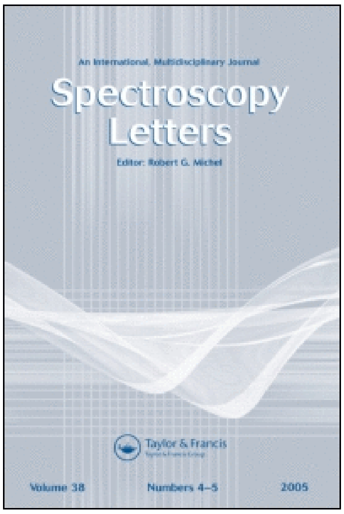

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EPR STUDIES OF THE LOW-TEMPERATURE PHASE TRANSITIONS IN $LiKSO_4$ BY Cu^{2+} IONS

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Electron paramagnetic resonance (EPR) spectra of Cu^{2+} doped lithium potassium sulphate (LPS) have been studied at different temperatures. The spin-Hamiltonian g and A parameters have been evaluated. Phase transitions in LPS were observed at low temperature. The measured g-values indicate a rhombic field for Cu^{2+} in the lattice at the temperature range 300 - 215 K. Between 215 K and 123 K an orthorhombic field suggested. The bonding parameter (α^2), Fermi-contact term (K) and the free ion dipolar term (P) are evaluated using the principal g and A values. The ground state were function for Cu^{2+} ion in (LPS) is determined.

INTRODUCTION

Lithium potassium sulphate ($LiKSO_4$), due to its interesting properties has been subjected to various investigations, including

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EPR studies (1-6). The crystal structures, the existance of positional disorder and domain structures in particular have been investigated by X-ray and neutron diffraction (3,7,8). Low temperature structural phase transitions have been studied by Raman scattering (2,6), and EPR (4,9,10). However, there is no enough informations in literature on the EPR spectra of Cu^{2+} ions in these materials. The EPR method provides in detail description of the electric field symmetry produced by the ligands around the paramagnetic ions (11). It can be used also to obtain informations about the influence of defects on the low -temperature phase transitions (10,11,12). Hefni et al (13-16) studied the EPR spectra of Cu^{2+} doped in a variety of host lattices.

In the present work, we report the results of the EPR study of Cu^{2+} ion doped LPS. The interest of this study is to find the site symmetry and the ground state wave function of the ion. Also, the attention has been focused to certain selected temperature ranges to illustrate the low phase transitions which take place in this material.

EXPERIMENTAL

LPS crystals doped with Cu^{2+} which is used in this work were grown by slow evaporation at room temperature from an aqueous solutions made up of equi-molar quantities of potassium sulphate and lithium sulphate monohydrate to which 0.05 to 0.1 mole percent of copper sulphate was added as impurity. All the reagent used in the present investigation are of analytical grade.

The morphology of the grown crystals agrees with that in (17). LPS crystals are hexagonal at room temperature and its space group is $P6_3$ (C_6^6), with a bimolecular unit cell of dimensions a = 5.1457 A° and C = 8.6298 A°. The four oxygens of the SO_4 group are situated at the four corners of a regular tetrahedron with the sulpher atom at the center. The lithium ion alternate with the sulphur ions. Each potassium ion is surrounded by six sulphate ions and each sulphate ion contributes one oxygen to the potassium ion forming approximately an octahedron.

The EPR measurements were carried out on powder samples using a Brucker ER 200E-SRC X-band Spectrometer with a 100 KHz modulation and TM_{110} cavity. The sample temperature was controlled with an Oxford Instruments Model ESR 900. The g values were determined using the DPPH resonance as a standard and are accurate to ±0.0005.

RESULTS AND DISCUSSION

EPR spectra of the sample were recorded at different temperatures in the temperature ranged from 300 K to 120 K. A selection of the first-derivative EPR spectra of the powdered crystals recorded at various temperatures are shown in Fig. 1&2. They show a typical three g-values spectra. From these spectra one can obtain the salient features pertinent to the calculation of the spin-Hamiltonian parametries (12,13,18). Furthermore, such observation provides a convenient way for studying the temperature variations of the EPR spectra of LPS : Cu^{2+}

The variation with temperature of the g-values and ^{63}Cu hyperfine tensors is conventiently studied in the powder samples to obviate the need for lengthly study of the crystal in three planes.

The EPR spectrum at room temperature (300 K) consists of four lines in the low field side (corresponding to g_z), one broad line in the mid-field (corresponding to g_x) and four lines in the high -field side (corresponding to g_y). The structure of the broad line is well resolved at low temperatures. It could be distinctly seen in the g_x part below T = 190 K. The general form of the spectra in the temperature range from 300 K to 230 K is that expected for a six-coordinated copper complex having tetragonal symmetry with a slight rhombic distortion (19). These spectra are essentially similar to that reported previously (20).

However, important differences were observed in our temperature dependence spectra, especially below 230 K where the best-resolved

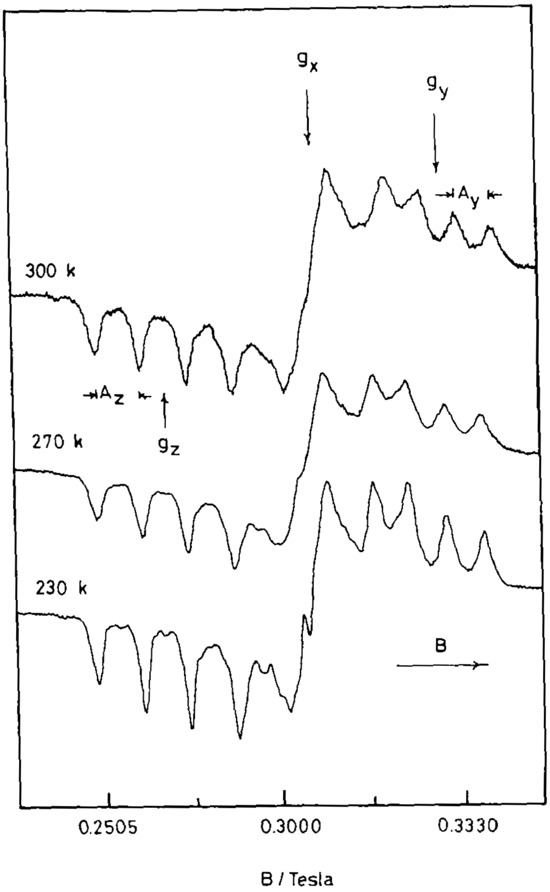

Figure 1. First-derivative EPR spectra of Cu^{2+} in $LiKSO_4$ polycrystalline sample taken at T = 300 K, 270 K and 230 K (during cooling).

spectra is obtained (Fig. 2). We observed that the intensity of the lines increased and their line-widths decreased. The hyperfine peaks, particularly those occuring in the low-field side, show additional splitting at T = 215 K and down. We have observed weak doublets and singlest between the main EPR peaks (Fig. 2). These weak peaks represent, in all probability, the forbidden transitions

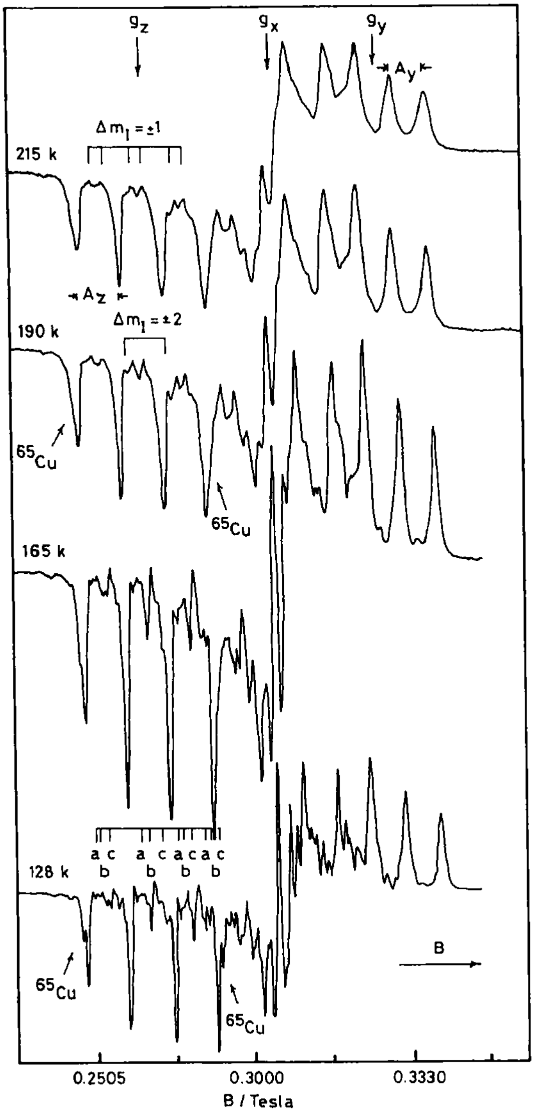

Figure 2. First-derivative EPR spectra of Cu^{2+} in $LiKSO_4$ polycrystalline sample taken at T = 215 K,. 190 K, 165 K and 123 K (during cooling). Weak lines marked at the extreme positions are components of the ^{65}Cu isotop which appear below T = 190 K. Forbidden hyperfine peaks $\Delta m_I = \pm 1$ and $\Delta\ m_I = \pm 2$ are shown.

$\Delta M_S = \pm 1$, $\Delta m_I = \pm 1$ and $\Delta M_S = \pm 1$, $\Delta m_I = \pm 2$, permitted by the second order perturbation, due to the quadrupole moment of the copper nucleus and partialy due to the large hyperfine coupling constant A. The little departure from equidistance between the four lines of Cu^{2+} ion can be assigned to low symmetry effects. The EPR spectra at the temperature range 215 - 123 K could be attributed to Cu^{2+} ion in orthorhombic symmetry. This is an experimental evidence to assume a phase transitions in LPS at T = 215 K. Tomaszewski and Lukaszewicz (3) show that a freezing of the oxygen in a definite position results in tilting of the SO_4 tetrahedra and lowering the symmetry down orthorhombic cmc_1^2. The tilting of the sulphate tetrahedra explains well an elongation of the lattice in a-direction and shortening in the b-direction as a result of the phase transition from the hexagonal to orthorhombic phase. They studied structural analysis of LPS at low temperatures by X-ray differaction. They provide that LPS has a first-order structural phase transition into an orthorhombic phase (cmc_1^2) at 190 K on cooling, and that between 190 K and 164 K the hexagonal phase and orthorhompic phase are coexist. At 170 K, the lattice parameters for the orthorhombic phase are a = 5.202 A^o, b = 8.701 A^o and c = 8.619 A^o. In addition, an intermediate hexagonal $P6_3$ mc phase was proposed at temperatures between 216 K and 190 K on cooling. On the basis of Raman scattering, Bansal et al (2) suggested this phase to be trigonal.

On passing through 165 K, a sudden changes in the spectra were observed. Due to the reduction of the line-width to about its half value (11 G), some additional feature are observed. The EPR peaks due to the less abundant isotope ^{65}Cu (I = 3/2) were resolved. At 165 K the ^{65}Cu weak peaks appeared as shoulders in the $m_I = \pm 3/2$ hyperfine components at the low field side. These weak peaks were resolved in the $m_I = \pm 3/2$ components and also appeared as shoulders in the $m_I = \pm 1/2$ components at T 123 K.

On cooling further the spectra of the sample underwent drastic changes at 123 K. The main results were as a maximum of a new three

Table 1. The spin-Hamiltonian parameters for Cu^{2+} ions in LPS evaluated at different temperatures.

Temp. (T) K	g_z	g_x	g_y	A_z (10^{-4} cm^{-1})	A_x (10^{-4} cm^{-1})	A_y (10^{-4} cm^{-1})	R	P (10^{-4} cm^{-1})	^{2}	K
300	2.3802	2.1842	2.0301	96.2	33.3	74.5	0.7862	-220	0.6214	-0.150
270	2.3859	2.1827	2.0301	98.0	33.3	75.5	0.7510	-223	0.6228	-0.145
250	2.3878	2.1789	2.0311	98.0	34.4	76.0	0.7075	-232	0.6488	-0.133
240	2.3842	2.1783	2.0315	98.0	35.3	76.5	0.7130	-231	0.6152	-0.166
230	2.3816	2.1839	2.0337	98.0	35.3	76.5	0.7180	-234	0.6094	-0.148
215	2.3910	2.1713	2.0335	98.0	35.3	76.5	0.7202	-226	0.6219	-0.153
190	2.3816	2.1713	2.0304	98.0	35.3	76.5	0.6700	-241	0.6214	-0.138
183	2.3816	2.1713	2.0376	98.0	29.4	76.5	0.6371	-290	0.5812	-0.097
170	2.3816	2.1713	2.0376	100.0	29.4	78.5	0.6371	-303	0.5776	-0.086
165	2.3816	2.1713	2.0376	100.0	29.4	78.5	0.6371	-303	0.5776	-0.087
150	2.3816	2.1713	2.0376	100.0	29.4	78.5	0.6371	-303	0.5776	-0.086
140	2.3816	2.1713	2.0373	102.0	29.4	78.5	0.6371	-301	0.5784	-0.089
133	2.3816	2.1678	2.0313	102.0	31.4	80.4	0.6384	-297	0.5836	-0.098
123	2.3816	2.1655	2.0346	102.0	29.4	80.4	0.6057	-321	0.5730	-0.084

sets of four lines "a", "b" and "c" each could be located which is shown in Fig. 2. These lines are too weak to be analyzed.

Our study clearly shown EPR spectra from Cu-O complex in LPS at the temperature range from 300 K to 215 K, characteristic of a rhombic compressed system. while the observed EPR spectra through the temperature range from 215 K to 123 K is characteristic of orthorohmbic field around the Cu^{2+} ion. From the observed EPR spectra, the spin-Hamiltonian parametrs have been evaluated and are given in Table 1. The observed variation of the g-factors with temperatures are similar to these observed for copper doped Zinc Tutton's salt (21) and Zinc(II) bis(pyridine-3-sulphate) hydrate (22) systems in which Cu^{2+} experiences a rhombic distortion. The large value g_z is typical of Cu-O bonding (23). From the obtained g-values we allow to get information on the electronic ground state of the impurity Cu^{2+} ion in LPS.

Dudley and Hathaway (24) suggested that for rhombic g-values (with $g_z > g_x > g_y$), if $(g_x - g_y)/(g_z - g_x) = R$ is greater than unity, then a predominantly d_z2 ground state is present. For a $d_{x^2-y^2}$ ground state, the value of R is expected to be less than unity. The principal g-values obtained at the various temperatures give $R < 1$, as shown in Table 1. From the calculated R values, we suggest that the electronic ground state of copper ion in LPS is predominantly $d_{x^2-y^2}$.

Koto and Abe (24) reported the following exprissions to calculate the free ion dipolar term (P), Fermi-contact term (K) and the bonding parameter (α^2):

$$P = 14(A_x - A_y)/17(\Delta g_y - \Delta g_x)$$

$$\alpha^2 = (7/6)\left[(A_y - A_z)/P - \Delta g_z + (11/14)\Delta g_y - (6/14)\Delta g_x\right],$$

$$K = (A_x/p) + (2/7)\alpha^2 + \Delta g_x - (3/14)\Delta g_y$$

where $\Delta g_z = g_e - g_z$, $\Delta g_x = g_e - g_x$ and $\Delta g_y = g_e - g_y$ (g_e is the free-spin g-value and equal to 2.0023). The values of ^{2} are shown in Table 1. The value of α^2 is close to unity for ionic bonds and becomes smaller with increasing covalent bonding.

From the values of the parameters p, α^2 and K (Table 1) which give the nature of the bonding, it is found that Cu^{2+} doped in LPS is bound by a mixture of ionic and covalent bonds with the surrouding atoms (25).

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