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EPR and optical study of Mn²⁺ doped ammonium oxalate monohydrate

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Abstract

Studies on fine and hyperfine structures of paramagnetic resonance spectra in single crystals of Mn^{2+} : ammonium oxalate monohydrate are reported. As sufficient numbers of lines were not obtained at room temperature, measurements have been done at liquid nitrogen temperature and at the frequency of X-band. The Mn^{2+} spin Hamiltonian parameters have been evaluated employing a large number of resonant line positions observed for various orientations of the external magnetic field and the surrounding crystalline field has been discussed. The values of the zero field parameters that give good fit to the observed EPR spectra have been evaluated. The values obtained for g, A, B, D, E and a are 2.0002 ± 0.0002 , $(100 \pm 2) \times 10^{-4}$, $(79.5 \pm 2) \times 10^{-4}$, $(257 \pm 2) \times 10^{-4}$, $(85 \pm 2) \times 10^{-4}$ and $(-18 \pm 1) \times 10^{-4}$ cm⁻¹, respectively. The percentage of covalency of the metalligand bond is also determined. The optical absorption study has been done at room temperature. The observed bands are assigned as transitions from the ${}^{6}A_{1g}(S)$ ground state to various excited quartet levels of Mn^{2+} ion in a cubic crystalline field. The electron repulsion parameters (*B* and *C*), the crystal field splitting parameter(Dq) and the Trees correction (α) providing good fit to the observed optical spectra have been estimated and the values obtained for the parameters are B=897, C=2144, Dq=910 and $\alpha=76$ cm⁻¹.

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1. Introduction

EPR provides a great deal of information about the magnetic properties of transition metal ions and enables to identify site symmetry around the metal ion [1]. Optical absorption is important in studying the electronic structure of transition ions in crystals giving knowledge of the energy levels and crystal field parameters. Thus EPR and optical absorption are two

In the present investigation, the EPR and optical study of Mn^{2+} ions doped in ammonium oxalate monohydrate are reported in order to obtain information whether Mn^{2+} ion enters the lattice substitutionally or interstitially and to have better understanding of the physical interactions present in the system. The study is further used to find energy of

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supplementary tools to investigate the site symmetry and the dynamic behaviour of the substituents of the lattice. EPR of Mn^{2+} , high spin d^5 ion, has been studied quite extensively, particularly in octahedral coordination [2–6]. Mn^{2+} has five 3d electrons and the ground state is ${}^6S_{5/2}$. As the resultant angular momentum is zero, only the electron spin is responsible for the paramagnetism. The zero-field splittings in these ions are sensitive with respect to small structural changes.

various orbital levels as well as to describe the nature of bonding in the complex.

2. Crystal structure

The crystal structure [7] of ammonium oxalate monohydrate (NH₄)₂ C₂O₄·H₂O, is orthorhombic with the space group $P_{2_12_1}$, containing two formula units per unit cell. The unit cell dimensions are a=8.04, b=10.27 and c=3.82 Å. Distances within the oxalate group are: C-C=1.581±0.01, O₁-C=1.25±0.02, and O₂-C=1.23±0.02 Å the angle O-C-O=129±2°. The angle between the O-C-O plane and (001) is 14° and thus the angle between the two O-C-O planes of an oxalate group is 28°.

3. Experimental

Single crystals of ammonium oxalate monohydrate are grown at room temperature by slow evaporation of an aqueous solution of ammonia and oxalic acid. For Mn²⁺ doped crystals 0.1 wt% manganese sulphate is added as paramagnetic impurity to the mixture. The colourless crystals grow in about 15-20 days. The ESR spectra are recorded using X-band Varian E-112 ESR spectrometer with 100 kHz field modulation. As sufficient numbers of lines were not obtained at room temperature, spectra have been recorded at liquid nitrogen temperature. The single crystals are mounted at the end of a quartz-rod using quickfix and the crystal rotations are performed along the three mutually perpendicular axes a, b and c using a goniometer. The magnetic field was measured using a Varian flux meter and a proton probe having 0.2 cm³ of 0.25 molar solution of GdCl₃ in H₂O with the help of a Hewlet–Packard frequency counter. The optical absorption spectra have been recorded on a Unicam-5625 spectrophotometer in the wavelength range 195-1100 nm at room temperature.

4. Results and discussion

A typical EPR spectrum of Mn^{2+} in ammonium oxalate monohydrate recorded at 77 K when the applied magnetic field **B** is parallel to the '*a*' axis given in Fig. 1 shows five sets with six lines in each set. The five sets of lines are the fine structure of Mn^{2+} (*S*=5/2), and the six lines within each set are the hyperfine structure of ⁵⁵Mn(*I*=5/2, 100% abundance).

Crystal rotations have been performed in the three orthogonal crystallographic planes ab, bc, and ca. The rotation pattern of fine structure in ab plane is shown in Fig. 2. However, it is to be noted here that in all the three planes only one magnetically distinct site is observed.

When the Mn^{2+} , an S-state ion, is introduced in a crystal, it experiences an intense crystal field produced by



Fig. 1. EPR spectra of Mn^{2+} doped ammonium oxalate monohydrate when the applied magnetic field (*B*) is parallel to the *a* axis.

the surrounding ions. Consequently, fine structure results from the crystal field and the spin–spin interactions, and the hyperfine structure arises from the interaction between the nuclear spin of ${}^{55}Mn(I=5/2)$ and its electronic spin. Accordingly, the experimental results for the resonance fields can be analysed with the usual spin Hamiltonian

$$\mathcal{H} = \mathcal{H}_{z} + \mathcal{H}_{zfs} + \mathcal{H}_{h} \tag{1}$$

where \mathcal{H}_z is the Zeeman interaction term, \mathcal{H}_{zfs} the fine structure(zero-field splitting) term and \mathcal{H}_h the hyperfine interaction term, respectively. The Zeeman term is

$$\mathcal{H}_{z} = \mu_{\rm B} \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} \tag{2}$$

where $\mu_{\rm B}$ is the Bohr magneton, **B** is the external magnetic field vector, **g** is the spectroscopic splitting factor, and **S** is the effective electron spin vector. The zero-field splitting term for orthorhombic symmetry is [8,9]



Fig. 2. Angular variation of the fine structure of Mn^{2+} doped ammonium oxalate monohydrate in *ab* plane (showing the experimental points and the calculated curves).

$$\mathcal{H}_{zfs} = D[S_z^2 - 1/3S(S+1)] + E(S_x^2 - S_y^2) + a/6[S_x^4 + S_y^4 + S_z^4 - 1/5S(S+1)(3S^2 + 3S - 1)]$$
(3)

where D and E are the second order axial and the rhombic zero-field splitting parameters and a is the cubic splitting parameter, respectively.

The hyperfine interaction is

$$\mathcal{H}_{h} = \mathbf{A}S_{z}I_{z} + \mathbf{B}(S_{x}I_{x} + S_{y}I_{y}) \tag{4}$$

where A and B are hyperfine structure constants.

Bleaney and Trenum [10] gave the allowed transitions assuming the Zeeman interaction to be dominant occurring at fields **B** given by [8]

$$M = |\pm 5/2\rangle \leftrightarrow |\pm 3/2\rangle \tag{5}$$

 $g\mu_{\rm B}\mathbf{B} = g\mu_{\rm B}\mathbf{B}_0 - [2D(3\cos^2\theta - 1) + 2pa] - 32\delta_1 + 4\delta_2$

$$+ \varepsilon_1$$

 $M = |\pm 3/2\rangle \leftrightarrow |\pm 1/2\rangle$

 $g\mu_{\rm B}\mathbf{B} = g\mu_{\rm B}\mathbf{B}_0 - [D(3\cos^2\theta - 1) - 5pa/2] + 4\delta_1 - 5\delta_2$ $+ \varepsilon_2$

$$M = |\pm 1/2\rangle \leftrightarrow |-1/2\rangle$$

 $g\mu_{\rm B}\mathbf{B} = g\mu_{\rm B}\mathbf{B}_0 + 16\delta_1 - 8\delta_2 + \varepsilon_3$

where $\mathbf{B}_0 = h\nu/g\mu_B$ is the field at which a line would have occurred if all the fine structure terms had been zero. θ is the angle of rotation and the remaining terms have been explained elsewhere [8].

Direction cosines of the distortion axis have been determined using the method of Rao and Subramanian [11] and are given in Table 1 together with the direction cosines of some NH₄–O bonds. The EPR parameters were obtained by computer fitting of the experimental data and we selected the parameters which best satisfy simultaneously the resonance fields measured on the crystallographic *ab*, *bc* and *ca* planes. The values of *g*, **A**, **B**, *D*, *E* and *a* obtained for Mn²⁺ in ammonium oxalate monohydrate are summarized in Table 2.

The percentage of covalency of the Mn-O bond is also

Table 1

Direction cosines of NH_4 with surrounding oxygen; $NH_4\text{--}O_2$ and the distortion axis of Mn $^{2+}$ derived from EPR

Direction	l	т	n
C–NH ₄	± 0.6890	± 0.6043	± 0.3998
O ₁ -O ₂	± 0.2981	± 0.9235	± 0.2412
NH ₄ -O ₁	± 0.4316	± 0.8455	± 0.3189
NH ₄ -O ₂	± 0.7564	± 0.3113	± 0.5752
Distortion axis	± 0.7655	± 0.1061	± 0.6346

evaluated [12] using Matumura's plot [13] and is found as 14. The value of hyperfine splitting constant 78×10^{-4} cm⁻¹ predicted from the graph is in a reasonable agreement with the observed value of 86×10^{-4} cm⁻¹, (**A**+2**B**)/3.

The spin-orbit coupling parameter for the transition ions in a crystal are different from those of the free ion due to the covalency [14,15]. In fact, experimental values in a crystal are less than those of the free ion. The covalent bonding modifies the spin-orbit coupling ζ_d in a crystal as

$$\zeta_{\rm d} = N^2 \zeta_{\rm d}^0 \tag{6}$$

where ζ_d^0 is the free ion spin-orbit coupling and N is the average covalency parameter [15].

The deviations $\Delta g = g - 2.0023$ are observed in crystals where a fair amount of covalent bonding is present. It has been suggested [16] that in the presence of covalent bonding excited sextets ${}^{6}T_{1g}$ are present, whose single electron states tend to be full or empty according to whether electrons are transferred to or from the central ion by the action of bonding. A second order shift is then possible in the *g*-value, whose sign depends upon the direction of electron transfer. The value -0.0021 of Δg in the present study is consistent with this explanation.

5. Optical spectra

In a cubic crystalline field $Mn^{2+} 3d^5$ electron configuration yields various electronic states ${}^6A_{1g}$, ${}^4A_{1g}$, 4E_g , ${}^4T_{1g}$, ${}^4T_{2g}$, ${}^4A_{2g}$, ${}^4A_{2g}(F)$, ${}^4T_{1g}(F)$ and to a number of doublet states as discussed earlier [12]. ${}^6A_{1g}$ of these lies lowest and all the absorption bands of high spin Mn^{2+} result from spin forbidden transitions.

The observed optical absorption spectrum at room temperature is shown in Figs. 3 and 4. The spectrum consists of seven main bands located at 13,623, 14,430, 15,220, 21,186, 21,691, 26,455, 29,585 cm⁻¹. In addition, to the above, one weak band at 16,271 cm⁻¹ is observed. Among the bands observed in the present study, the bands at 15,220, 21,186, and 26,455 cm⁻¹ are found to be sharp. Using the Tanabe–Sugano diagram [17] and our earlier study [12] the assignments of different bands has been done. The wavelengths and the wave numbers of the bands are given in Table 3, together with the assignments.

The energy values for different electronic states have been calculated [12] using computer for different values of crystal field splitting parameter Dq with Racah parameters $B=897 \text{ cm}^{-1}$, $C=2144 \text{ cm}^{-1}$ and Trees correction $\alpha =$ 76 cm⁻¹ [18]. A good fit of the observed band positions is obtained for Dq=910 cm⁻¹ as can be seen from the graph in Fig. 5. It is interesting to note that the observed and calculated values are in good agreement, justifying the assignments.

The Racah parameters *B* and *C* are reduced considerably in crystals from those of free ion value due to the covalency [14].

Table 2

Spin Hamiltonian parameters for Mn^{2+} in ammonium oxalate monohydrate

g	Α	В	D	Ε	а
2.0002	100	79.5	257	85	-18

A, **B**, *D*, *E* and *a* all in units of $\times 10^{-4}$ cm⁻¹. Estimated error for *g* is ± 0.0002 . Estimated error for *A*, *B*, *D* are $\pm 2 \times 10^{-4}$ cm⁻¹. Estimated error for *a* is $\pm 1 \times 10^{-4}$ cm⁻¹.

These parameters in terms of N are given by the following relations [15]

$$B = N^4 B_0, \quad C = N^4 C_0 \tag{7}$$

where 0 < N < 1(N=1 for the pure ionic bond) and B_0 and C_0 are free ion values of Racah parameters. In Fe³⁺:YAG, the value of *N* is in the range of 0.8–0.9 for the Fe³⁺–O²⁻ bond [15]. Experimental evidence for a reduction of the parameters *B* and *C* in octahedral crystals is given in the literature [19].

Powell, Gabriel and Johnston [20] showed that the spin-doublet contribution to the ground state via the spinorbit interaction, is of major importance, using a value of $\zeta_d = 400 \text{ cm}^{-1}$, they found that for a range + 1200 to -1200 cm^{-1} of Dq, the cubic splitting parameter *a* varied widely. They also found possible to fit observed value of $z_d < 300 \text{ cm}^{-1}$ [21]. A value for ζ_d of $320 \pm 10 \text{ cm}^{-1}$ has been obtained from the optical spectrum of Mn^{2+} in RbMnF₃ [22]. In the range + 1000 \text{ cm}^{-1} \le \text{Dq} \le +1500 \text{ cm}^{-1} the parameter *a* was found to be a sensitive function of ζ_d and Dq.

Zhao et al. [23] have given the contribution of the sixthorder and the eighth-order perturbation to cubic splitting parameter a and showed that the eighth-order perturbation cannot be neglected for large Dq. In the present study the sixth-order perturbation magnitude to a has been obtained



Fig. 3. Absorption spectrum of Mn^{2+} in ammonium oxalate monohydrate in the wavelength range 325–1100 nm (the incident beam is perpendicular to the *ab* face of the crystal).

using Table 1 of Zhao et al. [23] and eighth-order perturbation contribution from the formula

$$a^{(8)} = \frac{1}{3} \left[(2.023050 \times 10^{-26}) \zeta_d^4 \text{Dq}^4 N^{-28} \right]$$

+ (1.269239 × 10^{-26}) \zeta_d^5 \text{Dq}^3 N^{-28} + (1.511472 \times 10^{-27}) \zeta_d^6 \text{Dq}^2 N^{-28} + (5.453156 \times 10^{-28}) \zeta_d^7 \text{Dq} N^{-28} \right] (8)

where *N* is obtained to be 0.939 using $B_0=960$ and $C_0=3325 \text{ cm}^{-1}$ for free Mn²⁺ ion [19] and $\zeta_d=N^2 \zeta_d^0$ with $\zeta_d^0=336.6 \text{ cm}^{-1}$ [23]. The value of *a* estimated comes out to be $13.4 \times 10^{-4} \text{ cm}^{-1}$ which is in good agreement with the experimental value given in Table 2.

The free ion values of the Racah parameters B_0 and C_0 are 960 and 3325 cm⁻¹ [19]. In the present investigation, we obtained the values of B=897 and C=2144 cm⁻¹. The considerable decrease in the values of the Racah parameters B and C from the free ion values indicates that there exists a fair amount of covalent bonding between the central metal ion and the ligand.

Arrangements of atoms surrounding NH_4^+ ions and water molecules [7] are shown in Fig. 6. Water molecules are tetrahedrally surrounded by two NH_4^+ ions and two oxygen atoms. Interatomic distances for one set are near 2.80 Å and for the other near 3.20 Å. The planes of the O–C–O parts of the $C_2O_4^-$ group are at an angle of 28° to one another.

The principal models of charge compensation when divalent impurity cations are substituted for the monovalent cations in a crystal lattice have been discussed earlier [24–26]. In these models the magnetic tensors have their unique axes pointing towards the divalent impurity-positive ion vacancy directions. Watkins [24] as well as Yokozawa and Kazumata [27] have obtained a spectrum IV showing orthorhombic symmetry which they assigned to an associated pair Mn^{2+} : X^{2-} where X^{2-} is an impurity like O^{2-} , S^{2-} etc. occupying a nearest neighbour anion site. The spin Hamiltonian parameters in the present case are given in

Table 3

The experimental data and the analysis of the absorption spectrum of Mn^{2+} ions in ammonium oxalate monohydrate

Transition from ⁶ A _{1g} (S)	Observed (Å)	Observed (cm ⁻¹)	Calculated (cm^{-1})
$^{4}T_{1g}(G)$	7340	13,623	13,646
${}^{4}T_{2g}(G)$	6930	14,430	
${}^{4}E_{g}(G)$	6570	15,220	22,293
${}^{4}A_{1g}(G)$	6146	16,271	21,210
0	4720	21,186	
${}^{4}T_{2g}(D)$	4610	21,691	20,822
${}^{4}E_{g}(D)$	3780	26,455	26,342
${}^{4}T_{1g}(P)$	3380	29,585	29,846

 $(B=897 \text{ cm}^{-1}, C=2144 \text{ cm}^{-1}, \text{Dq}=910 \text{ cm}^{-1}, \alpha=76 \text{ cm}^{-1}).$



Fig. 4. Absorption spectrum of Mn^{2+} in ammonium oxalate monohydrate in the wavelength range 195–325 nm (incident beam is perpendicular to the *ab* face of the crystal).

Table 2. The orthorhombic symmetry is evident due to the presence of the *E* term. The values of $D(814.9 \times 10^{-4} \text{ cm}^{-1})$ and $E(163.8 \times 10^{-4} \text{ cm}^{-1})$ for Mn^{2+} in BiVO₄ with Mn^{2+} substituting for Bi³⁺ [28] having approximately orthorhombic local field symmetry, are larger as compared to this study($D=257 \times 10^{-4} \text{ cm}^{-1}$). This may be due to different local ionic arrangement around



Fig. 5. The energy level diagram of Mn^{2+} in ammonium oxalate monohydrate showing the variation of the levels with Dq for a case with $B=897 \text{ cm}^{-1}$, $C=2144 \text{ cm}^{-1}$ and $a=76 \text{ cm}^{-1}$ (the circles show the experimental energies).

the metal ion. The direction cosine of the distortion axis calculated from EPR spectra nearly coincides with the direction of NH₄-O₂ bond. Therefore, Mn²⁺ is expected to be substituted for NH_4^+ in $(NH_4)_2$ C₂O₄·H₂O,similar to spectrum IV of Mn²⁺ in NaCl, corresponding to an associated pair Mn^{2+} : O^{2-} where O^{2-} occupies a nearest neighbour site. As the ion O^{2-} is next to Mn^{2+} ion, a large Coulombic binding energy is expected. The close proximity of the negative charge also explains the observed crystal field splittings. The asymmetry, as measured by E, could arise as a result of partial electron transfer away from the O^{2-} leaving a partial hole whose orbital degeneracy could be lifted by the Jahn-Teller distortion [8]. As only one set of allowed hyperfine lines is observed in all the three planes of rotation, it appears that only one type of site is preferentially occupied by Mn²⁺. Thus in our case though the Mn²⁺ ion enters the lattice of $(NH_4)_2 C_2 O_4 \cdot H_2 O$ substitutionally, the charge compensation model is different to that of Cu^{2+} doped $(NH_4)_2 C_2 O_4 \cdot H_2 O$ [29]. According to theory [30] the degeneracy of the ${}^{4}E_{g}(G)$ level is expected to be lifted in tetragonal or rhombic but not in trigonal distortion. The splitting of the sharp band ${}^{6}A_{1g}(S) \rightarrow {}^{4}E_{g}(G)$ in the present study suggests that Mn^{2+} is in a rhombically distorted octahedral site.

The comparison of the present EPR investigation with the previous EPR study [12] of Mn^{2+} doped KHSO₄ ($\mathbf{A}=66 \times 10^{-4} \text{ cm}^{-1}$, $\mathbf{B}=26 \times 10^{-4} \text{ cm}^{-1}$, $D=59 \times 10^{-4} \text{ cm}^{-1}$, $E=32 \times 10^{-4} \text{ cm}^{-1}$, $a=-8 \times 10^{-4} \text{ cm}^{-1}$, B=627 cm⁻¹, $C=2580 \text{ cm}^{-1}$ and $\text{Dq}=790 \text{ cm}^{-1}$) shows that the parameters **A**, **B**, *D*, *E*, *a*, *B*, *C* and Dq are larger in the present case. This can be explained on the basis of bonding. The hyperfine splitting for Mn^{2+} substituted in a number of crystals depends on the host lattice, it is appreciably larger for ionic crystals as compared to covalent ones [31]. The mechanism of covalent reduced hyperfine splitting involved covalency hindered $3s \rightarrow 4s$ excitation with a partially occupied 4s orbital. It was suggested [32] that the reduction of hyperfine splitting was due to the



Fig. 6. The configuration of the oxalate group and the atomic surroundings of the water molecule and the ammonium ion in $(NH_4)_2C_2O_4.H_2O.$

decrease of the 3d electron spin density at the Mn^{2+} site due to covalency. The relative amount of 4s-bonding increases on going to more covalent crystals. The reduction of hyperfine splitting of Mn²⁺ doped KHSO₄ is consistent with the larger covalency (20%) in it as compared to the present system (14%). The larger D and E values of Mn^{2+} doped ammonium oxalate monohydrate than that of Mn^{2+} doped KHSO₄ are because of NH₄-O bond length (2.85 Å) being shorter than the K–O bond length (2.98 Å). However, the local ionic arrangement around Mn²⁺ is different in the two cases giving different crystal field strength and consequently different zero field splitting parameters [15]. The rise in a in Mn²⁺ doped KHSO₄ would be expected to be associated with the decrease of ionicity of the Mn²⁺ ion [8]. The smaller B, C and Dq values of Mn^{2+} doped KHSO₄ as compared to the present case may also be expected to be associated with the larger covalency of Mn^{2+} in KHSO₄ [8, 191.

The ionic radii of Mn^{2+} , K^+ and NH_4^+ are 0.80, 1.33 and 1.43 Å, respectively. Thus for the substitutional Mn^{2+} in KHSO₄ and $(NH_4)_2C_2O_4 \cdot H_2O$, the amount of local distortion may be expected to be slightly larger in the former lattice than that in the latter. According to Owen [33] and Stevens [34] the d ϵ electrons of manganese having $(d\epsilon)^3(d\gamma)^2$ configuration will move into the orbits of the adjacent oxygen ions $(2p\pi \text{ orbits})$ and form π bonding and the d γ electrons will interact with $2p\sigma$ and 2s electrons of the oxygen ions and form σ bonding. The effect of π and σ bonding increases the crystal field strength and consequently the crystal field splitting. The smaller the strength of π bond the smaller will be the amount of local distortion [35]. Thus stronger covalent bonding in Mn^{2+} doped KHSO₄ gives larger amount of distortion in the lattice.

6. Conclusion

The EPR study of Mn^{2+} doped Ammonium Oxalate Monohydrate has been done at 77 K. The spin Hamiltonian parameters g, **A**, **B**, D, E and a have been determined. From the results a rhombically distorted octahedral substitutional site is predicted for the Mn^{2+} species. The optical absorption study has been done at room temperature and the bands observed have been assigned to transitions from the ${}^{6}A_{1g}(S)$ ground state to various excited levels of Mn^{2+} ion in cubic crystalline field. The observed band positions have been fitted with four parameters B, C, Dq and α and covalency of the metal–ligand bond has been discussed. The results of this investigation have been compared with that of the previous study of Mn^{2+} doped KHSO₄ and a brief discussion has been presented.

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