Electron Spin Resonance of Cr^{3+} in $K_{1-x}Tl_xAl(SO_4)_2 \cdot 12\ H_2O$

V. K. Jain

Department of Physics, M. D. University, Rohtak-124001, India

Reprint requests to Dr. V. K. J.; E-mail: liggavansh@yahoo.com

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The electron spin resonance (ESR) of Cr^{3+} in $K_{1-x}Tl_xAl(SO_4)_2{\cdot}12H_2O$ has been studied at 300 K and 9.45 GHz. The ESR spectrum for x between 30 and 90% shows several chromium complexes. The variation of the zero-field splitting parameter D suggests that monovalent ions play an important role in the trigonal distortion of the water octahedron around the trivalent metal ion in alums. – *PASC:* 76.30 F.

Key words: ESR; Cr^{3+}; Zero-field Splitting.

The potassium, ammonium and thallium alums form continuous series of solid solutions. By means of x-ray diffraction Klug and Alexander [1] have shown that these solid solutions are ideal from the stand point of Vegard's law [2], particularly solid solutions of ammonium and thallium alum [1]. Jain [3] has studied the electron spin resonance (ESR) of Cr^{3+} in single crystals of mixed alums of ammonium and thallium and observed the presence of four magnetically inequivalent but otherwise identical Cr^{3+} complexes (formed by the substitution of Al^{3+} by Cr^{3+}). The zero-field splitting (ZFS) was found to vary with the composition. Garrett and Boop [4] concluded those from the ESR of powder spectra the presence of other chromium complexes beside those observed by Jain [3]. Chand et al. [5] have studied the ESR of Cr^{3+} in the mixed alums $(NH_4)_xM_{1-x}Al(SO_4)_2{\cdot}12H_2O$ (M=Na,K) and have observed only one kind of chromium complexes. It seemed of interest to investigate the ESR of Cr^{3+} diluted in $K_{1-x}Tl_xAl(SO_4)_2{\cdot}12H_2O$ (Potanium-Thallium-Alum = PTA) in order to understand the variation of the ZFS with composition. The ESR of PTA for $x = 0$ and 1 has been previously studied [6, 7]. The potassium aluminium and thallium aluminium alums which belong to the α type of alum [8, 9], form a continuous series of solid solutions [1, 10].

The alum belongs to the cubic system with space group $T_h{}^6$(Pa3). Because of different atomic arrangements they exists in three types, namely α, β, and γ [8]. The K and Tl alum belong to the α type. The lattice constant a of the K alum is 1.2158 nm, and of the Tl alum is 1.2232 nm [9]. The Al^{3+} has six water molecules as nearest neighbours, forming a nearly regular octahedron. On the other hand, the octahedron of water molecules around the monovalent ion is strongly distorted with the distortion being along the three-fold axis of the cell. The [111] axis of the octahedron surrounding the Al^{3+} coincides with the [111] axis of the crystal, but the axes of the octahedron deviate from the cubic axes of the crystal by an angle of rotation $\sim 9.5^\circ$ about the [111] direction [8].

Experimental

Single crystals of PTA ($x = 0$ to 1) were grown at ~ 300 K by slow evaporation of the saturated aqueous solutions of appropriate metal sulphates. Cr^{3+} was introduced into the host lattice by adding chromic sulphate (1% by weight). The ESR experiments were performed on a JEOL FE-3X homodyne spectrometer operating at ~ 9.45 GHz equipped with a TE_{011} cylindrical cavity and 100 kHz field modulation. A speck of powdered diphenyl picrylhydrazil (DPPH) used as a field marker (taking $g_{DPPH} = 2.0036$) was inserted simultaneously into the sample cavity. The crystals were mounted on quartz rods. The angular variation studies were made using a JES-UCR-2X sample angular rotating device. Powder spectra were recorded from powder in quartz tubes. Each powdered ESR sample was obtained by grinding an individual untwinned crystal.

For an arbitrary orientation of the crystal, the ESR spectrum consists of a number of intense lines besides some weak lines on the low magnetic field side of the spectrum in all the crystals studied. For $x = 0$

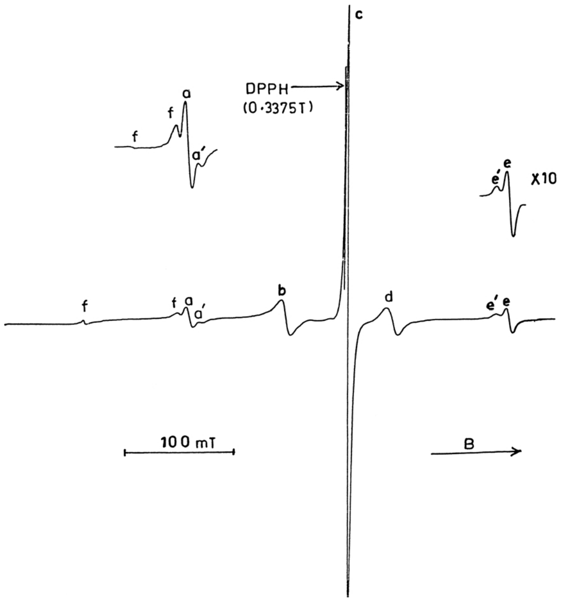

Fig. 1. The z-axis room temperature (300 K) spectrum of Cr^{3+} in $K_{0.1}Tl_{0.9}Al(SO_4)_2\cdot 12H_2O$ single crystals. The lines marked a,a' and e,e' are single, b and d triple, and c consists of four lines. The lines belonging to the z-axis of intense chromium complexes are a,e and one of c. a' and e' belong to the z-axis of the weak chromium complex. f represents high order ESR transitions of the intense chromium complexes.

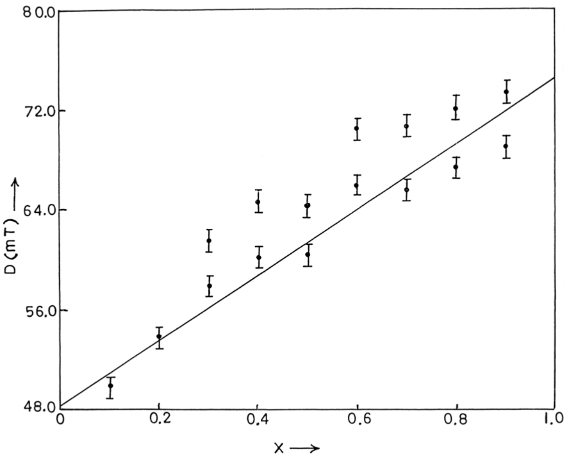

Fig. 2. The zero-field splitting parameter D for Cr^{3+} in $K_{1-x}Tl_xAl(SO_4)_2\cdot 12H_2O$ vs. x at 300 K.

and 1, angular variation studies reveal the presence of four magnetically inequivalent but chemically equivalent Cr^{3+} complexes (formed by the substitution of Al^{3+} by Cr^{3+}) with their z-axes along the $\langle 111\rangle$ direction. The ESR spectrum shows an axial symmetry about the z-axis. Samples having a Tl concentration between 30 – 90% show at least two chemically inequivalent chromium complexes. For certain compositions even three chromium complexes have been observed. Along the z-axis, the $M = \pm 3/2 \leftrightarrow \pm 1/2$ transitions are not single lines but there are broader spectra in the wings which would give a ZFS different from the intense spectrum. The spectrum taken at 300 K with the magnetic field along z-axis of the chromium complexes in PTA for $x = 0.9$ is shown in Figure 1. The weak lines at the low magnetic field side of the spectrum are identified as high order ESR transitions of Cr^{3+} [6]. Powder-spectra have been recorded for all the samples.

The ESR measurements on PTA were analysed using the spin-Hamiltonian appropriate for Cr^{3+} in an axial crystalline field [6],

$$H = \beta_e \boldsymbol{S}\cdot g\cdot \boldsymbol{B} + D[S_z^2 - (1/3)\boldsymbol{S}(\boldsymbol{S}+1)],$$

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

The parameters D and g have been evaluated using the resonance field positions [6] of the above spin-Hamiltonian. The g values in all the samples studied lie in the range 1.978 ± 0.005. The sign of D was taken to be positive in accordance with the results of Manoogian and Leclerc [7]. The values of D for different compositions of the samples are shown graphically in Figure 2. A straight line has been drawn through the points representing of D of Cr^{3+} in the pure alum [6, 7]. It is found that D of all chromium complexes in PTA lies between that of pure potassium and thallium alum. The results suggest that we are observing a series of spectra corresponding to different local crystalline environments. Since local distortions of the primary coordination shell of the paramagnetic ion control the ZFS, one would expect a different spectrum for each set of mixed neighbours and perhaps further differentiation due to second neighbour substitution. The low amplitude broad spectrum is perhaps due to overlapping of spectra arising from slightly different ZFS's. This is perhaps because many surroundings may have a significant probability. Thus the variation of the ESR spectra with composition is probably a sequential growth and diminuition of spectra corresponding to specific configurations of near neighbours. Chand et al. [5] have studied the ESR of Cr^{3+} in mixed alums of ammonium and potassium (sodium) and have observed only one species. One of the reasons for not observing multiplet spectra may be that the components of the species are not resolved because of the small difference in the ZFS's of Cr^{3+} in pure alums, and the large linewidths.

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