ELECTRON PARAMAGNETIC RESONANCE OF Mn^{2+} IN Tl$_2$Mg(SeO$_4$)$_2$·6H$_2$O SINGLE CRYSTALS

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The electron paramagnetic resonance of Mn^{2+} in Tl$_2$Mg(SeO$_4$)$_2$·6H$_2$O single crystals has been observed at 298 K and 77 K at $\sim$ 9.45 GHz. Mn^{2+} has been found to substitute for Mg^{2+} exhibiting two magnetically inequivalent complexes. The electron paramagnetic resonance spectra have been analysed using the spin Hamiltonian appropriate for rhombic symmetry.
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1. Introduction

The hydrated double sulfates and selenates with the general formula M$'_2$M$''_2$(XO$_4$)$_2$ · 6H$_2$O, where M$'$ is a monovalent cation and M$''$ is a divalent cation, X = S or Se, form an isomorphous series of monoclinic compounds [1]. Hence it is easy to prepare solid solution of the paramagnetic salts in diamagnetic ones over a wide range (0 − 100%) of relative concentration. There has been a considerable interest in the electron paramagnetic resonance (EPR) of these salts because they provide a series of simple structurally related molecules to test bonding models of transition metal complexes [2, 3], temperature-dependent spectra [4], spin quenching effects [5] and host spin lattice relaxation narrowing effects [4, 6]. In this paper we describe an EPR study of Mn^{2+} in Tl$_2$Mg(SeO$_4$)$_2$·6H$_2$O (TMSeH) single crystals at 298 K and 77 K.

2. Crystal structure

The crystals of TMSeH are isomorphous to (NH$_4$)$_2$Mg(SO$_4$)$_2$·6H$_2$O. The crystal structure is known to be monoclinic with space group $P(2_1/a)$ (C^5_{2h}) [7]. The crystallographic axes (a, b, c) are approximately in the ratio 3:4:2 and the angle $\beta \approx 105°$. There are two formula units in each unit cell. Six water molecules surround the divalent inversion symmetric (C_i) site. The divalent atoms in the unit cell are located at $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, 0)$ while all other atoms are in the general positions.

3. Experimental

Single crystals of TMSeH doped with Mn^{2+} were grown by slow evaporation of an aqueous solution at 300 K. Mn^{2+} was introduced into the host lattice by adding 0.5–1 wt% of manganese sulfate. The EPR experiments were performed on a JEOL FE-3X homodyne spectrometer operating at $\sim$ 9.45 GHz equipped with a TE_{011} cylindrical cavity and 100 kHz field modulation. The liquid nitrogen temperature measurements have been made using a JES-UCD-2X insertion type dewar. As a reference for the magnetic field strength the resonance line of DPPH with $g = 2.0036$ is used.

4. Results and discussion

For an arbitrary orientation of the crystal, a complex spectrum corresponding to two identical but differently oriented Mn^{2+} complexes is observed in TMSeH. When the magnetic field is in the a, c plane, the EPR spectrum shows only one set of five sextets ($\Delta M = \pm 1$, $\Delta m = 0$ transitions). This conforms with the fact that the a, c plane is a mirror plane perpendicular to the b axis, in which two Mn^{2+} sites become equivalent. The Mn^{2+} ions substitute for Mg^{2+} sites and consequently $[Mn(H_2O)_6]^{2+}$ complexes are obtained. The principal axes of the Mn^{2+} complexes were obtained by locating extrema in the fine structure spread. The two z axes make an angle of $72°(2°)$ with each other. The spectra reveal rhombic symmetry. Figure 1 shows the angular variation of the positions of fine structure transitions $\Delta M = \pm 1$ in the z, x plane of the one of the Mn^{2+} complexes.

The EPR spectrum of Mn^{2+} in TMSeH was also studied at liquid nitrogen temperature. It was found that as the temperature is lowered from 298 K, only the spread of the spectrum increases indicating the absence of any phase transition in the host in this temperature range.

The EPR spectrum of Mn^{2+} in TMSeH is described by a spin Hamiltonian appropriate for rhombic (or lower) symmetry of the form [4]:

$$\mathcal{H} = \beta_e(S_x g_x B_x + S_y g_y B_y + S_z g_z B_z)$$
$$+D[S_z^2 - (1/3)S(S+1)] + E(S_x^2 - S_y^2)$$
$$+(a/6)[S_x^4 + S_y^4 + S_z^4 - (1/5)S(S+1)(3S + 3S^2 - 1)]$$
$$+A_z S_z I_z + A_x S_x I_x + A_y S_y I_y,$$

where the symbols have their usual meaning and $S = I = 5/2$.

Magnetic field measurements were made for the allowed lines with the magnetic field B parallel to the z and x axes, respectively. No measurement could be made for B parallel to the y axis, since the lines got mixed up and consequently the various fine structure transitions could not be distinguished. Therefore, it was necessary to assume that $A_x = A_y$ and $g_x = g_y$ in the calculations (the hyperfine and g tensors are normally isotropic for the Mn^{2+} ion). Using the above spin Hamiltonian the Mn^{2+} EPR spectra are analysed and the best-fit parameters are given in Table. The signs of the parameters are only relative and have been determined from the observed second-order hyperfine shift assuming A_z to be negative [8, 9].
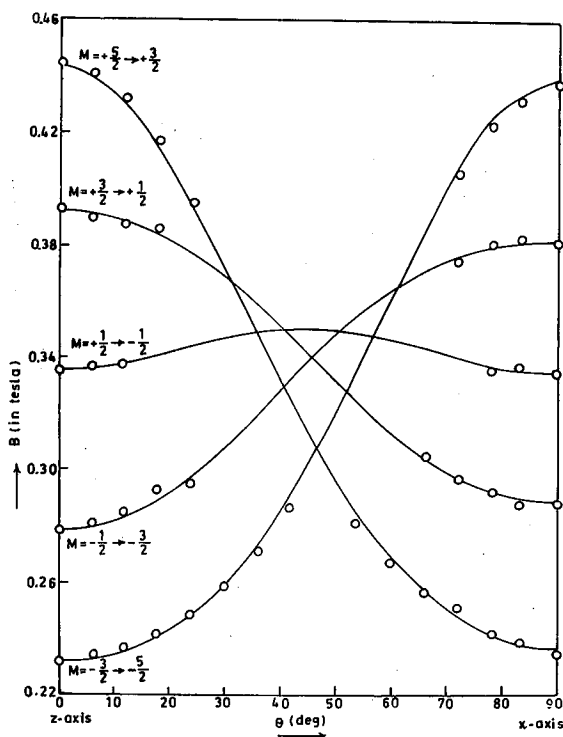
Fig. 1. Angular variation of the allowed fine structure transitions in the z, x plane of one of the magnetic complexes of Mn^{2+} in $Tl_2Mg(SeO_4)_2 \cdot 6H_2O$ single crystals at 298 K. Theoretical curve ———, experimental points o.

TABLE

Spin-Hamiltonian parameters of Mn^{2+} in $Tl_2Mg(SeO_4)_2 \cdot 6H_2O$ single crystals. All the zero field and hyperfine parameters are in units of 10^{-4} cm^{-1}.

Spin-Hamiltonian parameters	298 K	77 K
D	−256(2)	−308(3)
E	71(3)	75(2)
a	10(1)	8(1)
g_z	2.009(2)	2.011(2)
g_x	2.006(2)	1.997(2)
A_z	−87(1)	−87(1)
A_x	−88(1)	−88(1)

The values of the parameters D and E are nearly of the same magnitude for Mn^{2+} in TMSeH, $Tl_2Zn(SeO_4)_2 \cdot 6H_2O$ ($D = -258.6 \times 10^{-4}$ cm^{-1}, $E = 75 \times 10^{-4}$ cm^{-1}) [10] and $Tl_2Co(SeO_4)_2 \cdot 6H_2O$ ($D = -256 \times 10^{-4}$ cm^{-1}, $E = 66 \times 10^{-4}$ cm^{-1}) [11]. This gives a qualitative idea of the local symmetry at divalent cation sites, especially in the system where no detailed crystal structure is available. Qualitatively, it can be concluded that the coordination of water molecules at the Mn^{2+} is nearly the same for all the three systems, as regards the symmetry and distances from the Mn^{2+}. Although, the divalent metal–H_2O distances may be different in all the three hosts, however, it is shown that if R (metal–ligand bond distance) $>$ normal Mn–ligand bond distance, the introduction of substitutional Mn^{2+} gives rise to an inward relaxation while the opposite situation occurs for $R <$ Mn–ligand bond distance [12]. The ionic radii of Mg^{2+} (0.066 nm), Co^{2+} (0.072 nm) and Zn^{2+} (0.074 nm) are smaller than that of Mn^{2+} (0.08 nm) [13]. Therefore, substitution of Mn^{2+} in place of Mg^{2+}, Co^{2+} and Zn^{2+} in Tl salts may cause an outward relaxation and resulting in perhaps nearly the same configuration around Mn^{2+} in these salts as regards to symmetry and Mn–H_2O distances.

The EPR spectrum of the system was also studied at 77 K. As the crystal cools from 298 K to 77 K, the D parameter increases. The observed increase of D with decrease of temperature can be described in terms of explicit contributions resulting from the thermal expansion of the lattice and implicit contributions resulting from the lattice vibrations [9].

Acknowledgements

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