

# OPTICAL ABSORPTION SPECTRUM OF Cr<sup>3+</sup> ION IN STRONTIUM FORMATE CRYSTAL

S. V. J. LAKSHMAN\* and P. RAMAA DEVI

(Received 24 June 1978; after revision 22 November 1978)

The optical absorption spectrum of Cr<sup>3+</sup> ion in strontium formate dihydrate crystal has been studied. The observed ligand field bands have been explained assuming an octahedral site symmetry for the Cr<sup>3+</sup> ion in the crystal. The values of the crystal field and Racah parameters derived are as follows :

$$Dq = 1720 \text{ cm}^{-1} \quad B = 625 \text{ cm}^{-1} \quad c = 5.0 B$$

An explanation for the charge compensation is presented.

## INTRODUCTION

STRONTIUM formate dihydrate unlike other formates is orthorhombic (Galigne, 1971). It belongs to the space group  $P_{2_1,2_1,2_1}$  and has four molecules per unit cell. The dimensions reported are

$$a = 7.332 \text{ \AA}, \quad b = 12.040 \text{ \AA} \quad \text{and} \quad c = 7.144 \text{ \AA}$$

Strontium is surrounded by eight oxygen atoms.

The e. s. r. of Mn<sup>2+</sup> ion doped in strontium formate dihydrate was reported by Narayan *et al.* (1976). They concluded that Mn<sup>2+</sup> ion takes up substitutional site in place of strontium in the crystal Lattice. With a view to investigate how different transition metal ions enter into the crystal lattice of strontium formate dihydrate, the authors took up the present work.

## EXPERIMENTAL

Large single crystals of chromium doped strontium formate dihydrate were grown from an aqueous solution of freshly prepared strontium formate to which was added one mole percent of chromium trichloride hexahydrate (A.R.). The solution was acidified by the addition of two to three drops of formic acid and was maintained at a temperature of 40 °C throughout the growth process. The well-formed green rhombic crystals were taken out of the solution and dried.

Qualitative emission spectrochemical analysis was made following the usual procedure (Ahrens & Taylor, 1961).

A crystal of 0.2 cm thickness was found suitable in the present investigation. The optical absorption spectrum of Cr<sup>3+</sup> ion in strontium formate dihydrate crystal (Fig. 1) was recorded at room temperature from  $\lambda$  9000 Å to  $\lambda$  3000 Å on a Hitachi double beam recording spectrophotometer at Bhabha Atomic Research Centre. A pure undoped crystal of the same thickness as the experimental crystal was used to standardise the reference beam.

---

\*For authors' address, see p. 348.

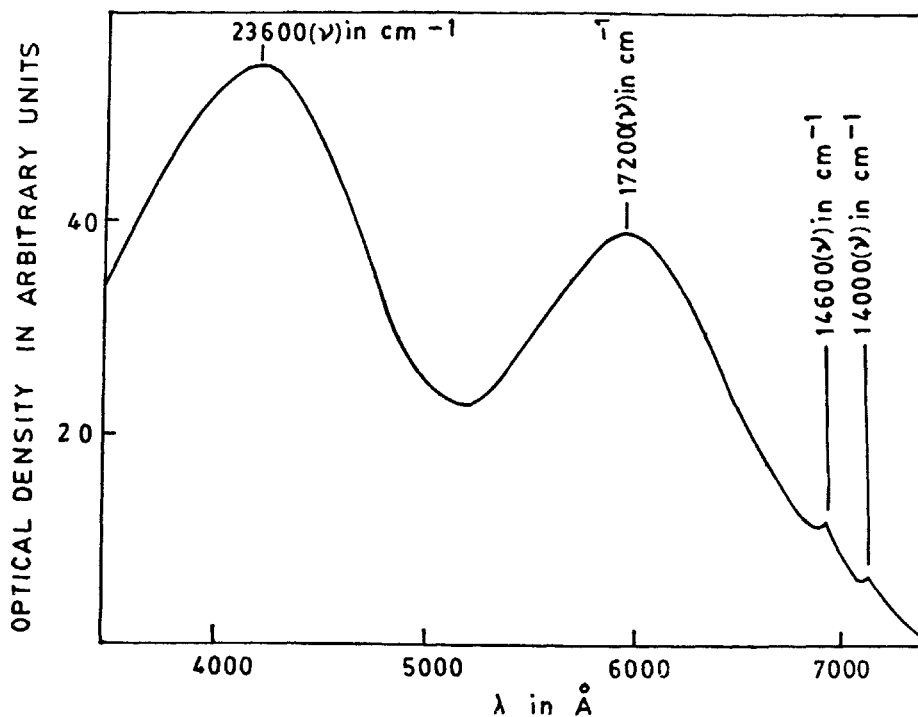


FIG. 1. Optical absorption spectrum of  $\text{Cr}^{3+}$  ion in strontium formate dihydrate crystal at 300 °K.

### RESULTS AND ANALYSIS

Two intense and broad bands were recorded at  $23600\text{ cm}^{-1}$  and  $17200\text{ cm}^{-1}$ . In addition, two sharp line like bands were recorded at  $14600\text{ cm}^{-1}$  and  $14000\text{ cm}^{-1}$ . Since the sharp line like bands are characteristic of the  $\text{Cr}^{3+}$  ion in octahedral symmetry, the analysis of the observed bands was made assuming  $o_h$  site symmetry for the  $\text{Cr}^{3+}$  ion in the crystal. The observed band positions, their wavelengths and wave numbers together with oscillator strengths and assignments are presented in Table I.

TABLE I

Wave length ( $\lambda$ ), wave number ( $\nu$ ), oscillator strengths ( $f$ ) and assignments for the bands of  $\text{Cr}^{3+}$  in strontium formate dihydrate

Band positions		Oscillator strengths ( $\times 10^6$ ) $f$	Assignment w.r.t. the ground state ${}^4A_2$
Wavelength ( $\lambda$ ) Å	Wavenumber ( $\nu$ ) $\text{cm}^{-1}$		
4235	23600	1.38	${}^4T_1$
5815	17200	1.43	${}^4T_2$
6855	14600	—	${}^2T_1$
7140	14000	—	${}^2E$

The ground state electronic configuration of  $\text{Cr}^{3+}$  ion in  $o_h$  symmetry can be written as  ${}^4A_2$ . Thus we expect three spin allowed transitions in the increasing order of energy as  ${}^4T_2 \leftarrow {}^4A_2$ ,  ${}^4T_1 \leftarrow {}^4A_2$  and  ${}^4T_1 \leftarrow {}^4A_2$ .

The two observed intense bands at  $17200\text{ cm}^{-1}$  and  $23600\text{ cm}^{-1}$  have been attributed to the electronic transitions,  ${}^4T_2 \leftarrow {}^4A_2$  and  ${}^4T_1 \leftarrow {}^4A_2$  respectively. In contrast to the broad spin allowed transitions, the spin forbidden transitions of  $\text{Cr}^{3+}$  ion in  $o_h$  symmetry, i.e.,  ${}^2E \leftarrow {}^4A_2$ ,  ${}^2T_1 \leftarrow {}^4A_2$  and  ${}^2T_2 \leftarrow {}^4A_2$  are expected to give rise to sharp line like bands since they represent intra-configurational transitions belonging to  $t_2^3$  configuration. The energy of the  ${}^2T_2$  level would be considerably higher than that of either  ${}^2T_1$ , or  ${}^2E$ . Since the bands observed at  $14600\text{ cm}^{-1}$  and  $14000\text{ cm}^{-1}$  are quite sharp and close to one another, they are attributed to the transitions  ${}^2T_1 \leftarrow {}^4A_2$  and  ${}^2E \leftarrow {}^4A_2$  respectively.

The energy diagrams for  $d^3$  configuration for different values of  $C/B$  were drawn by diagonalising the energy matrices of the  $d^3$  configuration (Tanabe *et al.*, 1954), on an IBM 370/155 computer. The best fit of the observed values could be obtained for  $C/B = 5.0$  at  $Dq/B = 2.75$ . The experimental and calculated values of the energies of the different transitions are presented in Table II. The values of  $B$  and  $Dq$  obtained by fitting the experimental values with the energy diagram for  $C/B = 5.0$  (Fig. 2.), are

$$Dq = 1720\text{ cm}^{-1} \quad B = 625\text{ cm}^{-1} \quad \text{and} \quad C = 3125\text{ cm}^{-1}.$$

#### DISCUSSION

The width of a band in a crystal field spectrum is proportional to  $dE/dDq$ , where  $E$  is the energy of the transition (Orgel, 1955). 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. In general, intraconfigurational spin-forbidden transitions are quite sharp since the ground and excited state equilibrium geometries are nearly the same in this case. Their energies are independent of  $Dq$ . On the other hand, spin-allowed transitions  ${}^4T_1 \leftarrow {}^4A_2$  and  ${}^4T_2 \leftarrow {}^4A_2$  are associated with configurational charge  $t_2^3 \rightarrow t_2^2 e$  and hence are expected to give rise to broad and intense bands.

TABLE II

*Experimental and calculated energies of transitions of  $\text{Cr}^{3+}$  in strontium formate dihydrate crystal*

$Dq = 1720\text{ cm}^{-1}$ ;  $B = 625\text{ cm}^{-1}$ ;  $C = 5B$

Transitions from ${}^4A_2$	Band positions	
	Observed ( $\nu$ ) $\text{cm}^{-1}$	Calculated ( $\nu$ ) $\text{cm}^{-1}$
${}^4T_1$	23600	23600
${}^4T_2$	17200	17200
${}^2T_1$	14600	14600
${}^2E$	14000	14000

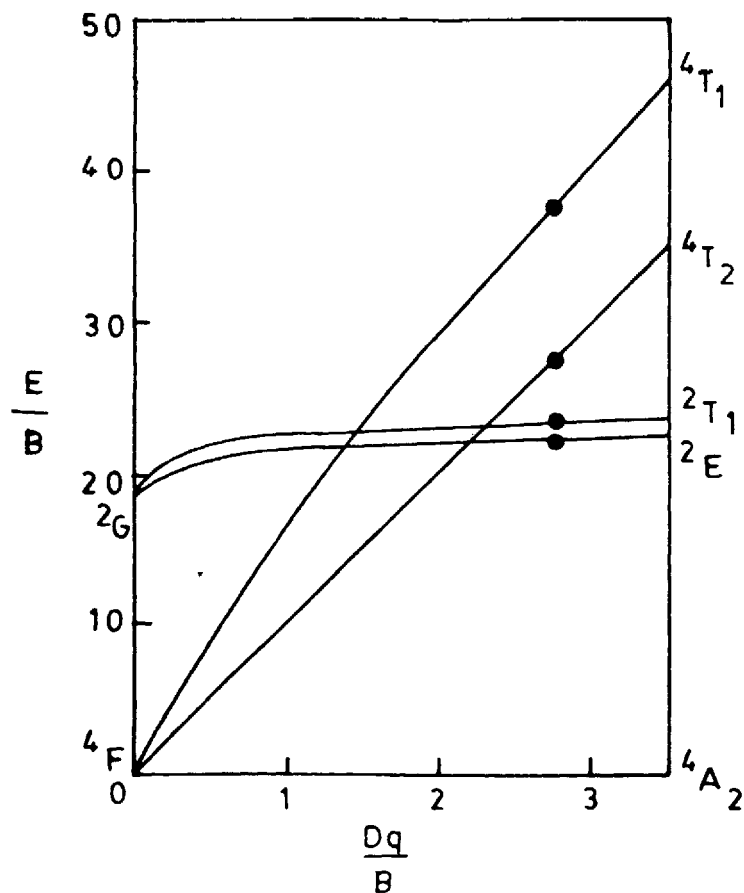


FIG. 2. Energy level diagram of  $\text{Cr}^{3+}$  ion in strontium formate dihydrate crystal in  $o_h$  symmetry, with  $C = 5B$ . The solid circles represent the energies at 300 °K.

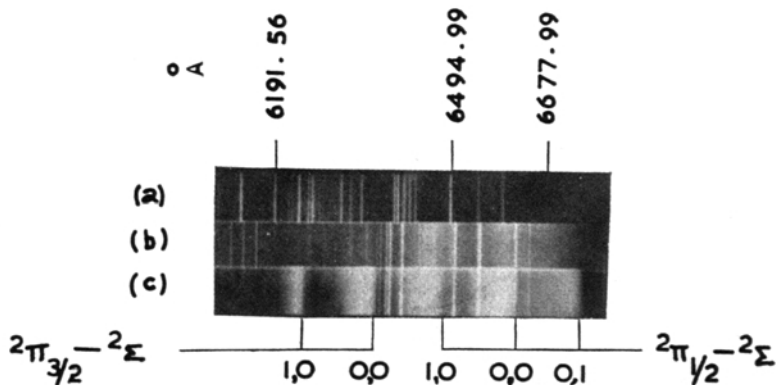


FIG. 3. Quartz-Littrow spectrogram of the emission spectrum of the crystal sample excited in spec pure carbon electrodes in the region  $\lambda$  6800 Å —  $\lambda$  6200 Å. Vibrational assignments of the bands of  $A^2 \pi - X^2 \Sigma$  system of  $\text{SrCl}$  molecule are shown. (a) Iron spectrum; (b) Crystal Spectrum; and (c) Spectrum of Strontium chloride (for comparison).

In the crystal lattice, strontium is surrounded by eight oxygen atoms. If strontium were to be replaced (substitutional) by chromium, an altogether different spectrum should have been obtained. In this case, the order of the observed bands should be  $4A_2 \leftarrow 4T_1$ ,  $2T_1 \leftarrow 4T_1$ ,  $2T_2 \leftarrow 4T_1$  and  $4T_1 \leftarrow 4T_1$ , from low to high frequency end of the spectrum. If on the other hand chromium ion takes an interstitial position between the strontium atoms, we should obtain  $2E \leftarrow 4A_2$ ,  $2T_1 \leftarrow 4A_2$ ,  $4T_2 \leftarrow 4A_2$ ,  $2T_2 \leftarrow 4A_2$  and  $4T_1 \leftarrow 4A_2$  transitions from low to high energy end of the spectrum, as has been observed in the present case. Thus we could conclude that the chromium ion takes up an interstitial position in the crystal. It may be pointed out here that it is not understandable as to how  $Mn^{2+}$  ion could take the substitutional site while  $Cr^{3+}$  ion takes an interstitial site.

In growing the crystal chromium trichloride hexahydrate has been used. An emission spectrochemical analysis of the crystal sample has therefore been made to detect the presence of chlorine if any, in it. As is shown in Fig. 3, its presence is, revealed from the observed  $A^2 \pi - X^2 \Sigma$  system of bands of the SrCl molecule (Pearse & Gaydon, 1965).

From X-ray studies, Galigne (1971) reported that the strontium ion in the strontium formate dihydrate crystal is surrounded by eight oxygens, three of which belong to water molecules and five to formate groups as shown in Fig. 4.

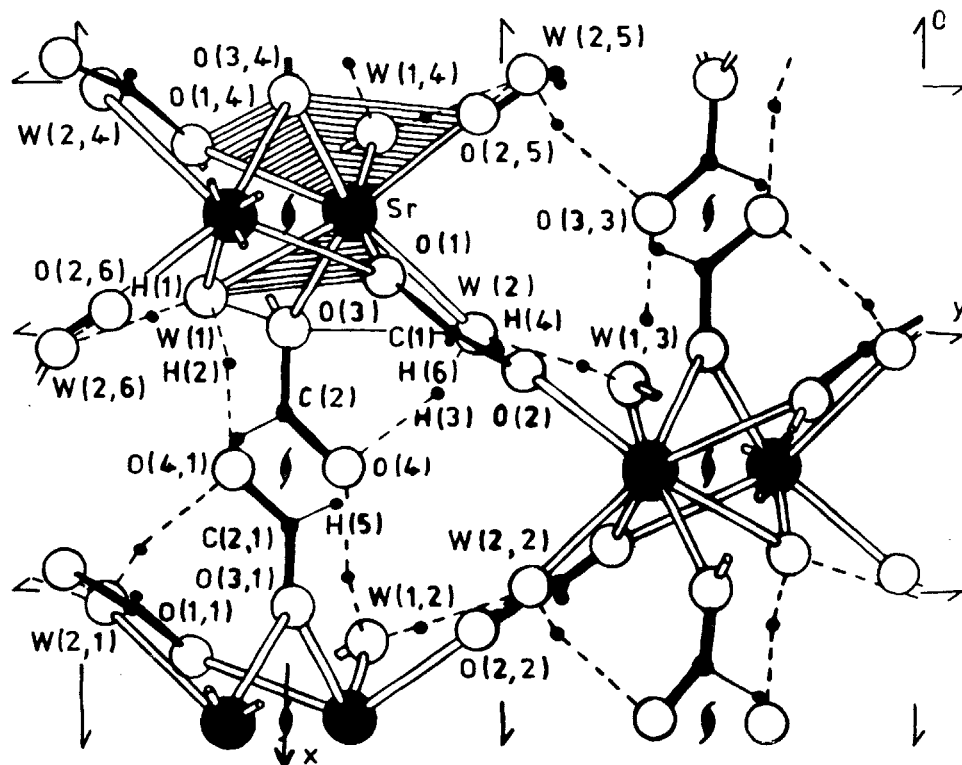


FIG. 4. Structure of strontium formate dihydrate crystal [(Galigné, 1971) viewed from the (001) axis]

The charge compensation can in all probability be explained as achieved by the replacement of three neutral water molecules surrounding the strontium ion such as  $W(1, 4)$ ,  $W(2,4)$  and  $W(1)$  (Fig. 4) by three negatively charged chloride ions, when the  $\text{Cr}^{3+}$  ion enters into an interstitial position.

#### ACKNOWLEDGEMENTS

Thanks are due to Dr. Narasimham and Dr. Ranganatham of BARC, Bombay, for permitting the use of the Spectrophotometer. One of the authors (P.R.) is grateful to the University Grants Commission, New Delhi for financial assistance.

#### REFERENCES

- Ahrens, L. H., and Taylor, S. R. (1961). *Spectrochemical Analysis*. Addison Wesley Publishing Company Inc., U. S. A.
- Galigné, J. L. (1971). Refinement of the crystal structure of strontium formate dihydrate. *Acta Cryst.*, B-27, 2429.
- Narayan, M., Satyanarayana, S. G., and Sastry, G. Sivarama. (1976). E. P. R. of  $\text{Mn}^{2+}$  in single crystals of strontium formate dihydrate. *Indian J. pure appl. Phys.* 14 (6) 511-512.
- Orgel, L. E. (1955). Band widths in the spectra of manganous and other transition metal ions. *J. chem. Phys.*, 23, 1824.
- Pearse, R. W. B., and Gaydon, A. G. (1963). *The Identification of Molecular Spectra*. Chapman and Hall Ltd., London.
- Tanabe, Y., and Sugano, S. (1954). *J. phys. Soc. Japan*, 9, 753.