HIGH-ORDER EPR TRANSITIONS OF Cr^{3+} IN $CH_3NH_3Al(SO_4)_2 \cdot 12H_2O$ SINGLE CRYSTALS

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The EPR spectrum of Cr^{3+} in $CH_3NH_3Al(SO_4)_2 \cdot 12H_2O$ shows a number of weak lines on the low magnetic field side of the allowed ($\Delta M = \pm 1$) fine structure lines. These weak lines are found to arise from the high-order EPR ($\Delta M > \pm 1$) transitions of Cr^{3+} centres.

1. Introduction

Methylammonium aluminium sulphate dodecahydrate $CH_3NH_3Al(SO_4)_2 \cdot 12H_2O$ which is usually referred to as MASD, due to its interesting ferroelectric properties, has been the subject of a number of studies by different workers [1]. The electron paramagnetic resonance (EPR) studies of Cr^{3+} in this compound have been made by Baker [2] and O'Reilly and Tsang [3]. These studies give information about the environment of the Cr^{3+} in MASD and the influence of the latter on the EPR spectrum of the ion. The temperature variation study gives information about the phase transition. The Cr^{3+} in MASD exhibits a number of weak lines on the low magnetic field side of its allowed fine structure EPR lines. These weak lines of the spectrum have not been studied so far. This paper presents the investigations carried out on these weak lines.

2. Crystal structure

MASD crystallizes in β-type alum structure [4–6]. The alums belong to cubic system with space group $Th^6(Pa3)$ and exist in three form α, β and ν [7] due to different atomic arrangements. The unit cell of MASD has lattice constant $a = 12.502$ Å and contains

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four formula units. The nearest neighbours of Al^{3+} are six water molecules forming a nearly regular octahedron. The $(CH_3NH_3)^+$ is also surrounded by six water molecules forming an octahedron which is strongly distorted. The cubic axes of the octahedron surrounding Al^{3+} are directed along the cubic axes of the crystal. MASD undergoes a ferroelectric phase transition at 177K. The crystal structure in ferroelectric phase is monoclinic ($P2_1$).

3. Experimental

Single crystals of MASD were grown by slow evaporation of a solution of sulphuric acid, methyl ammonium chloride and aluminium sulphate in proportions corresponding to the formula $CH_3NH_3Al(SO_4)_2 \cdot 12H_2O$. Cr^{3+} was introduced into the host by adding a small amount (1 % by weight) of chromic sulphate. Large single crystals with well developed faces were readily grown; usually the (111) and (210) faces are predominant. A Varian V-4502 X-band EPR spectrometer with a 9-inch magnet and 100 kHz field modulation was used to record the spectra. As a reference for the magnetic field strength, the resonance line of DPPH with $g = 2.0036$ was used. The crystals were mounted on quartz rods. Angular variation studies were made using a Varian E-229 goniometer. Experiments were carried out at 310 K.

4. Results and discussion

For an arbitrary orientation of the crystal, the EPR spectrum consists of a number of intense lines between ~0.15 T and 0.54 T. These arise from the allowed fine structure transition ($\Delta M = \pm 1$) of the Cr^{3+} centres. In addition to these lines there are some weak

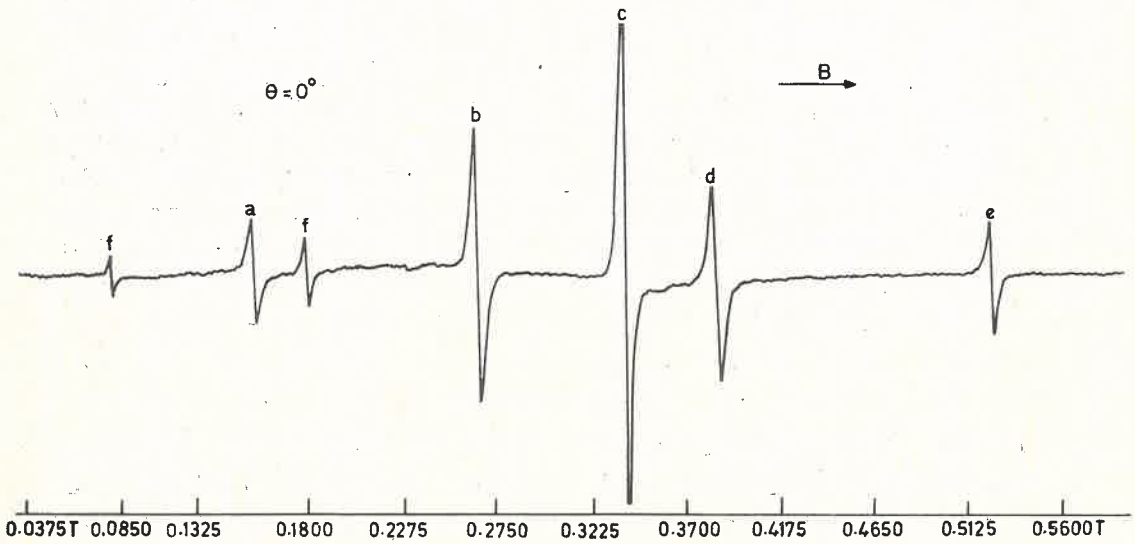

Fig. 1. The principal z-axis spectrum of Cr^{3+} in $CH_3NH_3Al(SO_4)_2 \cdot 12H_2O$ at 310 K. *a* and *e* are single lines, *b* and *d* are triple and *c* consists of four lines. *a*, *e*, and one of the *c* belong to the z-axis in question. *f*'s represent high-order (forbidden) transitions of other Cr^{3+} centres with different principal z-axes

lines below ~0.27 T. Angular variation studies reveal the presence of four identical but differently oriented Cr^{3+} complexes (Cr^{3+} substituting for Al^{3+}) with their principal z-axes along the $\langle 111 \rangle$ directions. The principal z-axes make an angle ~70° with each other. This angle can be compared to an angle of 70.5° between $\langle 111 \rangle$ directions in a cubic crystal. Fig. 1 shows the EPR spectrum of Cr^{3+} when the magnetic field is along the principal z-axis of one of the four Cr^{3+} complexes. In the figure, lines marked *a*, *e* and *d* are triple, and *c* consists of four lines. *a*, *e* and one of the *c* belong to the principal z-axis in question. *f*'s represent the weak lines of other Cr^{3+} complexes with different principal z-axes. The intensity of allowed lines ($\Delta M = \pm 1$), *a*, *e* and one of the *c* is maximum along the principal z-axis whereas the intensity of weak lines is zero for the Cr^{3+} complex in question. As the magnetic field deviates from the z-axis, weak lines for this Cr^{3+} complex appear and their intensity increases. The intensity is very small along the direction perpendicular to the z-axis also.

In a plane perpendicular to the z-axis of a particular complex, there is no angular variation of the positions of the corresponding fine structure lines indicating that the spectrum exhibits axial symmetry about the [111] axis. Since the four complexes of Cr^{3+} are identical, magnetic field measurements were made only for one of them. Hyperfine structure of ^{53}Cr was not observed in the present study.

The EPR measurements on MASD were analysed using a spin-Hamiltonian appropriate for Cr^{3+} in an axial crystalline field

$$\mathcal{H} = \beta \vec{B} \vec{g} \vec{S} + D[S_z^2 - \tfrac{1}{3} S(S+1)], \tag{1}$$

where the terms have their usual meaning. The g factor is isotropic within the experimental error and for Cr^{3+}, $S = 3/2$.

To identify the low-field weak lines, we have investigated high-order EPR transitions ($\Delta M > \pm 1$) for the Cr^{3+} centres. For this purpose, we have used the third order perturbation to evaluate the positions of all the fine structure transitions.

The field positions $B_{M \to M-R}$ at which a line due to the EPR transition ($M \to M-R$) occurs is obtained by using the eigen-values of the spin-Hamiltomian to the third order of perturbation [8]. For the present case where no hyperfine structure is observed and the symmetry is axial, the line position $B_{M \to M-R}$ is given by

$$B_{M \to M-R} = \frac{B_0}{R} - \frac{D}{2}(3\cos^2\theta - 1)(2M - R) - \tfrac{1}{8}\frac{D^2}{B_0}\sin^4\theta U$$

$$- \tfrac{1}{2}\frac{D^2}{B_0}\sin^2\theta\cos^2\theta V - \tfrac{1}{8}\frac{D^3}{B_0}\sin^2\theta\cos^2\theta(3\cos^2\theta - 1)W$$

$$- \tfrac{1}{32}\frac{D^3}{B_0^2}\sin^4\theta(3\cos^2\theta - 1)X, \tag{2}$$

where

$$U = -6M^2 + 6MR - 2R^2 - 1 + 2S(S+1),$$

$$V = 24M^2 - 24MR + 8R^2 + 1 - 4S(S+1),$$

$$W = (2M-R)\,[-80M^2-40R^2+80MR-14+24S(S+1)],$$
$$X = (2M-R)\,[20M^2-20MR+10R^2+14-12S(S+1)]$$

and $M = 3/2, \pm 1/2$; $R = 1, 2, 3$. Using Eq. (2) for $R = 1, 2$ and the observed spectra the following values for the constants of the spin-Hamiltonian (1) are obtained at 310 K:

$$D = -0.0935\text{T} \pm 0.001\text{T}, g = 1.980 \pm 0.004.$$

These values are consistent with those reported earlier [2, 3]. The sign of D is taken to be negative in accordance with the earlier results [2, 3].

Angular variation of the spectrum of one of the four Cr^{3+} complexes in the zx plane obtained by substituting the values of D and g in Eq. (2) is shown in Fig. 2. In the figure, angle θ is the angle between the external magnetic field and the z-axis of the Cr^{3+} centre. The satisfactory agreement of the calculated angular variation with the experimental

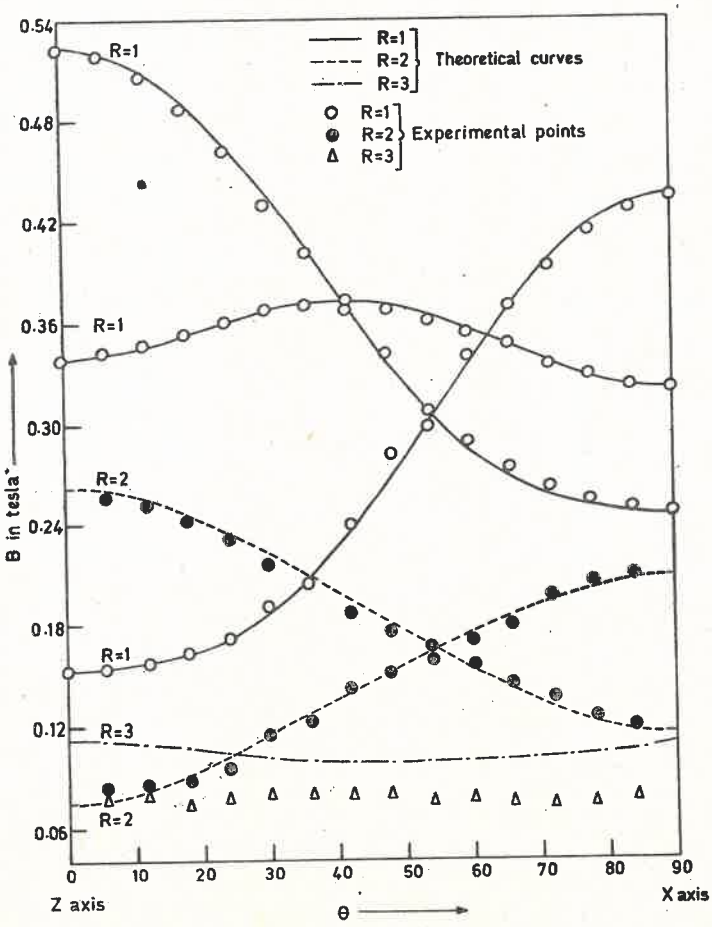

Fig. 2. Angular variation of the EPR spectrum in the zx plane of one of the Cr^{3+} complexes in $CH_3NH_3Al(SO_4)_2 \cdot 12H_2O$ single crystals at 310 K

one (except for $\Delta M = \pm 3$ transition where the agreement is poor) confirms that the assumed axial symmetry is valid and the weak lines on the low magnetic field side of the allowed transition ($\Delta M = \pm 1$) are due to $\Delta M = \pm 2, \pm 3$ transitions.

The appearance of $\Delta M \neq \pm 1$ transitions in the EPR spectra of Cr^{3+} is connected with the crystalline field symmetry. The presence of the off-diagonal terms in the spin-Hamiltonian gives rise to admixtures into the pure state when the magnetic field is not along the z-axis (i.e. $\theta \neq 0$) and in this case, all the transitions become allowed. Farcas et al. [9] have given the theoretical expressions for the transition probability of $\Delta M = \pm 1, \pm 2, \pm 3$ of Cr^{3+} in trigonal field. However, we could not obtain the angular variation dependence of the intensity of high-order transitions because of very poor intensity. Further at some orientations, the allowed lines masked the high-order transitions.

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