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ELECTRONIC ABSORPTION SPECTRUM OF Cr^{3+} IONS DOPED IN LITHIUM CAESIUM SULPHATE SINGLE CRYSTAL

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The electronic absorption spectra of the Cr^{3+} ions in Lithium caesium sulphate were studied both at room and liquid nitrogen temperatures. The observed bands were explained satisfactorily assuming octahedral symmetry for the Cr^{+3} ion in the crystal. The values of the crystal field and Racah parameters have been calculated.

Key Words : Absorption Spectrum; Energy Levels; Crystal Field Parameters; Oscillator Strengths

INTRODUCTION

LITHIUM caesium sulphate ($LiCsSO_4$) belongs to a list of pseudohexagonal crystal of general formula $A'A''BX_4$. At room temperature $LiCsSO_4$ is orthorhombic (Phase I) with space group Pcmn. At low temperatures it is monoclinic (Phase III) with space group $P2_1/n$. Kruglik *et al.*[1] studied the crystal structures of phase I and III of $LiCsSO_4$, Aleksandrov *et al.*[2] studied the investigation of structural and physical properties of $LiCsSO_4$, Pietraszko *et al.*[3] studied the X-ray and optical studies of the phase transition in $LiCsSO_4$ and Pakulski *et al.*[4] studied the ferroelectric properties of $LiCsSO_4$. Though extensive studies have been done on $LiCsSO_4$, no absorption work has so far been reported about Cr^{3+} ions doped in $LiCsSO_4$ in literature, the present investigation is carried out.

EXPERIMENTAL

Cr^{3+} ions doped Lithium caesium sulphate single crystals were grown by slow evaporation method at room temperature. The electronic absorption spectra were recorded both at room and liquid nitrogen temperatures in the wavelength region 8000Å to 3500Å on Cary-2300 Spectrophotometer with a crystal of thickness about 1mm. By computing the area under the absorption curves, the oscillator strengths were determined.

THEORY

The electronic configuration for Cr^{3+} ion is Ar $(3d)^3$ where Ar stands for the closed argon shell. In the lowest field configuration $(t_{2g})^3$, the states $^4A_{2g}(F)$, $^2E_g(G)$,

$^2T_{1g}(G)$ and $^2T_{2g}$ (G) arise. In a medium strong field configuration $(t_{2g})^2$ $(t_g)^1$, the states $^4T_{1g}(F)$ and $^4T_{2g}(F)$ arise. In a strong field configuration $(t_{2g})^1$ $(e_g)^2$, the states $^4T_{1g}(P)$ arises Among all $^4A_{2g}(F)$ lies lowest and forms the ground state of the ion as per Hund's rule.

Results and Analysis

The spectra recorded at room and liquid nitrogen temperatures are shown in Fig 1 and 2 respectively. At room temperature it consists of two strong and broad bands and a weak band The two broad bands are located at 17606cm^{-1} and 23148cm^{-1} and the weak band observed at 13089cm^{-1}.

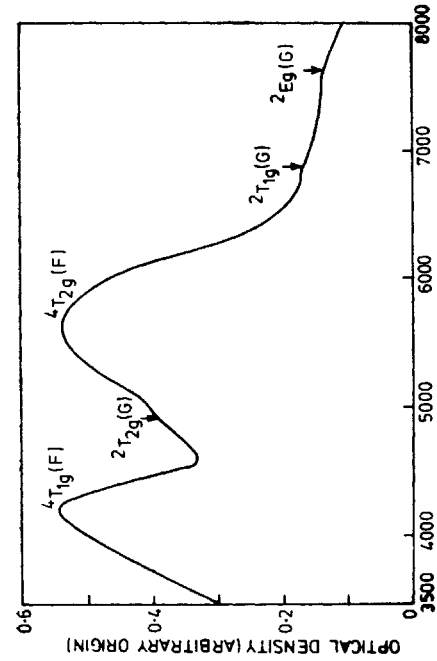
When the crystal is cooled to liquid nitrogen temperature a general sharpening of the bands have been observed. In addition to the three bands observed at room temperature two more extra bands are found at liquid nitrogen temperature at 14535cm^{-1} and 20325cm^{-1}. The wavelengths, wavenumbers and the assignments for the bands at room and liquid nitrogen temperatures are presented in Table 1.

The two broad bands are characteristic of Cr^{3+} ion in octahedral (O_h) symmetry and have been observed in almost all the crystals. Therefore the analysis of the observed spectrum is done assuming octahedral site symmetry for the Cr^{3+} ion. In O_h symmetry, we expect three spin allowed bands corresponding to $^4A_{2g}(F) \rightarrow {}^4T_{2g}$ (F), $^4A_2g(F) \rightarrow {}^4T_{1g}(F)$ and $^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$. The two broad and intense bands observed both at room an liquid nitrogen temperatures are assigned to the transitions. $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ and $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$. At 77 K these bands were centered at 17857cm^{-1} and 23697cm$^{-\alpha}$. The weak bands observed at 13089cm^{-1} at room temperature and at 14535cm^{-1} and 20325cm^{-1} at liquid nitrogen temperature are assigned to the spin forbidden transitions $^4A_{2g}(F) \rightarrow {}^2E_g(G)$, $^4A_{2g}(F) \rightarrow {}^2T_{1g}(G)$ and $^4A_{2g}(F) \rightarrow {}^2T_{2g}(G)$ respectively.

The linear energy expression for the energy states of Cr^{3+} given by Boxall *et al.*[5] has been solved for different values of Dq, B and C. It has been found that the best fit for the observed bands at 77 K could be obtained for Dq = 1785cm^{-1}, B = 680cm^{-1} and C = 2820cm^{-1}: The corresponding energy level diagram Dq versus E is shown in Fig. 3. The observed and calculated band maxima positions along with their oscillator strengths at 77 K are presented in Table II.

Discussion

Orgell[6] stated that the energies of the intra configurational spin forbidden transitions are independent of Dq. As such, the bands show no appreciable shift at low temperature. This has been observed for the transition $^4A_{2g}(F) \rightarrow {}^2E_g(G)$ in the present work. On the other hand Carlin[7] stated that the spin-allowed transition $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ and $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ are associated with configurational change namely $(t_{2g})^3 \rightarrow (t_{2g})^2$ $(e_g)^1$ and hence the ground and excited potential energy curves have different equillibrium inter-nuclear seperation and this leads to excitation of many vibrations and results in broad bands.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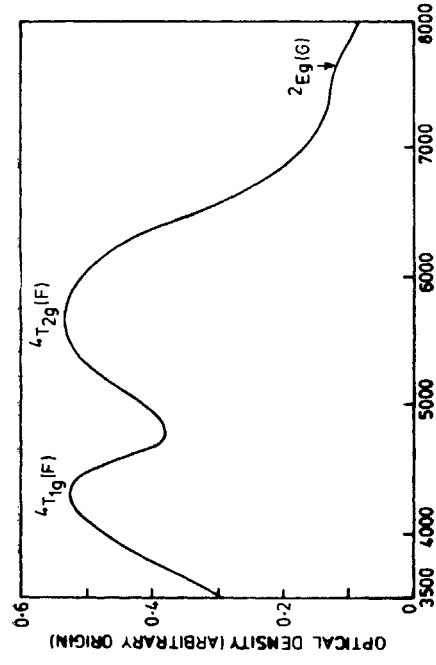
$^2Eg(G)$

FIG 2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$^4T_{2g}(F)$
$^2Eg(G)$

FIG 1

TABLE I

Wavelength (λ), *wavenumber* (ν) *and assignments for the bands of* Cr^{3+} *in* $LiCsSO_4$

Transitions from	Band Positions			
	300 K		77 K	
$^4A_{2g}(F)$	λ(Å)	ν(cm^{-1})	λ(Å)	ν(cm^{-})
$^2E_g(G)$	7640	13089	7640	13089
$^2T_{1g}(G)$	——	——	6880	14535
$^4T_{2g}(F)$	5680	17606	5600	17857
$^2T_{2g}(G)$	——	——	4920	20325
$^4T_{1g}(F)$	4320	23148	4220	23697

TABLE II

The observed and calculated energies, oscillator strengths and the assignments of the bands of Cr^{3+} *in* $LiCsSO_4$ *at 77 K*

(B = 680cm^{-1}; C = 2820cm^{-1}; and Dq = 1785cm^{-1})

Transitions from	Band Position (cm^{-1})		Oscillator strengths
	Observed	Calculated	
$^4A_{2g}(F)$			(f)
$^2E_g(G)$	13089	13388	—
$^2T_{1g}(G)$	14535	13979	—
$^4T_{2g}(F)$	17857	17850	29.79×10^{-5}
$^2T_{2g}(G)$	20325	20159	—
$^4T_{1g}(F)$	23697	23353	43.09×10^{-5}

When the crystal is cooled to liquid nitrogen temperature, both the spin allowed bands shift to higher energy. This is primarily due to the depopulation of the excited vibrational levels of the ground electronic state and secondarily to a change in Dq with lattice contraction. The Dq value observed at room temperature is 1760cm^{-1} whereas at liquid nitrogen temperature, the value is 1785cm^{-1}. The blue shifts of 251cm^{-1} (17857—17606) for $^4T_{2g}(F)$ and 549cm^{-1} (22697—23148) for $^4T_{1g}(F)$ are also in accordance with the theory as the corresponding energy levels are having positive slopes in the Tanabe-Sugano[8] energy level diagram ford[3] configuration.

The spin-orbit splitting can be evaluated from the empirical relation given by Cole and Garrett[9] connecting the Racah interelectronic repulsion parameter B in kK and spin orbit coupling constant λ in kK.

$$\lambda = 0.011\,(B + 1.08)^3 + 0.0062$$

The value of λ, thus evaluated from the above expression is 65cm^{-1}. It is interesting to find that this value is in the range expected for Cr^{3+} ion given by Figgis.[10]

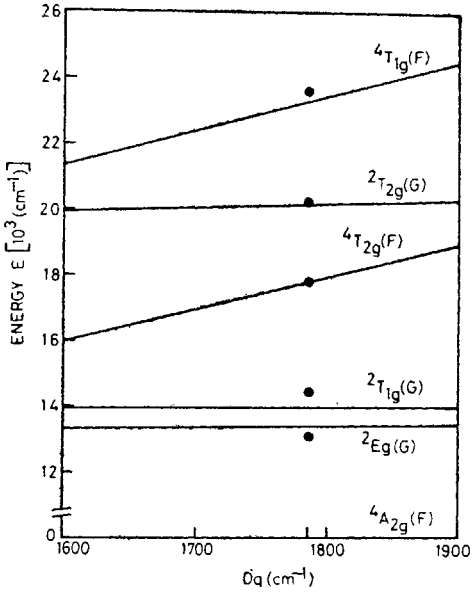

FIG 3

The observed bands did not show any splitting at 77 K, indicating a predominantly octahedral site symmetry for the Cr^{3+} ion in Lithium caesium sulphate. Though the crystal structure indicates a slightly distorted octahedral symmetry, the bands did not exhibit any splitting even at liquid nitrogen temperature. They may in all probability exhibit splitting at a still lower temperature such as that of liquid hydrogen or liquid helium.

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