ESR of Cr^{3+} in Aluminium Chloride Hexahydrate

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The angular dependence of the ESR spectrum of Cr^{3+} ions in $AlCl_3 \cdot 6H_2O$ has been studied. In addition to the allowed fine structure lines some weak low field lines, identified as fine forbidden transitions, have been observed.

The electron spin resonance (ESR) of Cr^{3+} has been studied by various workers in a number of host lattices [1–6]. This note describes the ESR of Cr^{3+} in aluminium chloride hexahydrate $AlCl_3 \cdot 6H_2O$. Weak intensity lines have been observed at low fields in the alums [3, 4]. The aim of the present study is to understand the nature and cause of appearance of these lines. Previous studies by Emch and Lacroix [5] and by Wong [6] did not report these lines.

The crystal structure of $AlCl_3 \cdot 6H_2O$ is rhombohedral with space group D_{3d}^6-$R\bar{3}c$ [7, 8]. The unit cell contains two formula units. Each aluminium atom is surrounded by an octahedron of water molecules. A [111]-direction in each octahedron coincides with the crystal c axis and the two types of $Al \cdot 6H_2O$ complexes per unit cell are distinguished from each other by a rotation of approximately 28° about the c axis.

Crystals of $AlCl_3 \cdot 6H_2O$ doped with Cr^{3+} were grown by slow evaporation of the saturated aqueous solution at room temperature. The Cr^{3+} impurity was introduced into the host lattice by adding a small amount (0.05% by weight) of $CrCl_3 \cdot 6H_2O$. ESR experiments were performed on a Varian V-4502 spectrometer operating at X-band provided with 100 kHz field modulation.

For an arbitrary orientation of the magnetic field, the ESR spectrum consists of three intense lines besides some weak lines at low fields (Figure 1). Angular variation studies of Cr^{3+} spectra reveal the presence of only one type of spectrum, indicating that all the Cr^{3+} complexes are equivalent. The Cr^{3+} substitute Al^{3+} in the lattice and form $Cr(H_2O)_6{}^{3+}$ complexes. The chromium complex exhibits axial symmetry with the principal z axis along the crystal c axis.

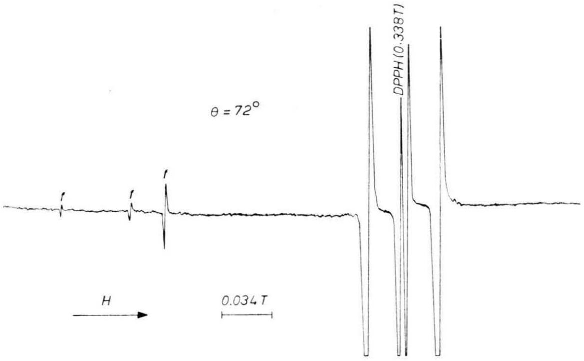

Fig. 1. ESR spectrum of Cr^{3+} in $AlCl_3 \cdot 6H_2O$ single crystals at 308 K. Fine structure forbidden lines are marked f.

The ESR spectrum of the Cr^{3+} complex in $AlCl_3 \cdot 6H_2O$ can be described by a spin Hamiltonian of the form

$$\mathscr{H} = \beta g H \cdot S + D[S_z^2 - \tfrac{1}{3} S(S+1)]$$

where the z axis is parallel to the c axis. The symbols have their usual meaning and $S = \frac{3}{2}$ for Cr^{3+}.

The field position $H_{M \to M-R}$ at which a line due to the ESR transition ($M \to M - R$) occurs was obtained by using the eigenvalue (to third order of perturbation theory) given by Bir [9]. For Cr^{3+}, the line position is given by the expression

$$\begin{aligned} H_{M \to M-R} = {} & \frac{H_0}{R} - \frac{D}{2}(3\cos^2\theta - 1)(2M - R) \\ & - \frac{2D^2}{H_0} \sin^2\theta \cos^2\theta \\ & [6M(M-R) + 2R^2 - S(S+1) + \tfrac{1}{4}] \\ & - \frac{D^2}{8H_0} \sin^4\theta \\ & [2S(S+1) - 6M(M-R) - 2R^2 - 1] \\ & - \frac{TD^3}{H_0{}^2} \sin^2\theta \cos^2\theta \\ & (3\cos^2\theta - 1) - \frac{U}{16H_0{}^2} D^3 \sin^4\theta (3\cos^2\theta - 1) \\ & - \frac{V}{4H_0{}^2} D^3 \sin^4\theta \cos^2\theta , \end{aligned} \tag{1}$$

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where

$$\begin{aligned} T = {} & (2M - R)[3S(S+1) - 5(M^2 - R^2) \\ & - 5M(M+2R) - 7/4 + 6MR(M-R) \\ & + 2R^3 - RS(S+1) + R/4], \end{aligned}$$

$$\begin{aligned} U = {} & 20M^3 - 30M^2R + 20MR^2 - 5R^3 \\ & - 7R + 14M - 6S(S+1)(2M-R) \\ & + 2R(2M-R)S(S+1) \\ & - 6MR(2M-R)(M-R) \\ & - 2R^3(2M-R) - R(2M-R), \end{aligned}$$

$$\begin{aligned} V = {} & 120M^3 - 180M^2R + 120MR^2 \\ & - 30R^3 + 3(2M-R)[5 - 8S(S+1)] \end{aligned}$$

and $M = \frac{3}{2}$, $\pm\frac{1}{2}$, $R = 1, 2, 3$. Employing Eq. (1) in conjunction with the experimental spectra the following values for the constants of the spin Hamiltonian were obtained at 308 K.

$$D = -0.035 \pm 0.0002\ T,$$
$$g = 1.978 \pm 0.001.$$

The sign of D was taken negative in accordance with the results of Manoogian and Leclerc [2]. The angular dependence of the spectrum obtained on inserting these value of D and g in Eq. (1) is shown in the Figure 2. The agreement between the experimental and theoretical values (Fig. 2) confirms that the assumed axial symmetry is correct. The lines are identified as $\Delta M = 1, 2, 3$ transitions in the spectrum of Cr^{3+} in $AlCl_3 \cdot 6H_2O$. The appearance of fine structure forbidden transitions is connected with the crystalline field symmetry.

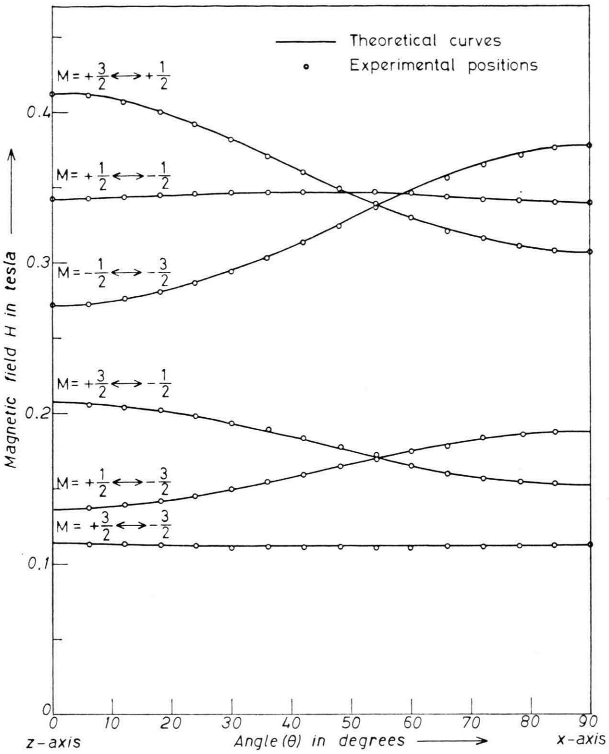

Fig. 2. Angular dependence of Cr^{3+} ESR lines in the zx plane for $AlCl_3 \cdot 6\,H_2O$ at 308 K.

The presence of the zero field splitting term in the spin Hamiltonian gives rise to a mixing of the pure state when H is not parallel to the z axis. In this case all transitions are allowed. Hyperfine lines due to ^{53}Cr isotopes were not observed in this work.

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