EPR of Cu^{2+} in Ferroelectric $LiH_3(SeO_2)_2$ Single Crystals

Mohd. Waseem, R. Dayal
Department of Physics, Aligarh Muslim University,
Aligarh-202001, India

Vimal Kumar Jain
Department of Physics, M.D. University,
Rohtak-124001, India

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The electron paramagnetic resonance of Cu^{2+} in ferroelectric $LiH_3(SeO_3)_2$ has been studied at 298 K in X-band. The Cu^{2+} appears to substitute Li^+ in the lattice with the z-axis nearly along the Li-O(6) bond direction. The spectra have been analysed using the spin-Hamiltonian appropriate for Cu^{2+} in orthorhombic symmetry.

Lithium trihydrogen selenite, $LiH_3(SeO_3)_2$ (LHS) [1], due to its interesting features such as large dielectric polarization, presence of ferroelectricity up to its melting point, role of hydrogen bonds in the onset of ferroelectric behaviour, and so on, has been the subject of a number of investigations [2–5]. Jain and Venkateswarlu [6–7] have reported the EPR of Mn^{2+} and VO^{2+} in LHS from 298 K down to 77 K. The present note describes an EPR study of Cu^{2+} in LHS single crystal at 298 K.

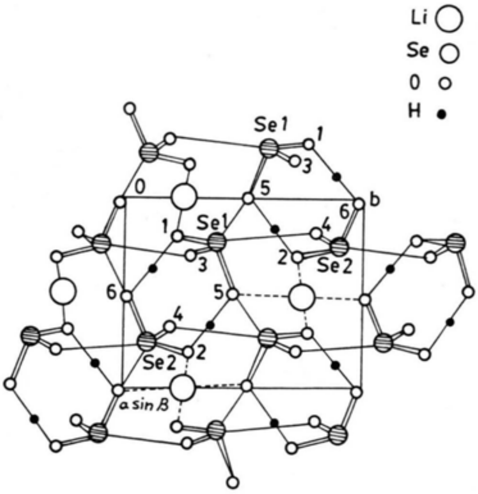

Fig. 1. The unit cell of $LiH_3(SeO_3)_2$ as viewed down the c-axis. Broken lines link the Li atom to oxygen atoms (only four oxygen atoms are shown).

The LHS is monoclinic with a bimolecular unit cell (Fig. 1) of dimensions [8, 9] $a = 6.2554$ Å, $b = 7.882$ Å, $c = 5.4339$ Å and $\beta = 105° \, 32.5'$. The space group is $C_s{}^1(P_n)$ and the point group is $C_s(m)$. The Li^+ is surrounded by six oxygen atoms arranged in a slightly distorted octahedron. Two linear bonds O(1)—H(1)—O(6) and O(5)—H(2)—O(2) link two SeO_3 groups. Third hydrogen bond O(4)—H(3)—O(3) forms S-shaped chains of selenite groups running along the c-direction. The Li^+ ions form Li-O bonds with four different chains creating a three-dimensional network. Figure 1, shows four oxygen atoms of the octahedron surrounding the Li^+ ion.

Single crystals of $LiH_3(SeO_3)_2$ doped with Cu^{2+} were grown at room temperature by slow evaporation of an aqueous solution of one mole of Li_2CO_3 and four moles of SeO_2, to which cupric sulphate (0.5% by weight) was added. The crystals have poor faces but perfect cleavage in a plane perpendicular to the b-axis [10]. The EPR spectra were recorded on a Varian V-4502 EPR Spectrometer operating at X-band and provided with a 9-inch electromagnet and 100 kHz field modulation.

The EPR spectrum of $Cu^{2+}(S = 1/2,\ I = 3/2)$ in LHS consists of two overlapping, angle-dependent, four-line hyperfine patterns (Figure 2) arising from two differently oriented but magnetically equivalent Cu^{2+} complexes, the principal z-axes of which are found at ±12° from the b-axis. The angular variation of the spectra shows orthorhombic symmetry. The spectra at 298 K have been analysed using the spin Hamiltonian

$$\begin{aligned}\mathscr{H} &= \mu_\beta(S_x g_x B_x + S_y g_y B_y + S_z g_z B_z)\\ &\quad + (S_x A_x I_x + S_y A_y I_y + S_z A_z I_z),\end{aligned}$$

where the symbols have their usual meaning. The values of the spin Hamiltonian parameters obtained are:

$$\begin{gathered} g_z = 2.417 \pm 0.005, \quad g_x = 2.029 \pm 0.008, \\ g_y = 2.160 \pm 0.008, \quad A_z = 91.0 \pm 1, \\ A_x = 48.0 \pm 4, \quad A_y = 35.0 \pm 4, \\ \theta = 12° \pm 2°, \quad \Phi = \sim -20°, \end{gathered}$$

where the A values are in units of $10^{-4}\,\mathrm{cm}^{-1}$, θ is

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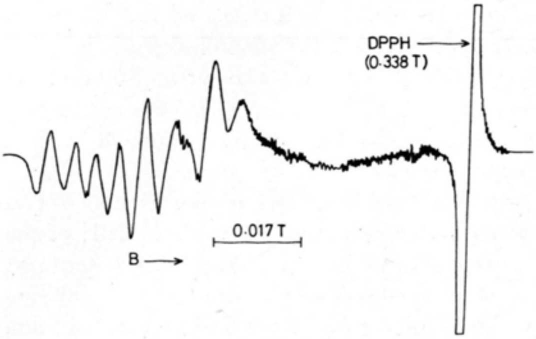

Fig. 2. The EPR spectrum Cu^{2+} doped $LiH_3(SeO_3)_2$ single crystals at 298 K with B parallel to the one of the two *z*-axes.

the angle between the *z*-axis and the *b*-axis, and Φ is the angle between the *x*-axis and the projection of *z* on the *ac* plane. The value of Φ could not be determined accurately because the EPR spectrum nearly merges to a band in the *ac* plane. Since Cu^{2+} has a d^9 configuration and $g_z > g_y > g_x$, the single hole must be in a $d_{x^2-y^2}$ type orbital. The values of the components of the *g*-factor indicate that Cu^{2+} in the lattice is surrounded by six oxygen atoms [11].

If Cu^{2+} enters substitutionally in LHS, the sites available to it are those of Li^+ and Se^{6+}. As there is a small difference in the ionic radii of Li^+ and Cu^{2+} and their valence states do not differ much, Cu^{2+} would prefer to occupy Li^+ sites. It would be surrounded by an oxygen octahedron and would give rise to two equivalent Cu^{2+} complexes. Cu^{2+} in place of Li^+ would produce a positive ion vacancy resulting in an extra contribution to the crystal field at the Cu^{2+} position, and the *z*axis would be expected to lie along the Cu^{2+} — vacancy direction such as in NaCl : Mn^{2+} [12, 13].

The observed *z*-axes of the Cu^{2+} complexes are found nearly along Li-O(6) bonds. The lower energy of the Li-O bond compared to the H-O bond favours the absence of Li^+ in vacancy formation [14]. Further, an aqueous solution of SeO_2 forms selenious acid, a weak acid, which is very slightly dissociated. On the other hand the salts like $LiH_3(SeO_3)_2$ are strongly ionized in solution and give Li^+ ions more frequently [15]. Therefore an addition of Cu^{2+} will be balanced by Li^+ ions and hardly by H^+ ions. The Cu^{2+} ions at the Li^+ sites will thus form complexes with a large distortion of the surrounding oxygen octahedron along the Li-O(6) direction. The nature of the Li^+-vacancy association [12—13] with Cu^{2+} can not be ascertained because Cu^{2+} is already at a site of low symmetry and a further lowering of the symmetry due to vacancy association [12—13] does not affect the EPR spectra.

The EPR spectrum shows no appreciable change at liquid nitrogen temperature; only the linewidth decreases slightly as the temperature is lowered to liquid nitrogen temperature.

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[1] R. Pepinsky and K. Vedam, Phys. Rev. **114**, 1217 (1959).
[2] G. A. Samara, Phys. Rev. **173**, 605 (1968).
[3] S. A. Seryshev, I. S. Vinogradova, and A. G. Lundin, Soc. Phys. — Solid State **17**, 281 (1975).
[4] H. Iwasaki, J. Phys. Soc. Japan **20**, 1783 (1965).
[5] O. Edlund and A. Lund, J. Magn. Reson. **21**, 197 (1976).
[6] V. K. Jain and P. Venkateswarlu, Can. J. Phys. **56**, 807 (1978).
[7] V. K. Jain and P. Venkateswarlu, J. Chem. Phys. Lett. **62**, 320 (1979).
[8] R. Tellegren and R. Liminga, J. Sol. State Chem. **4**, 255 (1972).
[9] J. K. Mohna Rao and M. A. Visawamitra, Acta Crystallogr. **B27**, 1765 (1971).
[10] V. P. Konstantinova, I. M. Sil'vestrova, L. A. Shuvalov, and Y. A. Yurin, Bull. Acad. Sci. (Phys. Serv.) USSR **24**, 1317 (1960).
[11] J. R. Pilbrow and M. R. Lowrey, Rep. Prog. Physics **43**, 471 (1980).
[12] G. D. Watkin, Phys. Rev. **113**, 79 (1959).
[13] K. N. Shrivastava and P. Venkateswarlu, Proc. Ind. Acad. Sci. **63A**, 284 (1966).
[14] F. A. Cotton and G. Wilkinson, Adv. Inorg. Chem., Wiley East. Priv. Lim., Page 112, (1966).
[15] R. B. Helslop and P. L. Robinson, Inorganic Chemistry, Elsevier Publishing Comp., Amsterdam 1967, p. 490.