

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

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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

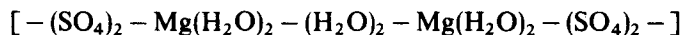
Kainite has the chemical formula $KMgClSO_4 \cdot 3H_2O$ (Meyerhoffer 1903; Mellor 1952) and is a mineral well known for its use in fertilizers (Hieltzes 1937) and health eradication in coniferous cultures (Brückner and Bujakowsky 1936). $Mn(II)$ ion is employed as a probe in kainite host lattice to 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 $MgSO_4 \cdot 7H_2O$. Well-developed crystals are obtained having unit cell dimensions

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

and crystallizing in the monoclinic space group $C_{2h}^3 - C2/m$ 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



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 $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ 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 $\Delta m_l = 0$) corresponding to $M_s = m_l = \frac{5}{2}$ 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)

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

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).

$$\begin{aligned} H = & H_0 - (M_s - \frac{1}{2}) [D(3 \cos^2 \theta - 1) - 3E \cos 2\phi (\cos^2 \theta - 1)] + Am_l \\ & + \frac{1}{2H_0} [4S(S+1) - 24M_s(M_s - 1) - 9] \\ & \times \{ (D - E \cos 2\phi)^2 (\sin \theta \cos \theta)^2 + (E \sin 2\phi)^2 \sin^2 \theta \} \\ & - \frac{1}{8H_0} [2S(S+1) - 6M_s(M_s - 1) - 3] \\ & \times \{ [D \sin^2 \theta + E \cos 2\phi (1 + \cos^2 \theta)]^2 + 4(E \cos \theta \sin 2\phi)^2 \}, \quad (2) \end{aligned}$$

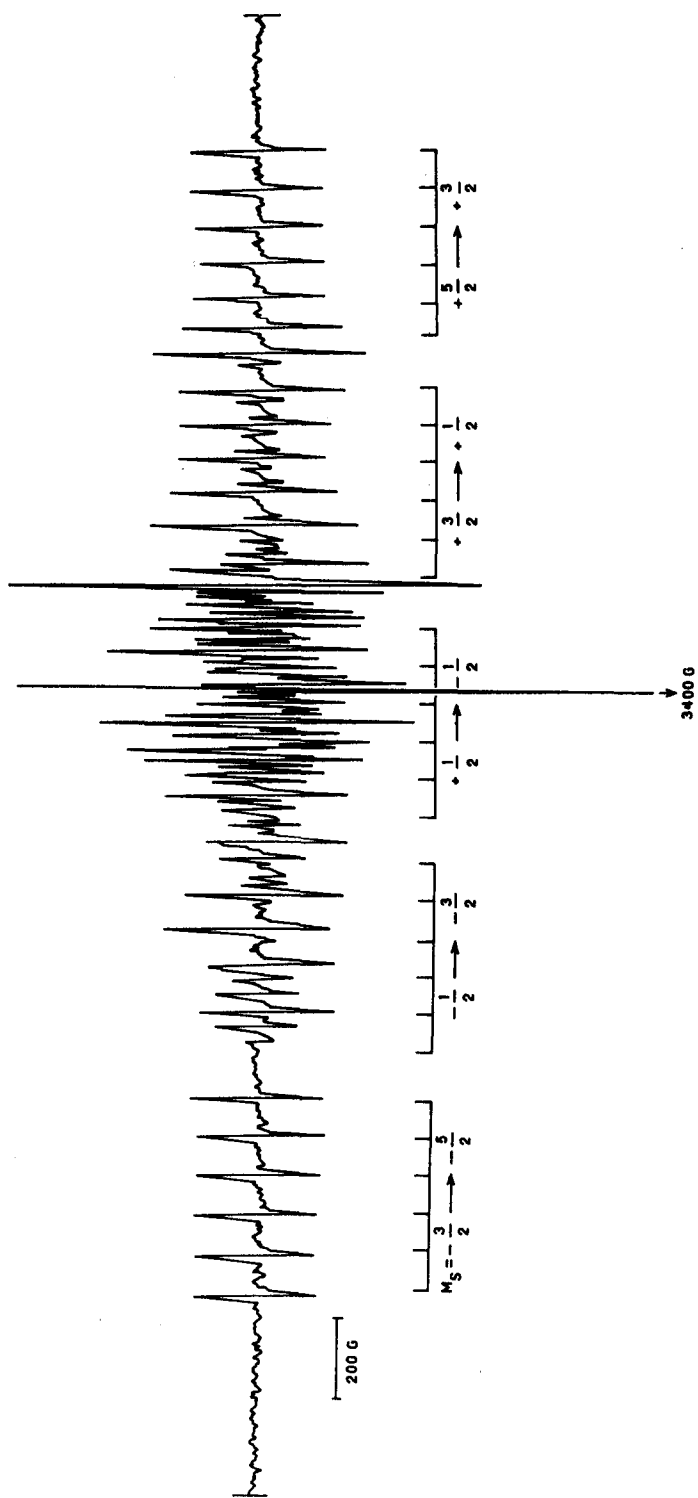


Figure 1. X-band EPR spectrum of Mn^{2+} ions when c^* -axis is 40° away from magnetic field direction in c^* plane at room temperature. The computed hyperfine field positions are marked by vertical lines beneath the spectrum.

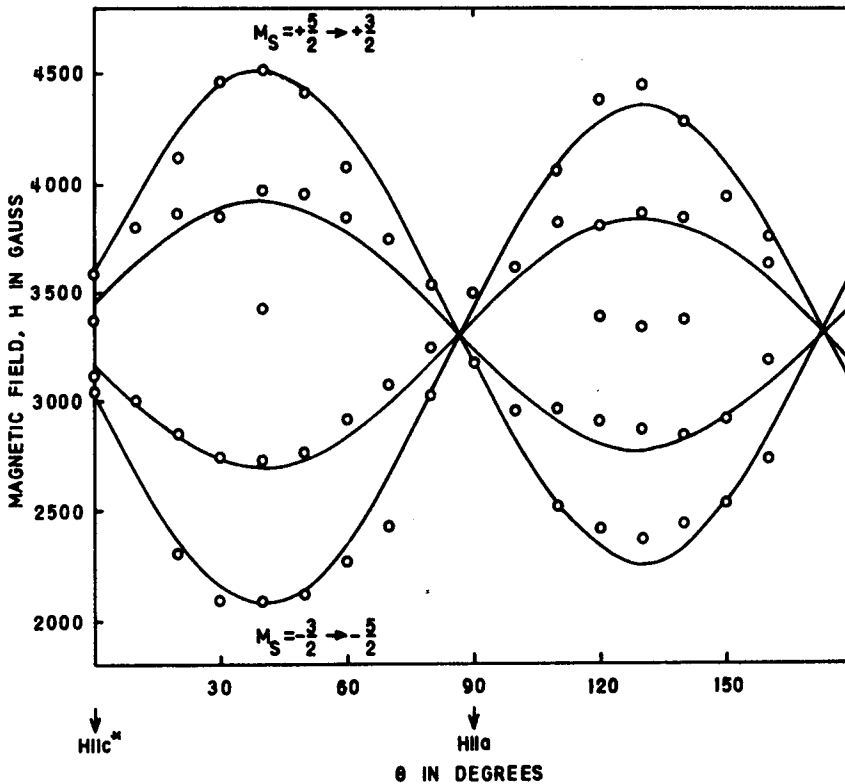


Figure 2. Finestructure lines variation of Mn^{2+} ions in kainite lattice in c^*a plane. Solid lines indicate theoretical values and open circles indicate experimental values.

Table 1. Spin Hamiltonian parameters of Mn^{2+} ions in different systems. D , E and A are in units of 10^{-4} cm^{-1} .

System	D	E	A	g
$Mg_2SiO_4^{(a)}$	-730 ± 10	-109 ± 3	-84 ± 1	2.003 ± 0.001
$CdNa_2(SO_4)_2 \cdot 2H_2O^{(b)}$	550 ± 2	-94 ± 3	-85 ± 1	2.004 ± 0.002
$CdGa_2Se_4^{(c)}$	-919 ± 3	15 ± 2	-61 ± 3	2.003 ± 0.001
$KMgClSO_4 \cdot 3H_2O$	642 ± 5	261 ± 5	95 ± 5	2.04 ± 0.02

References: ^(a) Chatelian and Weeks (1970); ^(b) Jain and Venkateswarlu (1979); ^(c) Schlaak and Weiss (1972)

where $H_0 = \frac{h\nu}{g\beta}$; $M_S = +\frac{5}{2}, +\frac{3}{2}, +\frac{1}{2}, -\frac{1}{2}$ and $-\frac{3}{2}$;

$m_l = +\frac{5}{2}, +\frac{3}{2}, +\frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$ and $-\frac{5}{2}$; $S = \frac{5}{2}$.

D , E and A represent axial, rhombic and hyperfine structure constants respectively. θ is the angle between the magnetic field direction and the z -axis while ϕ is the angle between the projection of the z -axis on ac^* plane of the crystal and the c^* -axis. In (2), D

and E terms are used in erg units and the resultant terms containing D and E have to be divided by $g\beta$ to convert them into gauss units. H_0 and A terms are in units of gauss.

Spin Hamiltonian parameters are evaluated from (2) by fixing the θ value. Various sets of D and E values are incorporated for $\phi = 0$ to 180° . All the parameters θ , ϕ , D and E are then varied until a good fit to the experimental data in ac^* plane for the fine-structure transitions versus angular variation could be obtained.

Figure 1 illustrates Mn^{2+} spectrum in kainite crystal, when the c^* -axis is 40° away from the magnetic field direction in c^*a plane. The computed field positions are marked by vertical markings beneath the spectrum. The fine structure transitions in all orientations in c^*a plane are plotted in figure 2. The spin Hamiltonian parameters which fit the observed spectra are

$$\begin{aligned} D &= 642 \pm 2 \times 10^{-4} \text{ cm}^{-1}, & E &= 261 \pm 2 \times 10^{-4} \text{ cm}^{-1}, \\ A &= 91 \pm 5 \times 10^{-4} \text{ cm}^{-1}, & g &= 2.04 \pm 0.02, \\ \theta &= 56 \pm 1^\circ, & \phi &= 40 \pm 1^\circ. \end{aligned}$$

These results suggest that the z -axis of the complex raises by 56° from c^*a plane and the projection of the z -axis on the c^*a plane is rotated by 40° from c^* -axis.

The spin Hamiltonian parameters in a few systems are compared with that of Mn^{2+} in kainite as shown in table 1. The signs of D , E and A in kainite are not determined. The D value is found to be large in kainite. Also the E value is very large when compared to the other systems (Chatelian and Weeks 1970; Jain and Venkateswarlu 1979; Schlaak and Weiss 1972). This indicates that the surrounding ligand interaction with $Mn(II)$ is highly distorted (low symmetry) resulting in strong orthorhombic nature of crystal field. The hyperfine constant is found to be isotropic and has the similar value as in Tutton salts (Jain and Venkateswarlu 1979).

5. Conclusion

Spin Hamiltonian parameters are derived for a single Mn^{2+} site from EPR investigations in kainite. The $Mn(II)$ ion is influenced by a very strong orthorhombic crystal field and this reveals that the metal coordination is highly distorted.

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