ELECTRON PARAMAGNETIC RESONANCE OF Mn^{2+} IN $(NH_4)_2SO_4$ SINGLE CRYSTAL

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ABSTRACT

Electron paramagnetic resonance investigation of Mn^{2+} in $(NH_4)_2SO_4$ single crystal is discussed both in paraelectric and ferroelectric phases of the crystal. Mn^{2+} is found to substitute one of the two possible types (α and β) of NH_4^+ ions and get associated with the second type of NH_4^+ vacancy, the vacancy being the second distant neighbour in the *bc*-plane. The line joining Mn^{2+} substituted NH_4^+ site and NH_4^+ vacancy lies at an angle of 18° from the crystallographic *b*-axis in the *bc*-plane. As the temperature is lowered to — 56° C the crystal becomes ferroelectric and the spectrum in the paraelectric phase splits into two from which it appears that two sets of Mn^{2+} sites which are magnetically equivalent in the paraelectric phase become inequivalent in the ferroelectric phase. The spin Hamiltonian analysis is presented for the spectrum in the paraelectric phase.

INTRODUCTION

ELECTRON paramagnetic resonance is known to give valuable information about lattice defects (Forrester and Schneider, 1956; Wertz and Auzins, 1957; Watkins, 1959; Yokozawa and Kazumata, 1961; Srivastava and Venkateswarlu, 1966 and Chowdari and Venkateswarlu, 1967) and phase transitions (Chowdari and Venkateswarlu, 1967; Sastry, 1967; Muller, 1963; Rimai and de Mars, 1963; Rimai, Deutsch and Silverman, 1964; and Chambers, Datars and Calvo, 1964). Our recent studies (Chowdari and Venkateswarlu, 1967) on the EPR of Mn^{2+} in K_2SO_4 gave indication regarding the existence of a probable new crystallographic phase below —130° C. in that crystal, in addition to the information about the locations of Mn^{2+} in the crystal and the associated alkali vacancies. The present paper

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deals with the results obtained in a study of EPR of Mn^{2+} in $(NH_4)_2SO_4$ single crystals in the paraelectric and ferroelectric phases. It is known from the work of Matthias and Remeika (1956) that ammonium sulphate becomes ferroelectric below $-50°$ C. It was suggested that the phase transition might be due to a change in the hydrogen bonding. Since that time nuclear magnetic resonance, neutron inelastic scattering and infrared spectroscopic studies (Blinc and Levstek, 1960; Burns, 1961; Richards and Schaefer, 1961; Chiho, 1962; Rush and Taylor, 1965; and Miller, Blinc, Brenman and Waugh, 1962) as well as X-ray, neutron and electron diffraction studies (Singh, 1962; Udalova and Pinsker, 1963, 1964 and Schlemper and Hamilton, 1966) have been carried out. Recently deuteron magnetic resonance studies (O'Reilly and Tsang, 1967) in ammonium sulphate were carried out by O'Reilly and Tasang (1967). Shrivastava (1966) of our laboratory carried out the preliminary work of EPR of Mn^{2+} doped $(NH_4)_2SO_4$ single crystal but the nature of the complex responsible for the spectrum obtained by him is still not definitely clear. The main purpose of this paper is to present a detailed study of the EPR of Mn^{2+} in $(NH_4)_2SO_4$ single crystal corresponding to a particular type of complex whose nature appears to have become clear in the present experiments.

Crystal Structure

A detailed investigation of the structure of $(NH_4)_2SO_4$ was carried out by Ogg (1928, 1930). Later Singh (1962) re-examined the room temperature structure by X-ray studies and also by a two-dimensional neutron study. Very recently neutron diffraction study of the structure of ammonium sulphate both in paraelectric and ferroelectric phases was reported by Schlemper and Hamilton (1966). The dimensions of the unit cell at room temperature according to this study are $a = 5{\cdot}993$ Å, $b = 10{\cdot}636$ Å and $c = 7{\cdot}782$ Å. The arrangement of the positive and negative ions in $(NH_4)_2SO_4$ is similar to that in K_2SO_4. The sulphur atoms lie on reflection planes, the reflection plane being a plane of symmetry of the SO_4 group. Two oxygen atoms of the SO_4 group lie on the plane and two others are equidistant from the plane. The structure consists of layers of atoms parallel to (100) with a spacing of $a/2$. The mirror planes or reflection planes are designated as $(100)_{\frac{1}{4}}$ and $(100)_{-\frac{1}{4}}$ referred to the centre of the unit as the origin of co-ordinates. Figure 1 shows that the projection of the atoms of ammonium sulphate crystal contains two different sets of ammonium ions called α and β, the oxygen environment of the ammonium ions being different for the two sets in the structure. In each unit

cell there are four ammonium ions of α type and four of β type. In Fig. 1 the atoms are represented by circles of different radii but the radii are not intended to represent atomic radii to scale. Since the atoms within the unit cell lie mostly in two layers parallel to (100), the atoms projected on the plane (100) have been shaded to distinguish these layers. The white circles represent atoms on the front plane, and the black circles represent atoms on a parallel plane at a distance $a/2$ behind it. The other shaded atoms lie between the planes. The SO_4 groups are shown by joining the S atoms to the oxygen atoms with lines. The symmetry of the crystal is orthorhombic at room temperature. Below the curie point the mirror symmetry disappears and the space group of $(NH_4)_2SO_4$ becomes $Pna\,2_1$. Thus the symmetry is still orthorhombic, but the a-axis gets polarised. The dimensions of the unit cell in the ferroelectric phase (Schlemper and Hamilton, 1966) are: $a = 5{\cdot}967 \pm 0{\cdot}006$ Å, $b = 10{\cdot}61 \pm 0{\cdot}01$ Å and $c = 7{\cdot}837 \pm 0{\cdot}007$ Å.

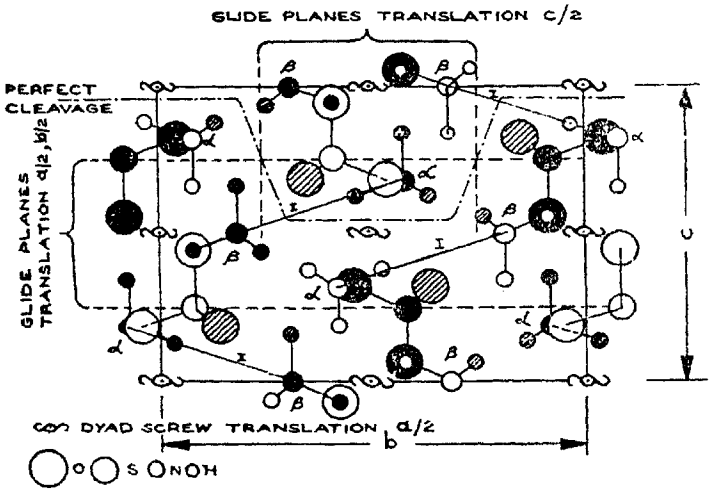

FIG. 1. Projection of ammonium sulphate single crystal in the *bc*-plane. The white circles represent atoms in the front plane and the black circles represent atoms in a parallel plane at a distance $a/2$ behind it.

EXPERIMENT, RESULTS AND DISCUSSION

The experimental details are similar to those given in the earlier paper (Chowdari and Venkateswarlu, 1967). $(NH_4)_2SO_4$ crystals doped with Mn^{2+} are grown from water solution mainly by slow evaporation of a saturated solution at constant temperature and the spectra are taken with a varian V-4502 EPR spectrometer using a 9″ magnet and 100 KC modulation. The crystallographic axes were confirmed by X-ray diffraction photographs.

The EPR spectrum of Mn^{2+} in orthorhombic fields is expected to show five fine structure transitions, each of which will show six hyperfine components. The spectrum that will be discussed here is taken in the crystallographic *bc*-plane keeping the *a*-axis of the crystal perpendicular to the direction of magnetic field. It is found to be largely angular dependent. It gets well resolved and shows maximum spread when the magnetic field H makes an angle of 18° on either side of the *b*-axis. This suggests that the site symmetry axis (*Z*-axis) of the complex makes an angle of 18° with the *b*-axis in the *bc*-plane of the crystal. Further it can be seen from Fig. 1 that the directions $\alpha\beta$ and $\beta\alpha$ the second distant neighbours in the *bc*-plane make also angles of 18° with the *b*-axis on either side. Thus these observations indicate that Mn^{2+} substitutes either α-NH_4^+ and gets associated with β–NH_4^+ vacancy or *vice versa*. One can see that there exist four such complexes in a single unit cell as marked I in Fig. 1 and they form two pairs. When H is parallel to the symmetry axes of one pair of complexes it makes an angle of 36° with that of the other pair. The individual complexes of each pair will probably be magnetically indistinguishable in the paraelectric phase and therefore one expects only one set of five sextets when H is making 18° angle with *b*-axis. However, additional weak lines due to the complexes with $\theta = 36°$ will also be present in addition to weak angular parts of the spectra of other

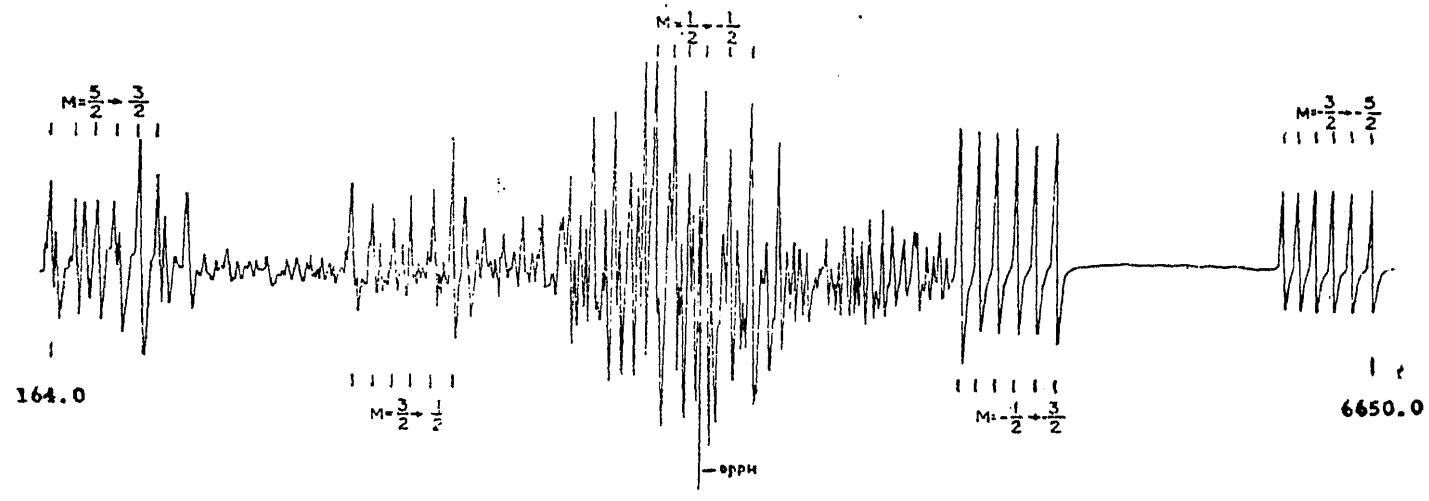

FIG. 2. EPR spectrum of Mn^{2+} in $(NH_4)_2SO_4$ single crystal at room temperature, the direction of magnetic field making an angle of 18° with the crystallographic *b*-axis in the *bc*-plane.

unidentified complexes, if any. Figure 2 shows the spectrum taken at room temperature with $H \parallel z$ where *z* is the site symmetry axis of the complex. This spectrum has been analysed using the spin-Hamiltonian

$$H = g\beta H \cdot S + D' [S_z^2 - \tfrac{1}{3} S(S+1)] + E' (S_x^2 - S_y^2) + S \cdot A' \cdot I$$

which includes in turn terms describing the electronic Zeeman splitting, axial crystalline field, rhombic field and the nuclear Zeeman splitting. The constants D′, E′ and A′ in the above equation are all expressed in cm.$^{-1}$ and are related to D, E and A expressed in gauss in the rest of the paper through a multiplication factor of $g\beta$ (*viz.*, $D' = g\beta D$). The expressions used to obtain energy differences are:

(*a*) for fine structure (expressed in gauss) with $H \| z$

$$H_1\left(M = \frac{5}{2} \rightarrow \frac{3}{2}\right) = H_0 - 4D + \frac{9E^2}{(H_1 + D)} - \frac{5E^2}{(H_1 + 3D)}$$

$$H_2\left(M = \frac{3}{2} \rightarrow \frac{1}{2}\right) = H_0 - 2D - \frac{9E^2}{(H_2 + D)} + \frac{9E^2}{(H_2 - D)} - \frac{5E^2}{(H_2 + 3D)}$$

$$H_3\left(M = \frac{1}{2} \rightarrow -\frac{1}{2}\right) = H_0 - \frac{9E^2}{(H_3 - D)} + \frac{5E^2}{(H_3 + 3D)} + \frac{5E^2}{(H_3 - 3D)} - \frac{9E^2}{(H_3 + D)}$$

$$H_4\left(M = -\frac{1}{2} \rightarrow -\frac{3}{2}\right) = H_0 + 2D + \frac{9E^2}{(H_4 + D)} - \frac{9E^2}{(H_4 - D)} - \frac{5E^2}{(H_4 - 3D)}$$

$$H_5\left(M = -\frac{3}{2} \rightarrow -\frac{5}{2}\right) = H_0 + 4D + \frac{9E^2}{(H_5 - D)} - \frac{5E^2}{(H_5 - 3D)}$$

(*b*) for hyperfine structure (expressed in gauss) with $H \| z$

$$H(m \leftrightarrow m) = -Am - \frac{A^2}{2H}[I(I+1) - m^2 + (2M - 1)m].$$

The fine structure parameters have been obtained by solving equations for H_2, H_4 and H_5. Iteration procedure was followed to get the best possible fit with the experimental values for all the fine structure transitions. The hyperfine structure parameter A is calculated from the above equation. The spin Hamiltonian parameters obtained are $g = 1{\cdot}992$, $D = 760$ gauss, $E = 120$ gauss and $A = 93$ gauss. The value for A given above corresponds to the one obtained from H_2, H_3, H_4 and H_5. It is found that the value of A obtained from H_1 is inconsistent with the value of A obtained from H_2, H_3, H_4 and H_5. The reason for this might be that the contribution of higher order terms (A^2D/H^2, E^2A/H^2, E^4A/H^4, etc.) for H_1 is more than that for other H values because of the very low value of H_1. However it may be noted that if one uses H_0 in the above equation instead of H, one obtains again $A = 94 \pm 1$ which is consistent for all the sextets H_1, H_2, H_3, H_4 and H_5.

Comparison of the experimental and calculated field values for the fine structure positions H_1 to H_5 is shown in Table I.

TABLE I

A comparison of the experimental and the calculated resonant field values (fine structure)

Experimental (gauss)	Calculated (gauss)
436·4	404·4
1862·0	1888·7
3333·1	3358·1
4865·5	4843·3
6413·3	64·055

As the temperature is lowered the spectrum persists up to $-55°$ C. and at $-56°$ C. phase transition takes place.* Figure 3 shows the spectrum recorded at $-57°$ C. The spectrum in the low field side is complicated both in the paraelectric and the ferroelectric phases of the crystal because of the presence of angular parts of other complexes in that field region. By comparing Figs. 2 and 3 one can see four high field sextets in Fig. 3 instead of two high field sextets in Fig. 2 ($M = -1/2 \rightarrow -3/2$ and

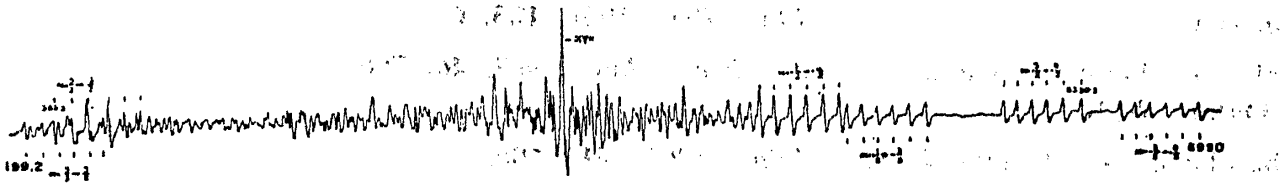

FIG. 3. EPR spectrum of Mn^{2+} in $(NH_4)_2SO_4$ single crystal at $-57°$ C., the direction magnetic field marking an angle of 18° with the crystallographic *b*-axis in the *bc*-plane.

$M = -3/2 \rightarrow -5/2$). It is known that there is a loss of mirror symmetry in the ferroelectric phase which obviously means that the crystalline field around a particular ammonium ion in the upper reflection plane $(100)_{\frac{1}{2}}$ is not the same as the field around the corresponding ammonium ion in the lower reflection plane $(100)_{-\frac{1}{2}}$. Thus the two magnetically equivalent Mn^{2+} complexes in the paraelectric phase that exist in different reflection planes become inequivalent in the ferroelectric phase and therefore the

* This differs from the transition temperature of $-50°$ C. obtained by earlier workers and the difference might be due to the presence of Mn^{2+} impurity.

spectrum splits into two. Very recently O'Reilly and Tsang (1967) have studied the deuteron magnetic resonance in ferroelectric ammonium sulphate. They have observed twice the resonance lines in the ferroelectric phase than what they have observed in the paraelectric phase. They have two resonance lines at $-40°$ C. which have been assigned as due to two inequivalent ammonium ions in the unit cell. Below the curie point each line is observed to split into two. The reason attributed to this was also the disappearance of the mirror plane in the ferroclectric phase. This supports the information we have obtained here from the EPR studies.

The superposition of the resonance lines due to several complexes added complexity to the spectrum and a detailed analysis of the spectrum in the ferroelectric phase has become difficult. It may be noted that the intensities of the two spectra that one gets in the ferroelectric phase (Fig. 3) are different indicating that the number of spins responsible for these spectra is different. However, the reason for this is not yet clear.

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