EPR and Optical Absorption Study of Mn$^{2+}$ Doped Lithium Potassium Sulphate Single Crystals

R. Kripal$^1$*, H. Govind$^2$#, C. Rudowicz$^3$, and Y.Y. Yeung$^4$

Received 6 November 2015; Published online 12 December 2015

Abstract

EPR study of Mn$^{2+}$ doped lithium potassium sulphate (LiKSO$_4$) single crystals is carried out at room temperature. The Mn$^{2+}$ spin Hamiltonian (SH) parameters are evaluated using positions of a large number of resonance lines observed for different orientations of the external magnetic field. The estimated SH parameters are: $g = 1.9986 \pm 0.0002$ (dimensionless), $D = 244 \pm 2$, $E = 76 \pm 2$, $a = 4 \pm 1$, $A = 118 \pm 2$ and $B = 105 \pm 2$ (in $10^{-4}$ cm$^{-1}$), for site I and $g = 2.0016 \pm 0.0002$ (dimensionless), $D = 231 \pm 2$, $E = 68 \pm 2$, $a = 7 \pm 2$, $A = 97 \pm 2$ and $B = 86 \pm 2$ (in $10^{-4}$ cm$^{-1}$), for site II. The optical absorption study of the crystal is also carried out at room temperature. The observed bands are assigned to the transitions from the $^6A_{1g}(S)$ ground state to various excited states of Mn$^{2+}$ ion. These transitions are matched within the crystal field framework using the inter-electronic Racah parameters ($B$ and $C$), cubic crystal field parameter ($D_q$), and Trees correction ($\alpha$). The energy levels are calculated using the crystal field analysis (CFA) computer package, whereas the parameter values are obtained using approximated analytical expressions as: $B = 842$, $C = 2277$, $D_q = 745$, and $\alpha = 76$ cm$^{-1}$. On the basis of the data obtained the surrounding crystal field and the nature of metal-ligand.

Keywords: EPR (electron paramagnetic resonance); Optical absorption; Spin Hamiltonian; Crystal field; Fine structure; Covalency; Hyperfine coupling; Racah parameters

PACS numbers: 76.30.-v; 75.10.Dq; 71.70.Ch; 71.70.Ej.

1. Introduction

The paramagnetic compounds with divalent manganese are of great interest because the Mn$^{2+}$ ($3d^5$)-electrons responsible for the paramagnetism exhibit the quenched orbital angular
momentum in the ground $6S$-state. The crystal field (CF) can affect the electron spins only through higher-order interactions so that the spins are almost completely free to orient themselves in an applied magnetic field. The EPR spectrum of the $S$–state Mn$^{2+}$ ion provides plentiful information about the local atomic environment in a wide variety of the materials. This is due to the fact that the spectrum is often observed at room temperature and shows both fine structure as well as hyperfine structure (Abragam and Bleaney, 1970). The magnitudes of the spin Hamiltonian (SH) parameters and the orientation of SH ‘tensors’ are very sensitive to the CF strength and the geometry of the local surroundings. Thus the 3d5 ions are ideal probes to study the site symmetry and phase transitions (Weil et al., 1994; Misra, 1999). The main objectives of the EPR studies of Mn$^{2+}$ impurity in crystals have been, e.g., the determination of site symmetry and orientation of the local symmetry axes, understanding of phase transitions and magnetic properties of materials (Jain and Lehmann, 1990). On the other hand, the optical studies provide the energy level structure of paramagnetic ions and the CF strength in the host lattice. 

Thus EPR and optical absorption are two supplementary powerful tools to investigate the site symmetry and associated distortions in the lattice. In the present paper we report EPR and optical absorption studies of Mn$^{2+}$ doped lithium potassium sulphate (LPS). Our aim is to obtain information on the site symmetry, associated distortion in the lattice, and the energy level scheme of Mn$^{2+}$ (3d$^5$) ion as well as to determine the respective CF and SH parameters. These data enable discussion of the surrounding CF and the nature of bonding of metal ion with its different ligands.

2. Experimental Aspects

Single crystals of LPS were grown by slow evaporation at room temperature of an aqueous solution containing stoichiometric proportion of K$_2$SO$_4$.2H$_2$O and Li$_2$SO$_4$. To grow the Mn$^{2+}$ doped crystals aqueous solution of 0.1 wt% of MnCl$_2$.4H$_2$O was added to the mixture. The crystals were obtained after 25 days. LPS crystals (LiKSO$_4$) belong to the hexagonal class (Karipinen et al., 1983) with the space group $P6_3$. The unit cell dimensions are $a = 0.51452 \pm 0.002$ and $c = 0.86343 \pm 0.002$ nm. There are two molecules in the unit cell.

The EPR spectra were recorded using X-band, reflection type spectrometer (Varian, E-LINE century, Series E-112). The single crystal was mounted on quartz rod fitted in a goniometer and then aligned in TE$_{102}$ cavity center to avoid RF field deterioration. Magnetic field was modulated at 100 kHz frequency and small voltage (10 mV) microwave power was used to avoid saturation effects in spectra. The EPR spectra were measured along three mutually perpendicular crystallographic axes $a^*$, $b$ and $c$ ($b$ is perpendicular to $c$ and $a^*$ is perpendicular to the plane $bc$) at an interval of $10^o$.

A Varian flux meter with a proton probe having 0.2 cm$^3$ of 0.25 molar solution of GdCl$_3$ in H$_2$O was used for magnetic field measurement along with a Hewlett-Packard frequency counter. The optical absorption spectrum of Mn$^{2+}$: LPS single crystal was recorded at room temperature by UNICAM-5625 spectrophotometer in UV-VIS-NIR (195-925 nm) region.

3. EPR Spectroscopy

The room temperature EPR spectrum of Mn$^{2+}$ ion doped in LPS exhibits two distinct sites each of
five sets with six lines in each set. This spectrum is characteristic of a system with \( S = \frac{5}{2} \) and \( I = \frac{5}{2} \). A typical EPR spectrum of Mn\(^{2+}\): LPS recorded with the applied magnetic field \( B \) parallel to the \( \mathbf{a}^* \) axis is shown in Fig. 1. The crystal rotations are performed in the three orthogonal planes \( \mathbf{ab} \), \( \mathbf{bc} \) and \( \mathbf{ca}^* \). The angular variation of the resonance field for Mn\(^{2+}\): LPS (site I) in the respective planes is shown in Fig. 2(a), 2(b), and 2(c).

**Fig. 1.** EPR spectra of Mn\(^{2+}\) doped in lithium potassium sulphate (LPS) single crystal with the applied magnetic field parallel to the \( \mathbf{a}^* \)-axis.

**Fig. 2(a).** Angular variation of the resonance field in the \( \mathbf{ab} \) plane for Mn\(^{2+}\): LPS (site I)
Fig. 2(b). Angular variation of the resonance field in the bc plane for Mn$^{2+}$: LPS (site I).

Fig. 2(c). Angular variation of the resonance field in the ca* plane for Mn$^{2+}$: LPS (site I).

In the absence of an external magnetic field $B$, the ground state ($^6S_{5/2}$) of Mn$^{2+}$ ion splits into three Kramer's doublets, due to combined action of spin-orbit coupling and (to a lesser extent) the electronic spin–spin interaction with separation of $4D$ and $2D$. The $B$-field splits the three Kramer doublets further into six spin levels. When the strong $B$-field is along the symmetry axis, the successive separations between the spin levels (correct up to the first order in the second-rank zero-field splitting (ZFS) parameter $D$) are $(g\mu_B B + 4D)$, $(g\mu_B B + 2D)$, $(g\mu_B B)$, $(g\mu_B B - 2D)$ and $(g\mu_B B - 4D)$ (Abragam and Bleaney, 1970; Bleaney and Ingram, 1951). Hence the transitions between these levels yield five equally spaced resonance lines. However, each of these resonances further splits into a sextet, due to hyperfine interaction resulting from the nuclear spin of $^{55}$Mn, $I = 5/2$. Therefore a five set pattern of six components is obtained separately (i.e. 30 line pattern). Due to the second-order effects, other ZFS terms in SH will also contribute to the spin energy levels and as a result the sextets in each group are not equally spaced.
The SH in the conventional form (Rudowicz, 1987; Rudowicz and Sung, 2001) for the spin \( S = \frac{5}{2} \) ground state of Mn\(^{2+} \) ion at orthorhombic symmetry sites is taken as (Kripal and Mishra, 2005; Kripal et al., 2007):

\[
\mathcal{H} = g \mu_B \mathbf{B} \cdot \mathbf{S} + D(S_z^2 - \frac{1}{3} S(S+1)) + E(S_x^2 - S_y^2) + \left( \frac{a}{6} \right) [S_x^4 + S_y^4 + S_z^4 + \frac{1}{5} S(S+1)(3S^2 + 3S - 1)] \\
+ \frac{F}{180} [35 S_z^4 - 30 S(S+1)S_x^2 + 25 S_z^2 - 6S(S+1) + 3S^2(S+1)] + \frac{K}{4} [(7S_z^2 - S(S+1) - 5) \\
(S_x^2 - S_y^2) + (S_z^2 - S_x^2) (7S_z^2 - S(S+1) - 5)] + A S_z I_z + B (S_x I_x + S_y I_y)
\]  

(1)

where, \( g \) is the isotropic spectroscopic splitting factor, \( \mu_B \) - the Bohr magneton, \( B \) - the external magnetic field. The parameters \( D \) and \( E \) are the second-rank axial and rhombic ZFS parameters, whereas \( a, F, \) and \( K \) are the fourth-rank cubic, axial and rhombic ones, respectively. For relationships between the conventional ZFS parameters and those in the (extended) Stevens notation refer to Refs. (Bleaney and Ingram, 1951) and (Rudowicz, 1987). It may also be useful to consult the review (Rudowicz, 1987) on the spin Hamiltonian formalisms, the review (Rudowicz and Sung, 2001) on the often confused interrelations between the CF and ZFS quantities and the note (Rudowicz, 2000) on the incorrect orthorhombic ZFSPs relations. The last two terms in Eq. (1) represent the hyperfine (\( I = \frac{5}{2} \)) interaction. The \( F \) and \( K \) ZFS terms are omitted here as their effect is small (Abragam and Bleaney, 1970; Rudowicz and Misra, 2001; Radnell et al., 1975). The isotropic approximation used for the electronic Zeeman interaction is generally valid for Mn\(^{2+} \) ions (Abragam and Bleaney, 1970; Weil et al., 1994). The two approximations in question may slightly affect the fitted value of \( a \) (Rudowicz and Madhu, 1999). The direction of the maximum overall splitting of EPR spectrum is taken as the z-axis and that of the minimum as the x-axis (Rudowicz and Bramley, 1985). The laboratory axes (x, y, z) determined from EPR spectra are found to coincide with the crystallographic axes (CA). The Z-axis of the local site symmetry axes, i.e. the symmetry adapted axes (SAA) is along the metal oxygen bond and the other two axes (X, Y) are perpendicular to the Z-axis (discussed later). The allowed transitions and the corresponding resonance fields \( B \) for the case of dominant Zeeman interaction are given by the equations in Appendix A of (Kripal et al., 2007).

The values of \( g, D, E, a, A, \) and \( B \) for Mn\(^{2+} \) in LPS obtained (Kripal and Mishra, 2005) using the equations in Appendix A of (Kripal et al., 2007) and a computer program are given in Table 1. The fitted \( D \) and \( E \) values appear to belong to the standard range (Rudowicz and Madhu, 1999; Rudowicz, 1986). This case represents the 'nearly rhombic’ \( D \) and \( E \) (Rudowicz and Madhu, 1999). Note that the \( D \) and \( E \) values are expressed in the laboratory axes defined above. The best fit (Anandlakshmi et al., 2004) of the theoretical and experimental values of the separation between the extreme sets of hyperfine sextets is obtained if \( D \) is positive. The sign of the parameter \( A \) and \( B \) is taken to be negative (Abragam and Bleaney, 1970), whereas, \( D \) and \( a \) have opposite signs (Abragam and Bleaney, 1970), this yields negative \( a \).
Table 1  The experimentally fitted spin Hamiltonian parameters for the two Mn$^{2+}$ sites in LPS; except of g (dimensionless) all values in units of $10^{-4}$ cm$^{-1}$; estimated errors are for g: ± 0.0002, D, E, A and B: ± 2 × $10^{-4}$ cm$^{-1}$, a: ± 1 × $10^{-4}$ cm$^{-1}$.

<table>
<thead>
<tr>
<th>SITE</th>
<th>g</th>
<th>D</th>
<th>E</th>
<th>a</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1.9986</td>
<td>244</td>
<td>76</td>
<td>4</td>
<td>118</td>
<td>105</td>
</tr>
<tr>
<td>II</td>
<td>2.0016</td>
<td>231</td>
<td>68</td>
<td>7</td>
<td>97</td>
<td>86</td>
</tr>
</tbody>
</table>

The percentage of covalency (Simanek and Muller, 1970; Rao and Subramanian, 1985) of bond between manganese and its ligands affects the value of isotropic hyperfine coupling constant. The covalency $C$ of a bond between atoms P and Q is approximately related to their electro negativities $X_P$ and $X_Q$ by the relation (Simanek and Muller, 1970).

\[ C = \frac{1 - 0.16(X_P - X_Q) - 0.035(X_P - X_Q)^2}{n} \]  

where, $n$ is the number of the neighbour bond atoms. Using the values of $X_{Mn} = 1.4$ and $X_Q = 3.5$ [20], the percentage covalency is obtained to be 8.5 %. The value of hyperfine splitting constant $118 \times 10^{-4}$ cm$^{-1}$ predicted from the graph also agrees reasonably well with the observed value of $109 \times 10^{-4}$ cm$^{-1}$ of the average hyperfine splitting constant, i.e. $(A + 2 B)/3$.

4. Optical Absorption Spectroscopy

In a strong cubic CF (Griffith, 1961) 3d$^5$ electrons of Mn$^{2+}$ are distributed in the $t_{2g}$ and $e_g$ orbitals, with three in the former and two in the later. Thus the ground state configuration is written as $(t_{2g})^3(e_g)^2$. This configuration gives rise to the electronic states $^6A_{1g}$ (ground state), $^4A_{1g}$, $^4E_{g}$, $^4T_{1g}$, $^4T_{2g}$, $^4A_{2g}$ and a number of higher-lying spin doublet state. The other exited electron configurations like $(t_{2g})^4(e_g)$, $(t_{2g})^2(e_g)^3$ and $(t_{2g})(e_g)^4$ give rise to several spin doublet and quartet states. Thus all the absorption bands of the high-spin Mn$^{2+}$ ion correspond to spin-forbidden transitions.

The observed optical absorption spectrum at room temperature is shown in Figs. 3(a) and 3(b).
Fig. 3(a). Optical absorption spectrum of Mn$^{2+}$: LPS measured in the wavelength range 195-325 nm at room temperature.

Fig. 3(b). Optical absorption spectrum of Mn$^{2+}$: LPS measured in the wavelength range 325-1100 nm at room temperature.

The spectrum consists of ten bands located at 14905, 15408, 21299, 21349, 22232, 26185, 30157, 32690, 35361 and 37147 (in cm$^{-1}$). Among the observed bands, the bands at 21299, 26185 and 30157 (in cm$^{-1}$) are sharp and intense. Ligand field bands are sharp when the energy does not depend on the cubic CF parameter (Dq), since the number of t$_{2g}$ electrons is the same in both the ground state and excited ones (Ballhausen, 1962). These sharp bands are assigned to the transitions $^6$A$_{1g}$(S)$\rightarrow$$^4$E$_{g}$(G), $^6$A$_{1g}$(S)$\rightarrow$$^4$E$_{g}$(D), and $^6$A$_{1g}$(S)$\rightarrow$$^4$T$_{1g}$(P), respectively, since the energy expressions are independent of Dq. The two states $^4$A$_{1g}$(G) and $^4$E$_{g}$(G) are normally degenerate, but their degeneracy is often lifted by covalency in the crystal (Ferguson et al., 1974). The transitions that are CF independent may be classified into three main groups depending on the type of the molecular orbitals appearing in the repulsion integrals responsible for the transition energy. These
groups are: (1) very sharp transitions whose energy is given by \([t_2e^2 t_2 t_2]\) integrals, \(4A_2(t^2) \rightarrow 2E(t^2)\), \(E = (9B_0 + 3C_0) f_{12 f_{12}}^2\); (2) moderately sharp transitions arising from \([t_2e e t_2]\) integrals, \(6A_1(t_2^3 e^2) \rightarrow 4A_1, 4E(t_2^3 e^2), E = (10B_0 + 5C_0) f_{12 f_{12}}^2\); (3) relatively broad transitions arising from \([e e e e]\) integrals, \(4A_1(t_2^3 e^2) \rightarrow 4A_2(t_2^3 e^2), E = (16B_0 + 4C_0) f_{12}^2 + (6B_0 + 3C_0) f_{2 f_{12}} \) (\(B_0, C_0\) are free ion Racah parameters). This classification applies for six-fold coordinated, nearly octahedral systems, where \(f_e < f_{12} < 1\) (\(f_e\) and \(f_{12}\) are covalency factors, also termed the localization factors (Abragam and Bleaney, 1970; Owen and Thornley, 1966)). As the covalency factors vary with metal-ligand overlap and hence with the metal-ligand distance, the energy of a crystal-field independent transition is not necessarily independent of the totally symmetric motion of the ligands. The greater the dependence of the transition energy on \(f_e\) in octahedral systems the greater the Franck-Condon shift and the greater the dependence on any geometrical perturbation. When \(f_{12} > f_e\) as in octahedral complexes, \(E(4A_1) < E(4E)\) for \(1 > f_e/f_{12}\) being of the order of 7/8. Koide and Pryce (1958) by plotting the variation of the energy levels as function of the covalency parameters have shown the separation between the levels \(4A_{1g}(G)\) and \(4E_g(G)\) to be of about 100 cm\(^{-1}\). Using the Tanabe-Sugano diagram (Tanabe and Sugano, 1954), the other bands at 14905, 15408, 21349, 2223 \(cm\(^{-1}\)) are assigned to the transitions from the ground state \(6A_{1g}(S)\) to the excited states: \(4T_{1g}(G), 4T_{2g}(G), 4A_{1g}(G), 4T_{2g}(D), 4A_{2g}(F), 4T_{1g}(F),\) and \(4T_{2g}(F)\), respectively. The wavelengths and the wave numbers of the bands are given in Table 2, together with their assignments.

The theoretical energy levels have been calculated using the crystal field analysis (CFA) computer package (Yeung and Rudowicz, 1992; 1993). The inter-electronic repulsion parameters (B and C), the cubic CF splitting parameter (D\(_q\)) are obtained using Eqs given in Appendix B of (Krippal et al., 2007). The correction term (Trees correction \(\alpha\)) is relatively small, and therefore it is arbitrarily fixed at the free ion value of 76 cm\(^{-1}\). The CF parameters \(B_{\text{eq}}\) (in the Wybourne notation) required for calculation of the theoretical energy levels have been obtained using the superposition model (SPM). The SPM enables to express the CF parameters as (Yu and Zhao, 1988):

\[
B_{\text{eq}} = \sum_j A_k(R_j) K_{\text{eq}}(\Theta_j, \Phi_j) \tag{3}
\]

where the coordination factors \(K_{\text{eq}}(\Theta_j, \Phi_j)\) are explicit functions of the angular positions of the ligands. The intrinsic parameters \(A_k(R_j)\) are approximated as:

\[
A_k(R_j) = A_k(R_0)(R_0/R_j)^{\delta_k} \tag{4}
\]

where \(R_j\) is the distance between the \(d^6\) ion and the \(j\)-th ligand, \(A_k(R_0)\) is the intrinsic parameter of the reference crystal, and \(\delta_k\) is the power-law exponent. The Mn\(^{2+}\) ions substitute for K\(^+\) ions at the octahedral site I and II (discussed later), each surrounded by six O\(^2-\) ions (see, Fig. 4). The Cartesian and angular coordinates of ligands with respect to the crystallographic axes centered at Mn\(^{2+}\) ions obtained using the X-ray structural data (Karipinen et al., 1983) are listed in Table 3. For the Mn\(^{2+}\)-O\(^2-\) bonds, the values \(t_2 = 3\) and \(t_4 = 7\) (Yu and Zhao, 1987) are found to be consistent with experimental data. The \(B_{\text{eq}}\) parameters for Mn\(^{2+}\) doped LPS in orthorhombic symmetry obtained from Eqs. (3) and (4) can be expressed (Han and Kim, 1996) as

\[
B_{20} = A_2(R_0) \sum_j (R_0/R_j)^{3(3\cos^2\Theta_j - 1)}
\]
B_{22} = \frac{\sqrt{6}}{2} A_2(R_0) \sum_j (R_0/R_j)^3 \sin^2 \theta_j \cos 2 \phi_j

B_{40} = A_4(R_0) \sum_j (R_0/R_j)^7 (35 \cos^4 \theta_j - 30 \cos^2 \theta_j + 3)

B_{42} = \sqrt{10} A_4(R_0) \sum_j (R_0/R_j)^7 \sin^2 \theta_j (7 \cos^2 \theta_j - 1) \cos 2 \phi_j

B_{44} = \sqrt{\frac{35}{2}} A_4(R_0) \sum_j (R_0/R_j)^7 \sin^4 \theta_j \cos 4 \phi_j

Table 2 The experimental data and the analysis of the absorption spectrum of Mn^{2+} ions doped in LPS single crystals; Dq = 745 cm\(^{-1}\).

<table>
<thead>
<tr>
<th>Transition from</th>
<th>Wavelength (nm)</th>
<th>Wave number (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^6)A(_{1g})(S)</td>
<td>670.9</td>
<td>14905</td>
</tr>
<tr>
<td>(^4)T(_{1g}) (G)</td>
<td>649.0</td>
<td>15408</td>
</tr>
<tr>
<td>(^4)E(_g) (G)</td>
<td>469.5</td>
<td>21299</td>
</tr>
<tr>
<td>(^4)A(_{1g}) (G)</td>
<td>468.4</td>
<td>21349</td>
</tr>
<tr>
<td>(^4)T(_{2g}) (D)</td>
<td>449.8</td>
<td>22232</td>
</tr>
<tr>
<td>(^4)E(_g) (D)</td>
<td>381.9</td>
<td>26185</td>
</tr>
<tr>
<td>(^4)T(_{1g}) (P)</td>
<td>331.6</td>
<td>30157</td>
</tr>
<tr>
<td>(^4)A(_{2g}) (F)</td>
<td>305.9</td>
<td>32690</td>
</tr>
<tr>
<td>(^4)T(_{1g}) (F)</td>
<td>282.8</td>
<td>35361</td>
</tr>
<tr>
<td>(^4)T(_{2g}) (F)</td>
<td>265.4</td>
<td>37679</td>
</tr>
</tbody>
</table>

(a) Cubic approximation: \(B_{40} = -1500.18\) cm\(^{-1}\) and \(B_{44} = 528.66\) cm\(^{-1}\); \(B = 842\) cm\(^{-1}\), and \(C = 2277\) cm\(^{-1}\); \(\alpha = 76\) cm\(^{-1}\).

(b) Non-cubic fitting: \(B_{40} = 26,750\) cm\(^{-1}\) and \(B_{44} = 8,831\) cm\(^{-1}\); \(B = 822\) cm\(^{-1}\), and \(C = 2364\) cm\(^{-1}\); \(\alpha = 76\) cm\(^{-1}\).
Fig. 4. Nearest ligands around the $K^+$ ion in LPS; the $Z$ axis is directed upward; the $\text{Mn}^{2+}$ ion is at the center of the oxygen octahedron, whereas the three oxygen ions connected by the solid and dashed lines are located above and below the $XY$ plane, respectively; the positions of atoms are listed in Table 1.
Table 3 Cartesian (X, Y, Z) (in nm) and angular (R, Θ, φ) coordinates of O\(^{2-}\) ligands in LPS referred to the (X, Y, Z) coordinate frame centred at Mn\(^{2+}\) (0, 0, 0) obtained using the X-ray structural data [5].

<table>
<thead>
<tr>
<th>Site I</th>
<th>Ion</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>R(nm)</th>
<th>Θ</th>
<th>φ</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(^{2-})</td>
<td>0</td>
<td>-0.240036</td>
<td>0.178112</td>
<td>0.2989</td>
<td>53</td>
<td>270</td>
<td></td>
</tr>
<tr>
<td>O(^{2-})</td>
<td>-0.207877</td>
<td>0.120019</td>
<td>0.178112</td>
<td>0.2989</td>
<td>53</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td>O(^{2-})</td>
<td>0.207877</td>
<td>0.120019</td>
<td>0.178112</td>
<td>0.2989</td>
<td>53</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>O(^{2-})</td>
<td>0</td>
<td>0.240036</td>
<td>-0.178112</td>
<td>0.2989</td>
<td>127</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>O(^{2-})</td>
<td>-0.207877</td>
<td>-0.120019</td>
<td>-0.178112</td>
<td>0.2989</td>
<td>127</td>
<td>330</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Site II</th>
<th>Ion</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>R(nm)</th>
<th>Θ</th>
<th>φ</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(^{2-})</td>
<td>0</td>
<td>-0.238591</td>
<td>-0.167036</td>
<td>0.29125</td>
<td>125</td>
<td>270</td>
<td></td>
</tr>
<tr>
<td>O(^{2-})</td>
<td>0.206626</td>
<td>0.119295</td>
<td>-0.167036</td>
<td>0.29125</td>
<td>125</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>O(^{2-})</td>
<td>-0.206626</td>
<td>0.119295</td>
<td>-0.167036</td>
<td>0.29125</td>
<td>125</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td>O(^{2-})</td>
<td>0.206626</td>
<td>-0.119295</td>
<td>0.167036</td>
<td>0.29125</td>
<td>55</td>
<td>330</td>
<td></td>
</tr>
<tr>
<td>O(^{2-})</td>
<td>-0.206626</td>
<td>-0.119295</td>
<td>0.167036</td>
<td>0.29125</td>
<td>55</td>
<td>210</td>
<td></td>
</tr>
<tr>
<td>O(^{2-})</td>
<td>0</td>
<td>0.238591</td>
<td>0.167036</td>
<td>0.29125</td>
<td>55</td>
<td>90</td>
<td></td>
</tr>
</tbody>
</table>

For octahedral coordination, \(A_4(R_0)\) is related with cubic CF parameter \(D_q\) (Yu and Zhao, 1988) as

\[
A_4(R_0) = \frac{3}{4}D_q \tag{6}
\]

Various workers have obtained the value of \(A_2/A_4\) as practically constant (Yeung and Newman, 1986) for \(3d^\text{h}\) ions and being in the range between 8 - 12. \(A_2/A_4 = 8.4\) has been used in the present calculation to have good match with the experimental data. Taking \(R_0 = 0.220\) nm for the Mn-O bonds (Lohr Jr., 1966), \(R_1 = 0.2989\) nm (Table 3), \(R_2 = 0.2840\) nm (Karipinen et al., 1983), the \(B_{\text{eq}}\) parameters are evaluated as \(B_{20} = 281.81, B_{22} = 2556.91, B_{40} = -1500.18, B_{42} = 781.90\) and \(B_{44} = 528.66\) [in cm\(^{-1}\)], respectively. The energy values for the spin quartet states have been calculated for different values of \(D_q\) with \(B = 842\) cm\(^{-1}\), \(C = 2277\) cm\(^{-1}\), and \(\alpha = 76\) cm\(^{-1}\). A good match of the experimentally observed band positions is obtained for \(D_q = 745\) cm\(^{-1}\) as it is seen from Fig. 5.
Fig. 5. The energy level diagram of Mn$^{2+}$: LPS showing the variation of the levels with Dq for B = 842, C = 2277 and $\alpha$ = 76 [in cm$^{-1}$]; the circles represent the experimental energies).

Table 2 indicates that the observed and calculated values of band positions in the cubic approximation are in good agreement and thus justifying the assignments. A non-cubic fitting of the band positions has also been carried out which shows better agreement with the experimental ones (Table 2). The free ion values of the Racah inter-electronic repulsion parameters $B_0$ and $C_0$ are 960 and 3325 cm$^{-1}$ (Figgis, 1976). The considerable decrease in the values of B and C indicates that there exists a strong covalent bonding between the central metal ion and its ligands.

5. Analysis of EPR and Optical Absorption Spectroscopy Results

It is worthwhile to consider the structural implications of the EPR and optical absorption spectroscopy studies presented in Section 3 and 4, respectively. The structure of LPS consists of Li$^+$ and SO$_4^{2-}$ ions lying on threefold axes and K$^+$ ions on six-fold axes. The Li$^+$ ion has a tetrahedral coordination with Li-O distances in the range 0.199 - 0.1923 nm. The K$^+$ ion is surrounded by nine sulphate O atoms at distances of 0.2840 - 0.2989 nm. The arrangement of O ligands may be described as a distorted octahedron with additional O atoms outside three of its edges (Fig. 6).
It can be seen from the crystal structure (Karipinen et al., 1983) that two magnetically inequivalent K⁺ sites are available to the Mn²⁺ ion for substitution. The ionic radii of K⁺, Li⁺ and Mn²⁺ are 0.133, 0.068 and 0.080 nm (West, 1976), respectively. Because of the smaller ionic radius of Mn²⁺ as compared to K⁺, Mn²⁺ seems fit to enter the lattice substitutionally in place of K⁺ but then one can expect two magnetically inequivalent sites per unit cell as LPS contains two potassium atoms in the unit cell (Karipinen et al., 1983). In the present investigation two magnetically distinct sites are observed. Therefore, the Mn²⁺ ions may be expected to occupy the distorted octahedral substitutional K⁺ site in LPS. When divalent impurity cations are substituted for the monovalent cations, the charge compensation occurs. The simplest mechanism for the charge compensation in the Mn²⁺: LPS lattice is for one of the neighbouring Li⁺ ions to be missing. There are three equivalent Li⁺ ions in the vicinity of the K⁺ site. A deficiency of one Li⁺ ion will ensure the charge balance. If one of the Li⁺ ions is missing the local symmetry at the Mn²⁺ site is greatly reduced. The only symmetry element which remains is the mirror plane containing Mn²⁺ ion and the vacant Li⁺ site. The second-rank zero-field splitting tensor $D$ for a Mn²⁺-Li⁺ center may hence be expected to be rhombic, similar to the Cr³⁺-Cs⁺(1) center in Cs₂CdCl₄ (Kay and McPherson, 1981). The angular variation of the hyperfine resonances of the Mn²⁺ ions in LPS is complicated by the fact that there are two magnetically inequivalent sites. The principal X- and Y-axes of the tensor $D$ lie in the planes, which contain Li⁺ ions. In one of the sites these axes lie in the (110) plane while in the other site in the (1̅10) plane. In each case the principal X-axis of the tensor $D$ is directed away from the c-axis by about 30°. The principal Z-axes are along the metal-oxygen bond directions (Fig. 6). The non-zero value $E$ confirms the expected rhombic distortion. The value of $D$ (814.9 x 10⁻⁴ cm⁻¹) and $E$ (163.8 x 10⁻⁴ cm⁻¹) for Mn²⁺ in BiVO₄ (Yeom et al., 1992) with Mn²⁺ substituting at the Bi³⁺ sites having
approximately orthorhombic symmetry are larger as compared with those determined in this study, see Table 1. This may be due to different local ionic arrangement around Mn\textsuperscript{2+} ion in the two crystals. Using the CF parameters (B_{\text{sq}}), Racah inter-electronic repulsion parameters (B and C) and spin-orbit parameter (\xi = 337 cm\textsuperscript{-1} [28]), the ZFSPs are calculated from the theoretical Eqs. (16) and (17) of (Yu and Zhao, 1988) to be \( D = 256 \) and \( E = 71 \) cm\textsuperscript{-1}. These calculated values are in good agreement with the experimental ones.

Table 4 The direction cosines of different bonds in the host LPS and the distortion axes for Mn\textsuperscript{2+} in LPS.

<table>
<thead>
<tr>
<th>Bond</th>
<th>a*</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>K-Li</td>
<td>±0.4242</td>
<td>±0.8483</td>
<td>±0.6784</td>
</tr>
<tr>
<td>K-S</td>
<td>±0.2529</td>
<td>±0.5059</td>
<td>±0.8989</td>
</tr>
<tr>
<td>K-O(1)</td>
<td>±0.3107</td>
<td>±0.6214</td>
<td>±0.8428</td>
</tr>
<tr>
<td>K-O(2)</td>
<td>±0.2603</td>
<td>±0.3045</td>
<td>±0.9585</td>
</tr>
<tr>
<td>Li-S</td>
<td>±0.0000</td>
<td>±0.0000</td>
<td>±1.0000</td>
</tr>
<tr>
<td>Li-O(1)</td>
<td>±0.0000</td>
<td>±0.0000</td>
<td>±1.0000</td>
</tr>
<tr>
<td>Li-O(2)</td>
<td>±0.0127</td>
<td>±0.3297</td>
<td>±0.9409</td>
</tr>
<tr>
<td>S-O(1)</td>
<td>±0.0000</td>
<td>±0.0000</td>
<td>±1.0000</td>
</tr>
<tr>
<td>S-O(2)</td>
<td>±0.0479</td>
<td>±0.9201</td>
<td>±0.3273</td>
</tr>
<tr>
<td>O(1)-O(2)</td>
<td>±0.0295</td>
<td>±0.8677</td>
<td>±0.8125</td>
</tr>
<tr>
<td>Distortion axis</td>
<td>0.2941</td>
<td>0.5826</td>
<td>0.8130</td>
</tr>
<tr>
<td>Distortion axis</td>
<td>0.2571</td>
<td>0.2901</td>
<td>0.9462</td>
</tr>
</tbody>
</table>

For identification of the distortion axis at either of the two Mn\textsuperscript{2+} sites, i.e. the axis of distortion from the cubic symmetry, the crystal is first rotated about three mutually perpendicular axes \( a^\ast, b \) and \( c \) and the maximum value of fine structure splitting is calculated for each of these rotations. The maximum splitting for the extreme lines in the \( i \)-th plane is \( 4D'(3\cos^2\theta_i'-1) \). The value of \( D' \) can be estimated from a powder spectrum by measuring the separation between the extreme lines of the set of sextets. The determination of \( \theta_1', \theta_2' \) and \( \theta_3' \) yields the angles between the magnetic field and the distortion axis in each rotation when the magnetic field, the distortion axis and the axis of rotation are in the same plane. Therefore, the angles the distortion axis makes with the mutually
perpendicular axes of rotation are simply (90-0') (Rao and Subramanian, 1985). These values provide a rough idea about the orientation of the distortion axis. For further confirmation, this result should be correlated with the X-ray structure of the host crystal. There are two distortion axes corresponding to each of the two sites of Mn$^{2+}$ ion in LPS, which are determined by the above procedure taking into account the respective fine structure splitting for the two sites. The direction cosines of the distortion axes calculated from EPR spectra nearly coincide with the direction of K-O(1) and, K-O(2) bonds, see Table 4.

Therefore, the Mn$^{2+}$ ions are expected to substitute for the K$^+$ ions in LPS. The band assigned to $^{6}A_{1g}(S) \rightarrow {^{4}E_g}(G)$ is sharp and exhibits splitting. The degeneracy of the $E_g(G)$ level is expected to be lifted by a tetragonal or rhombic distortion but not a trigonal one (Lohr Jr., 1966). The observed splitting of this sharp band suggests that Mn$^{2+}$ ions enter rhombically distorted octahedral sites.

6. Conclusions

EPR and optical absorption studies of Mn$^{2+}$ doped lithium potassium sulphate monohydrate have been carried out at room temperature. The spin Hamiltonian parameters $g$, $D$, $E$, $a$, $A$ and $B$ have been determined. The optical absorption bands have been assigned to various transitions and the correctness of these assignments has been verified by theoretical calculations using the crystal field analysis (CFA) computer package. The Racah parameters $B$ and $C$ as well as the cubic CF parameter $D_q$ have been evaluated. A good match between the observed band positions and the calculated values has been obtained for $D_q = 745 \text{ cm}^{-1}$ with $B = 842 \text{ cm}^{-1}$ and $C = 2277 \text{ cm}^{-1}$ and Trees correction $\alpha = 76 \text{ cm}^{-1}$. A non-cubic fitting of the band positions shows better agreement with the experimentally observed ones. The percentage covalency has also been estimated and a strong covalent bonding between the central metal ion and the ligand has been revealed. Our results indicate that the Mn$^{2+}$ ions doped into lithium potassium sulphate enter the host lattice substitutionally at two magnetically inequivalent K$^+$ sites.

Acknowledgements

The authors are thankful to Dr. T.K. Gundu Rao of SAIF, IIT Powai, Mumbai for providing EPR Spectrometer facilities. This work was partially supported by the research grant (to CZR) from the Polish Ministry of Science and Tertiary Education in the years 2006-2009.

References


http://dx.doi.org/10.1007/BF02704427


