Pressure dependence of the alexandrite emission spectrum

T. Kottke and F. Williams

Physics Department, University of Delaware, Newark, Delaware 19711

(Received 27 December 1982)

The dependence on hydrostatic pressure of the photoluminescent spectrum of alexandrite has been measured to 40 kbar, at 300 and 167 K. The R_1 and R_2 lines red shift linearly 0.27 ± 0.01 and 0.33 ± 0.01 Å/kbar, the same for both temperatures. Narrowing of the R lines with pressure is observed. The phonon sidebands are blue shifted with pressure. By analysis of these spectral shifts we calculate the anharmonicities of the $^4A_2$ and ^2E states and explain the line narrowing. Thus from these analyses we propose that the linear dependency of the R-line transition energies on hydrostatic pressure results from anharmonic effects on the zero-point levels of the $^4A_2$ and ^2E states, for Cr^{3+}-doped materials in general.

I. INTRODUCTION

Alexandrite, $BeAl_2O_4$:Cr^{3+}, has recently been studied as the active lasing medium for broadly tunable lasers.[1] The Cr^{3+} ions enter the orthorhombic alexandrite structure predominantly by substitution at mirror symmetry Al sites. Such aluminum sites are surrounded by approximately hexagonally close-packed oxygen ions with the Cr^{3+} being displaced from the central position of this octagon of oxygen ions.[2] Interatomic distances between Cr^{3+} ions at Al mirror symmetry sites and nearest-neighbor oxygen ions range from 1.71 to 2.14 Å.[3] The pressure dependence of the emission spectrum of chromium-doped ruby has been extensively studied[4,5] and offers a convenient comparison with that of alexandrite. The Cr^{3+} ions in ruby are also surrounded by an approximately octahedral arrangement of O^{2-} ions with the Cr^{3+} ion being located closer to the central position of the O ions.

We have studied the alexandrite emission spectrum at hydrostatic pressures up to 40 kbar at both room temperature and 167 K. Spectral changes are noted for the R lines, which arise from ^2E to $^4A_2$ transitions, and the high- and low-energy sidebands associated with these R-line transitions. Major emphasis is placed on explaining the linear shifts of the R lines with applied hydrostatic pressure, with various pressure models being considered. The role that anharmonic forces can have in affecting the pressure dependence of fluorescence spectra is used in interpreting the experimental results. The changes in local phonon modes with pressure for the ^2E and $^4A_2$ states are obtained from analysis of the shifts of the zero-phonon lines and phonon sidebands. These changes in local modes are used to explain the R-line narrowing with pressure.

II. EXPERIMENTAL

Crystals of alexandrite used in this investigation were obtained from Allied Corporation and were doped with 0.2 at. % chromium with respect to aluminum concentration. High-pressure measurements were made using a diamond anvil pressure cell utilizing a metal gasket and 4:1 methanol-ethanol pressure transmitting fluid to obtain a hydrostatic environment. Pressures were determined by monitoring the spectral shifts of the R lines from a ruby chip that was included in the pressure chamber. The alexandrite samples were optically excited with the use of the 514.4-nm line from an argon-ion laser with excitation intensities below 0.1 W to avoid sample heating. Fluorescence spectra were resolved using a Spex 1702 three-quarter meter monochromator and detected with a Hamamatsu R446 photomultiplier tube. For high-pressure measurements at reduced temperatures, the diamond anvil pressure cell was cooled with the use of chilled nitrogen gas with type-K thermocouples for temperature monitoring. Pressure measurements were specifically performed at 167 K, at which temperature the pressure dependence of ruby has been calibrated.[6]

III. RESULTS

Figure 1 shows the general pressure-dependent characteristics of the alexandrite emission spectrum at room temperature. With the application of hydrostatic pressure, the relative intensity and structure of the high-energy sideband are enhanced, while the relative intensity of the low-energy sideband decreases. The structure of the high-energy sideband is due to $^2T_1$ to $^4A_2$ transitions and R-line anti-Stokes transitions (phonon annihilation replicas), as
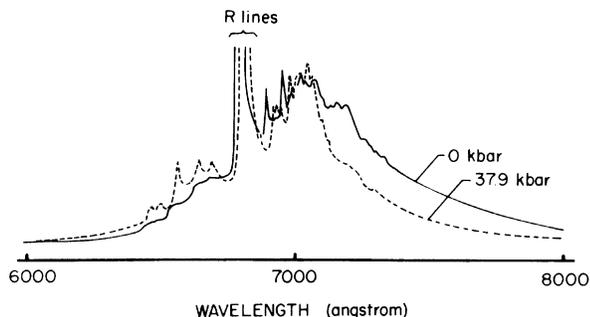
FIG. 1. Luminescent spectra of alexandrite without and with hydrostatic pressure.

FIG. 3. Full width at half maximum of R lines vs hydrostatic pressure.

with ruby. Spectral shifts of the R lines with applied hydrostatic pressure are also evident in this figure. On the low-energy side of the R lines there are pair lines and then a continuum of phonon creation replicas. From these sidebands a phonon density of states can be determined, as will be discussed later.

The red shifts of the R lines with pressure at room temperature and 167 K are shown quantitatively in Fig. 2. At both temperatures the R-line spectral positions are linearly shifted with applied hydrostatic pressure over the pressure range 0–40 kbar. The pressure coefficients of the R_1 and R_2 lines at room temperature are 0.27±0.01 and 0.33±0.01 Å/kbar, respectively. To within the accuracy of the measurements, these pressure coefficients are unchanged at 167 K. The difference between the pressure coefficients of the R lines in alexandrite is in contrast to the ruby system, where both R lines exhibit the same pressure coefficient of 0.36 Å/kbar. This difference between the pressure dependence of the R lines for these two chromium-doped systems may be due to the fact that the chromium site in alexandrite is displaced farther from the central position of the surrounding oxygen ions than in ruby, or to alexandrite's greater compressibility. With the application of pressure, the chromium in
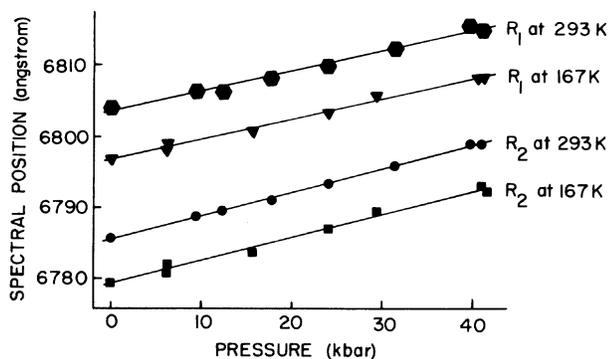
alexandrite is probably displaced more towards the central position of the surrounding oxygen ions than is the corresponding chromium site in ruby at the same pressure. The lower-symmetry nonoctahedral crystal field which causes the splitting of the chromium R line is therefore reduced at the alexandrite chromium site with the result that the spectral separation between the two R lines decreases with increasing pressure.[7]

The application of hydrostatic pressure decreases the observed linewidths of the R lines. Figure 3 shows the pressure dependences of the linewidth of the alexandrite R_1 and R_2 lines.

IV. THEORETICAL

Various models are considered as possible explanations of the linear pressure dependence of the alexandrite R lines. These models include existing pressure theories that make use of the harmonic approximation, consideration of the effects of anharmonic forces on the equilibrium position energies, consideration of the effects of anharmonic forces on zero-phonon-level energies, and multiple configuration coordinate models.

A number of pressure theories exist which make use of the harmonic approximation.[8-11] These are mainly focused at broadband spectra, for which a linear pressure dependence of peak transition energy exists. The broadband spectra are the envelope of vibronic spectra which have changes in both transition energies and intensities with pressure. For spectra with well-resolved vibronic spectra, the changes in transition energies and intensities can be separated. Thus the change in transition energies with hydrostatic pressure, for example, of zero-phonon lines such as R lines, can be considered in the harmonic

FIG. 2. Wavelengths of spectral maxima of R lines vs hydrostatic pressure.

approximation rather simply, as follows: When pressure is applied quasistatically against harmonic crystal forces, the work added is quadratic in the pressure and thus the zero-phonon transition which involves levels tied to the minima of the quasistatic potentials for the excited and ground electronic states has no linear but only quadratic pressure dependence. Therefore, the linear shifts with hydrostatic pressure of the alexandrite R lines, and, for that matter, the linear pressure shifts of the R lines of a variety of materials doped with trivalent chromium,[4] do not appear explainable using theories which include only harmonic forces.

The possibility is considered that the forces acting on a fluorescence center are not totally harmonic. This possibility is particularly plausible for, although not limited to, materials such as alexandrite where the impurity ions occupy sites of low symmetry. Effects of anharmonicity are considered for the pressure dependence of the equilibrium configuration energies and the zero-point energies in relation to the equilibrium energies using the generalized force expression

$$F(x) = a + b(x - x_0) + c(x - x_{00})^2 + PA , \quad (1)$$

where a, b, and c are coefficients characteristic of the zero-pressure system, x_0 and x_{00} are the equilibrium positions associated with each term, and A is the coupling constant between the system and the pressure P. Anharmonic forces are found not to add a linear pressure term to the pressure dependence of the equilibrium configuration energies. Instead, anharmonic forces simply modify the quadratic pressure dependence of the equilibrium configuration energies predicted using the harmonic approximation. The pressure dependence for the equilibrium configuration energy including anharmonicity becomes

$$E_{eq}(P) - E_{eq}(P = 0)$$
$$= P^2 A^2 / 2b \{ 1 + 4c [b(x_0 - x_{00}) - a] / b^2 \}^{1/2} . \quad (2)$$

As a result, the effect of anharmonicity on the pressure dependence of the equilibrium configuration energies cannot explain the linear shifts of the alexandrite R-line energies with pressure.

An additional effect of anharmonicity is the introduction of a pressure-dependent effective force constant. A pressure-dependent force constant causes the frequencies of vibrational states to be pressure dependent with the result that vibronic level energies measured with respect to the minimum energy are also pressure dependent. Energies of zero-phonon levels, when measured from the energy minimum, are predicted to shift with pressure for

anharmonic systems according to the relation[11]:

$$E_{zp}(P) = (3\hbar/2)[(b_g/M_g)^{1/2}(A_g c_g / b_g^2)$$
$$- (b_e/M_e)^{1/2}(A_e c_e / b_e^2)]P$$
$$+ [(A_e^2/b_e) - (A_g^2/b_g)]P^2/2$$
$$+ E_{zp}(P = 0) , \quad (3)$$

where M refers to the reduced mass of the vibrational system, and the subscripts refer to the ground and excited states. Phonon replicas (vibronic transitions) are similarly shifted. The magnitudes of linear pressure shifts of zero-phonon lines due to the effect of anharmonicity on vibronic energy levels have been estimated using the approximation that 10% of the deformation energy is due to the anharmonic force terms and are found to be large enough to account for the linear pressure dependence of the zero-phonon R-line transition energies. Thus, the pressure dependence of the alexandrite R-line transition energies appear to be due, at least in part, to the effects of anharmonicity on the energy levels of the initial and final zero-phonon states.

Additional sources of linear shifts of the alexandrite R lines may be masked by basic assumptions of the pressure models. The configurational coordinate pressure models that have been considered all utilize the approximation that the configuration coordinate that describes the effects of applied pressure is the same coordinate that is relevant to optical processes. Models which allow multiple configuration coordinates may predict additional linear pressure dependences of spectral positions.[12]

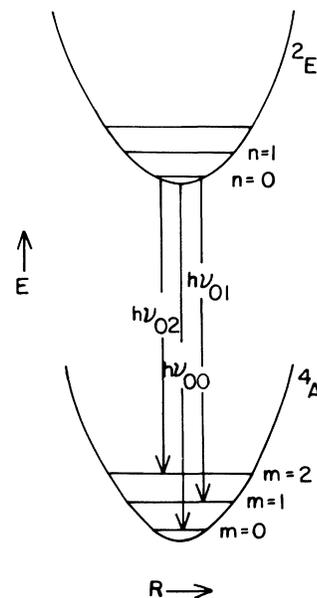The generalization to any vibronic transition of

FIG. 4. Anharmonic adiabatic potentials, vibrational levels, and vibronic transitions for Cr^{3+} in alexandrite.

the linear pressure term of Eq. (3) can be written in the following form:

$$\Delta_P(h\nu_{nm}) = (n + \tfrac{1}{2})\Delta_P(\hbar\omega_e) - (m + \tfrac{1}{2})\Delta_P(\hbar\omega_g) ,$$

(4)

where Δ_P indicates the incremental change with pressure P, $\hbar\omega_e$ and $\hbar\omega_g$ are, respectively, the local phonon energies for the excited and ground electronic states, and n and m index the vibrational levels. These levels and the vibronic transitions $h\nu_{nm}$ are illustrated in Fig. 4. The adiabatic potentials (configuration coordinate curves) for the $^4A_2$ and ^2E states of Fig. 4 anticipate the anharmonicities which will be obtained from analysis of the spectral changes with pressure.

We use the zero-phonon $h\nu_{00}$ and first phonon replica $h\nu_{01}$, obtained from Eq. (4), in the analysis. Experimentally, $\Delta_{39\ kbar}(h\nu_{00}) = -3.2$ meV for the average of the two R lines; $\Delta_{39\ kbar}(h\nu_{01})$ can be estimated from the change in density of local phonon levels obtained from the single-phonon creation replica. At 10 K this replica shows structure and the high-frequency limit of the local modes can be estimated. In other words, we use the 10 K spectrum to determine the spectral cutoff of 660 cm^{-1} for one-phonon replicas, and then analyze the spectral change with pressure at higher temperatures using the same cutoff. The effective densities of phonon levels are shown in Fig. 5. The $\Delta_{39\ kbar}(h\nu_{01})$ is thus found to be approximately $+1.4$ meV. Substitution of $\Delta_{39\ kbar}(h\nu_{00})$ and $\Delta_{39\ kbar}(h\nu_{01})$ yields $\Delta_{39\ kbar}(\hbar\omega_g) = -4.6$ meV and $\Delta_{39\ kbar}(\hbar\omega_e) = -11$ meV. The higher anharmonicity for the excited state is expected. The negative anharmonicities are somewhat unexpected but appear plausible from the viewpoint that for the A (breathing) mode of the near neighbors the oxygens move in against the un-
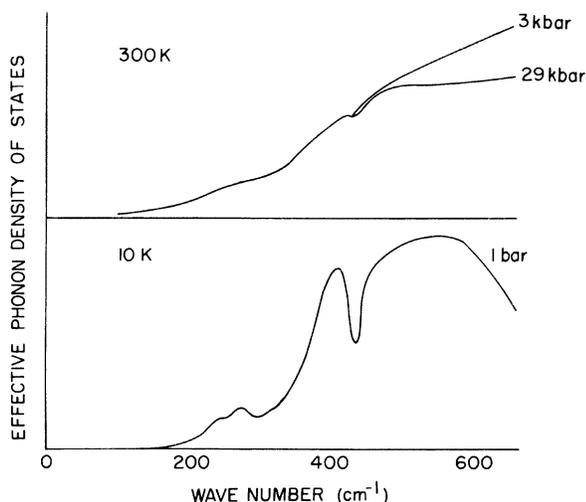
filled shell Cr^{3+} $3d^3$ electrons and out against the filled shell Al^{3+} $2s^2 2p^6$ electrons.

From the estimated values of $\Delta_P(\hbar\omega_e)$ and of $\Delta_P(\hbar\omega_g)$, other phonon replicas can be calculated. For example, we predict $\Delta_{39\ kbar}(h\nu_{02}) = +6$ meV; experimentally, the value is about half the predicted value.

The phonon sidebands can also be used to obtain the narrowing of the linewidths with pressure of the R lines. This is done by modifying the analysis of Imbusch et al.,[13] which was developed to explain the temperature dependence of linewidth, to the problem of the pressure dependence of linewidth. The linewidth at pressure P is thus of the following form:

$$W(P,T) = W(0,0) + \kappa \int [\rho(P,T,\omega)]^2 f(T,\omega)$$

$$\times [1 + f(T,\omega)] d\omega , \quad (5)$$

where $\rho(P,T,\omega)$ is the density of phonon states of frequency ω and $f(T,\omega)$ is the occupational probability. The $W(P,T)$ can thus be obtained using the results in Fig. 5. From this analysis linewidth reductions to 0.8 are predicted for 30 kbar; 0.7 and 0.8 are observed for R_1 and R_2, respectively, as shown in Fig. 3. The $\rho(\omega)$ is obtained from the phonon sideband and, since the phonon sideband changes with pressure, $\rho(\omega)$ changes with pressure and thus the width changes with pressure.

It is concluded that the linewidths of the R lines of alexandrite are pressure dependent due to the effect of anharmonicity through the pressure dependence of the effective phonon spectrum that interacts with the chromium ions to broaden the R lines.

V. CONCLUSION

The major outcome of this study of the pressure dependence of the alexandrite emission spectrum is the important role of anharmonic forces. It has been shown that the linear pressure shifts of the R-line energies can be explained by pressure-dependent force constants which results from anharmonic forces. The magnitudes of the linear pressure shifts that would result from typical anharmonic forces have been estimated and are found to be in agreement with what is observed experimentally. From an analysis of the red shifts of the R lines and the blue shifts of the phonon sidebands, we obtain the anharmonicities of the $^4A_2$ and ^2E states. The same pressure dependence of phonon sidebands are used to explain the narrowing with pressure of the R lines.

Although our measurements of the spectral shifts of the R lines are quite accurate, the corresponding

FIG. 5. Effective densities of local modes vs their wave number.

shifts of the phonon replicas and the separation of the one-phonon replicas from multiphonon replicas are approximate and thus the calculated changes in anharmonicities are approximate. Nevertheless, the observations of R-line shifts, changes in effective phonon densities, and line narrowing are all consistent, based on this analysis. We note that additional measurements such as resonant Raman scattering and inelastic neutron scattering as a function of hydrostatic pressure can lead to more accurate values for the anharmonicities and their changes with pressure.

[1]J. C. Walling, H. P. Jenssen, R. C. Morris, E. W. O'Dell, and O. G. Peterson, Opt. Lett. **4**, 182 (1979).

[2]C. F. Cline, J. Mater. Sci. **14**, 941 (1979).

[3]R. Wyckoff, *Crystal Structures*, (Interscience, New York, 1960), Vol. II.

[4]R. A. Forman, B. A. Weinstein, and G. Piermarini, Colloq. Int. CNRS (Lyon), No. 255 (1977).

[5]G. J. Piermarini, S. Block, J. D. Barnett, and R. A. Forman, J. Appl. Phys. **46**, 2774 (1975).

[6]D. M. Adams, R. Appleby, and S. K. Sharma, J. Phys. E **9**, 1140 (1976).

[7]G. F. Imbusch, *Luminescence of Inorganic Solids*, edited by B. DiBartolo, (Plenum, New York, 1978).

[8]P. D. Johnson and F. E. Williams, Phys. Rev. **95**, 69 (1954).

[9]P. B. Alers and R. L. Dolecek, J. Chem. Phys. **38**, 1046 (1963).

[10]H. G. Drickamer, C. W. Frank, and C. P. Slichter, Proc. Natl. Acad. Sci. USA **69**, 933 (1972).

[11]D. Curie, D. E. Berry, and F. Williams, Phys. Rev. B **20**, 2323 (1979).

[12]D. E. Berry, R. C. Tompkins, and F. Williams, J. Chem. Phys. **76**, 3362 (1982).

[13]G. F. Imbusch, W. M. Yen, A. L. Schawlow, D. E. McCumber, and M. D. Sturge, Phys. Rev. **133**, 1029 (1964).