Electron Spin Resonance of VO^{2+} in $LiKSO_4$ Single Crystals

Manu Jain

Department of Physics, St. Stephen's College, Delhi-110006, India

Reprint requests to M. J.; E-mail: es_prit_de_corps@rediffmail.com

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Electron spin resonance of VO^{2+} doped in $LiKSO_4$ single crystals has been studied at 295 K, using an X-band spectrometer. Three sites have been observed. VO^{2+} enters the lattice at Li and K substitutional sites. The ESR spectra have been analysed and spin-Hamiltonian parameters evaluated.

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Lithium potassium sulfate, $LiKSO_4$, belongs to the family of compounds $LiMAB_4$ (M=Na,K,Rb,Cs,NH_4; AB_4=SO_4,BeF_4). $LiKSO_4$ has been investigated in great detail because of its large variety of physical properties found in different structural phases [1, 2]. This paper reports the electron spin resonance (ESR) of vanadyl, VO^{2+}, ion impurities in single crystals of $LiKSO_4$ at 295 K. The crystal structure of $LiKSO_4$ at 295 K is hexagonal with space group $P6_3$ [3, 4]. The unit cell has the dimensions $a = 0.5146$ nm, $c = 0.8636$ nm and contains two formula units [4]. The potassium atoms occupy positions on the hexagonal c-axis. They are coordinated by nine oxygens. The Li atoms are coordinated with four oxygens.

Single crystals of $LiKSO_4$, doped with VO^{2+}, were grown at $\sim$ 300 K by slow evaporation of an aqueous solution containing an equimolar mixture of corresponding sulfate to which 0.5 wt % VO^{2+} was added. The crystal grows in flat hexagonal plates, the plane of which is perpendicular to the c-axis. The ESR experiments were performed with a JEOL FE-3X homodyne spectrometer operating at ~ 9.45 GHz, equipped with a TE_{001}-cylindrical cavity and 100 kHz field modulation. A speck of powdered DPPH used as a field marker (taking $g_{DPPH} = 2.0036$) was inserted simultaneously into the sample cavity. The angular variation studies were done using a JES-UCR-2X sample angular rotating device. Powder spectra were recorded by powder in quartz tubes. The powder ESR samples were obtained by grinding an individual crystal.

For an arbitrary orientation of the crystal, the ESR spectrum of the vanadyl ions consists of a large number of resonance lines. In addition to weak lines from unidentified vanadyl complexes, at least three chemically different sites, having differing intensities, were observed. For an arbitrary orientation of the crystal, the crystal symmetry allows two symmetries, related but with magnetically inequivalent orientations for a given site. These orientations become equivalent, when the magnetic field is along the c-axis or perpendicular to it. The three different patterns of different intensities were observed, corresponding to three sites, will be called site I, II and III (Figure 1). Because of the low intensity of vanadyl at site III, only its lines along the z-axis could be identified. Angular variation studies did show that the z-axes of site I, II and III make, respectively, an angle of 10°, 65°, and 40°to the c-axis.

The ESR spectra have been analysed using the spin-Hamiltonian

$$\mathcal{H} = \beta_e \boldsymbol{S.g.B} + \boldsymbol{S.A.I},$$

where the terms have their usual meaning. Additional terms, including the nuclear Zeeman and quadrupole coupling terms, are ignored, because these terms are sufficiently small to be neglected. The spin-Hamiltonian parameters observed for VO^{2+} in $LiKSO_4$ are given in Table 1. The parameters were also determined from the spectra taken with finely crushed crystals (Fig. 2) and are included in the table. The powder spectrum indicates the presence of two different sites, and the extreme lines are marked in the Figure 2. The accuracy of the constants determined from the powder spectra is limited by the linewidth.

In vanadyl containing materials, including complexes in solution, the V^{4+} ion is usually coordinated with other groups, particularly with oxygens. The

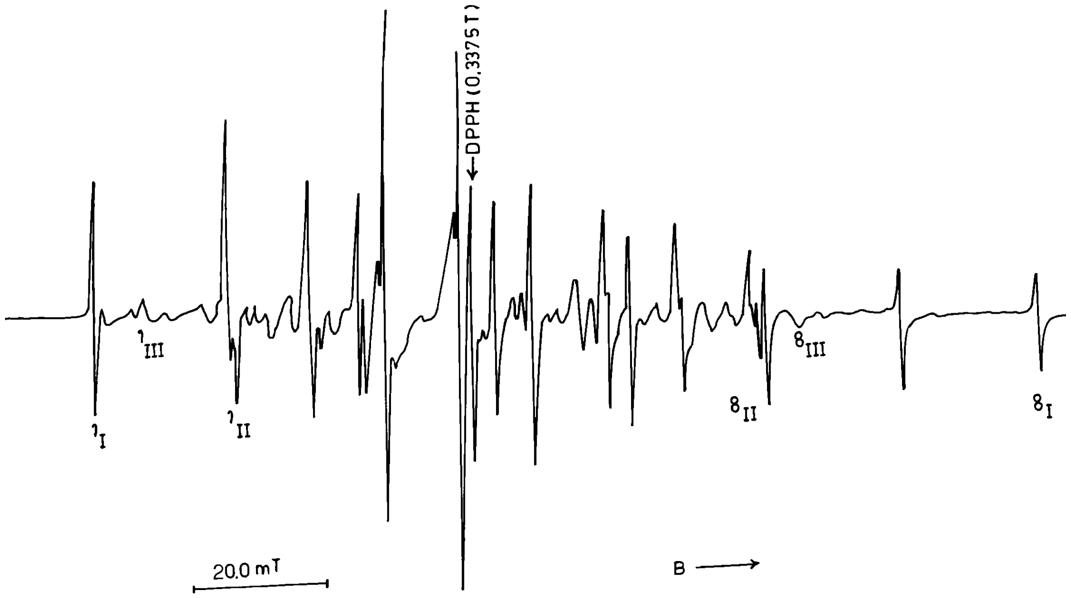

Fig. 1. ESR spectrum of VO^{2+} doped $LiKSO_4$ single crystals at 295 K with B parallel to the c-axis.

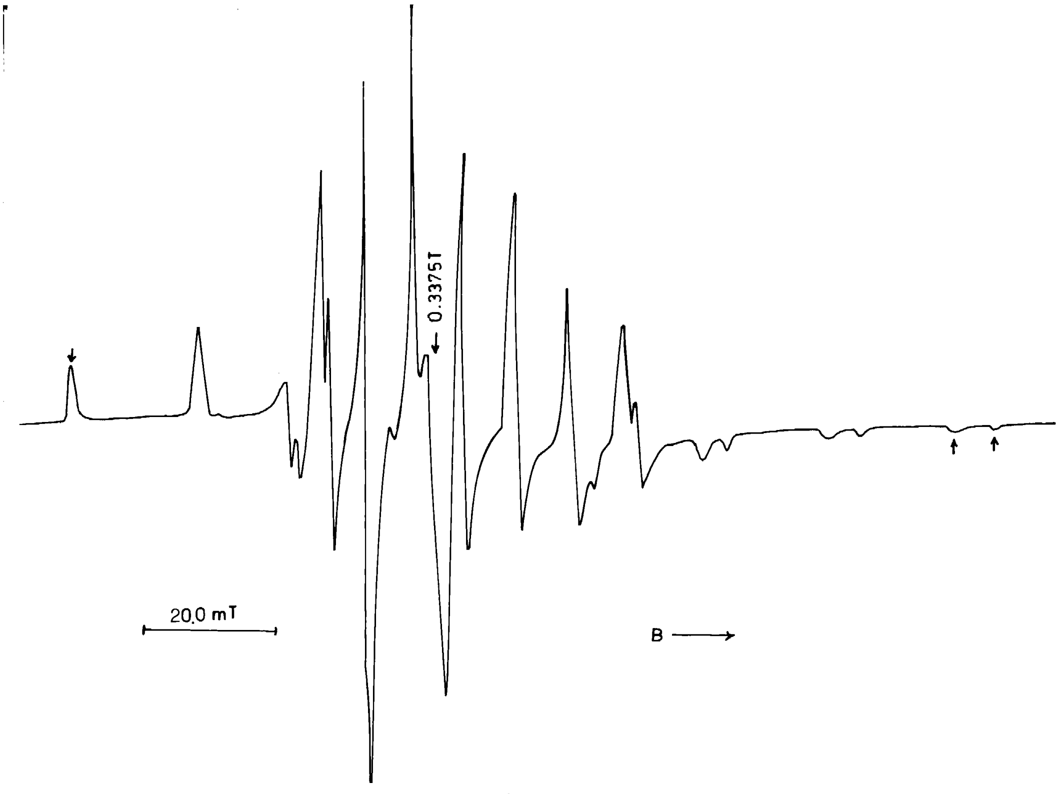

Fig. 2. ESR spectrum of a powder sample (crushed) of VO^{2+} doped $LiKSO_4$ at 295 K.

Table 1. Spin-Hamiltonian parameters for VO^{2+} ions in $LiKSO_4$ single crystals at 295 K. A values are in units of 10^{-4} cm^{-1}.

	Crystal			Powder	
Parameters	Site I	Site II	Site III	Site I	Site II
$g_\parallel$	1.919(2)	1.919(2)	1.935	1.919	1.930
$g_\perp$	1.984(4)	1.982(4)	–	1.977	1.975
$A_\parallel$	181(1)	182(1)	174	182	174
$A_\perp$	70(2)	77(2)	–	77	68

potassium site in $LiKSO_4$ is surrounded by a polyhedron of nine oxygens with K-O distances 0.2850 nm, 0.2957 nm and 0.2987 nm [4]. The lithium site is surrounded by four oxygens with Li-O distances 0.1911 nm and 0.1925 nm [4]. An attempt is made to correlate the direction of the V-O bond with the K-O and Li-O bond direction. The direction of the K-O and Li-O bonds relative to the c-axis were calculated using neutron diffraction data [4]. The angle, which K-O_1 (0.2987 nm) and K-O_2 (0.2957 nm, 0.2850 nm) make with the c-axis are 84°, 41°and 43°, respectively. On the other hand, the angle which Li-O_2 (0.1925 nm) makes with the c-axis is 75.4°, while Li-O_1 (0.1911 nm) lies along the c-axis. Comparing these values with those obtained experimentally, the direction of V-O for site I is found to be nearly along the direction of Li-O_1 while that for site II is close to the direction of Li-O_2 and for site III it is along the K-O_2 bond direction. Jayaram and Sobhanadri [5] concluded from ESR studies of VO^{2+} in $LiNH_4SO_4$ that vanadyl occupies tetrahedral Li sites. It appears that the Li site is preferred in comparison to NH_4 and K site.

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