

## ABSORPTION SPECTRUM OF $\text{Cr}^{3+}$ ION IN $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$

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The optical absorption spectrum of  $\text{Cr}^{3+}$  ion in Potassium Aluminium Sulphate single crystal has been studied. The bands observed with maxima at about 14833, 15193, 17356, 20570, 24746 and  $37026\text{cm}^{-1}$  are assigned to the  ${}^4\text{A}_2 \rightarrow {}^2\text{E}$ ,  ${}^4\text{A}_2 \rightarrow {}^2\text{T}_1$ ,  ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ ,  ${}^4\text{A}_2 \rightarrow {}^2\text{T}_2$ ,  ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$  and  ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$  (P) transitions respectively. The values of the crystal field and Racah parameters derived are as follows :

$$Dq = 1735\text{cm}^{-1} \quad B = 695\text{cm}^{-1} \quad C = 3128\text{cm}^{-1}$$

**Keywords:** Absorption Spectrum; Potassium Aluminium Sulphate; Crystal Field and Racah Parameters

### INTRODUCTION

THE electron spin resonance of  $\text{Cr}^{3+}$  ion in alums has been studied by several authors (Bagguley & Griffiths, 1950; Bleaney, 1950; Bendt, 1970; Radhakrishna & Bhaskara Rao, 1976; Manoogian & Leclerc 1976; and Jain, 1978). The alums belong to the cubic system with space group  $T_h^6$  (Pa3). Because of different atomic arrangements they exist in three types, namely  $\alpha$ ,  $\beta$  and  $\gamma$  (Lipson, 1935). The  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  is an  $\alpha$ -type alum. The unit cell contains four formula units. The  $\text{K}^+$  and  $\text{Al}^{3+}$  have six water molecules as nearest neighbours forming a regular octahedron.

### EXPERIMENTAL

Single crystals of  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  doped with  $\text{Cr}^{3+}$  were grown at room temperature by slow evaporation of the saturated aqueous solution. The spectrum at room temperature was recorded in the wavelength range  $8500\text{\AA}$  to  $2000\text{\AA}$  on Perkin-Elmer 551 UV-VIS Spectrophotometer.

### THEORY

The electronic configuration for  $\text{Cr}^{3+}$  ion is written as (A)  $(3d)^3$ , where A stands for a closed argon shell. In an octahedrally coordinated  $\text{Cr}^{3+}$  complex, the ground state electron configuration gives rise to  ${}^4\text{A}_2$ ,  ${}^2\text{E}$ ,  ${}^2\text{T}_1$  and  ${}^2\text{T}_2$  states of which  ${}^4\text{A}_2$  lies lowest and forms the ground state of the ion. The excited configurations  $t_2^2 e^1$  and  $t_2^1 e^2$  give rise to  ${}^4\text{T}_2$ ,  ${}^4\text{T}_1$  (F) and  ${}^4\text{T}_1$  (P) states respectively in addition to several doublet states.

## RESULTS AND ANALYSIS

The spectrum recorded at room temperature is shown in Fig. 1. The wavelengths and wave numbers together with oscillator strengths and assignments are presented in Table I.

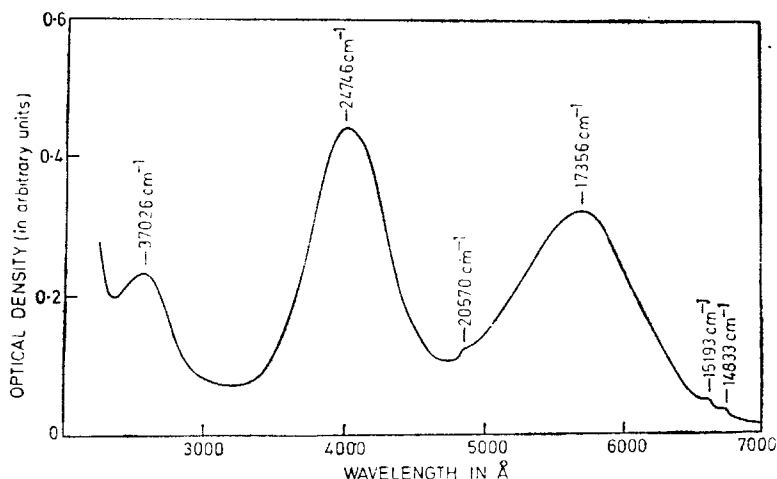


FIG. 1.

TABLE I

Wavelength ( $\lambda$ ) wave number ( $\nu$ ), oscillator strengths ( $f$ ) and assignments for the bands of  $\text{Cr}^{3+}$  in  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$

Band positions		Oscillator strengths ( $f$ )	Assignment w.r.t. the ground state ${}^4\text{A}_2$
Wavelength ( $\lambda$ ) Å	Wavenumber ( $\nu$ ) $\text{cm}^{-1}$		
6740	14833	—	${}^2\text{E}$
6580	15193	—	${}^2\text{T}_1$
5760	17356	$3.82 \times 10^{-4}$	${}^4\text{T}_2$
4860	20570	—	${}^2\text{T}_2$
4040	24746	$6.84 \times 10^{-4}$	${}^4\text{T}_1$
2700	37026	$3.46 \times 10^{-4}$	${}^4\text{T}_1(\text{P})$

At room temperature, two broad and intense bands at 17356 and 24746  $\text{cm}^{-1}$ , one moderately broad and intense band at 37026  $\text{cm}^{-1}$  and three weak and sharp bands at 14833, 15193 and 20570  $\text{cm}^{-1}$  have been recorded.

Since the sharp line like bands are characteristic of  $\text{Cr}^{3+}$  ion in octahedral symmetry, the analysis of the observed spectrum has been made assuming  $O_h$  site symmetry for  $\text{Cr}^{3+}$  ion in the crystal. In  $O_h$  symmetry, we can expect three spin-allowed transitions  ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ ,  ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$  and  ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{P})$  in the increasing order of

energy. The three bands at 17356, 24746, 37026  $\text{cm}^{-1}$  have therefore been attributed to the electronic transitions  ${}^4A_2 \rightarrow {}^4T_2$  and  ${}^4A_2 \rightarrow {}^4T_1$  and  ${}^4A_2 \rightarrow {}^4T_1(P)$  respectively. The spin-forbidden transitions  ${}^4A_2 \rightarrow {}^2E$ ,  ${}^4A_2 \rightarrow {}^2T_1$  and  ${}^4A_2 \rightarrow {}^2T_2$  are expected to give sharp line like bands since they represent intraconfigurational transitions belonging to  $t_2^3$  configuration. The energy of  ${}^2T_2$  level would be considerably higher than  ${}^2E$  or  ${}^2T_1$ . Therefore, the observed sharp peaks at 14833, 15193 and 20570  $\text{cm}^{-1}$  have been attributed to the transitions  ${}^4A_2 \rightarrow {}^2E$ ,  ${}^4A_2 \rightarrow {}^2T_1$  and  ${}^4A_2 \rightarrow {}^2T_2$  respectively.

The energy level diagrams for different values of  $C/B$  were drawn by diagonalising the energy matrices of the  $d^3$  configuration (Tanabe & Sugano, 1954) on IBM 370/155 computer. The best fit of the observed values could be obtained for  $C/B = 4.5$  at  $Dq/B = 2.5$  as shown in Fig. 2. The experimental and calculated values of the energies of different transitions are presented in Table II.

The values of  $Dq$  and  $B$  obtained by fitting the experimental values with the energy level diagram for  $C/B = 4.5$  are

$$Dq = 1735\text{cm}^{-1} \quad B = 695\text{cm}^{-1} \quad \text{and} \quad C = 3128\text{cm}^{-1}.$$

#### DISCUSSION

The spin-forbidden transitions  ${}^4A_2 \rightarrow {}^2E$ ,  ${}^4A_2 \rightarrow {}^2T_1$  and  ${}^4A_2 \rightarrow {}^2T_2$  are all sharp since all the states involved in these transitions arise from the same configuration

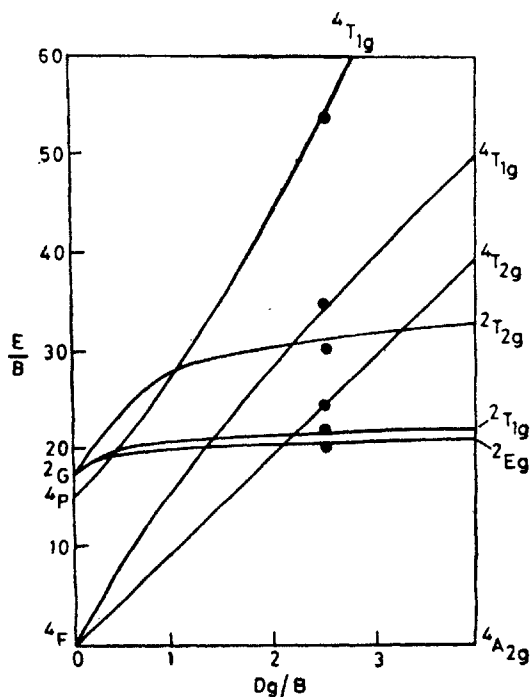


FIG. 2.

TABLE II

The observed and calculated energies of the bands of  $\text{Cr}^{3+}$  in  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$

$$Dq = 1735\text{cm}^{-1}; \quad B = 695\text{cm}^{-1}; \quad C = 4.5B.$$

Transitions from ${}^4\text{A}_2$	Band positions	
	Observed ( $\nu$ ) $\text{cm}^{-1}$	Calculated ( $\nu$ ) $\text{cm}^{-1}$
${}^3\text{E}$	14833	14595
${}^4\text{T}_1$	15193	15290
${}^4\text{T}_2$	17356	17375
${}^2\text{T}_2$	20570	20850
${}^4\text{T}_1$	24746	24673
${}^4\text{T}_1(\text{P})$	37026	37183

$t_2^3$  and hence the ground and excited state equilibrium geometries are nearly the same. It is interesting to note that the energies of the intraconfigurational spin-forbidden transitions are independent of  $Dq$  (Orgel, 1955). On the other hand, the spin allowed transitions  ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ ,  ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$  and  ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{P})$  are associated with configurational change namely  $t_2^2 e^1$  and  $t_2^1 e^2$  and hence the ground and excited potential energy curves have different equilibrium intranuclear separations (Carlin, 1969). This, therefore, leads to excitation of many vibrations and results in broad bands.

The width of a band in a crystal field spectrum is proportional to  $dE/dDq$ , where  $E$  is the energy of the transition. Thus transitions to levels having large slope in the energy level diagram should give rise to broad bands while transitions to levels having lesser slope tend to be sharper.

The spectra were also recorded for two mutually perpendicular orientations of the incident light beam. However no change in the spectra was observed indicating a predominantly octahedral site symmetry for the  $\text{Cr}^{3+}$  ions which are incorporated substitutionally into the trivalent metal sites of the  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  crystal.

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