Electron paramagnetic resonance study of Mn$^{2+}$ in kainite

P SUBRAMANIAN and N HARIHARAN*

School of Physics, Madurai Kamaraj University, Madurai 625021, India
* Present address: Department of Physical Science, Federal University of Lagos, Abeokuta, PMB 2240 Ogun State, Nigeria

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Abstract. EPR measurements on kainite containing Mn$^{2+}$ impurities are made at x-band microwave frequencies at room temperature. The fine structure transitions observed in $ac^*$ plane have helped to extract the spin Hamiltonian parameters of Mn$^{2+}$ ions in the crystalline environment. The results indicate strong orthorhombic crystalline field and the rhombic field parameter is larger than those observed in the other similar systems. The $z$-axis of the $D$-tensor is determined with respect to $ac^*$ plane by theoretically fitting the experimental fine structure transitions.

Keywords. Electron paramagnetic resonance; kainite; spin Hamiltonian parameters; orthorhombic crystalline field.

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1. Introduction

Kainite has the chemical formula KMgClSO$_4$·3H$_2$O (Meyerhoffer 1903; Mellor 1952) and is a mineral well known for its use in fertilizers (Hieltzes 1937) and health eradication in coniferous cultures (Brückner and Bujakowsky 1936). Mn(II) ion is employed as a probe in kainite host lattice to determine the nature and strength of the crystal field surrounding the Mn(II) ion. The results of our EPR measurements on this system are reported in this paper.

2. Crystal structure

The crystals are grown by slow evaporation technique at room temperature from an aqueous solution containing equimolar ratios of the constituents KCl and MgSO$_4$·7H$_2$O. Well-developed crystals are obtained having unit cell dimensions

$$a = 19.75 \text{ Å}, \quad b = 16.25 \text{ Å}, \quad c = 9.54 \text{ Å} \quad \text{and} \quad \beta = 94.9^\circ$$

and crystallizing in the monoclinic space group $C_{2h}^2 - C2/m$ with $z = 16$. Detailed crystal structure data such as positional coordinates are not available (Ilse Ness 1958; Lindstedt 1951). However, it is known that the structure consists of four chains of groups of atoms

$$[-(SO_4)_2 - Mg(H_2O)_2 -(H_2O)_2 - Mg(H_2O)_2 -(SO_4)_2 -]$$
running along crystalline $b$-axis and the SO$_4$ tetrahedra lie in the mirror plane. The chains are distributed on the (010) cross-section of the cell. K$^+$ and Cl$^-$ ions in free fields hold the chains vertically.

3. Experimental

To obtain kainite with Mn(II) impurities, the saturated solution is mixed with less than 1% molecular weight of MnCl$_2$·4H$_2$O and the solution under slow evaporation at room temperature gives well-defined transparent crystals. Cell dimensions measured using x-ray diffraction agree well with reported values (Ilse Ness 1958; Lindstedt 1951). Crystals of suitable dimensions are chosen and EPR measurements are carried out at room temperature at X-band using the homebuilt EPR spectrometer at the Chemical Physics Division of TIFR, Bombay. The sample is kept in a TE$_{102}$ cavity operating at 100 kHz field modulation. DPPH is used in all spectra as internal field marker.

4. Results and discussion

The ground state of Mn(II) being an $^6S_{5/2}$ state, five sextets of allowed EPR transitions ($\Delta M_s = \pm 1$ and $\Delta m_I = 0$) corresponding to $M_s = m_I = \frac{3}{2}$ may be expected. For an arbitrary orientation of the crystal a number of 30-line pattern corresponding to different Mn$^{2+}$ sites are observed. Since there are many sites for Mn$^{2+}$ in the crystal, several such EPR transitions are possible. But, we have identified only one set of 30-line pattern corresponding to a particular Mn$^{2+}$ site in our spectra with the magnetic field in the crystal $ac^*$ plane. The spin Hamiltonian parameters are extracted from these data.

The observed spectrum can be described by a spin Hamiltonian (Orton 1968; Low 1960)

$$\mathcal{H} = g\beta H \cdot S + D[S_z^2 - \frac{1}{3}S(S + 1)] + E(S_x^2 - S_y^2) + A m_I \cdot S.$$  

(1)

The various terms in the spin Hamiltonian correspond to Zeeman, crystal field and nuclear hyperfine interactions respectively. Assuming $g$ and $A$ to be isotropic for an ion in $^6S$ state, the crystal field terms are considered as a perturbation on Zeeman term and the line positions for an arbitrary orientation are expressed with second order corrections as (Low 1960; Chatelian and Weeks 1970).

$$H = H_0 - (M_s - \frac{3}{2})[D(3 \cos^2 \theta - 1) - 3E \cos 2\phi (\cos^2 \theta - 1)] + Am_I$$

$$+ \frac{1}{2H_0} [4S(S + 1) - 24M_s (M_s - 1) - 9]$$

$$\times \{(D - E \cos 2\phi)^2 (\sin \theta \cos \theta)^2 + (E \sin 2\phi)^2 \sin^2 \theta\}$$

$$- \frac{1}{8H_0} [2S(S + 1) - 6M_s (M_s - 1) - 3]$$

$$\times \{[D \sin^2 \theta + E \cos 2\phi (1 + \cos^2 \theta)]^2 + 4(E \cos \theta \sin 2\phi)^2\},$$  

(2)