Electron Paramagnetic Resonance and DTA Investigation of Cr^{3+} in Tris(guanidinium) Hexafluoroaluminate Single Crystals

T. Lakshmi Kasturi and V. G. Krishnan

Physics Department, Osmania University, Hyderabad 500 007, India

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Electron Paramagnetic Resonance (EPR) studies of Cr^{3+} in single crystals of tris(guanidinium) hexafluoroaluminate, $[C(NH_2)_3]_3AlF_6$, have been carried out in the X-band region. A temperature dependent study of the zero-field splitting parameter D in the range 77– 398 K shows the presence of a phase transition, which is supported by Differential Thermal Analysis. In addition, ^{19}F superhyperfine structure has been observed in the 9.3% naturally abundant ^{53}Cr isotope hyperfine structure. D shows a large decrease with increasing temperature. The phase transition brings about a chemical inequivalence in the two chemically equivalent but magnetically inequivalent room temperature $(CrF_6)^{3-}$ species. Comparison is made with the alums $AlCl_3 \cdot 6H_2O$, as well as other guanidinium aluminum salts.

1. Introduction

In the last four decades the majority of electron paramagnetic resonance (EPR) studies on Cr^{3+} at high point symmetry have been mostly made on hydrated crystals viz., a) $M^I M^{III} (XO_4) \cdot 12H_2O$ with M^I = NH_4, K, Rb, Cs, T1, M^{III} = Al, Ga, In, Cr, X = S, Se, b) $AlCl_3 \cdot 6H_2O$, c) $[C(NH_2)_3]Al(XO_4)_2 \cdot 6H_2O$ with X = S, Se. Alums are cubic with space group Pa3. They are further classified into the α, β, and γ type due to small differences in the atomic arrangements. Each trivalent ion is surrounded by an octahedron of water molecules. In the α type alums, the [111] axis of the octahedron coincides with the [111] axes of the crystal. However, the cubic axes of the octahedron are displaced from the cubic axes of the crystal by a rotation of approximately 9.5° about the [111] direction. In the β type, the [111] axis of the octahedron and the crystal as well as the cubic axes of the octahedron and the crystal coincide. RbAl and RbGa alums are of α type, CsAl and CsGa are of β type, and NaAl alum is of γ type. The α structure was said to be represented by medium sized monovalent ions, the β by large ions and the γ by the small ions [1–5]. The variation with temperature of the zero-field splitting parameter D gave an additional measure of the behavior of the various types of alums. In contrast, $AlCl_3 \cdot 6H_2O$, crystallizing in the rhombohedral system with R 3c space group [6], was relatively simple as all the six molecules in the unit cell were equivalent, giving only one set of triplet fine structure lines and a small temperature dependence of the D parameter.

However, the ferroelectric guanidinium aluminum and guanidinium gallium sulphates, which crystallize in the hexagonal system with P 31 m space group, are more complicated [7]. The three molecules in the unit cell could be devided into two groups with C_1 and C_3 site symmetries, respectively, with the C_1 site twice in number compared to the C_3 site. Our EPR study also reflected this feature with the spectra for Cr^{3+} ion replacing the site with C_1 symmetry twice as intense than the spectra for the site with C_3 symmetry. In all the above described lattices one common feature was the relatively large zero-field splitting, indicating a large trigonal distortion in the form of either a compression or an elongation. An EPR study of Cr^{3+} doped in $LiSrAlF_6$, where the impurity replaced Al^{3+} ions, showed three different sites, one having axial symmetry and the remaining two possessing rhombic symmetry [8]. The D parameter was large (0.15 cm^{-1}). No Cr^{3+} hyperfine or ^{19}F superhyperfine structure was reported. The existence of the low symmetry sites was attributed to defects that were created during the growth of the crystal from the melt.

Due to the lack of investigations on crystals with high symmetry MF_6 sites, we have taken up this study on tris(guanidinium)MF_6 (GAF) crystals (M = Al, Ga, In) by introducing impurities like Cu^{2+}, Cr^{2+}, Mn^{2+}, VO^{2+} and Eu^{2+}. It has been observed that the phase transitions in crystals containing the guanidinium cation is generally initiated by the arresting of the cationic rotational motion [9–13]. The Cu^{2+} doped $[C(NH_2)_3]AlF_6$ (GAF) crystals show dynamic Jahn-Teller effect features from

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Reprint requests to Dr. V. G. Krishnan;
E-mail: sathyan@hd1.vsnl.net.in

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400 K down to 77 K, requiring static features to appear below 50 K [14]. Recently we reported an EPR investigation of the VO^{2+} ion in GAF [15], where three $V{=}O$ orientations in the AlF_6 octahedron are observed, but with different occupancy factors. Here we report the results of a study on Cr^{3+} impurity in GAF single crystals in the temperature range of 77–398 K and the observation of a phase transition below 140 K.

A room temperature X-ray structure investigation, and ^{1}H and ^{19}F NMR studies between 100 and 513 K have been reported on GAF [16]. The changes in the proton and fluorine NMR second moments in this temperature range did not indicate the presence of any phase transition. Also the Differential Thermal Analysis (DTA) scan between room temperature and 620 K failed to show any phase transition.

Experiment and Crystal Structure

Single crystals were grown from aqueous solution containing an excess of $[C(NH_2)_3]F$ and AlF_3 with 1% of Cr^{3+} impurity by slow evaporation. EPR spectra were recorred on a Varian E-12 spectrometer operating in the X-band region (9.07–9.51 GHz) with 100 kHz magnetic field modulation. Variable temperature measurements were made with Varian accessories. A DTA scan was carried out between 77 and 330 K.

Tris(guanidinium)AlF_2 crystallizes in the cubic system with space group P $2_1 3$, with $a = 13.953$ Å, $Z = 8$, $V = 2716.46$ Å^3 [17]. Six fluorines form a regular octahedron around Al^{3+}. AlF_6 anions are arranged as Na and Cl in the NaCl lattice. Unlike in other guanidinium salts, the guanidinium cation does not show any symmetry and the $(AlF_6)^{3-}$ exhibits only the 3-fold (C_6) symmetry. As a consequence, all guanidinium cations are distributed on 24 fold general positions, and the Al atoms occupy two inequivalent positions having different molecular environments. Since the C in the $[C(NH_2)_3]$ cation is not on the 3 fold axis there is a significant lowering from its ideal symmetry, 6m2(D_{3h}).

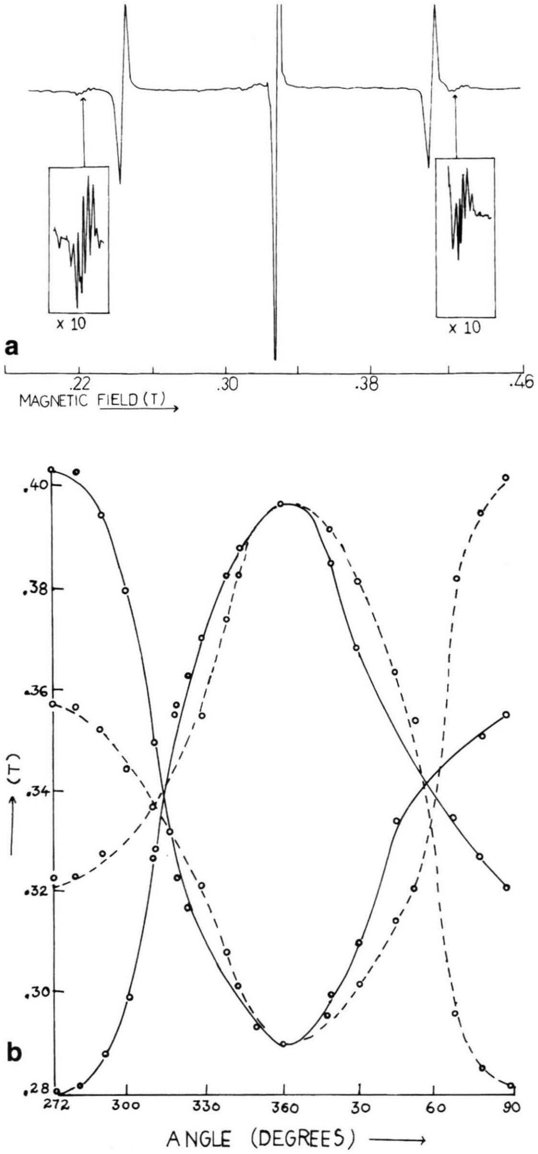

Fig. 1. a) EPR spectrum for **B** along c-axis. b) Angular variation study with the magnetic field in the plane containing the c-axis.

Results and Discussion

EPR spectra at room temperature, with B along the crystallographic c-axis, showed only one triplet, as expected for the d^3 ion. The linewidth of the fine structure lines is ca. 4.5 mT. The separation between the $-(3/2) \leftrightarrow -(1/2)$ and the $+(1/2) \leftrightarrow +(1/2)$ fine-structure lines is considerably less than that reported for alums. Figure 1(a) shows the spectrum along the c-axis. Also shown is the ^{19}F superhyperfine structure (SHFS) recorded at high receiver gain on the hyperfine lines due to the 9.6% naturally abundant Cr^{3+} ($I = 3/2$) isotope flanking the intense central fine-structure transition. The angular variation study, carried out with magnetic field in the plane containing the crystallographic c-axis, is shown in Figure 1(b). The maxima for the two magnetically inequivalent Cr^{3+} sites in the unit cell occur at an angle of 88° on either side of the c-axis. This implies that the [111] axes of the two AlF_6 octahedra are i) not coincident with the crystal [111] axis and ii) rotated by nearly 88° with respect to the crystal [111] axis. In the case of α Alums, this was reported to be only 9.5°. The intensity of the low field fine structure transition was found to be greater than that of the high field transition at 298 K as well as at 77 K. Hence we assign a negative sign to D.

The spectra could be fitted to an axial spin Hamiltonian

$$\mathcal{H}=\beta B\, \tilde{g}\, S + \mathrm{D}\, [\hat{S}_z^2 - 1/3\, S\, (S+1)] + \mathrm{S}.\tilde{\mathrm{A}}.\mathrm{I}.$$

For the ^{53}Cr isotope, $I = 3/2$ and both $\tilde{g}$ and $\tilde{A}$ are isotropic in our case. The expression for the angular dependence of the resonance field for the $\Delta M = \pm 1$ transitions (ignoring initially the hyperfine structure) is

$$g\, \beta B = -h\, \nu + (M - 1/2)\, [D\, (3 \cos^2\theta - 1)],$$

corresponding to trigonal symmetry at the metal ion site.

Table 1 lists the spin Hamiltonian parameters for Cr^{3+} in GAF along with those of alums and other guanidinium salts. While the g values reported for $[Cr(H_2O)_6]^{3+}$ in various alums as well as in $AlCl_3 \cdot 6\,H_2O$ are in good agreement with that in GAF, the D values are considerably smaller in the present lattice, indicating only a small trigonal distortion of the AlF_6 octahedron. In guanidinium aluminum sulphate hexahydrate and guanidinium aluminum selenate hexahydrate, the guanidinium cation is located on the crystallographic 3-fold axis [7], whereas in GAF the C–N skeleton of the $[C(NH_2)_3]$ cation is almost parallel to the [001] plane. The ^{19}F SHFS on the hyperfine lines of naturally abundant ^{53}Cr isotope ($I = 3/2$) is observed perhaps for the first time. However, the anisotropy of the hyperfine as well as the superhyperfine transitions could not be followed due to their close proximity to the intense fine structure transitions. It was reported for $AlCl_3 \cdot 6\,H_2O$ [6] that due to the small hyperfine splitting, two of the four lines appear on the wings of the fine structure transitions. The observation of the seven component SHFS is in agreement with the six equivalent fluorines ($I = 1/2$) along the [111] direction. The measured value of $\tilde{A}$ (^{19}F) is 25.1×10^{-4} cm^{-1}.

For the investigation of the temperature dependence, the crystal was oriented along the c-axis in the variable temperature accessory. Above room temperature, the zero field splitting parameter was found to decrease with increasing temperature. Above 373 K there is also a rapid decrease in intensity. As the temperature is lowered, D is found to increase steadily down to 147 K. Figures 2(a) and 2(b) show the variation of D as well as the line positions of the $\pm (3/2) \leftrightarrow \pm (1/2)$ fine structure transitions in the temperature range 77–398 K.

Due to the limitations of the Varian temperature control unit it was not possible to record spectra with any accuracy for $T < 147$ K. The spectrum recorded at 77 K along the c-axis shows a decrease in the separation of the $\pm 1/2 \leftrightarrow \pm 3/2$ fine structure lines (Figure 2b). The plot of D vs. T also shows this change at 77 K (Figure 2a). This suggests a phase transition below 147 K. Hence a DTA scan was carried out between 77 and 330 K. A heat anomaly was detected at (89 ± 1) K, confirming the presence of a phase transition.

Table 1. Spin Hamiltonian D parameter of Cr^{3+} in some high symmetry lattices at given temperatures.

Lattice	D (in units of 10^{-4} cm^{-1})				Ref.
	4.2 K	77 K	195 K	297 K	
I. Cubic systems					
$[C(NH_2)_3]_3AlF_6$	–	392	362	268	This work
$NH_4Al(SO_4)_2 \cdot 12\,H_2O$	–	–	232	485	[3]
$CsAl(SO_4)_2 \cdot 12\,H_2O$	715	723	744	762	[3]
$CsCr(SO_4)_2 \cdot 12\,H_2O$	652	649	679	710	[3]
$RbAl(SO_4)_2 \cdot 12\,H_2O$	349	348	474	681	[3]
$RbCr(SO_4)_2 \cdot 12\,H_2O$	567	565	663	838	[3]
II. Hexagonal systems					
$AlCl_3 \cdot 6\,H_2O$	341	338	337	326	[6]
$(Urea)_6Al(ClO_4)_3$	–	155	110	105	[8]
$(Urea)_6Ga(ClO_4)_3$	–	135	90	75	[8]
$[C(NH_2)_3]Al(SO_1)_2 \cdot 6\,H_2O$	889	839	712	577	[8]
$[C(NH_2)_3]Gal(SO_4)_2 \cdot 6\,H_2O$	695	651	547	450	[8]

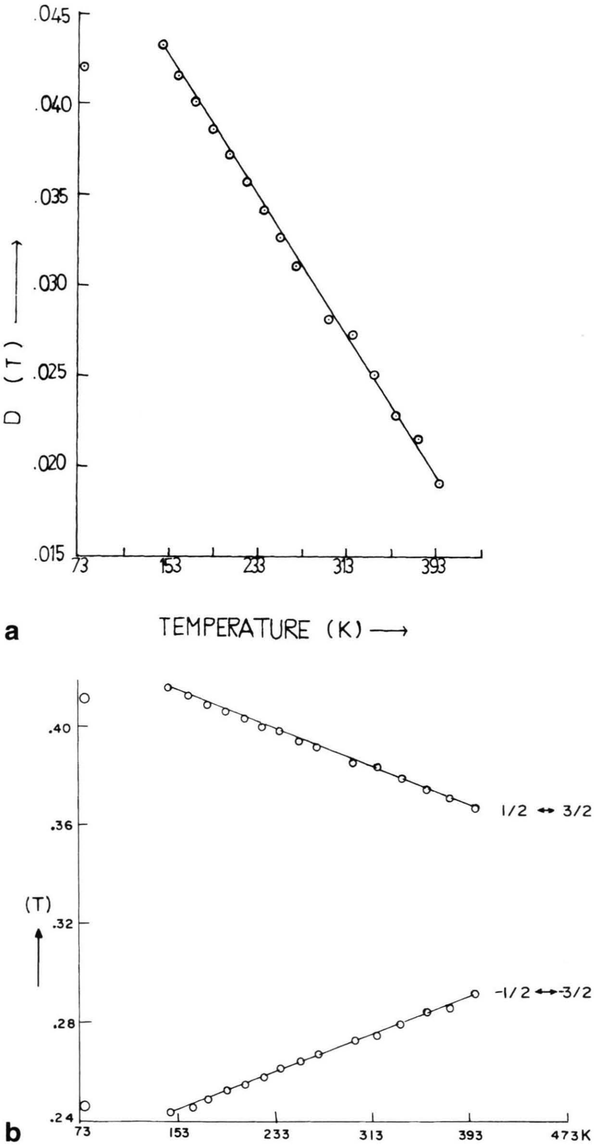

Fig. 2. Temperature variation of a) the zero-field splitting parameter (D). b) The line positions of the + (3/2) ↔ + (1/2) and − (3/2) ↔ − (1/2) fine structure transitions in the range 77–398 K.

In the crystal structure investigation of guanidinium aluminum sulphate hexahydrate (GASH) [7], rotational motion of the cation was inferred from the large isotropic thermal parameters of the nitrogens. The symmetry axis of the guanidinium cation as well as the $[Al(H_2O)_6]$ octahedron is along the [111] direction of the crystal forming a chain. Since neighbouring chains are well separated, the guanidinium cation is free to rotate. In tris-guanidinium hexachloroantimonate [10] a phase transition was observed at 146 K. A change in the thermal expansion coefficients indicated a distortion of the anion sublattice. Thus, on lowering the temperature, the room temperature phase with the overall motion of the guanidinium cation gave rise to the low temperature phase in which the motion about the C–N axis and the motion of the individual NH_2 groups are progressively arrested. From the NMR study reported on GAF [14], the proton and fluorine second moments show a gradual decrease at 210 K, which ruled out the possibility of a phase transition. A sharper change is seen to occur at 270 K for protons and 433 K for fluorines. In their DTA study in the temperature range 300 to 620 K no structural phase transition was seen.

In our study also the zero-field splitting parameter did not show any anomaly between 147 and 396 K. But the D value at 77 K is markedly less than that at 147 K (Figure 2a). Unlike in GASH, in GAF the cations occupy various positions and lie on the [001] plane. A close link exists with the neighbouring AlF_6 octahedra through hydrogen bonds. The isotropic thermal parameters for nitrogen are considerably smaller than those in GASH, indicating the absence of any rapid rotation. Hence the phase transition cannot be associated with cationic motion. Thus it can be concluded that the phase transition is due to changes occurring in the AlF_6 octahedra. If there is a rotation of the two AlF_6 octahedra with respect to the crystallographic c-axis, it should have been reflected in the loss of the c-axis and an introduction of a rhombic parameter E. From the spectrum recorded along c-axis at 77 K it is seen that the phase transition has not destroyed the three fold axis of symmetry. If this symmetry were lost, each of the transitions would have split. This is not seen when the magnetic field is rotated away from the c-axis by 10°. If the phase transition introduces small but opposite changes in the extent of trigonal distortion in the two octahedra, this would alter their D values marginally.

That this is the case can be seen in the powder EPR spectra (Fig. 3), where each of the lines at 295 K is split into two at 77 K. These are placed symmetrically with respect to the room temperature line. An introduction of the rhombic component should have split only the secondary maxima, with a separation of 6 E, leaving the extreme low and high field line positions unchanged. Since these extreme lines also show the splitting, it can be concluded that the two AlF_6 octahedra have unequal trigonal distortions and consequently different D values and do not show any indication of having rotated. Hence

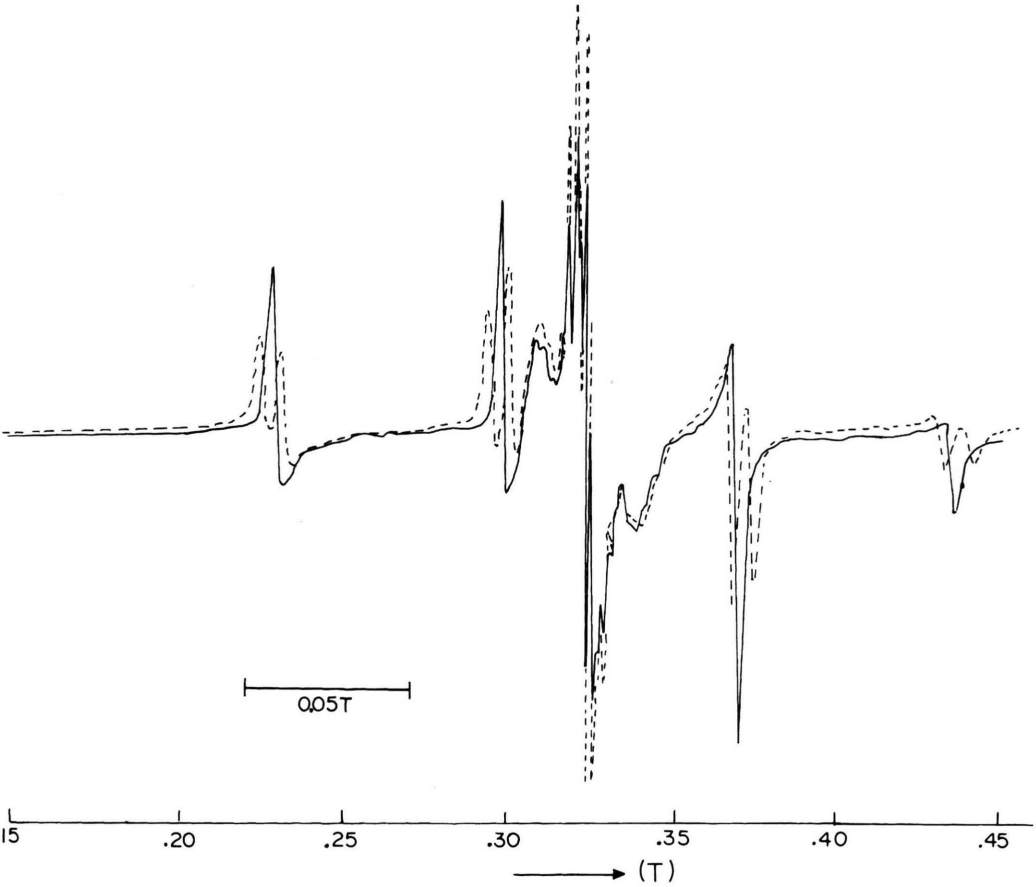

Fig. 3. Powder EPR spectra in which each of the lines at 295 K is shown to split into two at 77 K.

the phase transition has resulted in two magnetically inequivalent but chemically equivalent $(CrF_6)^{3-}$ species becoming magnetically as well as chemically inequivalent.

Conclusions

In the high symmetry (GAF) lattice, EPR spectra of Cr^{3+}, substituting for Al^{3+}, indicate an axially symmetric D tensor with two magnetically inequivalent AlF_6 octahedra which are symmetric about the crystallographic c-axis. Hyperfine structure (HF) due to the naturally abundant $^{53}Cr^{3+}$ (9.6%) was observed. These hyperfine lines show an additional splitting into seven components along the [111] direction due to superhyperfine (SHFS) interaction with six equivalent fluorines. A structural phase transition is observed below 147 K, which suggests a change in the relative strengths of the trigonal distortions in the two magnetically inequivalent AlF_6 octahedra, rendering them chemically inequivalent. The phase transition is ascribed to the freezing of the rotation of guanidinium cations, which instead of resulting in the customary reorientation of the AlF_6 octahedron introduces different components of trigonal distortion. The room temperature c-axis is seen to be retained as the symmetry axis.

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