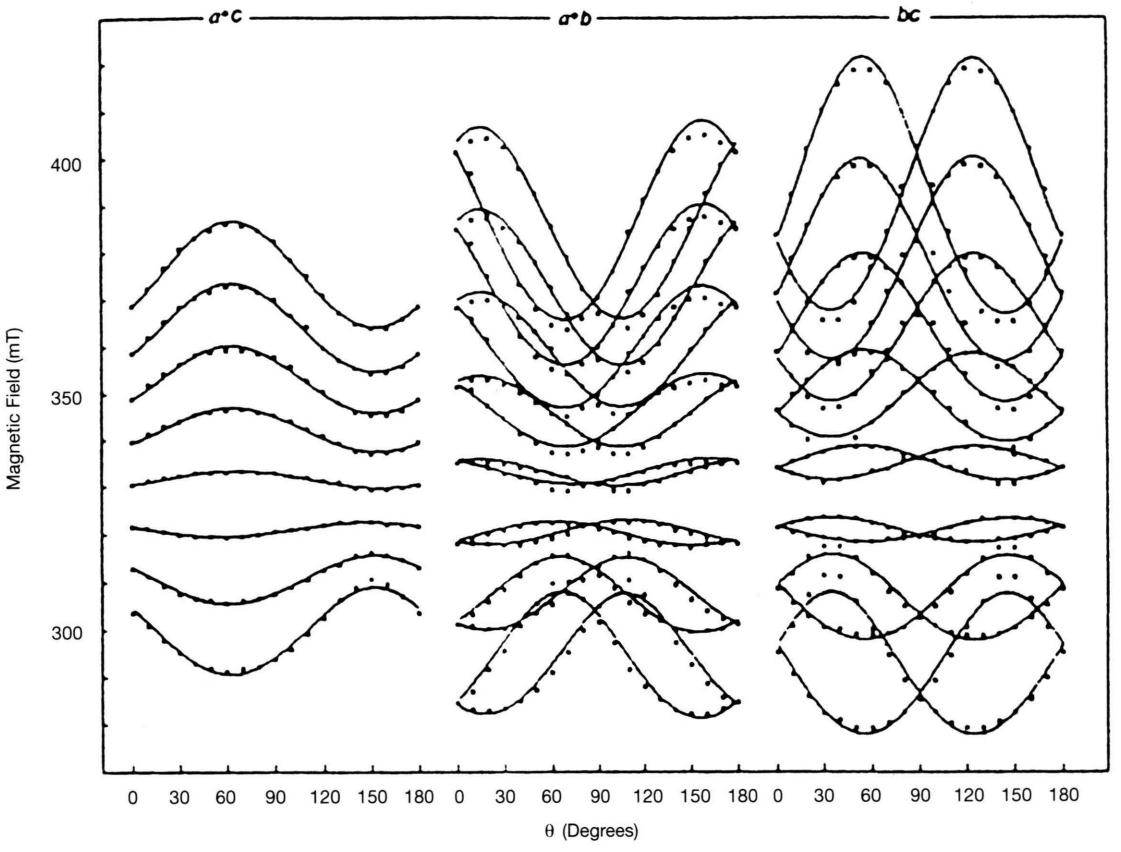

Fig. 4. Variations of the hyperfine line positions of VO^{2+} in $Li_2SO_4 \cdot H_2O$ single crystal. The angles indicate the orientations of the magnetic field in the a^*c, a^*b and bc planes.

the usual diagonalization procedures [10, 11]. The results are listed in Table 1 for the two sites. The isotropic values of the **g** and the **A** tensors for both sites are equal and $g_{av} = 1.971$ and $a = 11.73$ mT. However, the principal values of g and A deviate somewhat from axial symmetry. As an approximation we take $A_{//} = A_{bb}$, $A_{\perp} = \frac{1}{2}(A_{a^*a^*} + A_{cc})$ and $g_{//} = g_{bb}$, $g_{\perp} = \frac{1}{2}(g_{a^*a^*} + g_{cc})$, and use these values in the following equations for the spin Hamiltonian parameters [4, 12, 13]:

$$-\frac{A_{//}}{P} = K + \frac{4}{7} - \Delta g_{//} - \frac{3}{7}\Delta g_{\perp}, \tag{1}$$

$$-\frac{A_{\perp}}{P} = K - \frac{2}{7} - \frac{11}{14}\Delta g_{\perp}. \tag{2}$$

In these equations P is the dipolar hyperfine coupling constant given by $P = g_e g_N \beta_e \beta_N \langle r^{-3} \rangle$ where $\langle r^{-3} \rangle$ is the average value of r^{-3} between the vanadium $3d^1$ orbitals, K the dimensionless Fermi contact coupling parameter which represents the amount of the unpaired electron density at the nucleus, and the other symbols have their usual meaning [12]. From these and Table 1 we obtained $P = 13.97$ mT and $K = 0.8$ for one site; and $P = 14.08$ mT and $K = 0.79$ for the other. These P values are close to the ones observed for VO^{2+} in other lattices [12], and the K values are in the same order as that for VO^{2+} in other crystals where the ion is surrounded by oxygens [12, 14, 15]. Therefore, this study is consistent with the single crystal data given above as the two types of Li atoms are surrounded by the O atoms forming a LiO_4 polyhedron [7–9]. Consequently it becomes obvious that VO^{2+} enters the lattice substitutionally in place of Li^+ ions, Li_1^+ or Li_2^+, using one of the oxygen atoms in LiO_4 polyhedra. For the charge compensation we suggest that when a VO^{2+} replaces a Li^+ and an oxygen atom, another Li^+ vacancy sould appear. However, neither of the direction cosines of the princi-

Table 1. EPR parameters of VO^{2+} doped in $Li_2SO_4 \cdot H_2O$. The direction cosines are referred to the crystalline b,c and a^* axes.

Site	g A(mT)	Direction cosines		
		b	c	a^*
I	1.999	0.2844	−0.9448	0.1620
	1.992	0.7802	0.3264	0.5335
	1.924	0.5570	−0.0253	0.8301
II	1.997	0.4743	−0.8565	−0.2032
	1.990	0.6908	0.5053	−0.5171
	1.925	0.5456	0.1048	0.8314
I	20.3	0.2423	−0.8912	0.3834
	7.9	0.5512	−0.1986	−0.8103
	7.0	0.7983	0.4077	0.4431
II	20.6	0.2902	−0.7853	0.5435
	8.0	0.5374	0.6074	0.5848
	6.6	0.7895	0.1188	0.6020

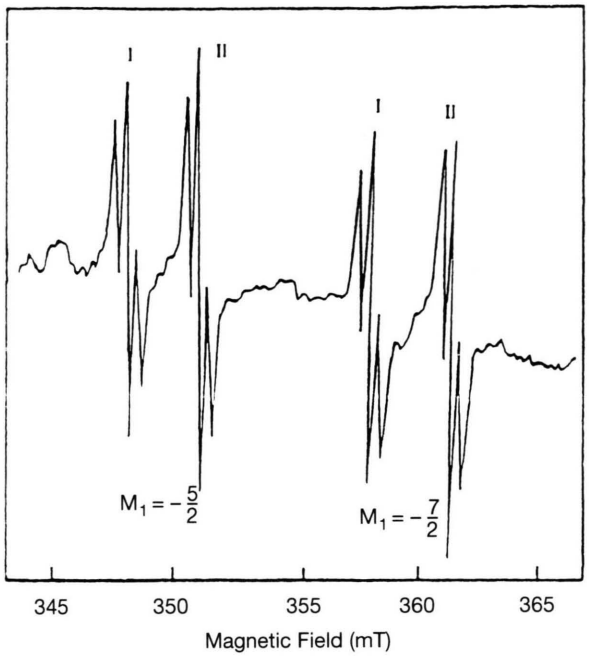

Fig. 5. Superhyperfine structure of the VO^{2+} hyperfine line corresponding to $m_I = -5/2, -7/2$. The magnetic field is in the a^*b plane and 5° away from the a^* axis.

pal values of the **g** or **A** tensor in Table 1 corresponds to the Li_1-Li_2 or LiO directions in the crystal. Therefore, the charge compensation seems to be effective in the occurence of this direction, as otherwise one of the principal directions of the **g** or **A** tensors would be in the V=O bond direction.

A further experimental observation is the superhyperfine interaction of the unpaired electron of VO^{2+} with the hydrogens of a water molecule in the crystal. Every hyperfine line in the two sites splits into 3 lines with an intensity distribution of 1:2:1 at some orientations of the magnetic field in the a^*b plane, as shown in Figure 5. The splitting constant varies from 0 to 0.5 mT, and the maximum value occurs at 5° from the a^* axis. This maximum splitting corresponds to a 9.88 per cent unpaired spin population on the hydrogen atoms, and it seems that at this orientation the magnetic field is in the $V=OH_2$ bond direction.

B) Cr^{3+}

The EPR spectrum of Cr^{3+} ($3d^3$) doped in $Li_2SO_4 \cdot H_2O$ consists of three lines when the magnetic field is along the crystalline b axis as shown in Figure 6. These are the characteristic allowed ($\Delta M_s = \pm 1$) fine structure EPR lines of Cr^{3+} with an effective spin $S=3/2$. However, when the magnetic field departs from the b axis, each line splits into two. The line positions against the orientation of the magnetic field in the bc plane are shown in Figure 7. These indicate the presence of magnetically inequivalent two sites for Cr^{3+} in this crystal. Forbidden transitions were not observed in this plane. However, in the a^*b and a^*c planes both the $\Delta M_s = \pm 2$ and $\Delta M_s = \pm 3$ lines were, observed similar to those in [16, 17].

The spectra can be described by the spin Hamiltonian for $3d^3$ ions ($S=3/2$),

$$\mathcal{H} = \beta g \mathbf{H} \cdot \mathbf{S} + D\left[S_z^2 - \frac{1}{3}S(S+1)\right] + E(S_x^2 - S_y^2), \quad (3)$$

where D and E are zero field splitting parameters and the other symbols have their usual meaning [1]. The spin Hamiltonian parameters were found to be $g = 1.970 \pm 0.005$ and $D = 152 \pm 2$ mT and $E = -19 \pm 2$ mT for both sites following the procedures of Darabont et al. [16]. These values are in the order of the parameters given in the literature for the Cr^{3+} doped in various compounds [18, 19]. Hyperfine interaction with the ^{53}Cr nucleus ($I=3/2$) and superhyperfine interaction, similar to VO^{2+}, with the hydrogens of the water molecules in the crystal were not observed. However, consistency of the EPR spectra with the monoclinic symmetry of the crystal indicates the

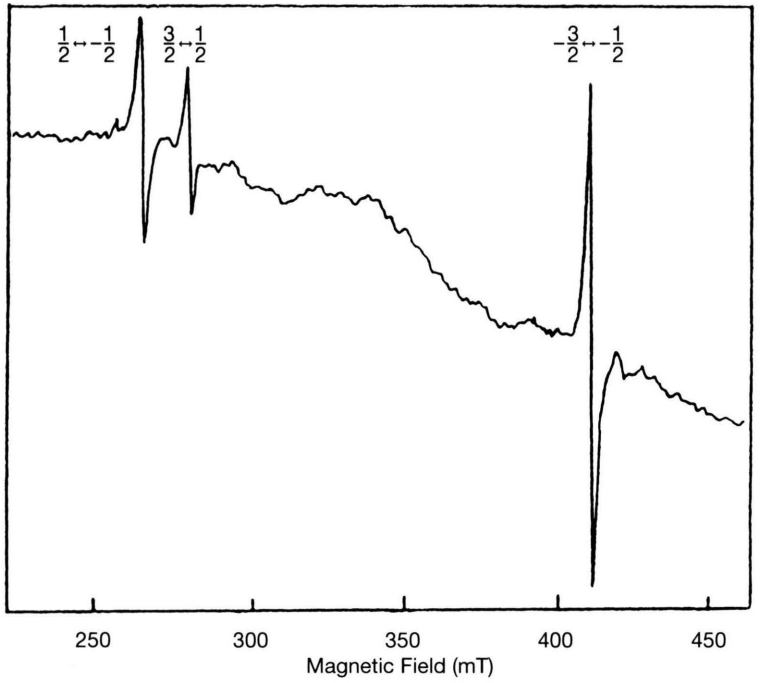

Fig. 6. EPR spectrum of Cr^{3+} doped in $Li_2SO_4 \cdot H_2O$ single crystal. The magnetic field is along the crystalline *b*-axis.

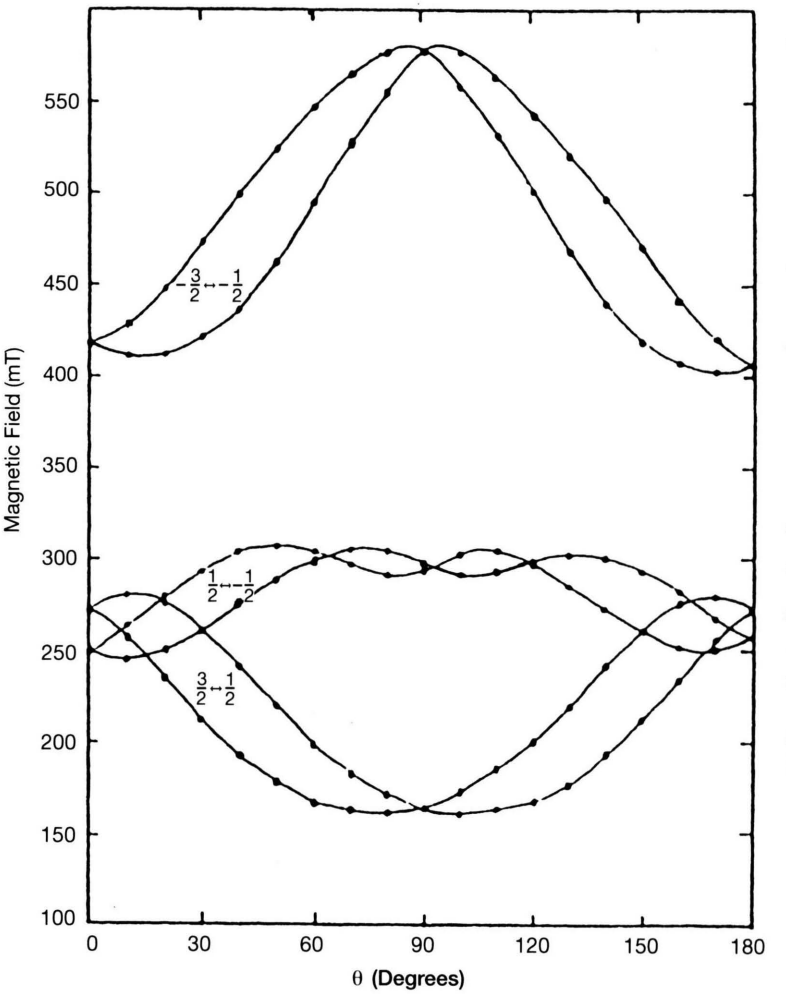

Fig. 7. Variations of the fine structure line positions of Cr^{3+} doped in $Li_2SO_4 \cdot H_2O$ single crystal in the crystalline *bc* plane.

substitution of Li^+ with Cr^{3+}. The ionic radius of Li^+ (78 pm) is larger than that of the Cr^{3+} (64 pm). Therefore we think that Cr^{3+} substitutes for one of the Li^+ ions in Fig. 1, and the charge compensation occurs in this case possibly by the proton vacancies, since no superhyperfine interaction of the protons with the electron spin of Cr^{3+} was observed. This makes it more reasonable to assume two protons, rather than two Li^+ vacancies, accompanying every Li^+–Cr^{3+} substitution.

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