EPR OF Cr^{3+} IN $Al(NO_3)_3 \cdot 9H_2O$ SINGLE CRYSTALS

By V. K. Jain

Department of Physics, M. D. University, Rohtak*

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The EPR spectrum of Cr^{3+} in single crystals of $Al(NO_3)_3 \cdot 9H_2O$ was studied in the X-band and at various temperatures between 90 K and 312 K. The Cr^{3+} in the lattice substitutes for Al^{3+} sites. The spectrum is satisfactorily described by a spin-Hamiltonian appropriate for Cr^{3+} in an orthorhombic (or lower) crystalline field.

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1. Introduction

The electron paramagnetic resonance (EPR) of Cr^{3+} has been studied in a variety of lattices [1–10]. These studies give information about the environment of the paramagnetic ions in the host lattices and the influence of the latter on the EPR sectra of the ions. On the other hand, such studies give aspect of the behaviour of lattices at different temperatures. EPR investigations of Cr^{3+} in hydrated crystals, however, have been restricted to a very small variety of lattices [3, 4, 8] and detailed studies have been carried out only for the alums. This paper reports EPR studies of Cr^{3+} in aluminium nitrate nonhydrate, $Al(NO_3)_3 \cdot 9H_2O$, single crystals at 312 K and at 90 K. The aim of this study is to understand the nature of the strength and symmetry of the crystalline field.

Crystals of $Al(NO_3)_3 \cdot 9H_2O : Fe^{3+}$ were used as working substances for a maser operating in a zero magnetic field [11, 12]. The Mössbauer spectra of $Al(NO_3)_3 \cdot 9H_2O : Fe^{3+}$ has been reported by Yakimov and Zarubin [13] and by Afanasev et al. [14]. The vibrational spectra of poly- and mono-crystalline aluminium nitrate nonahydrate was studied by Kondilenko et al. [15]. Rustgi [16] investigated the electron nuclear double resonance of X-irriadated deuterated compounds. The EPR of transition metal ions, except for Fe^{3+}, has not been investigated previously. Manekov and Milyav [17] studied the paramagnetic relaxation of $Al(NO_3)_3 \cdot 9H_2O : Fe^{3+}$ single crystals. To the best of our knowledge the detailed crystal structure is not available in the literature. Only preliminary information is available [18]. The crystal structure of $Al(NO_3)_3 \cdot 9H_2O$ is monoclinic and

* Address: Department of Physics, M. D. University, Rohtak 124001, India.

the space group is $P2_1/a$. The unit cell having the dimensions $a = 13.190$ Å, $b = 9.630$ Å, $c = 10.903$ Å, and $\beta = 84°48'$ contains four formula units [18]. The Al^{3+} are surrounded by a distorted octahedron of water molecules [15]. The symmetry of the Al^{3+} site is C_i.

2. Experimental

Single crystals of $Al(NO_3)_3 \cdot 9H_2O$ doped with Cr^{3+} were grown at room temperature by slow evaporation from a dilute nitric acid solution. The Cr^{3+} impurities were introduced into the lattice by adding a small amount of chromic nitrate (0.2% by weight). The crystal grew in the form of plates.

The experiments were performed on a Varian V-4502 EPR spectrometer operating in the X-band microwave frequency region and using a 9-in. rotating magnet and a 100 kHz field modulation. As a reference for the magnetic field strength, the resonance line of DPPH with $g = 2.0036$ was used. The magnetic field at the DPPH resonance was measured with the help of a Varian F-8A fluxmeter and the frequency of the proton signal was measured by a Systronic Type 701 frequency counter. The crystals were mounted on quartz rods. The angular variation studies were done using a E-229 Varian goniometer.

3. Results and discussion

For an arbitrary orientation of the crystal, the EPR spectrum consists of a number of intense lines between ~0.147 T and ~0.54 T and which arise from the allowed fine structure transition ($\Delta M = \pm 1$) of Cr^{3+} centers. In addition to these lines there are many weak lines below ~0.27 T. The weak lines at the low magnetic field side of the spectrum probably arise from the high-order EPR transitions of Cr^{3+} [3, 4]. Angular variation studies at 312 K reveal the presence of four magnetically inequivalent but otherwise identical Cr^{3+} complexes (formed by the substitution of Al^{3+} by Cr^{3+}). The principal axes of the Cr^{3+} complexes are determined by locating the directions corresponding to extrema in the spread of the spectrum. Figure 1 shows the EPR spectrum of Cr^{3+} when the magnetic field is along the z axis of one of the four magnetically inequivalent chromium complexes. The z axes corresponding to the four Cr^{3+} complexes were determined. The z axis of each Cr^{3+} complex in $Al(NO_3)_3 \cdot 9H_2O$ makes an angle of $14° \pm 2°$, $74° \pm 2°$, and $74° \pm 2°$ with the z axes of other complexes. In the absence of detailed crystal structure data for $Al(NO_3)_3 \cdot 9H_2O$, it is not possible in this study to relate the z axis with the water coordination to the cation.

Figure 2 shows the angular variation of the fine structure transitions of one of the four magnetically inequivalent Cr^{3+} complexes in the zx plane ($\varphi = 0°$, θ variable). It is seen from the angular variation plot that the fine structure transition lines ($\Delta M = \pm 1$) move rapidly from the z axis ($\theta = 0°$), as θ changes. The lines decrease to a very small spread at an orientation $\theta = \sim 50°$ away from the z axis. As θ increases further, the lines cross each other and spread out to a second maximum at $\theta = 90°$ (x axis). The angular variation behaviour of the spectrum in the zy plane ($\varphi = 90°$, θ variable) is much similar to the zx plane except for the spread of the spectrum along the y axis, which is less than

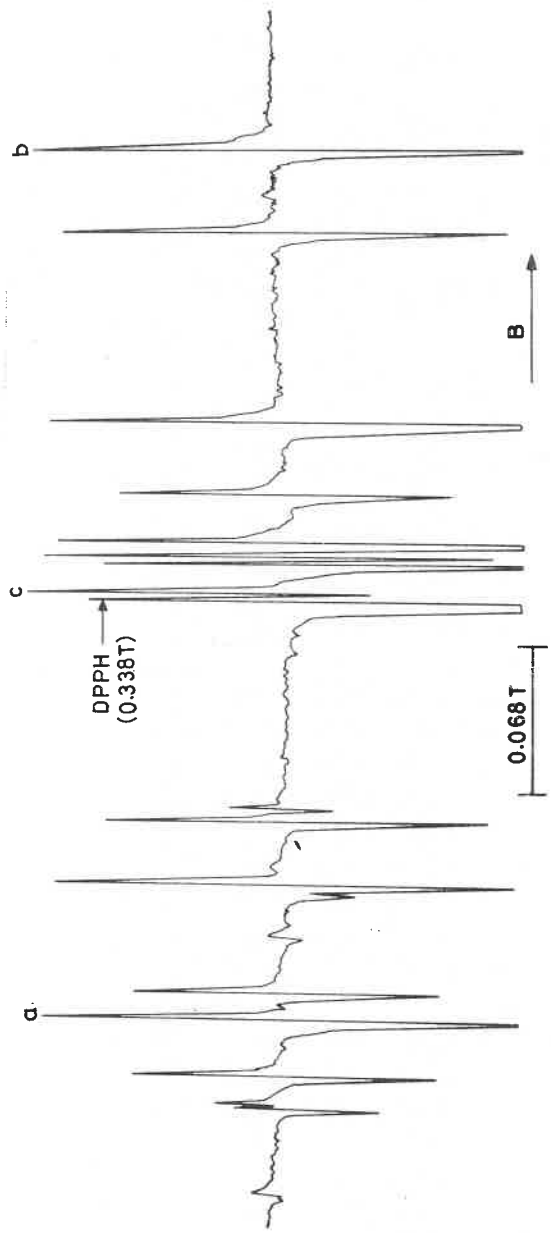

Fig. 1. The z axis EPR spectrum of Cr^{3+} in $Al(NO_3)_3 \cdot 9H_2O$ single crystals at 312 K. The lines belonging to the z axis are a, b, and c

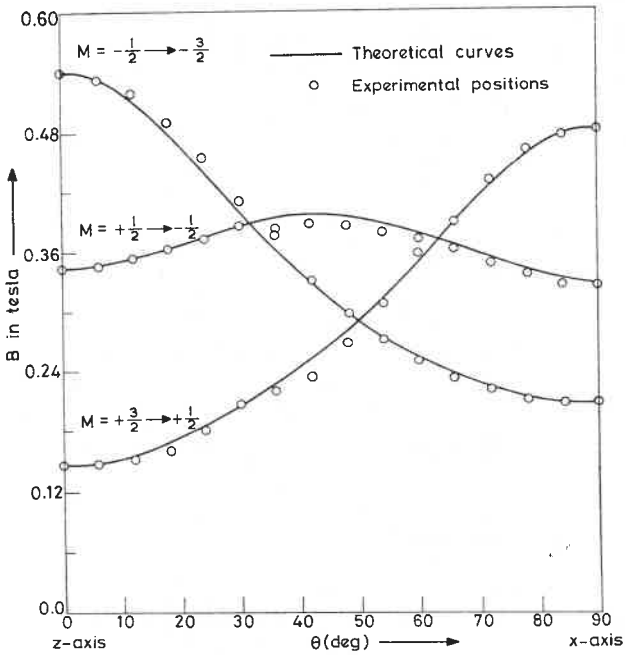

Fig. 2. The angular variation of the EPR spectrum in the *zx* plane of one of the chromium complexes in $Al(NO_3)_3 \cdot 9H_2O$ single crystals at 312 K

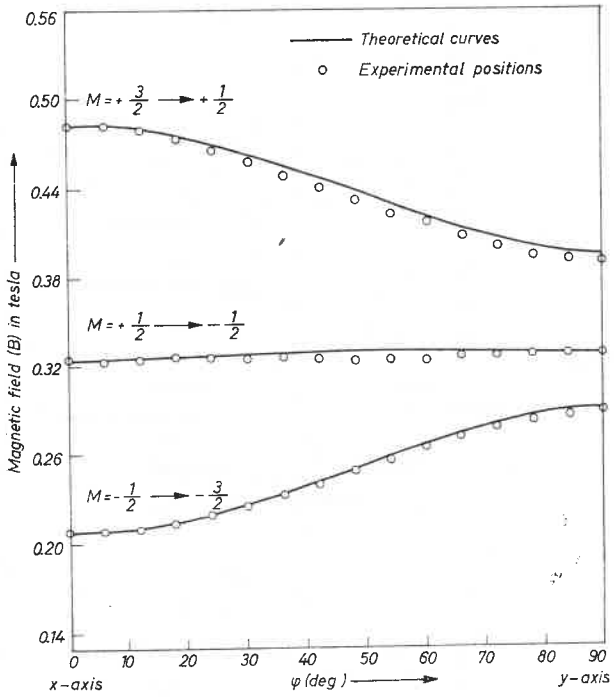

Fig. 3. The angular variation of the EPR spectrum in the *xy* plane of one of the chromium complexes in $Al(NO_3)_3 \cdot 9H_2O$ single crystals at 312 K

along the x axis. Figure 3 shows the angular variation of the allowed fine structure lines ($\Delta M = \pm 1$ transitions) of Cr^{3+} in the xy plane ($\theta = 90°$, φ variable). The behaviour of the angular variation in this plane is entirely different from that in the zx plane and the zy plane. The lines in the xy plane neither change to a low spread nor cross over in any orientation. The variation in the line position is much smaller in this plane.

The EPR spectrum shows orthorhombic symmetry. Since EPR in general does not distinguish between orthorhombic and lower symmetries [19] and as the site symmetry of Al^{3+} positions is C, the crystal field symmetry at the Cr^{3+} site may be either orthorhombic or more probably lower. The linewidth in the EPR spectra of $Al(NO_3)_3 \cdot 9H_2O : Cr^{3+}$ is ~ 1.2 mT at 312 K and it remains the same as the temperature is lowered to 90 K. The 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 hyperfine structure due to ^{53}Cr could not be observed in this study.

The experiment was repeated at various temperatures down to 90 K. The spectra, however, showed no noticeable change down to 90 K, indicating an absence of structural phase transition in this temperature range.

The EPR measurements on $Al(NO_3)_3 \cdot 9H_2O$ were analysed using a spin-Hamiltonian appropriate for Cr^{3+} in an orthorhombic (or lower) crystalline field

$$\mathcal{H} = \mu_B(S_x g_x B_x + S_y g_y B_y + S_z g_z B_z) + D[S_z^2 - (1/3)S(S+1)] + E(S_x^2 - S_y^2),$$

where the first term represents the Zeeman splitting due to the external magnetic field, where μ_B is the Bohr magneton and g_x, g_y, and g_z are the components of the g-factor along the principal axes of the crystalline field. The D and E term represent the stark (zero-field) splitting in fields of the axial and lower symmetries, respectively. For Cr^{3+}, $S = 3/2$.

Magnetic field measurements were made for the allowed lines along the principal axes. The spin-Hamiltonian parameters $g_i (i = x, y, z)$, D, and E were obtained by using the resonance field position up to second-order perturbation for the spin-Hamiltonian. The Hamiltonian parameters at 312 K are: $g_x = 1.964 \pm 0.003$, $g_y = 1.986 \pm 0.003$, $g_z = 1.976 \pm 0.002$, $D = 907 \pm 6.0 \times 10^{-4}\ cm^{-1}$, $E = -134 \pm 10 \times 10^{-4}\ cm^{-1}$. The sign of D was taken to be positive and the sign of E results from the choice of the x and y axes. The value of the spin-Hamiltonian parameters remain the same within the limits of experimental errors down to 90 K.

The g-factor shows a marked anisotropy in value and it deviates from the free spin value. Since the ground state of Cr^{3+} is orbitally non-degenerate, the observed shifts can be assumed to be completely orbital in origin. The sign of D is assumed to be positive. It is a well known fact that values of the resonance field alone cannot give the sign of D. Thus, they do not indicate which zerofield ground state level is highest. By going to low temperatures where the population in the four ground state levels are unequal, a variation in the intensity of the EPR signals with variation in temperature allows the sign of D to be determined. However, it is suggested that the sign of D and E can also be deduced from the g values in the spin-Hamiltonian [20, 21]. Using the expressions relating the g values with parameters D and E developed by Kurtz and Nilsen [21], however, it is found that within the accuracy of the spin-Hamiltonian parameters the sign of D may take a positive

as well as a negative value. From the values of D and E the zero-field splitting, represented by $\Delta_0 = 2(D^2+3E^2)^{1/2}$ [10], is 0.1872 cm^{-1}. The E/D ratio is $\sim 1/7$ which is of the same order as observed for $Al(NO_3)_3 \cdot 9H_2O : Fe^{3+}$ [17].

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