PHYSICAL REVIEW B VOLUME 7, NUMBER 4 15 FEBRUARY 1973

Relaxed Excited States of the *F* Center: A Study of the Nearly Degenerate States of a Bound Lattice Polaron*

S. Wang, M. Matsuura, C. C. Wong, and M. Inoue†
Department of Physics, University of Waterloo, Waterloo, Ontario, Canada

(Received 26 April 1972)

A method of calculating the nearly degenerate states of a bound lattice polaron is formulated treating the Hartree-type Hamiltonian as the unperturbed Hamiltonian and the interaction omitted in the Hartree-type approximation as a perturbation. This method is applied to study theoretically the relaxed excited states associated with the *F* emission in a typical alkali halide such as KCl. The resultant theoretical results imply that the lowest relaxed excited state contains about 70% $2s$ character and about 30% $2p$ character and that among all the higher relaxed excited states there are no states which can be well approximated either by the $2s$ or $2p$ type. In addition, adopting the Franck–Condon principle we extend the electronic-effective Hamiltonian derived for the relaxed excited state to the $1s$-like state to which the *F* emission occurs and calculate this $1s$-like state and thereby the *F*-emission energy. Finally, an expression for the radiative lifetime of a point defect is derived for the case in which the initial states are nearly degenerate and applied to investigate the temperature dependence of the radiative lifetime of the *F* center.

I. INTRODUCTION

In previous theoretical studies, relaxed excited states of the *F* center (i.e., the *F*-electron excited states in the relaxed lattice, which refers to the lattice in the new equilibrium position after *F* absorption) were taken to be two separated $2s$- and $2p$-like states.[1,2] Therefore, the mixing of the $2p$ states into the $2s$ state due to the electron-phonon interaction, discussed in Ref. 3, was handled by nondegenerate perturbation theory. In Ref. 3, using the Fröhlich-type electron-phonon interaction and the obtained perturbed $2s$ state, the ratio of the transition probability of $2s \rightarrow 1s$ to that of $2p \rightarrow 1s$ was predicted to be 11.5 for the *F* center in KCl. As pointed out in Ref. 3, this value is too large. This may imply that the $2p$ and $2s$ state states are nearly degenerate rendering nondegenerate perturbation theory inappropriate for the calculation of the mixing of these states. As a result, the perturbed $2p$ or $2s$ state due to the electron-phonon interaction would no longer be approximately $2p$ or $2s$ like.

Further, in Ref. 4 the above-mentioned mixing was calculated by the Hartree-type self-consistent-field method in the continuum approximation. Thus, in this reference the effective electron-phonon interaction obtained from the Fröhlich-type electron-phonon interaction Hamiltonian cannot only shift the energy levels of the $2s$ and $2p$ states, but it can also mix these states. The mixing coefficients thus calculated are in good agreement with those expected from experimental work. However, this agreement must be considered as partly fortuitous in view of some rather crude approximations made, such as the continuum approximation and the Hartree-type self-consistent-field method, both of which require a justification for this problem.

In this work we first formulate a method to handle nearly degenerate states of a bound lattice polaron for the case in which the electronic frequency is much larger than the ionic frequency. Then this method is applied to the theoretical study of (a) relaxed excited states associated with the *F*-emission band in a typical alkali halide such as KCl, and (b) the temperature dependence of the lifetime of the excited *F* center in the range of low temperatures.

The method of calculating the nearly degenerate states of a bound lattice polaron is described in Sec. II. It is applied to investigate the relaxed excited states of the *F* center in KCl in Sec. III. The lifetime of the excited *F* center is calculated for KCl at a number of temperatures in Sec. IV. In Sec. V we summarize our results and compare them with the observed results and predictions of Refs. 5 and 6. Further, we comment on the construction of the wave functions for relaxed excited states of point defects.

II. METHOD OF CALCULATING NEARLY DEGENERATE STATES OF BOUND LATTICE POLARON

A. Hamiltonian

According to the work of Ref. 7, the Hamiltonian for a system consisting of an electron and a massive hole (effectively of infinite mass; for simplicity, we shall call it just "hole" in this work) in an insulator may be written as

$$H_e = \frac{p^2}{2m} + \sum_{\alpha} V(\vec{r} - \vec{R}_{\alpha 0}) - V(\vec{r}) + \left(1 - \frac{1}{\epsilon_\infty}\right)\frac{e^2}{r}\,\frac{2}{\pi}\int_0^{(\pi/d)r} \frac{\sin\mu}{\mu}\,d\mu + h \qquad (2.1)$$

when ignoring crystalline ionic polarization. The $\vec{p}$, m, and $\vec{r}$ are, respectively, the electronic momentum, the free-electron mass, and the electronic position vector with respect to the massive hole. The ϵ_∞ is the usual high-frequency dielectric constant. Here π/d is approximately the maximum value of the wave vector in the first Brillouin zone and d is the nearest-neighbor distance for alkali halides with NaCl structure. $V(\vec{r}-\vec{R}_{\alpha 0})$ represents the interaction of the electron with the αth ion at $\vec{R}_{\alpha 0}$ when the αth ion is at its equilibrium position and its core and valance electrons are in the ground state. Thus the second term in Eq. (2.1) is the interaction of the electron with all the ions making up the perfect insulator. The $-V(\vec{r})$ is the interaction between the bare electron and the hole. [In the F-center problem, because this problem consists of a perfect alkali halide minus a halogen ion plus an electron, $V(\vec{r})$ is, in fact, the interaction between the bare electron and a halogen ion. $-V(\vec{r})$ becomes $-e^2/r$ for large r.] The fourth term is the exchange interaction (i.e., the dielectric screening interaction) between the electron and the massive hole via the electronic-polarization field. h represents the electronic-polarization effect both on the massive hole and on the electron. Now the effect on the massive hole itself gives a constant energy and can be omitted hereafter. However, the effect on the electron itself yields (i) a self-energy, (ii) a mass correction to the electronic mass, and (iii) a Lamb-shift-type correction. The self-energy and the mass correction are given by

$$H_{se} = -\alpha_1 E_{ex} \tag{2.2}$$

and $-\frac{1}{6}\alpha_2 (p^2/2m)$, respectively. Here

$$\alpha_1 = (2\alpha/\pi)\tan^{-1}u \,, \tag{2.3}$$

$$\alpha_2 = \frac{2\alpha}{\pi}\left(\frac{-2u}{(1+u^2)^2} + \frac{u}{1+u^2} + \tan^{-1}u\right), \tag{2.4}$$

u and α being

$$u = (\hbar^2/2mE_{ex})^{1/2} w_m \,, \tag{2.5}$$

$$\alpha = \frac{e^2}{2E_{ex}}\left(1-\frac{1}{\epsilon_\infty}\right)\left(\frac{2mE_{ex}}{\hbar^2}\right)^{1/2} , \tag{2.6}$$

respectively. E_{ex} is the energy of a longitudinal exciton and w_m is the maximum value of $|\vec{w}|$ in the first Brillouin zone.

The above-mentioned mass correction can be taken into account simply by replacing m in Eq. (2.1) with m^* defined by

$$m^* = m/(1-\tfrac{1}{6}\alpha_2) \,. \tag{2.7}$$

We note that in the band-mass approximation, i.e.,

$$p^2/2m + \sum_\alpha V(\vec{r}-\vec{R}_{\alpha 0}) \rightarrow p^2/2m_b \,,$$

m becomes the band mass m_b and m^* becomes m_b^* so that the values of α and u in the band-mass approximation are different from those in the non-band-mass theory for the crystal under consideration.[7]

According to results obtained in Ref. 7, the Lamb-shift–type correction is very small compared to the total energy of the system. Although this correction shifts the $2p$ state downward and the $2s$ state upward for alkali halides such as KCl, the net correction in the energy difference between the $2s$ and $2p$ states is very small compared to a single phonon energy, and hence we shall omit this correction hereafter. (The net effect is less than $\frac{1}{10}$ of a single phonon energy when the size of the $2s$ and $2p$ orbitals, $\langle r\rangle$, is greater than $4d$.)

Thus H_e, Eq. (2.1), may be rewritten in the form

$$H_e = \frac{p^2}{2m^*} + \sum_\alpha V(\vec{r}-\vec{R}_{\alpha 0}) - V(\vec{r}) + \left(1-\frac{1}{\epsilon_\infty}\right)\frac{e^2}{r}\frac{2}{\pi}\int_0^{(\pi/d)r}\frac{\sin\mu}{\mu}\,d\mu - \alpha_1 E_{ex} \,. \tag{2.8}$$

We shall now adopt an argument used in Ref. 8 to consider the interaction between the electron-hole system and the phonons in an alkali halide at temperature T. When the electron moves in the region close to the center of the hole, i.e., the electron trap (having an effective charge of $+e$), it moves much faster than the ions of the crystal so that these ions do not follow the electronic motion and the positive charge of the trap is almost completely shielded by the electron. Hence when the electron moves in this region, the electron-hole system does not polarize the lattice and does not interact with phonons. On the other hand, when the electron is in a region far from the trap, it moves relatively slowly compared to its motion when nearby so that the ions can follow both the motion of the electron and of the hole and thus the electron-hole system interacts with phonons. Furthermore, the electron-hole system interacts strongly only with the longitudinal-optical phonons in the present problem. Thus, following lattice-polaron theory,[9,10] we write the Hamiltonian for the phonon system and its interaction with the electron and hole as

$$H_{ph} = \sum_{\vec{k}} a_{\vec{k}}^\dagger a_{\vec{k}} \hbar\omega_k \qquad \text{for } r < R_0 \,, \tag{2.9a}$$

$$H_{ph} = \sum_{\vec{k}} a_{\vec{k}}^\dagger a_{\vec{k}} \hbar\omega_k + \sum_{\vec{k}} (V_k a_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} + \text{c.c.}) - \sum_{\vec{k}} (V_k a_{\vec{k}} + \text{c.c.}) \qquad \text{for } r > R_0 \,, \tag{2.9b}$$

where the first term is the Hamiltonian of the longitudinal-optical phonons, written in terms of creation and annihilation operators $a_{\vec{k}}^\dagger$ and $a_{\vec{k}}$, respectively, for phonons of wave vector $\vec{k}$. The second term is the Fröhlich-type Hamiltonian describing the interaction between the electron and virtual phonons and is applicable for any temperature. The last term is the interaction of the (massive) hole with phonons. V_k, known as the coupling constant, is given by

$$V_k = -i\left(\frac{2\pi e^2 \hbar\omega_k}{k^2 V\epsilon^*}\right)^{1/2} , \tag{2.10}$$

where ω_k is the frequency of the longitudinal-optical modes and $1/\epsilon^* = 1/\epsilon_\infty - 1/\epsilon_s$, ϵ_s being the static dielectric constant for the crystal at temperature T. Note that the above coupling constant is renormalized such that the ionic screening has the expected macroscopic limiting behavior. Thus this coupling constant includes a host of other corrections.

It is known that $\epsilon_s = \epsilon_\infty + \Delta\epsilon$, where $\Delta\epsilon$ is the difference between the static and high-frequency dielectric constants and may be ascribed in ionic crystals to the ionic polarization. This polarization mainly arises from the relative displacement of ions of opposite sign because of ionic thermal vibration in the present problem. Therefore ϵ_s has a strong temperature dependence compared to other crystal constants in the coupling constant V_k and is mainly responsible for the temperature dependence of the Fröhlich-type interaction Hamiltonian.

Since it is hard to obtain a reasonable expression that explicitly includes the temperature dependence for ϵ_s, we shall use experimental values for this dielectric constant in our numerical calculations.

The R_0 is the radius of a spherical region drawn about the center of the hole and should be chosen such that the electron-hole system does not polarize the lattice for $r \le R_0$. R_0 is related to the ratio of the electronic frequency and the ionic frequency. However, the value of this ratio for which the ions begin to follow the electronic motion is not known and hence R_0 cannot be calculated accurately. In previous semicontinuum-model calculations of the F center,[8,11] this R_0 was chosen to be the Mott–Littleton radius R_{ML} for the negative-ion vacancy.[12] This choice is consistent with the established conclusion that the F-center electron spends most of its time inside the spherical region of radius R_{ML} centered at the center of the negative-ion vacancy so that the F center is nearly neutral and hardly polarizes the lattice, i.e., hardly interacts with the phonons in the case of the ground state.[2]

We note that it is not a very good approximation to treat the vanishing of the interaction between the electron-hole system and the phonon system for $r \le R_0$ as equivalent to the mutual cancellation of the two interactions of the phonons with the electron and the hole. This is because such a cancellation occurs only at $\vec{r} \simeq 0$.

Accordingly, the total Hamiltonian for the problem in question is given by Eq. (2.8) plus Eq. (2.9), i.e.,

$$H = H_e + H_{\mathrm{ph}} . \tag{2.11}$$

B. Equivalent Hamiltonian

With the use of the operator

$$A_{\vec{k}} = a_{\vec{k}} - V_k^* / \hbar\omega_k \tag{2.12}$$

employed in Ref. 8, the H_{ph} in Eq. (2.11) can be transformed to

$$H_{\mathrm{ph}} = \sum_{\vec{k}} \hbar\omega_k A_{\vec{k}}^\dagger A_{\vec{k}} + \sum_{\vec{k}} (V_k A_{\vec{k}} + \mathrm{c.c.}) + \sum_{\vec{k}} \frac{|V_k|^2}{\hbar\omega_k} \quad \text{for } r < R_0 \tag{2.13}$$

and

$$H_{\mathrm{ph}} = \sum_{\vec{k}} \hbar\omega_k A_{\vec{k}}^\dagger A_{\vec{k}} + \sum_{\vec{k}} (V_k A_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} + \mathrm{c.c.}) + V_{\mathrm{ip}}(r) - \sum_{\vec{k}} \frac{|V_k|^2}{\hbar\omega_k} \quad \text{for } r > R_0 \tag{2.14}$$

with

$$V_{\mathrm{ip}}(r) = \sum_{\vec{k}} \frac{|V_k|^2}{\hbar\omega_k} (e^{i\vec{k}\cdot\vec{r}} + \mathrm{c.c.}) . \tag{2.15}$$

The operator $A_{\vec{k}}$ and its complex conjugate, i.e., $A_{\vec{k}}^\dagger$, satisfy the commutation relations for boson operators. Thus $A_{\vec{k}}$ and $A_{\vec{k}}^\dagger$ can be defined as an annihilation operator and a creation operator for bosons of wave vector $\vec{k}$, respectively. Then the first term in Eq. (2.14) or (2.13) can be regarded as the Hamiltonian of the phonon system in the $A_{\vec{k}}$ representation. (A representation actually refers to a reference system here.) The second term in Eq. (2.14) is thus the interaction of the electron with phonons characterized by the operator $A_{\vec{k}}$. The second term and the last term in Eq. (2.13) are, respectively, some interaction and a constant energy resulting from the transformation of H_{ph} for $r < R_0$. The last term in Eq. (2.14) is the self-energy of the hole due to its own ionic polarization field.[7] The $V_{\mathrm{ip}}(r)$ can be written as

$$V_{\mathrm{ip}}(r) = \frac{e^2}{\epsilon^* r} \frac{2}{\pi} \int_0^{k_m r} \frac{\sin\mu}{\mu} d\mu$$

when replacing the summation over the wave vector $\vec{k}$ in the first Brillouin zone by the $\vec{k}$ integration, where k_m is the maximum value of k in this zone. When the trapped electron is in a very diffused state, r is very much larger than the lattice constant d and $V_{\mathrm{ip}}(r)$ reduces to $e^2/\epsilon^* r$ because of the decreasing nature of the integrand with increasing r. In this case (a) the effective-mass theory becomes valid and Eq. (2.8) can be written as H_e

$=(p^2/2m_b^*)-e^2/\epsilon_\infty r$ plus a constant energy, and (b) R_0 is effectively zero. Hence, for very diffused states, H given by Eq. (2.11) reduces to

$$H=\frac{p^2}{2m_b^*}-\frac{e^2}{\epsilon_s r}+\sum_{\vec{k}}\hbar\omega_k A_k^\dagger A_k+\sum_{\vec{k}}(V_k A_{\vec{k}}^* e^{i\vec{k}\cdot\vec{r}}+\text{c.c.}),$$

where the constant energies are omitted. Here $-e^2/\epsilon_s r$ is the sum of $-e^2/\epsilon_\infty r$ and $V_{\text{ip}}(r)$ for large r, i.e., $e^2/\epsilon^* r$. Hence $V_{\text{ip}}(r)$ is nothing but the screened interaction between the electron and the hole via the ionic polarization field.[7] Further, the H just given above is essentially the Hamiltonian used widely in the theory of a lattice polaron bound in a Coulomb potential.[13] For the present problem, however, such a Hamiltonian is not appropriate, since the above approximations (a) and (b) are not reasonable.

In order to obtain another form of the Hamiltonian by which the eigenstates can be calculated rather readily, let us use the boson operator

$$C_{\vec{k}}=A_{\vec{k}}+V_k^*\rho_{\vec{k}}^*/\hbar\omega_k\,, \tag{2.16}$$

and its complex conjugate $C_{\vec{k}}^\dagger$ to transform H_{ph} once again. Here the complex conjugate of $\rho_{\vec{k}}^*$ is given by

$$\rho_{\vec{k}}=\langle\psi_i(\vec{r})\,|e^{i\vec{k}\cdot\vec{r}}|\,\psi_i(\vec{r})\rangle\,, \tag{2.17}$$

where $\psi_i(\vec{r})$ is the electronic wave function of its ith state. This transformation yields

$$H=H'+\sum_{\vec{k}}\hbar\omega_k C_{\vec{k}}^\dagger C_{\vec{k}}\,, \tag{2.18}$$

where

$$H'=H_e+\sum_{\vec{k}}\frac{|V_k|^2}{\hbar\omega_k}\,|\rho_{\vec{k}}-1|^2+\sum_{\vec{k}}[V_kC_{\vec{k}}(1-\rho_{\vec{k}})+\text{c.c.}]\quad\text{for } r<R_0 \tag{2.19}$$

and

$$H'=H_e+V_{\text{ip}}(r)+\sum_{\vec{k}}\frac{|V_k|^2}{\hbar\omega_k}(|\rho_{\vec{k}}|^2-1)-\sum_{\vec{k}}\frac{|V_k|^2}{\hbar\omega_k}\times(\rho_{\vec{k}}^*e^{i\vec{k}\cdot\vec{r}}+\text{c.c.})+\sum_{\vec{k}}[V_kC_{\vec{k}}(e^{i\vec{k}\cdot\vec{r}}-\rho_{\vec{k}})+\text{c.c.}]\quad\text{for } r>R_0\,. \tag{2.20}$$

Here H_e is still the electronic Hamiltonian given by Eq. (2.8).

It is evident that although the phonon part in the total Hamiltonian given by Eq. (2.18) is expressed in the $C_{\vec{k}}$ representation, the eigenvalues of this total Hamiltonian are the same as those of the original one, Eq. (2.11).

In this $C_{\vec{k}}$ representation, the total Hamiltonian for $r<R_0$ is Eq. (2.18) with H' given by Eq. (2.19), and thus the wave equation for the phonon system in this case is

$$\left\{\sum_{\vec{k}}\hbar\omega_kC_{\vec{k}}^\dagger C_{\vec{k}}+\sum_{\vec{k}}[V_kC_{\vec{k}}(1-\rho_{\vec{k}})+\text{c.c.}]\right\}\Phi=E_{\text{ph}}\Phi\,, \tag{2.21}$$

where Φ and E_{ph} are the corresponding eigenstate and eigenenergy, respectively. We write Φ in the Hartree form

$$\Phi=\prod_{\vec{k}}\phi_k\,, \tag{2.22}$$

where ϕ_k is the wave function of phonons of wave vector $\vec{k}$. Taking the second term in the bracket in (2.21) as a perturbation, we obtain by first-order perturbation theory

$$\phi_k=N\left(1-\frac{V_k^*(1-\rho_{\vec{k}}^*)}{\hbar\omega_k}C_{\vec{k}}^\dagger+\frac{V_k(1-\rho_{\vec{k}})}{\hbar\omega_k}C_{\vec{k}}\right)|n_k\rangle\,, \tag{2.23}$$

where n_k is the number of phonons with wave vector $\vec{k}$, $|n_k\rangle$ is the eigenstate of the operator $\hbar\omega_kC_{\vec{k}}^\dagger C_{\vec{k}}$, and N is a normalization factor given by

$$N=\left(1+\frac{|V_k|^2|1-\rho_{\vec{k}}|^2}{\hbar^2\omega_k^2}(1+2n_k)\right)^{-1/2}. \tag{2.24}$$

Here the value of $|1-\rho_{\vec{k}}|$ is between unity and zero (for $k=0$) for an allowed k, and $|V_k|^2\sim(k^2V)^{-1}$. For the face-centered-cubic crystals, the crystal volume $V\sim n^3$ and $k^2\sim n^{-2}$ for very small k and is of the order of unity for very large k. n is a large integer so that n times the length of one side of a primitive unit cell in the considered crystal is the length of one side of the crystal. Therefore, the order of magnitude of $|V_k|^2$ is between n^{-1} and n^{-3} for an allowed value of k. Consequently the second term in the large parentheses in Eq. (2.24) is virtually zero and the normalization factor N can be set equal to unity. Using Φ thus determined, we obtain the corresponding effective Hamiltonian

$$H_{\text{eff}}\equiv\langle\Phi|H|\Phi\rangle=H_e+\sum_{\vec{k}}\hbar\omega_k\,\langle\cdots n_k\cdots|C_{\vec{k}}^\dagger C_{\vec{k}}|\cdots n_k\cdots\rangle\quad\text{for } r<R_0\,, \tag{2.25}$$

where $|\cdots n_k\cdots\rangle$ represents an eigenfunction of $\sum_{\vec{k}}\hbar\omega_kC_{\vec{k}}^\dagger C_{\vec{k}}$. This equation is, in fact, $H_e+\sum_{\vec{k}}n_k\hbar\omega_k$, which is just that anticipated from Eq. (2.11) for $r<R_0$.

As a result, the total Hamiltonian is equivalently

$$H=H_e'+\sum_{\vec{k}}\hbar\omega_kC_{\vec{k}}^\dagger C_{\vec{k}}+H_I\,, \tag{2.26}$$

where H_e' is H_e, the original electron-part Hamiltonian, for $r<R_0$ and is

$$H_e'=H_e+V_{\text{ip}}(r)+\sum_{\vec{k}}\frac{|V_k|^2}{\hbar\omega_k}(|\rho_{\vec{k}}|^2-1)-\sum_{\vec{k}}\frac{|V_k|^2}{\hbar\omega_k}(\rho_{\vec{k}}^*e^{i\vec{k}\cdot\vec{r}}+\text{c.c.})\quad\text{for } r>R_0 \tag{2.27}$$

[cf. Eq. (2.20)]. H_I takes the form

$$H_I=\sum_{\vec{k}}[V_kC_kX(\vec{r})+\text{c.c.}]\,, \tag{2.28}$$

in which $X(\vec r)$ vanishes for $r < R_0$ and equals $e^{i\vec k\cdot\vec r} - \rho_{\vec k}$ for $r > R_0$.

C. Nearly Degenerate States of a Bound Lattice Polaron

We shall now take Eq. (2.26) as the total Hamiltonian to study the nearly degenerate states of a bound lattice polaron. Treating the last term in Eq. (2.26) as a perturbation, we obtain from the wave equation of the unperturbed Hamiltonian the equations

$$H_e'\,\psi_i(\vec r) = \epsilon_i\psi_i(\vec r) \tag{2.29}$$

and

$$\Big(\sum_{\vec k}\hbar\omega_k C_k^\dagger C_k\Big)|\cdots n_k\cdots\rangle = \epsilon_{\text{ph}}|\cdots n_k\cdots\rangle . \tag{2.30}$$

Here ψ_i and ϵ_i are, respectively, the eigenfunctions and eigenenergies of the effective electronic Hamiltonian H_e'. The ψ_i, centered at the center of the hole, can be expressed exactly in terms of the complete orthonormal set of hydrogenic wave functions ϕ_η, i.e.,

$$\psi_i = \sum_\eta C_\eta\phi_\eta . \tag{2.31}$$

The combination coefficients C_η depend not only on the original electronic Hamiltonian H_e but also on the other terms in H_e', Eq. (2.27). The last term in Eq. (2.27), the effective electron-phonon interaction, cannot only mix different hydrogenic states by virtue of the exponential function which may be expanded in powers of $\vec k\cdot\vec r$, but it can also shift the energy levels of hydrogenic states involved as such an expansion contains self-energy–type terms. The $|\cdots n_k\cdots\rangle$ are the eigenfunctions of the phonon system while the electron is in the state ψ_i, forming a complete orthonormal set, and ϵ_{ph} is the eigenenergy of the phonon system. Thus the energy of the unperturbed state $\psi_i(\vec r)|\cdots n_k\cdots\rangle$ is

$$\begin{aligned}E_i^0 = {}& \langle\psi_i|H_e|\psi_i\rangle + \langle\psi_i|V_{ip}(r)|\psi_i\rangle_o \\ &+ \sum_k \frac{|V_k|^2}{\hbar\omega_k}\big[(|\rho_{\vec k}|^2-1)\langle\psi_i|\psi_i\rangle_o \\ &- (\rho_{\vec k}^*\langle\psi_i|e^{i\vec k\cdot\vec r}|\psi_i\rangle_o + \text{c.c.})\big] + \sum_{\vec k} n_k\hbar\omega_k ,\end{aligned} \tag{2.32}$$

where the subscript o means the integration is to be taken over the outside of the spherical region of radius R_0 centered at the center of the hole.

When R_0 approaches zero, the E_i^0 becomes that in the usual Hartree-type approximation, i.e.,

$$\begin{aligned}E_H = {}& \langle\psi_i|[H_e + V_{ip}(r)]|\psi_i\rangle - \sum_{\vec k}\frac{|V_k|^2|\rho_{\vec k}|^2}{\hbar\omega_k} \\ &- \sum_{\vec k}\frac{|V_k|^2}{\hbar\omega_k} + \sum_{\vec k} n_k\hbar\omega_k .\end{aligned} \tag{2.33}$$

As mentioned earlier, the third term is the self-energy of the hole due to its own ionic-polarization field. The second term is the interaction energy between the electron and the phonon system and is exactly the same as that in the lattice-polaron theory of Pekar if the electronic wave function in $\rho_{\vec k}$ is approximated simply by a hydrogenic wave function.[14] Hence the unperturbed states stated above are just those in the Hartree-type approximation and may be calculated using a self-consistent-field method.

Suppose ϵ_i in Eq. (2.29) is nearly n-fold degenerate. Let the n unperturbed electronic states ψ_i involved in this degeneracy be $\psi_1, \psi_2, \ldots, \psi_n$. These states are supposed to be chosen such that they are orthogonal to each other and hence the unperturbed states $\psi_i|\cdots n_k\cdots\rangle$ belonging to an electron state i and those belonging to another electron state are orthogonal to one another. However, the phonon state for the electronic state ψ_i and that for another electronic state ψ_i' are, in general, not orthonormal. This is because the $C_{\vec k}$ and $C_{\vec k}^\dagger$ used to express the phonon system in the Hamiltonian ($C_{\vec k}^\dagger C_{\vec k}\hbar\omega_k$ is the Hamiltonian of a lattice harmonic oscillator of frequency ω_k) are electron-state dependent through the electron-state dependence of $\rho_{\vec k}$, as is indicated by Eq. (2.17). It is then seen that the difference between the $C_{\vec k}$ for ψ_i and that for $\psi_{i'}$ is eventually the difference between $\rho_{\vec k}$ for ψ_i and that for $\psi_{i'}$, corresponding essentially to the discrepancy between the equilibrium position of the lattice harmonic oscillator of frequency ω_k for the electronic state ψ_i and that for the electronic state $\psi_{i'}$.

When the electronic states ψ_i and $\psi_{i'}$ are nearly degenerate, however, the $\rho_{\vec k}$ for ψ_i is approximately the same as that for $\psi_{i'}$. The reason for this is the following. For ψ_i given by Eq. (2.31), $\rho_{\vec k}$ actually takes the form

$$\rho_{\vec k} = \sum_{\eta,\xi} C_\eta^* C_\xi\,\langle\phi_\eta|e^{i\vec k\cdot\vec r}|\phi_\xi\rangle . \tag{2.34}$$

This contains two types of integrals, $\langle\phi_\eta|e^{i\vec k\cdot\vec r}|\phi_\eta\rangle$ and $\langle\phi_\eta|e^{i\vec k\cdot\vec r}|\phi_\xi\rangle$, for which $\eta\neq\xi$. The latter is small compared to the former for small wave vector $\vec k$. The wave vector $\vec k$ involved in the present problem is *effectively* small, since the contribution from the electron-phonon interaction is mainly due to the interaction of the electron with phonons of small wave vector $\vec k$ [cf. the coupling constant given by Eq. (2.10)]. The main part of $\rho_{\vec k}$ is thus $\sum_\eta|C_\eta|^2 \times\langle\phi_\eta|e^{i\vec k\cdot\vec r}|\phi_\eta\rangle$, which is approximately the same for the nearly degenerate electronic states considered. Consequently we shall approximate the phonon Hamiltonian in Eq. (2.26) as the same for all n unperturbed electronic states ψ_i associated with the degeneracy of the unperturbed electronic energy ϵ_i in making the correction due to H_I. Thus the phonon states belonging to the unperturbed electronic state ψ_i are not only orthonormal to each other among themselves, but are also orthonormal to the phonon states belonging to the other unperturbed electronic states, being n-fold degenerate with the electronic state ψ_i.

We are now in the position to construct wave functions for the above case. The perturbation H_I operating on the unperturbed states $\psi_i|\cdots n_k\cdots\rangle$ produces all states with one more or one less phonon than the unperturbed states. Therefore, a reasonable wave function for the total Hamiltonian, Eq. (2.26), may be written in the form

$$\psi=\sum_{i=1}^{n}\left(a_i+\sum_{\vec{k}} S_{i\vec{k}}C_{\vec{k}}^{\dagger}+\sum_{\vec{k}} T_{i\vec{k}}C_{\vec{k}}\right)\psi_i|\cdots n_k\cdots\rangle\ , \tag{2.35}$$

where a_i, $S_{i\vec{k}}$, and $T_{i\vec{k}}$ denote, respectively, the amplitudes of the states $\psi_i|\cdots n_k\cdots\rangle$, $C_{\vec{k}}^{\dagger}\psi_i|\cdots n_k\cdots\rangle$, and $C_{\vec{k}}\psi_i|\cdots n_k\cdots\rangle$ in the combination of these states. These amplitudes satisfy the relation

$$\sum_{i=1}^{n}\left(|a_i|^2+\sum_{\vec{k}}|S_{i\vec{k}}|^2\,(n_k+1)+\sum_{\vec{k}}|T_{i\vec{k}}|^2 n_k\right)=1\ , \tag{2.36}$$

which was obtained from the normalization of Ψ with the aid of

$$C_{\vec{k}}^{\dagger}|\cdots n_k\cdots\rangle=(n_k+1)^{1/2}\,|\cdots n_k+1\cdots\rangle$$

and

$$C_{\vec{k}}|\cdots n_k\cdots\rangle=(n_k)^{1/2}\,|\cdots n_k-1\cdots\rangle\ .$$

Substituting the above Ψ into the wave equation of the total Hamiltonian, i.e.,

$$\left(H_e'+\sum_{\vec{k}}\hbar\omega_k C_{\vec{k}}^{\dagger}C_{\vec{k}}+H_I\right)\Psi=E\Psi\ , \tag{2.37}$$

and taking the scalar product of the state $\langle\cdots n_k\cdots|\psi_i$ with the resulting equation, we have

$$(E_i^0-E)a_i+\sum_j\sum_{\vec{k}}\,[S_{j\vec{k}}V_k\langle\psi_i|X(\vec{r})|\psi_j\rangle(n_k+1)$$
$$+T_{j\vec{k}}V_k^*\langle\psi_j|X(\vec{r})|\psi_i\rangle^* n_k]=0\ , \tag{2.38}$$

where E_i^0 is the unperturbed eigenenergy given by Eq. (2.32) and the summation over j is to be taken over all unperturbed electronic states associated with the nearly n-fold degenerate energy level ϵ_i. In order to determine $S_{i\vec{k}}$, we take the scalar product of the state $\langle\cdots n_k\cdots|C_{\vec{k}}\psi_i$ with Eq. (2.37) to obtain the equation

$$(E_i^0+\hbar\omega_k-E)S_{i\vec{k}}+\sum_j a_j V_k^*\langle\psi_j|X(\vec{r})|\psi_i\rangle^*=0\ . \tag{2.39}$$

Similarly, taking the scalar product of the state $\langle\cdots n_k\cdots|C_{\vec{k}}^{\dagger}\psi_i$ with Eq. (2.37) yields for $T_{i\vec{k}}$

$$(E_i^0-\hbar\omega_k-E)T_{i\vec{k}}+\sum_j a_j V_k\langle\psi_i|X(\vec{r})|\psi_j\rangle=0\ . \tag{2.40}$$

Substituting S_{ik} from Eq. (2.39) and T_{ik} from Eq. (2.40) into Eq. (2.38) leads to a set of equations

$$(E_i^0-E)a_i-\sum_{j,l}\sum_{\vec{k}}\left(\frac{|V_k|^2\langle\psi_i|X(\vec{r})|\psi_j\rangle\langle\psi_l|X(\vec{r})|\psi_j\rangle^*}{E_j^0+\hbar\omega_k-E}\right.$$
$$\left.\times(n_k+1)+\frac{|V_k|^2\langle\psi_j|X(\vec{r})|\psi_i\rangle^*\langle\psi_j|X(\vec{r})|\psi_l\rangle}{E_j^0-\hbar\omega_k-E}\,n_k\right)$$
$$a_l=0,\qquad i=1,2,\ldots,n\ . \tag{2.41}$$

These equations can be rearranged in the form

$$\sum_{l=1}^{n}(h_{il}-E\delta_{il})a_l=0,\qquad i=1,2,\ldots,n\ , \tag{2.42}$$

where

$$h_{il}=E_i^0\,\delta_{il}-\sum_j\sum_{\vec{k}}\left(\frac{|V_k|^2\langle\psi_i|X(\vec{r})|\psi_j\rangle\langle\psi_l|X(\vec{r})|\psi_j\rangle^*}{E_j^0+\hbar\omega_k-E}\right.$$
$$\left.\times(n_k+1)+\frac{|V_k|^2\langle\psi_j|X(\vec{r})|\psi_i\rangle^*\langle\psi_j|X(\vec{r})|\psi_l\rangle}{E_j^0-\hbar\omega_k-E}\,n_k\right)\ . \tag{2.43}$$

Equation (2.42) represents a set of homogeneous equations in the combination coefficients a_l. The corresponding secular equation to determine eigenenergies E is

$$\det\|h_{il}-E\delta_{il}\|=0\ . \tag{2.44}$$

Thus the combination coefficients a in the trial wave function (2.35) may be determined by solving Eqs. (2.42) and (2.36) for the energies given by Eq. (2.44)

If the n states are nondegenerate with unperturbed electronic energy levels widely spaced compared to the shift due to the perturbation, i.e., for E close to E_i^0, the nondiagonal elements in Eq. (2.44) become negligible compared to those in the degenerate case. Thus, for the nondegenerate case with E close to E_i^0, i.e., $E=E_i^0+\Delta E$, Eq. (2.44) leads to

$$E=E_i^0-\sum_j\sum_{\vec{k}}\left(\frac{|V_k|^2\,|\langle\psi_i|X(\vec{r})|\psi_j\rangle|^2}{E_j^0+\hbar\omega_k-E_i^0}\,(n_k+1)\right.$$
$$\left.+\frac{|V_k|^2\,|\langle\psi_j|X(\vec{r})|\psi_i\rangle|^2}{E_j^0-\hbar\omega_k-E_i^0}\,n_k\right)\ . \tag{2.45}$$

The second term in this equation is nothing more than the energy correction due to the perturbation H_I given by second-order nondegenerate perturbation theory. The corresponding wave function is

$$\Psi=\psi_i\,|\cdots n_k\cdots\rangle-\sum_j\sum_{\vec{k}}\left(\frac{V_k^*\langle\psi_i|X(\vec{r})|\psi_j\rangle^*}{E_j^0+\hbar\omega_k-E_i^0}\,C_{\vec{k}}^{\dagger}\right.$$
$$\left.+\frac{V_k\langle\psi_j|X(\vec{r})|\psi_i\rangle}{E_j^0-\hbar\omega_k-E_i^0}\,C_{\vec{k}}\right)\psi_j|\cdots n_k\cdots\rangle\ , \tag{2.46}$$

which was obtained from Eq. (2.35) using $S_{i\vec{k}}$ and $T_{i\vec{k}}$, found, respectively, from Eqs. (2.39) and (2.40) for the nondegenerate case in which $a_i=1$ and $a_j=0$ for $j\neq i$. However, it should be noted that in this nondegenerate case the approximation of $\rho_{\vec{k}}$ being independent of the electronic state used for the phonon Hamiltonian will introduce an error larger than in the degenerate case.

Nevertheless, it can be concluded from Eqs.

(2.45) and (2.46) that when $|E_j^0 - E_i^0|$ is very large compared to the energy of a single phonon so that $|\langle \psi_i | X(\vec{r}) | \psi_j \rangle|$ is small, the second term in each of these equations is very small so that E and Ψ approach the Hartree-type results E_i^0 and $\psi_i | \cdots n_k \cdots \rangle$, respectively.

III. RELAXED EXCITED STATES OF *F* CENTER

In this section we apply the method developed in Sec. II to study the relaxed excited states associated with the $2s$ and $2p$ states for the F center in a typical alkali halide such as KCl.

A. Effective Hamiltonian

As was mentioned in Sec. II A, the $V(\vec{r})$ in the electronic Hamiltonian H_e, given by Eq. (2.8), is the interaction of the electron with a halogen ion at the origin of the position vectors for an F center in an alkali halide. Hence, for the F center this $V(\vec{r}) \equiv V_0(\vec{r}) + v$ includes both a polarization potential energy $v \equiv -|v|$ and $V_0(\vec{r})$ which is $V(\vec{r})$ when the halogen ion just mentioned above is at its equilibrium position and its core and valence electrons are in the ground state. This $V_0(\vec{r})$ is the same as $V(\vec{r} - 0)$ in the second term of Eq. (2.8), $\sum_\alpha V(\vec{r} - \vec{R}_{\alpha 0})$ being the interaction of the electron with all the ions making up the perfect alkali halide [see the discussion following Eq. (2.1)].

We now write the sum of the first three terms in H_e, Eq. (2.8), as

$$\frac{p_2}{2m^*} + \sum_\alpha V(\vec{r} - \vec{R}_{\alpha 0}) - V(r)$$

$$= \frac{p^2}{2m} + \sum_\alpha V(\vec{r} - \vec{R}_{\alpha 0}) - V_0(\vec{r}) + |v| - \tfrac{1}{6}\alpha_2 \frac{p^2}{2m}, \tag{3.1}$$

where the last term on the right-hand side is the mass correction term and combines with $p^2/2m$ to give $p^2/2m^*$. As in the semicontinuum-model calculation of the F center,[11] we write the sum of the first three terms on the right-hand side of Eq. (3.1), h_e^0 say, as

$$h_e^0 = \frac{p^2}{2m} - \frac{Me^2}{d} \qquad \text{for } r < R_{\text{ML}} \tag{3.2a}$$

$$= E_0 + \frac{p^2}{2m_b} - \frac{e^2}{r} \qquad \text{for } r > R_{\text{ML}}\,. \tag{3.2b}$$

Here R_{ML} is the Mott–Littleton radius for the negative-ion vacancy and is approximately $0.85 d_0$ for KCl,[12] d_0 being the distance between the center of the negative-ion vacancy and its first nearest neighbors. M is the Madelung constant and d is the distance between any two nearest ions in the crystal. E_0 is the energy of the lowest state of the conduction band which is not corrected for the influence of the electronic and ionic polarizations and m_b is the corresponding electronic band mass. The approximation (3.2a), based on the point-ion model of the lattice, may be understood rather easily from the point of view of pseudopotential theory.[15] The approximation (3.2b), amounting to the effective-mass approximation, can be justified reasonably well by the pseudopotential theory of impurity states developed by Hermanson and Phillips.[16] According to this theory the effective-mass approximation can also hold for r not very large. This is because for r not very large the negative correction to the electronic kinetic energy in the effective mass approximation is largely canceled by a positive correction to the Coulombic potential energy resulting from the orthogonality of the electronic wave function to the ion-core states of the impurity (the massive hole $-\text{Cl}^-$ for the case of an F center as mentioned in Sec. II). Note that in Eqs. (3.2) there is a discontinuity of the kinetic-energy operator at R_{ML}. In reality, the possible error resulting from such a discontinuity might not be very significant when the trapped electron spends most of its time either outside the negative-ion vacancy, as in the case of relaxed excited states of the F center considered, or inside the vacancy. Thus we shall omit the correction to this discontinuity in this work.

On considering both Eqs. (3.1) and (3.2), we write, from Eq. (2.8), the electronic Hamiltonian H_e for the F center as

$$H_e = \frac{p^2}{2m^*} - \frac{Me^2}{d} + |\chi| + |v| + \left(1 - \frac{1}{\epsilon_\infty}\right)\frac{e^2}{r}\,\frac{2}{\pi}\int_0^{(\pi/d)r} \frac{\sin\mu}{\mu}\,d\mu - \alpha_1 E_{\text{ex}} \qquad \text{for } r < R_{\text{ML}} \tag{3.3a}$$

$$= \frac{p^2}{2m_b^*} - \frac{e^2}{r} + |v| + \left(1 - \frac{1}{\epsilon_\infty}\right)\frac{e^2}{r}\,\frac{2}{\pi}\int_0^{(\pi/d)r} \frac{\sin\mu}{\mu}\,d\mu \qquad \text{for } r > R_{\text{ML}}\,. \tag{3.3b}$$

Here, as in the semicontinuum model, the energy of the lowest state of the conduction band E_0 plus the electronic self-energy due to the electronic polarization in H_e for $r > R_{\text{ML}}$ was dropped by adding the electron affinity $|\chi|$ to Eq. (3.3a). This brings the zero of energy to the bottom of the conduction band which is corrected for the influence of the electronic polarization, but not for influence of the ionic polarization. Therefore $|\chi|$ can be set as $|\chi| = |\chi|_{\text{obs}} - \alpha_0 \hbar\omega$, where $|\chi|_{\text{obs}}$ is the observed $|\chi|$ including both the electronic- and ionic-polarization effects. $-\alpha_0\hbar\omega$ is the energy shift of the bottom of the conduction band (i.e., the electronic self-energy) due to the ionic-polarization effect[7] and is about 0.1 eV for KCl in the low-temperature range (for which the coupling constant $\alpha_0 \simeq 3.90$ and the phonon energy $\hbar\omega$ is about 0.026 eV). m_b^* is the electronic band mass corrected for the influence of the electronic polarization and should be regarded as the so-called band mass in the work of Hodby[17] because the band mass determined by him includes the electronic-polarization effect.

It is very difficult to find a reasonable form for $|v|$ to use in Eqs. (3.3). According to the calculation of the quantum-defect data for free atoms and ions,[18,19] however, $|v|$ may be written as $\alpha_e e^2/2r^4$ for r greater than the ion-core radius, where α_e is the polarizability of the halogen ion and is $\sim 3.10^{-24}$ cm^3 for Cl$^-$.[18(b)] For small r, the orthogonality of the electronic wave function to the ion-core states of the halogen ion becomes important and hence the contribution from $|v|$ to the total energy will be reduced by the effect of such an orthogonality. This amounts to $|v|$ for small r being *effectively* small. Consequently we may approximate $|v|$ by

$$\begin{aligned} |v| &= 0 && \text{for } r \leq R \\ &= \alpha_e e^2/2r^4 && \text{for } r > R \ , \end{aligned} \qquad (3.4)$$

where R is the ion-core radius of the halogen ion and is about 1.81 Å.[20] In the following we shall use this form of $|v|$ in Eqs. (3.3) without considering the crystal effect on it. This may not be very serious in an order-of-magnitude numerical calculation of the present type.

Accordingly, we write, from Eq. (2.11), the total Hamiltonian for the F center as

$$H = H_e + \sum_{\vec{k}} a^\dagger_{\vec{k}} a_{\vec{k}} \hbar\omega_k \qquad \text{for } r < R_{\text{ML}} \ , \qquad (3.5\text{a})$$

where H_e is given by Eq. (3.3a), and

$$\begin{aligned} H = H_e &+ \sum_{\vec{k}} a^\dagger_{\vec{k}} a_{\vec{k}} \hbar\,\omega_k + \sum_{\vec{k}} (V_k\, a_{\vec{k}}\, e^{i\vec{k}\cdot\vec{r}} + \text{c.c.}) \\ &- \sum_{\vec{k}} (V_k\, a_{\vec{k}} + \text{c.c.}) \quad \text{for } r > R_{\text{ML}}, \end{aligned} \qquad (3.5\text{b})$$

where H_e is given by Eq. (3.3b).

In the usual semicontinuum calculation for large-orbit states, the term

$$\frac{6e^2}{d}\left(1 - \frac{1}{1+\delta}\right)$$

is added to Eq. (3.3a), where δ is the percent of the static displacement of one of the first nearest neighbors (six positive ions) of the negative-ion vacancy from its original equilibrium position when the electron is outside the vacancy. This term, as mentioned in the semicontinuum calculation, was added as the electronic potential due to the static distortion of the lattice. In reality such a correction also should be made for the massive hole when one retains the lattice part of the Hamiltonian for $r < R_{\text{ML}}$ as for $r > R_{\text{ML}}$, since the change in energy of the total system during the optical transitions is due not only to the change of the electronic energy but also to the change of the lattice energy. Such a correction for the massive hole is similar to that for the electron in magnitude but opposite in sign. In the following we keep the lattice part of the Hamiltonian as the same for both $r < R_{\text{ML}}$ and $r > R_{\text{ML}}$ and omit the corrections due to the static distortion of the first nearest neighbors of the vacancy.

B. Hartree-Type Results

Taking H given by Eqs. (3.5) as the total Hamiltonian and applying the results derived in Sec. II, we may write from Eq. (2.32) the energy for the relaxed excited states of the F center in the Hartree-type approximation as

$$\begin{aligned} E_i^0 = \langle \psi_i | H_e | \psi_i \rangle + \sum_{\vec{k}} \frac{|V_k|^2}{\hbar\omega_k} \big[& (|\rho_{\vec{k}}|^2 - 1) \langle \psi_i | \psi_i \rangle_o \\ & - \rho^*_{\vec{k}} \rho'_{\vec{k}} - \rho_{\vec{k}} \rho'^*_{\vec{k}} + \rho'_{\vec{k}} + \rho'^*_{\vec{k}} \big] \ , \end{aligned} \qquad (3.6)$$

where $\rho'_{\vec{k}}$ is given by

$$\rho'_{\vec{k}} = \langle \psi_i | e^{i\vec{k}\cdot\vec{r}} | \psi_i \rangle_o \ . \qquad (3.7)$$

We remark that in Eq. (3.6), the energy of the phonon system $\sum_{\vec{k}} n_k \hbar\omega_k$ is omitted, since for the approximations being used this energy remains unchanged during the optical transition at a given temperature.

Since the relaxed excited states considered here are primarily associated with $2p$ and $2s$ states, we approximate ψ_i by a linear combination of hydrogenic $2s$, $2px$, $2py$, and $2pz$ wave functions:

$$\phi_s = (\alpha^3/\pi)^{1/2} (1 - \alpha r) e^{-\alpha r} \ , \qquad (3.8)$$

$$\phi_x = (\beta^5/\pi)^{1/2}\, r e^{-\beta r} \sin\theta \cos\phi \ , \qquad (3.9)$$

$$\phi_y = (\beta^5/\pi)^{1/2}\, r e^{-\beta r} \sin\theta \sin\phi \ , \qquad (3.10)$$

$$\phi_z = (\beta^5/\pi)^{1/2}\, r e^{-\beta r} \cos\theta \ , \qquad (3.11)$$

that is,

$$\psi_i(\vec{r}) = \sum_\eta C_\eta \phi_\eta , \qquad \eta = s, x, y, z \ . \qquad (3.12)$$

Here the C_η are the combination coefficients. For this ψ_i, $\rho_{\vec{k}}$ and $\rho'_{\vec{k}}$ are

$$\rho_{\vec{k}} = \sum_{\eta,\xi} C^*_\eta C_\xi \rho_{\vec{k},\eta\xi}$$

and

$$\rho'_{\vec{k}} = \sum_{\eta,\xi} C^*_\eta C_\xi \rho'_{\vec{k},\eta\xi} \ , \qquad (3.13)$$

respectively, where

$$\rho_{\vec{k},\eta\xi} = \langle \phi_\eta | e^{i\vec{k}\cdot\vec{r}} | \phi_\xi \rangle$$

and

$$\rho'_{\vec{k},\eta\xi}=\langle \phi_\eta \mid e^{i\vec{k}\cdot\vec{r}} \mid \phi_\xi\rangle_o \ . \qquad (3.14)$$

Correspondingly, Eq. (3.6) can be written as

$$E_1^0=\sum_\eta |C_\eta|^2\langle \phi_\eta \mid H_e \mid \phi_\eta\rangle + \sum_{\eta,\xi}\sum_{\eta',\xi'} C_\eta^* C_\xi C_{\eta'}^* C_{\xi'}(I_{\eta\xi,\eta'\xi'}\langle \psi_i \mid \psi_i\rangle_o - I'_{\eta\xi,\eta'\xi'} - I'^{*}_{\eta\xi,\eta'\xi'}) + \sum_{\eta,\xi}(C_\eta^* C_\xi J'_{\eta\xi} + \mathrm{c.\,c.}) - \sum_{\vec{k}} \frac{|V_k|^2}{\hbar\omega_k}\langle\psi_i \mid \psi_i\rangle_o \ , \qquad (3.15)$$

in which

$$I_{\eta\xi,\eta'\xi'}=\sum_{\vec{k}}\frac{|V_k|^2}{\hbar\omega_k}\rho_{\vec{k},\eta\xi}\,\rho^*_{\vec{k},\eta'\xi'} \ , \qquad (3.16)$$

$$J'_{\eta,\xi}=\sum_{\vec{k}}\frac{|V_k|^2}{\hbar\omega_k}\rho'_{\vec{k},\eta\xi} \ , \qquad (3.17)$$

and $I'_{\eta\xi,\eta'\xi'}$ is given by Eq. (3.16) with $\rho^*_{\vec{k},\eta'\xi'} \to \rho'^*_{\vec{k},\eta'\xi'}$.

Transforming the sum over $\vec{k}$ in the first Brillouin zone into the k integral and replacing the zone by a sphere of radius $|k_m|$ (equal to π/d for NaCl-type crystals), we have the following nonvanishing $I_{\eta\xi,\eta'\xi'}$:

$$\begin{aligned} &I_{ss,xx}=I_{ss,yy}=I_{ss,zz}\equiv I_{sp0} \ ,\\ &I_{xx,ss}=I_{yy,ss}=I_{zz,ss}\equiv I_{ps0} \ ,\\ &I_{sx,sx}=I_{sy,sy}=I_{sz,sz}\equiv I_{sp1} \ ,\\ &I_{xx,xx}=I_{yy,yy}=I_{zz,zz}\equiv I_{p0} \ ,\\ &I_{xx,yy}=I_{yy,zz}=I_{zz,xx}\equiv I_{p1} \ ,\\ &I_{xy,xy}=I_{yz,yz}=I_{zx,zx}\equiv I_{p2} \ . \end{aligned} \qquad (3.18)$$

In the same manner, the nonvanishing $I'_{\eta\xi,\eta'\xi'}$ are just those obtained from Eqs. (3.18) by replacing $I_{\eta\xi,\eta'\xi'}$ with $I'_{\eta\xi,\eta'\xi'}$. Further, the nonvanishing $J'_{\eta,\xi}$ are found to be

$$J'_{x,x}=J'_{y,y}=J'_{z,z}\equiv J'_p \ . \qquad (3.19)$$

In order to complete the simplification in subscripts, we hereafter set $I_{ss,ss}\equiv I_{ss}$, $I'_{ss,ss}\equiv I'_{ss}$, and $J'_{s,s}\equiv J'_s$. Applying the above relations to Eq. (3.15) reduces E_i^0 to

$$E_i^0=\sum_\eta |C_\eta|^2\langle \phi_\eta \mid H_e \mid \phi_\eta\rangle + C_s^4(I_{ss}\langle\psi_i \mid \psi_i\rangle_o - 2I'_{ss}) + (C_x^2+C_y^2+C_z^2)^2(I_{p0}\langle\psi_i \mid \psi_i\rangle_o - 2I'_{p0}) + 2C_s^2(C_x^2+C_y^2+C_z^2)[(I_{sp0}+2I_{sp1})\langle\psi_i \mid \psi_i\rangle_o - I'_{sp0} - I'_{ps0} - 4I'_{sp1}] + 2C_s^2 J'_s + 2(C_x^2+C_y^2+C_z^2)J'_p - \frac{e^2}{\epsilon^* d}\langle\psi_i \mid \psi_i\rangle_o \ . \qquad (3.20)$$

Note that in this equation terms containing $C_x^2C_y^2 + C_y^2C_z^2 + C_z^2C_x^2$ do not appear because of the result $I_{p1}+2I_{p2}-I_{p0}=0$. This result is exactly true when the first Brillouin zone is a sphere. The form of E_i^0 given by Eq. (3.20) and the normalization of ψ_i lead to one of ψ_i being

$$\psi_1=a\phi_s+b(\alpha_1\phi_x+\alpha_2\phi_y+\alpha_3\phi_z) \ , \qquad (3.21)$$

where the α, and a and b satisfy, respectively, the relations

$$\sum_{i=1}^3 \alpha_i^2=1 \quad \text{and} \quad b=(1-a^2)^{1/2} \ . \qquad (3.22)$$

The corresponding energy E_1^0 is

$$E_1^0=a^2\langle\phi_s \mid H_e \mid \phi_s\rangle + b^2\langle\phi_x \mid H_e \mid \phi_x\rangle + a^4(I_{ss}\langle\psi_1 \mid \psi_1\rangle_o - 2I'_{ss}) + b^4(I_{p0}\langle\psi_1 \mid \psi_1\rangle_o - 2I'_{p0}) + 2a^2b^2[(I_{sp0}+2I_{sp1})\langle\psi_1 \mid \psi_1\rangle_o - I'_{sp0} - I'_{ps0} - 4I'_{sp1}] + 2a^2J'_s + 2b^2J'_p - (e^2/\epsilon^*d)\langle\psi_1 \mid \psi_1\rangle_o \ , \qquad (3.23)$$

which is obtained from Eq. (3.20) by replacing ψ_i, C_s, C_x, C_y, and C_z by ψ_1, a, $b\alpha_1$, $b\alpha_2$, and $b\alpha_3$, respectively.

As regards the wave functions of the other relaxed excited states, associated with the hydrogenic 2*s*, 2*px*, 2*py*, and 2*pz* functions, we follow the rule that eigenfunctions of a Hamiltonian are orthogonal to one another and choose the following functions as the wave functions for these relaxed states:

$$\psi_2=b\phi_s-a(\alpha_1\phi_x+\alpha_2\phi_y+\alpha_3\phi_z) \ , \qquad (3.24)$$

$$\psi_3=\beta_1\phi_x+\beta_2\phi_y+\beta_3\phi_z \ , \qquad (3.25)$$

$$\psi_4=\gamma_1\phi_x+\gamma_2\phi_y+\gamma_3\phi_z \ , \qquad (3.26)$$

where the β and γ satisfy the relations

$$\sum_{i=1}^3 \beta_i^2=\sum_{i=1}^3 \gamma_i^2=1 \ , \qquad (3.27)$$

$$\sum_{i=1}^3 \alpha_i\beta_i=\sum_{i=1}^3 \beta_i\gamma_i=\sum_{i=1}^3 \gamma_i\alpha_i=0 \ , \qquad (3.28)$$

so that ψ_1, ψ_2, ψ_3, and ψ_4 are orthogonal to each other. Note that the mixing of hydrogenic 2*s*, 2*px*, 2*py*, and 2*pz* states in the relaxed excited states considered above is mainly due to the terms capable of mixing *s* and *p* states in the expansion of the exponential function in the effective electron-phonon interaction, i.e., the fourth term of Eq. (2.20). The second term in that expression, being of the form

$$i\vec{k}\cdot\vec{r}\equiv i(k_x x+k_y y+k_z z) \ , \qquad (3.29)$$

is one such term. The corresponding force has no preferred direction. Hence, if the $2s$ state can mix with the $2p$ state via the electron-phonon interaction, it will mix with all three $2p$ states as indicated in Eq. (3.21) for ψ_1 and in Eq. (3.24) for ψ_2. As regards ψ_3 and ψ_4, because of the requirement that ψ_3 and ψ_4 be orthogonal to ψ_1 and ψ_2, ψ_3 and ψ_4 should be written, respectively, as Eqs. (3.25) and (3.26) in which the $2s$ component is not present. This is only true when one of the ψ can be approximated by Eq. (3.21).

The energy for the state ψ_2 is obtained from Eq. (3.23) by simply interchanging a and b. The energy expressions for ψ_3 and for ψ_4 are obtained from Eq. (3.23) by putting $a=0$ and $b=1$. Hence the ψ_3 and ψ_4 states are degenerate. This result is valid in the approximation of replacing the first Brillouin zone by a sphere. If this approximation were not made, terms containing $C_x^2C_y^2+C_y^2C_z^2+C_z^2C_x^2$ would also appear in Eq. (3.20) [see the discussion following Eq. (3.20)], so that the ψ_i do not become those given by Eqs. (3.21) and (3.24)–(3.26). Consequently, the combination coefficients of the three $2p$ states could have particular values, corresponding to the splitting of $2p$ states. This is analogous to the dynamic Jahn–Teller effect on the p states due to an electron-phonon interaction having a symmetry like the terms $k_x k_y xy$, $k_y k_z yz$, and $k_z k_x zx$ in the expansion of the exponential function in the fourth term of Eq. (2.20). However, since replacing the first Brillouin zone by a sphere is reasonable for NaCl-type crystals (where the first Brillouin zone is a truncated octahedron), the splitting among $2p$ states themselves, if any, should be expected to be very small for these crystals.

We use the values of the constants listed in Tables I and II and minimize E_1^0 expressed by Eq. (3.23) with respect to the variational parameters α and β in the wave functions ϕ and the combination coefficient a to determine the lowest relaxed excited state of the F center in KCl. It is found that the lowest of the above-mentioned four relaxed excited states is ψ_1, with $a=0.91$ in the low-temperature range. The value of a and the corresponding values for α, β, and E_1^0 are summarized in Table II. The energies for the other relaxed excited states, calculated with a, α, and β determined from the calculation of E_1^0, are also summarized in this table. Note that the values of the energy levels in Table II and the following tables are measured from the zero of energy in this calculation. This zero of energy, as will be seen later, is $\alpha_0\hbar\omega+(e^2/\epsilon^* d)$ above the thermally highest bound state (or the lowest state of the ionized states, corresponding to the case in which the electronic wave function is completely diffused).

We now comment on the values used for some of the constants used herein. As is seen in Tables I and II, the present numerical calculation omits the effect of the temperature dependence of crystal constants other than ϵ_s and d, since (a) no accurate data are available for this effect, and (b) this temperature dependence is expected to be small compared to that of ϵ_s and d. The Mott–Littleton radius R_{ML} for the negative-ion vacancy involved in the calculation of the first two terms in Eq. (3.23) was set equal to $0.85d$, as in the case of the F-center absorption. This $0.85d$ was also used for R_0, R_0 being involved in the terms associated with the interactions of the electron and the hole with the phonons in Eq. (3.23) for a reason stated after Eq. (2.10). This choice for R_0 probably does not introduce a significant error, since the contribution from the interaction between the electron-hole system and the phonons to the energy is found to be not very sensitive to the choice of R_0. The value of $|\chi|$, listed in Table I, was obtained from $|\chi| = |\chi|_{\mathrm{obs}} - \alpha_0\hbar\omega$ using $|\chi|_{\mathrm{obs}} = 0.5$ eV for KCl [see the discussion following Eq. (3.3b)]. In reality, the $|\chi|_{\mathrm{obs}}$ for KCl reported in Ref. 25 is 0.6 eV, whereas that reported in Ref. 26 is 0.3 eV. We compromise and set $|\chi|_{\mathrm{obs}}$ equal to 0.5 eV for KCl.

TABLE I. Input data for the numerical calculation for KCl (see text for details).

ϵ_∞	m_b^*/m	E_{ex} (eV)	$\lvert\chi\rvert$ (eV)	M
2.13[a]	0.48[b]	7.8[a]	0.398	1.74756[c]

[a]Reference 21. [b]Reference 17. [c]Reference 12.

C. Corrected Results

We shall now consider the correction due to the perturbation H_I, Eq. (2.28), which was omitted in the above Hartree-type calculation of the relaxed excited states of the F center. The procedure is to solve Eq. (2.42) for the relaxed excited states of interest taking the Hartree-type results obtained in Sec. III B as the unperturbed results in the present theory.

The calculated values listed in Table II for the variational parameters in the wave functions imply that the wave functions ψ_i of the present unperturbed states are almost entirely outside the spherical region of radius R_{ML}. Hence in solving Eq. (2.42) for the relaxed excited states in question we shall approximate $\langle \psi_i | X(\vec{r}) | \psi_i \rangle = 0$ and $\langle \psi_i | \psi_j \rangle_o = 0$ for simplicity.

For the four Hartree-type solutions obtained in Sec. III B, viz., ψ_1, ψ_2, ψ_3, and ψ_4, the matrix elements other than h_{11}, h_{12}, h_{21}, h_{22}, h_{33}, and h_{44} are calculated to be zero using relations like those given in Eqs. (3.18) and (3.19). As a result, the equations expressed by Eq. (2.42) become

TABLE II. Input data, which are relatively strongly temperature dependent, for the numerical calculation, the numerical results of variational parameters (α, β, and a), energy levels of the relaxed excited states of the F center in the Hartree-type calculation, and the self-energies of the hole and electron due to the ionic polarization for KCl. The superscript a refers to data of the nearest-neighbor distance d of Ref. 22, the superscript b to data of the static dielectric constant ϵ_s of Ref. 23, and the superscript c to data of the phonon energy $\hbar\omega$ of Ref. 24.

T (°K)	d^a (Å)	ϵ_s^b	$\hbar\omega^c$ (10^{-2} eV)	α (Å^{-1})	β (Å^{-1})	a	E_1^0 (eV)	E_2^0 (eV)	E_p^0 (eV)	$-\frac{e^2}{\epsilon^* d}$ (eV)	$-\alpha_0\hbar\omega$ (eV)
4	3.122	4.496	2.591	0.210	0.160	0.91	−1.3618	−1.3260	−1.3051	−1.1395	−0.1016
50	3.123	4.501	2.593	0.210	0.160	0.91	−1.3624	−1.3266	−1.3058	−1.1403	−0.1018
100	3.135	4.554	2.608	0.209	0.160	0.91	−1.3713	−1.3357	−1.3148	−1.1511	−0.1031

$$[E - E_1^0 + F(E_2^0)A + 2F(E_p^0)B]a_1 + 2F(E_p^0)Da_2 = 0 \; , \tag{3.30a}$$

$$2F(E_p^0)Da_1 + [E - E_2^0 + F(E_1^0)A + 2F(E_p^0)C]a_2 = 0 \; , \tag{3.30b}$$

$$[E - E_p^0 + F(E_1^0)B + F(E_2^0)C + F(E_p^0)\hbar\omega I_{p2}]a_p = 0 \tag{3.30c}$$

for the relaxed excited states under study. In these equations, $p = 3$ or 4,

$$F(E_i^0) = \frac{\bar{n}+1}{E_i^0 + \hbar\omega - E} + \frac{\bar{n}}{E_i^0 - \hbar\omega - E} \; , \tag{3.31a}$$

$$A = a^2 b^2 \hbar\omega(I''_{ss} + I''_{p0} - 2I''_{sp0}) + (a^2 - b^2)^2 \hbar\omega I''_{sp1} \; , \tag{3.31b}$$

$$B = a^2 \hbar\omega I''_{sp1} + b^2 \hbar\omega I''_{p2} \; , \tag{3.31c}$$

$$C = b^2 \hbar\omega I''_{sp1} + a^2 \hbar\omega I''_{p2} \; , \tag{3.31d}$$

$$D = ab\hbar\omega(I''_{sp1} - I''_{p2}) \; , \tag{3.31e}$$

where $I''_{\eta\xi,\eta'\xi'}$ are those given by Eqs. (3.16) and (3.18) with $\rho_{\vec{k},\eta\xi} \rightarrow \rho'_{\vec{k},\eta\xi}$ and $\rho^*_{\vec{k},\eta'\xi'} \rightarrow \rho'^*_{\vec{k},\eta'\xi'}$, respectively. Here, for simplicity, we ignore the wave-vector dependence of the phonon frequency. This omission is not serious because the optical phonons involved are weakly wave-vector dependent. $\bar{n}$ is the average number of phonons per mode at the temperature T.

Now, the eigenenergies of interest corresponding to Ψ in Eq. (2.35) can be determined numerically on an electronic computer by solving the secular equation built up from Eqs. (3.30a) and (3.30b), i.e.,

$$\begin{vmatrix} E - E_1^0 + F(E_2^0)A + 2F(E_p^0)B & 2F(E_p^0)D \\ 2F(E_p^0)D & E - E_2^0 + F(E_1^0)A + 2F(E_p^0)C \end{vmatrix} = 0 \; , \tag{3.32}$$

and the equation

$$E - E_p^0 + F(E_1^0)B + F(E_2^0)C + F(E_p^0)\hbar\omega I_{p2} = 0 \; , \tag{3.33}$$

which is obtained from Eq. (3.30c). We note that Eq. (3.32) has six roots at $T = 0$ and ten roots at $T \neq 0$, whereas Eq. (3.33) has four roots at $T = 0$ and seven roots at $T \neq 0$.[27] Further, E obtained from Eq. (3.33) is doubly degenerate because this equation is the same for $p = 3$ and $p = 4$.

It is then seen that for Ψ corresponding to E, obtained from Eq. (3.32), a_3 and a_4 in Eq. (2.35) are zero. Hence its normalization leads, from Eq. (2.36), to

$$\langle \Psi | \Psi \rangle = K_s \langle \phi_s | \phi_s \rangle + K_{p\alpha} \langle \phi_{p\alpha} | \phi_{p\alpha} \rangle + K_{p\beta} \langle \phi_{p\beta} | \phi_{p\beta} \rangle + K_{p\gamma} \langle \phi_{p\gamma} | \phi_{p\gamma} \rangle = 1 \; , \tag{3.34}$$

where $\phi_{p\alpha} = \alpha_1\phi_x + \alpha_2\phi_y + \alpha_3\phi_z$, $\phi_{p\beta} \equiv \psi_3$, and $\phi_{p\gamma} \equiv \psi_4$. The coefficients K_s, $K_{p\alpha}$, and $K_{p\beta}$ are given by

$$K_s = a^2[a_1^2 + a_2^2 G(E_1^0)A] + b^2[a_2^2 + a_1^2 G(E_2^0)A] \; , \tag{3.35a}$$

$$K_{p\alpha} = b^2[a_1^2 + a_2^2 G(E_1^0)A] + a^2[a_2^2 + a_1^2 G(E_2^0)A] \; , \tag{3.35b}$$

$$K_{p\beta} = K_{p\gamma} = G(E_p^0)[a_1^2 B + 2a_1 a_2 D + a_2^2 C] \; , \tag{3.35c}$$

in which

$$G(E_i^0) = \frac{\bar{n}+1}{(E_i^0 + \hbar\omega - E)^2} + \frac{\bar{n}}{(E_i^0 - \hbar\omega - E)^2} \; . \tag{3.35d}$$

Whereas for Ψ corresponding to E obtained from Eq. (3.33), since the a_1, a_2, and a_4 (or a_3) are zero, the coefficients in its normalization equation similar to Eq. (3.34) are

$$K_s = [a^2 G(E_1^0)B + b^2 G(E_2^0)C]a_p^2 \; , \tag{3.36a}$$

$$K_{p\alpha} = [b^2 G(E_1^0)B + a^2 G(E_2^0)C]a_p^2 \; , \tag{3.36b}$$

$$\left.\begin{aligned} &K_{p\beta}(\text{or } K_{p\gamma}) = a_p^2 \; , \\ &K_{p\gamma}(\text{or } K_{p\beta}) = G(E_p^0)\hbar\omega I''_{p2} a_p^2 \; , \end{aligned}\right. \tag{3.36c}$$

where $p = 3$ (or 4). Application of the usual normalization condition for the ϕ in Eq. (3.34) yields

TABLE III. Results for the lowest relaxed excited state of the *F* center in KCl, corrected for the influence of an interaction being neglected in the Hartree-type calculation, H_I. The listed values for *K*'s are obtained from Eq. (3.35) by using the solutions of Eq. (3.30), i.e., a_1 and a_2.

T (°K)	E (eV)	a_1	a_2	K_s	$K_{p\alpha}$	$K_{p\beta}=K_{p\gamma}$
4	−1.3759	0.927	0.065	0.719	0.185	0.048
50	−1.3767	0.924	0.083	0.715	0.187	0.049
100	−1.3877	0.906	0.079	0.690	0.194	0.058

$K_s+(K_{p\alpha}+K_{p\beta}+K_{p\gamma})=1$. Hence the ratio $K_s/(K_{p\alpha}+K_{p\beta}+K_{p\gamma})$ may be interpreted as the ratio of the mixing between the single 2*s* state and the triplet of 2*p* states. Having determined the eigenenergies, the a_i can be determined by solving Eqs. (3.30) and (3.34) and hence the *K* may be determined by Eqs. (3.35) and (3.36).

The energies, a_i, and *K* thus determined for the lowest relaxed excited state Ψ_1 are summarized in Table III. We find that the change in the mixing coefficients of the 2*s* and 2*p* states due to H_I is significant and that the state Ψ_1 (when including the effect of H_I) has less 2*s* component (~70%) than that of the state ψ_1 (the lowest relaxed excited state in the Hartree-type approximation, containing ~83% 2*s* character). Further, the 2*s* component in Ψ_1 decreases slowly with increasing temperature, as is seen from the value of K_s in Table III. This temperature dependence is essentially due to the phonon number $\bar{n}$, coming in via H_I. This can be seen by varying only $\bar{n}$ from its 100 to its 4 °K value, causing K_s to change from 0.690 to 0.717 instead of 0.719. However, the effect of H_I on the energy levels is not very significant, being relatively much less than its effect on the mixing coefficients of the 2*s* and 2*p* components (cf. the theoretical values in Tables II and III).

The second-lowest relaxed excited state, say Ψ_2, is found to lie about 0.025 eV above Ψ_1. This Ψ_2 mainly consists of the two states $\psi_2|\cdots n_k\cdots\rangle$ and $\psi_1 C_{\vec{k}}^\dagger|\cdots n_k\cdots\rangle$. These two states are strongly mixed because their unperturbed energies are approximately the same. The corresponding *K* are calculated to be $K_s=0.52$, $K_{p\alpha}=0.44$, and $K_{p\beta}=K_{p\gamma}=0.02$ at 4 °K.

It is found that the higher relaxed excited states, Ψ other than the above Ψ_1 and Ψ_2, also contain both 2*s* and 2*p* components. However, most of them contain more of the 2*p* component than the 2*s* component. The probability of finding the present system in these higher states is very small in the low-temperature range considered in this work. Hence we shall not discuss further these higher relaxed excited states.

In order to see the position of the zero of energy in this calculation, we now calculate the energy of the thermally highest bound state of the present system. The highest bound state corresponds to the case in which the electronic wave function is completely diffused so that the corresponding $\rho_{\vec{k}}\to 0$. Thus, in this limit, the operator $C_{\vec{k}}$, defined by Eq. (2.16), approaches $A_{\vec{k}}$, and the unperturbed wave equations, given by Eqs. (2.29) and (2.30), and H_I, given by Eq. (2.28), all become those of the usual perturbation theory [treating

$$H_e+V_{\mathrm{ip}}(r)-\sum_{\vec{k}}\frac{|V_k|^2}{\hbar\omega}+\sum_k \hbar\omega A_k^\dagger A_k$$

as the unperturbed Hamiltonian and $\sum_k(V_kA_ke^{i\vec{k}\cdot\vec{r}}+\mathrm{c.c.})$ as a perturbation].[7] Correspondingly, the energy expressed by Eq. (2.45) approaches that of the usual perturbation theory, i.e., $E_h=-\alpha_0\hbar\omega-e^2/\epsilon^*d$ at very low temperatures.[7] This means that the zero of the energy is $\alpha_0\hbar\omega+e^2/\epsilon^*d\approx 1.24$ eV above the highest bound state. Thus the energy difference between the highest bound state and the lowest relaxed excited state (the calculated energy of which is, as seen in Table III, $E=-1.38$ eV) is $|E_h-E|\simeq 0.14$ eV in the low-temperature range for the *F* center in KCl, as compared with experimental value 0.15 eV [28] being the ionization energy of the excited *F* center in the corresponding crystal.

Finally, the picture that emerges for the lowest relaxed excited state of interest is that this state is about 0.14 eV below the highest bound state and contains ~70% 2*s* component and ~30% 2*p* component. This percentage is within the range predicted using the hydrogenic model (for the *F* center) and some experimental data in Refs. 5 and 6. A further discussion of the calculated results for the relaxed excited states in relation to predicted results of these references will be given in Sec. V.

IV. EMISSION AND RADIATIVE LIFETIME OF CENTER

In this section we first calculate the 1*s*-like state involved in the *F*-center emission in a crystal such as KCl. We then examine the lifetime of the excited *F* center, associated with its radiative decays from excited states to the 1*s*-like state. Hereafter we call this 1*s*-like state simply the relaxed 1*s* state.

A. Relaxed 1*s* State and *F*-Emission Energy

During the radiative decays of the *F* center the effect of the lattice on the *F* center may be expected to remain virtually unchanged, since these decays (i.e., the spontaneous optical transitions giving rise to the *F* emission) satisfy the Franck–Condon principle. Hence the effective electronic Hamiltonian used for the relaxed excited states can also be taken as the effective Hamiltonian for the relaxed 1s state. This effective Hamiltonian in the Hartree-type approximation is $H_{\mathrm{eff},i} = \langle \ldots n_k \ldots | H | \ldots n_k \ldots \rangle$, where H is given by Eq. (2.26) and $| \ldots n_k \ldots \rangle$ is one of a set of the eigenfunctions of the phonon system when the electron is in the excited state ψ_i. Thus, for corrected wave functions given by Eq. (2.35), the effective electronic Hamiltonian may be written as $H_{\mathrm{eff}} = \sum_i \alpha_i H_{\mathrm{eff},i}$, where α_i is a combination coefficient introduced to weight the Hartree-type potential in $H_{\mathrm{eff},i}$, that is, the terms containing $\rho_{\vec{k}}$ and $\rho_{\vec{k}}^*$ in Eq. (2.27). For the relaxed excited states of the F center considered here, the Hartree-type potential, and thereby $H_{\mathrm{eff},i}$, is, in fact, weakly electron-state dependent and therefore H_{eff} may be simply approximated by $H_{\mathrm{eff}} = H_{\mathrm{eff},i}$. This effective Hamiltonian is, from Eq. (2.26),

$$H_{\mathrm{eff}} \equiv \langle \cdots n_k \cdots | H | \cdots n_k \cdots \rangle = H_e' + \sum_{\vec{k}} n_k \hbar \omega_k \ . \tag{4.1}$$

For the relaxed states of the F center, H_e' is just H_e given by Eq. (3.3a) for $r < R_{\mathrm{ML}}$ and is given by Eq. (2.27) with H_e having the form of Eq. (3.3b) for $r > R_{\mathrm{ML}}$. Actually, this effective Hamiltonian is exactly the same as that for the relaxed excited state ψ_i in the Hartree-type approximation and does not include the effect of H_I. In view of the fact that the correction due to H_I to the energy of the relaxed excited state in the Hartree-type approximation is very small, we expect the effect of H_I on the relaxed 1s state to be small also.

Thus the energy of the relaxed 1s state $\psi_{1s}(\vec{r})$ may be calculated as

$$\begin{aligned} E_{1s} \equiv \langle \psi_{1s} | H_{\mathrm{eff}} | \psi_{1s} \rangle &= \langle \psi_{1s} | H_e | \psi_{1s} \rangle \\ &+ \sum_{\vec{k}} \frac{|V_k|^2}{\hbar\omega} [(|\rho_{\vec{k}}|^2 - 1) \langle \psi_{1s} | \psi_{1s} \rangle_o \\ &+ (1 - \rho_{\vec{k}}^*) \langle \psi_{1s} | e^{i\vec{k}\cdot\vec{r}} | \psi_{1s} \rangle_o \\ &+ (1 - \rho_{\vec{k}}) \langle \psi_{1s} | e^{-i\vec{k}\cdot\vec{r}} | \psi_{1s} \rangle_o] , \end{aligned} \tag{4.2}$$

where the phonon energy $\sum_{\vec{k}} n_k \hbar \omega_k$ was omitted as in the case of relaxed excited states for the reason stated following Eq. (3.7). It should be noted that after the F emission, Eq. (4.2) is no longer true. This is because after the F emission is made, the lattice will be affected by the Coulomb field of the electron in the 1s-like state rather than that in the relaxed excited states and the $\rho_{\vec{k}}$ is not the one involved in the relaxed excited state.

As in the semicontinuum calculation, the ψ_{1s} in Eq. (4.2) may be chosen as

$$\psi_{1s} = (\lambda^3 / 7\pi)^{1/2} (1 + \lambda r) e^{-\lambda r} , \tag{4.3}$$

where λ is a variational parameter. This ψ_{1s} is a modified hydrogen 1s wave function. Substituting the above-determined $\rho_{\vec{k}}$ for the lowest relaxed excited state and the above ψ_{1s} into Eq. (4.2) and then minimizing E_{1s} with respect to the variational parameter λ, we determine the relaxed 1s state corresponding to the lowest relaxed excited state for the F center in KCl at $T = 4$, 50, and 100 °K. The resultant 1s energies and the corresponding λ are given in Table IV.

The corresponding F-emission energy E_{em} defined as the difference between the calculated energies of the lowest relaxed excited state and the relaxed 1s state is also given in this table. It is seen from the comparison of the calculated emission energy with the experimental value listed in Table IV that the present calculation underestimates the F-emission energy by about 14%. This error could arise mainly from the form of the Hamiltonian used for the relaxed 1s state, since the present Hamiltonian is more reasonable for large-orbit electronic states than for small-orbit electronic states such as the electronic state in the relaxed 1s state of interest (see Sec. V for details). Hence, the calculated variation of the F-emission energy with respect to temperature agrees only qualitatively with the experimental results (see Table IV).

B. Radiative Lifetime

Following the basic theory of Ref. 30, we may write the inverse of the radiative lifetime τ of the F center in its lowest relaxed excited state as

$$1/\tau = \int W_{ba}(E) dE , \tag{4.4a}$$

where $W_{ba}(E)$ is given by

$$W_{ba}(E) = \left(\frac{\epsilon_{\mathrm{eff}}}{\epsilon_0}\right)^2 \frac{4ne^2}{3\hbar^4 c^3} \left\langle\left\langle \sum_a |E_b - E_a|^3 |\langle a | \vec{r} | b \rangle|^2 \delta(E_b - E_a - E) \right\rangle\right\rangle_b \ . \tag{4.4b}$$

Here $\vec{r}$ is the position vector of the F-center electron; $|b\rangle$ and $|a\rangle$ are, respectively, the initial and final states of the total system consisting of the F-center electron and the phonons; E_b and E_a are, respectively, the energies of the initial and final states involved in the radiative decays. E is the energy of the photon; $\langle\langle \ldots \rangle\rangle_b$ stands for the thermal average over the initial states $|b\rangle$ of the radiative decays; c is the velocity of light and n is the (real) index of refraction; and ϵ_{eff} is the magnitude of the field effective in the radiative decays if ϵ_0 is the average field in the crystal.

TABLE IV. Calculated values of the variational parameter λ in ψ_{1s}, the energy of the relaxed 1s state E_{1s}, the emission energy E_{em}, the square of the dipole matrix element M_d, the lifetime τ multiplied by the square of the local-field ratio, and experimental values of emission energy and lifetime for the F center in KCl. The superscripts a and b refer, respectively, to data of Refs. 29 and 6(b).

T (°K)	λ (Å^{-1})	E_{1s} (eV)	E_{en} (eV)	M_d (Å^2)	$\tau\,\frac{(\epsilon_{\text{eff}})^2}{\epsilon_0}$ (10^{-6} sec)	$E^a_{\text{em,ex}}$ (eV)	τ^b_{ex} (10^{-6} sec)
4	0.89	−2.393	1.017	0.182	4.45	1.18	0.72
50	0.89	−2.392	1.016	0.182	4.27	1.18	0.69
100	0.89	−2.393	1.006	0.182	3.85	1.13	0.55

In the present work the initial states $|b\rangle$ of the radiative decays from the lowest relaxed excited states of the F center are of the form, from Eq. (2.35),

$$|b\rangle=\sum_{i=1}^{4}\Big(a_i+\sum_{\vec{k}}S_{i\vec{k}}C^{\dagger}_{\vec{k}}+\sum_{\vec{k}}T_{i\vec{k}}C_{\vec{k}}\Big)\psi_i\,\Phi_\beta\,. \tag{4.5}$$

Here $\Phi_\beta\equiv|\cdots n_k\cdots\rangle$ are the eigenfunctions of the phonon system and form a complete orthonormal set, as mentioned in Sec. IIC. $S_{i\vec{k}}$ and $T_{i\vec{k}}$ are given by

$$S_{i\vec{k}}=-\frac{\sum_j' a_j V^*_{\vec{k}}\langle\psi_i\,|X(\vec{r})\,|\,\psi_j\rangle^*}{E^0_i+\hbar\omega-E}\,, \tag{4.6}$$

$$T_{i\vec{k}}=-\frac{\sum_j' a_j V_k\langle\psi_i\,|X(\vec{r})\,|\,\psi_j\rangle}{E^0_i-\hbar\omega-E}\,. \tag{4.7}$$

These are obtained from Eqs. (2.39) and (2.40), respectively. The prime on the sum over j means that $j=i$ is to be excluded from the sum, because $\langle\psi_i\,|X(\vec{r})\,|\,\psi_i\rangle$ was approximated to be zero in the calculation of the relaxed excited states in Sec. IIIC. For the lowest relaxed excited state, a_3 and a_4 are zero and the values of a_1 and a_2, calculated in Sec. III, are given in Table III. The final states in this work are essentially approximated by

$$|a\rangle=\psi_{1s}(\vec{r})\Phi_\alpha\,, \tag{4.8}$$

as is seen in Sec. IVA. Substituting Eqs. (4.5) and (4.8) into $W_{ba}(E)$ in Eq. (4.4) and setting $|E_b-E_a|$ equal to the emission energy E_{em} yields

$$\frac{1}{\tau}=\left(\frac{e_{\text{eff}}}{\epsilon_0}\right)^2\frac{4ne^2E^3_{\text{em}}}{3\hbar^4c^3}\,R\,, \tag{4.9}$$

where R is given by

$$R=\Big\langle\Big\langle\sum_{\alpha}\sum_{i,j}\langle\Phi_\beta\,|\Big(a^*_i+\sum_{\vec{k}}S^*_{i\vec{k}}C_{\vec{k}}+\sum_{\vec{k}}T^*_{i\vec{k}}C^{\dagger}_{\vec{k}}\Big)|\,\Phi_\alpha\rangle$$
$$\times\langle\Phi_\alpha\,|\Big(a_j+\sum_{\vec{k}}S_{j\vec{k}}C^{\dagger}_{\vec{k}}+\sum_{\vec{k}}T_{j\vec{k}}C_{\vec{k}}\Big)|\,\Phi_\beta\rangle$$
$$\times\langle\psi_i\,|\vec{r}\,|\,\psi_{1s}\rangle\langle\psi_{1s}\,|\vec{r}\,|\,\psi_j\rangle\Big\rangle\Big\rangle_\beta\,. \tag{4.10}$$

The phonon wave functions Φ_α constitute a complete set and hence $\sum_\alpha|\Phi_\alpha\rangle\langle\Phi_\alpha|$ in Eq. (4.10) equals unity. Considering this and an approximation used earlier, i.e., the Φ_β are independent of electronic excited states [cf. the discussion following Eq. (2.34)], we have after a straightforward calculation

$$R=\sum_{i,j}\Big(a^*_i a_j+\sum_{\vec{k}}S^*_{i\vec{k}}S_{j\vec{k}}(\bar{n}+1)+\sum_{\vec{k}}T^*_{i\vec{k}}T_{j\vec{k}}\bar{n}\Big)$$
$$\times\langle\psi_i\,|\vec{r}\,|\,\psi_{1s}\rangle\langle\psi_{1s}\,|\vec{r}\,|\,\psi_j\rangle\,. \tag{4.11}$$

Substitution of the complex conjugates of Eqs. (4.6) and (4.7), and $S_{j\vec{k}}$ and $T_{j\vec{k}}$ obtained, respectively, from Eqs. (4.6) and (4.7), into Eq. (4.11), yields

$$R=\sum_{i,j}\Big(a^*_i a_j+G(E^0_i,E^0_j)\sum_q{}'\sum_l{}'a^*_q a_l\sum_{\vec{k}}|V_k|^2$$
$$\times\langle\psi_q\,|X(\vec{r})\,|\,\psi_i\rangle\langle\psi_l\,|X(\vec{r})\,|\,\psi_j\rangle^*\Big)$$
$$\times\langle\psi_i\,|\vec{r}\,|\,\psi_{1s}\rangle\langle\psi_{1s}\,|\vec{r}\,|\,\psi_j\rangle\,, \tag{4.12}$$

where

$$G(E^0_i,E^0_j)=\frac{\bar{n}+1}{(E^0_i+\hbar\omega-E)(E^0_j+\hbar\omega-E)}$$
$$+\frac{\bar{n}}{(E^0_i-\hbar\omega-E)(E^0_j-\hbar\omega-E)}\,. \tag{4.13}$$

The prime on the sum over q and that on the sum over l mean that the former excludes $q=i$ and the latter excludes $l=j$. As mentioned above, for the lowest relaxed excited state only a_1 and a_2 are not zero. Hence the ψ in Eq. (4.12) are those given by Eqs. (3.21) and (3.24) in the present work. When substituting these ψ into Eq. (4.12), R can be reduced to

$$R=M_d(a_1^2b^2+a_2^2a^2-2a_1a_2ab)$$
$$+M_d[(a_2^2b^2G(E^0_1,E^0_1)+a_1^2a^2G(E^0_2,E^0_2)$$
$$-2a_1a_2abG(E^0_2,E^0_1))A+2G(E^0_3,E^0_3)\,Y]\,, \tag{4.14}$$

with Y having the form

$$Y=a_1^2B+2a_1a_2D+a_2^2C\,, \tag{4.15}$$

where A, B, C, and D are those given in Eq. (3.31). M_d is the square of the dipole matrix element and is given by

$$M_d=|\langle\phi_z\,|Z\,|\,\psi_{1s}\rangle|^2\,. \tag{4.16}$$

For the case in which the ψ_1 component in the lowest relaxed excited state is far removed in energy from the other ψ_i compared to a single phonon energy, i.e., for the nondegenerate case, we may replace E in Eqs. (4.6) and (4.7) by E_1 and set $a_1=1$ and $a_i=0$ for $i\neq1$, as was discussed in

Sec. II C. Now the corresponding total wave function is given by Eq. (2.46) in general. Thus, in this case, Eq. (4.5) becomes

$$|b\rangle=\psi_1\Phi_\beta-\sum_{j(\neq 1)}\sum_{\vec{k}}\left(\frac{V_k^*\langle\psi_1|X(\vec{r})|\psi_j\rangle^*}{E_j^0+\hbar\omega_k-E_1^0}C_{\vec{k}}^\dagger+\frac{V_k\langle\psi_j|X(\vec{r})|\psi_1\rangle}{E_j-\hbar\omega_k-E_1^0}C_{\vec{k}}\right)\psi_j\Phi_\beta\,, \tag{4.17}$$

and Eq. (4.12) becomes

$$R=|\langle\psi_1|\vec{r}|\psi_{1s}\rangle|^2+\sum_{i(\neq 1)}\sum_{j(\neq 1)}\left(G(E_i^0,E_j^0)\sum_{\vec{k}}|V_k|^2\langle\psi_1|X(\vec{r})|\psi_i\rangle\times\langle\psi_1|X(\vec{r})|\psi_j\rangle^*\right)\langle\psi_i|\vec{r}|\psi_{1s}\rangle\langle\psi_{1s}|\vec{r}|\psi_j\rangle\,, \tag{4.18}$$

where G is given by Eq. (4.13) with $E\rightarrow E_1^0$. Equation (4.18) is to be regarded as that R in nondegenerate perturbation theory.

If we further treat ψ_1 and the other ψ in Eq. (4.18), respectively, as the hydrogenic $2s$ and $2p$, rather than those used in Sec. III, as in the usual theoretical study of the mixing of the three $2p$ states into the $2s$ state,[3] then R can be reduced to

$$R=\frac{3M_d\sum_{\vec{k}}|V_k|^2|\langle\phi_s|e^{i\vec{k}\cdot\vec{r}}|\phi_z\rangle|^2}{(E_p^0-E_s^0)^2}\coth\frac{\hbar\omega}{2\kappa T}\,, \tag{4.19}$$

where E_p^0 and E_s^0 are the energies of the $2p$ and $2s$ states, respectively, and κ is the Boltzmann constant. In deriving Eq. (4.19) we have used $\langle\phi_s|\vec{r}|\psi_{1s}\rangle=0$ and the relation

$$G(E_p^0,E_p^0)=\frac{\bar{n}+1}{(E_p^0+\hbar\omega-E_s)^2}+\frac{\bar{n}}{(E_p^0-\hbar\omega-E_s^0)^2}\simeq\frac{1}{(E_p^0-E_s^0)^2}(2\bar{n}+1)\,, \tag{4.20}$$

since the energy of a single phonon is small compared to $|E_p^0-E_s^0|$ in the nondegenerate case. $2\bar{n}+1$ in Eq. (4.20) equals $\coth(\hbar\omega/2\kappa T)$. The corresponding $1/\tau$ is thus, from Eq. (4.9):

$$\frac{1}{\tau}=\frac{1}{\tau_0}\coth\left(\frac{\hbar\omega}{2\kappa T}\right), \tag{4.21}$$

where τ_0 is the lifetime at $T=0$. This result is known as the inverse of the radiative lifetime in the case of weak mixing.[31] In contrast, the inverse of the radiative lifetime in the strong-mixing (or nearly degenerate) case, as is seen in Eq. (4.14), consists of two terms; one of them depends upon temperature implicitly and the other depends upon temperature explicitly but is not proportional to $\coth(\hbar\omega/2\kappa T)$.

It has been demonstrated in Ref. 32 that Eq. (4.21) with $1/\tau_0=1.2\times10^6$ sec^{-1} and $\hbar\omega=0.014$ eV can fit the observed variation of $1/\tau$ with respect to T for the F center in KCl. These values of $1/\tau_0$ and $\hbar\omega$ differ significantly from the true values and hence such a good fit cannot be interpreted to imply that Eq. (4.21) is actually valid with the conclusion that the mixing of the $2s$ and $2p$ states in the F center in a typical alkali halide is weak.

The values of M_d calculated from Eq. (4.16) and $\tau(\epsilon_{\text{eff}}/\epsilon_0)^2$ calculated from Eq. (4.9) with R having the form of Eq. (4.14) using the above-obtained results are given in Table IV. A reasonable value for the ratio $\epsilon_{\text{eff}}/\epsilon_0$ to use in the numerical calculation of τ is not readily available. If this ratio is replaced, as a rough estimate, by the so-called Lorentz local-field ratio[33] $1+\frac{1}{3}(n^2-1)$, then the value of τ is that of $\tau(\epsilon_{\text{eff}}/\epsilon_0)^2$ given in Table IV divided by the square of the Lorentz local-field ratio, i.e., $\simeq 1.9$. The radiative lifetime thus calculated is a factor of 3 larger than the experimental value listed in Table IV. This discrepancy is largely due to the insufficient accuracy of the theoretical results for E_{em} and the wave function of the relaxed $1s$ state.

V. SUMMARY AND DISCUSSION

A method of calculating the nearly degenerate states of a bound lattice polaron has been developed by taking the Hartree-type Hamiltonian as the unperturbed Hamiltonian and the interaction omitted in the Hartree-type approximation as a small perturbation. This method was then applied to investigate the relaxed excited states associated with the F emission in KCl. In this application, the electronic part of the Hamiltonian was treated as in the usual semicontinuum-model calculation but the electronic polarization was not. This latter effect was included following the procedure of Ref. 7. The calculated results for the relaxed excited states lead to the following conclusions: (i) The lowest relaxed excited state is about 0.14 eV below the thermally highest bound state at low temperatures, as compared to the experimental value of 0.15 eV.[28] (ii) As was predicted in Refs. 5 and 6, the lowest relaxed excited state contains ~70% $2s$ character and ~30% $2p$ character and is not approximately a $2s$- or $2p$-like state as in the unrelaxed excited states (the F-abosrption case).[2,8,11] Further, the size of the electronic orbit in this relaxed excited state, $\langle\Psi_1|r|\Psi_1\rangle\simeq 14.5$ Å, is much greater than that in the lowest unrelaxed excited state, $\langle 2p|r|2p\rangle$, being 5.1 Å in Ref. 2 and 7.8 Å in Ref. 8. (iii) Among all the higher relaxed excited states, there are no states that can be well approximated either by the $2s$ or $2p$ type and so the higher relaxed excited states are not as simple in structure as those given in Refs. 5 and 6.

The mixing of the $2s$ and $2p$ electronic states of the F center due to the electron-phonon interaction was studied in Refs. 5 and 6 by using (a) the hydrogenlike model for the F-center electron, (b) an interaction having a nature similar to Eq. (3.29) for the interaction of the electron with the lattice, and (c) some experimental data. Thus the picture that emerges for the relaxed excited states in these references is rather simple and, qualitatively, is not much different from that obtained from the present Hartree-type results.

Conclusion (ii) above implies that the mixing of the $2s$ and $2p$ electronic states due to the electron-phonon interaction is not in the strong-coupling regime where an approximately equal mixing of these electronic states occurs. This is consistent with a conclusion drawn very recently by Ham.[34] This conclusion has been based on a comparison of the results of his solution to a vibronic model for the relaxed excited state of the F center in the strong-coupling limit with the relevant experimental data. According to the numerical results of our calculations, the interaction of the electron with the lattice mode A_{1g} [which corresponds to a term having the symmetry as $k_x^2x^2+k_y^2y^2+k_z^2z^2$ in the expansion of exponential function in the fourth term of our Eq. (2.20)] very much affects the splitting of the $2s$ and $2p$ electronic states of the F center, as was expected in the work of Ham.[34] Because of this effect and because of the fact that the splitting between the energy levels of the $2s$ and $2p$ electronic states of the F center in the relaxed KCl-type crystal, including the effect of the ionic dielectric screened interaction, is not negligible compared to the single-phonon energy, the mixing of these electronic states due to the interaction of the electron with the T_{1u} mode [which corresponds to an interaction having a symmetry like our Eq. (3.29)] is not in the strong-coupling regime.

The electronic effective Hamiltonian used for the relaxed excited states was extended to the relaxed $1s$ state to calculate the $1s$ energy relative to the lowest-relaxed-excited-state energy and thereby the F-emission energy in the low-temperature range. The F-emission energy thus calculated is smaller than the experimental value by about 14% and agrees only qualitatively with the experimentally observed temperature dependence of the F-emission energy (cf. the results in Table IV). This discrepancy arises mainly from the application of Eq. (3.3) as the Hamiltonian of the electronic part to the present relaxed $1s$ state. This is because the orbit of the present relaxed $1s$ state is so small that a correction to $\sum_\alpha V(\vec{r}-\vec{R}_{\alpha 0})-V_0(\vec{r})$ in the point-ion approximation, i.e., the Madelung potential $-Me^2/d$, and some correction to the electronic-polarization potential in Eqs. (3.3) and (3.5) becomes necessary.

An expression for the radiative lifetime of a point defect was derived for the case in which the initial states are nearly degenerate. This expression has been used to calculate the lifetime of the excited F center in KCl at low temperatures using the calculated results for the lowest relaxed excited state and the relaxed $1s$ state. Only order-of-magnitude agreement is obtained between the calculated lifetime and the experimental value. This is largely because the theoretical results used for the relaxed $1s$ state are not accurate enough. Further, the variation of the present calculated lifetime with respect to temperatures agrees qualitatively with the experimental one in the range of temperature below 100 °K. Note that this agreement exists even without considering the effect of the relaxed excited states higher than the lowest relaxed excited states and is due to the presence of the phonon number in the expression used for the lifetime.

It is interesting to compare the features of the present $2s$-$2p$ mixing-model calculation for the radiative lifetime with those of the p-state model. Fowler[11] has used the p-state model for F emission to show that differential spreading of the wave functions of the relaxed $2p$ and $1s$ states is important and can give the lifetime of the excited F center to the correct order of magnitude. In order to assess the additional effect on the lifetime of the mixing of the $2s$ state into the $2p$ state, we have also calculated the lifetime for KCl on the basis of the p-state model. We obtain the value for $\tau(\epsilon_{\text{eff}}/\epsilon_0)^2$ to be 0.97×10^{-6} sec, which is one-fourth of that calculated using the $2s$-$2p$ mixing model (cf. Table IV). Further, the wave-function parameters for the relaxed excited and $1s$ states in the p-state model are, respectively, $\beta=0.15$ Å^{-1} (for which $E_{2p}=-1.305$ eV) and $\lambda=0.89$ Å^{-1} (for which $E_{1s}=-2.386$ eV). These parameters are essentially the same as those found in the present $2s$-$2b$ mixing-model calculation and hence the mixing of the $2s$ state into the $2p$ state does not appear to affect the spreading out of the relaxed $2p$-state wave function, but merely reduces the $2p$ component making the lifetime longer. We conclude that both the spreading out of the relaxed $2p$-state wave function (which can make the lifetime long[11]) and $2s$-$2p$ mixing (which can lengthen the lifetime by up to an order of magnitude) produce significant effects on the lifetime.

It seems to us that because of the uncertainty in $\epsilon_{\text{eff}}/\epsilon_0$, the calculated magnitude of the lifetime cannot be used to distinguish between the p-state model and the $2s$-$2p$ mixing model for F emissions in typical alkali halides. However, the temperature dependence of the lifetime is very sensitive to the model. The p-state model, which, according to the present work, assumes that the Hartree-type approximation for treating the electron-phonon interaction is valid so that the phonon number does not appear in the effective electron-phonon interaction, cannot adequately account for the temperature dependence of the radiative lifetime of the F center in the range of temperature below 100 °K. On the other hand, the $2s$-$2p$ mixing model does give the correct temperature dependence when the $2s$ state lies *below* the $2p$ state before the mixing. Because of the similarity between the temperature dependence of the lifetime of the excited F center in KI and that in KCl, it is hard to understand from the above discussion the conclusion, drawn very recently by Mollenauer and Baldacchini[35] from their analysis of the electron-nuclear-double-resonance spectrum of the F center, that for KI the relaxed excited state associated with the F emission is $2p$-like rather than a mixing of the $2p$ and $2s$ states.

Our results prompt us to discuss the applicability of the idea of Conway *et al.*[36] for the mixing of a p state into an s state due to the electron-phonon interaction when used for the case of the F center. The validity of this approach was first examined by Fowler[3] in the calculation of the ratio R of the transition probability of $2s \rightarrow 1s$ to that of $2p \rightarrow 1s$ for the F center. In his calculation (a) the $1s$ and $2p$ were chosen, respectively, to be the hydrogenic $1s$ and $2p$ states, and (b) the perturbed $2s$ state was treated by nondegenerate perturbation theory, as in the work of Conway *et al.*,[36] and is given by

$$|2s'\rangle = |2s\rangle - \sum_i \frac{\langle 2pi|H_I|2s\rangle}{E_{2pi} - E_{2s}} |2pi\rangle , \quad (5.1)$$

where the hydrogenic states $|2s\rangle$ and $|2pi\rangle$ correspond, respectively, to the unperturbed energies E_{2s} and E_{2pi}, and H_I denotes the electron-phonon interaction. In the sum, the states other than the $2p$ states are omitted because of the large-energy denominators. The best values for R in the work of Fowler[3] were obtained by using the Fröhlich-type Hamiltonian for the electron-phonon interaction [which should correspond to the second term in Eq. (2.14)] for H_I rather than that derived in the work of Conway *et al.*[36] and these values are 0.2 for absorption and 11.5 for emission for the F center in KCl. The latter result is too large (as Fowler also pointed out). The origin of the discrepancy probably lies to a large extent in the form of the wave function used for the relaxed excited state. This can be seen in the following discussion.

It is clear that Eq. (5.1) is valid only if

$$|\langle 2pi|H_I|2s\rangle| \ll |E_{2pi} - E_{2s}| . \quad (5.2)$$

This condition will presumably be satisfied in the case of absorption of F centers in typical alkali halides, because the phonon effect in optical excited states is small.[2] For the case of emission, however, the phonon effect involved in the relaxed excited states is much larger than that in absorption and hence $|E_{2pi} - E_{2s}|$ and $|\langle 2pi|H_I|2s\rangle|$ become, respectively, smaller and larger, leading to a possible breakdown of the condition given by Eq. (5.2). This implies that the use of nondegenerate perturbation theory to construct wave functions, as in Ref. 36, could be inappropriate for the relaxed excited states of the F center.

Finally we remark that if the condition given by Eq. (5.2) is not satisfied such that $|E_{2pi} - E_{2s}|$ is effectively negligible, then the wave functions for mixed states should be constructed along the lines of degenerate perturbation theory. Such wave functions are generally appropriate in a discussion of the electron-phonon mixing of np and ns states. This is because the results of degenerate perturbation theory reduce to those of nondegenerate perturbation theory as the relation between $|\langle npi|H_I|ns\rangle|$ and $|E_{npi} - E_{ns}|$ approaches $|\langle npi|H_I|ns\rangle| \ll |E_{npi} - E_{ns}|$.

ACKNOWLEDGMENT

The authors are grateful to Dr. R. A. Moore for many valuable discussions.

---

*Work supported by the National Research Council of Canada.

†Physics Department, Tokyo Metropolitan University, Tokyo, Japan.

[1] W. B. Fowler, E. Calabrese, and D. Y. Smith, Solid State Commun. **5**, 569 (1967).

[2] R. F. Wood and U. Öpik, Phys. Rev. **179**, 783 (1969).

[3] W. B. Fowler, J. Lumin. 1/2,755 (1970).

[4] C. C. Wong and S. Wang, Bull. Am. Phys. Soc. **15**, 788 (1970).

[5] L. D. Bogan, L. F. Stiles, Jr., and D. B. Fitchen, Phys. Rev. Lett. **23**, 1495 (1969).

[6] (a) L. D. Bogan and D. B. Fitchen, Phys. Rev. B 1, 4122 (1970); (b) L. F. Stiles, Jr., M. P. Fontana, and D. B. Fitchen, Phys. Rev. B **2**, 2077 (1970).

[7] S. Wang, H. L. Arora, and M. Matsuura, Phys. Rev. B **4**, 3685 (1971).

[8] S. Wang, Phys. Rev. **153**, 939 (1967).

[9] H. Fröhlich, H. Pelzer, and S. Zienau, Philos. Mag. **41**, 221 (1950).

[10] H. Haken, Nuovo Cimento **10**, 1230 (1956).

[11] W. B. Fowler, Phys. Rev. A **135**, 1725 (1964).

[12] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Clarendon, Oxford, England, 1948).

[13] (a) P. M. Platzman, Phys. Rev. **125**, 1961 (1962); (b) D. M. Larsen, Phys. Rev. **187**, 1147 (1969); (c) J. Sak, Phys. Rev. B **3**, 3356 (1971); (d) M. H. Engineer and N. Tzoar, Phys. Rev. B **5**, 3029 (1972).

[14] S. I. Pekar, Usp. Fiz. Nauk **50**, 193 (1953); see also, for example, B. S. Gourary and F. J. Adrian, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1960), Vol. 10, p. 171.

[15] (a) J. K. Kübler and R. J. Friauf, Phys. Rev. A **140**, 1742 (1965); (b) M. I. Petrashen, I. V. Abarenkov, A. A. Berezin, and R. A. Evarestov, Phys. Status Solidi **40**, 9 (1970); Phys. Status Solidi **40**, 433 (1970).

[16] (a) J. Hermanson and J. C. Phillips, Phys. Rev. **150**, 652 (1966); (b) J. Hermanson, Phys. Rev. **150**, 660 (1966).

[17] J. W. Hodby, Solid State Commun. **7**, 811 (1969).

[18] (a) J. H. Van Vleck, *The Theory of Electronic and Magnetic Susceptibilities* (Oxford U.P., London, 1932); (b) C. J. F. Böttcher, Recl. Trav. Chim. Pays-Bas **62**, 325 (1943); Recl. Trav. Chim. Pays-Bas **62**, 503 (1943).

[19] R. F. Wood, Phys. Rev. **151**, 629 (1966).

[20] C. Kittel, *Introduction to Solid State Physics*, 3rd ed. (Wiley, New York, 1968).

[21] W. B. Fowler, Phys. Rev. **151**, 657 (1966).

[22] Calculated using $d(298\,°\mathrm{K}) = 3.146$ Å [*Inorganic and Theoretical Chemistry* (Longmans, Green, 1963), Vol. 2, Suppl. III, Pt. 2] and the thermal-expansion data [P. M. Meincke and G. M. Graham, Can. J. Phys. **43**, 1853 (1965)].

[23] M. C. Robinson and A. C. H. Hallett, Can. J. Phys. **44**, 2211 (1966).

[24] The frequency of the longitudinal-optical phonons ω is calculated using the relation $\omega = (\epsilon_s/\epsilon_\infty)^{1/2}\omega_T$ given in Ref. 20. The values of the frequency of transverse-optical phonons ω_T is taken from the work of G. O. Jones, D. H. Martin, P. A. Mavir, and C. H. Perry, Proc. R. Soc. A **261**, 10 (1961).

[25] T. Timusk and W. Martienssen, Phys. Rev. **128**, 1656 (1962).

[26] S. C. Jain and G. D. Sootha, J. Phys. Chem. Solids **26**, 267 (1965).

[27] This implies that the perturbation H_I removes partly the degeneracy of the states $C_k^\dagger \psi_i | \ldots n_k \ldots >$ in $\Sigma_k S_{ik} C_k^\dagger \psi_i | \ldots n_k \ldots >$ and that of the states $C_k \psi_i | \ldots n_k \ldots >$ in $\Sigma_k T_{ik} C_k \psi_i | \ldots n_k \ldots \rangle$ in the total wave function Ψ given in Eq. (2.35).

[28] R. K. Swank and F. C. Brown, Phys. Rev. Lett. **8**, 10 (1962); Phys. Rev. **130**, 34 (1963).

[29] W. Gebhardt and M. Kühnert, Phys. Status Solidi **14**, 159 (1966).

[30] D. L. Dexter, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1958), Vol. 6, p. 353.

[31] (a) R. Kubo and Y. Toyozawa, Prog. Theor. Phys. **13**, 160 (1955); (b) A. D. Liehr and C. J. Ballhausen, Phys. Rev. **106**, 1161 (1957).

[32] M. Tamura, T. Kitada, and S. Honda, J. Phys. Soc. Jap. **22**, 454 (1967).

[33] S. I. Pekar and Yu. E. Perlin, Zh. Eksp. Teor. Fiz. **43**, 1108 (1962) [Sov. Phys.-JETP **16**, 782 (1963)].

[34] F. S. Ham, Phys. Rev. Lett. **28**, 1048 (1972).

[35] L. F. Mollenauer and G. Baldacchini, Phys. Rev. Lett. **29**, 465 (1972).

[36] J. M. Conway, D. A. Greenwood, J. A. Krumhansl, and W. Martienssen, J. Phys. Chem. Solids **24**, 239 (1963).

PHYSICAL REVIEW B VOLUME 7, NUMBER 4 15 FEBRUARY 1973

Contribution to Sound Absorption in Disordered Solids at Low Temperatures[*]

Steven Brawer[†]
Department of Physics, University of Colorado, Boulder, Colorado 80302

(Received 31 January 1972)

A new mechanism for sound absorption in disordered solids is proposed. The mechanism combines the following two effects: (i) A sound wave modulates the frequencies of the thermal phonons (phonons of frequency kT/h). (ii) In a disordered solid, phonons are elastically scattered by the disorder. Because of (i), the sound wave may bring about an instantaneous equalization of the frequencies of thermal phonons whose frequencies, in the absence of the sound wave, are different. When this happens then because of (ii), thermal phonons are scattered among these modes. It is shown that this process alters the distribution of thermal phonons and always leads to an absorption of sound. This mechanism applies to all disordered solids, and in particular is expected to be very important in neutron-irradiated quartz.

The absorption of 1-GHz longitudinal sound waves has been measured in vitreous silica[1] and quartz irradiated with fast neutrons,[2] and is shown in Fig. 1. Vitreous silica is a glass with the composition SiO_2, while quartz is a crystalline form of SiO_2. In vitreous silica and irradiated quartz, the absorption at 10 °K is, respectively, a factor of 2.75×10^4 and 500 greater than in quartz crystal at the same temperature.[3]

Both vitreous silica and irradiated quartz are called disordered solids, because unlike crystals their atoms are not arranged in a regular array. The properties of such solids are unusual compared to the properties of crystalline solids, both because of the disorder and because point defects probably exist which are intrinsic to the amorphous state.[4,5] For example, it has been proposed that the large absorption peak occurring at 50–65 °K, depending on the sound frequency, is due to an oxygen atom in a potential with two equivalent equilibrium positions.[6] In disordered solids, then, it is important to distinguish between the effects of disorder and those of point defects on the sound absorption. In this article, the effects of disorder on the sound absorption in disordered solids will be considered.

This article is divided into two parts. In the first part, known absorption mechanisms which may pertain to disordered solids are briefly reviewed. In the second part, a new mechanism is proposed which leads to sound absorption only in solids which are disordered.

The theories discussed here apply to all disordered solids. Vitreous silica and irradiated quartz are used as examples throughout because of the experimental and theoretical interest in these materials. The conclusions are that at temperatures below 20 °K, the proposed mechanism for acoustic absorption is important in irradiated quartz, while in vitreous silica it is expected to lead to only a very small fraction (< 10%) of the observed sound