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Analysis of the absorption spectrum of ruby at high pressures

Surinder M. Sharma* and Y. M. Gupta

Shock Dynamics Laboratory, Department of Physics, Washington State University, Pullman, Washington 99164-2814

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It is shown that at high pressures, results of absorption measurements are inconsistent with R-line fluorescence data. The observed constancy of R_1-R_2 splitting under hydrostatic conditions is supported by crystal-field analysis. The present findings suggest the need for absorption measurements in ruby crystals under more well-defined stress conditions.

Ruby spectra have been the subject of numerous experimental and theoretical investigations due to the utility of ruby as a laser material and as a high-pressure sensor in diamond anvil cell studies.[1-7] At ambient conditions, various details of the spectrum consisting of multiplets of R, R' and B lines, and U and Y absorption bands can be quantitatively understood with a symmetry-based crystal-field-theory approach.[5,8-10] Significant crystal-field parameters for description of ruby spectrum turn out to be the following.[5] Racah parameters B and C, representing electron-electron repulsion of d electrons of Cr^{3+}; $10Dq$, characterizing the strength of crystal field of octahedral symmetry; V_{trig}, the crystal field of only C_3 point-group symmetry which is the local site symmetry around Cr^{3+} in the corrundum lattice.[11-13] The trigonal field is characterized by the magnitude of two matrix elements of this field (between the bases of symmetry adapted sets $\{t_{2g}\}$ and $\{e_g\}$, namely $v = -3\langle t_{2g}x_+|V_{\text{trig}}|t_{2g}x_+\rangle$ and $v' = \langle t_{2g}x_+|V_{\text{trig}}|e_g u_+\rangle$ as defined by Pryce and Runciman.[14] Fine multiplet structure of energy levels emerges from the simultaneous presence of the trigonal field and spin-orbit interaction and can be explained quantitatively.[5,8,9]

Attempts to understand variations in ruby spectrum due to hydrostatic pressure, in terms of the crystal-field approach, have aimed at broad correlations.[15,16] The fine multiplet structure of lines and bands is completely ignored, thereby approximating the crystal field to have octahedral symmetry only. Variations in crystal-field parameters, in the assumed octahedral symmetry, are represented by two independent "scale parameters,"[15,16] which are determined by the best fit to appropriately averaged experimental data. Such a procedure, by its very nature, overemphasizes the consistency of pressure-dependent changes in the spectrum. For example, over 80% of the measured shift of the Y band (representing a ${}^4T_1 \rightarrow {}^4A_2$ transition) is due to changes in $10Dq$ and, therefore, a considerable variation in the pressure dependence of Racah parameters with pressure will not impair the quality of agreement.

In this paper we analyze the consistency between the pressure variation of the absorption bands,[17] and R_1,R_2 lines[18] in detail, i.e., beyond the octahedral approximation in the crystal-field analysis. The consistency analysis is restricted to this part of the spectrum for two reasons. First, no other lines have such a well-defined spectrum as R lines;[19] second, this restricted analysis suggests the need for experimental measurements of the absorption bands under well-characterized conditions of stress, and with improved statistical precision. An accurate determination of the details of the ruby spectrum at high pressure would permit a detailed crystal-field analysis similar to that performed by Macfarlane[9] at ambient conditions.

The results describing the pressure variation of the absorption spectrum, which enter as input to our calculation, have been taken from the polarized light absorption measurements of Stephens and Drickamer.[17] They measured the absorption bands up to 120 kbar and used a crystal-field description to derive $10Dq$, B, and trigonal field as a function of pressure. These authors assumed that both the bands, viz., U (${}^4T_2$) and Y (${}^4T_1$) split by the same amount $v/2$. Subsequent analysis of Macfarlane[9] showed that the splitting of the Y band is given by $v/2+v'$. Hence, only the experimental results of the U (${}^4T_2$) band should be used to estimate changes in the trigonal field. Further, by comparing the splitting of the U and Y bands, we conclude that variation in v' with pressure, within experimental errors, is zero. The observed variations of absorption bands from Ref. 17 are summarized as follows: (i) the Racah parameter B decreases as $0.205\ \text{cm}^{-1}\,\text{kbar}^{-1}$; (ii) $10Dq$ increases at a rate $10.9\ \text{cm}^{-1}\,\text{kbar}^{-1}$; (iii) the trigonal field parameter v shows little or no change up to ≈ 75 kbar, beyond which it increases rapidly. We now use these results to calculate the variations in R_1,R_2 lines with pressure. The calculation of the red shift is followed by the calculation for R-lines splitting.

Reduction in the Racah parameter B with pressure implies a red shift of the R lines and is, therefore, in qualitative agreement with experimental observations.[18] If there is no change in the trigonal field with pressure, then the rate of the red shift with pressure can be deduced by diagonalizing the 4×4 matrix representing Coulomb interaction.[5] With the above-mentioned observed values,[17] the red shift of R lines is given by $4.26\ \text{cm}^{-1}\,\text{kbar}^{-1}$ (assume that $C/B = 5.1245$ to get the position of R lines at ambient conditions). This is to be compared with the measured[18] red shift of $0.76025\ \text{cm}^{-1}\,\text{kbar}^{-1}$; this is smaller by a factor of 5 when compared to the calculated shift. A calculation based on sensitivity analysis, after Macfarlane,[9] which includes configuration interaction, confirms that the calculated red shift is about a factor of

5 larger than the observed value. This implies that the variation of the Racah parameter, obtained from absorption experiments, is in significant disagreement with the red shift of the R lines.

As pointed out earlier, coexistence of the trigonal field and spin-orbit interaction bring about splitting of ^2E giving rise to the R_1,R_2 lines. Within second-order perturbation theory, the splitting between R_1,R_2 lines can be written as

$$\Delta(R_1-R_2)=\frac{\frac{4}{3}v\zeta}{\epsilon(^2T_2)-\epsilon(^2E)}\ , \tag{1}$$

where ζ represents the strength of the spin-orbit interaction. Equation (1) can be used to predict the change in splitting with changes in the trigonal field. We shall assume that spin-orbit interaction does not change with pressure—an approximation that is consistent with an analysis of the lifetime variation of the R_1 line with pressure.[20] Alternatively, we can use the following result due to Macfarlane[21] to evaluate the changes in R-line splitting due to variations in the trigonal field:

$$\Delta(R_1-R_2)=D_0-0.027v_p-0.008v_p'\ . \tag{2}$$

Here, D_0 represents splitting at $P=0$, and v_p and v_p' are pressure-dependent changes in v and v'. For the same input, Eq. (1) gives a larger splitting than Eq. (2) and so we term the results of Eq. (1) as upper bound and that of Eq. (2) as lower bound. In principle, Eq. (2) should be more accurate, as it includes configuration interaction. We have used both equations because experimental results[19] of relative movements of R and R' lines do not confirm the predictions of Macfarlane's calculation.[9]

We now calculate the R-line splitting due to the trigonal field changes, reported on the basis of the absorption measurements.[17] We take $\epsilon(^2T_2)-\epsilon(^2E)$ from Ref. 9 and $\zeta=186.1\ \text{cm}^{-1}$ to reproduce R-line splitting at ambient pressure. Results for a few representative pressures are given in Table I.

Therefore, the absorption data of Stephens and Driackmer[17] imply no change in splitting up to about 75 kbar and then a large change. At 120 kbar, the splitting increases by approximately 30% compared to that at 75 kbar. However, the experimental results for R lines, consisting of 38 sets of data up to 150 kbar, tested for statistical consistency,[18] are incompatible with the results above 75 kbar. The experimentally observed rate of change of splitting is[18] $0.0025\pm0.004\ \text{cm}^{-1}\,\text{kbar}^{-1}$. This result implies that within the experimental accuracy there is no change in splitting up to 150 kbar, in contrast to the results shown in Table I.

Experimental results of R lines, aside from better precision and mutual statistical compatibility,[18] are also consistent with crystal-field analysis as shown below. We use the point-ion approximation to estimate changes in the crystal field. Although this approximation is known to be inadequate for calculation of crystal-field parameters at ambient conditions,[10,22] it gives a reasonable estimate of stress-induced changes.[21,23,24]

As the site symmetry of Cr^{3+} site is C_3, the potential function for an electron can be written[3] as

$$\begin{aligned}V={}&B_0^0+B_1^0r\cos\theta+B_2^0r^2(3\cos^2\theta-1)+B_3^0r^3(5\cos^3\theta-3\cos\theta)+B_3^3r^3\sin^3\theta\cos3\phi+C_3^3r^3\sin^3\theta\sin3\phi\\&+B_4^0r^4(35\cos^4\theta-30\cos^2\theta+3)+B_4^3r^4\sin^3\theta\cos\theta\cos3\phi+\cdots\ ,\end{aligned} \tag{3}$$

where B_n^m and C_n^m are the lattice sums over real and imaginary part of functions of the type $(j/R^{n+1})Y_{lm}$ as defined and calculated by McClure[3] at ambient conditions (the constant j depends on the position of the atom with respect to the symmetry axis and R represents lattice vectors).

The trigonal field parameters v and v' can now be represented in terms of B_n^m as follows:[3,23]

$$v=\tfrac{6}{7}B_2^0\langle r^2\rangle+\tfrac{160}{63}\left[B_4^0+\frac{B_4^3}{20\sqrt{2}}\right]\langle r^4\rangle\ , \tag{4}$$

$$v'=\frac{-2\sqrt{2}}{7}B_2^0\langle r^2\rangle+\frac{40\sqrt{2}}{63}\left[B_4^0+\frac{B_4^3}{20\sqrt{2}}\right]\langle r^4\rangle\ . \tag{5}$$

We assume that hydrostatic pressure results in an isotropic compression of the rhombohedral cell[25–28] of ruby and that all interatomic distances change uniformly and proportionally to unit cell dimensions a. This assumption seems to be reasonable up to $\approx3\%$ compression (≈100 kbar).[29] Then it can be shown that $\delta B_n^m/B_n^m=(n+1)\delta a/a$ for small $\delta a/a$. Such an approximation gives reasonable agreement with experiments.[30] The changes in v and v' under pressure can then be written as follows:

$$\delta v=-\frac{\delta a}{a}\left[\tfrac{18}{7}B_2^0\langle r^2\rangle+\tfrac{800}{63}\langle r^4\rangle\left[B_4^0+\frac{B_4^3}{20\sqrt{2}}\right]\right]\ , \tag{6}$$

$$\delta v'=\frac{\delta a}{a}\left[\frac{6\sqrt{2}}{4}\langle r^2\rangle B_2^0-\frac{200\sqrt{2}}{63}\langle r^4\rangle\left[B_4^0+\frac{B_4^3}{20\sqrt{2}}\right]\right]\ . \tag{7}$$

TABLE I. Variation in R_1-R_2 splitting due to observed (Ref. 17) changes of the trigonal field. Equation (1) gives the upper bound and Eq. (2) gives the lower bound.

Pressure (kbar)	Upper bound (cm^{-1})	Lower bound (cm^{-1})
0	29.6	29.6
↓		
75	29.6	29.6
92	33.4	32.4
102	36.4	34.6
120	39.7	37.0

Taking

$$\langle r^4\rangle/\langle r^2\rangle=3.0732 \tag{8}$$

as estimated by Schawlow *et al.*,[24] from Hartree-Fock solutions for a free Cr^{3+} ion, we get

$$\delta v=\frac{\delta a}{a}\langle r^2\rangle 0.101\,803\ , \tag{9}$$

$$\delta v'=\frac{-\delta a}{a}\langle r^2\rangle 0.256\,326\ . \tag{10}$$

Equations (9) and (10) give a negative δv and a positive $\delta v'$ consistent with earlier conclusions.[21] Substituting these values in Eq. (2) gives

$$\Delta(R_1-R_2)=D_0+6.981\times10^{-4}\langle r^2\rangle\frac{\delta a}{a}\ . \tag{11}$$

For ruby $\delta a/a=-1.28\times10^{-4}P$, where P is pressure in kbar.[25-27] This gives a splitting of

$$\Delta(R_1-R_2)=D_0-C_1P\ , \tag{12}$$

where $C_1=8.935\times10^{-8}\langle r^2\rangle$ eV kbar^{-1}. The value of $\langle r^2\rangle$ has been estimated to be 0.4048 A^2 with Hartree-Fock wave function and 1.38 A^2 with Slater's wave function by Schawlow *et al.*[24] These give $[C_1]_{HF}=2.92\times10^{-4}$ cm^{-1} kbar^{-1} and $[C_1]_{Slater}=9.95\times10^{-4}$ cm^{-1} kbar^{-1}, implying that the splitting changes at the rate 0.001 cm^{-1} kbar^{-1} or less and is negligible. This finding is consistent with observed results. At compressions larger than 3%, local compressibility around Cr^{3+} may be smaller than the bulk compressibility[29] of Al_2O_3. Then the above analysis would give an upper limit on variation of trigonal field within the point ion approximation.

On the basis of the above analysis, we conclude that the R-line data are consistent with the crystal-field model. The high-pressure, absorption results reported in Ref. 17 are not consistent with R-line data on both counts—the red shift as well as splitting of R_1,R_2 lines. However, the splitting results are consistent to 75 kbar. We conjecture that the inconsistency between the absorption and the R-line results may arise, in part, due to the possibility of nonhydrostatic stresses. It is known that nonhydrostatic stresses due to either uniaxial stress[31] or uniaxial strain[32] bring about changes in the trigonal field. Hence, the existence of nonhydrostatic stresses beyond 75 kbar in the experimental configuration used in Ref. 17 may explain the increase in the trigonal field. Experimental data are needed to verify this conjecture. In addition, to accurately determine the adequacy of the crystal-field description for modeling ruby spectrum at high pressures, there is a need for high-precision absorption data under well-defined hydrostatic pressures.

Before concluding, we would like to make another observation. Ma *et al.*[16] assume an effective interaction between ^2E and $^2T_1$ states which is an increasing function of trigonal field. To explain the experimental observations of the relative shift of the R and R' lines they require a large variation of the trigonal field with pressure. This is in contrast with our conclusion that the trigonal field does not change significantly with hydrostatic pressure. Therefore, the assumed interaction of Ma *et al.*[16] requires a reconsideration. In fact, V_{trig} does not couple the ^2E and $^2T_1$ states to the first order.[1,5] Significant configuration interaction is through $^2T_2$ and is, therefore, second order in perturbation. Ma *et al.*[16] require a fairly strong interaction between ^2E and $^2T_1$ states and, further, it needs to increase rapidly with pressure. We feel that such an effective interaction actually emerges because of increased mixing of oxygen p orbitals with that of Cr^{3+} d orbitals.[33] Such a mixing is expected to be mainly responsible for the removal of accidental degeneracy of ^2E and $^2T_1$ levels which exists within first-order perturbative treatment with d orbitals.[5] The same could well be the cause of disagreement of observed sensitivity of R' lines[19] with crystal-field theoretical predictions.[9]

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*Permanent address: Neutron Physics Division, Bhabha Atomic Research Centre, Bombay 400 085, India.

[1] S. Sugano and Y. Tanabe, J. Phys. Soc. Jpn. **13**, 880 (1958).

[2] A. L. Schawlow, in *Advances in Quantum Electronics*, edited by T. R. Singer (Columbia University Press, New York, 1961), p. 50.

[3] D. S. McClure, J. Chem. Phys. **36**, 2757 (1962).

[4] D. C. Cronemeyer, J. Opt. Soc. Am. **56**, 1703 (1966).

[5] S. Sugano, Y. Tanabe, and H. Kamimura, *Multiplets of Transition Metal Ions in Crystal* (Academic, New York, 1970).

[6] R. A. Forman, G. J. Piermarini, J. D. Barnett, and S. Block, Science **176**, 284 (1972).

[7] A. Jayaraman, Rev. Mod. Phys. **55**, 65 (1983).

[8] S. Sugano and M. Peter, Phys. Rev. **122**, 381 (1961).

[9] R. M. Macfarlane, J. Chem. Phys. **39**, 3118 (1963).

[10] D. E. Rimmer and D. F. Johnson, Proc. Phys. Soc., London **89**, 943 (1966).

[11] R. W. G. Wyckoff, *Crystal Structures* (Interscience, New York, 1948), Chap. VA, p. 6.

[12] S. C. Moss and R. E. Newnham, Z. Kristallogr. **120**, S. 359 (1964).

[13] J. W. McCauley and G. V. Gibbs, Z. Kristallogr. **135**, S. 453 (1972).

[14] M. H. L. Pryce and W. A. Runciman, Discuss. Faraday Soc. **26**, 34 (1958).

[15] R. G. Munro, J. Chem. Phys. **67**, 3146 (1977).

[16] D. Ma, J. Chen, and Z. Wang, Phys. Lett. A **126**, 377 (1988).

[17] D. R. Stephens and H. G. Drickamer, J. Chem. Phys. **35**, 427 (1961).

[18] R. G. Munro, G. J. Piermarini, S. Block, and W. B. Holzapfel, J. Appl. Phys. **57**, 165 (1985).

[19] R. A. Forman, B. A. Weinstein, and G. Piermarini, *Proceedings of Colloques. Internationaux Centre National de la Recherche Scientifique*, Vol. 255 of *Spectroscopie des Elements de Transition et des Elements Lourds Daus Les Solides, Lyon, France, 1976* (CNRS, Paris, 1977), p. 51.

[20] Surinder M. Sharma and Y. M. Gupta, Appl. Phys. Lett. **54**, 84 (1989).

[21] R. M. Macfarlane, Phys. Rev. **158**, 252 (1967).

[22] S. Sugano and R. G. Schulman, Phys. Rev. **130**, 517 (1963).

[23] G. E. Stedman, J. Chem. Phys. **50**, 1461 (1969).

[24] A. L. Schawlow, A. H. Piksis, and S. Sugano, Phys. Rev. **122**, 1469 (1961).

[25] H. d'Amour, D. Schiferl, W. Denner, H. Schulz, and W. B. Holzapfel, J. Appl. Phys. **49**, 4411 (1978).

[26] L. W. Finger and R. M. Hazen, J. Appl. Phys. **49**, 5823 (1978).

[27] Y. Sato and S. Akimoto, J. Appl. Phys. **50**, 5285 (1979).

[28] T. Kottke and F. Williams, J. Appl. Phys. **54**, 6749 (1983).

[29] R. Goto, T. J. Ahrens, and G. R. Rossman, Phys. Chem. Miner. **4**, 253 (1979).

[30] If we use this result to calculate changes in $10Dq$ then we get $\delta(10Dq)/10Dq=\delta D/D=5(\delta R/R)$. From Ref. 15 we know that this is more than 97% of the change in $10Dq$.

[31] Elsa Feher and M. D. Sturge, Phys. Rev. **172**, 244 (1968).

[32] P. D. Horn and Y. M. Gupta, Phys. Rev. B **39**, 973 (1989).

[33] Xu Jian and Zhao Minguang, Sci. Sin. **XXIV**, 721 (1981).