

## Pressure shift of $\text{Cr}^{3+}$ -ion-pair emission lines in ruby

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The shifts of the  $N_1$  (3A2),  $N_2$  (4A1), {4C2, 4D2, 4E2}, and 4F1 near-neighbor  $\text{Cr}^{3+}$ -pair emission lines in ruby [see P. Kisliuk *et al.*, Phys. Rev. **184**, 367 (1969), for notation] have been measured under hydrostatic pressure up to 11 GPa. With increasing pressure, all near-neighbor pair lines shift to lower energy at rates between  $-7.4$  and  $-10.3 \text{ cm}^{-1}/\text{GPa}$ . These shifts are larger than, or approximately equal to, that of the isolated- $\text{Cr}^{3+}$ -ion  $R$  lines ( $-7.53 \text{ cm}^{-1}/\text{GPa}$ ), and therefore near-neighbor pair lines are not expected to overlap the  $R$  lines used in the calibration of hydrostatic high-pressure experiments. Our results demonstrate that hydrostatic pressure shifts of the near-neighbor pair lines are not accurately modeled by an elastic-constant analysis of shifts measured under uniaxial stress. We evaluate our data in terms of Munro's scaling-theory model, and find our results to correspond to a pressure shift of the orbital exchange parameter of  $dJ/dP = 3 \times 10^{-2} \text{ cm}^{-1}/\text{GPa}$ .

### INTRODUCTION

In the fluorescence spectrum of ruby, the relatively intense isolated- $\text{Cr}^{3+}$ -ion  $R_1$  and  $R_2$  lines are accompanied by nearby lines which have been assigned to two separate phenomena: (1) neighbor-neighbor interactions between exchange-coupled  $\text{Cr}^{3+}$  pairs,<sup>1-3</sup> and (2) phonon-shifted vibronic peaks. For the near-neighbor  $\text{Cr}^{3+}$ -ion-pair lines, Munro<sup>4</sup> has made a theoretical prediction, using a scaling-theory model, of the value of the shift with pressure of the exchange integral  $J$ . The purpose of this study, therefore, was to measure the hydrostatic pressure shifts of the most intense near-neighbor pair lines in heavily doped ruby in order to draw a more accurate constraint on  $dJ/dP$ . For comparison, the effect of uniaxial stress on near-neighbor pair lines has previously been documented.<sup>5-7</sup> Also, one other study has been made of the hydrostatic pressure shift of near-neighbor pair lines, but in lower- $\text{Cr}^{3+}$ -concentration ruby (0.03 at. %  $\text{Cr}^{3+}$ ).<sup>8</sup>

### EXPERIMENTAL PROCEDURE

Synthetic ruby, with 5000 ppm  $\text{Cr}^{3+}$  nominal concentration, was used in these experiments. Identical results were obtained from the three sets of samples, obtained from Barksowski International Corporation (Charlotte, N.C.), from the Carnegie Institution Geophysical Laboratory (Washington D.C.), and from Union Carbide Corporation. Ruby with a concentration of 5000 ppm  $\text{Cr}^{3+}$  was selected because the near-neighbor pair lines are plainly visible in its fluorescence spectrum. Also, this concentration ruby is commonly used for calibration in high-pressure experiments. For the  $N_1$  near-neighbor pair line, there is some overlap with the high-energy edge of the vibronic line whose peak is at  $14133 \text{ cm}^{-1}$ .

Single ruby chips, 10–40  $\mu\text{m}$  in diameter, and not more than 10  $\mu\text{m}$  in thickness, were loaded into a gasketed diamond cell,<sup>9,10</sup> with a 4:1 methanol-ethanol mixture used as a hydrostatic-pressure medium. Pressure was calibrated by the  $R_1$  shift with an uncertainty of 0.1 GPa. If pinning of the sample between the two diamonds or spectral broadening of the  $R$  lines (indicative of a nonhydrostatic stress com-

ponent)<sup>11</sup> was observed, results were discarded. All runs were performed at ambient temperature. At low temperatures, the methanol-ethanol solution is expected to become nonhydrostatic at lower pressures than the 10–12-GPa hydrostatic limit at 290 K.

Samples were excited with use of a 13-mW He-Cd laser, and spectra were collected with a GaAs detector coupled to a  $\frac{1}{4}$ -m monochromator with a 300-g/mm echelle grating.<sup>12</sup> The monochromator was used in eighth order and calibrated with Ne emission lines, and He-Cd and He-Ne laser lines. Spectral resolution was estimated to be  $\pm 2 \text{ cm}^{-1}$  for the relatively sharp neighbor lines but resolution of the broader vibronic band was estimated to be  $\pm 4 \text{ cm}^{-1}$ . Judging from the temperature-dependent zero-pressure position of the  $R_1$  line, the 13-mW He-Cd laser used for excitation heated the sample by less than  $10^\circ\text{C}$ .

### RESULTS AND DISCUSSION

The separation from  $R_1$  of the four strongest near-neighbor pair lines and the nearby vibronic line are plotted in Fig. 1 as a function of pressure; the data are summarized in Table I. To within the experimental resolution, all near-neighbor-pair-line shifts are linear with pressure, and all but 4F1 have shifts greater than that of  $R_1$ . As 4F1 shifts nearly at the same rate as  $R_1$ , no superposition of lines will occur at high pressures. A small component of the broadening in  $R_1$  observed at ultrahigh pressures (see Ref. 13, for example) may, however, be due to the presence of near-neighbor pair lines on, or beneath, the leading (low-energy) edge of  $R_1$ .

The notation used in identifying the near-neighbor pair lines is that of Kisliuk, Chang, Scott, and Pryce,<sup>3</sup> in which the first digit indicates the set of near neighbors (e.g, third or fourth) to which the pair line belongs; the letter is the designation of the excited-state level of the line, and the last numeral is the ground-state spin of the ion pair. Although their data were taken at 77 K, the temperature shift of the principal near-neighbor pair lines ( $N_1$  and  $N_2$ , or 3A2 and 4A1) is well documented<sup>14</sup> and correlations can readily be drawn between our data and those of Kisliuk *et al.* The one vibronic line measured in our experiments corresponds well

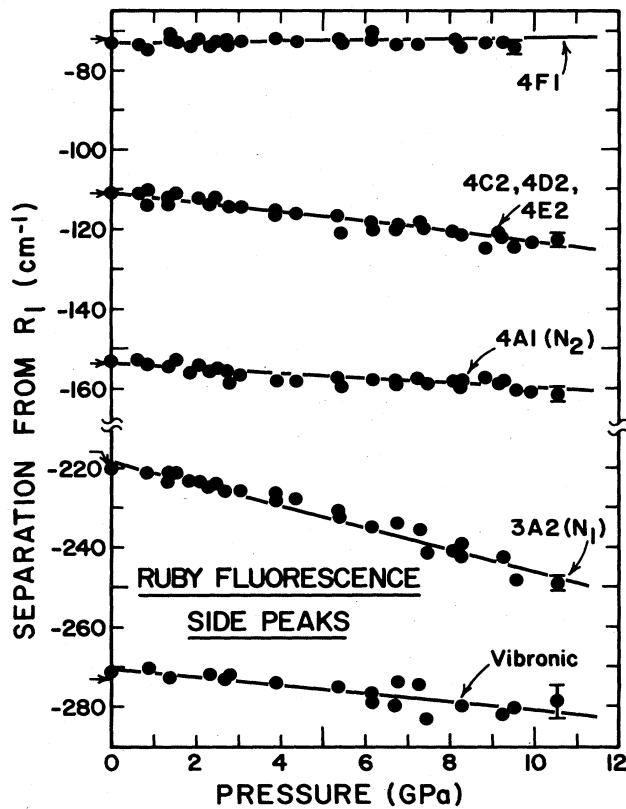


FIG. 1. Separation of ruby near-neighbor-pair-line peaks from  $R_1$  as a function of pressure at room temperature. Representative uncertainties are indicated on the highest pressure point for each peak, and the accepted zero-pressure values are shown by arrows (Ref. 8).

with that observed by Merkle, Spain, and Powell.<sup>8</sup> The location of the vibronic line does not correspond with any corundum vibrational modes observed in either Raman<sup>15</sup> or infrared reflection spectra,<sup>16</sup> although evidence of low-frequency vibrations has been reported in the visible absorption spectra of transition-metal-doped corundum,<sup>17</sup> and in an early infrared investigation of ruby.<sup>18</sup> The mode Grüneisen parameter, computed using a bulk modulus of 251.1 GPa,<sup>19</sup> is  $1.0 (\pm 0.4)$ , a value which is in accord with

the high-temperature thermodynamic value of 1.32.

The line observed at  $14293 \text{ cm}^{-1}$  at zero pressure is identified as a manifold of  $4C2$ ,  $4D2$ , and  $4E2$ , which at 77 K are separated by  $4 \text{ cm}^{-1}$  and are of approximately equal intensities.<sup>3</sup> The lack of resolution of these lines is probably due to thermal broadening of the linewidth. No splitting and a minimal broadening of this line are observed with pressure, and so it can be concluded that the  $4C$ ,  $4D$ , and  $4E$  levels of the excited near-neighbor pair states have, to within the resolution of the experiment, identical pressure shifts. As these lines correspond to the same eigenvalue of the excited-state exchange Hamiltonian, split by the crystal anisotropy,<sup>20</sup> the nearly identical pressure dependencies are not surprising.

An estimate of the hydrostatic pressure shift of near-neighbor pair lines was made by Kaplyanskii, Przhvuski, and Rozenbaum,<sup>21</sup> for  $N_1$  and  $N_2$ , based on an elastic-constant analysis of data collected under uniaxial stress. Their calculated values of  $-14.1$  and  $-10.7 \text{ cm}^{-1}/\text{GPa}$  for  $3A2 (N_1)$  and  $4A1 (N_2)$ , respectively, differ substantially from our values of  $-10.3$  and  $-8.1 \text{ cm}^{-1}/\text{GPa}$ , illustrating that the effect of hydrostatic stress on the anisotropic excited-pair interaction is not accurately extrapolated from the effects of uniaxial stress.

The pressure shifts of the near-neighbor pair lines are a combination of two separate phenomena: changes in the ground-state energy levels and changes in the excited-state energy levels. Both involve exchange between  $3d$ -type orbitals: the former between two  $^4A_{2g}$  states, and the latter between an  $^4A_{2g}$  state and an  $^2E_g$  state. The ground-state energy is expressed as<sup>5</sup>

$$E = \frac{-15}{4}J + \frac{J}{2}S(S+1), \quad (1)$$

where  $J$  is an orbital exchange parameter and  $S$  the total spin of the ion pair.

Naito<sup>20</sup> has described the energies of the  $4A$  and  $4F$  excited levels as

$$E(1) = R' - 5J/4 \pm N - |5L \pm K| + E_{\text{an}}, \quad (2)$$

where  $+$  is the  $4F$  level and  $-$  the  $4A$  level, and that of the  $4C, D, E$  levels as

$$E(2) = R' + 3J/4 + 3N - |3L - 3K| + E_{\text{an}}. \quad (3)$$

$R'$  is the energy difference between the  $^2E$  and  $^4A_2$  states in

TABLE I. Pressure shifts of the near-neighbor pair lines, with shifts relative to  $R_1$  (column 4) and shifts determined by Merkle, Spain, and Powell (column 5).

Location ( $\text{cm}^{-1}$ )	Identification	$dv/dP$ ( $\text{cm}^{-1}/\text{GPa}$ )	$[dv - dv(R_1)]/dP$ ( $\text{cm}^{-1}/\text{GPa}$ )	$dv/dP$ (Ref. 8) ( $\text{cm}^{-1}/\text{GPa}$ )
14404	$R_1$	$-7.53 (\pm 0.05)^a$		
14330	$4F_1$	$-7.4 (\pm 0.15)$	$+0.1 (\pm 0.2)$	$-8.2 (\pm 0.3)$
14293	$\{4C2, 4D2, 4E2\}$	$-8.8 (\pm 0.12)$	$-1.3 (\pm 0.2)$	$-8.8 (\pm 0.3)$
14249	$4A1 (N_2)$	$-8.1 (\pm 0.12)$	$-0.6 (\pm 0.2)$	$-8.7 (\pm 0.3)$
14183	$3A2 (N_1)$	$-10.3 (\pm 0.15)$	$-2.8 (\pm 0.2)$	$-10.8 (\pm 0.3)$
14133	Vibronic	$-8.6 (\pm 0.3)$	$-1.1 (\pm 0.35)$	$-8.6 (\pm 0.4)$

<sup>a</sup>References 10 and 22.

a singly excited pair (i.e., the average energy of the  $R$  line transition for a  $\text{Cr}^{3+}$  with a neighboring  $\text{Cr}^{3+}$  ion).  $E_{\text{an}}$  is a pair anisotropy energy induced by spin-orbit interaction, and  $J$ ,  $N$ ,  $L$ , and  $K$  are expressed in terms of exchange integrals as follows:

$$J = \frac{1}{9} \sum_{j,k} J_{1j,2k} \quad (4a)$$

$$K = \frac{1}{18} \sum_{j,k} \omega^{-j+k} J_{1j,2k} \quad (4b)$$

$$L = \frac{1}{18} \sum_{j,k} \omega^j J_{1j,2k} \quad (4c)$$

$$N = \frac{1}{18} \sum_{j,k} \omega^{-j-k} J_{1j,2k} \quad (4d)$$

where  $\omega = \exp(\frac{2}{3}\pi i)$ , and  $i$  and  $j$  assume the values 1, 2, and 3, which refer, respectively, to the three  $t_{2g}$  single-ion orbitals  $d_{yz}$ ,  $d_{zx}$ , and  $d_{xy}$  (or  $\epsilon$ ,  $\eta$ , and  $\zeta$ ). Naito<sup>20</sup> has found values for the six interorbital exchange integrals of  $J_{1\epsilon,2\epsilon} = -36.4 \text{ cm}^{-1}$ ,  $J_{1\zeta,2\zeta} = 57.0 \text{ cm}^{-1}$ ,  $J_{1\epsilon,2\epsilon} = 96.9 \text{ cm}^{-1}$ ,  $J_{1\epsilon,2\zeta} = 77.7 \text{ cm}^{-1}$ ,  $J_{1\epsilon,2\zeta} = -4.3 \text{ cm}^{-1}$ , and  $J_{1\eta,2\epsilon} = -392.1 \text{ cm}^{-1}$ .

To obtain a value for the shift in frequency with pressure of the near-neighbor pair lines, we assume a constant value for  $J^{-1}dJ/dP$ .<sup>4</sup> Thus, the value of each  $J_{i,j}$  at a selected high pressure (10 GPa) may be calculated. Equations (4a)–(4d) may then be used to solve for the respective high-pressure values of  $J$ ,  $N$ ,  $|L - K|$ ,  $|5L + K|$ , and  $|5L - K|$ . From these values, and Eqs. (1)–(3), the actual shifts of the near-neighbor pair lines can then be estimated by assuming that the pressure shift of  $R'$  is equal to that of  $R$ , the single-ion  ${}^2E \rightarrow {}^4A_{2g}$  transition,  $-7.53 \text{ cm}^{-1}/\text{GPa}$ .<sup>11,22</sup> The chief discrepancy in value between  $R'$  and  $R$  is due to the charge-charge interaction between the two

ions, estimated by Naito<sup>20</sup> to be  $\sim 20 \text{ cm}^{-1}$ . The magnitude of this interaction should vary as the reciprocal of the square of the interionic distance; for the maximum change in volume of our experiments ( $\sim 4\%$ ), the pressure-induced change in this parameter should be not more than 2.5%, or about  $0.5 \text{ cm}^{-1}$ . We also assume that the pressure shift of  $E_{\text{an}}$ , the anisotropy energy, is negligible. It has been shown that the separation of  $R_1$  and  $R_2$  (an energy corresponding to the single-ion anisotropy energy) undergoes only a very slight decrease with pressure of  $> 0.1 \text{ cm}^{-1}/\text{GPa}$ .<sup>23</sup> By analogy with the single ion, therefore, it is unlikely that the anisotropy energy has a significant pressure dependence.

Thus, the absolute shift with pressure of the near-neighbor-pair-line energy may be calculated, as a function of  $dJ/dP$ . We find the greatest consistency (using a least-squares criterion) between values obtained from the above approach and our data to be produced for  $J^{-1}dJ/dP = 4 \times 10^{-3} \text{ GPa}^{-1}$ , or  $dJ/dP = -0.028 \text{ cm}^{-1}/\text{GPa}$ . For the data of Merkle *et al.*<sup>8</sup> (listed in the last column of Table I) we find the most consistent value of  $J^{-1}dJ/dP = 7 \times 10^{-3} \text{ GPa}^{-1}$ , or  $-0.049 \text{ cm}^{-1}/\text{GPa}$ . Both values lie beneath Munro's value of  $0.01 \text{ cm}^{-1}/\text{GPa}^{-1}$  for the fourth-nearest-neighbor pair  $J^{-1}dJ/dP$ , but within his estimated uncertainty of an order of magnitude.

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