

## Optical absorption spectrum of $\text{Cr}^{3+}$ in natural ruby

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**Abstract.** Two sharp line-like bands called *N* and *R* lines on the red side, a close doublet (*B* lines) on the violet side and two broad bands are observed for natural ruby. At liquid air temperature the splitting of *R* line was found and also three sharp-bands called *R*, *R'* and *B* lines are identified with spin-forbidden transitions of  ${}^3E$ ,  ${}^2T_1$  and  ${}^2T_2$ . The two broad bands called *U* band and *Y* band are assigned accordingly to the spin-allowed transitions  ${}^4T_2$  and  ${}^4T_1$ , respectively. The observed bands of natural ruby have been attributed to  $\text{Cr}^{3+}$  ion in an octahedral environment with trigonal distortion. The crystal field parameters which gave a good fit to the observed band positions are  $B = 732 \text{ cm}^{-1}$ ,  $C = 4.25 B$ ,  $Dq = 1830 \text{ cm}^{-1}$ ,  $V = -1996 \text{ cm}^{-1}$  and  $\lambda = 34 \text{ cm}^{-1}$ .

**Keywords.** Optical absorption; electronic spectra, natural ruby; crystal field parameters; oscillator strengths; emission spectrochemical analysis.

### 1. Introduction

Ruby contains a moderate amount of chromium (Deer *et al* 1962). Natural ruby occurs in hexagonal structure and its chemical composition is  $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ . The red colour of ruby is due to the replacement of aluminium ion by the larger chromium ion (Bragg 1958). Since no detailed analysis of the bands of natural ruby is available the present work was undertaken to study the absorption spectrum of ruby both at room and liquid air temperatures and to confirm the characteristic features of the chromium ion and its site symmetry.

### 2. Experimental

The optical absorption spectrum of red-coloured ruby (collected from Mysore, Karnataka State, India) was recorded in the region 1000–400 nm on Hilger medium quartz spectrograph at room and liquid air temperatures. Two sections each of 0.8mm thick crystals were cut carefully with *C* axis parallel to its face in one and perpendicular in the other. When the spectra were recorded with these two sections, interesting features could be observed with the crystal *C* axis perpendicular to its face. The spectra were recorded in about 10 to 20 minutes on Kodak IN, IM and Ilford Astra plates. The dispersion of the instrument was  $15 \text{ \AA/mm}$  at  $3000 \text{ \AA}$  and  $5 \text{ \AA/mm}$  at  $2000 \text{ \AA}$ . Spectrochemical (emission) analysis of the sample was carried out on Hilger Littrow spectrograph with dispersion  $5 \text{ \AA/mm}$  at  $3000 \text{ \AA}$  and  $1.2 \text{ \AA/mm}$  at  $2000 \text{ \AA}$ . Only two elements of the iron group namely chromium and

iron were found in the sample. The chromium content was found to be about 50 times higher than that of iron.

From the microphotometric profiles of the bands and the iron spectrum, both the wavelengths and oscillator strengths were determined in the same way as Pappalardo (1957) and Lakshman *et al* (1972).

### 3. Results

The absorption spectrum of ruby was recorded both at room and liquid air temperatures and microphotometric profiles were taken. The microphotometric trace of the bands obtained at 80 K is shown in figure 1. The band maxima and oscillator strengths of the bands are presented in table 1 along with their assignments. At room temperature two sharp bands called *N* and *R* lines respectively at 14053 and 14272  $\text{cm}^{-1}$  and one broad band (*U* band) at 18170  $\text{cm}^{-1}$  and a close doublet called *B* lines at 21025 and 21343  $\text{cm}^{-1}$  were recorded. When the crystal was cooled down to liquid air temperature the sharp line at 14272  $\text{cm}^{-1}$  split into two lines at 14262 and 14296  $\text{cm}^{-1}$ . Three sharp bands called *R'* lines were observed at 16725, 16919 and 17042  $\text{cm}^{-1}$ . A small blue shift of about 73  $\text{cm}^{-1}$  was observed for the *U* band. The sharp band at 21025  $\text{cm}^{-1}$  was also found to split up into two lines at 21012 and 21058  $\text{cm}^{-1}$ . Further an edge absorption was recorded from 22200  $\text{cm}^{-1}$  towards violet side. However this was confirmed by a broad band at 24993  $\text{cm}^{-1}$  by Cary-14 R spectrophotometer record. The band recorded at room temperature at 18170  $\text{cm}^{-1}$  is broad and when the crystal is cooled to 80 K it was found to split into two with maxima at 17245 and 18243  $\text{cm}^{-1}$ .

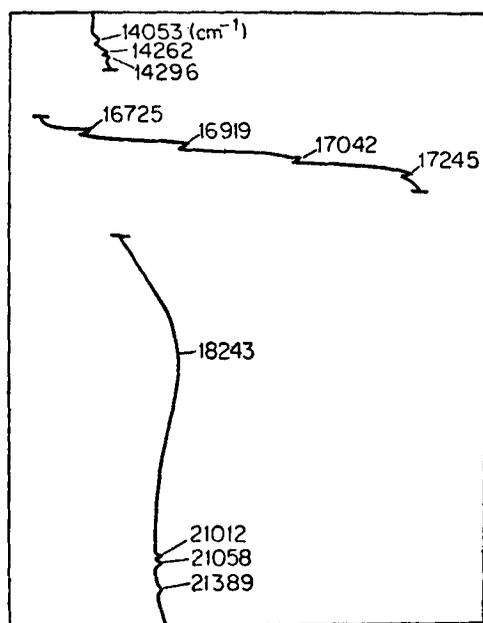


Figure 1. Microphotometric trace of the absorption spectrum of  $\text{Cr}^{3+}$  in natural ruby at 80°K.

**Table 1** Wavelength (nm), wavenumber ( $\nu$ ), assignments and oscillator strengths for the bands of  $\text{Cr}^{3+}$  in natural ruby.

	Assignments w.r.t. the ground state ${}^4A_2$	Band position				$f$ value		
		300 K		80 K		300 K	80 K	
		(nm)	( $\text{cm}^{-1}$ )	(nm)	( $\text{cm}^{-1}$ )			
<i>N</i> line	<i>N</i> line	711.4	14053	711.4	14053		$1.4 \times 10^{-6}$	
<i>R</i> lines	${}^2E$	700.5	14272	701.0	14262		$1.5 \times 10^{-6}$	
				699.3	14296			
<i>R'</i> lines	${}^2T_1$			597.8	16725		$5.6 \times 10^{-6}$	
				590.9	16919		$3.6 \times 10^{-6*}$	
				586.6	17042		$1.2 \times 10^{-6}$	
<i>U</i> band	${}^4T_2$	550.2	18170	579.7	17245	$3.9 \times 10^{-4}$	$3.2 \times 10^{-4}$	
				548.0	18243			
<i>B</i> lines	${}^2T_2$	475.5	21025	475.8	21012		$3.0 \times 10^{-6}$	
				474.7	21058			
		468.4	21343	467.4	21389			$2.1 \times 10^{-6}$
<i>Y</i> band	${}^4T_1$	400.0	24993					

\* $3.5 \times 10^{-6}$  average intensity of  ${}^2T_1$  bands.

#### 4. Analysis

Since the chromium content is in higher percentage than that of iron, the absorption bands are attributed to the chromium ion. The sharp *R* and *R'* lines in the red and the *B* lines in the violet side further support the view that the ion responsible for the lines is  $\text{Cr}^{3+}$ .

The line or band is sharp if the number of  $t_2$  electrons is the same in both its excited and ground states (Ballhausen 1962). Therefore the two sharp *R* lines at 14262 and 14296  $\text{cm}^{-1}$  are attributed to the electronic transition  ${}^4A_2 \rightarrow {}^2E$ . The other three sharp lines at 16725, 16919 and 17042  $\text{cm}^{-1}$  termed as *R'* lines are assigned to  ${}^4A_2 \rightarrow {}^2T_1$  transition. Schawlow *et al* (1959) observed *N* lines on the red side of *R* lines in synthetic ruby and also in  $\text{Cr}^{3+}:\text{MgO}$ . Therefore the line at 14053  $\text{cm}^{-1}$  is termed as *N* line. Considering the experimental facts (Sugano *et al* 1970) one may conclude that the broad absorption bands are due to the intrasystem (spin-allowed) combinations and sharp absorption lines are due to the intersystem (spin-forbidden) combinations. Therefore the broad bands at 18170  $\text{cm}^{-1}$  and 24993  $\text{cm}^{-1}$  are assigned to the spin-allowed transitions  ${}^4A_2 \rightarrow {}^4T_2$  and  ${}^4A_2 \rightarrow {}^4T_1$  respectively. The *B* lines observed at 21012, 21058 and 21389  $\text{cm}^{-1}$  are attributed to the spin-forbidden transition  ${}^4A_2 \rightarrow {}^2T_2$ . The energy matrices for  $d^3$  configuration were diagonalised and solved on IBM 370/155 computer system. Several sets of graphs were drawn between  $Dq/B$  and  $E/B$  with different values of  $C/B$  where  $E$  is the energy,  $Dq$  is the crystal field parameter and  $B$  and  $C$  are Racah parameters. The observed band positions gave a good fit for  $C/B = 4.25$  which is shown in figure 2. The *B* and *Dq* values evaluated therefrom are  $B = 732 \text{ cm}^{-1}$  and  $Dq = 1830 \text{ cm}^{-1}$ .

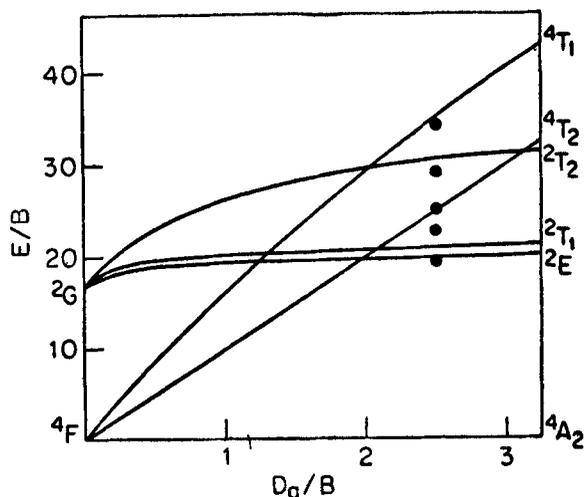


Figure 2. Energy level diagram of  $\text{Cr}^{3+}$  in cubic environment.  $E/B$  plotted as a function of  $Dq/B$  with  $C/B = 4.25$ . The solid circles show the experimental values at  $80^\circ\text{K}$ .

## 5. Discussion

The spin-forbidden transitions are allowed by the mixing of states of different multiplicity through spin-orbit coupling (Carlin 1969). Thus  ${}^2E$  and  ${}^2T_1$  contain admixtures of  ${}^4T_1$  and  ${}^4T_2$ . Assuming that the transitions to  ${}^2E$  and  ${}^2T_1$  'steal' all their intensity from the first spin-allowed transition  ${}^4A_2 \rightarrow {}^4T_2$ , we obtain (Carlin 1969)

$$\frac{f({}^4A_2 \rightarrow {}^2E)}{f({}^4A_2 \rightarrow {}^2T_1)} = \frac{[({}^4T_2 | V_{\text{so}} | {}^2E)]^2}{[({}^4T_2 | V_{\text{so}} | {}^2T_1)]^2} \quad (1)$$

where  $f({}^4A_2 \rightarrow {}^2E)$  and  $f({}^4A_2 \rightarrow {}^2T_1)$  are oscillator strengths for the  ${}^2E$  and  ${}^2T_1$  bands respectively and  $[({}^4T_2 | V_{\text{so}} | {}^2E)]^2$  and  $[({}^4T_2 | V_{\text{so}} | {}^2T_1)]^2$  are the squares of spin-orbit matrix elements. Since the squares of spin-orbit matrix elements are equal to  $16\xi^2$  and  $6\xi^2$  respectively ( $\xi$  is the spin-orbit coupling coefficient), we have

$$\frac{f({}^4A_2 \rightarrow {}^2E)}{f({}^4A_2 \rightarrow {}^2T_1)} = \frac{16\xi^2}{6\xi^2} = 2.7. \quad (2)$$

It is quite interesting to note from the observed oscillator strengths given in table 1, that this theoretical ratio of 2.7 is in excellent agreement with the experimental ratio of  $(3.5 \times 10^{-6}/1.5 \times 10^{-6}) = 2.3$ . The splitting of  $R$  and  $R'$  lines in the present work indicates a lowering of symmetry for the  $\text{Cr}^{3+}$  ion. This may be either due to tetragonal or trigonal distortion. Since the  $r$  lines correspond to the transition  ${}^4A_2 \rightarrow {}^2E$ , the splitting of  ${}^2E$  band (splitting of  ${}^4A_2$  would be very small of the order  $1 \text{ cm}^{-1}$ ) may be interpreted as due to the tetragonal distortion, but not in a trigonal field (Wood 1965). However the splitting of  ${}^2E$  can also be attributed to a trigonal distortion combined with spin-orbit coupling. The trigonal field splittings are charac-

terized by two parameters  $v$  and  $v'$ . MacFarlane (1963, 1965) reported the trigonal field splittings for the  ${}^4T_1$  and  ${}^4T_2$  states as follows

$${}^4T_1 \begin{cases} {}^4A_2 \\ {}^4E \end{cases} (\frac{1}{2} v) + v' \text{ (Approximately),}$$

$${}^4T_2 \begin{cases} {}^4A_1 \\ {}^4E \end{cases} (\frac{1}{2} v) \text{ (Approximately).}$$

According to the polarization selection rules valid for  $D_3$  symmetry (Ballhausen 1962) the  $\pi$  polarized lines are  $A_2 \leftrightarrow A_1$  while the  $A_2 \leftrightarrow E$  transitions are  $\sigma$  polarized. The band at  $18243 \text{ cm}^{-1}$  is recorded with more intensity in the presence of parallel-polarized light ( $\pi$ ). Therefore this band is attributed to the transition  ${}^4A_2 \rightarrow {}^4A_1$ . In perpendicular polarized light the band at  $17245 \text{ cm}^{-1}$  (component of  $18243 \text{ cm}^{-1}$ ) was observed with more intensity than the  $18243 \text{ cm}^{-1}$  band. Therefore the  $17245 \text{ cm}^{-1}$  band is attributed to the  ${}^4A_2 \rightarrow {}^4E$  transition. The above assignments agree with the spectra reported on ruby (McClure 1962).

From the observed separation of the two components of  ${}^4T_2$ , the trigonal field parameter  $v$  is calculated by equating it to  $\frac{1}{2} v$  and is found to be equal to  $1996 \text{ cm}^{-1}$ . From the trigonal splitting parameter  $v$ , the spin-orbit coupling coefficient  $\xi$  and the energy separation between the states  ${}^2E$  and  ${}^2T_2$ , it is possible to evaluate  ${}^2E$  splitting,  $\lambda$  ascribed to mixing (*via* the trigonal field and spin-orbit coupling) with  ${}^2T_2$  from the following formula (Sugano and Tanabe 1958 and MacFarlane 1967)

$$\lambda = -\frac{4}{3} \frac{v \xi}{W({}^2E) - W({}^2T_2)}. \quad (3)$$

The value of  $W({}^2E) - W({}^2T_2)$  which is the energy difference between the  ${}^2E$  and  ${}^2T_2$  states is calculated from the formula (Jorgensen 1962)

$$6B + 2C - \frac{(98.5) B^2}{10 Dq} = 7732 \text{ cm}^{-1}. \quad (4)$$

The theoretical value of  $7732 \text{ cm}^{-1}$  is also in good agreement with the observed mean energy difference of  ${}^2E$  and  ${}^2T_2$  states ( $21153 - 14271 = 6882 \text{ cm}^{-1}$ ). The value of  $\xi$  is calculated using the formula

$$g = 2.0029 - \frac{8}{3} \frac{\xi}{10Dq}, \quad (5)$$

with  $g = 1.988$  (Geusic 1956). Thus the  $\xi$  value is equal to  $102 \text{ cm}^{-1}$ . Knowing the values of  $\xi$ ,  $v$ ,  $B$  and  $10 Dq$ , the value of  $\lambda$  evaluated to be equal to  $39.5 \text{ cm}^{-1}$ , which is in good agreement with the observed value of  $34 \text{ cm}^{-1}$ . The splitting of  ${}^2E$  ( $34 \text{ cm}^{-1}$ ) in natural ruby is very close to that of synthetic ruby ( $29 \text{ cm}^{-1}$ ) (Carlin 1969).

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