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Theoretical calculations of pressure-induced shifts of the entire energy spectrum of ruby

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Abstract. The d^3 ions in trigonal crystal fields are considered. On the basis of the expansion of the electron wavefunctions under pressure, the expressions for the parameters Dq , B , C , K , K' and ζ as functions of the linear compression ratio χ are derived, and the complete d^3 energy matrix in trigonal field is constructed. With the P - χ dependence, by diagonalization of this matrix to fit only the experimental data of the red shifts of ruby R_1 line under quasi-hydrostatic pressure, the values of three parameters for the pressure shift (S_0 , D_1 and t) are determined. Then, the values of Dq , B , C , K , K' and ζ at various pressures are evaluated, and the pressure shifts of the entire energy spectrum of ruby are theoretically calculated uniformly by diagonalization of the complete d^3 matrix. The contributions of changes of Dq , B , C , K , K' and ζ to the R_1 and R_2 red shifts and the pressure-induced change in the R_1 - R_2 splitting are obtained. The calculated results of the pressure shifts are in good agreement with all the experimental data of the R-, R'- and B-line groups and U and Y bands. A discussion is given and conclusions drawn.

1. Introduction

The pressure-induced red shift of the ruby R_1 line has been used extensively for the measurement of pressure in the diamond anvil cell. The ruby R_1 pressure scale has been calibrated to 180 GPa non-hydrostatically [1] and to 110 GPa quasi-hydrostatically [2]. The pressure-induced shifts of the energy spectra of ruby have been studied both experimentally and theoretically [1–15].

In our previous work [9, 10], we have calculated the pressure shifts of three groups of sharp lines and two broad bands of ruby. However, the spin-orbit interaction was omitted and the trigonal field was taken into account approximately. In [10], we fitted the experimental data of the R_1 -line and the R' -line red shifts [5, 6] and the U-band blue shifts [3, 7] of ruby by using seven adjustable parameters. However, the data for the U-band and Y-band blue shifts in [7] are considerably smaller than the new data given in [12, 13].

A thorough investigation of the entire electronic energy spectrum of ruby and its pressure shift is important to understand the pressure dependence of the electronic states and optical spectral properties of ruby. In this paper, we shall need only three adjustable parameters and will determine their values by fitting only more accurate and newer experimental data on the R_1 -line red shift under quasi-hydrostatic pressure [2]. Then, the pressure shifts of the entire crystal-field energy spectrum of ruby will be theoretically calculated by means of diagonalization of the 120×120 complete d^3 energy matrix in which the cubic-field, trigonal-field, Coulomb and spin-orbit interactions are all taken into account.

2. Expansion of the electron wavefunctions and expressions for B , C , Dq , K , K' and ζ

As is well known in ligand-field theory, when the distance between the central metal ion and the ligands is reduced, the electron wavefunctions expand. This expansion results from screening of the nuclear charge by the overlapping electron clouds and the partial transference of electrons [16–18].

According to [19], ruby does not undergo any structural transition to at least 175 GPa and the c/a -ratio remains approximately constant. In [20] it was pointed out that, to a close approximation, the compression of ruby up to 46 kbar may be represented by a simple scaling of structure at normal pressure, with all distances compressed equally and all the interatomic angles unchanged. Therefore, we can assume that, under isotropic compression, the angular part of the d-electron wavefunction of the Cr^{3+} ion remains unchanged, while the radial part varies with the substitution of $r\Phi(\chi)$ for r . The expansion function $\Phi(\chi)$ represents the expansion behaviour of the electron wavefunction, where $\chi = (V/V_0)^{1/3} = R/R_0$, V_0 and R_0 are the crystal volume and the interionic distance at normal pressure, and V and R are the corresponding quantities under compression. We shall justify this assumption in section 5.

We have derived that [9]

$$\Phi(\chi) = \chi^{S_0} \exp[-\frac{1}{2}D_1(1-\chi)^2 - \frac{1}{3}D_2(1-\chi)^3 - \dots] \quad (1)$$

where S_0 , D_1 and D_2 are the parameters depending on the crystal properties.

On the basis of the expansion of the electron wavefunctions, we can microscopically derive expressions for the parameters B , C , Dq , K , K' and ζ as functions of χ . B and C are Racah parameters; Dq is the cubic-field parameter; K and K' are the trigonal-field parameters; ζ is the spin-orbit coupling parameter. We always use the subscript 0 to indicate the quantities at normal pressure ($\chi = 1$), and the quantities without a subscript 0 are those under compression ($\chi < 1$).

It has been proved that [9–11]

$$B/B_0 = C/C_0 = \Phi(\chi) \quad (2)$$

$$Dq/Dq_0 = \chi^{-5}\Phi^{-4}(\chi)q_{\text{eff}}/(q_{\text{eff}})_0 \quad (3)$$

$$q_{\text{eff}}/(q_{\text{eff}})_0 = \exp\{-t[\Phi^{-1}(\chi) - 1] - u[\Phi^{-1}(\chi) - 1]^2 - \dots\} \quad (4)$$

where q_{eff} is the effective charge of a ligand ion under compression, and $(q_{\text{eff}})_0$ is the value at normal pressure. We can call S_0 , D_1 , D_2 , t and u the parameters for pressure shift. They depend on the crystal properties and are considered to be adjustable parameters.

Let us derive the expressions for K and K' .

According to Sugano and co-workers [16, 21], K and K' can be defined as

$$K = \langle t_2x_+ | V_{\text{trig}} | t_2x_+ \rangle = -\frac{1}{7}\langle A(r) \rangle - \frac{20}{189}\langle B(r) \rangle \quad (5)$$

$$K' = -\frac{1}{\sqrt{2}}\langle t_2x_+ | V_{\text{trig}} | eu_+ \rangle = \frac{1}{7}\langle A(r) \rangle - \frac{5}{63}\langle B(r) \rangle \quad (6)$$

where

$$V_{\text{trig}} = V_c^0 + V_{\text{ax},z} \quad (7)$$

$$V_c^0 = D(r)\{C_0^{(4)}(\theta\varphi) + (\frac{10}{7})^{1/2}[C_3^{(4)}(\theta\varphi) - C_{-3}^{(4)}(\theta\varphi)]\} \quad (8)$$

$$V_{\text{ax},z} = A(r)C_0^{(2)}(\theta\varphi) + B(r)C_0^{(4)}(\theta\varphi) \quad (9)$$

Similar to the derivation in [11], we have

$$\frac{\langle A(r) \rangle}{\langle A(r) \rangle_0} = \frac{\langle r^2 \rangle q_{\text{eff}} R_0^3}{\langle r^2 \rangle_0 (q_{\text{eff}})_0 R^3} \quad (10)$$

$$\frac{\langle B(r) \rangle}{\langle B(r) \rangle_0} = \frac{\langle r^4 \rangle q_{\text{eff}} R_0^5}{\langle r^4 \rangle_0 (q_{\text{eff}})_0 R^5} \quad (11)$$

where $\langle r^n \rangle = \int_0^\infty r^n R_d^2(r) r^2 dr$ ($R_d(r)$ is the radial wavefunction of the d electron); R is the distance between the centre metal ion and the ligand ions. As we have proved in [11], because both the radial wavefunction at $\chi = 1$ and that at $\chi < 1$ must satisfy the normalization condition, after changing the variable r to $r' = r\Phi(\chi)$, the extra $\Phi^{-n}(\chi)$ will appear only from the factor r^n in $\langle r^n \rangle$. We then have

$$\langle r^n \rangle / \langle r^n \rangle_0 = \Phi^{-n}(\chi). \quad (12)$$

Finally we obtain

$$K = \left(-\frac{\langle A(r) \rangle_0}{7} \chi^{-3} \Phi^{-2}(\chi) - \frac{20 \langle B(r) \rangle_0}{189} \chi^{-5} \Phi^{-4}(\chi) \right) \frac{q_{\text{eff}}}{(q_{\text{eff}})_0} \quad (13)$$

$$K' = \left(\frac{\langle A(r) \rangle_0}{7} \chi^{-3} \Phi^{-2}(\chi) - \frac{5 \langle B(r) \rangle_0}{63} \chi^{-5} \Phi^{-4}(\chi) \right) \frac{q_{\text{eff}}}{(q_{\text{eff}})_0}. \quad (14)$$

From equations (5) and (6), we can obtain

$$\langle A(r) \rangle_0 = 4K'_0 - 3K_0 \quad (15)$$

$$\langle B(r) \rangle_0 = -\frac{27}{5}(K'_0 + K_0). \quad (16)$$

From equations (13), (14) and (16) we have

$$\frac{K + K'}{K_0 + K'_0} = \chi^{-5} \Phi^{-4}(\chi) \frac{q_{\text{eff}}}{(q_{\text{eff}})_0} = \frac{Dq}{Dq_0}. \quad (17)$$

Now we derive the expression for ζ as follows: ζ is given as [16]

$$\zeta = \int_0^\infty \xi(r) R_d^2(r) r^2 dr \quad (18)$$

where

$$\xi(r) = \frac{\hbar^2}{2m^2 c^2 r} \frac{1}{dr} \frac{dV(r)}{dr}. \quad (19)$$

According to ligand-field theory, usually the potential energy for the d electron can be approximately taken as $V(r) = -Z_{\text{eff}}e^2/r$, where Z_{eff} is the effective nuclear charge number 'seen' by the d electron. Therefore we obtain

$$\frac{\zeta}{\zeta_0} = \frac{Z_{\text{eff}}}{(Z_{\text{eff}})_0} \frac{\langle r^{-3} \rangle}{\langle r^{-3} \rangle_0}. \quad (20)$$

We can further adopt the simplified approximation that $R_d(r)$ is a hydrogen-like wavefunction or a Slater-type orbital, then we can obtain [22]

$$\langle r^{-3} \rangle = \frac{Z_{\text{eff}}^3}{a_0^3 n^3 l(l + \frac{1}{2})(l + 1)}. \quad (21)$$

From equations (12) and (21) we get

$$\frac{\langle r^{-3} \rangle}{\langle r^{-3} \rangle_0} = \left(\frac{Z_{\text{eff}}}{(Z_{\text{eff}})_0} \right)^3 = \Phi^3(\chi). \quad (22)$$

Finally we obtain

$$\frac{\zeta}{\zeta_0} = \Phi^4(\chi). \quad (23)$$

In [10, 11], the factor $Z_{\text{eff}}/(Z_{\text{eff}})_0$ was not taken into account.

Because the spin-orbit interaction of rare-earth ions is much larger than that of transition-metal ions, it is easier to measure the variation in ζ for rare-earth ions in crystals by experiment. Huber *et al* [18] obtained the variation in ζ with pressure by using the experimental values for the centres of gravity of the manifolds of Eu^{3+} in $\text{EuP}_5\text{O}_{14}$. They found that the percentage of decrease in ζ with increasing pressure is much higher than the percentage of decrease in B or C , and that the volume dependence of $\langle r_{4f}^{-3} \rangle$ is about an order of magnitude smaller than the volume dependence of $\langle r_{3d}^{-3} \rangle$. Similar results were reported in [23]. Thus, equations (2) and (23) are reasonable.

3. Construction of the d^3 energy matrix and its diagonalization at normal pressure and P - χ dependence

As is well known, the Cr^{3+} ions in ruby ($\alpha\text{-Al}_2\text{O}_3:\text{Cr}^{3+}$) are surrounded by trigonally distorted octahedra of oxygen ions. The sites of the Cr^{3+} ions possess the trigonal symmetry C_3 , and Cr^{3+} has a $3d^3$ electronic configuration. Therefore, first of all, we must construct the complete energy matrix of the d^3 electron configuration in a trigonal field. For this we adopt the strong-field scheme [16, 21]. The matrix elements of the cubic-field and electrostatic interactions have been given by Sugano *et al* [16]. Because only the reduced matrix elements of the trigonal field within the t_2^3 and t_2^2e strong-field configurations were given in [21] and among these there were several mistakes, we have calculated all the reduced matrix elements and the matrix elements of the trigonal field of all the strong-field configurations t_2^3 , t_2^2e , t_2e^2 and e^3 . We have also calculated all the spin-orbit matrix elements. With all the matrix elements of the cubic-field, electrostatic, trigonal-field and spin-orbit interactions, thus, we have constructed the 120×120 complete energy matrix of the d^3 configuration. We have made a check which shows the correctness of this matrix.

Next, by diagonalizing this matrix to perform a least-squares fit to the optical and microwave spectral experimental data of ruby at normal pressure (including all the data adopted in [24, 25]), we obtain the values of the parameters at normal pressure: $Dq_0 = 1765 \text{ cm}^{-1}$, $B_0 = 685 \text{ cm}^{-1}$, $C_0 = 3075 \text{ cm}^{-1}$, $K_0 = -230 \text{ cm}^{-1}$, $K'_0 = -421 \text{ cm}^{-1}$ and $\zeta_0 = 205 \text{ cm}^{-1}$. The corresponding calculated results of the energy spectrum, especially those of the ground-state splitting and the sharp lines, are better than those of previous

work [21, 24, 25]. The calculation of the energy spectrum of ruby at normal pressure will be reported later.

The P - χ dependence is calculated from the three-parameter Birch equation

$$P = \frac{3B_0}{2} \left(\frac{V}{V_0} \right)^{-5/3} \sum_{i=1}^3 b_i \left[\left(\frac{V}{V_0} \right)^{-2/3} - 1 \right]^i \quad (24)$$

where $B_0 = 2504.1$ kbar, $B'_0 = 4.00$, $b_1 = 1$, $b_2 = \frac{3}{4}(B'_0 - 4)$ and $b_3 = -0.4020$ [9]. The P - χ dependence is shown in table 1. For convenience in calculation we keep many digits in the values of χ .

Table 1. The p - χ dependence and the values of the parameters at various pressures ($Dq_0 = 1765.00$ cm⁻¹, $B_0 = 685.00$ cm⁻¹, $C_0 = 3075.00$ cm⁻¹, $\zeta_0 = 205.00$ cm⁻¹, $K_0 = -230.00$ cm⁻¹ and $K'_0 = -421.00$ cm⁻¹).

P (kbar)	χ	Dq (cm ⁻¹)	B (cm ⁻¹)	C (cm ⁻¹)	ζ (cm ⁻¹)	K (cm ⁻¹)	K' (cm ⁻¹)
20.00	0.99738264	1782.53	684.06	3070.78	203.88	-233.43	-424.04
40.00	0.99485090	1799.60	683.14	3066.64	202.78	-236.77	-426.99
60.00	0.99239889	1816.25	682.23	3062.58	201.71	-240.05	-429.85
80.00	0.99002133	1832.50	681.34	3058.59	200.66	-243.26	-432.64
100.00	0.98771346	1848.38	680.47	3054.68	199.63	-246.41	-435.35
200.00	0.97708217	1922.75	676.33	3036.09	194.82	-261.28	-447.90
300.00	0.96768731	1990.15	672.50	3018.89	190.44	-274.94	-459.10
350.00	0.96336406	2021.69	670.69	3010.74	188.39	-281.39	-464.28
400.00	0.95925453	2051.95	668.93	3002.86	186.43	-287.62	-469.22
500.00	0.95159362	2109.13	665.58	2987.80	182.72	-299.47	-478.46
600.00	0.94456679	2162.41	662.41	2973.59	179.27	-310.61	-486.97
700.00	0.93807086	2212.33	659.41	2960.12	176.04	-321.14	-494.85
800.00	0.93202640	2259.35	656.55	2947.29	173.01	-331.13	-502.20
1000.00	0.92105414	2345.97	651.21	2923.31	167.44	-349.74	-515.55
1100.00	0.91603526	2386.11	648.70	2912.04	164.88	-358.44	-521.65

4. Calculations and results of pressure shifts of the entire energy spectrum of ruby

With the above-mentioned values of the parameters at normal pressure and the P - χ dependence, by using the theoretical formulae for $\Phi(\chi)$, Dq , B , C , ζ , K and K' and diagonalizing the complete d^3 energy matrix so that it is a least-squares fit to only the experimental data of the R_1 -line red shifts under quasi-hydrostatic pressure up to 110 GPa [2], we have determined the values of the parameters for the pressure shift. We found that it is sufficient to keep the first term of the series in equation (1) and the first term of the series in equation (4), i.e. we need only three adjustable parameters. In this way, we have obtained the values of the parameters: $S_0 = 0.5212$, $D_1 = 2.48$ and $t = 6.34$.

Using these results, the values of Dq , B , C , ζ , K and K' at various pressures have been calculated (see table 1). Then, at each pressure, the pressure shifts of all the levels of ruby have been theoretically evaluated uniformly and simultaneously by diagonalization of the complete d^3 matrix, without further parameter adjustments. It is shown that the R_1 -line red shifts obtained by the fit calculation are in excellent agreement with the experimental

data [2] (table 2 and figure 1), and the pressure shifts theoretically predicted for the R_2 line, the R' and B lines, and the U and Y bands are also in very good agreement with the experimental data [5, 12, 13, 26–28] (tables 2 and 3, and figure 1). Therefore, the pressure shifts of all of the sharp lines and broad bands of ruby have been calculated uniformly, consistently and successfully.

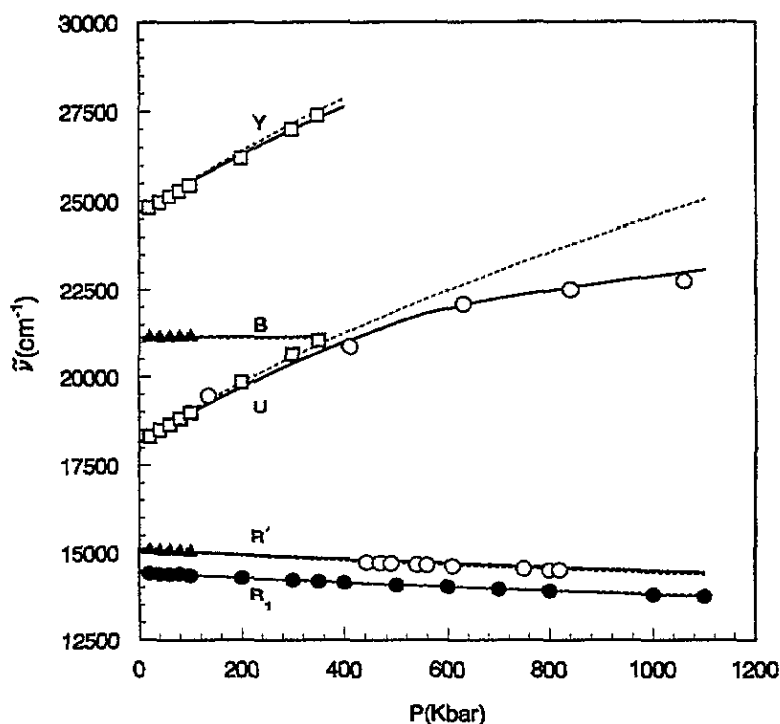


Figure 1. Pressure shifts of R_1 line and cubic-field centres of R' and B lines and U and Y bands: —, results calculated in this work; ·····, results calculated in [12]; ●, experimental data from [2]; ○, experimental data from [12]; □, experimental data from [13]; ▲, experimental data from [5].

For the U and Y bands and the R' -line group and B-line group, in order to compare with the experimental data of pressure shifts of cubic-field band (or line) centres, the weighted averages of pressure shifts of split components are given in table 3 and figure 1, respectively.

From table 2 it is shown that the theoretically calculated red shift of the R_2 line is almost the same as that of the R_1 line up to about 100 kbar. This is in good agreement with the experimental results under hydrostatic conditions [26–28]. It is worth noting that our theory corresponds to the situation of isotropic strain (see the assumption in section 2). From table 2, the increase in R_1 – R_2 separation with increasing pressure from 1 bar to 110 GPa is 4.4 cm^{-1} . However, the increase given in [2] is about 12 cm^{-1} . The larger increase in R_1 – R_2 separation is indicative of non-hydrostatic strain [2, 12, 15].

By diagonalization of the complete d^3 matrix, we have obtained the rates of change in the levels with respect to various parameters. The rates of change in the R_1 and R_2 levels are shown in table 4. From table 1 and table 4, we get table 5. Obviously, the results in table 5 cannot be obtained by the perturbation method.

Table 2. The red shifts of the R₁ and R₂ lines.

P (kbar)	$\Delta\tilde{\nu}_{R_1}$ (cm ⁻¹)			$\Delta\tilde{\nu}_{R_2}$ (cm ⁻¹)
	Observed ^a	Calculated ^b	Calculated ^c	Calculated ^d
20.00	-15.06	-14.94	-17.5	-14.93
40.00	-29.99	-29.82	-34.6	-29.77
60.00	-44.78	-44.61	-51.3	-44.51
80.00	-59.45	-59.30	-67.6	-59.14
100.00	-73.98	-73.89	-83.5	-73.66
200.00	-144.8	-145.05	-158.6	-144.39
300.00	-212.7	-213.20	-227.4	-212.06
350.00	-245.6	-246.18	-259.8	-244.79
400.00	-277.9	-278.46	-291.1	-276.83
500.00	-340.6	-341.04	-350.8	-338.94
600.00	-400.9	-401.18	-407.0	-398.64
700.00	-459.1	-459.10	-460.2	-456.14
800.00	-515.3	-514.98	-511.0	-511.64
1000.00	-622.0	-621.33	-606.2	-617.28
1100.00	-672.8	-672.07	-651.1	-667.70

^a From [2].^b This work, $\sigma = \sqrt{\sum_{i=1}^{15} (\Delta\tilde{\nu}_i^{\text{obs}} - \Delta\tilde{\nu}_i^{\text{cal}})^2} / 15 = 0.40$ cm⁻¹.^c The calculated results using the formulae and the values of parameters given in [12] (see text); $\sigma = 11$ cm⁻¹.^d This work.

Table 3. The pressure shifts of the cubic-field centres of R' and B lines, and U and Y bands.

P (kbar)	$\Delta\tilde{\nu}_{R'}$ (cm ⁻¹)	$\Delta\tilde{\nu}_U$ (10 ³ cm ⁻¹)	$\Delta\tilde{\nu}_B$ (cm ⁻¹)	$\Delta\tilde{\nu}_Y$ (10 ³ cm ⁻¹)
20.00	-15.91	0.17	5.62	0.18
40.00	-31.65	0.34	10.4	0.36
60.00	-47.23	0.51	14.5	0.54
80.00	-62.63	0.67	17.9	0.71
100.00	-77.85	0.83	20.7	0.87
200.00	-151.43	1.57	27.3	1.64
300.00	-221.03	2.24	25.1	2.33
350.00	-254.46	2.56	22.0	2.65
400.00	-287.04	2.86		
500.00	-349.86	3.42		
600.00	-409.82	3.82		
700.00	-467.21	4.12		
800.00	-522.27	4.34		
1000.00	-626.27	4.74		
1100.00	-675.54	4.93		

Table 4. The rates of change in the energies of R₁ and R₂ levels with respect to various parameters.

Level	$\Delta E / \Delta Dq$	$\Delta E / \Delta B$	$\Delta E / \Delta C$	$\Delta E / \Delta \zeta$	$\Delta E / \Delta K $	$\Delta E / \Delta K' $
$t_2^3 {}^2E\bar{E}(R_1)$	0.3858	6.4077	3.0512	-0.2476	-0.6662	-0.2257
$t_2^3 {}^2E2\bar{A}(R_2)$	0.3732	6.4124	3.0474	-0.0968	-0.5674	-0.2111

Table 5. The pressure-induced shifts $\Delta\tilde{\nu}_{R_1}$ of the R_1 level, the pressure-induced shifts $\Delta\tilde{\nu}_{R_2}$ of the R_2 level, the pressure-induced change $\Delta\tilde{\nu}_{R_2} - \Delta\tilde{\nu}_{R_1}$ in R_1 - R_2 splitting (with pressure from 1 bar to 20 kbar) and the contributions to these by changes in various parameters. $\Delta\tilde{\nu}(Dq)$, $\Delta\tilde{\nu}(B)$, $\Delta\tilde{\nu}(C)$, $\Delta\tilde{\nu}(\zeta)$, $\Delta\tilde{\nu}(K)$ and $\Delta\tilde{\nu}(K')$ indicate the contributions to $\Delta\tilde{\nu}_{R_1}$, $\Delta\tilde{\nu}_{R_2}$ and $\Delta\tilde{\nu}_{R_2} - \Delta\tilde{\nu}_{R_1}$ by the changes in Dq , B , C , ζ , K and K' , respectively.

	$\Delta\tilde{\nu}(Dq)$ (cm^{-1})	$\Delta\tilde{\nu}(B)$ (cm^{-1})	$\Delta\tilde{\nu}(C)$ (cm^{-1})	$\Delta\tilde{\nu}(\zeta)$ (cm^{-1})	$\Delta\tilde{\nu}(K)$ (cm^{-1})	$\Delta\tilde{\nu}(K')$ (cm^{-1})	Total (cm^{-1})
$\Delta\tilde{\nu}_{R_1}$	6.76	-6.03	-12.89	0.28	-2.29	-0.69	-14.9
$\Delta\tilde{\nu}_{R_2}$	6.54	-6.04	-12.87	0.11	-1.95	-0.64	-14.9
$\Delta\tilde{\nu}_{R_2} - \Delta\tilde{\nu}_{R_1}$	-0.22	-0.01	0.02	-0.17	0.34	0.05	0

From table 5 we can further find the following: the contributions to the pressure-induced change in the R_1 - R_2 splitting $\Delta\tilde{\nu}_{R_2} - \Delta\tilde{\nu}_{R_1}$ by the changes in K and K' are 0.34 cm^{-1} and 0.05 cm^{-1} , respectively; the contributions by the changes in Dq and ζ are -0.22 cm^{-1} and -0.17 cm^{-1} , respectively; the contributions by the changes in B and C are insignificant; it is because these contributions cancel that $\Delta\tilde{\nu}_{R_2} - \Delta\tilde{\nu}_{R_1}$ becomes zero (under hydrostatic conditions). However, Sharma and Gupta [14] assume that the spin-orbit interaction does not change with pressure. Then, they calculated the variation in R_1 - R_2 splitting by taking into account only the trigonal-field change and concluded that the trigonal field does not change significantly with hydrostatic pressure. These are inappropriate (see equation (23) and discussion about it).

From table 5, we can also see that the contributions to the R_1 -line red shift $\Delta\tilde{\nu}_{R_1}$ from the changes in B and C are partly eliminated by the contribution from the change in Dq ; the contributions to $\Delta\tilde{\nu}_{R_1}$ from the changes in K and K' are -2.98 cm^{-1} (i.e. 20% of the total $\Delta\tilde{\nu}_{R_1}$), which shows the importance of the contributions to $\Delta\tilde{\nu}_{R_1}$ from the change in the trigonal field.

We found that, if we adopt a Birch-Murnaghan equation of state (with $K_0 = 254 \text{ GPa}$ and $K'_0 = 4.3$) [19] and slightly adjust the values of the parameters S_0 , D_1 and t , the calculated results differ only slightly from the above-mentioned results.

5. Discussion and conclusions

(i) We compare this paper with [10, 12] as follows. In [10], by using incomplete matrices, we fitted the experimental data of the R_1 -line and R' -line red shifts [5, 6] and the U-band blue shifts [3, 7]. However, the new data on U-band and Y-band blue shifts given in [12, 13] are considerably larger than the shock-wave data in [7]. Because of fit to the data of the U-band blue shifts in [7], of course, the calculated results of U-band and Y-band blue shifts in [10] are not in agreement with the data in [12, 13] and the value of Dq has a turn-over at about 50 GPa. In this paper, therefore, we have carried out much stricter theoretical calculations. Firstly, by diagonalization of the complete d^3 matrix (taking into account the cubic-field, electrostatic, trigonal-field and spin-orbit interactions), the pressure shifts of the entire energy spectrum of ruby have been evaluated uniformly and simultaneously (We found that, when the effects of ζ and/or K and K' are neglected, the calculated results are obviously worse than the results in tables 2 and 3); secondly, we have fitted only the improved experimental data of the R_1 -line red shifts under quasi-hydrostatic pressure given in [2] (which are the most accurate of all the experimental data of the pressure shifts of the sharp lines and broad bands of ruby) and have theoretically calculated all other pressure shifts (including those of the R_2 , R' and B lines, and the U and Y bands); thirdly, the

number of the adjustable parameters has been reduced from 7 to 3. It is shown that the theoretically predicted pressure shifts are all in very good agreement with the experimental data (the data on U and Y bands are the new values given in [12, 13]; the data of the R' lines include the new values given in [12]; see figure 1) and are much better than the fitted and predicted results in [10]. In particular, the theoretically predicted pressure shifts of U and Y bands are in excellent agreement with the new experimental data given in [12, 13]. This shows clearly that the data on U- and Y-band blue shifts in [12, 13] are consistent with the experimental data of the pressure shifts of R₁, R₂, R' and B lines [2, 5, 12, 26–28], and the present work is very successful and in good agreement with the physical reality.

The theories of Munro [8] and Eggert *et al* [12] use pressure and volume, respectively, to scale the electronic charge e and nuclear charge number Z . By fitting the pressure-shift experimental data in the cubic Coulomb approximation, Eggert *et al* [12, 15] have calculated the pressure shifts of the R, R', B, U and Y transitions. Furthermore, by using an empirical function to fit the R₁–R₂ splitting and combining the line-centre fits, they have calculated the red shifts of R₁ and R₂ lines. It seems that their assumption ($\zeta \sim Dq$) is unreasonable. From table 2, our fitted results of the R₁-line red shifts are much better than the fitted results obtained by Eggert *et al*. From table 3 and figure 1, furthermore, our theoretically calculated results of the pressure shifts of B-line, U-band and Y-band centres are better than the results found by Eggert *et al*. In particular, the pressure shift of the B-line centre given by Eggert *et al* is the red shift. However, the experimental data is the blue shift (the average blue-shift rate $(\Delta\bar{\nu}_B/P) \simeq 0.18 \text{ cm}^{-1} \text{ kbar}^{-1}$) [5]. Our results in table 3 give the average blue-shift rate in the range up to 200 kbar, $(\Delta\bar{\nu}_B/P) = 0.21 \text{ cm}^{-1} \text{ kbar}^{-1}$, which is in good agreement with the experimental data.

(ii) By diagonalization of the complete energy matrix, we have obtained results that cannot be given by the perturbation method [12, 14], such as the contributions of Dq , B , C , K , K' and ζ to the R₁ and R₂ red shifts and the pressure-induced change in the R₁–R₂ splitting (see table 5 and the discussion in section 4).

Furthermore, by making use of the complete d^3 matrix and the theoretical formulae for the pressure dependence of all the parameters Dq , B , C , ζ , K and K' , and fitting appropriate and accurate experimental data, good results on the pressure dependence of Dq , B , C , ζ , K and K' have been obtained; otherwise inaccurate results may be given. We have obtained the monotonically increasing behaviour of Dq (see table 1), which is different from the result in [10]. In [3], B and $10Dq$, as functions of pressure, were directly calculated using incomplete matrices and the experimental data of U and Y bands. The obtained rates of change in B and $10Dq$ up to about 100 kbar (which are $-0.205 \text{ cm}^{-1} \text{ kbar}^{-1}$ and $10.9 \text{ cm}^{-1} \text{ kbar}^{-1}$, respectively [3, 14]) are inaccurate. From table 1, they are $-0.0453 \text{ cm}^{-1} \text{ kbar}^{-1}$ and $8.34 \text{ cm}^{-1} \text{ kbar}^{-1}$, respectively. In particular, the result for the rate of change in B given by [3] is a factor of about 5 larger than the result from table 1 (noting that the U and Y bands are insensitive to B). Using the inaccurate rate of change in B given by [3], therefore, Sharma and Gupta [14] obtained the red shift of R lines which is a factor of about 5 larger than the observed value. Similarly, because of the approximation of the calculation (see equation (12) in [13]) and data in [13] the result that C remains constant while B decreases with increasing pressure was given. This is in contrast with our results. Physically, both B and C are parameters representing the electrostatic interaction between d electrons of Cr^{3+} ; therefore a difference between their pressure dependences should not be expected.

Ohnishi and Sugano [29] pointed out that the dependence of physical parameters (B , C , Dq , etc) upon R (or χ) is one of the main subjects of the optical studies of transition-metal ions in crystals under high pressure. Thus, equations (1)–(4), (13), (14) and (23) demonstrate

the important progress made in the theory; making use of them and diagonalization of the complete energy matrix is very important to obtain good results.

(iii) Finally, we justify the assumption in section 2 and discuss some differences between the theory in [8, 12] and the theory in this work.

When the distance between the central metal ion and the ligands is reduced under pressure, the screening of the nuclear charge of central ion by the overlapping electron clouds from the ligands is enhanced, the effective nuclear charge number 'seen' or experienced by d electrons decreases from $(Z_{\text{eff}})_0$ to $(Z_{\text{eff}})_0\Phi(\chi)$ ($\Phi(\chi) < 1$). With the potential energy $V(r) = -(Z_{\text{eff}})_0\Phi(\chi)e^2/r$, the d-electron wavefunction (as a hydrogen-like wavefunction or a Slater-type orbital or, more generally, an expansion in terms of the Slater-type orbitals) varies with the substitution of $r\Phi(\chi)$ for r . Of course, in order to satisfy the normalization condition, the normalization factor should be changed appropriately. It is worth noting that the relative changes in Dq , B , C , ζ , K and K' depend only on $\Phi(\chi)$ and χ and do not depend on the details of the wavefunction. In fact, in order to prove equations (2)–(4), (13) and (14), we can use the general expression for the wavefunction, which is an expansion in terms of the Slater-type orbitals. In this way, we have justified the assumption in section 2; we see that the key point is the expansion of the electron radial wavefunction (correspondingly, we need only the expansion function $\Phi(\chi)$) and we do not have to introduce two scaling parameters, such as $\Omega(p)$ and $\Lambda(p)$ in [8, 12]. By using $\Phi(\chi)$, we can obtain the changes in Dq , B , C , ζ , K and K' with pressure and calculate the pressure shifts of the entire energy spectrum. Hence, the physical essentials of the pressure shifts of the crystal-field spectra can be microscopically attributed to the expansion of the electron radial wavefunctions when the interionic distance is reduced under compression.

According to Munro [8], $\delta q/q_0 + 1 = q/q_0 = \langle r^4 \rangle / \langle r^4 \rangle_0 = \Omega^{-4}(p)$. Eggert et al [12] gave $\delta\Omega = -0.051$; so $\Omega(p) = 1 + \delta\Omega[1 - V_0/V(p)] > 1$ (Munro [8] also gave $\Omega(p) > 1$), so then $\langle r^4 \rangle < \langle r^4 \rangle_0$. This is contrary to the expansion of wavefunctions under pressure.

Munro [8] considered the charges of ligands as point charges ($-ze$). In view of the shortcomings of the point-charge model, we should consider the effective charge q_{eff} of a ligand ion 'seen' or experienced by d electrons [30, 31] and its change with pressure (see equation (4) [10]), by taking into account the expansion of the electron wavefunctions of the central metal ion and the ligands. We found that, if this effect is not taken into account appropriately, the pressure shifts of the U and Y bands are markedly larger than the experimental data, and this is similar to the results given by Eggart et al [12].

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