PHYSICAL REVIEW B VOLUME 8, NUMBER 6 15 SEPTEMBER 1973

Vibronic Model for the Relaxed Excited State of the *F* Center. II. Perturbation Analysis for Weak-Coupling Limit

Frank S. Ham
General Electric Research and Development Center, Schenectady, New York 12301

U. Grevsmühl
Department of Theoretical Physics, Oxford University, Oxford, England

(Received 14 March 1973)

A perturbation solution is given for a vibronic model for the relaxed excited state of the *F* center, in the limiting case of weak electron-phonon coupling. The resulting predictions of the model are compared with available data on radiative lifetimes, Stark effects, magnetic circular polarization, and stress-induced polarization of *F*-band luminescence in alkali halides. It is shown that a consistent quantitative interpretation of most of these data is possible on this basis if the 2*s* electronic state lies below the 2*p* state in the relaxed cubic configuration by an energy difference which is ∽ 0.09 eV for KCl and ∽ 0.15 eV for KF. The long radiative lifetime should then be attributed predominantly to the 2*s* state being only weakly coupled to the 2*p* state by the phonons, rather than to spatial diffuseness of the 2*p* state. The model also accounts for the observed ratio of the electric-field-induced change in the radiative lifetime to the field-induced polarization of the luminescence, for the temperature dependence of the radiative lifetime and field-induced polarization, and for the absence of any such temperature dependence in the stress-induced polarization.

I. INTRODUCTION

In the preceding paper (I)[1] a general solution was given for a vibronic model applicable to an interpretation of recent experiments on Stark effects and other phenomena in the *F*-band luminescence of alkali halides. This model comprises nondegenerate 2*s* and 2*p* electronic states interacting in cubic symmetry via a triply degenerate odd-parity Γ_4^- vibrational mode. It was shown there that the experimental data indicate that this coupling, although very important in determining the properties of the relaxed excited state of the *F* center, is actually rather weak. It was concluded further that the 2*s* electronic state must lie about 0.1 eV below the 2*p* state in the relaxed cubic configuration corresponding to the equilibrium position of the totally symmetric modes in the excited electronic state. The purpose of this paper is to give a direct perturbation treatment of the coupling to the Γ_4^- mode in this situation, for the weak-coupling limit, and to compare the resulting predictions of the model with the experimental data.

II. LOW-ENERGY VIBRONIC STATES WITH NO EXTERNAL PERTURBATION

We consider the same vibronic model as in I, except that we take the 2*s* electronic state to be below the 2*p* state in the cubic configuration by an energy difference $|E_{sp}|$ appreciably larger than the vibrational quantum $\hbar\omega$, and for convenience we take the zero of energy to coincide with the 2*s* state. Using the same notation as in I, we take for our unperturbed Hamiltonian

$$\mathcal{H}_0 = +\tfrac{1}{2}|E_{sp}|(1-\rho_0) + (2\mu)^{-1}[P_x^2+P_y^2+P_z^2 + \mu^2\omega^2(Q_x^2+Q_y^2+Q_z^2)] \quad , \qquad (2.1)$$

and we treat the coupling

$$\mathcal{H}_{eL} = G(Q_x\rho_x + Q_y\rho_y + Q_z\rho_z) \qquad (2.2)$$

by perturbation theory. We will assume in particular that G is sufficiently small so that we have $E_G = G^2/2\mu\omega^2 \lesssim \frac{1}{4}|E_{sp}|$. This was the condition found in paper I, Eq. (3.3) [hereafter we use, e.g., Eq. (I3.3)] for the minimum energy of the static problem to occur for the 2*s* state in the cubic configuration, and, together with $|E_{sp}| \gg \hbar\omega$, this appears to be a sufficient condition for the usefulness of perturbation theory in treating the low-energy vibronic states.

The unperturbed eigenstates of $\mathcal{H}_0$ are given by the simple product functions $\Phi_{lmn}(\vec{Q})|2s\rangle$ and $\Phi_{lmn}(\vec{Q})|p_i\rangle$ $(i = x, y, z)$ having energies $(l+m+n+\frac{3}{2})\hbar\omega$ and $|E_{sp}| + (l+m+n+\frac{3}{2})\hbar\omega$, respectively, where

$$\Phi_{lmn}(\vec{Q}) = F_l(Q_x)F_m(Q_y)F_n(Q_z) \quad . \qquad (2.3)$$

Here $F_n(Q)$ is the nth eigenfunction of the one-dimensional simple harmonic oscillator.

The perturbed wave function for the vibronic ground state is then given to first order in G by

$$\Psi(0) = b_0\Phi_{000}|2s\rangle + b_1(\Phi_{100}|p_x\rangle + \Phi_{010}|p_y\rangle + \Phi_{001}|p_z\rangle), \qquad (2.4)$$

where

$$b_1 = \frac{-G(\hbar/2\mu\omega)^{1/2}}{|E_{sp}| + \hbar\omega} \quad , \qquad (2.5)$$

and

$$b_0 = 1 - \tfrac{3}{2} b_1^2 \qquad (2.6)$$

gives the normalization correct to order G^2. The energy of this level to order G^2 is therefore given by

$$E(0) = \tfrac{3}{2}\hbar\omega - 3E_G \hbar\omega (|E_{sp}| + \hbar\omega)^{-1} . \qquad (2.7)$$

The probability per unit time that this level will decay radiatively to the 1s electronic ground state with emission of a photon of polarization η is found from Eqs. (2.4) and (I5.7) to be given to the same accuracy by

$$I_\eta(0) = \tau_r^{-1}(p) E_G \hbar\omega (|E_{sp}| + \hbar\omega)^{-2} . \qquad (2.8)$$

The ratio of the radiative lifetime of the vibronic ground state to that of the 2p electronic state is accordingly

$$\tau_r(0)/\tau_r(p) = (|E_{sp}| + \hbar\omega)^2 / 3E_G \hbar\omega . \qquad (2.9)$$

Under our assumption that we have $|E_{sp}| \gg \hbar\omega$, the first excited vibronic level above the ground state is a p-like triplet which in zero order has one vibrational mode excited while the electronic system remains in the 2s state. To first order in G, the component of this state transforming like x is given by

$$\Psi_x(1) = c_0 \Phi_{100} |2s\rangle + c_1 \Phi_{000} |p_x\rangle + c_2 \Phi_{200} |p_x\rangle + c_3 (\Phi_{110} |p_y\rangle + \Phi_{101} |p_z\rangle) , \qquad (2.10)$$

where

$$c_1 = \frac{-G(\hbar/2\mu\omega)^{1/2}}{|E_{sp}| - \hbar\omega} ,$$

$$c_2 = (2)^{1/2} c_3 = \frac{-G(\hbar/\mu\omega)^{1/2}}{|E_{sp}| + \hbar\omega} , \qquad (2.11)$$

$$c_0 = 1 - \tfrac{1}{2}(c_1^2 + c_2^2 + 2c_3^2) .$$

The energy of this level relative to the ground state is then found to be

$$\delta E = E(1) - E(0)$$

$$= \hbar\omega \{1 - 2E_G |E_{sp}| [E_{sp}^2 - (\hbar\omega)^2]^{-1}\} . \qquad (2.12)$$

The ratio R of $\tau_r(0)$ to the radiative lifetime $\tau_r(1)$ of this level is given by Eqs. (2.11, (I5.8), and (2.9) to be

$$R = \tau_r(0)/\tau_r(1)$$

$$= \tfrac{4}{3}[1 + \tfrac{1}{4}(|E_{sp}| + \hbar\omega)^2 (|E_{sp}| - \hbar\omega)^{-2}] . \qquad (2.13)$$

III. EFFECTS OF EXTERNAL PERTURBATIONS

In treating the effects of external perturbations, such as electric and magnetic fields and applied uniaxial stresses, we can in every case of interest give an exact solution for the 2s and 2p electronic states under the effect of the perturbation. Solving first for these perturbed electronic states and energies, we will then treat the vibronic coupling, Eq. (2.2), by first-order perturbation theory. The polarization of the luminescence, the induced change in lifetime, and other properties may then be calculated for the resulting vibronic levels. Expanding these expressions to the appropriate power of the perturbing field, we thus obtain the results desired for comparison with the experimental data. We will give this calculation below for the case of the magnetic circular polarization of the luminescence, but since the theory is so simple and straightforward we will merely cite the results in the other cases with only the briefest sketch of the derivation.

A. Magnetic Circular Polarization

With a magnetic field H along the z direction, the electronic state $|2s\rangle$ is of course unaffected, but the 2p states are split, with $|p_+\rangle = -(2)^{-1/2}(|p_x\rangle + i|p_y\rangle)$, $|p_z\rangle$, and $|p_-\rangle = +(2)^{-1/2}(|p_x\rangle - i|p_y\rangle)$ having energies $|E_{sp}| + g_L \mu_B H$, $|E_{sp}|$, and $|E_{sp}| - g_L \mu_B H$, respectively. Treating $\mathcal{H}_{eL}$ in Eq. (2.2) by perturbation theory, we now have for the ground-state wave function to first order in G,

$$\Psi(0) = b_{000} \Phi_{000} |2s\rangle + (c_{100}^{+} \Phi_{100} + c_{010}^{+} \Phi_{010}) |p_+\rangle + (c_{100}^{-} \Phi_{100} + c_{010}^{-} \Phi_{010}) |p_-\rangle + c_{001}^{z} \Phi_{001} |p_z\rangle , \qquad (3.1)$$

where

$$c_{100}^{+} = i c_{010}^{+} = + G(\hbar/4\mu\omega)^{1/2} (|E_{sp}| + \hbar\omega + g_L \mu_B H)^{-1} ,$$

$$c_{100}^{-} = - i c_{010}^{-} = - G(\hbar/4\mu\omega)^{1/2} (|E_{sp}| + \hbar\omega - g_L \mu_B H)^{-1} ,$$

$$c_{001}^{z} = - G(\hbar/2\mu\omega)^{1/2} (|E_{sp}| + \hbar\omega)^{-1} . \qquad (3.2)$$

The emission probabilities $I_+(0)$ and $I_-(0)$ for light with left- and right-handed circular polarization, respectively, along the magnetic field are then found from Eq. (I5.7) to be given by

$$I_+(0) = \tau_r^{-1}(p) (|c_{100}^{+}|^2 + |c_{010}^{+}|^2) ,$$

$$I_-(0) = \tau_r^{-1}(p) (|c_{100}^{-}|^2 + |c_{010}^{-}|^2) , \qquad (3.3)$$

Expanding these results to first order in H, we obtain for the diamagnetic part of the circular polarization,

$$\Delta_d(0) = \frac{I_+(0) - I_-(0)}{I_+(0) + I_-(0)} = \frac{-2 g_L \mu_B H}{|E_{sp}| + \hbar\omega} . \qquad (3.4)$$

This expression agrees with the general result obtained in Eq. (I5.37), as seen from Eq. (I6.4b) (where $\hbar\omega$ was neglected in the energy denominator). Similarly, we may include the effect of spin-orbit interaction and of a net spin polarization $\langle S_z \rangle$ in the excited state by adding $+2\lambda\langle S_z \rangle$ to the numerator of Eq. (3.4), as in Eq. (I5.40). We thus obtain for the total circular polarization of the emission from the vibronic ground state in the weak-coupling limit the result

$$\Delta(0) = -(2g_L \mu_B H + \lambda\langle S_z\rangle)/(|E_{sp}| + \hbar\omega) \,. \qquad (3.5)$$

B. Stress-Induced Linear Polarization

The coupling of the electronic $2p$ states to stress-induced strain was given in Eq. (I5.41). For an applied uniaxial stress X along [001] we have $e_\theta = +X/(c_{11} - c_{12})$ with the other strain components zero. The electronic state $|p_z\rangle$ has energy $|E_{sp}| - V_2 e_\theta$, while $|p_x\rangle$ and $|p_y\rangle$ have $|E_{sp}| + \frac{1}{2}V_2 e_\theta$. The perturbed vibronic ground-state wave function is then given as in Eq. (2.4) but with the strain splitting included in the energy denominator of the first-order terms. Expanding the resulting polarized emission probabilities, given as in Eq. (2.8), to first order in $V_2 e_\theta$, we obtain for the linear polarization

$$P(0) = \frac{I_z(0) - I_x(0)}{I_z(0) + I_x(0)} = \frac{\frac{3}{2} V_2 e_\theta}{|E_{sp}| + \hbar\omega} \,. \qquad (3.6)$$

Similarly, for a stress X along [110] we have $e_\theta = -\frac{1}{2}X/(c_{11} - c_{12})$ and $e_{xy} = +\frac{1}{4}X/c_{44}$. The $2p$ strain eigenstates are now $|p_{x'}\rangle = (2)^{-1/2}(|p_x\rangle + |p_y\rangle)$, $|p_{y'}\rangle = (2)^{-1/2}(|p_x\rangle - |p_y\rangle)$, and $|p_z\rangle$ with energies $+\frac{1}{2}V_2 e_\theta - V_3 e_{xy}$, $+\frac{1}{2}V_2 e_\theta + V_3 e_{xy}$, and $-V_2 e_\theta$, respectively. The resulting polarization as viewed along [001] is given by

$$P_z(0) = \frac{I_{x'}(0) - I_{y'}(0)}{I_{x'}(0) + I_{y'}(0)} = \frac{+2V_3 e_{xy}}{|E_{sp}| + \hbar\omega} \,. \qquad (3.7)$$

where x' denotes polarization along [110] and y' that along [$1\bar{1}0$]. For the polarization as viewed along [$1\bar{1}0$], we obtain

$$P_{y'}(0) = \frac{I_{x'}(0) - I_z(0)}{I_{x'}(0) + I_z(0)} = \frac{+V_3 e_{xy} - \frac{3}{2}V_2 e_\theta}{|E_{sp}| + \hbar\omega} \,. \qquad (3.8)$$

To investigate the temperature dependence of the stress-induced polarization, we have made a similar calculation of the polarization $P(1)$ that results for stress applied along [001] if the luminescence originates from the first excited triplet level. Using the wave function for $\Psi_x(1)$ as given in Eq. (2.10), together with the similar expressions for $\Psi_y(1)$ and $\Psi_z(1)$, and modifying the coefficients c_1, c_2, and c_3 in Eq. (2.11) to include the strain splitting of the p states in the energy denominator, we find

$$P(1) = \frac{I_z(1) - I_x(1)}{I_z(1) + I_x(1)} = \frac{+\frac{3}{2}V_2 e_\theta}{|E_{sp}| + \hbar\omega} u \,. \qquad (3.9)$$

The factor u is given by

$$u = \frac{4 + [(|E_{sp}| + \hbar\omega)/(|E_{sp}| - \hbar\omega)]^3}{4 + [(|E_{sp}| + \hbar\omega)/(|E_{sp}| - \hbar\omega)]^2} \,, \qquad (3.10)$$

so that we have $u \sim 1$ if $\hbar\omega$ is small compared to $|E_{sp}|$. $P(1)$ is then equal to $P(0)$ to a good approximation, so that the stress-induced polarization should be independent of temperature even up to temperatures at which the first excited vibronic triplet level is appreciably populated. Whether this temperature independence persists to even higher temperatures as higher levels become populated has not been investigated, but presumably it does not persist to temperatures at which the electronic $2p$ states are appreciably populated, $kT \sim |E_{sp}|$.

The calculation of Eq. (3.9) has ignored any Boltzmann-factor population difference between the three states of the triplet, because the strain splitting of this triplet is reduced by a factor $\sim(2E_G\hbar\omega/E_{sp}^2)$ compared to the splitting of the $2p$ electronic state. The additional contribution to P due to this splitting is smaller than $P(1)$ in Eq. (3.9) by a factor $\sim(E_G\hbar\omega/2kT|E_{sp}|)$, which is small under our assumption $E_G < \frac{1}{4}|E_{sp}|$ at temperatures at which the excited level is appreciably populated.

A similar conclusion for the temperature independence of P, with the ratio $P(1)/P(0)$ again given by the same factor u in Eq. (3.10), is obtained for [110] stress and also for the magnetic circular polarization, Eqs. (3.4) and (3.5).

C. Stark Effects

In the case of a magnetic field or applied stress, the polarization induced in the luminescence from the vibronic ground state results from the splitting of the $2p$ electronic states, through the change in the amount by which these states are mixed into the ground state by the vibronic coupling. On the other hand, an applied electric field directly mixes the $2s$ and $2p$ electronic states and thus leads to an induced polarized luminescence from the $2s$ level even if the vibronic coupling is negligible. For simplicity we shall consider only the effect of this zero-order mixing, while neglecting the change caused by the field in the vibrational mixing. The latter would lead to corrections to the polarization and change in radiative lifetime that are relatively smaller than what we calculate by a factor $\sim(E_G/|E_{sp}|)$.

The change in the unperturbed Hamiltonian $\mathcal{H}_0$ as a result of an electric field in the z direction is taken as in Eq. (I5.12) to be

$$\mathcal{H}_F = -D_z F_e \,. \qquad (3.11)$$

To first order in the local field F_e, the resulting perturbation in the ground state wave function (2.4) is

$$\Psi^F(0) = \Phi_{000}|2s\rangle + (dF_e/|E_{sp}|)\Phi_{000}|p_z\rangle \,, \qquad (3.12)$$

where $d = \langle 2s|D_z|p_z\rangle$. In calculating $I_z(0)$ from Eq. (I5.7), we note that there is no interference between the total transition probability resulting from the field-induced term in Eq. (3.12) and the vibrationally induced term in Eq. (2.4), because of the orthogonality of Φ_{000} and Φ_{001}. We therefore have

$$I_z(0)=\tau_r^{-1}(p)\left(\frac{d^2F_e^2}{|E_{sp}|^2}+\frac{E_G\hbar\omega}{(|E_{sp}|+\hbar\omega)^2}\right) , \qquad (3.13)$$

while $I_x(0)$ and $I_y(0)$ continue to be given by Eq. (2.8). We accordingly have for the induced polarization, to order F_e^2,

$$P(0)=\frac{I_z(0)-I_x(0)}{I_z(0)+I_x(0)}$$

$$=\frac{\frac{1}{2}d^2F_e^2}{E_G\hbar\omega}\left(\frac{|E_{sp}|+\hbar\omega}{E_{sp}}\right)^2 , \qquad (3.14)$$

and for the change in radiative lifetime,

$$\Delta[\tau_r^{-1}(0)]=\tau_r^{-1}(p)(d^2F_e^2/E_{sp}^2) . \qquad (3.15)$$

Comparing Eqs. (3.14) and (3.15) and using Eq. (2.9), we find then the relation

$$P(0)=-\tfrac{3}{2}\tau_r^{-1}(0)\Delta\tau_r(0) . \qquad (3.16)$$

This is the same relation obtained by Bogan[2] when we take his mixing coefficient $a\sim 0$.

The perturbing field causes a change in energy $\Delta E(0)$ of the ground state given by

$$\Delta E(0)=-d^2F_e^2/|E_{sp}| , \qquad (3.17)$$

corresponding to the approximations in Eq. (3.12). Assuming a negligible field-induced shift in the 1*s* electronic state, we then expect the field-induced change of the first moment of the *F*-band emission at 0 °K, for light polarized perpendicular to the field, to be simply

$$\langle\Delta E_x\rangle=\langle\Delta E_y\rangle=\Delta E(0) . \qquad (3.18)$$

This follows since the perturbation in Eq. (3.12) does not affect the transition probabilities for the emission of light polarized in the *x* or *y* direction, which in the approximation of Eq. (2.4) goes entirely to the vibrational level of the 1*s* state that has one phonon excited. For light polarized parallel to the field, on the other hand, the perturbation in Eq. (3.12) induces a transition to the no-phonon level of the 1*s* state. Weighting the transitions to the no- and one-phonon levels at 0 °K with their respective probabilities for *z* polarization, we obtain to order F_e^2 the result

$$\langle\Delta E_z(0)\rangle=-\Delta E(0)\left(\frac{(|E_{sp}|+\hbar\omega)^2}{|E_{sp}|E_G}-1\right) . \qquad (3.19)$$

Since $\Delta E(0)$ is negative, and because we have $|E_{sp}|/E_G>4$ under our assumptions of weak coupling, we see that $\langle\Delta E_z\rangle$ should be positive and larger in magnitude than $\langle\Delta E_x\rangle$ and $\langle\Delta E_y\rangle$, which are negative.

Finally, to obtain the temperature dependence of the field-induced polarization, we note that the change in the wave functions $\Psi_x(1)$, $\Psi_y(1)$, and $\Psi_z(1)$ of the first excited level is identical with Eq. (3.12) except for the different vibrational factor Φ_{100}, Φ_{010}, or Φ_{001}. We accordingly find that $[I_z(1)-I_x(1)]$ has the same value as $[I_z(0)-I_x(0)]$. However, $[I_z(1)+I_x(1)]$ is not equal to $[I_z(0)+I_x(0)]$ because of the lifetime ratio *R* in Eq. (2.13), and we have therefore

$$P(1)/P(0)=\tau_r(1)/\tau_r(0)=R^{-1} . \qquad (3.20)$$

The temperature dependence of the polarization is given, for temperatures at which only the ground state and first excited state are significantly populated, by

$$P(T)=\frac{P(0)+3RP(1)e^{-\delta E/kT}}{1+3Re^{-\delta E/kT}} . \qquad (3.21)$$

Using Eq. (3.20), we find therefore that the ratio $P(0)/P(T)$ should be given by

$$P(0)/P(T)=M^2(T)/M^2(0) , \qquad (3.22)$$

where $M^2(T)/M^2(0)$ is given by Eq. (I6.2) and represents the temperature variation of the radiative lifetime.

IV. COMPARISON WITH EXPERIMENT

The evidence was reviewed in I (Sec. VI) that leads us to the conclusion that for the *F* center in KCl and other alkali halides the coupling of the 2*s* and 2*p* electronic states via the Γ_4^- vibrational modes cannot be so strong as to place the system in or near the strong-coupling regime. Arguments were also given there to show that this coupling is probably weak. We will now compare the experimental data with the theoretical results we have obtained in this paper for the weak-coupling model. These data are most complete for KCl and KF, and we will devote our discussion below mainly to these two crystals. As we will see, the weak-coupling model does appear to account successfully for most of these data. However, there remain a number of puzzling points and one major discrepancy, the shift induced by an applied electric field in the energy of the luminescence band. Whether these reflect an inadequacy of the weak-coupling model in representing the actual situation, or perhaps some experimental difficulties, is not clear. We will discuss in Sec. V the extent to which we might hope better to explain the data by including the Jahn-Teller coupling of the 2*p* states with the Γ_3^+ and Γ_5^+ modes in our treatment, or by extending the analysis to consider stronger coupling with the Γ_4^- modes than can be handled by the simple perturbation treatment. However, a detailed study of these latter possibilities is left for future work.

It was already shown in I that if 2*s* lies below 2*p* in the cubic configuration the separation $|E_{sp}|$ may be found in the weak-coupling case from the diamagnetic part of the circular polarization $\Delta_d(0)$ of the emission induced by a magnetic field. Substituting the experimental values $\Delta_d(0)/H = -(9\pm 1)\times 10^{-8}$ (H in gauss) for KCl[3] and $\Delta_d(0)/H = -(6\pm 1)\times 10^{-8}$ for KF[4] into Eq. (3.4), and using $g_L = 0.95 \pm 0.1$ for KCl[5] and $g_L \sim 1$ for KF[6] (the g value obtained for the unrelaxed configuration from the circular dichroism of the optical absorption, which we assume approximates that for the relaxed configuration as well), we obtain the values

$$\begin{aligned} |E_{sp}| + \hbar\omega &\sim 0.12 \text{ eV} \quad (\text{KCl}) \\ &\sim 0.19 \text{ eV} \quad (\text{KF}) \ . \end{aligned} \tag{4.1}$$

The energy difference $|E_{sp}|$ of the electronic states in the relaxed cubic configuration is therefore smaller than the values (4.1) by one vibrational quantum, which should lie in the range 0.02–0.04 eV.

There are several alternative ways in which we may interpret the data to obtain a value for the strength of the vibronic coupling, and we will consider these in turn. We begin by postulating that the principal coupling between the $2s$ and $2p$ states is with a vibrational mode having a frequency near that of the LO lattice phonon, and we will use Eq. (2.12) together with the observed value for δE, the excitation energy of the first excited level above the vibronic ground state in the relaxed configuration, to estimate the coupling energy E_G from the ratio $\delta E/\hbar\omega$. We would expect coupling with the long-wavelength LO phonons to predominate if the $2s$ and $2p$ states are diffuse and if their interaction occurs primarily via the electric field associated with these vibrational modes. This estimate of E_G should be an upper bound, since the LO phonon has the highest energy of all phonons of the perfect lattice, and since one expects coupling to phonons of lower energy to be enhanced by the presence of the anion vacancy, as McCombie *et al.*[7] have shown for the symmetric modes, even when no truly localized mode occurs.

Accordingly, if we take $\hbar\omega = \hbar\omega_{\text{LO}} = 26.8$ meV for KCl and 40.2 meV for KF, we have

$$\begin{aligned} |E_{sp}| &\sim 0.09 \text{ eV} \quad (\text{KCl}) \\ &\sim 0.15 \text{ eV} \quad (\text{KF}) \ . \end{aligned} \tag{4.2}$$

from Eq. (4.1). The data of Bogan and Fitchen[2] for the temperature dependence of the electric-field-induced polarization [Eq. (3.21)] and those of Stiles *et al.*[8] for the temperature variation of the radiative lifetime [Eq. (I6.2)] give $\delta E = 18$ meV for KCl and ~ 17 meV for KF. From the values 0.67 and 0.42 for the ratio $\delta E/\hbar\omega$ for KCl and KF, respectively, we obtain from Eq. (2.12) the estimate of the coupling energy,

$$\begin{aligned} E_G &\sim 0.014 \text{ eV} \quad (\text{KCl}) \\ &\sim 0.040 \text{ eV} \quad (\text{KF}) \ . \end{aligned} \tag{4.3}$$

These values are consistent with our conclusion in I that the coupling to the Γ_4^- modes is weak.

We now use the values (4.1) and (4.3) for $|E_{sp}| + \hbar\omega$ and E_G to evaluate the radiative lifetime ratio $\tau_r(0)/\tau_r(p)$ from Eq. (2.9), obtaining

$$\begin{aligned} \tau_r(0)/\tau_r(p) &\sim 12 \quad (\text{KCl}) \\ &\sim 7.5 \quad (\text{KF}) \ . \end{aligned} \tag{4.4}$$

This ratio gives the factor by which the radiative lifetime is enhanced at the lowest temperatures, relative to that of the $2p$ state, as a result of the $2s$ state being below $2p$. The values (4.4) agree well with Fowler's estimate[9,10] of the enhancement factor needed to account for the observed lifetime, which he attributed in an increase in $\tau_r(p)$ caused by the $2p$ state (the initial state for the luminescence transition in his model) becoming spatially diffuse as a result of lattice relaxation. If the values (4.1) and (4.3) are roughly correct, the long radiative lifetime of the F center in KCl and KF must therefore to a large extent be because the $2s$ state is below $2p$ and is only weakly coupled to it by the phonons, as originally suggested by Swank and Brown,[11] rather than because the dipole matrix element $\langle 1s|D_\eta|2p_\eta\rangle$ is strongly reduced in the relaxed configuration. A large reduction in this matrix element for the diffuse $2p$ state indeed was obtained by Fowler in his calculations for NaCl[9]; however the recent calculations of Wood and Opik[12] show that a reduced matrix element is not a necessary consequence of a large expansion of the $2p$ state, because the $1s$ wave function concomitantly may develop an extended tail in the modified potential of the relaxed configuration.

An alternative estimate of the lifetime ratio $\tau_r(0)/\tau_r(p)$ is given by combining Eq. (2.9) with Eq. (3.14) for the electric-field-induced polarization $P(0)$, so that we have

$$P(0) = \frac{3}{2}\frac{\tau_r(0)}{\tau_r(p)}\frac{d^2F_e^2}{|E_{sp}|^2} \ . \tag{4.5}$$

Bogan and Fitchen[2] have measured $P(0)$ for KCl and KF (as well as for NaF, NaCl, RbCl, and CsF), so that using the values for $|E_{sp}|$ from Eq. (4.2) we can evaluate $\tau_r(0)/\tau_r(p)$ once we have determined $d^2F_e^2$. This last quantity is given directly for the unrelaxed configuration in KCl by the measurements of Chiarotti *et al.*[13] of the change $\langle \Delta E_e^2 \rangle$ in the second moment of the F absorption band for light polarized parallel to the applied field, since as shown by Henry *et al.*[14,15]

$$\langle \Delta E_e^2 \rangle = d^2F_e^2 \ . \tag{4.6}$$

This experimental value presumably provides a lower bound for the value of $d^2F_e^2$ that should be used in Eq. (4.5), since the calculations of Wood and Opik[12] show that the $2s$ and $2p$ states should both become more diffuse in the relaxed configuration. The results of Chiarotti *et al.*[13] place the value of $\langle\Delta E_z^2\rangle$ in the range between 2.4×10^{-7} eV^2 (obtained by integrating over the region of the F and K bands) and 4.8×10^{-7} eV^2 (obtained from the region of the F band alone) for an applied field $F=40$ kV/cm (where F denotes the applied field, F_e the local field, in our notation). Substituting the larger of these values for $d^2F_e^2$ in Eq. (4.5), together with Bogan's experimental value[2] $P(0)/F^2 = (1.0\pm0.3)\times10^{-5}$($F$ in kV/cm), we obtain

$$\tau_r(0)/\tau_r(p) \sim 180 \qquad (4.7)$$

for KCl. Substituting this result in turn into Eq. (2.9), and using $\hbar\omega = 26.8$ meV and Eq. (4.1) for $(|E_{sp}| + \hbar\omega)$, we obtain a value for the coupling energy of $E_G \sim 1.0$ meV. This interpretation of the data would therefore indicate a very much weaker coupling to the Γ_4^- modes than that given by Eq. (4.3). However, the value (4.7) for the lifetime ratio seems unreasonably large, since it would require a value $\tau_r(p) \sim 4$ nsec in order to be consistent with the experimental low-temperature lifetime in KCl,[8] $\tau_r(0) = 717 \pm 15$ nsec. We could bring Eq. (4.7) into agreement with Eq. (4.4) by increasing $d^2F_e^2$ for the relaxed configuration by a factor ~ 15 compared with the experimental value of Chiarotti *et al.*[13] obtained from the absorption data. A large change in this quantity due to lattice relaxation is possible, and indeed Wood and Opik[12] did find an increase by a factor ~3 in the dipole matrix element d from their theoretical wave functions. The correct value for the lifetime should in any case be intermediate between Eq. (4.4) and (4.7), since the way we obtained Eq. (4.4) indicates it is a lower bound.

The weak-coupling model is certainly consistent with the fact, already discussed in I (Sec. VI), that the experimental value for δE is found not to be strongly reduced compared to optical-phonon energies of the crystal. The ratio of δE to the effective mode energy $\hbar\omega$ is given for weak coupling by Eq. (2.12), and we have already used this relationship, together with the assumption $\hbar\omega \sim \hbar\omega_{\mathrm{LO}}$, in obtaining the estimates of the coupling energy E_G given by Eq. (4.3). Alternatively, the value $E_G \sim 1$ meV corresponding to the value of the lifetime ratio given by Eq. (4.7) would indicate that δE is reduced below $\hbar\omega$ by only 2–3%. If this were the case, the effective mode energy in KCl would have to be close to that of the TO modes, $\hbar\omega_{\mathrm{TO}} = 18.5$ meV. Whatever value for $\hbar\omega$ we use, we see that the coupling energy E_G for KCl and KF cannot be significantly larger than the values given by Eq. (4.3) without causing δE to be smaller than what is observed.[16]

Another way to estimate $\tau_r(0)/\tau_r(p)$ and E_G from the Stark-effect data, which does not require having a value for the dipole matrix element d in the relaxed excited state, is to take the ratio of the induced polarization $P(0)$, given by Eq. (4.5), to $\langle\Delta E_x\rangle$, the induced shift of the F emission for light polarized perpendicular to the applied electric field, given by Eqs. (3.17) and (3.18). Using the value given by Eq. (4.2) for $|E_{sp}|$, Bogan and Fitchen's value[2] for $P(0)$, and their result $\langle\Delta E_x\rangle/F^2 = -(2.0\pm0.4)\times10^{-7}$ eV, we obtain in this way the value $\tau_r(0)/\tau_r(p) \sim 3$ for KCl. The corresponding value of this ratio for KF is 5. Both of these results correspond to values for $E_G \sim 0.06$ eV according to Eq. (2.9). These results for KF are not seriously in disagreement with the values given by Eqs. (4.3) and (4.4). However, for KCl this approach leads to a value for E_G four times larger than what we have previously argued must be an upper bound for E_G in view of the observed value of δE. This result indicates that Bogan and Fitchen's value for $\langle\Delta E_x\rangle/F^2$ for KCl is some four times larger than it should be in order to be consistent with the other data on the basis of our weak-coupling model.

We encounter a further discrepancy when we consider the induced shift $\langle\Delta E_z\rangle$ for light polarized parallel to the applied electric field. According to Eq. (3.19) this shift should be to higher energy, in contrast to the smaller red shift predicted for $\langle\Delta E_x\rangle$ by Eqs. (3.17) and (3.18). However, Bogan and Fitchen[2] found the same red shift for both signs of polarization in all of the crystals they investigated. This result is in clear disagreement with the weak-coupling model.

The weak-coupling model predicts a definite value for the ratio of the electric-field-induced polarization $P(0)$ to the change in radiative lifetime, as given by Eq. (3.16). Because our derivation of this relation ignored the dependence of the radiative lifetime on the energy of the transition, the data for the lifetime change should be compensated for the field induced shift of the emission by defining $M^2 = (\tau_r\langle E^3\rangle)^{-1}$ as in Eq. (I6.1). The ratio of $P(0)$ to $\Delta M^2/M^2$ then equals $+\frac{3}{2}$ in the weak-coupling model. The data of Bogan and Fitchen[2] and Stiles *et al.*[8] for KCl, KF, and NaF as given in Table I are consistent with this relation. We have noted previously in I that a larger value for this ratio would be expected for stronger coupling.

The lifetime ratio R for the lowest two vibronic levels is given by Eq. (2.13) and our values for $|E_{sp}|$ in Eq. (4.2), using $\hbar\omega$ as 26.8 meV for KCl and 40.2 meV for KF, to be

$$\begin{aligned} R &\sim 2.4 \ \ (\text{KCl}) \\ &\sim 2.3 \ \ (\text{KF}) \ . \end{aligned} \qquad (4.8)$$

TABLE I. Electric-field-induced linear polarization of F-band emission and change in radiative lifetime.[a]

Crystal	$\Delta M^2/M^2$ [10^{-6} (kV/cm)$^{-2}$]	$P(0)$ [10^{-6} (kV/cm)$^{-2}$]
KCl	6.0 ± 1.0[b]	10 ± 3[c]
KF	4.2 ± 0.6[b]	8 ± 3[c]
NaF	3.0 ± 0.5[b]	4 ± 1[c]

[a] The radiative lifetime τ_r is related to M^2 by the relation $M^2 = (\tau_r \langle E^3 \rangle)^{-1}$, where E is the energy of the transition.

[b] Stiles *et al.* (Ref. 8).

[c] Bogan and Fitchen (Ref. 2).

TABLE II. Stress-induced linear polarization of F-band emission for uniaxial stress X along [001].[a]

Crystal	P/X [10^{-3} (kg/mm^2)$^{-1}$]
KCl	9.9
RbCl	11.1
NaCl	3.9
NaF	3.1

[a] These data are taken from the slopes of the lines in Fig. 1 of the paper by Hetrick and Compton (Ref. 17).

These values may be compared with the observed ratio ~2.75 found by Stiles *et al.*[8] for both KCl and KF. The difference is probably within the limits of experimental uncertainty, since Stiles *et al.* did not take into account in their analysis the likelihood that additional vibronic levels lying above the first excited level have an even shorter radiative lifetime. We may note that the large experimental value for R again favors the weak-coupling model, since R presumably becomes smaller than the values (4.8) as the coupling strength increases, approaching unity in the strong-coupling limit as we have seen in I.

The stress-induced linear polarization of the F-band luminescence in KCl, NaCl, NaF, and RbCl has been measured by Hetrick and Compton,[17] for uniaxial stress applied along the [001] and [110] directions, and found to be consistent with Eqs. (3.6)–(3.8) if we have for the strain-coupling coefficients $V_2 \gg V_3 \sim 0$. We can therefore obtain an independent estimate of $|E_{sp}| + \hbar\omega$ from Eq. (3.6) if we assume that V_2 is the same as in the unrelaxed configuration, for which it may be obtained from the stress-induced change in the first moment of the F-band absorption. Taking a uniaxial stress X along [001], we have for the difference in the first moment change for light polarized parallel and perpendicular the stress axis,

$$\langle \Delta E_z \rangle - \langle \Delta E_x \rangle = -\tfrac{3}{2} V_2 e_\theta = -A_3 X \quad . \tag{4.9}$$

Equation (4.9) defines a stress-coupling coefficient A_3, in terms of which we may express Eq. (3.6) as

$$P(0)/X = A_3/(|E_{sp}| + \hbar\omega) \quad . \tag{4.10}$$

Combining the data of Hetrick and Compton[17] for $P(0)/X$ (Table II) with the value of A_3 obtained by Schnatterly[18] and Hetrick[19] (Table III), we obtain from Eq. (4.10) a value $(|E_{sp}| + \hbar\omega) \sim 0.06$ eV for KCl, NaCl, and RbCl. This is only half the value for $(|E_{sp}| + \hbar\omega)$ for KCl given in Eq. (4.1) and obtained from the magnetic circular polarization. We regard the latter value as the more reliable, however, because of the likelihood that the value of A_3 that should be used in Eq. (4.10) may differ substantially from that measured in absorption because of the large symmetric-mode relaxation. A large change in the coupling coefficient accompanying the relaxation seems to be the only plausible explanation for Hetrick and Compton's surprising observation[17] that no polarization occurred with any of their crystals for [110] stress and light viewed along [001]. The expected polarization in this case is given by Eq. (3.7), so that V_3 is evidently zero in the relaxed configuration. This result contrasts with Schnatterly's absorption measurements,[18] which show that in the unrelaxed configuration the coupling to the shear e_{xy} is as strong as that to e_θ in all of the crystals measured. For [110] uniaxial stress and light incident along [001] the relation analogous to Eq. (4.9) is

$$\langle \Delta E_{x'} \rangle - \langle \Delta E_{y'} \rangle = -2 V_3 e_{xy} = -A_5 X \quad , \tag{4.11}$$

where x' denotes [110] and y', [1$\bar{1}$0]. The values of A_5 measured by Schnatterly[18] are given in Table III.

A surprising feature of the data of Hetrick and Compton[17] was the complete absence of any temperature dependence of the induced polarization

TABLE III. Stress-coupling coefficients for the $2p$ electronic states in the unrelaxed configuration, obtained from stress-induced linear dichroism data in F-band adsorption.[a]

Crystal	A_3 [10^{-4} eV (kg/mm^2)$^{-1}$]	A_5 [10^{-4} eV (kg/mm^2)$^{-1}$]
KCl	6.1 ± 0.9[b]	8.8 ± 1.2[b]
	5.9 ± 0.8[c]	8.0 ± 1.1[c]
KBr	4.4 ± 0.6[b]	6.3 ± 0.9[b]
KI	6.2 ± 0.9[b]	9.8 ± 1.4[b]
NaCl	2.4 ± 0.4[b]	6.7 ± 1.0[b]
RbCl	7.0 ± 1.0[b]	5.8 ± 0.8[b]

[a] The coefficients A_3 and A_5 are defined by Eqs. (4.9) and (4.11) of the text from the stress-induced changes in the first moment of the F-band adsorption.

[b] Schnatterly (Ref. 18): data at 80 °K.

[c] Hetrick (Ref. 19): data at 7 °K.

between 20 and 140 °K, for all of the crystals studied. This result would be consistent with the weak-coupling model if we had $|E_{sp}| \gg \hbar\omega$, as we have seen in Sec. III B, since the ratio $P(1)/P(0) = u$ is then unity. For the values $|E_{sp}| = 0.09$ eV, $\hbar\omega = 26.8$ meV, which we have taken to be appropriate to KCl, we obtain $u = 1.39$, a result which would lead us to expect an increase in polarization by ~ 15% as the temperature is raised to 140 °K. No such change was observed by Hetrick and Compton,[17] although this is close to their limit of experimental uncertainty. On the basis of the weak-coupling model, it therefore appears that their results require that $|E_{sp}|$ be no smaller than ~ 0.10 eV for any of the crystals in Table II.

In contrast to the temperature independence of the stress-induced polarization, Bogan and Fitchen[2] found the polarization induced by an electric field to be strongly dependent on temperature. This result and the general form of the variation found by Bogan and Fitchen are also consistent with the weak-coupling model, as shown by Eq. (3.21). Indeed, this model predicts [Eq. (3.22)] that the temperature dependence of the polarization as given by $P(0)/P(T)$ should be identical with that of the radiative lifetime as given by $M^2(T)/M^2(0)$, at least at temperatures low enough so that only the vibronic ground state and first excited state are appreciably populated. This relation is satisfied at least approximately by the data of Bogan and Fitchen[2] for the polarization and that of Stiles *et al.*[8] for the radiative lifetime. The lifetime data gave values for δE for KCl (18 meV) and KF (17 meV), in good agreement with those obtained from the polarization measurements (18 and 16 meV, respectively), although some discrepancy was found for NaF (17 vs 12 meV).

To data there has been no successful determination of the paramagnetic component Δ_p of the magnetic circular polarization of the emission for KCl or KF, interesting as such data would be, because of the difficulty in producing a net spin polarization $\langle S_z \rangle$ in the excited state.[3,6] However, such measurements have recently been made by Baldacchini and Mollenauer[20] for KBr and KI, although no Stark-effect data exist as yet for these crystals. Baldacchini and Mollenauer[20] have also obtained the diamagnetic component $|\Delta_d(0)|/H = (16.3 \pm 1.7) \times 10^{-8}$ for KBr and $(18.5 \pm 1.2) \times 10^{-8}$ for KI at 1.7 °K, although the sign of $\Delta_d(0)$ was not established. Assuming that Eq. (3.4) is applicable also for KBr and KI and that the sign of $\Delta_d(0)$ is negative, and taking $g_L \sim 1$,[21] we obtain from these results the values

$$\begin{aligned}(|E_{sp}| + \hbar\omega) &\sim 0.07 \text{ eV} \quad (\text{KBr}) \\ &\sim 0.06 \text{ eV} \quad (\text{KI}) \; . \end{aligned} \tag{4.12}$$

This result for KI is consistent with the finding of Park and Faust[22] that strong optical absorption from the relaxed excited state (the $2s$ state in our model) occurs to another state lying not more than 0.1 eV higher in energy, which we would identify on the basis of Eq. (4.12) with the $2p$ state. Baldacchini and Mollenauer's data[20] for the paramagnetic component of the emission from the vibronic ground state gave the results $|\Delta_p(0)| = 1.27 \times 10^{-3}$ for KBr and 2.16×10^{-3} for KI, corresponding to spin polarization $P' = 2\langle S_z \rangle$ in the excited state of 0.14 and 0.21, respectively. Combining these results with the values for $|E_{sp}| + \hbar\omega$ from Eq. (4.12), and substituting these in Eq. (3.5), we obtain for the spin-orbit parameter λ of the $2p$ states in the relaxed configuration the result

$$|\lambda| \sim 0.6 \text{ meV} \tag{4.13}$$

for both KBr and KI. This result contrasts with the values of the spin-orbit parameter $\lambda = -15$ meV for KBr and $\lambda = -26$ meV for KI in the unrelaxed configuration as determined from the magnetic circular dichroism of the absorption.[5] One would expect some reduction in $|\lambda|$ as a result of a more diffuse $2p$ wave function in the relaxed configuration, but the very strong reduction indicated by Eq. (4.13) is surprising, particularly when contrasted with Smith's result[23] that λ as calculated from theoretical wave functions for RbCl is only a factor ~ 5 smaller in the $3p$ state than in $2p$. Alternatively, if λ in the relaxed configuration is not really as small as indicated by Eq. (4.13), one would apparently have to conclude that the spin polarization P' in the excited state is not as large as calculated by Baldacchini and Mollenauer.[20] The question of possible Jahn-Teller effects in these data is discussed in Sec. V.

V. SUMMARY AND DISCUSSION

We have shown that the weak-coupling model is able to account quantitatively for most of the available experimental data for KCl and KF, if the $2s$ electronic state is about 0.1 eV below $2p$ in the relaxed configuration. There is, however, one major discrepancy which we have been unable to explain, in the shift induced in the energy of the emission by an applied electric field. Moreover, agreement with the model appears a little forced when we try to fit simultaneously all the various data. It is therefore tempting to speculate that such agreement with the weak-coupling model as we have obtained is fortuitous and that a better explanation of the data could be obtained if we included in our treatment the Jahn-Teller coupling of the $2p$ states to the Γ_3^+ and Γ_5^+ modes, or if we extended our perturbation analysis to consider somewhat stronger coupling with the Γ_4^- modes. The possibility that the separation E_{sp} is smaller than we have assumed must also be considered, since our perturbation results will not be accurate if $|E_{sp}|$ should be less than $\sim 4E_G$, if the condition $|E_{sp}| \gg \hbar\omega$ is not satisfied, or if $2p$ should lie below $2s$. These cases can be investigated in the range of intermediate coupling by setting up the matrix equation for the exact energies of the vibronic states using as a basis the unperturbed eigenstates of Eq. (2.3), and obtaining numerical solutions. Such calculations should certainly be made in the course of further investigation of this problem. However, the chances of improving the agreement with the data in this way are limited, as the following discussion shows.

Strong evidence that the coupling energy E_G cannot be larger for KCl and KF than the values given by Eq. (4.3) is the fact, already discussed, that the excitation energy δE is not strongly reduced compared to optical-phonon energies of the crystal. Supporting this conclusion is the large value ~ 2.75 found for the lifetime ratio R, which will approach unity for stronger coupling as the mixing of $2s$ and $2p$ in the vibronic states becomes more nearly equal. Also supporting weak coupling is the fact that the lifetime change in an applied electric field, as given by $\Delta M^2/M^2$ in Table I, is about two-thirds as large as the induced polarization $P(0)$, since a smaller lifetime change will result if the $2s$ and $2p$ states are more fully mixed by the vibronic coupling, as discussed in I. This estimate of E_G is of course consistent with the conclusion from I (Table I) that we must have $2s$ below $2p$ and $E_G < \frac{1}{4}|E_{sp}|$, in order to have a nondegenerate ground state.

In assessing the accuracy of our estimate for $|E_{sp}|$ as obtained from the diamagnetic part of the circular polarization of the emission, we should recall that Eq. (3.4) is but a special case of the general result given by Eq. (I5.37), which is valid for any coupling strength for which the vibronic ground state is an s-like type-I state. The energy denominator which we have taken to be $(|E_{sp}| + \hbar\omega)$ in Eq. (4.1) is therefore in the general case $\overline{E}_{\mathrm{II}} - E_{\mathrm{I}}(0)$, the average energy difference between the ground state and the type-II states that have matrix elements of orbital angular momentum with the ground state. We recall, however, that the type-II states are completely unaffected by the vibronic coupling to the Γ_4^- modes and that they therefore coincide with vibrational levels of the unperturbed $2p$ electronic states. The ground-state energy $E_{\mathrm{I}}(0)$, on the other hand, is depressed by the coupling in proportion to E_G. The energy difference $\overline{E}_{\mathrm{II}} - E_{\mathrm{I}}(0)$ therefore lies between its weak-coupling value $|E_{sp}| + \hbar\omega$ and its strong-coupling limit $2E_G$ (valid only if we have both $E_G \gg |E_{sp}|$ and $E_G \gg \hbar\omega$). Taking the value for E_G given by Eq. (4.3) as an upper bound for the coupling strength, we see from these considerations that, in order to account for a value of $\overline{E}_{\mathrm{II}} - E_{\mathrm{I}}(0)$ as large as given by Eq. (4.1), we must have $|E_{sp}| \gtrsim 0.1$ eV for KCl and KF. This interpretation of the diamagnetic part of the circular polarization is therefore not compatible with a value for $|E_{sp}|$ smaller than this (unless of course we should have g_L substantially smaller than unity for the diffuse $2p$ state in the relaxed configuration).

The possibility of important effects of the Jahn-Teller coupling to the Γ_3^+ and Γ_5^+ modes would seem at first sight large, since our estimates of the Jahn-Teller energies $(E_{JT})_E$ and $(E_{JT})_T$ for KCl in I $[(E_{JT})_E \lesssim 0.07$ eV, and 0.04 eV $\lesssim (E_{JT})_T \lesssim 0.06$ eV$]$ indicated these were larger than the values we have now obtained for the coupling energy E_G to the Γ_4^- modes. Nevertheless, it seems clear that we can rule out the possibility that the Jahn-Teller coupling is strong enough to bring the energy minimum of the Jahn-Teller-distorted $2p$ states below that of the $2s$ state, since it follows from Table I of I that the vibronic ground state should then be degenerate. We can similarly rule out the possibility that the ground state is one of a number of closely spaced tunneling levels of the "s-p mixed type" (Table I of I) resulting from strong coupling both to the Γ_4^- modes and to the Γ_3^+ or Γ_5^+ modes. Either of these situations should cause the polarization of the emission produced by an applied electric field, magnetic field, or stress to be strongly temperature dependent at low temperatures, contrary to observation. We are left then with the likelihood that the Jahn-Teller coupling significantly affects the $2p$ states, but that the minimum in the adiabatic energy surfaces for these states remains above the energy of the $2s$ state in the cubic configuration, as in Fig. 1. In other words, we have the situation described in Table I of I by the conditions $E_{sp} < 0$, $(E_{JT})_E < |E_{sp}|$, $(E_{JT})_T < |E_{sp}|$, $E_G < \frac{1}{4}|E_{sp}|$. We recall that this is the only situation in which the ground state is nondegenerate.

Nevertheless, we believe that appreciable Jahn-Teller coupling of the $2p$ states in this situation will not greatly change the results obtained in Sec. IV by neglecting this coupling, as long as the Jahn-Teller energy [the larger of $(E_{JT})_E$ and $(E_{JT})_T$] is appreciably smaller than $|E_{sp}|$, as in Fig. 1. The $2s$ state in this situation is not directly affected at all by the coupling to Γ_3^+ and Γ_5^+ modes, so that this coupling affects the vibronic ground state only through the $2p$ states which are mixed with $2s$ by the Γ_4^- coupling or by an applied electric field. However, from Fig. 1 it is clear that mixing of the $2p$ states into the lowest vibrational state of $2s$ occurs only near $Q = 0$, where this state has appreciable amplitude, and that the average separation of the $2s$ and $2p$ energy surfaces in this region is the cubic energy difference

$|E_{sp}|$. The properties of the lowest vibrational states of the $2p$ energy surfaces, which would show such effects of the Jahn-Teller coupling as the quenching of orbital angular momentum,[24] are thus not relevant in determining the properties of the perturbed vibronic ground state. To a good approximation, we should therefore be able to neglect the Jahn-Teller coupling of the $2p$ states in calculating the effects of the $2s$-$2p$ mixing on the vibronic ground state. This qualitative argument based on Fig. 1 is supported by modifying the perturbation treatment of Secs. II and III to include coupling the $2p$ states to the Γ_3^+ modes; sums over the vibronic states of these modes may be eliminated by replacing energy differences between vibronic levels by an average approximately equal to the cubic energy separation $|E_{sp}|$.

Moreover, it is likely that the estimates of $(E_{JT})_E$ and $(E_{JT})_T$ cited above and based on the data of Schnatterly[18] and Hetrick[19] for the stress-induced linear dichroism of the F-band absorption should be reduced for the relaxed configuration. The $2p$ wave functions are probably much more diffuse in this configuration than in absorption, and the number of phonons with which they can interact strongly is consequently reduced to those of long wavelength lying in the central part of the Brillouin zone. Moreover, Hetrick and Compton's data[17] show that the stress-coupling coefficient A_5 is very small in the relaxed configuration, so that coupling with long-wavelength Γ_5^+ phonons should be negligible.

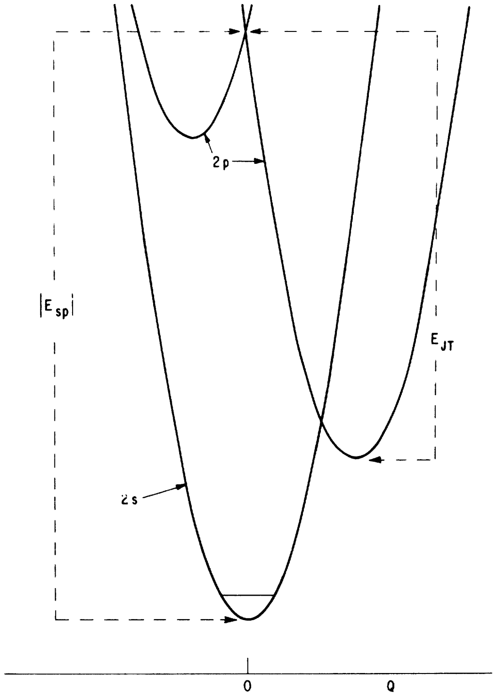

FIG. 1. Adiabatic energy surfaces for electronic $2s$ and $2p$ states as functions of a Γ_3^+ or Γ_5^+ distortion mode Q which splits the $2p$ degeneracy in first order (Jahn-Teller coupling). The figure illustrates the situation in which $2s$ is below $2p$ in the cubic configuration ($Q=0$) by an energy difference $|E_{sp}|$ and the Jahn-Teller energy E_{JT} of the $2p$ states is less than $|E_{sp}|$. The minima of the $2p$ energy surfaces in this case therefore lie above the minimum of the $2s$ surface, which occurs in the cubic configuration. There is no coupling of the $2s$ and $2p$ states via a Γ_3^+ or Γ_5^+ distortion mode. The energy of the lowest vibrational state on the $2s$ surface is indicated by a horizontal line within the $2s$ well, which also shows the approximate spatial extent in Q of the vibrational wave function of this state.

We conclude, therefore, that the Jahn-Teller energy of the $2p$ states in the relaxed configuration is probably much smaller than the cubic energy difference $|E_{sp}| \gtrsim 0.1$ eV. In this situation our previous arguments lead us to conclude that we can ignore this coupling in evaluating the various excited-state parameters for the weak-coupling model as in Sec. IV. This conclusion contrasts with that of Iida *et al.*,[25] who attributed the small value of the circular polarization $\Delta_d(0)$ to the partial quenching of the orbital angular momentum by the Jahn-Teller coupling. Their calculation is not directly comparable with our work, since they took the $2s$-$2p$ mixing to result from an internal field which they treated adiabatically. However, it appears to us that their interpretation of their numerical results is wrong and that the small value of the magnetic circular polarization is caused in their model, as in our present work, by the $2s$ electronic state being appreciably lower in energy than the $2p$ states in the relaxed cubic configuration.

The possibility was raised in Sec. IV that the small value obtained for the spin-orbit parameter λ in the relaxed configuration for KI might somehow be caused by the Jahn-Teller coupling. The arguments just presented lead us to discount this possibility if the general behavior of the excited states is the same for KI as for KCl and KF. But even if these states are somehow different for KI and there could be a Jahn-Teller quenching of the effect of the spin-orbit interaction in producing the paramagnetic component of the circular polarization of the luminescence, there should then be a corresponding reduction in the orbital Zeeman interaction responsible for the diamagnetic component,[24] since both interactions depend on matrix elements of the orbital angular momentum. The very small value for $|\lambda|$ given by Eq. (4.13) was in fact obtained by taking the excited states coupled to the ground state by the spin-orbit interaction to be the same as those that are admixed by the orbital Zeeman interaction. There is therefore apparently no basis for hoping that the Jahn-Teller effect can resolve the puzzle why this value for $|\lambda|$ is so small.

In our treatment we have taken the vibronic coupling to be with a single Γ_4^- mode. If this coupling is with the long-wavelength longitudinal-optical phonons, as seems likely for diffuse $2s$ and $2p$ states, this is a good approximation since we can form a linear combination of these modes, all having roughly the same frequency, such that the coupling is only with this effective mode. Alternatively, if the coupling is with a number of modes of different frequencies, the results of our simple perturbation treatment in Secs. II and III need only be modified by summing the effects of the various modes. In the latter case, if the coupling were stronger so that perturbation theory could not be used, a good approximation could be obtained using a single suitably averaged Γ_4^- mode chosen in the manner described recently by O'Brien.[26]

It was shown in I that one can obtain a simple general expression [Eq. (I5.43)] for the change δg in the g factor of the excited state resulting from the vibronic mixing of the $2s$ and $2p$ states. For our weak-coupling model this result becomes

$$\delta g = -\tfrac{4}{3}\,\frac{\tau_r(p)}{\tau_r(0)}\,\frac{\lambda g_L}{|E_{sp}| + \hbar\omega}\quad , \tag{5.1}$$

so that δg should be positive since λ is presumably negative as in the unrelaxed configuration. The g factor in the relaxed excited state has recently been determined for KCl, KBr, and KI by Mollenauer and co-workers,[27,28] using a method of optical detection of spin resonance, and for these crystals and a number of others by a different method by Ruedin.[29] These results are given in Table IV, from which it is seen that in all cases the observed g shift is *negative*. Moreover, if we calculate δg for KCl and KF using the values for $|E_{sp}| + \hbar\omega$ and $\tau_r(0)/\tau_r(p)$ given by Eqs. (4.1) and (4.4) and the values found for λ in the unrelaxed configuration[5,6] (– 5.0 and – 3.2 meV for KCl and KF, respectively), we obtain $\delta g \sim +0.0046$ for KCl and $\delta g \sim +0.0020$ for KF. The results for δg, which ought to yield an upper bound for the vibronic g shift since $|\lambda|$ should be smaller for the more diffuse $2p$ wave function in the relaxed configuration, are thus considerably smaller in magnitude than the experimental shift, in addition to having the opposite sign. We conclude that the dominant component of the experimental g shift must have another origin having nothing to do with the vibronic coupling.

TABLE IV. Experimental values of electron g factors in the ground state and relaxed excited state of the F center.

Crystal	Relaxed excited state MP[a]	R[b]	$1s$ ground state SW[c]
NaCl	···	1.973	1.997
KF	···	1.993	1.996
KCl	1.976 ± 0.001	1.981	1.995
KBr	1.862 ± 0.002	1.873	1.982
KI	1.627 ± 0.002	1.630	1.964
RbBr	···	1.845	1.967
RbI	···	1.634	1.949

[a] L. F. Mollenauer and S. Pan (Ref. 27).
[b] Y. Ruedin (Ref. 29).
[c] H. Seidel and H. C. Wolf (Ref. 30).

There is of course a significant negative g shift in the $1s$ ground state (Table IV).[30] This has been explained by Adrian[31] as resulting from the spatial variation of the $1s$ F-center wave function near the neighboring ions due to the orthogonality requirement to their p core states. The spin-orbit interaction due to the nuclear potential of these ions couples the F-center wave function to excited states, thereby causing a negative g shift. The same mechanism should operate in the excited $2s$ state as well, and we attribute the negative shift observed in the relaxed excited state to this cause. The fact that this shift is so much larger than in the $1s$ ground state indicates that, while the strength of the spin-orbit interaction in the vicinity of the neighboring ions should be weaker because the $2s$ state is more diffuse than $1s$, the excitation energy of the excited states coupled by this interaction must be very much smaller for the $2s$ state. (Adrian[31] and Schmid[32] took this energy for the $1s$ state to be approximately the F-band energy, which is 2.3 eV for KCl). This argument indicates that the spin-orbit interaction cannot also be very much smaller for the $2s$ state than for $1s$, and it therefore serves to cast further doubt on the accuracy of the very strongly reduced value of $|\lambda|$ for the $2p$ state of KI inferred in Eq. (4.13).

Recently Mollenauer and Baldacchini[28] have proposed an interpretation for the optically detected electron-nuclear-double-resonance (ENDOR) spectrum of KI and KBr in the relaxed excited state,[27] in terms of the radial distribution expected for a pure $2p$ wave function with no $2s$ admixture. This interpretation contrasts with the picture of the excited state developed by the present analysis, although a direct conflict is perhaps avoided because the Stark-effect data do not yet exist for KI and KBr, and it is these data for KCl and KF that provide much of the evidence that the $2s$ state is below $2p$. Nevertheless, the low-temperature radiative lifetime in KI and KBr is even longer than in KCl and KF (3.2 μsec for KI,[33] 1.1 μsec for KBr,[11] 717 nsec for KCl,[8] and 380 nsec for KF[8]), and it would be surprising if this were not an indication that the order of the states was the same and the vibronic coupling weak in all four crystals. Moreover, the observation[28] that the excited-state g factor in KI is isotropic is itself evidence that the vibronic ground state has no orbital degeneracy. Mollenauer and Baldacchini have suggested that a suitable nondegenerate state comprising equal admixtures only of the $2p$ orbitals $|2p_x\rangle$, $|2p_y\rangle$, and $|2p_z\rangle$ may result from a dynamic treatment of the vibronic coupling. However, in our analysis of this problem in I for the general case, the $2p$ admixture into the nondegenerate type-I s-like ground state was only 50% in the strong-coupling limit, whereas for weaker coupling such a state is predominantly $2s$. The only situation in which the ground state is made up predominantly from the $2p$ states is when $2p$ is below $2s$ ($E_{sp} > 0$) and the vibronic coupling to the Γ_4^- modes is weak, but the ground state is then triply degenerate (a type-I p-like state). If this were the case we might expect to find a true dynamic Jahn-Teller effect[24] for an orbital triplet state, as a result of the coupling to Γ_3^+ and Γ_5^+ modes, but the degeneracy of the ground state then remains. This degeneracy would of course be lifted in part by the spin-orbit interaction, itself reduced by the Jahn-Teller coupling, but with λ negative the $J = \frac{3}{2}$ state should be below $J = \frac{1}{2}$. In any case, the observed g factors show no resemblance to the values expected for such states. Alternatively, if the Jahn-Teller coupling is strong enough we would expect to see a static Jahn-Teller effect at sufficiently low temperature, but the resonance spectrum should then be the superposition of anisotropic spectra for the several axially distorted states. An isotropic spectrum could result in this case if sufficiently rapid thermally induced electronic transitions occur between the different distorted states, but such a "motionally averaged" spectrum would certainly be replaced by the anisotropic one as these transitions are slowed by going to low temperatures. The observation of the isotropic spectrum at 1.6 °K therefore appears to be conclusive proof that the vibronic ground state is a simple nondegenerate state with none of these complications, and from all the other evidence we would then expect it to have a radial distribution compatible with a predominantly $2s$ state. Mollenauer and Baldacchini's conclusion that this distribution as inferred from the ENDOR data is consistent with a $2p$ state but not with $2s$ is thus very puzzling. It would clearly be desirable to reconsider this conclusion using more accurately calculated wave functions such as those of Wood and Opik,[12] and also to carry through for KI and KBr the various experiments on Stark effects, stress-induced polarization, etc., that could further test the possible degeneracy of the ground state of the relaxed excited state.

We have remarked previously that the interpretation of the Stark-effect data based on Bogan's adiabatic model has overestimated the strength of the vibronic coupling. According to the present theory the reciprocal of the lifetime ratio $\tau_r(0)/\tau_r(p)$ gives the fractional mixing of the $2p$ electronic state into the vibronic ground state, as we recognize from Eqs. (2.4), (2.5), and (2.9) or from the general Eqs. (I5.8) and (I5.9). The corresponding quantity in Bogan's theory is $a^2/(1+a^2)$. From the lifetime ratios given by Eq. (4.4), which should give an upper bound for this quantity, we thus have the values 0.08 and 0.13, respectively, for KCl and KF, compared to the estimates $a^2/(1+a^2) \sim 0.3$ made by Stiles *et al.*[8]

Our treatment has ignored the broadening of the luminescence resulting from the difference in the coupling to the totally symmetric Γ_1^+ modes between the $1s$ state and the excited state. However, this should not affect any of our results provided all the measured quantities are determined from the appropriate moment obtained by integrating over the full F-band emission. There should be no corresponding broadening of the emission by the Γ_3^+ or Γ_5^+ modes, at least at low temperatures, since the $2s$ state is not linearly coupled to these modes.

Some years ago Tomura, Kitada, and Honda[34] pointed out that the temperature dependence of the F-center radiative lifetime in KCl below about 120 °K could be fitted to the expression

$$\tau_r^{-1}(T) = \tau_r^{-1}(0) \coth(\hbar\omega/2kT) \qquad (5.2)$$

and that such a behavior would be expected for a forbidden $2s$ to $1s$ transition made allowed by coupling to an odd-parity phonon of energy $\hbar\omega$. This suggestion is fully consistent with the model used in this paper, if the coupling is sufficiently weak so that the excitation energy δE in Eq. (2.12) is not appreciably smaller than $\hbar\omega \ll |E_{sp}|$. When this latter condition is satisfied the lifetime ratio R given by Eq. (2.13) is equal simply to $\frac{5}{3}$, and Eq. (5.2) then agrees with the expression for the lifetime [Eq. (I6.2)] used by Stiles *et al.*[8] to the accuracy of neglecting terms of order $e^{-2\hbar\omega/kT}$. Equation (I6.2) and the related Eq. (3.21) for the field-induced polarization were indeed obtained by assuming that higher levels were not significantly populated, and this neglect is probably responsible for the difficulty in fitting these equations to the data of Stiles *et al.*[8] at the higher temperatures. The weak-coupling model developed in this paper may therefore be regarded as an extension of this suggestion by Tomura *et al.*

ACKNOWLEDGMENT

One of the authors (F. S. H.) would like to thank Professor B. Bleaney and the Clarendon Laboratory, Oxford University, for their hospitality during the time in which this research was done. He would also like to thank the John Simon Guggenheim Memorial Foundation for its fellowship support and the General Electric Research and Development Center for the grant of a Research Sabbatical. The other author (U.G.) would like to thank Queen's College, Oxford, and the Foundation of the Florey European Studentships for their support.

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