

EPR OF Mn^{2+} IN $MgCs_2(SeO_4)_2 \cdot 6H_2O$ SINGLE CRYSTALS

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The EPR spectrum of Mn^{2+} substituted for Mg^{2+} in $MgCs_2(SeO_4)_2 \cdot 6H_2O$ is measured at X-band frequencies at 298 K and 77 K.

We have studied electron paramagnetic resonance (EPR) spectra of divalent manganese in the Tutton salt $MgCs_2(SeO_4)_2 \cdot 6H_2O$ (MCsSeH) single crystals from 298 K down to 77 K. The MCsSeH crystals are monoclinic with two formula units per unit cell. The space group is $P2_1/a$. The lattice constants are approximately in the ratio 3:4:2 and monoclinic angle β is $106^\circ 17'$ [1]. The Mg^{2+} is surrounded by a distorted octahedron of water molecules. Thus the unit cell contains two inequivalent $Mg(H_2O)_6^{2+}$ complexes which are interchanged on mirror reflection in the ac plane.

Single crystals of MCsSeH doped with Mn^{2+} were grown by slow evaporation of aqueous solution at constant temperature. The Mn^{2+} were introduced into the lattice by adding a small amount (0.1% by weight) of manganese sulfate. The experiments were performed on a Varian V-4502 EPR spectrometer, operating at X-band, provided with 100 kHz field modulation.

For an arbitrary orientation of the magnetic field, a complex spectrum corresponding to the two identical but differently oriented Mn^{2+} complexes is observed. When the magnetic field is varied in the ac plane the EPR spectrum showed only one set of five sextets ($\Delta M = \pm 1$, $\Delta m = 0$ transitions). This is in conformity with the fact that the ac is a mirror plane perpendicular to the b axis, in which two divalent sites becomes equivalent. The Mn^{2+} substitutes Mg^{2+} sites and shows the rhombic spectrum. The angle between the z axis of two inequivalent Mn^{2+} complexes is $66^\circ \pm 2^\circ$. Fig 1 shows the angular variation of the positions of fine structure transitions $\Delta M = \pm 1$ in the zx plane of the one of the Mn^{2+} complexes. The linewidths in the EPR spectra is of the order of 11 gauss, which can be explained as due to local magnetic fields of the proton nuclear moments in the water molecules [2].

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Magnetic field measurements were made for the allowed lines along z and x axes. No measurements could be made along the y axis since the lines are all mixed together and consequently the various transitions could not be distinguished. The results were fitted to a spin-Hamiltonian of the form [3]

$$\mathcal{H} = \beta(g_x H_x S_x + g_y H_y S_y + g_z H_z S_z) + D[S_z^2 - (1/3)S(S+1)] + E(S_x^2 - S_y^2) + (a/6)[S_x^4 + S_y^4 + S_z^4 - (1/5)(3S^2 + 3S - 1)S(S+1)] + AS_z I_z + BS_x I_x + CS_y I_y,$$

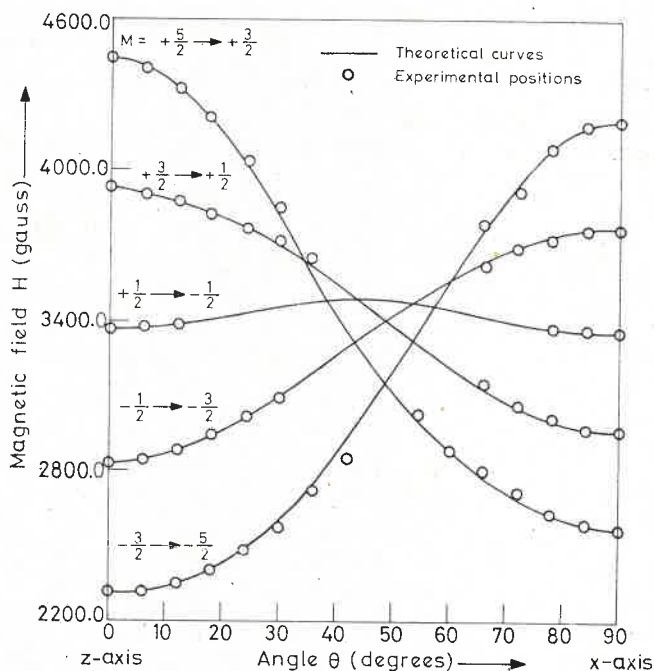


Fig. 1. Angular variation in zx plane of the allowed fine structure transitions in the EPR spectrum of $\text{MgCs}_2(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O} : \text{Mn}^{2+}$ single crystals at 298 K.

where the symbols have their usual meaning and for Mn^{2+} , $S = I = 5/2$. Since no measurements were made along y axis, it was necessary to assume that $B = C$ and $g_x = g_y$ in the calculations.

Using the above spin-Hamiltonian, the Mn^{2+} EPR spectra are analysed, and the values of the best fit parameters, thus obtained, are listed in Table I at 298 K and 77 K. The signs of the parameters (given in Table I) are only relative and have been determined from the observed second-order hyperfine shifts, assuming A to be negative [4, 5]. The values of g and A are independent of temperature within the experimental error. The work of van Wieringen [6] shows that the magnitude of the hyperfine coupling constant depends on the amount of covalent bonding in the crystal. That is, the greater the covalent bonding the smaller will be the hyperfine splitting. The observed value of A (average hyperfine coupling constant) indicates that Mn^{2+} are surrounded by six water molecules

TABLE I

Spin-Hamiltonian parameters of Mn^{2+} in $MgCs_2(SeO_4)_2 \cdot 6H_2O$ single crystals. All the crystal field and hyperfine parameters are in units of $10^{-4} cm^{-1}$

Spin-Hamiltonian parameters	298 K	77 K
D	-249.5 ± 1	-271.3 ± 1
E	43.0 ± 2	44.5 ± 2
a	6.3 ± 1	6.0 ± 1
g_z	2.0069 ± 0.0005	2.0066 ± 0.0005
g_x	2.0061 ± 0.0008	2.0061 ± 0.0008
A	-89.0 ± 1	-89.0 ± 1
B	-88.0 ± 1	-88.0 ± 1

as the covalency parameter determined from the curve (hyperfine parameter vs covalency) given by Simanek and Müller [7] indicates the characteristic covalency of $Mn^{2+} - 6H_2O$ complex. The value of the axial parameter D is sensitive to temperature. The value of D increases as temperature decreases. An increase in the value of D at low temperature can probably be explained as due to thermal contraction of the lattice [8].

TABLE II

Comparison of the spin-Hamiltonian parameters and angle between the z axis of two inequivalent Mn^{2+} complexes in Mn^{2+} doped Tutton salt single crystals. All the parameters are in units of $10^{-4} cm^{-1}$

Host lattice	D	E	A	B	Angle between z axis of two inequivalent Mn^{2+} complexes	References
$Mg(NH_4)_2(SO_4)_2 \cdot 6H_2O$	231	60	90	90	75°	[9]
$Zn(NH_4)_2(SO_4)_2 \cdot 6H_2O$	243	100	-91	-91	64°	[10]
$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	-232.5	45	-87.8	90.8	$70 \pm 5^\circ$	[11]
$ZnK_2(SO_4)_2 \cdot 6H_2O$	-261	72	-87.3	88	64°	[12]
$MgCs_2(SeO_4)_2 \cdot 6H_2O$	-249.5 ± 1	43.0 ± 2	-89.0 ± 1	-88 ± 1	$66 \pm 2^\circ$	Present work

A comparison of our observations with the EPR studies of Mn^{2+} in other Tutton salts [9-12] gives an idea of the local symmetry at divalent cation sites, especially in the system where no detailed crystal structure is available. The comparison is given in Table II. In all the salts quoted above, D and E parameters have nearly the same magnitude. The values of the angle between the z axis of two inequivalent Mn^{2+} complexes has been found to be of very nearly the same magnitude. Thus qualitatively it can be concluded that the co-ordination of water octahedra at the divalent ion site is nearly the same for all the systems.

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