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Calculation of stress-induced polarization of *F*-center luminescence for a vibronic model of the relaxed excited state

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The polarization of F-center luminescence caused by an applied stress is calculated from a direct numerical diagonalization of the matrix of the interaction Hamiltonian that includes the stress splitting of the electronic states for the simplest vibronic model of the relaxed excited state consistent with cubic symmetry. In this model the $2s$ electronic state is coupled to $2p$ by a triply degenerate odd-parity vibrational mode of frequency ω, and the $2s$ state is taken to lie below $2p$ by an energy $|E_{sp}| = \Delta \hbar\omega$. The polarization is found in general to increase from its value at 0 K as the temperature rises, reach a maximum, and then fall, eventually approaching a limiting rate of decrease that is independent of Δ and of the vibronic coupling strength. For $\Delta \lesssim 2$ this variation with temperature is found to be too large to be consistent with the experimental observation by Hetrick and Compton for KCl, NaCl, RbCl, and NaF that the polarization is effectively independent of temperature below 140 K. The conclusion from our work that we must have $\Delta > 2$ for these materials agrees with an earlier estimate for KCl from magnetic-polarization data but is not in agreement with other published estimates based on the temperature dependence of the radiative lifetime and of the Stark polarization. The implications of these results are discussed.

I. INTRODUCTION

Research has been under way for more than a decade in an attempt to learn the nature of the relaxed excited state (RES) of the F center in alkali halides and to develop a full understanding of the processes involved in F-band luminescence. The discovery by Swank and Brown[1] that the radiative lifetime of the F center in KCl, KBr, KI, and NaCl is anomalously long provided the first indication[2] that the lowest level of the RES might be a state of even parity rather than the electronic $2p$ state expected from studies of optical absorption in the F band. Subsequent theoretical calculations by Fowler *et al.*[3] and by Wood and Opik[4] showed that the $2s$ state should be close in energy to $2p$ and might be below it in the relaxed configuration. This last possibility was given strong additional support by Stark-effect studies on KCl, KF, RbCl, and NaF by Bogan and Fitchen,[5] Kühnert,[6] and Stiles *et al.*[7] which have since been extended to KBr, KI, RbBr, and RbI by Ohkura *et al.*[8]

If the $2s$ electronic state is indeed close to or below $2p$, coupling of these states by odd-parity vibrational modes of the lattice plays a crucial role in determining the radiative lifetime and other properties of the RES. An interpretation of the temperature dependence of the radiative lifetime on the basis of such a model was first proposed by Tomura *et al.*[9] The implications of this model were developed more fully by Bogan and Fitchen[5] and by Honda and Tomura,[10] using a semiclassical approximate theory of the vibrational-electronic ("vibronic") coupling. A quantum-mechanical treatment of this problem was first given by Ham,[11] who used similarities between this problem and that of the dynamic Jahn-Teller effect to give a general method of solution and to show how various properties of the RES might be calculated. This theory was used by Ham and Grevsmühl[12] to propose a quantitative interpretation of the experimental data for KCl and KF, using a perturbation treatment of the vibronic coupling for the weak-coupling limit. Numerical calculations of vibronic states and energies for intermediate coupling strengths were subsequently given by Grevsmühl[13] and by Kayanuma and Toyozawa.[14] The latter authors[14] also extended the theoretical model to include the possibility of coupling to additional vibrational modes of different symmetry type, and on this basis Kayanuma[15] proposed a reinterpretation of the data for KCl. More recently, the theory has been applied by Imanaka, Iida, and Ohkura[16] to give a quantitative interpretation of Stark-effect and lifetime data on seven alkali halides, and by Ohkura *et al.*,[17] Imanaka *et al.*,[18] and Iwahana *et al.*[19] to interpret stress and magnetic effects in the RES. A further extension of the theory has also been made by Kayanuma and Kondo[20] to include vibronic coupling among higher states ($3s$, $3p$, $3d$) of the RES and to propose an interpretation on this basis for the transient optical absorption within the RES observed by Kondo and Kanzaki[21] and by Schneider.[22]

While these attempts to account for the experimental results in terms of a vibronic model of the RES have led to general agreement that for *F* centers in alkali halides the 2*s* electronic state is nearly degenerate with or below the 2*p* state in the relaxed configuration, no consensus has yet developed concerning the values of the parameters in such a model that give the best quantitative fit to the data. In particular, quite different values have been inferred for the energy difference Δ between the 2*s* and 2*p* states, depending on the type of experiment emphasized in fitting the theory. For example, from the circular polarization of the luminescence induced by a magnetic field, Ham and Grevsmühl[12] obtained the values $\Delta \simeq 3.75$ and 3.5 for KF and KCl, respectively (with Δ given in units of the vibrational quantum $\hbar\omega$ of the *p*-like mode that couples these states), while Imanaka *et al.*,[16] using the same vibronic model, found instead that the values $\Delta = 0.0$ and 1.25 for the same two materials gave the best fit to the temperature dependence of the radiative lifetime and of the electric-field-induced linear polarization. So large an uncertainty in the fundamental quantity Δ is clearly of crucial importance in seeking a consistent interpretation of these and other experiments.

One of the arguments advanced by Ham and Grevsmühl[12] in favor of a large value for Δ was the temperature independence of the stress-induced linear polarization of the *F*-band luminescence found by Hetrick and Compton[23] for KCl, NaCl, RbCl, and NaF over the range 20 to 140 K. From their perturbation treatment of the vibronic coupling Ham and Grevsmühl showed that the stress-induced polarization should increase appreciably with increasing temperature as higher levels of the RES become populated, if Δ were not sufficiently large. In particular, if Δ were as small as some of the values proposed by Imanaka *et al.*,[16] the results of Ham and Grevsmühl[12] would lead one to expect a strong temperature dependence of the polarization, contrary to the observations of Hetrick and Compton.[23] However, it is now clear from the calculations of Grevsmühl,[13] Kayanuma,[15] and Imanaka *et al.*[16] for intermediate coupling that treating the vibronic coupling by perturbation theory does not provide a quantitatively reliable means of analysis except in the limit of vanishingly small coupling, since the calculations show that many of the parameters of the vibronic levels depend very strongly on the strength of the coupling and may change their values by a factor of 2 or more as the coupling strength S_1 increases from 0 to 0.5. Clearly, we need to make numerical calculations valid for intermediate coupling in order to determine what limits can be placed on Δ as a consequence of the temperature independence of the stress-induced polarization.

The purpose of this paper is to outline a calculation of this type for the stress-induced polarization and to give the results in a more complete form than was possible in an earlier preliminary report.[24] These results are found to lend support to the original arguments of Ham and Grevsmühl[12] (paper II) in favor of a value for Δ larger than those proposed by Imanaka *et al.*[16] In Sec. II we give the necessary background on the vibronic model for the RES based on the treatment by Ham[11] (paper I). In Sec. III the matrix elements are obtained that give the effect of stress (or strain) on the vibronic energy levels, and formulas are derived giving the resulting polarization of the luminescence originating from one of these levels when the RES decays radiatively to the 1*s* electronic ground state. Section IV gives the results obtained from the numerical calculations: First, in Sec. IV A values for the stress-induced polarization of luminescence from the vibronic ground state (0 K) are presented for various values of Δ as a function of S_1 $(0 \leq \Delta, S_1 \leq 5)$; in Sec. IV B graphs showing the temperature dependence of this polarization are shown; in Sec. IV C an approximate formula is derived which is useful in describing the initial dependence on temperature when only the lowest and first excited levels of the RES are appreciably populated. This formula is also useful in assessing the relative importance of contributions to the polarization from stress-induced splitting and mixing of the vibronic states. A discussion is given in Sec. V comparing the conclusions of this work with the values of Δ and S_1 inferred from the various other types of experiments. We also discuss the contrast between our conclusions and those of Ohkura *et al.*[17] and Iwahana *et al.*,[19] who have independently made calculations of the stress-induced polarization. Finally, in an Appendix we derive for the stress-induced polarization an asymptotic formula which is independent of the coupling strength and which gives the limiting behavior at high temperatures of the calculated curves.

The calculations given in this paper are limited to the simplest vibronic model for the RES that is consistent with the cubic symmetry of the *F* center. In particular, of the possible vibrational modes that couple to the 2*s* and 2*p* electronic states we have included only the *p*-like mode that couples 2*s* with 2*p*. While coupling to additional modes of different symmetry may be significant, as Kayanuma[15] and Iwahana *et al.*[19] have proposed, it has not yet been demonstrated to our satisfaction that this additional coupling is necessary to explain the data. In any case, it is important to establish the limitations of the simple model before complicating features are added. Moreover, the simple model is much easier to handle mathematically, and one can easily ensure the accuracy of the numerical calculations by including enough vibronic states without making the matrices too large for efficient computation. We consider the possible effects of additional types of coupling in a qualitative discussion in Sec. V.

II. REVIEW OF THE VIBRONIC MODEL

We consider the same vibronic model used in papers I (Ref. 11) and II (Ref. 12) with the 2*s* (Γ_1^+) and 2*p* (Γ_4^-) electronic states[25] interacting in cubic symmetry (point group O_h) via a triply degenerate odd-parity Γ_4^- vibrational mode Q_x, Q_y, Q_z. In this model the Hamiltonian

$$\mathcal{H} = \mathcal{H}_e + \mathcal{H}_L + \mathcal{H}_{eL} \tag{2.1}$$

has three parts, the first of which gives the relative energies of the electronic states in the cubic configuration ($Q_x = Q_y = Q_z = 0$)

$$\mathcal{H}_e = +\tfrac{1}{2}E_{sp}\rho_0 , \tag{2.2}$$

where we denote by ρ_0 the operator

$$\rho_0 = +|2s\rangle\langle 2s| - |2p_x\rangle\langle 2p_x| - |2p_y\rangle\langle 2p_y| - |2p_z\rangle\langle 2p_z| . \tag{2.3}$$

The vibrational part $\mathcal{H}_L$ describes a three-dimensional simple harmonic oscillator of frequency ω and effective mass μ,

$$\mathcal{H}_L = (2\mu)^{-1}[P_x^2 + P_y^2 + P_z^2 + (\mu\omega)^2(Q_x^2 + Q_y^2 + Q_z^2)] . \tag{2.4}$$

Finally, the linear coupling of the electronic states by the distortion is given by

$$\mathcal{H}_{eL} = G(Q_x\rho_x + Q_y\rho_y + Q_z\rho_z) , \tag{2.5}$$

where

$$\rho_i = |2p_i\rangle\langle 2s| + |2s\rangle\langle 2p_i| , \tag{2.6}$$

and the coupling energy[11] is given by

$$E_G = G^2/2\mu\omega^2 . \tag{2.7}$$

In units of the vibrational energy quantum $\hbar\omega$, we denote by Δ and S_1 the ratios

$$\Delta = -E_{sp}/\hbar\omega , \tag{2.8}$$

$$S_1 = E_G/\hbar\omega . \tag{2.9}$$

We shall be particularly concerned with the case in which the 2*s* state lies below 2*p*, so that the energy separation E_{sp} is negative and Δ is positive.

In seeking eigenstates of $\mathcal{H}$ in the regime of weak and intermediate coupling, and in determining the effect of lattice strain on these states (Sec. III), it is convenient to adopt as a basis the vibronic eigenstates of the simplified Hamiltonian

$$\mathcal{H}_0 = \mathcal{H}_e + \mathcal{H}_L , \tag{2.10}$$

which describes the system when the coupling G is zero. We introduce linear combinations of the 2*p* states

$$|2p_0\rangle = |2p_z\rangle , \quad |2p_{\pm 1}\rangle = \mp (2)^{-1/2}(|2p_x\rangle \pm i|2p_y\rangle) \tag{2.11}$$

which are eigenstates, with the conventional phase relations,[26] of the *z* component of the electronic orbital angular momentum operator $\vec{l}$. Within the basis of the 2*s* and 2*p* electronic states the components of $\vec{l}$ have the representation

$$l_z = -i|2p_x\rangle\langle 2p_y| + i|2p_y\rangle\langle 2p_x| , \tag{2.12}$$

etc. In the space of the Q's we introduce the vibrational angular momentum operator $\vec{L}$ with components L_x, L_y, L_z given by

$$L_z = \hbar^{-1}(Q_xP_y - Q_yP_x) , \tag{2.13}$$

etc., and define polar coordinates r, θ, φ ($Q_z = r\cos\theta$, $Q_x = r\sin\theta\cos\varphi$, $Q_y = r\sin\theta\sin\varphi$), so that the normalized spherical harmonics $Y_{LM'}(\theta,\varphi)$ (defined[11] with the phase relationship of Condon and Shortley[26]) are eigenfunctions of $\vec{L}^2$ and L_z. Harmonic oscillator eigenfunctions $|n, L, M'\rangle$ having the angular dependence of $Y_{LM'}(\theta,\varphi)$, satisfying

$$\mathcal{H}_L|n, L, M'\rangle = (n + \tfrac{3}{2})\hbar\omega|n, L, M'\rangle , \tag{2.14}$$

and therefore corresponding to a vibrational energy

$$E = (n + \tfrac{3}{2})\hbar\omega \tag{2.15}$$

with $n = L + 2N$ ($N = 0, 1, 2, 3, \ldots$), are given by

$$|L+2N, L, M'\rangle = \frac{[2\Gamma(N+1)]^{1/2}\alpha^{3/2}}{[\Gamma(N+L+\frac{3}{2})]^{1/2}}(\alpha r)^L \exp(-\tfrac{1}{2}\alpha^2 r^2) \times L_N^{L+1/2}(\alpha^2 r^2)Y_{LM'}(\theta,\varphi) , \tag{2.16}$$

where $\alpha = (\mu\omega/\hbar)^{1/2}$ and $L_N^a(z)$ is the Laguerre polynomial defined by the generating function[27]

$$(1-t)^{-(1+a)}\exp\left(\frac{-zt}{(1-t)}\right) = \sum_{N=0}^{\infty} t^N[\Gamma(N+a+1)]^{-1}L_N^a(z) . \tag{2.17}$$

The full Hamiltonian $\mathcal{H}$ including the coupling $\mathcal{H}_{eL}$ is invariant under a continuous group of simultaneous rotations of the electronic and vibrational coordinates.[11] Thus, although $\mathcal{H}$ does not commute with $\vec{I}$ or $\vec{L}$ separately (except when G is zero), it does commute with the components of

$$\vec{J} = \vec{I} + \vec{L}\,. \tag{2.18}$$

Accordingly, it is convenient to classify eigenstates of $\mathcal{H}$ by the eigenvalues $J(J+1)$ and M of $\vec{J}^2$ and J_z, respectively. Eigenstates of $\mathcal{H}_0$ classified in this fashion are easily obtained by forming linear combinations of products of the electronic states with the vibrational eigenstates (2.16), using a table of Wigner coefficients.[26] We use the designation

$$|J, M; (J+2N), J, 2s\rangle = |J+2N, J, M\rangle\,|2s\rangle \tag{2.19}$$

for the state formed by the simple product of the electronic state $|2s\rangle$ with the vibrational state given by Eq. (2.16) with $L = J$. The Wigner coefficients[26] in the linear combinations

$$|J, M; (2N+L), L, 2p\rangle\,, \tag{2.20}$$

formed from the electronic $2p$ states (2.11) for $J = L-1, L, L+1$ are listed in Table I.

Because $\mathcal{H}_{eL}$ commutes with $\vec{J}$, the only nonzero matrix elements of $\mathcal{H}_{eL}$ between the states (2.19) and (2.20) are those between states with the same values of J and M, and these are independent of M. To obtain these explicitly, we make use of Eq. (3.17) of paper I to perform the integration over the electronic coordinates and the angular part of the integration in Q space. The radial integration in Q space is then easily done using the radial part of the oscillator wave functions in Eq. (2.16) and the generating function for the Laguerre polynomials in Eq. (2.17). We find in this way that the only nonzero matrix elements of $\mathcal{H}_{eL}$ are the following:

$$\langle J, M; (J+2N\pm 1), J-1, 2p|\mathcal{H}_{eL}|J, M; (J+2N), J, 2s\rangle = \mp (S_1)^{1/2}\hbar\omega[J/(2J+1)]^{1/2}[(J+2N+\tfrac{3}{2}) \mp (J-\tfrac{1}{2})]^{1/2}\,, \tag{2.21a}$$

$$\langle J, M; (J+2N\pm 1), J+1, 2p|\mathcal{H}_{eL}|J, M; (J+2N), J, 2s\rangle = \mp (S_1)^{1/2}\hbar\omega[(J+1)/(2J+1)]^{1/2}[(J+2N+\tfrac{3}{2}) \pm (J+\tfrac{3}{2})]^{1/2}\,, \tag{2.21b}$$

where either the upper or lower sign is to be taken throughout the equation. These matrix elements of $\mathcal{H}_{eL}$ were first given by Grevsmühl[13] and can be obtained also (apart from some nonessential sign differences) from the work of Kayanuma and Toyozawa.[14]

$\mathcal{H}$ and $\mathcal{H}_{eL}$ also commute with the inversion operator[11]

$$\Lambda = I\rho_0\,, \tag{2.22}$$

where I is the inversion operator in Q space, and ρ_0 as defined by Eq. (2.3) plays the role of the electronic inversion operator for the $2s$ and $2p$ states. Vibronic eigenstates of $\mathcal{H}$ may therefore be labeled also by their parity $\Lambda' = \pm 1$. Since the oscillator state $|L+2N, L, M'\rangle$ as given by Eq. (2.16) has the parity $(-1)^L$ of $Y_{LM'}(\theta, \varphi)$, we see from Eq. (2.21) that $\mathcal{H}_{eL}$ couples only those vibronic states for a given J which have the parity $\Lambda' = (-1)^J$, and we give such states the designation[11] type I. The states of type I comprise all the states formed from the $2s$ electronic state as in Eq. (2.19) and the states $|J, M, (2N+L), L, 2p\rangle$ with $J = L \pm 1$ given by the first and third rows of Table I. A second class[11] of states, called type

TABLE I. Wigner coefficients for the linear combinations of product states, formed from the vibrational eigenstates $|L+2N, L, M'\rangle$ of $\mathcal{H}_L$ and the electronic $2p$ states, which are eigenstates of $\vec{J}^2$ and J_z with $J = L-1, L, L+1$ and $J_z = M$ (from Condon and Shortley, Ref. 26, Table 2^3, p. 76).

$\|J, M; (2N+L), L, 2p\rangle$	$\|2N+L, L, M-1\rangle\|2p_{+1}\rangle$	$\|2N+L, L, M\rangle\|2p_0\rangle$	$\|2N+L, L, M+1\rangle\|2p_{-1}\rangle$
$\|L-1, M; (2N+L), L, 2p\rangle$	$+\left(\frac{(L-M)(L-M+1)}{2L(2L+1)}\right)^{1/2}$	$-\left(\frac{(L-M)(L+M)}{L(2L+1)}\right)^{1/2}$	$+\left(\frac{(L+M+1)(L+M)}{2L(2L+1)}\right)^{1/2}$
$\|L, M; (2N+L), L, 2p\rangle$	$-\left(\frac{(L+M)(L-M+1)}{2L(L+1)}\right)^{1/2}$	$+\frac{M}{[L(L+1)]^{1/2}}$	$+\left(\frac{(L-M)(L+M+1)}{2L(L+1)}\right)^{1/2}$
$\|L+1, M; (2N+L), L, 2p\rangle$	$+\left(\frac{(L+M)(L+M+1)}{(2L+1)(2L+2)}\right)^{1/2}$	$+\left(\frac{(L-M+1)(L+M+1)}{(2L+1)(L+1)}\right)^{1/2}$	$+\left(\frac{(L-M)(L-M+1)}{(2L+1)(2L+2)}\right)^{1/2}$

II, also belongs to J but has the parity $\Lambda' = (-1)^{J+1}$ and is completely independent of $\mathcal{H}_{eL}$. These states are formed entirely from the $2p$ states and are given by the second row of Table I with $J = L$. The states of type II exist for all values of J except $J = 0$.

Any eigenstate of the full Hamiltonian $\mathcal{H}$ that belongs to J and M and is of type I is then easily shown from the form of the matrix elements in Eq. (2.21) to have the general form

$$\begin{aligned}\Psi_{\text{I}}(J, M, \Lambda') = &\sum_{N=0}^{\infty} a(J, J+2N) | J, M; (J+2N), J, 2s\rangle \\ &+ \sum_{N=0}^{\infty} b(J, J+2N-1) | J, M; (J+2N-1), J-1, 2p\rangle \\ &+ \sum_{N=0}^{\infty} c(J, J+2N+1) | J, M; (J+2N+1), J+1, 2p\rangle \qquad (2.23)\end{aligned}$$

with $\Lambda' = (-1)^J$. The coefficients in this expansion are independent of M and may be determined, together with the energy eigenvalue, by diagonalizing the matrix of $\mathcal{H}$ obtained from Eqs. (2.2), (2.15), and (2.21) for the chosen value of J. In practice this diagonalization may be carried out by truncating the matrix of $\mathcal{H}$ by omitting states having N larger than a value chosen large enough to make the eigenstates and energies of interest independent of this choice to a suitable accuracy. Since the states of type II are not affected by $\mathcal{H}_{eL}$, these eigenstates $\Psi_{\text{II}}(J, M, \Lambda')$ of $\mathcal{H}$ which belong to J and M and have $\Lambda' = (-1)^{J+1}$ are simply the eigenstates of $\mathcal{H}_0$

$$\Psi_{\text{II}}(J, M, \Lambda') = | J, M; (2N+J), J, 2p\rangle , \qquad (2.24)$$

with energies given by adding the electronic energy $-\frac{1}{2}E_{sp}$ of the $2p$ states to the vibrational energy $(2N + J + \frac{3}{2})\hbar\omega$ given by Eq. (2.15).

Numerical calculations of the energies of eigenstates of $\mathcal{H}$ of type I, carried out in a manner similar to that outlined above, have been made for selected values of Δ and S_1 by Grevsmühl[13] and by Kayanuma and Toyozawa.[14] For $\Delta > 0$ the lowest vibronic level (including those of type II) is always found to be a nondegenerate state of type I with $J = 0$, with the nearest excited level a triplet of type I with $J = 1$. This is then the expected order for the lowest states in the situation with which we are concerned in this paper. Even with $\Delta < 0$, however, the same order is obtained provided S_1 exceeds a critical value which depends on Δ. For sufficiently large S_1 the relative energies of the lowest states (all of type I) approach values given by the asymptotic formula[11]

$$E_{\text{I}}(J) - E_{\text{I}}(0) = J(J+1)\hbar\omega/4S_1 , \qquad (2.25)$$

which is independent of Δ.

III. STRESS-INDUCED POLARIZATION OF LUMINESCENCE

In this section we consider how the vibronic eigenstates and energy levels of Sec. II are changed by an externally applied stress. In particular, we will formulate the calculation of the stress-induced polarization of the luminescence that results when the F center decays radiatively from the RES to its nondegenerate $1s$ electronic ground state.

An applied stress induces strain in the crystal and thus lowers the symmetry of the F center from cubic. We will be concerned primarily with effects linear in the stress, so that we could treat an arbitrary stress to this order by superimposing effects of uniaxial stress directed along suitable axes. For convenience, therefore, we will limit our considerations to uniaxial stress X applied along the [001] crystal axis, which produces a strain

$$e_\theta = +X/(c_{11} - c_{12}) \qquad (3.1)$$

in the crystal. Here e_θ is the combination[11]

$$e_\theta = e_{zz} - \tfrac{1}{2}(e_{xx} + e_{yy}) \qquad (3.2)$$

of the components e_{ij} of the strain tensor, while c_{ij} denotes the crystal elastic constants. We will assume that the principal consequence of the reduction in symmetry is the splitting of the triple degeneracy of the $2p$ electronic state and that we may ignore any similar splitting of the degeneracy of the vibrational modes and any change in their coupling to the electronic states. The modified Hamiltonian is then taken to be

$$\mathcal{H}' = \mathcal{H} + \mathcal{H}_S , \qquad (3.3)$$

where $\mathcal{H}$ is identical with Eq. (2.1) and $\mathcal{H}_S$ describes the splitting of the $2p$ state linear in the strain e_θ,

$$\mathcal{H}_S = V_2 e_\theta \mathcal{E}_\theta . \qquad (3.4)$$

Here V_2 is the strain coupling coefficient[11] of the $2p$ states, and $\mathcal{E}_\theta$ is the electronic operator

$$\mathcal{E}_\theta = -|2p_z\rangle\langle 2p_z| + \tfrac{1}{2}|2p_x\rangle\langle 2p_x| + \tfrac{1}{2}|2p_y\rangle\langle 2p_y| , \qquad (3.5a)$$

or equivalently, in terms of the states in Eq. (2.11),

$$\mathcal{E}_\theta = -|2p_0\rangle\langle 2p_0| + \tfrac{1}{2}|2p_{+1}\rangle\langle 2p_{+1}| + \tfrac{1}{2}|2p_{-1}\rangle\langle 2p_{-1}| . \qquad (3.5b)$$

From the form of $\mathcal{E}_\theta$ in Eq. (3.5b) it is evident that $\mathcal{E}_\theta$ commutes with l_z and ρ_0 and therefore with J_z and Λ, so that eigenstates of the modified Hamiltonian $\mathcal{H}'$ remain eigenstates of J_z and Λ and can continue to be labeled by the eigenvalue M and by parity. J is no longer a good quantum number, but because $\mathcal{E}_\theta$ transforms under rotations in the same way as the $M=0$ component of a spherical harmonic with $J=2$, nonzero matrix elements of $\mathcal{H}_S$ must satisfy the restriction $\Delta J \leq 2$. Moreover, since $\mathcal{E}_\theta$ is a purely electronic operator coupling only the $2p$ states, the only nonzero matrix elements of $\mathcal{H}_S$ among the states (2.19) and (2.20) are those between states $|J, M; (2N+L), L, 2p\rangle$ having the same values for L and N, otherwise the orthogonality of the vibrational factors makes the matrix element vanish. From these restrictions it is clear that $\mathcal{H}_S$ couples directly two states of type I having $M=M'$ and $|J-J'|=2$, and such matrix elements are easily found from Eq. (3.5b) and Table I to be given by

$$\langle L+1, M; (2N+L), L, 2p|\mathcal{H}_S|L-1, M; (2N+L), L, 2p\rangle = +\tfrac{3}{2}V_2 e_\theta (2L+1)^{-1}(L^2-M^2)^{1/2}[(L+1)^2-M^2]^{1/2}[L(L+1)]^{-1/2} . \qquad (3.6)$$

$\mathcal{H}_S$ also couples states of type I to states of type II if $M=M'\neq 0$ and $|J-J'|=1$, and these matrix elements may be expressed as

$$\langle L\pm 1, M; (2N+L), L, 2p|\mathcal{H}_S|L, M; (2N+L), L, 2p\rangle = \mp \tfrac{3}{2} M V_2 e_\theta [L(L+1)(2L+1)]^{-1/2}[(U^2-M^2)/U]^{1/2} , \qquad (3.7)$$

where U takes the value $U=L+1$ for $J=L+1$ [the upper sign in Eq. (3.7)] and $U=L$ for $J=L-1$. Diagonal matrix elements of $\mathcal{H}_S$ with respect to these states are similarly found to be given for the states of type I by

$$\langle J, M; (2N+L), L, 2p|\mathcal{H}_S|J, M; (2N+L), L, 2p\rangle = +V_2 e_\theta [3M^2 - J(J+1)][(2L+1)(J+L+1)]^{-1} , \qquad (3.8)$$

where J takes only the values $(L+1)$ and $(L-1)$. The diagonal matrix elements for the states of type II $(J=L)$ are given by

$$\langle L, M; (2N+L), L, 2p|\mathcal{H}_S|L, M; (2N+L), L, 2p\rangle = -V_2 e_\theta [3M^2 - L(L+1)][2L(L+1)]^{-1} . \qquad (3.9)$$

All other matrix elements of $\mathcal{H}_S$ among the states (2.19) and (2.20) are zero.

To obtain eigenstates and eigenvalues of the modified Hamiltonian $\mathcal{H}'$ of Eq. (3.3), including the effect of a small strain e_θ, we proceed as in Sec. II to set up and diagonalize the matrix of the Hamiltonian in the basis of the states (2.19) and (2.20). Since J is no longer a good quantum number, however, we must now include states of both types I and II with different values of J, do the diagonalization separately for each value of M and the parity Λ', and include the matrix elements of $\mathcal{H}_S$ as given by Eqs. (3.6)–(3.9), using a suitably chosen small value for the ratio $\sigma = V_2 e_\theta/\hbar\omega$. The eigenstate of $\mathcal{H}'$ for the ith level now takes the general form

$$\begin{aligned}\Psi_i(M,\Lambda') = &\sum_{N,L}{}' a_i(L, M, 2N+L)|L, M; (2N+L), L, 2s\rangle \\ &+ \sum_{N,L}{}'' c_i(L-1, M, 2N+L)|L-1, M; (2N+L), L, 2p\rangle \\ &+ \sum_{N,L}{}'' b_i(L+1, M, 2N+L)|L+1, M; (2N+L), L, 2p\rangle \\ &+ \sum_{N,L}{}'' d_i(L, M, 2N+L)|L, M; (2N+L), L, 2p\rangle , \end{aligned} \qquad (3.10)$$

where, in contrast to Eq. (2.23), the coefficients now depend in general on M. The primes on the summations in Eq. (3.10) indicate that only those values of L are included in the sums that are consistent with the given parity Λ'; thus for $\Lambda' = +1(-1)$ L must be even (odd) in the sum labeled with a single prime, and odd (even) in the three doubly primed sums. Certain coefficients in these sums may be zero in special cases; for example, for $M=0$ the coupling of states of type I with those of type II vanishes, according to Eq. (3.7), so that for a state with $M=0$ either all coefficients $d(L, 0, 2N+L)$ are zero or all the a, b, and c coefficients are zero and only a single coefficient $d(L, 0, 2N+L)$ (which then equals unity) is nonzero.

Except for $M=0$, energy levels corresponding to the states (3.10) are doubly degenerate, since matrix elements of the Hamiltonian $\mathcal{H}'$ for positive and negative values of M differ only in the sign of the off-diagonal elements of $\mathcal{H}_S$ which couple states of type I with states of type II and which are given by Eq. (3.7). This sign difference does not affect the energy eigenvalues, since the matrices for $\pm M$ could be made identical if, in defining the basis states, we chose to reverse the sign of every state of type II having a negative value of M, instead of using the sign conventions given in Table I. The coefficients in the expansion (3.10) of an eigenstate for a negative value of M may therefore be obtained from those of the corresponding state with M positive by reversing the sign of all the coefficients $d(L, M, 2N+L)$ of the states of type II. As we will see below, this sign difference is just what is required in order that states with $\pm M$ contribute equally to the stress-induced polarization of the luminescence.

To determine the polarization of the light emitted when the excited state of the F center decays to its ground state, we use the result proved in paper I (Ref. 11) that I_η^i, the probability per unit time of emission from the vibronic state Ψ_i of a photon of linear polarization η ($\eta = x, x, z$), is given by

$$I_\eta^i = [\tau_r(2p)]^{-1} \int |\Phi_\eta^i|^2 dQ \,. \tag{3.11}$$

Here $\tau_r(2p)$ is the radiative lifetime of the $2p$ electronic state, and Φ_η^i is the vibrational factor multiplying the electronic state $|2p_\eta\rangle$ when we write the vibronic wave function Ψ_i in the form

$$\Psi_i = \Phi_S^i |2s\rangle + \Phi_x^i |2p_x\rangle + \Phi_y^i |2p_y\rangle + \Phi_z^i |2p_z\rangle \,. \tag{3.12}$$

To correspond with the form of the states given in Table I, it is more convenient to write Ψ_i in the alternative form

$$\Psi_i = \Phi_s^i |2s\rangle + \Phi_{+1}^i |2p_{+1}\rangle + \Phi_0^i |2p_0\rangle + \Phi_{-1}^i |2p_{-1}\rangle \tag{3.13}$$

and then use Eq. (2.11) to obtain the relations

$$\Phi_z^i = \Phi_0^i \,, \quad \Phi_x^i = -2^{-1/2}\Phi_{+1}^i + 2^{-1/2}\Phi_{-1}^i \,, \tag{3.14}$$

etc. If Ψ_i is an eigenstate of J_z characterized by M, as in Eq. (3.10), it can be shown from Table I that Φ_{+1}^i and Φ_{-1}^i are orthogonal under integration in Q space, so that we have from Eq. (3.14)

$$\int |\Phi_x^i|^2 dQ = \tfrac{1}{2} \int (|\Phi_{+1}^i|^2 + |\Phi_{-1}^i|^2)\, dQ \,. \tag{3.15}$$

We can obtain Φ_{+1}^i, Φ_{-1}^i, and Φ_0^i for the state $\Psi_i(M, \Lambda')$ in Eq. (3.10) by combining from Table I all terms that have a common vibrational state. For example, Φ_{+1}^i takes the form

$$\Phi_{+1}^i(M, \Lambda') = \sum_{N,L}{}'' k_i(L, M, N) |2N+L, L, M-1\rangle \,, \tag{3.16}$$

where k_i involves the Wigner coefficients from the first column of Table I and the coefficients b_i, c_i, and d_i from Eq. (3.10). Using the orthonormality of the states $|2N+L, L, M'\rangle$, we obtain in this way the results

$$\begin{aligned}\int |\Phi_0^i(M, \Lambda')|^2 dQ = \sum_{N,L}{}'' |\{&[(L-M+1)(L+M+1)/(2L+1)(L+1)]^{1/2} b_i(L+1, M, 2N+L) \\ &- [(L-M)(L+M)/L(2L+1)]^{1/2} c_i(L-1, M, 2N+L) + M[L(L+1)]^{-1/2} d_i(L, M, 2N+L)\}|^2 \,,\end{aligned} \tag{3.17a}$$

$$\begin{aligned}\int |\Phi_{+1}^i(M, \Lambda')|^2 dQ = \sum_{N,L}{}'' |\{&[(L+M)(L+M+1)/(2L+1)(2L+2)]^{1/2} b_i(L+1, M, 2N+L) \\ &+ [(L-M)(L-M+1)/2L(2L+1)]^{1/2} c_i(L-1, M, 2N+L) \\ &- [(L+M)(L-M+1)/2L(L+1)]^{1/2}\, d_i(L, M, 2N+L)\}|^2 \,,\end{aligned} \tag{3.17b}$$

$$\begin{aligned}\int |\Phi^i_{-1}(M,\Lambda')|^2 dQ = \sum_{N,L}{}'' \big|\{&[(L-M)(L-M+1)/(2L+1)(2L+2)]^{1/2} b_i(L+1,M,2N+L)\\ &+[(L+M)(L+M+1)/2L(2L+1)]^{1/2} c_i(L-1,M,2N+L)\\ &+[(L-M)(L+M+1)/2L(L+1)]^{1/2} d_i(L,M,2N+L)\}\big|^2 .\end{aligned} \tag{3.17c}$$

Together with Eqs. (3.11), (3.14), and (3.15), Eqs. (3.17a)–(3.17c) provide the expressions we need for the probabilities I^i_x (or I^i_y) and I^i_z for emission from the state $\Psi_i(M,\Lambda')$ in Eq. (3.10).

It was noted earlier that in the calculation of the eigenstates of $\mathcal{H}'$ for an axial strain e_θ, the coefficients of corresponding states $\Psi_i(M,\Lambda')$ of positive and negative M are identical except for the sign difference

$$d_i(L,-M,2N+L) = -d_i(L,M,2N+L) . \tag{3.18}$$

Using this relationship of the coefficients in Eq. (3.17a), we find that states of $\pm M$ have equal values for the integral of $|\Phi^i_0|^2$ and thus of I^i_z. The same is true for I^i_x, as we see by noting from Eqs. (3.17b) and (3.17c) that the expressions for the integrals of $|\Phi^i_{+1}|^2$ and $|\Phi^i_{-1}|^2$ are exchanged if the sign of M is changed and the relationship (3.18) used.

At a temperature T, the probability per unit time $I_\eta(T)$ that a photon of polarization η is emitted is then obtained by averaging I^i_η over all vibronic levels of the $2s$ and $2p$ excited state, weighted with the probability of level occupancy. Assuming an equilibrium Boltzmann distribution, we have

$$I_\eta(T) = \mathfrak{z}^{-1} \sum_i I^i_\eta \exp\left(\frac{-E_i}{kT}\right) , \tag{3.19}$$

where E_i denotes the level energy and $\mathfrak{z}$ the partition function

$$\mathfrak{z} = \sum_i \exp\left(\frac{-E_i}{kT}\right) . \tag{3.20}$$

The linear polarization of the luminescence is then defined[5,11] by

$$P_S(T) = [I_z(T) - I_x(T)]/[I_z(T) + I_x(T)] . \tag{3.21}$$

IV. RESULTS

A. Stress-induced polarization at $T = 0$ K

At $T = 0$ K only the lowest vibronic level of the RES is occupied, if the RES is assumed to be in thermal equilibrium. As discussed in Sec. II, this state has $J = 0$ in the absence of stress for all values of S_1 and all positive values of Δ. The effect of a strain e_θ is to mix this state with the $M = 0$ component of states of type I having $J = 2, 4, 6, \ldots,$ but to first order in the strain parameter $\sigma = V_2 e_\theta/\hbar\omega$ the polarization of the emission from this level arises solely from mixing with states having $J = 2$. Treating the strain interaction $\mathcal{H}_S$ [Eq. (3.4)] by perturbation theory, we may show easily from the matrix elements of Eqs. (3.6)–(3.9) that the coefficients $b_0(2,0,2N+1)$ in Eq. (3.10) for this lowest level are proportional to σ in lowest order, whereas the coefficients $d_0(L,0,2N+L)$ are zero. The coefficients $c_0(0,0,2N+1)$ are independent of σ in lowest order, their size being determined by the strength S_1 of the vibronic coupling. It follows then from Eqs. (3.11)–(3.17) that $P_S(0)$, the stress-induced polarization at $T = 0$ K as defined by Eq. (3.21), is given to first order in σ by

$$P_S(0) = -\frac{3}{(2)^{1/2}} \frac{\sum_N b_0(2,0,2N+1)c_0(0,0,2N+1)}{\sum_N [c_0(0,0,2N+1)]^2} \tag{4.1}$$

In Fig. 1 is shown the ratio $P_S(0)/\sigma$ as calculated for various positive values of Δ as a function of S_1. In making these calculations, we obtained values for the coefficients $c_0(0,0,2N+1)$ and $b_0(2,0,2N+1)$ for the lowest level from a numerical diagonalization of the matrix of $\mathcal{H}' = \mathcal{H} + \mathcal{H}_S$

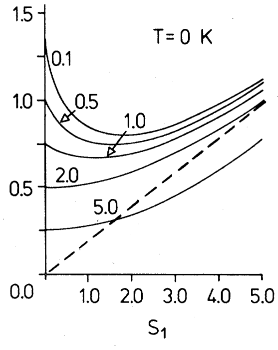

FIG. 1. Stress-induced polarization $P_S(0)$ of luminescence at $T = 0$ K, when all luminescence originates in the lowest vibronic level of the RES, as a function of the coupling strength S_1. The ordinate is the ratio of $P_S(0)$ to the strain parameter σ, and the curves are labeled with the corresponding value of Δ, the energy of the $2p$ electronic state with respect to the $2s$ state in units of $\hbar\omega$. The curves were obtained from calculations described in the text using a value $\sigma = 0.1$. The dashed line represents the asymptotic relation given by Eq. (4.4) of the text.

for $M=0$, $\Lambda'=+1$, as discussed in Sec. III, using standard computer routines.[28] The matrix was truncated in these calculations by excluding states with $N>9$ and also states with $J\geq 4$, and a value $\sigma=0.1$ was used. This value of σ is small enough to cause no significant difference between $P_S(0)$ as given by Eq. (4.1) and that calculated from the more general formulas in Eqs. (3.17), which were actually used in obtaining the results in Fig. 1 and which include terms of order σ^2 or higher that are omitted in Eq. (4.1).

The results shown in Fig. 1 may be compared, in the limit $S_1 \rightarrow 0$, with the formula obtained in paper II (Ref. 12) [Eq. (3.6) of paper II] by treating the vibronic coupling by perturbation theory,

$$\lim_{S_1\to 0} P_S(0)=\tfrac{3}{2}V_2 e_\theta/(|E_{sp}|+\hbar\omega)\,, \tag{4.2a}$$

or, in the notation of Fig. 1,

$$\lim_{S_1\to 0} P_S(0)/\sigma=3/[2(\Delta+1)]\,. \tag{4.2b}$$

Good agreement with Fig. 1 is found.

A further check in the limit of strong coupling is provided by the asymptotic relation obtained in paper I (Ref. 11) [Eq. (5.50) of paper I, where the numerical factor was erroneously given as $\frac{3}{20}$],

$$P_S(0)\sim(\tfrac{3}{10})V_2 e_\theta[E_{\mathrm{I}}(2)-E_{\mathrm{I}}(0)]^{-1}\,. \tag{4.3}$$

Taking the energy-level difference from Eq. (2.25), which is independent of Δ for sufficiently large S_1, we have

$$P_S(0)/\sigma\sim\tfrac{1}{5}S_1\,. \tag{4.4}$$

The curves of Fig. 1 appear to be converging toward this limiting relation, shown by the dashed line.

B. Temperature dependence of stress-induced polarization

At a temperature T above 0 K, higher vibronic levels of the RES have a finite probability of being occupied, and calculation of $P_S(T)/\sigma$ requires averaging the polarized emission probabilities over possible initial states in accord with Eqs. (3.19)–(3.21). To obtain the relative energies of these states in the presence of a small strain e_θ, together with the coefficients in the perturbed wave function of Eq. (3.10) needed to calculate the emission probabilities from Eqs. (3.11) and (3.17), we have used standard computer routines[28] as in Sec. IV A to diagonalize the matrices of $\mathcal{H}'=\mathcal{H}+\mathcal{H}_S$ for different values of M and Λ', again using a value $\sigma=0.1$ and truncating the matrices by excluding states with $N>9$. For sufficiently low temperatures and the order of levels expected for $\Delta>0$, as described in Sec. II, only levels having $J=0, 1, 2$ in the absence of strain will be significantly populated, and accordingly we have carried through the matrix diagonalization only for $M=0, 1, 2$ but for both values of the parity $\Lambda'=\pm 1$. To ensure that all contributions to Eqs. (3.17a)–(3.17c) linear in σ are included for these populated states, we have included in these matrices all states of the same value of M with $J=3$ or 4 that have nonzero matrix elements of $\mathcal{H}_S$ with those of $J=1$ or 2 as given by Eqs. (3.6) and (3.7). According to this scheme, we used the following six nonmixing sets of basis states $\Psi(J,M)$ from Eqs. (2.23) and (2.24) in setting up the matrices to be diagonalized for the various values of M and Λ':

$$M=0,\ \Lambda'=+1:\ [\Psi_{\mathrm{I}}(0,0),\Psi_{\mathrm{I}}(2,0),\Psi_{\mathrm{I}}(4,0)]\,, \tag{4.5a}$$

$$M=0,\ \Lambda'=-1:\ [\Psi_{\mathrm{I}}(1,0),\Psi_{\mathrm{I}}(3,0)]\,, \tag{4.5b}$$

$$M=+1,\ \Lambda'=-1:\ [\Psi_{\mathrm{I}}(1,+1),\Psi_{\mathrm{II}}(2,+1),\Psi_{\mathrm{I}}(3,+1)]\,, \tag{4.5c}$$

$$M=+1,\ \Lambda'=+1:\ [\Psi_{\mathrm{I}}(2,+1),\Psi_{\mathrm{II}}(1,+1),\Psi_{\mathrm{II}}(3,+1),\Psi_{\mathrm{I}}(4,+1)]\,, \tag{4.5d}$$

$$M=+2,\ \Lambda'=+1:\ [\Psi_{\mathrm{I}}(2,+2),\Psi_{\mathrm{II}}(3,+2),\Psi_{\mathrm{I}}(4,+2)]\,, \tag{4.5e}$$

$$M=+2,\ \Lambda'=-1:\ [\Psi_{\mathrm{II}}(2,+2),\Psi_{\mathrm{I}}(3,+2)]\,. \tag{4.5f}$$

Including all states with $N\leq 9$, we then used the following number of basis states in diagonalizing these matrices: (4.5a) 80, (4.5b) 60, (4.5c) 70, (4.5d) 80, (4.5e) 70, (4.5f) 40. A separate matrix diagonalization for states with $M=-1$ and -2 is unnecessary, since according to Sec. III such states are degenerate with the corresponding states of positive M and make an identical contribution to $P_S(T)$. Not included among the states (4.5a)–(4.5f) but also required in calculating $P_S(T)$ are the additional states of type II

$$M=0,\ \Lambda'=+1:\ \Psi_{\mathrm{II}}(1,0),\quad \Psi_{\mathrm{II}}(3,0)\,, \tag{4.6a}$$

$$M=0,\ \Lambda'=-1:\ \Psi_{\mathrm{II}}(2,0) \tag{4.6b}$$

which we found in Sec. II are not affected at all by $\mathcal{H}_{eL}$ and which, having $M=0$, are not coupled to any other state by the strain perturbation $\mathcal{H}_S=V_2 e_\theta \mathcal{E}_\theta$ according to Eq. (3.7). These states are shifted in energy to first order in the strain, however, according to Eq. (3.9), and this shift must be included in forming the Boltzmann factor for these states used in calculating $P_S(T)$. Finally, in obtaining $P_S(T)$ we have included emission from the states (again including all those with $N\leq 9$)

$$\Psi_{\rm I}(3,\pm3),\quad \Psi_{\rm I}(4,\pm3),\quad \Psi_{\rm I}(4,\pm4),\quad \Psi_{\rm II}(3,\pm3) \tag{4.7}$$

which are not coupled by $\mathcal{H}_S$ to any of the states with $J=0, 1, 2$, and for which we obtained vibronic energy levels and wave functions as in Sec. II by treating the interaction $\mathcal{H}_{eL}$ alone. Had we omitted these states in calculating $P_S(T)$ from those included in the sets (4.5a)–(4.5f) and (4.6a) and (4.6b), we would have obtained a spurious nonzero value for $P_S(T)$ even for a zero value of the strain e_θ, because of the asymmetry in the emission from individual states. Even though levels having $J=3$ and 4 have only a small probability of being occupied for temperatures $kT/\hbar\omega < 0.5$, the spurious value for $P_S(T)$ obtained when not all their component states are included becomes comparable in the higher end of this temperature range with the correct value of the stress-stress-induced $P_S(T)$ obtained for $\sigma=0.1$. For this reason the additional states (4.7) must be included in the calculation even though their interaction with the strain may be ignored.

Results for $P_S(T)/\sigma$ as a function of temperature are shown in Figs. 2(a)–2(e) for values of Δ ranging from $+0.25$ to $+5.0$ and values of the coupling strength S_1 from 0.1 to 1.5. The intercepts of these curves with the vertical axis agree with the values of $P_S(0)/\sigma$ for $T=0$ K shown in Fig. 1. With increasing T, the polarization is seen to rise initially, reach a peak, and then fall, the relative change with temperature being larger the smaller the value of Δ and the weaker the coupling S_1.

It is of interest to contrast the stress-induced polarization shown in Fig. 2 for the $2s$ and $2p$ states coupled by the vibronic interaction with the polarization that would occur if the vibronic coupling were zero. In that case, emission would occur only from the electronic $2p$ state, and in the presence of a strain e_θ, the $2p_z$ state would lie below the $2p_x$ and $2p_y$ states by the energy difference $(\frac{3}{2})V_2e_\theta$ in accord with Eqs. (3.4) and (3.5). Since emission from the $2p_z$ state is polarized entirely along the z axis and from $2p_x$ along x, and since the radiative lifetimes of both states are equal to $\tau_r\,(2p)$, we obtain for the polarization $P_S(T)$ from Eq. (3.21)

$$P_S(T)=\tanh(3V_2e_\theta/4kT)\,, \tag{4.8}$$

where we have taken into account the energy difference of the states in forming the Boltzmann factors. Expanding Eq. (4.8) to lowest order in $\sigma=V_2e_\theta/\hbar\omega$, we have then

$$P_S(T)/\sigma=\tfrac{3}{4}(\hbar\omega/kT)\,. \tag{4.9}$$

This expression is plotted as the dashed curve in Fig. 2(a) and is seen to lie above the curves for the vibronically coupled states, approaching them as T increases. Indeed, it may be shown (Appendix) that Eq. (4.9) provides the asymptotic limit for large T for all of the curves in Fig. 2. This asymptotic behavior is evidently reached sooner, the smaller the value of Δ and the weaker the coupling S_1.

C. Approximate formula for temperature dependence of polarization at low temperatures

At temperatures such that only the ground state and first excited state (assumed to be type-I states with $J=0$ and $J=1$, respectively) are significantly populated, the temperature dependence of the stress-induced polarization can be represented approximately by a formula

$$\frac{P_S(T)}{P_S(0)}=\frac{1+C(T)\exp(-\delta E/kT)}{1+3R\exp(-\delta E/kT)} \tag{4.10}$$

of a form similar to that used previously[5,8,12,16] in describing the electric-field-induced polarization (Stark effect), as we will now show. Here δE denotes the excitation energy of the $J=1$ triplet when there is no applied stress

$$\delta E=E_{\rm I}(1)-E_{\rm I}(0)\,, \tag{4.11}$$

while R denotes the ratio of the radiative lifetimes of these states

$$R=\tau_r(0)/\tau_r(1)\,. \tag{4.12}$$

An interesting conclusion of our analysis is that for the stress-induced polarization we always have for sufficiently low temperatures (and nonvanishing coupling $S_1>0$)

$$C(T)>3R\,, \tag{4.13}$$

so that the initial effect of raising the temperature above 0 K is always an increase in the polarization. By contrast, when the Stark polarization is approximated by the same type of formula as in Eq. (4.10), the inequality (4.13) may be shown to be reversed, so that a rise in temperature decreases the polarization, as observed.[5,8]

To prove Eq. (4.10) from Eq. (3.21), we must evaluate the contributions to $I_z(T)$ and $I_x(T)$ from the $J=0$ ground state and from the three components of the excited triplet as perturbed by the strain e_θ. From Eqs. (3.11) and (2.23), we have for the ground state in the absence of strain

$$I_\eta^0=[3\tau_r(0)]^{-1}=[3\tau_r(2p)]^{-1}\sum_{N=0}^{\infty}[c(0,2N+1)]^2\,. \tag{4.14}$$

Taking $P_S(0)$ to denote the polarization of the luminescence from this level that results from

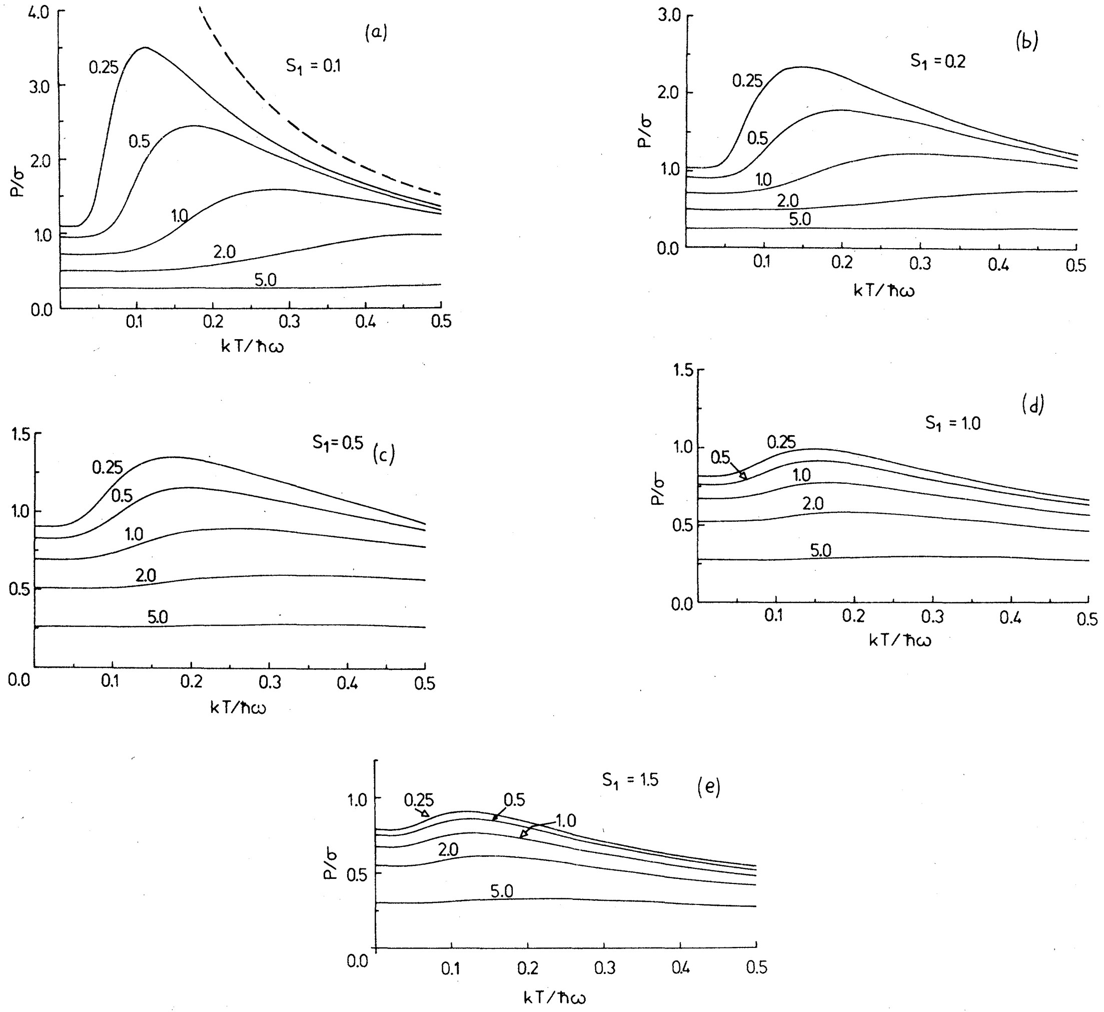

FIG. 2. Temperature dependence of the stress-induced polarization $P_S(T)$ of luminescence when the occupation probability of vibronic levels of the RES is given by a Boltzmann distribution corresponding to a temperature T. The ordinate is the ratio of $P_S(T)$ to the strain parameter σ. The solid curves were calculated as described in the text, using $\sigma = 0.1$, for the value of Δ indicated on each curve and the following values of the coupling strength S_1: (a) 0.1, (b) 0.2, (c) 0.5, (d) 1.0, (e) 1.5. The dashed curve in (a) represents the polarization in the limit of vanishing coupling ($S_1 = 0$) as given by Eq. (4.9) of the text and also represents the asymptotic relation [Eq. (A15)] derived in the Appendix.

the strain mixing with the $J=2$ states, we have for the contribution to $[I_z(T) - I_x(T)]$ from this level, to first order in the strain,

$$\Delta I(0) = [2/3\tau_r(0)]P_S(0)\mathfrak{s}^{-1}. \tag{4.15}$$

Similarly, for the triplet we have as the average over the three components

$$I^1_\eta = [3\tau_r(1)]^{-1} = [3\tau_r(2p)]^{-1} \sum_{N=0}^{\infty} \{[b(1, 2N)]^2 + [c(1, 2N+2)]^2\} \tag{4.16}$$

and

$$\Delta I_M(1) = [2/\tau_r(1)]P_S(1)\mathfrak{s}^{-1} \exp(-\delta E/kT), \tag{4.17}$$

where $P_S(1)$ denotes the polarization of the luminescence from the $J=1$ level that results from strain mixing with states of type I with $J=3$ and states of type II with $J=2$. $\Delta I_M(1)$ as given by Eq. (4.17) includes the contributions of all three components of the triplet but omits any contribution to the polarization from the splitting of the triplet caused by the strain. To include this latter contribution, we note from Eqs. (2.23) and (3.8) that the direct strain splitting of the $J=1$ triplet places the $M=0$ component below the $M=\pm 1$ components by an energy difference $\frac{3}{2}V_2 e_\theta K_1(E)$, where $K_1(E)$ is the reduction factor[11]

$$K_1(E)=\sum_{N=0}^{\infty}\{[b(1,2N)]^2+\tfrac{1}{10}[c(1,2N+2)]^2\}\,. \tag{4.18}$$

The same factor appears in the difference

$$\begin{aligned} I_z^{1(0)}-I_x^{1(0)} &= [\tau_r(2p)]^{-1} \\ &\quad\times\sum_{N=0}^{\infty}\{[b(1,2N)]^2+\tfrac{1}{10}[c(1,2N+2)]^2\} \\ &= [\tau_r(2p)]^{-1}K_1(E) \end{aligned} \tag{4.19}$$

obtained from Eqs. (3.11) and (3.17) using the wave function of the $M=0$ component of the triplet from Eq. (2.23) (zero stress). Similarly, for the $M=+1$ component we obtain

$$I_z^{1(+1)}-I_x^{1(+1)}=-\tfrac{1}{2}[\tau_r(2p)]^{-1}K_1(E) \tag{4.20}$$

with an identical result for $M=-1$. Weighting Eqs. (4.19) and (4.20) with the Boltzmann factors of the respective states and thus taking account of the strain splitting of the triplet, we then obtain to first order in $\sigma=V_2 e_\theta/\hbar\omega$ the contribution of this splitting to $[I_z(T)-I_x(T)]$

$$\Delta I_S(1)=\tfrac{3}{2}\sigma(\hbar\omega/kT)[K_1(E)]^2[\tau_r(2p)]^{-1}\mathfrak{z}^{-1}\exp(-\delta E/kT)\,. \tag{4.21}$$

Adding the three contributions to $[I_z(T)-I_x(T)]$ from Eqs. (4.15), (4.17), and (4.21) and dividing by

$$\begin{aligned} I_z(T)+I_x(T) \\ &= \mathfrak{z}^{-1}\{2[3\tau_r(0)]^{-1}+2[\tau_r(1)]^{-1}\exp(-\delta E/kT)\} \end{aligned} \tag{4.22}$$

from Eqs. (4.14) and (4.16), we obtain from Eq. (3.21) the desired result, to first order in σ, in the form of Eq. (4.10) with

$$\begin{aligned} C(T) &= 3R[P_S(1)/P_S(0)] \\ &\quad+\tfrac{9}{4}R(\hbar\omega/kT)[\sigma/P_S(0)][K_1(E)]^2[\tau_r(1)/\tau_r(2p)]\,. \end{aligned} \tag{4.23}$$

Since the second term in Eq. (4.23) is positive and varies as $1/T$, the inequality (4.13) is necessarily satisfied at a sufficiently low temperature. The effect of an increase in temperature from 0 K therefore is always an initial increase in the polarization, and it is the strain splitting of the excited triplet state that ensures that this is so. In addition, it was shown in paper II (Ref. 12) [Eqs. (3.6) and (3.9)] that in the limit $S_1\to 0$ the ratio $P_S(1)/P_S(0)$ in the first term in Eq. (4.23) is greater than unity for $\Delta>1$, approaching unity as Δ becomes large. Therefore, at least for sufficiently small S_1 and $\Delta>1$, the first term in Eq. (4.23) alone satisfies the inequality (4.13) and thus would suffice by itself to cause the polarization to increase with increasing temperature, at least until levels above the first triplet become appreciably populated.[29]

In contrast to this behavior of the stress-induced polarization, for the Stark effect one finds [paper II, Eq. (3.20)] $P_E(1)/P_E(0)=R^{-1}$ in the limit of S_1 small (for $\Delta>1$), and Imanaka *et al.*[30] have shown that this ratio decreases as S_1 increases. Thus, since we have $R>1$, for the Stark effect the first term in the expression corresponding to Eq. (4.23) is always less than $3R$. Moreover, in the second-order splitting of the $J=1$ triplet by an electric field, calculations for representative values of Δ and S_1 show that the $M=0$ state is raised in energy relative to the $M=\pm 1$ states, so that the term in the polarization resulting from this splitting and analogous to the second term in Eq. (4.23) is therefore negative. This second term therefore acts to reduce $C(T)$ further relative to $3R$. The inequality (4.13) is thus reversed for the Stark effect, and the polarization decreases with temperature, as observed.[5,8]

The relative size of the two terms in $C(T)$ in Eq. (4.23) provides a measure of the importance of the stress-induced splitting of degenerate levels in contributing to the polarization, as compared with the change of the wave functions of the states caused by the mixing of states of different J. As noted earlier,[29] we have used the vibronic eigenstates calculated for zero stress to evaluate the second term in Eq. (4.23) for representative values of Δ and S_1, and we have then used these results in comparing the curves in Fig. 2 to an expression of the form of Eq. (4.10). We have found that this approximation reproduces the calculated curves quite accurately for temperatures up to or somewhat beyond their peak but that the calculated drop at higher temperatures is more rapid than given by Eq. (4.10), evidently because of contributions of higher levels at these temperatures. Near the peak we have found that the second term in Eq. (4.23) is typically appreciably smaller than the temperature-independent first term. However, the second term is large enough to contribute most of the increase in polarization above its value at 0 K. Thus, although at any given temperature the polarization due to the level splitting is smaller than that due to the mixing of the states, the effect of the splitting is crucial in obtaining the correct temperature variation of the polarization.

V. DISCUSSION

We are particularly interested in learning from our calculations what lower bound we can place on Δ from the observations of Hetrick and Compton[23] that the stress-induced polarization is independent of temperature. Their data, taken for KCl, NaCl, RbCl, and NaF, showed no evidence of any variation of more than ~10% (the limit indicated by the scatter of their experimental points and their estimate of the accuracy of the measurements) over the temperature range 20 to 140 K. Comparing with Fig. 2, we see that all of the curves for $\Delta \leq 2.0$ show a variation greater than 10% over the range $0 < kT/\hbar\omega < 0.5$ (which for KCl, with $\hbar\omega = 26.8$ meV,[12,16] corresponds to $0 < T < 155$ K). Accordingly, we conclude from our calculations that for KCl, NaCl, RbCl, and NaF we must have a value $\Delta > 2$ in order that the simple vibronic model used in our work be consistent with the observations of Hetrick and Compton.

This conclusion contrasts with that of Imanaka *et al.*,[16] who determined Δ and S_1 for KF, KCl, KBr, and RbCl, using the same vibronic model, by simultaneously fitting the temperature dependence of the radiative lifetime and of the polarization induced by an electric field. They obtained in this way for the best fit the values $\Delta = 1.25$, $S_1 = 0.35$ for KCl and $\Delta = 1.5$, $S_1 = 0.3$ for RbCl. For these values of S_1, which lie between those of Figs. 2(b) and 2(c), and for values of Δ from 1.25 to 1.5, we see from our calculated curves that one expects a variation of the stress-induced polarization with temperature much larger than anything compatible with the observations of Hetrick and Compton. Evidently, therefore, a discrepancy exists between the values of the parameters of the vibronic model needed to fit the temperature dependence of the radiative lifetime and the Stark polarization, on one hand, and those needed to fit the stress-induced polarization on the other.

A similar but even larger discrepancy occurs for NaF, for which Kayanuma[15] estimated $\Delta = 0.3$, $S_1 = 0.2$ (with $\hbar\omega = 53.4$ meV) from the temperature dependence of the radiative lifetime alone. As we see from Fig. 2(b), on the basis of these values we would expect Hetrick and Compton to have observed the stress-induced polarization to roughly double over the temperature range of their observations, in contrast to the temperature-independent result reported.

Unpublished experimental results of Ishiguro and Asami[31] are cited by Ohkura *et al.*[17,19] as showing that the stress-induced polarization is independent of temperature for KBr and RbBr also. For these materials Imanaka *et al.*[16] obtained the values $\Delta = 1.50$, $S_1 = 0.25$ for KBr and $\Delta = 2.0$, $S_1 = 0.2$ for RbBr by fitting the Stark polarization alone. Again, from these values of the parameters we would expect from Fig. 2(b) a much larger variation of the stress-induced polarization than evidently shown by the data of Ishiguro and Asami.

No experimental data for the stress-induced polarization so far are available for KF, for which Imanaka *et al.*[16] obtained the values $\Delta = 0.0$, $S_1 = 0.5$, and Kayanuma[15] the values $\Delta = 0.0$, $S_1 = 0.7$. It would clearly be of interest to do the stress experiments for this material, since we would expect from Fig. 2(c) a very pronounced peak in the stress-induced polarization *versus* temperature if a value of Δ near zero were correct. KF should thus provide a particularly good additional test of the compatibility of the values of Δ and S_1 obtained from the Stark effect and radiative lifetime with those consistent with the stress results.

The values $\Delta \sim 3.5$ and 3.75 for KCl and KF, respectively, obtained by Ham and Grevsmühl[12,32] from the circular polarization[33,34] of the luminescence in a magnetic field, would lead one, by contrast, to expect from Fig. 2 that the stress-induced polarization should be very nearly independent of temperature. The stress data of Hetrick and Compton[23] therefore seem to support these larger values for Δ. It must be emphasized, however, that these values for Δ were obtained from the magnetic data with the assumption[12] that the orbital g factor for the electronic $2p$ state in the relaxed configuration had the same value [$g_L = 0.95 \pm 0.1$ for KCl,[35] $g_L \sim 1$ for KF (Ref. 36)] as that measured for the unrelaxed configuration in optical-absorption experiments. As Ham and Grevsmühl[12] and Kayanuma[15] have noted, the magnetic-polarization data would be compatible with a smaller value for Δ if g_L were appreciably reduced in the relaxed configuration. From Kayanuma's theoretical curves[15] for the magnetic polarization as a function of S_1, we find that a value $g_L \sim 0.6$ would be needed in order that the magnetic data be compatible for KCl with the values $\Delta = 1.25$, $S_1 = 0.35$ of Imanaka *et al.*[16] It is, of course, quite possible that g_L is changed appreciably by the lattice relaxation, although this change could very well be an increase because of the orthogonality of the extended $2p$ wave function to the core states of neighboring ions.[37] We cannot therefore regard the larger values of Δ obtained by Ham and Grevsmühl as definitely determined by the magnetic data, in the absence of an independent determination of g_L, but we can conclude that the stress data of Hetrick and Compton, in supporting such values for Δ, do suggest that there is no large reduction in g_L in the relaxed configuration.

If the simple vibronic model used by Imanaka *et al.*[16] and in the present work cannot account simultaneously for the radiative lifetime, the Stark polarization, and the stress polarization, some modification of the model is evidently required. Kayanuma[15] has shown, in fact, that in order to account for the observed red shift of the luminescence caused by an electric field one can postulate that the 2*s* and 2*p* states are coupled differently to a symmetric (Γ_1^+) vibrational mode. Extending Kayanuma's work to include possible coupling of the 2*p* states to a Γ_3^+ mode, Iwahana *et al.*[19] have asserted in a very recent paper that both the Γ_1^+ and Γ_3^+ modes must be included in order to explain all the experimental data. While it seems quite possible to us that coupling to these additional modes may play a significant role in the RES, we consider it unlikely, for the reasons outlined below, that such coupling will serve to suppress the temperature dependence of the stress polarization if Δ is as small as these workers suggest. We believe, in fact, that Iwahana *et al.*[19] have obtained the wrong temperature dependence in calculating $P_S(T)$ because they have omitted the contribution to the polarization of the stress-induced splitting of degenerate levels, the importance of which we noted in Sec. IV C. We discuss the contrast between their results and ours in more detail below, but it is our conclusion that their results concerning the role of the Γ_1^+ and Γ_3^+ modes cannot be relied upon as a basis for improving the simple vibronic model of the RES. What modification of this model is needed to reconcile the data from the different experiments is not yet apparent to us. Nevertheless, the results we have obtained suggest that in any such modified model the difference between the 2*s* and 2*p* electronic energies must be significantly larger than the values of Δ proposed by the various Japanese workers, if we are to explain the temperature independence of the stress data.

In trying to assess the effect on the stress polarization of Kayanuma's proposal[15] of different coupling of the 2*s* and 2*p* states to a Γ_1^+ mode, we note from the curves in Fig. 2 that what is needed to diminish the temperature variation of $P_S(T)$ is an increase in the effective value of Δ. Kayanuma's modification should have the opposite effect of somewhat reducing the average energy difference between the vibronic states derived from 2*s* and 2*p* that are mixed by the coupling to the Γ_4^- mode, and thus this modification should actually enhance the temperature variation of $P_S(T)$ for a given Δ. To see this, we note that the difference in coupling the 2*s* and 2*p* states to a symmetric mode Q_0 causes the minimum energy of the two states to occur at different values of Q_0. If we continue to define Δ as the 2*s* – 2*p* electronic energy difference in the equilibrium configuration of the 2*s* state[38] (in units of $\hbar\omega$ of the Γ_4^- mode, which for simplicity we assume equal to $\hbar\omega$ of the Γ_1^+ mode), the 2*p* minimum then has an energy $(\Delta - S_0)$ relative to the 2*s* minimum, where S_0 is the Huang-Rhys parameter[39] reflecting the coupling difference to the symmetric mode. (We assume $\Delta > S_0$ so that the 2*s* minimum is lower.) Vibronic states derived from 2*p* and near the 2*p* minimum energy have their mixing with low-energy vibronic states derived from 2*s* enhanced by the inverse dependence of the mixing on the energy difference of the states. Of course, the mixing of all states is reduced in proportion to their overlap in the space of Q_0, but the net effect of the coupling to the Γ_1^+ mode is a reduction in the average energy of the 2*p* states mixed with the low-energy 2*s* states, and thus a reduction in the effective value of Δ. We therefore expect in analogy with the behavior shown in Fig. 2 that the coupling to the Γ_1^+ mode should enhance the temperature variation of $P_S(T)$ as compared with that found for the simpler model with the same value of Δ and coupling only to the Γ_4^- mode. A similar argument leads to the same conclusion if we consider the effect of coupling the 2*p* states to Γ_3^+ and/or Γ_5^+ modes.

Ohkura *et al.*[17] and Iwahana *et al.*[19] have claimed that by including coupling to Γ_1^+ and Γ_3^+ modes, using $\Delta = 1.05$, $S_1 = 0.6$, $S_0 = 0.5$, and $S_3 = 0.15$ (with S_3 the corresponding parameter for the coupling of the 2*p* states to a Γ_3^+ mode) they have obtained a temperature-independent stress polarization for KCl while also fitting the temperature dependence of the radiative lifetime and that of the Stark polarization. These claims are clearly in disagreement with the argument we have made above. In addition, Iwahana *et al.*[19] claim similar results for RbCl, KBr, and RbBr for values for Δ and S_1 similar to those obtained by Imanaka *et al.*[16] However, the temperature variation of $P_S(T)$ calculated by Iwahana *et al.*[19] when the coupling to Γ_1^+ and Γ_3^+ modes vanishes is completely different from what we have obtained in Fig. 2. For example, for $\Delta = 1.0$, $S_1 = 0.5$, $S_0 = S_3 = 0$ Iwahana *et al.* [see Fig. 3(a) of Ref. 19] find that $P_S(T)$ *decreases* with increasing temperature instead of increasing initially as we found in Fig. 2(c). Iwahana *et al.* find (see Fig. 2 of Ref. 19) that $P_S(T)$ is independent of temperature for values of Δ falling along a curve running from $\Delta \sim 0.5$ at $S_1 = 0.1$ through $\Delta \sim 3$ at $S_1 = 0.7$, and that, while $P_S(T)$ increases initially for values of Δ larger than this limiting value, a decrease is found if

Δ is smaller. Our results in Fig. 2 show, by contrast, a relatively greater increase in $P_S(T)$ the smaller the value of Δ for any given S_1, and we have shown in Sec. IV C that the general behavior of $P_S(T)$ is always to increase initially with temperature (or to remain effectively constant if this increase is too small to be significant). We believe this difference in our results occurs because Iwahana *et al.*[19] and Ohkura *et al.*[17] neglect the stress-induced energy shift of the levels, as they state, in using perturbation theory to calculate the effect of stress on the wave functions and thus to determine the emission probabilities of the different levels. As we have discussed in Sec. IV C, this energy shift is responsible for the stress-induced splitting of degenerate levels, which makes a significant contribution to the polarization (to first order in the stress) because of the difference in the Boltzmann factors of the split states and the net polarization of the emission from individual component states even when the wave functions are unperturbed. As also discussed in Sec. IV C, this contribution from the splitting of the first excited triplet level always increases the polarization and is large enough to be responsible for most of the increase shown by the curves of Fig. 2 in going from 0 K to the polarization maximum. We believe that the omission of this contribution by Ohkura *et al.* and by Iwahana *et al.* is the principal reason for the difference between their results and ours.[40]

An important consequence of requiring a larger value for Δ than estimated by the Japanese workers, in order to account for the stress data, is that this will necessitate revising the interpretation of the transient optical absorption[21,22] within the RES proposed by Kondo and Kanzaki[21] and Kayanuma and Kondo.[20] On the assumption that Δ is sufficiently small so that transitions within the $2s$-$2p$ manifold of vibronic states occur at too low an energy to have been observed, these authors have interpreted these spectra as arising from transitions from the ground state of the RES (essentially the $2s$ state) to states derived from $3s$, $3p$, $3d$, and possibly $4p$. The $2s \rightarrow 2p$ transition should, however, have a much larger oscillator strength than $2s \rightarrow 3p$, and if Δ is at least as large as 2 the $2s \rightarrow 2p$ transition or at least some of its vibrational sidebands should occur within the spectral region studied. Identifying the $2s \rightarrow 2p$ transition with the observed absorption spectrum would, of course, provide an independent determination of $|E_{sp}|$ and thus of Δ. Calculation of the energies and relative intensities of the absorption peaks expected for different values of Δ and S_1 on the basis of the simple vibronic model used in this paper are in progress and will be reported in a later publication.

VI. SUMMARY AND CONCLUSIONS

From the numerical calculations we find that the stress-induced polarization either remains effectively constant or shows an initial increase as the temperature rises from 0 K and that this increase is pronounced if we have $\Delta \lesssim 2$. After reaching a maximum, the polarization then falls, eventually approaching a limiting rate of decrease that is independent of Δ and S_1. Only for $\Delta > 2$ is the initial increase sufficiently small to be consistent with the observation by Hetrick and Compton that for KCl, NaCl, RbCl, and NaF the polarization is independent of temperature between 20 and 140 K. While our conclusion that we must have $\Delta > 2$ for these materials agrees with estimates of Δ made by Ham and Grevsmühl from magnetic-polarization data, it disagrees with values for Δ obtained by Kayanuma and by Imanaka *et al.* by fitting the temperature dependence of the radiative lifetime and that of the Stark polarization. Extending the vibronic model to include coupling to additional vibrational modes of other symmetry types, as suggested by Kayanuma and by Iwahana *et al.*, does not appear to be sufficient to reconcile these differences. Evidently a vibronic model for the RES that provides a completely consistent quantitative explanation for all the data has not yet been achieved.

APPENDIX: DERIVATION OF ASYMPTOTIC HIGH-TEMPERATURE BEHAVIOR OF THE POLARIZATION

We start from an expression [Eq. (5.6) of paper I] equivalent to Eq. (3.11) for the probability per unit time of emission of a photon of polarization η if the system is initially in the vibronic state Ψ_i of the RES:

$$I_\eta^i = C \sum_m |\langle \Psi_i | D_\eta | \Psi_m(1s) \rangle|^2 . \tag{A.1}$$

Here D_η is the η component of the electric-dipole-moment operator for the electron, C [Eq. (5.5) of paper I] is a proportionality factor (the energy dependence of which we ignore), and $\Psi_m(1s)$ denotes the mth vibrational state associated with the electronic ground state $|1s\rangle$

$$\Psi_m(1s) = \Phi_m(Q)|1s\rangle . \tag{A2}$$

Averaging I_η^i over the levels of the RES weighted with the probability of occupation, we can write Eq. (3.19) in the form

$$I_\eta(T) = \mathfrak{z}^{-1}C \sum_m \sum_{i,j} \langle \Psi_m(1s) | D_\eta | \Psi_i \rangle \times \langle \Psi_i | \exp(-\mathcal{H}'/kT) | \Psi_j \rangle \times \langle \Psi_j | D_\eta | \Psi_m(1s) \rangle , \qquad \text{(A3)}$$

where we have used the fact that the orthonormal set of states Ψ_i are eigenstates of

$$\mathcal{H}' = \mathcal{H}_e + \mathcal{H}_L + \mathcal{H}_{eL} + \mathcal{H}_S \qquad \text{(A4)}$$

from Eqs. (2.1) and (3.3). Since the states Ψ_i form a complete set in the space of the vibrational modes and in the limited electronic space spanned by the 2*s* and 2*p* states, we can make the substitution

$$\sum_i | \Psi_i \rangle \langle \Psi_i | = \Big(\sum_{m'} | \Phi_{m'} \rangle \langle \Phi_{m'} | \Big) \Big(\sum_a | 2a \rangle \langle 2a | \Big) , \qquad \text{(A5)}$$

where $a = s, p_x, p_y, p_z$, for the sums over *i* and *j* in Eq. (A3). Since D_η is an electronic operator with only one nonzero matrix element

$$\langle 1s | D_\eta | 2p_\eta \rangle = D , \qquad \text{(A6)}$$

we can then simplify Eq. (A3):

$$I_\eta(T) = \mathfrak{z}^{-1}CD^2 \sum_m \Big\langle 2p_\eta \Big| \Big\langle \Phi_m \Big| \exp\Big(\frac{-\mathcal{H}'}{kT} \Big) \Big| \Phi_m \Big\rangle \Big| 2p_\eta \Big\rangle . \qquad \text{(A7)}$$

To proceed, we note that $\mathcal{H}_S$ and $\mathcal{H}_{eL}$ do not commute, so that to expand $\exp(-\mathcal{H}'/kT)$ in a power series in $\mathcal{H}_S$ we first need the general operator relationship,[41] which is exact

$$\exp(-\beta\mathcal{H}') = \exp[-\beta(\mathcal{H} + \mathcal{H}_S)] = \exp_{[-]} \Big(-\beta \int_0^1 \mathcal{H}_S(t)\, dt \Big) \exp(-\beta\mathcal{H}) , \qquad \text{(A8)}$$

where $\beta = 1/kT$,

$$\mathcal{H}_S(t) = \exp(-\beta\mathcal{H}t)\mathcal{H}_S \exp(\beta\mathcal{H}t) , \qquad \text{(A9)}$$

$[-]$ denotes the ordered operator as defined by Goldberger and Adams,[41] and $\mathcal{H}$ is given in Eq. (2.1). Expanding Eq. (A8) to first order in $\mathcal{H}_S$ and substituting into Eq. (A7), we obtain an expression for $I_\eta(T)$ that is exact to this order

$$I_\eta(T) = \mathfrak{z}^{-1}CD^2 \sum_m \Big\langle 2p_\eta \Big| \Big\langle \Phi_m \Big| \Big(1 - \beta \int_0^1 \mathcal{H}_S(t)\, dt \Big) \exp(-\beta\mathcal{H}) \Big| \Phi_m \Big\rangle \Big| 2p_\eta \Big\rangle . \qquad \text{(A10)}$$

Substituting Eq. (A10) into Eq. (3.21) for the polarization $P_S(T)$, we obtain

$$P_S(T) = -(2kTA)^{-1} \Big(\sum_m \Big\langle 2p_z \Big| \Big\langle \Phi_m \Big| \int_0^1 \mathcal{H}_S(t)\, dt \exp(-\beta\mathcal{H}) \Big| \Phi_m \Big\rangle \Big| 2p_z \Big\rangle - \sum_m \Big\langle 2p_x \Big| \Big\langle \Phi_m \Big| \int_0^1 \mathcal{H}_S(t)\, dt \exp(-\beta\mathcal{H}) \Big| \Phi_m \Big\rangle \Big| 2p_x \Big\rangle \Big) , \qquad \text{(A11)}$$

where

$$A = \sum_m \langle 2p_\eta | \langle \Phi_m | \exp(-\beta\mathcal{H}) | \Phi_m \rangle | 2p_\eta \rangle . \qquad \text{(A12)}$$

We have used the fact that *A* is independent of η (because $\mathcal{H}$ has cubic symmetry) and have dropped all terms of higher order than the first in $\mathcal{H}_S$. To this order, Eq. (A11) is still an exact expression for $P_S(T)$.

To evaluate Eq. (A11) in general, we would need the operator expansion

$$\mathcal{H}_S(t) = \mathcal{H}_S - \beta t [\mathcal{H}, \mathcal{H}_S] + \tfrac{1}{2}\beta^2 t^2 [\mathcal{H}, [\mathcal{H}, \mathcal{H}_S]] + \cdots . \qquad \text{(A13)}$$

However, in obtaining the asymptotic behavior of $P_S(T)$ to order $(1/T)$ it suffices to retain only the term in Eq. (A13) of lowest order in $\beta = 1/kT$, thus in effect ignoring all the commutators. (These commutators do equal zero if the vibronic coupling is zero.) Since $\mathcal{H}_S = V_2 e_\theta \mathcal{E}_\theta$ is a diagonal operator with respect to the electronic states $|2p_x\rangle$ and $|2p_z\rangle$, and since it is independent of the *Q*'s, this asymptotic expression for $P_S(T)$ becomes simply

$$P_S(T) \sim (2kT)^{-1} (\langle 2p_z | \mathcal{H}_S | 2p_z \rangle - \langle 2p_x | \mathcal{H}_S | 2p_x \rangle) \qquad \text{(A14)}$$

or

$$P_S(T) \sim +(3V_2 e_\theta / 4kT) . \qquad \text{(A15)}$$

This asymptotic result is thus independent of the strength S_1 of the vibronic coupling and agrees with Eq. (4.9).

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[38] In our usage Δ is defined as the $2s$–$2p$ electronic energy difference in the equilibrium configuration of the $2s$ state. Kayanuma (Ref. 15), on the other hand, takes Δ to be the energy of the $2p$ energy minimum relative to that of the $2s$ minimum. Kayanuma's value for Δ should therefore be increased by the symmetric mode-coupling parameter S_0 to obtain the energy difference corresponding to our definition of Δ.

[39] K. Huang and A. Rhys, Proc. R. Soc. London, Ser. A 204, 406 (1950). See also M. H. L. Pryce, in *Phonons in Perfect Lattices and in Lattices with Point Imperfections*, edited by R. W. H. Stevenson (Plenum, New York, 1966), p. 403.

[40] There may also be some difference because Iwahana *et al.* (Ref. 19) report including only states with up to two phonons excited in truncating their matrices, whereas we included states having $N \leq 9$, or at least eighteen phonons excited, in setting up our matrices from Eq. (4.5). Iwahana *et al.* have noted and rejected our criticism of their omission of the stress-induced splitting of the levels (see Note added in proof in Ref. 19), saying that this omission is allowed because realistic values of the stress correspond to a value for σ about one-tenth of the value $\sigma = 0.1$ used in our calculations. We have verified, however, that our results for $P_S(T)/\sigma$ are not significantly changed by using a smaller value of σ in the calculations, so that contributions to our results for $P_S(T)$ from terms of higher order than the first in σ cannot be of any importance. The contributions to $P_S(T)$ from the level splitting which Iwahana *et al.* have omitted are linear in σ and thus must be included if the results are to be accurate to this order.

[41] M. L. Goldberger and E. N. Adams II, J. Chem. Phys. 20, 240 (1952).