

Theory of the effects of hydrostatic pressure on the radiative transitions of impurities in crystals

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The effects of hydrostatic pressure on radiative electronic transitions of impurities in solids are analyzed in the adiabatic approximation. A procedure is established for including the effects of pressure on the adiabatic potential for each electronic state. From harmonic configuration coordinates the effects of pressure on peak energy and half-width are determined classically for broad-band, phonon-assisted, absorption and luminescent emission spectra. The conditions for linear dependence of the peaks on pressure are clarified. The impurity is then considered quantum mechanically, and the effects of pressure on vibronic transition energies and probabilities determined. The pressure at which the zero-phonon transition becomes most probable is predicted for some defects. Finally, the effect of anharmonicity on the pressure dependence of vibronic transition energies is evaluated. From this study it is concluded that impurities with vibronic structure can be understood in great detail from the application of the theory to experimental pressure-dependent spectra.

I. INTRODUCTION

The adiabatic approximation is assumed to be valid for the impurities and defects investigated. In other words, for the electronic states involved in the radiative transitions the orbital time for electronic motion is assumed to be short compared to the period of optical phonons and thus the stationary electron distribution for each electronic state smoothly adjusts to lattice displacements. The atomic motion is thus governed by an adiabatic potential that depends on the eigenvalue for each electronic state with its parametric dependence on nuclear coordinates. This is represented by the configuration coordinate model, such as shown in Fig. 1. Radiative transitions are usually assumed to occur vertically in accordance with the Franck-Condon principle: classically, the transition energies are the vertical differences between the adiabatic potential energies for the two electronic states; quantum mechanically, transitions occur between vibrational levels of the initial and final electronic states.

For those systems with well-defined modes, as illustrated in Fig. 2, vibrational structure in the spectra may be observed. For some molecular impurities, e.g., NO_2^- in KCl, the vibronic structure arises from a well-defined local mode; for dopants with effective-mass electronic states, e.g., S, Zn donor-acceptor pairs in GaP, optical-phonon replicas of the individual pair transitions occur.

The emphasis in the following analysis is on the

changes in optical spectra due to changes in the adiabatic potentials and in the configuration coordinate with hydrostatic pressure. In the classical analysis of broad-band, phonon-assisted spectra this leads to effects due to changes in the probability distribution of configurations and to changes in the transition energy for each configuration; in the quantum-mechanical

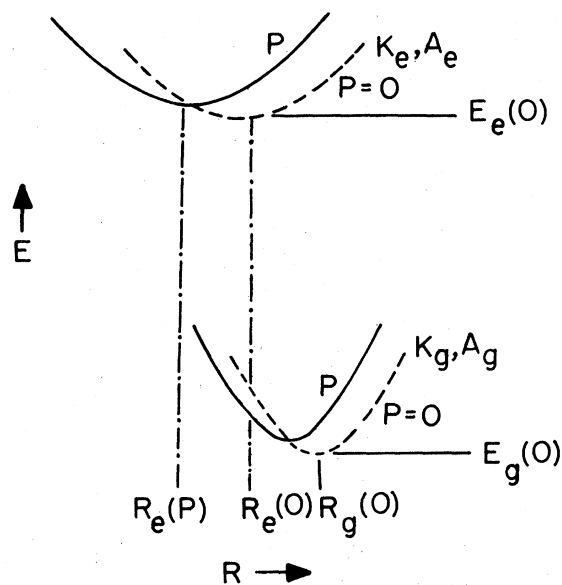


FIG. 1. Configurational coordinate model, with and without effects of hydrostatic pressure.

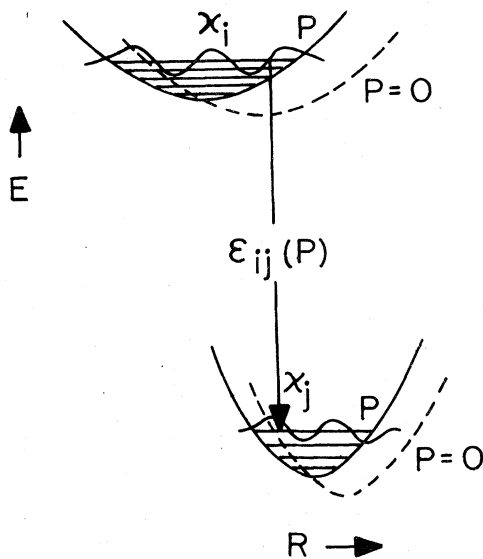


FIG. 2. Configurational coordinate diagram, showing the vibrational levels and representative wave functions.

analysis this leads to changes in the transition energy and transition matrix for each vibronic transition. Effects on the electronic transition matrix are included implicitly in the adiabatic changes in the electronic wave function with deformation.

The present analysis is limited to systems within a pressure range with no phase changes and to the effects of hydrostatic pressure, not to effects of uniaxial or other anisotropic stress. Because we use a single deformation parameter the analysis applies strictly only to cubic materials for which the deformation is isotropic.

Measurements of the pressure dependence of impurity spectra have become increasingly extensive during the past two decades. Most of these experimental studies have been on systems with broadband, phonon-assisted spectra (see for example, Drotning and Drickamer¹). A few experimental studies have been on systems with well-resolved vibronic structure (see for example, Laisaar²). One of the results of the analyses in the subsequent sections is to show that pressure-dependent spectra of systems with vibronic structure can provide detailed information on the electronic states of impurities and of their coupling with the lattice.

Concurrent with the aforementioned experimental work there have been advances in theoretical analysis of the effects of hydrostatic pressure on impurity spectra. The original basis for interpreting these spectra was provided by Johnson and Williams³ with the assumption that the main effect of pressure is to change the occupational probability of any arbitrary configuration of the initial electronic state; however, their resulting formulas also reflect the direct effect

of pressure on the system to linear terms in the pressure. Alers and Dolecek⁴ advanced the theory by including explicitly the effects of pressure on the final-state configuration coordinate contour and also by allowing for different coupling constants with the lattice for the different electronic states. More recently, Drickamer, Frank, and Slichter,⁵ Lin,⁶ Kelley,⁷ and Munro⁸ have made more general analyses of the pressure dependence of the optical spectra of localized systems in condensed matter; however, some effects appear to have been neglected (for details see Curie and Williams⁹). For example, Drickamer *et al.*⁵ do not include the effect of pressure on the transition energy at an arbitrary configuration and thus obtain different conditions for a linear dependence of the broad-band spectrum on pressure than did Alers and Dolecek⁴ and Curie and Williams.⁹

In an important generalization of the effects of applied fields on optical properties of color centers, Henry, Schnatterly and Slichter¹⁰ also do not include the direct effect of pressure on the transition energy.

In Secs. II–V we shall clarify the linear and quadratic dependence of these harmonic classical systems, calculate the pressure dependence of transition energies and probabilities of harmonic quantum-mechanical systems with vibronic structure, and evaluate some effects of anharmonicity.

II. PRESSURE DEPENDENCE OF IMPURITY SPECTRA IN THE HARMONIC APPROXIMATION

In this analysis we shall separate the effects of pressure on the occupational probability of each nuclear configuration, specified by R , of the initial electronic state involved in the transition from the effects of pressure on the radiative transition energy at that configuration R . In Fig. 1 the model is shown, with the ground and excited electronic states characterized by the force constants K_g and K_e , respectively, equilibrium configurations $R_g(0)$ and $R_e(0)$, and coupling constants between the microscopic impurity system and hydrostatic pressure A_g and A_e , which have the dimensionality of an area. In the present analysis the coupling constants are assumed to be independent of pressure.

The effect of hydrostatic pressure on the harmonic contours is to displace the minima of these curves both in the energy E and in the coordinate R . We shall let $[R(P), E(P)]$ be the position of the minimum, when the applied pressure is P , with appropriate subscripts for excited (e) and ground (g) states, see Fig. 1. The new contours are given by the following three steps: (a) the determination of $R(P)$ by the condition that the total force is zero at the minimum; (b) the determination of $E(P)$ as the sum of $E(0)$ and the work done to attain the new equilibrium (we will assume that this work is done adiabatically).

ically); and (c) the determination of an R -dependent adiabatic potential energy including the pressure, $U(R)$, which is zero at the new equilibrium position and where the new contours are the sum of the R -dependent term plus the energy of the new equilibrium. Implicit in this analysis is the assumption that the inertia of the pressure apparatus is large compared to that of the system undergoing the optical transition. This allows for adiabatic decoupling, but not complete decoupling, of the pressure apparatus from the optical system.

The first step is

$$F|_{R=R(P)} = \{-K[R - R(0)] - PA\}|_{R=R(P)} = 0,$$

which gives

$$R(P) = R(0) - PA/K.$$

The second step is explicitly

$$\begin{aligned} E(P) &= E(0) + \int_{R(0)}^{R(P)} (-PA) dR \\ &= E(0) + \int_{R(0)}^{R(P)} K[R - R(0)] dR, \end{aligned}$$

which gives

$$E(P) = E(0) + P^2 A^2 / 2K.$$

Finally the R -dependent force in the harmonic case is given by

$$\delta U(R) / \delta R = -F = K[R - R(0)] + PA, \quad (1)$$

which gives for $U(R)$

$$U(R) = \frac{1}{2} K [R - R(0)]^2 + PA [R - R(P)] + C,$$

where C is determined by

$$U(R(P)) = 0,$$

which gives

$$C = -P^2 A^2 / 2K.$$

Combining the above results, for the ground state, we get for the new contour

$$E_g(P, R) = \frac{1}{2} K_g [R - R_g(P)]^2 + P^2 A_g^2 / 2K_g + E_g(0). \quad (2)$$

There is a corresponding equation for the excited state given by replacing the subscript g by e . A special case is analyzed in detail in Appendix A.

We should note the following: (a) in the harmonic approximation the force constant is independent of pressure, (b) the ground- and excited-state minima are displaced different amounts if $A_e^2/K_e \neq A_g^2/K_g$, and (c) the equilibrium configuration coordinates of the two states are displaced differently if $A_e/K_e \neq A_g/K_g$. The unequal displacements of $R(P)$ cause the principal change in the intensity of a vi-

bronic transition and of $E(P)$ cause the change in the vibronic transition energy.

The above results are easily understood on the basis of the straightforward analogy which exists between the luminescent system in the harmonic approximation, and the well-known problem of a spring whose force constant is K : By an additional weight $mg = -PA$ we displace the equilibrium position to $R(P) = R(0) + mg/K$, and it is easily seen that the potential energy E depends on mg and R in the same way as in Eq. (2). The equations for the system in the excited states are the same except for a different force constant, coupling constant, and equilibrium position. From this analogy we confirm that the force constants K_g and K_e remain unchanged with pressure in the harmonic approximation. In Appendix B we further develop the spring analogy in order to clarify the interconnection between electronic states as affected by pressure.

The transition energy

$$\Delta E(P) \equiv \Delta E(P, R) = E_e(P, R) - E_g(P, R),$$

occurring vertically in accordance with the Franck-Condon principle, is thus given by the following:

$$\begin{aligned} \Delta E(P, R) &= \frac{1}{2} K_e \left[R - \left(R_e(0) - \frac{PA_e}{K_e} \right) \right]^2 + \frac{P^2 A_e^2}{2K_e} \\ &\quad - \frac{1}{2} K_g \left[R - \left(R_g(0) - \frac{PA_g}{K_g} \right) \right]^2 \\ &\quad - \frac{P^2 A_g^2}{2K_g} + \Delta E(0), \end{aligned} \quad (3)$$

where $\Delta E(0) = E_e(0) - E_g(0)$. See, for example, Alers and Dolecek.⁴

The differential of $\Delta E(P, R)$ is

$$\delta \Delta E = \left(\frac{\partial \Delta E}{\partial P} \right)_R \delta P + \left(\frac{\partial \Delta E}{\partial R} \right)_P \delta R,$$

and thus the complete derivative of the transition energy with pressure is

$$\frac{d \Delta E}{dP} = \left(\frac{\partial \Delta E}{\partial P} \right)_R + \left(\frac{\partial \Delta E}{\partial R} \right)_P \left(\frac{dR}{dP} \right). \quad (4a)$$

The partial derivatives are obtained from Eq. (3) and then substituted in Eq. (4a). Thus, we obtain for the change in the maximum in the phonon-assisted spectrum with pressure, which occurs at $R = R_e(0) - PA_e/K_e$ for emission,

$$\begin{aligned} \left(\frac{d \Delta E}{dP} \right)_m &= \left[A_e \frac{K_g}{K_e} - A_g \right] [R_e(0) - R_g(0)] \\ &\quad + \left[\left(\frac{A_e^2}{K_e} - \frac{A_g^2}{K_g} \right) - K_g \left(\frac{A_e}{K_e} - \frac{A_g}{K_g} \right)^2 \right] P. \end{aligned} \quad (4b)$$

TABLE I. Signs of $d\sigma/dP$ and $(d\Delta E/dP)_m$ are given for various combinations of the parameters to terms of first order in P for both emission and absorption. (See Ref. 11.)

		$\left(\frac{d\Delta E}{dP}\right)_m$		$\frac{d\sigma_e}{dP}$	$\frac{d\sigma_g}{dP}$
		emission	absorption		
$R_e(0) > R_g(0)$	$A_e/K_e > A_g/K_g$	+	-	-	-
$R_e(0) > R_g(0)$	$A_e/K_e < A_g/K_g$	-	+	+	+
$R_e(0) < R_g(0)$	$A_e/K_e > A_g/K_g$	-	+	+	+
$R_e(0) < R_g(0)$	$A_e/K_e < A_g/K_g$	+	-	-	-

We note that for $A_e = A_g$ and $K_e = K_g$ then $(d\Delta E/dP)_m$ is zero so that for this special case the phonon-assisted spectrum is independent of pressure.

In addition to the pressure dependence of the peak, we can also derive the expression for the half-width pressure and temperature dependences from the above considerations. If we use the usual derivation

for the second moment of the emission, then we find

$$\sigma_e(T, P) = \sigma_e(P) [\tanh(\hbar\omega_e/2kT)]^{-1/2},$$

where

$$\sigma_e^2(P) = 2K_g^2 [R_e(P) - R_g(P)]^2 (\hbar\omega_e/K_e),$$

which gives

$$\sigma_e(T, P) = K_g \left(\frac{2\hbar\omega_e}{K_e} \right)^{1/2} \left| R_e(0) - R_g(0) + \left(\frac{A_g}{K_g} - \frac{A_e}{K_e} \right) P \right| / \tanh^{1/2} \left(\frac{\hbar\omega_e}{2kT} \right). \quad (5)$$

The results for the absorption band are gotten from Eqs. (4b) and (5) by interchanging the subscripts e and g , plus a sign change in Eq. (4b).

The signs of $d\sigma/dP$ and $(d\Delta E/dP)_m$ for both emission and absorption with various combinations of the parameters are given in Table I, up to terms of first order in P .

In Fig. 2 the vibrational levels are included in the model. The dependence of the vibronic transition energy ϵ_{nm} on hydrostatic pressure is given by the following:

$$\epsilon_{nm}(P) = \frac{1}{2} \left[\left(\frac{A_e^2}{K_e} - \frac{A_g^2}{K_g} \right) P^2 \right] + \hbar \left[\left(n + \frac{1}{2} \right) \left(\frac{K_e}{M_e} \right)^{1/2} - \left(m + \frac{1}{2} \right) \left(\frac{K_g}{M_g} \right)^{1/2} \right] + E(0), \quad (6a)$$

$$= \frac{1}{2} \left[\left(\frac{A_e^2}{K_e} - \frac{A_g^2}{K_g} \right) P^2 \right] + \epsilon_{nm}(0), \quad (6b)$$

where the first term arises from the difference between the pressure-induced displacements of the minima for the two states involved in the transition and the second is the difference in vibrational energies for the levels before and after the transition. The quantities M_e and M_g are the masses of the vibrating system for the excited and ground states, respectively. We note that the transition energies for vibronic transitions are quadratically dependent on pressure and are all displaced the same amount, in the harmonic approximation.

The system behaves quite differently when a uniaxial stress is applied instead of a hydrostatic pressure, for except in very special cases the uniaxial stress changes the symmetry of the system and thus

produces a mixing of the normal vibrational modes. In other words, the effect of a uniaxial stress cannot in the general case be described in terms of a simple one-dimensional configurational diagram. However in a more sophisticated one-dimensional configurational coordinate model, uniaxial stress is describable in some cases.¹²

Now returning to the energy contours for any pressure, P , we should note that the new equilibrium position is on the energy contour for zero pressure, and that the position of the equilibrium is independent of the way the pressure is applied so long as it is done adiabatically.

We can show that the results are independent of path by considering the following two paths of going

from zero pressure to pressure $P_1 + P_2$; path one is zero pressure to P_1 and then to $P_1 + P_2$, and path two is zero pressure to $P_1 + P_2$. For path one the equilibrium for pressure P_1 is

$$[R(P_1), E(P_1)] = \left[R(0) - \frac{P_1 A}{K}, E(0) + \frac{P_1^2 A^2}{2K} \right]$$

and for the final equilibrium we get

$$[R(P_1 + P_2), E(P_1 + P_2)] = \left[R(P_1) - \frac{P_2 A}{K}, E(P_1) + \frac{1}{2} K [R(P_1 + P_2) - R(0)]^2 - \frac{1}{2} K [R(P_1) - R(0)]^2 \right], \quad (7)$$

where the balance of forces is given by

$$F|_{R=R(P_1+P_2)} = -K[R(P_1+P_2) - R(0)] - (P_1 + P_2)A = 0.$$

Simplifying the expression for $E(P_1 + P_2)$ gives

$$E(P_1 + P_2) = E(0) + (P_1 + P_2)^2 A^2 / 2K,$$

which is just the expression we would have gotten using path two, as is the expression for $R(P_1 + P_2)$ given in Eq. (7). Therefore, as it should be in the adiabatic approximation, the position of the equilibrium is path independent.

We should emphasize the unique position of the zero-pressure contour, that is, all the equilibrium positions are located on this curve. The zero-pressure curve differs from the non-zero-pressure curves in that this contour represents only the effects due to the crystal forces when R is changed, whereas the non-zero-pressure contour includes the effects due to the external pressure. That is, changes on the non-zero-pressure contour represent the work done against internal forces plus the external pressure.

III. PRESSURE DEPENDENCE OF THE PROBABILITY OF A VIBRONIC TRANSITION

In addition to the spectral displacements with hydrostatic pressure there is a change in intensity of each vibronic transition, principally as a consequence of the change in phase of the two vibrational wave functions χ_{gm} and χ_{en} with respect to each other (this is illustrated in Fig. 2) and also due to the changes in the transition energy. The relative displacement of the wave functions is, of course, directly connected with the displacement of the minima for the two electronic contours with respect to each other. In the adiabatic approximation the matrix element for the radiative transition, $M_{eg}(n, m)$, is given to first order¹³ by

$$M_{eg}(n, m) = S_{eg}(n, m) \int \phi_e^*(r; R_{nm}) \bar{e} \bar{\Gamma} \phi_g(r; R_{nm}) d^3 r, \quad (8)$$

where

$$S_{eg}(n, m) = \int \chi_{en}^*(R) \chi_{gm}(R) dR. \quad (9)$$

Here $\phi_e(r; R)$ and $\phi_g(r; R)$ are the electronic wave functions for the excited and ground states in the adiabatic approximation and

$$R_{nm} = \int \chi_{en}^*(R) R \chi_{gm}(R) dR / S_{eg}(n, m). \quad (10)$$

$M_{eg}(n, m)$ is pressure dependent mainly because $S_{eg}(n, m)$ and R_{nm} are pressure dependent, the latter being involved in the electronic matrix element. These effects arise because of the pressure dependence of the relative displacement of the two contours which make $S_{eg}(n, m)$ pressure dependent and because R_{nm} can be obtained as a linear combination of the $S_{eg}(n', m')$.

In this section we analyze the dependence of $S_{eg}(n, m)$ on pressure. The notation to be used is: $|n; K_e, R_e(0) : P\rangle$ is the n th vibronic wave function of the excited electronic state when a pressure P is applied to the system whose harmonic contour is parameterized by K_e and $R_e(0)$. A similar notation is used for the ground electronic state with g 's replacing e 's. In this notation $S_{eg}(n, m)$ is

$$S_{eg}(n, m) = \langle n; K_e, R_e(0) : P | m; K_g, R_g(0) : P \rangle. \quad (11)$$

Note that the transition probability, $W_{eg}(n, m)$, is given by

$$W_{eg}(n, m) = [\epsilon_{nm}(P)]^{-2} |S_{eg}(n, m)|^2 e^2 \left| \int \phi_e^*(r; R_{nm}) \bar{e} \bar{\Gamma} \phi_g(r; R_{nm}) d^3 r \right|^2. \quad (12)$$

$S_{eg}(n, m)$ is found to be

$$S_{eg}(n, m) = e^{\delta} [\Gamma(n+1)\Gamma(m+1)]^{1/2} (-\alpha)^{n/2} (-\mu)^{m/2} \times \sum_{r=0}^{\min(n, m)} \left(\frac{e^{2\gamma}}{\alpha\mu} \right)^{r/2} H_{n-r} \left(\frac{\beta}{2(-\alpha)^{1/2}} \right) H_{m-r} \left(\frac{\nu}{2(-\mu)^{1/2}} \right) / \Gamma(r+1)\Gamma(n-r+1)\Gamma(m-r+1), \quad (13)$$

where¹⁴

$$\begin{aligned}\alpha &= \frac{1}{2} \frac{M_e \omega_e - M_g \omega_g}{M_e \omega_e + M_g \omega_g}, \quad \mu = -\frac{1}{2} \frac{M_e \omega_e - M_g \omega_g}{M_e \omega_e + M_g \omega_g}, \quad \beta = \left(\frac{2}{\hbar M_e \omega_e} \right)^{1/2} \left(\frac{M_e M_g \omega_e \omega_g}{M_e \omega_e + M_g \omega_g} \right) [R_g(P) - R_e(P)], \\ \nu &= -\left(\frac{2}{\hbar M_g \omega_g} \right)^{1/2} \left(\frac{M_e M_g \omega_e \omega_g}{M_e \omega_e + M_g \omega_g} \right) [R_g(R) - R_e(P)], \quad \gamma = \ln \left(\frac{2(M_e M_g \omega_e \omega_g)^{1/2}}{M_e \omega_e + M_g \omega_g} \right), \\ \delta &= \frac{\gamma}{2} - \frac{[R_g(P) - R_e(P)]^2}{2\hbar} \left(\frac{M_e M_g \omega_e \omega_g}{M_e \omega_e + M_g \omega_g} \right), \quad \omega_e^2 = \frac{K_e}{M_e}, \quad \text{and} \quad \omega_g^2 = \frac{K_g}{M_g}.\end{aligned}\tag{14}$$

Two of the authors have given this result in an earlier work.¹⁵ Similar results have been obtained by W. Heinzel¹⁶ and also by S. Koide.¹⁷ Note that only β , ν , and δ are pressure dependent in the harmonic case. We can rewrite $S_{eg}(n, m)$ as follows:

$$\begin{aligned}S_{eg}(n, m) &= [\Gamma(n+1)\Gamma(m+1)]^{1/2} (-\alpha)^{n/2} (-\mu)^{m/2} \left(\frac{2(M_e M_g \omega_e \omega_g)^{1/2}}{M_e \omega_e + M_g \omega_g} \right)^{1/2} \\ &\times \sum_{r=0}^{\min(n, m)} \frac{(e^{2\gamma/\alpha\mu})^{r/2}}{\Gamma(r+1)\Gamma(n-r+1)\Gamma(m-r+1)} \kappa_{nm}(r: P),\end{aligned}\tag{15}$$

where

$$\begin{aligned}\kappa_{n, m}(r: P) &= \exp \left\{ -\frac{M_e M_g \omega_e \omega_g}{2\hbar(M_e \omega_e + M_g \omega_g)} \left[P \left(\frac{A_e}{K_e} - \frac{A_g}{K_g} \right) + [R_g(0) - R_e(0)] \right]^2 \right\} \\ &\times H_{n-r} \left\{ \frac{M_e M_g \omega_e \omega_g}{[\hbar M_e \omega_e (M_g^2 \omega_g^2 - M_e^2 \omega_e^2)]^{1/2}} \left[R_g(0) - R_e(0) + P \left(\frac{A_e}{K_e} - \frac{A_g}{K_g} \right) \right] \right\} \\ &\times H_{m-r} \left\{ \frac{M_e M_g \omega_e \omega_g}{[\hbar M_g \omega_g (M_e^2 \omega_e^2 - M_g^2 \omega_g^2)]^{1/2}} \left[R_g(0) - R_e(0) + P \left(\frac{A_e}{K_e} - \frac{A_g}{K_g} \right) \right] \right\}.\end{aligned}\tag{16}$$

We should note that the principal pressure dependence in $S_{eg}(n, m)$ is the exponential term which is quadratic in pressure, having the form $\exp[-AB^2(P - P_0)^2]$, where

$$A = \frac{M_e M_g \omega_e \omega_g}{2\hbar(M_e \omega_e + M_g \omega_g)}, \quad B = \frac{A_e}{K_e} - \frac{A_g}{K_g}, \quad P_0 = \frac{R_g(0) - R_e(0)}{A_g/K_g - A_e/K_e}.\tag{17}$$

This exponential factor is one when $P = P_0$ and decreases with a quadratic dependence on $(P - P_0)$. Note P_0 can be negative or positive.

We now give some special cases of $S_{eg}(n, m)$. [Note since $S_{eg}(n, m) = S_{ge}^*(m, n)$ as is evident from detail balance, we need only consider one of the pair $S_{eg}(n, m)$ and $S_{eg}(m, n)$.]

For the zero-phonon transition

$$S_{eg}(0, 0) = \left(\frac{2(M_e M_g \omega_e \omega_g)^{1/2}}{M_e \omega_e + M_g \omega_g} \right)^{1/2} \exp \left\{ -\frac{M_e M_g \omega_e \omega_g}{2\hbar(M_e \omega_e + M_g \omega_g)} \left[P \left(\frac{A_e}{K_e} - \frac{A_g}{K_g} \right) + [R_g(0) - R_e(0)] \right]^2 \right\}.\tag{18}$$

For the relaxed phonon-assisted emission

$$S_{eg}(0, m) = [\Gamma(m+1)]^{-1/2} \left(\frac{1}{2} \frac{M_e \omega_e - M_g \omega_g}{M_e \omega_e + M_g \omega_g} \right)^{m/2} \left(\frac{2(M_e M_g \omega_e \omega_g)^{1/2}}{M_e \omega_e + M_g \omega_g} \right)^{1/2} \kappa_{0m}(0: P),\tag{19}$$

where

$$\begin{aligned}\kappa_{0m}(0: P) &= \exp \left\{ -\frac{M_e M_g \omega_e \omega_g}{2\hbar(M_e \omega_e + M_g \omega_g)} \left[P \left(\frac{A_e}{K_e} - \frac{A_g}{K_g} \right) + R_g(0) - R_e(0) \right]^2 \right\} \\ &\times H_m \left\{ \frac{M_e M_g \omega_e \omega_g}{[\hbar M_g \omega_g (M_e^2 \omega_e^2 - M_g^2 \omega_g^2)]^{1/2}} \left[R_g(0) - R_e(0) + P \left(\frac{A_e}{K_e} - \frac{A_g}{K_g} \right) \right] \right\}.\end{aligned}$$

We now look at the conditions for $S_{eg}(0, m)$ having a maximum when m is fixed and the pressure is varied and also when P is fixed and m is varied. First consider the case of fixed m : Let P_m be the pressure at which $S_{eg}(0, m)$ has an extremum, then P_m must satisfy

$$\left. \frac{d}{dP} S_{eg}(0, m) \right|_{P=P_m} = 0. \quad (20)$$

Letting

$$C = \frac{M_e M_g \omega_e \omega_g}{[\hbar M_g \omega_g (M_e^2 \omega_e^2 - M_g^2 \omega_g^2)]^{1/2}},$$

then Eq. (20) becomes

$$(m+1) \frac{H_{m-1}(CB(P_m - P_0))}{H_m(CB(P_m - P_0))} = \frac{AB}{C} (P_m - P_0), \quad (21)$$

where $H_{-1}(x) = 0$. The P_m given by Eq. (21) can be either positive or negative, and therefore in some physical system it will be impossible to maximize some or all of the vibronic transitions. That is, the maximum obtainable value for $S_{eg}(0, m)$ is obtained at zero pressure, whenever P_m is less than or equal to zero. In particular, in the case of the zero-phonon transition, it is maximized at

$$P_0 = [R_g(0) - R_e(0)] \left/ \left(\frac{A_g}{K_g} - \frac{A_e}{K_e} \right) \right.$$

P_0 is positive in those systems for which

$$\text{sgn}[R_g(0) - R_e(0)] = \text{sgn} \left(\frac{A_g}{K_g} - \frac{A_e}{K_e} \right), \quad (22)$$

where

$$R_e(P_0) = R_g(P_0) = \frac{\frac{A_g}{K_g} R_e(0) - \frac{A_e}{K_e} R_g(0)}{\frac{A_g}{K_g} - \frac{A_e}{K_e}}.$$

For any system in which condition (22) is met, we can increase the zero-phonon line intensity by the application of pressure, and therefore if condition (22) is met for a system which shows no zero-phonon lines, then by the application of pressure we should be able to cause zero-phonon lines to appear.

We should note that for the harmonic case there are a total of seven parameters that specify the system. They are ω_e , ω_g , M_e , M_g , A_e , A_g , and $R_g(0) - R_e(0)$. Alers and Dolecek⁴ have shown that for broad-band emission and absorption measurements, where only peak transition energies and their dependences on pressure are used, only four of the parameters are determined. We, therefore, want to indicate some other measurements that can be used to gain and/or correlate information about more of the parameters of a given physical system.

Let m_M be the value of m at which $S_{eg}(0, m)$ has the maximum value for a given P , then m_M must satisfy

$$\begin{aligned} \frac{(m_M)^{1/2}}{|(-\mu)^{1/2}|} |H_{m_M-1}(BC(P - P_0))| \\ \leq |H_{m_M}(BC(P - P_0))| \\ \leq \frac{|(-\mu)^{1/2}|}{(m_M + 1)^{1/2}} |H_{m_M+1}(BC(P - P_0))|. \end{aligned} \quad (23)$$

Note a similar condition holds for m_M as for P_m . That is, if m_M is negative then the most intense real peak would be the zero-phonon peak. Also note that these conditions only specify complicated regions in the parameter space. On the other hand if we consider the equality signs, then the dimensions of these regions are reduced, that is, placing more restrictive conditions on the parameters of the system. If we let \bar{P}_- and \bar{P}_+ be the pressures for which the left and right hand equality signs hold, then given these values and m_M , we can further determine the parameters. It should be noted that it will not be possible in all cases to obtain a pressure so that either equality sign holds; then we must deal with the less restrictive conditions of Eq. (23). The pressure \bar{P}_- corresponds to the case when the peaks m_M and $m_M - 1$ have equal intensity, and similarly for \bar{P}_+ , the peaks m_M and $m_M + 1$.

It should be noted that Eqs. (22) and (23) are conditions for maximizing $S_{eg}(0, m)$ but not $W_{eg}(0, m)$. $W_{eg}(0, m)$ changes with m and P because of three factors: The principal change is due to $S_{eg}(0, m)$, the second factor is $[\epsilon_{0m}(P)]^{-2}$, and the last factor is the electronic matrix element which depends on m and P through R_{0m} .

We consider the change in Eqs. (22) and (23) due to the factor $[\epsilon_{0m}(P)]^{-2}$. Equation (22) is replaced by

$$\begin{aligned} \text{Re} \left\{ C(m+1) \frac{H_{m-1}(CB(P_m - P_0))}{H_m(CB(P_m - P_0))} - AB(P_m - P_0) \right\} \\ = \frac{D}{B} \frac{P_m}{DP_m^2 - m\omega_g + \epsilon_{00}(0)}, \end{aligned} \quad (22')$$

where

$$D = \frac{1}{2} \left(\frac{A_e^2}{K_e} - \frac{A_g^2}{K_g} \right)$$

and Eq. (23) is replaced by

$$\begin{aligned} \frac{m_M}{|\mu|} \left| \frac{H_{m_M-1}(CB(P - P_0))}{\epsilon_{0m_M}(P) + \omega_g} \right|^2 \leq \left| \frac{H_{m_M}(CB(P - P_0))}{\epsilon_{0m_M}(P)} \right|^2 \\ \leq \frac{|\mu|}{m_M} \left| \frac{H_{m_M+1}(CB(P - P_0))}{\epsilon_{0m_M}(P) - \omega_g} \right|^2. \end{aligned} \quad (23')$$

IV. EFFECTS OF ANHARMONICITY ON
THE PRESSURE DEPENDENCE OF
IMPURITY SPECTRA

By methods similar to those used for the harmonic approximation we can analyze the more general case including anharmonicity. We choose for the zero-pressure ground-state contour

$$E_g(0, R) = \frac{K_g}{2} [R - R_g(0)]^2 + \beta_g [R - R_g(0)]^3 + \alpha_g [R - R_g(0)]^4 + E_g(0), \quad (24)$$

where $\alpha_g > 0$ and where

$$|\beta_g| = \frac{2}{\sqrt{3}} e^{-\gamma_g^2} (K_g \alpha_g)^{1/2}.$$

This form is chosen so that $E_g(0, R)$ has a single minimum at $R_g(0)$ and is asymmetric about this minimum. Using the three steps given in Sec. II, we can find the contour at any pressure, P . The force

on the system is

$$F = -K_g [R - R_g(0)] - 3\beta_g [R - R_g(0)]^2 - 4\alpha_g [R - R_g(0)]^3 - PA_g. \quad (25)$$

Assuming that the first and last term of Eq. (25) are the largest terms we can solve Eq. (25) approximately for $R_g(P)$. To third order in P , $R_g(P)$ is

$$R_g(P) \approx R_g(0) - \frac{PA_g}{K_g} - 2\sqrt{3} e^{-\gamma_g^2} \left(\frac{\alpha_g}{K_g^5} \right)^{1/2} P^2 A_g^2 - \frac{4\alpha_g}{K_g^4} (6e^{-2\gamma_g^2} - 1) P^3 A_g^3. \quad (26)$$

The work done adiabatically, W , by the pressure is to third order in P

$$W \approx \frac{P^2 A_g^2}{2K_g} + \frac{4}{3} \left(\frac{\alpha_g}{K_g^5} \right)^{1/2} e^{-\gamma_g^2} P^3 A_g^3. \quad (27)$$

And finally the R -dependent term of the contour, to the same order in P is

$$U(R) = \frac{K_g(P)}{2} [R - R_g(P)]^2 + \beta_g(P) [R - R_g(P)]^3 + \alpha_g(P) [R - R_g(P)]^4, \quad (28)$$

where

$$K_g(P) \approx K_g - 4\sqrt{3} e^{-\gamma_g^2} \left(\frac{\alpha_g}{K_g} \right)^{1/2} PA_g + \frac{12\alpha_g}{K_g^2} (1 - 2e^{-2\gamma_g^2}) P^2 A_g^2 + 32\sqrt{3} e^{-\gamma_g^2} \left(\frac{\alpha_g^3}{K_g^7} \right)^{1/2} (2 - 3e^{-2\gamma_g^2}) P^3 A_g^3, \quad (29)$$

$$\beta_g(P) = \frac{2}{\sqrt{3}} e^{-\gamma_g^2(P)} [\alpha_g(P) K_g(P)]^{1/2}, \quad (30)$$

$$\alpha_g(P) = \alpha_g, \quad (31)$$

$$e^{-\gamma_g^2(P)} = e^{-\gamma_g^2} + 2\sqrt{3} \left(\frac{\alpha_g}{K_g^3} \right)^{1/2} (e^{-2\gamma_g^2} - 1) PA_g + 30 \left(\frac{\alpha_g}{K_g^3} \right) (e^{-3\gamma_g^2} - e^{-\gamma_g^2}) P^2 A_g^2 + 20\sqrt{3} \left(\frac{\alpha_g^3}{K_g^9} \right)^{1/2} (7 - 10e^{-2\gamma_g^2} + 9e^{-4\gamma_g^2}) P^3 A_g^3. \quad (32)$$

Combining Eqs. (27) and (28), we find for $E_g(P, R)$

$$E_g(P, R) \approx \frac{K_g(P)}{2} [R - R_g(P)]^2 + \frac{2}{\sqrt{3}} e^{-\gamma_g^2(P)} [\alpha_g(P) K_g(P)]^{1/2} [R - R_g(P)]^3 + \alpha_g(P) [R - R_g(P)]^4 + \frac{P^2 A_g^2}{2K_g} + \frac{4}{3} \left(\frac{\alpha_g}{K_g^5} \right)^{1/2} e^{-\gamma_g^2} P^3 A_g^3 + E_g(0), \quad (33)$$

where

$$\frac{2}{\sqrt{3}} e^{-\gamma_g^2(P)} [\alpha_g(P) K_g(P)]^{1/2} = \frac{2e^{-\gamma_g^2}}{\sqrt{3}} (\alpha_g K_g)^{1/2} - 4 \frac{\alpha_g}{K_g} PA_g - 8\sqrt{3} e^{-\gamma_g^2} \left(\frac{\alpha_g^3}{K_g^5} \right)^{1/2} P^2 A_g^2 - \frac{16\alpha_g^2}{K_g^4} (6e^{-2\gamma_g^2} - 1) P^3 A_g^3. \quad (34)$$

We note that as a consequence of the anharmonicity the effective force constant, $K_g(P)$, and the asymmetry constant, $\gamma_g^2(P)$, are pressure dependent. [If we had included terms in $E_g(0, R)$ of higher order than the fourth in $[R - R_g(0)]$ then α_g would also have been pressure dependent.] This results in a nonuniform displacement of the

vibronic transitions with pressure, as is evident from substituting the pressure-dependent force constants $K_e(P)$ and $K_g(P)$ into Eq. (6). In other words, the nonuniform displacement of the vibronic transitions with pressure is an additional measure of anharmonicity.

In addition, it is now clearly seen that when anharmonic forces are taken into account, then a linear displacement with pressure in the position of each vibronic line, including the zero-phonon line, occurs. This is shown by substituting the effective force constants given in Eq. (29) into Eq. (6a), and then expanding the square roots keeping linear terms in P . Equation (6b) for the dependence of the vibronic transition energies on pressure becomes

$$\begin{aligned} \epsilon_{nm}(P) & \approx 3\hbar \left[\left(m + \frac{1}{2}\right) \left(\frac{K_g}{M_g}\right)^{1/2} \frac{A_g}{K_g^2} \beta_g - \left(n + \frac{1}{2}\right) \left(\frac{K_e}{M_e}\right)^{1/2} \frac{A_e}{K_e^2} \beta_e \right] P \\ & + \left(\frac{A_e^2}{K_e} - \frac{A_g^2}{K_g} \right) \frac{P^2}{2} + \epsilon_{nm}(0), \end{aligned} \quad (35)$$

including the effects of anharmonicity in the change of the contours with pressure to first order in β_g and β_e , but not including the anharmonicity on the energy-level splitting. Note that the linear term in the pressure in Eq. (35) depends only on the second- and third-order coefficients of Eq. (24), that is on the K 's and β 's. Also note that if we included the anharmonicity in the energy-level splitting and assumed the anharmonicity to be small, then the added pressure dependence would be of an order of magnitude smaller than the linear term already included.

V. CONCLUSIONS

For impurity systems whose electronic states have harmonic adiabatic potentials, and pressure-independent coupling constants,¹⁸ the peak energy for broad-band phonon-assisted transitions is shown to have a linear pressure dependence if $K_g/K_e \neq A_g/A_e$ and a quadratic dependence if $K_e \neq K_g$ or $A_e \neq A_g$ [see Eq. (4b)], and vibronic transition energies have no linear dependence and have quadratic dependence if $K_g/K_e \neq A_g^2/A_e^2$ [see Eq. (6a)]. These conditions are corrections of some in current use. In the harmonic approximation, the peak positions for emission and absorption are displaced in opposite directions, while the bandwidths are both simultaneously increased or decreased, to first order in the pressure. It is proven that the equilibrium configuration coordinate for each state is independent of the way the pressure is applied so long as it is done adiabatically

and that the zero-pressure adiabatic potential is qualitatively different from all non-zero-pressure adiabatic potential curves.

The principal change in the transition matrix with hydrostatic pressure is a consequence of the change in phase of the two vibrational wave functions with respect to each other due to differential displacements in the adiabatic potentials for the two electronic states. The transition matrix is evaluated to first order for the zero-phonon transition [see Eq. (18)] and then for the most probable transition [see Eqs. (23) and (23')]. The types of centers for which hydrostatic pressure will enhance the zero-phonon transition are predicted [see Eq. (22)]. The parameters of impurity systems with vibronic spectra can be determined by applying the results of the theory to experimental spectra measured with different hydrostatic pressures.

We note that because the adiabatic potential curves are now pressure dependent the Franck-Condon principle must be generalized to include the condition $\Delta P = 0$, in addition to the usual conditions $\Delta R = 0$ and $\Delta \dot{R} = 0$.

Anharmonicity is shown to result in pressure-dependent force constant and asymmetry constant and thus is responsible for different energy displacements of different vibronic transitions, including the zero-phonon transition. The effect of anharmonicity on the pressure dependence of transition matrices remains to be calculated.

The present work assumes that the configuration coordinate associated with the Stokes shift or with the vibronic structure is the same as, or is simply related to, the deformation occurring with pressure. The relationship between these coordinates and its effects on spectra will be considered elsewhere.

Consideration of the pressure dependence of the envelope of the theoretical vibronic spectra, with and without anharmonicity, clarifies the origin of the pressure dependence of broad-band, phonon-assisted spectra. Analyses of the experimental broad-band spectrum and its pressure dependence result in a less complete determination of the parameters of the impurity system than is possible with the analysis herein developed for spectra with vibrational structure.

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APPENDIX A

The questions we want to answer are: What is the final-state energy in an optical transition from the re-

laxed initial state and how do you find this energy? We will give answers to these questions for the case of absorption, where the final state is the excited state for the simplest possible system that incorporates the essentials of the problem. The system we consider is one in which

$$R_g(0) = 0, \quad E_g(0) = 0, \quad A_e = A_g = A,$$

and

$$K_e = K_g = K.$$

We know from the balance of forces that $R_g(P) = -PA/K$, and the corresponding energy $E_g(P) = P^2A^2/2K$ when the pressure is applied adiabatically. Therefore, the initial state for the transition from the relaxed ground state is the state whose energy is $P^2A^2/2K$ and whose configuration is $R = -PA/K$. Note that the excited-state equilibrium is not at the same configuration as the ground-state equilibrium, when a pressure P is on the system, except accidentally, and therefore, we need to find the energy, not specifically for the excited-state equilibrium configuration, but for an arbitrary configuration.

Let R_1 be some arbitrary configurational coordinate, then we can ask what is the energy of the excited state for this configuration. We can determine this energy by finding the work done when changing from configuration R_1 to some configuration R_0 , for which we know the energy. We will choose R_0 to be $R_e(P)$, the relaxed configuration for the excited state when there is a pressure P applied to the system. The force on the system in the excited state is

$$F = -K[R - R_e(0)] - PA,$$

where the first term corresponds to the elastic energy and the second term corresponds to the constant pressure P . Now the work done by this force in going from R_1 to $R_e(P)$, the latter being where the force is zero, is

$$\begin{aligned} W &= \int_{R_1}^{R_e(P)} \{-K[R - R_e(0)] - PA\} dR \\ &= \frac{K}{2}[R_1 - R_e(0)]^2 + PA[R_1 - R_e(P)] \\ &\quad - \frac{K}{2}[R_e(P) - R_e(0)]^2. \end{aligned}$$

Note that this work involves a change at constant pressure. Now the energy of the excited state for the configuration R_1 , when a pressure P is on the system, is equal to the energy of the excited state for the configuration $R_e(P)$ plus W . We can find the energy of the configuration $R_e(P)$ by finding the work, W_1 , done by the system, when it is in the excited state as the pressure is removed adiabatically plus the energy of the configuration to which it goes, which is the excited-state zero-pressure equilibrium, $R_e(0)$. This work, W_1 , is just equal to the work done when

we apply a pressure P adiabatically to the system when it is in the excited state. That is,

$$W_1 = P^2A^2/2K.$$

If, when we remove the pressure, we did not go to the zero-pressure excited-state equilibrium, whose energy is $E_e(0)$, then: (a) If the state we went to had a higher energy, then we could let the system relax and then reapply the pressure coming to a state of lower energy than we relaxed to with the pressure P on the system. This contradicts the definition of the state at $R_e(P)$ to which we relaxed as being the equilibrium position state. Or (b), if the state we went to had a lower energy, then we have an inconsistency with the definition of the configuration at $R_e(0)$ being the equilibrium configuration for the excited state with zero pressure.

Now the energy of the excited state when the pressure P is on the system to which we make the optical transition from the ground state when the system is in the configuration R_1 is

$$\begin{aligned} E &= W + W_1 + E_e(0) \\ &= \frac{K}{2}[R_1 - R_e(0)]^2 + PA[R_1 - R_e(P)] \\ &\quad - \frac{K}{2}[R_e(P) - R_e(0)]^2 + \frac{P^2A^2}{2K} + E_e(0) \end{aligned}$$

which can be rewritten

$$E = \frac{K}{2}[R_e(P) - R_1]^2 + \frac{P^2A^2}{2K} + E_e(0),$$

which is just Eq. (2) for this special case.

APPENDIX B

In order to clarify some of the effects of hydrostatic pressure on radiative transitions of luminescent centers describable by a harmonic adiabatic potential we present here an extension of the spring analogy introduced in Sec. II, with and without pressure, for the ground and excited electronic states. For simplicity we shall consider the case for which the force constants for the two states and thus the spring constants are equal, $K_e = K_g$, and the coupling constants to the pressure are equal, $A_e = A_g$. Thus, the only difference in the two electronic states which exists in this spring analogy is the equilibrium positions, $R_e(0) \neq R_g(0)$; the difference in the electronic energies of the two states should be kept in mind but is not evident in the spring analogy.

If we assume that displacements of the right-hand end of the spring correspond to the configurational coordinate R then for springs of equal length the left-hand end of the spring must be fastened at dif-

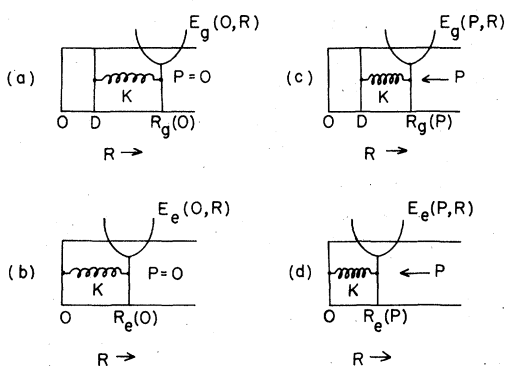


FIG. 3. Spring analogy to luminescent center for ground and excited states, without and with hydrostatic pressure.

ferent positions for the two different electronic states corresponding to $R_e(0) \neq R_g(0)$. Let us designate this difference by $D \equiv R_g(0) - R_e(0)$. Then the spring analogy for zero pressure is shown in Figs. 3(a) and 3(b), respectively, for the ground and excited states. Changes in energy with displacement in R from equilibrium are illustrated by the parabolas at the right-hand end of the springs.

With applied pressure P the equilibria are displaced to $R_g(P)$ and $R_e(P)$ for the two electronic states, respectively, as shown in Figs. 3(c) and 3(d). For these, the right-hand side of the spring experiences the spring force plus the force from the pressure; the force constant for the spring remains unchanged with pressure as proven in Sec. II; the D which in this analogy is the difference in positions of the left-hand end of the spring for the two electronic states remains unchanged with pressure because it describes the difference in crystal interactions alone for the two states.

We now consider optical transitions satisfying the Franck-Condon principle, that is $\Delta R = 0$ and $\Delta \dot{R} = 0$. For the transitions at $P = 0$, the most probable absorption corresponds to the difference in the parabolas for the two states with $R = R_g(0)$ on Figs. 3(a) and 3(b); the most probable emission, with $R = R_e(0)$ on the same pair of subfigures. Similarly, for the transitions at pressure, P , the peak absorption occurs at $R = R_g(P)$ on Figs. 3(c) and 3(d); the peak emission, at $R = R_e(P)$. The Franck-Condon princi-

ple is thus generalized to include an additional condition, $\Delta P = 0$.

Some authors, for example Drickamer, Frank, and Slichter,⁵ have obtained the dependence on hydrostatic pressure of the most probable radiative transitions by calculating the change in the most probable configuration of the initial state with pressure but neglecting the change in transition energy at any arbitrary configuration R with pressure. For absorption this corresponds in our analogy to a transition between Figs. 3(c) and 3(b) at $R_g(P)$; for emission, between Figs. 3(d) and 3(a) at $R_e(P)$. These transitions violate the condition $\Delta P = 0$, and thus do not include the effects of pressure on the dynamics for the final state of the transitions.

A recent analysis of Tompkins¹⁹ of experimental tests of the Drickamer, Frank, Slichter model "... revealed that the tests fail to verify the model, even qualitatively."

Several additional observations can be made by considering processes occurring between the subfigures of Fig. 3. The application of pressure to the crystal in its ground state corresponds to the adiabatic compression of the spring from $R_g(0)$ to $R_g(P)$ as shown from Figs. 3(a) to 3(c). After the previously described radiative transition from Fig. 3(c) to 3(d), there is a spontaneous relaxation from $R_g(P)$ to $R_e(P)$ on Fig. 3(d) during which work at constant pressure can be obtained from the system. The system then luminesces as previously described from Fig. 3(d) to 3(c), which is followed by relaxation from $R_e(P)$ to $R_g(P)$ on Fig. 3(c), during which work at constant pressure can be obtained.

The extension of the model to $K_e \neq K_g$ and $A_e \neq A_g$ is straightforward. The simple case, with only $R_e(0) \neq R_g(0)$, illustrates that the system in the two electronic states responds differently to pressure and the effect of pressure on the final state of the transition must be included in a complete theory. We emphasize in general: (a) a luminescent center in each electronic state is a distinct system with unique characteristics; (b) the connection between the center in its different electronic states is given by a single configuration coordinate diagram; and (c) the effects on optical spectra of perturbations of the luminescent center must include the effects on both the initial and final electronic states, particularly taking account of the connection between them.

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of two of the present authors (Ref. 12).

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$$H_n(x) = (2x)^n \Gamma(n+1) \sum_{m=0}^{[n/2]} \frac{(-4x^2)^{-m}}{\Gamma(m+1)\Gamma(n-2m+1)},$$

where $[\frac{1}{2}n]$ is the Legendre function ($[y]$ is the largest integer which is not greater than y).

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