EPR of Mn^{2+} in Tutton Salts*

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Electron paramagnetic resonance of divalent Mn^{2+} ions in the Tutton salts $M''M_2'(SO_4)_2 \cdot 6\,H_2O$, ($M' =$ Mg, Fe, Zn, Cd and $M'=$Rb, Cs) and $CdM_2'(SO_4)_2 \cdot 6\,H_2O$, ($M'=$K, NH_4) single crystals has been studied at 298 K. The Mn^{2+} is found to substitute divalent cation sites. The spectra have been analysed using the spin-Hamiltonian appropriate for rhombic symmetry.

1. Introduction

The hydrated double sulfates with the general formula $M''M_2'(SO_4)_2 \cdot 6\,H_2O$ (Tutton salts), where M'' is a divalent cation (Mg, Zn, Cd or an ion of the 3d group) and M' is a monovalent cation (K, Rb, Cs, Tl or NH_4) form an isomorphous series of compounds. Tutton salts have been widely used as host lattices for electron paramagnetic resonance (EPR) studies of various iron group ions[1]. Bleaney and Ingram[2] studied the EPR of Mn^{2+} in $Zn(NH_4)_2(SO_4)_2 \cdot 6\,H_2O$ as early as 1951. The EPR of Mn^{2+} in

$$Mg(NH_4)_2(SO_4)_2 \cdot 6\,H_2O, \quad Fe(NH_4)_2(SO_4)_2 \cdot 6\,H_2O \quad \text{and} \quad ZnK_2(SO_4)_2 \cdot 6\,H_2O$$

is also reported in the literature[3–5]. In this paper, an EPR study of Mn^{2+} in $M''M_2'(SO_4)_2 \cdot 6\,H_2O$ (where $M'' =$ Mg, Fe, Zn, Cd and $M' =$ Rb, Cs) and in $CdM_2'(SO_4)_2 \cdot 6\,H_2O$ (where $M' =$ K, NH_4) is reported at 298 K for the first time. A comparison of these results with those previously obtained in the other Tutton salts is expected to be helpful in understanding the orthorhombic field splitting of Mn^{2+} in Tutton salts.

2. Crystal Structure

The crystal structure of Tutton salts is known to be monoclinic with space group $P\,2_1/a$[6]. The crystallographic axes (a, b, c) are approximately in the ratio (3, 4, 2) and the angle β is about 105°. There are two formula units per unit cell. The two inequivalent divalent cations in the unit cell are situated at points (0, 0, 0) and ($\frac{1}{2}$, $\frac{1}{2}$, 0) and all others are in general positions. Each divalent cation is surrounded by a slightly distorted octahedron of water molecules.

3. Experimental

Single crystals of Tutton salts doped with Mn^{2+} were grown by slow evaporation of aqueous solutions at room temperature. The Mn^{2+} impurities were introduced into the host lattices by adding a small amount (0.1 percent by weight) of manganese sulfate. The experiments were performed on a Varian V-4502 EPR spectrometer, operating at X-band with 100 kHz field modulation. As a reference for the magnetic field strength the resonance line of DPPH with $g = 2.0036$ is used. The magnetic field at the DPPH resonance was measured with the help of a Varian Model F-8A fluxmeter, and the frequency of proton signal was measured by a Systronics type 701 frequency counter.

4. Results and Discussion

For an arbitrary orientation of the magnetic field, a complex spectrum corresponding to two identical but differently oriented Mn^{2+} complexes is observed in all the crystals studied. When the magnetic field is varied in the ac plane, the EPR spectrum shows only one set of five sextets ($\Delta M = \pm 1$, $\Delta m = 0$ transitions). This is in conformity with the fact that the ac plane is a mirror plane perpendicular to the b axis, in which two divalent sites become equivalent. Thus, it may be concluded that the Mn^{2+} ion enters the Tutton salt lattices in the divalent sites, and magnetic $[Mn(H_2O)_6]^{2+}$ complexes are obtained. The principal axes of the two inequivalent Mn^{2+} complexes were obtained by locating the extrema in fine structure spread. The spectrum at 298 K for magnetic field along the principal z axis of one set of equivalent Mn^{2+} complexes in $ZnRb_2(SO_4)_2 \cdot 6\,H_2O$ is shown in Figure 1. The angles between z axes of two inequivalent Mn^{2+}

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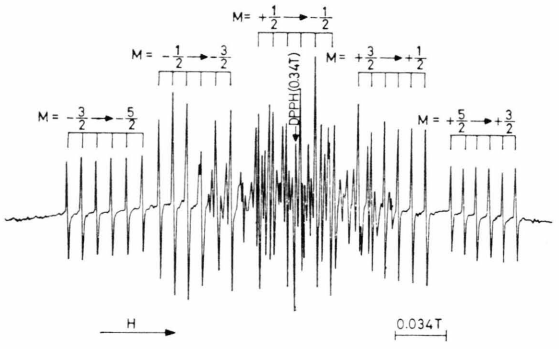

Fig. 1. EPR spectrum of $ZnRb_2(SO_4)_2 \cdot 6\,H_2O$: Mn^{2+} single crystals at 298 K; with H parallel to z axis of one of the magnetic complexes of Mn^{2+}.

complexes in all the crystals studied are given in Table I. The results of other Tutton salts are also included in this table [2–5]. Studies of the spectrum's angular variation showed that the crystal field symmetry is orthorhombic. Figure 2 shows the angular variation of the fine structure transitions ($\Delta M = \pm 1$)

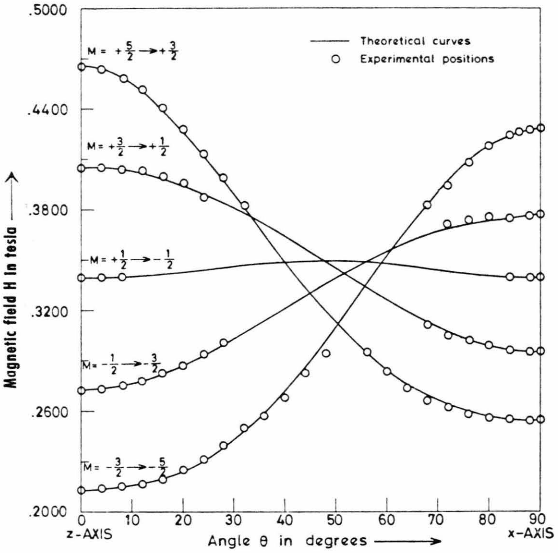

Fig. 2. Angular variation of the allowed fine structure transitions in the $z\,x$ plane of one of the magnetic complexes of Mn^{2+} in $ZnRb_2(SO_4)_2 \cdot 6\,H_2O$ single crystals.

Table I. Comparison of the spin-Hamiltonian parameters and angle α between z axes of the two magnetic inequivalent Mn^{2+} complexes in Tutton salt single crystals. All the crystal field and hyperfine parameters are in units of $10^{-4}\,cm^{-1}$.

Host lattice	D	E	a	g_z	g_x	A	B	α	References
$Zn(NH_4)_2(SO_4)_2 \cdot 6\,H_2O$	243.0	100.0	5.0	—	—	−91.0	−91.0	64°	2
$Mg(NH_4)_2(SO_4)_2 \cdot 6\,H_2O$	231.0	60.0	3.0	—	—	90.0	90.0	60°	3
$Fe(NH_4)_2(SO_4)_2 \cdot 6\,H_2O$	−232.5	45.0	—	2.004 ±0.001	—	−87.8	90.8	70°±5°	4
$ZnK_2(SO_4)_2 \cdot 6\,H_2O$	−245.8	67.8	8.7	2.0164	—	−82.2	−82.9	64°	5
$Cd(NH_4)_2(SO_4)_2 \cdot 6\,H_2O$	−250.0 ±2	50.0 ±5	7.7 ±1	2.0168 ±0.001	2.0204 ±0.002	−89.0±1	−88.0±2	66°±2°	
$CdK_2(SO_4)_2 \cdot 6\,H_2O$	−309.4 ±2	75.0 ±5	4.0 ±1	2.0054 ±0.0008	2.0095 ±0.0015	−90.5±1	−90.0±2	66°±2°	
$MgRb_2(SO_4)_2 \cdot 6\,H_2O$	−289.0 ±2	40.0 ±4	7.1 ±2	2.0101 ±0.0005	2.0105 ±0.001	−89.0±1	−88.0±1	70°±2°	
$FeRb_2(SO_4)_2 \cdot 6\,H_2O$	−297.0 ±2	46.0 ±4	6.9 ±2	2.0095 ±0.0005	2.0135 ±0.002	−90.0±1	−89.0±1	72°±2°	
$ZnRb_2(SO_4)_2 \cdot 6\,H_2O$	−300.0 ±2	55.0 ±4	9.4 ±2	2.0095 ±0.0005	2.0105 ±0.001	−89.0±1	−88.0±1	68°±2°	
$CdRb_2(SO_4)_2 \cdot 6\,H_2O$	−314.0 ±2	56.0 ±4	5.6 ±1	2.0069 ±0.0008	2.0101 ±0.002	−90.0±1	−89.0±2	67°±2°	
$MgCs_2(SO_4)_2 \cdot 6\,H_2O$	−257.8 ±2	32.0 ±4	4.3 ±2	2.0061 ±0.0005	2.0105 ±0.0015	−89.2±1	−88.0±1	68°±2°	
$FeCs_2(SO_4)_2 \cdot 6\,H_2O$	−265.8 ±2	24.0 ±4	5.5 ±1	2.0032 ±0.0005	2.0069 ±0.0015	−88.9±1	−88.6±1	68°±2°	
$ZnCs_2(SO_4)_2 \cdot 6\,H_2O$	−265.7 ±2	32.0 ±4	4.55 ±1	2.0081 ±0.0005	2.0114 ±0.0015	−89.5±1	−88.6±1	70°±2°	
$CdCs_2(SO_4)_2 \cdot 6\,H_2O$	−309.4 ±2	75.0 ±5	4.0 ±1	2.0054 ±0.0008	2.0095 ±0.0015	−90.5±1	−90.0±2	66°±2°	

in the zx plane of one of the Mn^{2+} complexes in $ZnRb_2(SO_4)_2 \cdot 6\,H_2O$. Similar curves have been found for the isomorphous crystals $M''M_2'(SO_4)_2 \cdot 6\,H_2O$ (M'' = Mg, Fe, Zn and Cd and M' = Rb, Cs) and $CdM_2'(SO_4)_2 \cdot 6\,H_2O$ (M' = K, NH_4). The similarity of these curves in all the crystals is indicative that the local environments have the same symmetry, with the spectra differing only in the magnitude of the splitting.

The linewidths in the EPR spectra of Mn^{2+} in magnesium and zinc Tutton salts at 298 K and at liquid nitrogen temperature are of the order of 1.2 mT and 1.0 mT, respectively. This linewidth is mainly due to the local magnetic fields of the proton nuclear moments in the water molecules surrounding the magnetic ion in the form of a distorted octahedron. The EPR studies in some hydrated crystals have shown that this linewidth can be reduced by a factor of about three in deuterated crystals [7]. The linewidths of Mn^{2+} resonance lines at 298 K in ferrous Tutton salts are of the order of 2.0 mT. The linewidth decreases slightly as the temperature is lowered to liquid nitrogen temperature. In cadmium Tutton salts, the linewidths are of the order of 4.0 mT, which is probably due to the crystalline imperfections, which cause distortions of the crystalline field. The large linewidths in cadmium Tutton salts cause uncertainty in the measurement of the line positions.

The observed orthorhombic spectra for a sample temperature of 298 K have been analysed using the spin-Hamiltonian

$$\begin{aligned}\mathcal{H} = {} & \beta(g_x H_x S_x + g_y H_y S_y + g_z H_z S_z) \\ & + D[S_z^2 - \tfrac{1}{3} S(S+1)] + E(S_x^2 - S_y^2) + \frac{a}{6} \\ & \times [S_x^4 + S_y^4 + S_z^4 - \tfrac{1}{5} S(S+1)(3\,S^2 + 3\,S - 1)] \\ & + A\,I_z S_z + B\,I_x S_x + C\,I_y S_y\,,\end{aligned}$$

where the symbols have their usual meaning and $S = I = 5/2$ for Mn^{2+}. The best-fit parameters were obtained from the resonance field positions given by Pandey and Upreti [8] up to third-order perturbation for the above spin-Hamiltonian. It was found that the contribution to the line positions from the fourth-order perturbation terms is negligibly small and must therefore not be considered.

To obtain the best-fit values of the spin-Hamiltonian parameters, the following procedure was adopted. Magnetic field measurements were made for the allowed lines along the z and x axes. No measurements could be made along the y axis since the lines got mixed up and consequently the various transitions could not be distinguished. Therefore, it was necessary to assume that $B = C$, $g_x = g_y$ in the calculations (the hyperfine and g tensors are isotropic for the Mn^{2+} ion). The spin-Hamiltonian parameters g_z, g_x, D, a, E, A and B were first estimated by solving the equations of resonance field positions up to second-order. Using these initial values of the parameter, an iterative procedure was adopted to get the best-fit parameters. The positions of thirty lines of Mn^{2+} spectra and root mean square deviations from the observed experimental values were then calculated. A computer programme was used, in which all the parameters were varied independently to minimize the root mean square deviations. In this procedure, the higher order terms were added one by one with the help of a computer programme by an iterative procedure. Final best-fit values of the parameters, thus obtained, are listed in Table I. The results of other Tutton salts are also included in this table.

The signs of the parameters (given in Table I) are relative. Since the hyperfine splitting constant is always found to be negative for a manganese ion [9, 10], this sign is taken for A in this case as well. The examination of the magnitude of the splitting of the hyperfine sextets appearing at high fields and at low fields when the magnetic field is parallel to z axis, attributes a sign to the parameter D [11]. The sign of the rhombic parameter E results from the sign of D and the choice of the x and y axes.

The g-factor and the hyperfine splitting were found to be almost isotropic within the experimental error for all the crystals studied. The work of van Wieringen shows that the magnitude of the hyperfine splitting depends on the amount of covalent bonding in the crystal [12]. That is, the greater the covalent bonding the smaller the hyperfine splitting will be. Schlaak and Weiss [13], while studying the EPR of Mn^{2+} in chalcogenides, discuss the influence of covalency on the spin-Hamiltonian parameters a, D, g and A. Plots of the average hyperfine splitting $= \frac{1}{3}(A + B + C)$ for Mn^{2+} as a function of covalency or ionicity parameters have been given for simple crystal systems [14–17]. The observed value of the average hyperfine splitting indicates that Mn^{2+} is surrounded by six water molecules in the Tutton salts since the covalency parameter as determined from the curve (hyperfine splitting vs covalency) given by Simanek and Müller[17] indicates the characteristic covalency of the $[Mn(H_2O)_6]^{2+}$ complex.

In all the salts quoted in Table I, the value of the angle between the z axes of twe inequivalent manganese complexes and the values of the parameters D and E are very nearly of the same magnitude. This gives a qualitative idea of the local symmetry at divalent cation sites, especially in the systems where no detailed crystal structure is available. Qualitatively, it can be concluded that the coordination of the octahedron of water molecules at the divalent cation is nearly the same for all the systems, both as regards the symmetry and the distances from the divalent cation. It is also noticed from Table I that the magnitude of D increases as the ionic radius of the divalent cation increases.

The sign of D for cadmium caesium Tutton salt is different from those for other caesium Tutton salts. Also, the ferrous and cadmium ammonium Tutton salts have a sign of D opposite to that for the other ammonium Tutton salts. It is interesting to note that in Mn^{2+} doped $CdCl_2$, the sign of D is positive below 380 ± 5 K and a reversal of sign of D takes place above 380 ± 5 K. The reversal of sign of D is deduced to be caused by the Cl^- octahedron surrounding the cadmium, changing from compression at lower temperatures to elongated at higher temperatures[18]. However, no detailed crystal structure studies are available for the Tutton salts studied in the present work. Therefore, a possible analogy with the above case as regards the correlation of the sign of D with the size and shape of the octahedron of the water molecules surrounding the divalent site could not be derived in the present case.

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