Relaxation of the Excited F Center*

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The electronic properties of the F center are considered on the basis of a semicontinuum model. It is shown that calculated absorption and emission energy levels and strengths agree closely with experimental values for NaCl, provided that certain reasonable values of parameters are chosen in the calculation. The resulting excited $2p$ state from which emission occurs has a very diffuse wave function, its maximum being at ≈ 4–5 nearest-neighbor distances, while the wave function of the ground state into which emission occurs remains largely confined to the potential well. This picture of the emitting system is consistent with a number of other experimental results, notably the emission associated with F_A centers.

INTRODUCTION

THE purpose of this paper is to examine in detail a suggestion regarding the nature of the relaxation of the F center in its excited electronic state, to investigate by means of a model calculation whether such relaxation can occur, and to relate the implications of this type of relaxation to experiment.

Although many properties of the F center associated with optical absorption have been at least semi-quantitatively understood for some time,[1–3] recent data on F- and F_A-center luminescence have not proven simple to analyze. In particular, the long lifetime for spontaneous emission[4–6] and the difficulties of fitting absorption and emission data with simple configuration coordinate models[7,8] strongly suggest that lattice relaxation associated with the large observed Stokes' shift has a pronounced effect on the electronic states of the F center. Such an effect may be manifested either by a modification of the ground and excited states or by a change in the relative energies of certain excited states.

The point of view that the nature of electronic states and/or wave functions may change between absorption and emission,[5,9] although fairly commonly held at present, is a relatively new idea. It can be stated schematically in terms of a simple configuration coordinate diagram, Fig. 1. The F center in its ground "$1s$" state (near position A) is excited into state B ("$2p$"), which is assumed to be a quasistationary state with an electronic wave function calculated from the same crystal potential as that used for state A. The lattice relaxes, and emission originates from state C. Since the lattice

relaxes, the crystal potential changes and the electronic wave function at C may be quite different from that at B (although it may be labeled by the same quantum numbers as that at B). In addition, the ordering of the excited electronic states may have changed. Emission now occurs into ground state D, which by similar reasoning may have an electronic wave function different from that at A. Thus, one speaks of two sets of electronic wave functions, one set for absorption ($A \rightarrow B$) and one for emission ($C \rightarrow D$). The validity of this point of view is not obvious. It depends on whether or not the electron spends enough time in states B and D for these to be considered stationary states. In the case of the F center this requirement is apparently satisfied (in $\approx 10^{-10}$ sec, the time for lattice relaxation, the electron can traverse a number of orbits), but in other systems it may well not be. Even in the case of the F center, several treatments of the problem proceed from the assumption that phonons are emitted simultaneously with the optical transition,[10,11] and that from the point of view of the electron the transitions are from A to C and from C to A.

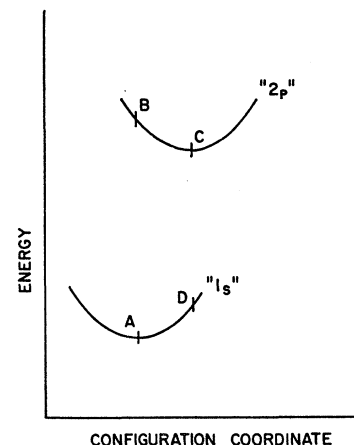To our knowledge only one detailed calculation of the properties of the F center in emission has been under-

Fig. 1. Simple configuration coordinate diagram. See text for details.

CONFIGURATION COORDINATE

[1] D. L. Dexter, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 6.
[2] J. J. Markham, Rev. Mod. Phys. **31**, 956 (1959).
[3] J. H. Schulman and W. Dale Compton, *Color Centers in Solids* (The Macmillan Company, New York, 1962).
[4] R. K. Swank and F. C. Brown, Phys. Rev. Letters **8**, 10 (1962).
[5] R. K. Swank and F. C. Brown, Phys. Rev. **130**, 34 (1963).
[6] G. Spinolo and F. C. Brown, Phys. Rev. **135**, A450 (1964).
[7] F. Lüty and W. Gebhardt, Z. Physik **169**, 475 (1962).
[8] C. C. Klick, D. A. Patterson, and R. S. Knox, Phys. Rev. **133**, A1717 (1964).
[9] W. Beall Fowler and D. L. Dexter, Phys. Rev. **128**, 2154 (1963).
[10] S. I. Pekar, Usp. Fiz. Nauk **50**, 197 (1953).
[11] K. Huang and A. Rhys, Proc. Roy. Soc. (London) **A204**, 406 (1950).

taken, that by Wood.[12] Wood has set up the emission problem using a Hartree-Fock approach. His complex calculations, when completed, should yield a quantitative understanding of the F center in a large number of crystals. There have been a number of speculations regarding the nature of the F-center states after absorption and subsequent lattice relaxation. Mott and Gurney[13] argued that the excited state of a hydrogenic F center would become less negative in energy after absorption than before, due to an increase in the effective dielectric constant associated with the excited state, whose orbit is inherently larger than that of the ground state. Such an increase in dielectric constant would tend to enlarge the orbit still further. Swank and Brown[5] pointed out that perhaps the long lifetime of the F center could be explained if the excited state for emission had a very diffuse wave function and thus a small overlap with the ground-state wave function. They argued that an alternative picture would be possible if the "2s" state ended up lower in energy than the $2p$ state, since then emission would be largely forbidden. Fowler and Dexter[9] discussed the last proposition and suggested also that a Jahn-Teller lattice relaxation could lead to large changes in the symmetries of the relevant wave functions and a consequent reduction in transition probability or, in other systems, a very large increase. In this paper we shall investigate the suggestion of the diffuse excited state.

It is well known that calculations employing a modified "particle-in-a-box" potential yield good absorption energies and oscillator strengths for the F-center problem.[14–17] The basic feature of this potential is that it consists of a well of depth V_0 (of the order of the Madelung energy) and radius R (of the order of the nearest-neighbor distance) and an external region whose behavior is not important for the absorption problem; we shall take it to be Coulombic, with an effective dielectric constant K_{eff}. The resulting electronic $1s$ and $2p$ wave functions in this potential are both rather compact, with the maxima in the charge distribution inside the potential well.

Let us now consider the possibility, along the lines suggested by Mott and Gurney and by Swank and Brown, that after the F center is excited into the $2p$ state the lattice relaxes in such a way that the $2p$ wave function is modified so as to penetrate into the lattice before emission with a mean radius several times that of the $2p$ function involved in absorption. The $1s$ state into which emission will occur, on the other hand, has a wave function which remains inside the

potential well, although the energy of the $1s$ state is raised considerably with respect to its value for absorption. Let us examine this suggestion by considering a semicontinuum model for the F center. We shall employ numerical values for the parameters applicable to the NaCl F center, but the conclusions are expected to be applicable to other F centers as well.

CALCULATION

The semicontinuum model is based on the one-electron Hamiltonian for the F center

$$H = p^2/2m + \sum_\nu' V_{perf}(\mathbf{r} - \mathbf{R}_\nu) + V_{pol}(\mathbf{r}), \qquad (1)$$

where the sum is over all lattice sites $\mathbf{R}_\nu$ except the vacancy, $V_{perf}(\mathbf{r} - \mathbf{R}_\nu)$ is the perfect-crystal potential centered at $\mathbf{R}_\nu$, and $V_{pol}(\mathbf{r})$ takes into account all polarization effects. In the semicontinuum approximation one may write H in the following way. Inside the vacancy (for $r < R$),

$$H \approx p^2/2m + V_0, \qquad (2)$$

where the constant V_0 contains a number of terms to be discussed below. Outside the vacancy

$$H = p^2/2m + \sum_\nu V_{perf}(\mathbf{r} - \mathbf{R}_\nu) - V_{perf}(\mathbf{r}) + V_{pol}(\mathbf{r}) \qquad (3)$$
$$\approx (p^2/2m^*) - (e^2/K_{eff}r).$$

In Eq. (3) we have added and subtracted $V_{perf}(\mathbf{r})$, thus removing the prime from the sum over ν, and have made an effective-mass approximation by simply replacing $p^2/2m + \sum_\nu V_{perf}(\mathbf{r} - \mathbf{R}_\nu)$ by $p^2/2m^*$, where m^* is the mass (assumed to be a scalar) at the bottom of the conduction band. $V_{pol}(\mathbf{r}) - V_{perf}(\mathbf{r})$ is written in terms of an effective dielectric constant $K_{eff}(r)$, assumed to be a function only of $|r|$.

We now use a treatment discussed by Gourary and Adrian in their review article[18] to determine several of these quantities. This treatment is based on the work of Simpson[14] and of Krumhansl and Schwartz.[15] The well depth is given by

$$V_0 = (-\alpha_m/a) + W - \chi, \qquad (4)$$

where $-\alpha_m/a$ is the Madelung energy, χ is the electron affinity, and

$$W = \frac{1}{2R}\left(1 - \frac{1}{K_0}\right) + \left(\frac{1}{K_0} - \frac{1}{K}\right)_R \int_R^\infty q(r)r^{-2}dr. \qquad (5)$$

Here R is the radius of the cavity, K_0 and K the high-frequency and static dielectric constants, and $q(r)$ is the fraction of the electronic charge outside a sphere of radius r;

$$q(r) = \int_r^\infty |\psi(\mathbf{s})|^2 d^3s, \qquad (6)$$

[12] H. W. Joy and R. F. Wood, Bull. Am. Phys. Soc. 9, 240 (1964).
[13] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (The Clarendon Press, Oxford, 1948), 2nd ed., p. 115.
[14] J. H. Simpson, Proc. Roy. Soc. (London) A197, 269 (1949).
[15] J. A. Krumhansl and N. Schwartz, Phys. Rev. 89, 1154 (1953).
[16] B. S. Gourary and F. J. Adrian, Phys. Rev. 105, 1180 (1957).
[17] R. F. Wood and J. Korringa, Phys. Rev. 123, 1138 (1961).

[18] B. S. Gourary and F. J. Adrian, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 10.

where ψ is the wave function of the state from which absorption or emission takes place. The last term of Eq. (5) arises from the self-energy of the vacancy with respect to the ionic polarization. This term is discussed further in the Appendix. As we see, V_0 and ψ must be evaluated self-consistently.

K_{eff} and ψ are similarly related. According to Krumhansl and Schwartz, and Simpson,

$$\frac{-e^2}{K_{\text{eff}}r}=\frac{-e^2}{K_0 r}+e^2\left(\frac{1}{K_0}-\frac{1}{K}\right)\int_r^\infty q(s)s^{-2}ds, \quad (7)$$

where K_0, K, $q(s)$ have been previously defined. Implicit in Eq. (7) is the assumption that the electron orbit will not become sufficiently large (or, equivalently, that the electron will not move so slowly) that the ionic polarization can follow the electronic motion. Such an assumption is generally made in F-center calculations, e.g., those of Huang and Rhys,[11] Pekar,[10] and Wang.[19] It is certainly valid when $q(s)$ is computed for the ground state, since the electron orbit is very small, and in fact the second term in Eq. (7) is very small. However, if the electron is in a large-orbit excited state of the type which we have suggested, ionic polarization will to some extent follow the motion of the $2p$ electron and the effective dielectric constant will be larger than Eq. (7) would yield and will approach the static value as the orbit becomes very large. A better, though still approximate, expression for the dielectric constant may be obtained on the basis of Haken's theory[20] of Wannier excitons.[21] As shown in the Appendix, the effective interaction between an electron and an infinite-mass hole (e.g., a vacancy) due to polarization is

$$\frac{-e^2}{K_{\text{eff}}r}=\frac{-e^2}{K_0 r}-\frac{e^2}{r}\left(\frac{1}{K}-\frac{1}{K_0}\right)\left(1-\frac{e^{-vr}+e^{-2r/a}}{2}\right), \quad (8)$$

where v is given by

$$v=(2m^*\hbar\omega/\hbar^2)^{1/2} \quad (9)$$

and a is the nearest-neighbor distance. In Eq. (9), m^* is the effective electron mass and ω is the frequency of longitudinal optical vibration for the crystal. The term $e^{-2r/a}$ will be negligible for the values of r in which we are interested ($r\approx 4a$).

The F-center calculation is now performed by means of a variational approach using hydrogenic wave functions

$$\psi_{1s}=[\alpha^{3/2}/(7\pi)^{1/2}](1+\alpha r)e^{-\alpha r},$$
$$\psi_{2p}=(\beta^{5/2}/\pi^{1/2})re^{-\beta r}\cos\theta, \quad (10)$$

where α and β are variational parameters. In this approach we do not exactly satisfy the boundary conditions for continuity of ψ and ψ' at $r=R$, since we neglect the fact that for $r>R$ a wave function is the product of a hydrogenic function and the conduction-band function at $k=0$.[22,23] This will be unimportant if the calculated wave functions spend most of their time either inside or outside of the vacancy. It may be not too important in any case, since the conduction-band wave function is probably rather flat over most of the boundary.

Thus, we are interested in minimizing the expectation values of the Hamiltonian with these wave functions [Eq. (10)] in the $1s$ and $2p$ states. In any state j, the quantity to be minimized W_j is given by

$$W_j=\langle\psi_j|p^2/2m|\psi_j\rangle_i+\langle\psi_j|p^2/2m^*|\psi_j\rangle_o$$
$$+V_0\langle\psi_j|\psi_j\rangle_i-(e^2/K_{\text{eff}})\left\langle\psi_j\left|\frac{1}{r}\right|\psi_j\right\rangle_o, \quad (11)$$

where i means the integration is to be taken over the inside of the potential well ($r<R$) and o means outside ($r>R$). Both V_0 and K_{eff} (as well as R) depend upon the initial state of the electron.

We thus find that

$$W_{1s}=\frac{\alpha^2}{28}\left[6-\left(1-\frac{1}{m^*}\right)\left(-\frac{t^4}{4}+3t^2+6t+6\right)e^{-t}\right]$$
$$+V_0\left\{1-\left[14(1+t)+7t^2+2t^3+\frac{t^4}{4}\right]\frac{e^{-t}}{14}\right\}$$
$$-\left[\frac{t^4}{2}+\frac{7t^3}{2}+9t^2+9t\right]\frac{e^{-t}}{28K_{\text{eff}}R}, \quad (12)$$

where t is equal to $2\alpha R$, and

$$W_{2p}=\frac{u^2}{8R^2}\left\{1-\left(1-\frac{1}{m^*}\right)\left[-\frac{u^4}{2}+2u^3+6u^2\right.\right.$$
$$\left.\left.+12(u+1)\right]\frac{e^{-u}}{12}\right\}+V_0\left\{1-[24(u+1)+12u^2\right.$$
$$\left.+4u^3+u^4]\frac{e^{-u}}{24}\right\}-\frac{\beta}{K_{\text{eff}}}[u^3+3u^2+6(u+1)]\frac{e^{-u}}{12}, \quad (13)$$

where u is equal to $2\beta R$. W_{1s} and W_{2p} are expressed in atomic units (1 a.u. = 27.2 eV). They are measured from the bottom of the conduction band.

For the absorption problem in NaCl we use $a=5.31a_0$, $R=5.0a_0$,[24] $K_0=2.31$,[25] $\chi=-0.02$ a.u.[26] V_0 is then

[19] S. F. Wang, Phys. Rev. **132**, 573 (1963).
[20] H. Haken, Nuovo Cimento **10**, 1230 (1956).
[21] R. S. Knox, *Theory of Excitons* (Academic Press Inc., New York, 1963).
[22] D. L. Dexter, Phys. Rev. **83**, 435 (1951); **93**, 244 (1954).
[23] J. A. Krumhansl, Phys. Rev. **93**, 245 (1954).
[24] N. F. Mott and M. J. Littleton, Trans. Faraday Soc. **34**, 485 (1938).
[25] H. Pick, *Landolt-Börnstein Tables* (Springer-Verlag, Berlin, 1955), Vol. 8, p. 415.
[26] N. F. Mott, Trans. Faraday Soc. **34**, 500 (1938).

−0.252 a.u. [plus the small second term of W, Eq. (5)], and we choose $K_{eff}=K_0$. The only real unknown is the effective mass m^*, which for reasons to be discussed later is chosen equal to $0.6m_e$. Minimization of Eqs. (12) and (13) then leads to the following results for absorption: $W_{1s}=-0.142$ a.u., $W_{2p}=-0.039$ a.u., $\alpha=0.56a_0^{-1}$, $\beta=0.42a_0^{-1}$. The predicted absorption energy is 2.80 eV.

After absorption, the lattice relaxes. This relaxation is expressed in our equations by letting K_{eff} and the positions of the nearest-neighbor ions change. We neglect any Jahn-Teller effect, assuming that the potential remains spherically symmetric. This assumption is probably quite good if the excited state for emission turns out to have a large orbit. To estimate the magnitude of K_{eff} we consider the possibility that W_{2p} will have a minimum for $\beta \approx 0.1$. The mean radius of the $2p$ state is then $5/(2\beta)$ or $25a_0$, and for $m^* \approx 0.5$ −1.0, v is in the range 0.035–0.04. In this range of parameters Eq. (8) tells us that K_{eff} is of the order 4.0–4.5. We shall see later that this choice of K_{eff} does in turn yield a minimum in W_{2p} for $\beta \approx 0.1$.

It is also assumed that the nearest-neighbor ions move outward by 10%. This assumption is discussed below. Hence R is changed to $5.5a_0$ and the Madelung energy becomes less negative. The constant part of V_0 then becomes −0.156 a.u., and in addition one must consider the second term of W, Eq. (5). Then

$$V_0=-0.156+(0.243/4R)[4+3u+u^2+(u^3/6)]e^{-u}.$$
(14)

Minimizing Eqs. (12) and (13) with $m^*=0.6m_e$ and $K_{eff}=4.2$ yields $W_{1s}=-0.05$ a.u., $W_{2p}=-0.0044$ a.u., $\alpha=0.436a_0^{-1}$, $\beta=0.08a_0^{-1}$. The predicted emission energy is 1.24 eV, and W_{2p} is −0.12 eV below the conduction band.

The squared dipole matrix element between $1s$ and $2p$ states [Eq. (10)] is given by

$$|\langle z \rangle|^2=(32^2/7)[\alpha^3\beta^5(\beta+6\alpha)^2/(\alpha+\beta)^{12}].$$
(15)

It is found that, for the values calculated above for α and β, the oscillator strength[1,27] for absorption is ≈ 1.0 and

$$|\langle z \rangle|^2_{emis}/|\langle z \rangle|^2_{abs}=0.13.$$

We thus see that the excited-state wave function for emission is much more diffuse than that for absorption, while the ground-state wave function changes only slightly. Our choice of K_{eff} is reasonably self-consistent

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[27] As is well known, the oscillator strength f may be calculated either in terms of dipole or gradient matrix elements. If the wave functions are eigenfunctions of the Hamiltonian, the results should be equal. In each case, however, an "effective" mass appears. This mass should in our case be between the band mass m^* and m_e, since the electron spends some time in the vacancy, where $m^*=m_e$, and some time in the dielectric, where $m^*=0.6m_e$. We find that if we calculate the oscillator strength both by dipole and gradient methods, and equate the results, the "effective" mass turns out to be 0.8 and $f\approx 1.0$. These results, while not particularly reliable, are nonetheless reasonable.

with the resulting value of β, and the violation of the boundary condition at $r=R$ is unimportant, since the excited-state wave function is very diffuse and the ground state is still rather compact. The squared dipole matrix element for emission is considerably smaller than that for absorption. The principal reason for this difference is the relatively small overlap between the excited- and ground-state wave functions for emission as compared with that for absorption.

We have evaluated the energies and matrix elements for a number of other values of V_0, K_{eff}, and m^*, and the tendency for the $2p$ state to stabilize in a large orbit while the $1s$ state remains confined to the well seems fairly strong. Making V_0 less negative, K_{eff} larger, and m^* smaller all have the effect of pushing out the $2p$ and $1s$ wave functions. The region of these parameters (in NaCl) for which large-orbit $2p$ states result is roughly $m^* \lesssim 0.7m_e$, $K_{eff} \gtrsim 3$, $V_0 \gtrsim -0.20$ a.u.

There exists the possibility that the $1s$ state would also have a large orbit. For this to occur V_0 would have to become very small, of the order of −0.07 a.u., in which case α would be $0.3a_0^{-1}$ and $W_{1s}-0.5$ eV. Under such circumstances it is possible that the dipole matrix elements for emission would actually become larger than those for absorption.[9]

DISCUSSION

Our model calculation has shown that in some ranges of parameters the F center relaxes into a large-orbit excited state, while the ground state into which emission occurs remains confined to the potential well. The important parameters are R, the radius of the well after relaxation, m^*, and K_{eff}. Although these have been chosen in the above illustration to yield good agreement with experimental results, we believe that the values chosen are, in fact, reasonable.

The determination of K_{eff} has already been discussed in some detail. Its validity rests upon the validity of Haken's theory[20] as extended in the Appendix. Even if the details of the theory are faulty, however, the result seems reasonable, as illustrated by the following simple argument. Assume that when the electron is at a radius greater than v^{-1} it "sees" the static dielectric constant, and when it is at a radius less than v^{-1} it "sees" the high-frequency dielectric constant. For $m^*=0.6m_e$, v^{-1} equals $26a_0$. For a β of 0.08, 60% of the electronic charge is outside this radius, 40% inside. Writing an average K_{eff} as $0.6K+0.4K_0$, we find that K_{eff} is 4.3, in excellent agreement with the value found by using Haken's theory in detail.

There is not very much evidence regarding conduction-band effective masses in the alkali halides. Ahrenkiel[28] has measured mobilities of conduction electrons in several alkali halides and his data, together with various mobility theories, yield effective band

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[28] R. Ahrenkiel, thesis, University of Illinois, 1963 (unpublished).

masses of ≈ 0.3 to 0.6, and polaron masses of ≈ 0.5 to 0.9 in KBr. Calculations of the lowest conduction band of NaCl have led to estimates of effective masses ranging from ≈ 0.4 to ≈ 0.9.[29-31] Phillips, in attempting to construct energy bands from uv absorption and reflectivity spectra, assumes an effective mass of 1 in constructing the lowest conduction band for all alkali halides.

If one assumes that the excitons in[32] NaCl are Wannier-like[21] with a series limit at 8.8 eV, the exciton binding energy G is 0.8 eV and the reduced exciton mass is given by $\mu = 0.8 K_0^2 m_e/13.6$. For NaCl this yields a μ of $0.3 m_e$; m^* is probably somewhat larger, 0.4 or $0.5 m_e$. Such a procedure is probably not very trustworthy, however.

Our choice of $\Delta R = 0.1 R$ is somewhat arbitrary. Since what is important is the relative distortion between ground- and excited-state configurations, we begin by considering the former. Kojima[33] calculates an *inward* motion of the nearest neighbors of 7.4% for the LiF ground state, and Feuchtwang[34] argues that electron nuclear double resonance data support this. Wood and Korringa,[17] on the other hand, calculate an *outward* displacement (for LiCl) of 1%.

For the large-orbit excited state, the nearest neighbors should approach the positions which they would assume if there were no electron at the vacancy. According to Mott and Littleton,[24] removal of a Cl$^-$ ion from NaCl causes the nearest-neighbor Na$^+$ ions to move outward $\approx 7-8\%$, while Kristofel[35] calculates for the same situation in KCl the nearest neighbors move outward 12.5%. Our assumption of a net outward motion of 10% between ground- and excited-state configurations then seems reasonable.

It would thus seem that the values of the parameters K_{eff}, m^*, and ΔR are reasonably consistent with what is known about NaCl. Furthermore, since the effective-mass method becomes exact in the limit of large orbit, we feel that the approach used to calculate the F-center excited state probably is valid. This method of calculation, although somewhat crude, is nevertheless an attractive one since polarization effects can be treated in a natural way. One would not expect, for example, that a simple point-ion or Hartree-Fock calculation would yield results such as those obtained here, since polarization effects are commonly ignored in the point-ion or Hartree-Fock approach (however, Kojima[33] has included these effects in the absorption problem).

We should point out that earlier calculations involving continuum or semicontinuum methods did not yield the key result of the present work, namely, that the relaxed excited state is characterized by a large-orbit wave function. The essential difference between these earlier calculations and ours in this respect lies in the determination of K_{eff}. As we have pointed out, Simpson[14] and Krumhansl and Schwartz[15] used Eq. (7) to determine K_{eff}. Huang and Rhys,[11] Pekar,[10] and Wang[19] utilized a more elegant formalism, quantizing the phonon field, but all of these treatments involve the assumption that the ionic polarization does not follow the motion of the electron, but that it responds only to the average electronic "charge distribution." A discussion of the Pekar approach which illustrates its close resemblance in this respect to the earlier Simpson treatment is given in Ref. 18.

These approaches all underestimate the interaction of the electron with the lattice polarization, at least for a large-orbit state. If one evaluates the matrix element of our $2p$ function [Eq. (10)] with respect to the interaction term [Eq. (7)], where $q(s)$ is determined also from ψ_{2p}, one finds that the relative contribution of polarization terms is independent of the $2p$ damping parameter β (in the limiting case in which the vacancy may be neglected). The interaction energy (for any value of β) is the same as would have been obtained by using a constant K_{eff} given by $(K_{eff})^{-1} = (K_0)^{-1} + 0.27[(K)^{-1} - (K_0)^{-1}]$. This result clearly does *not* approach $(K)^{-1}$ as β becomes very small. For NaCl, K_{eff} would be 2.76, a value not large enough to yield the large-orbit excited state.

The modified Haken theory [Eq. (8)] takes into account the fact that for diffuse states the lattice polarization may to some extent follow the motion of the electron. It yields a value of K_{eff} generally larger than one would obtain from Eq. (7) or its equivalent, a value which approaches K as β becomes small.

[*Note added in proof:* In a recent paper Buimistrov[35a] has presented a continuum calculation for an F center in AgBr. He has discussed the limitations of theories which allow the lattice to interact only with the average charge distribution of the trapped electron and has performed a calculation (using a method developed by himself and Pekar[35b]) in which this restriction is removed. There results a large-orbit F-center *ground* state in AgBr. This seems reasonable in view of the fact that the effective polaron mass in AgBr is $0.27 m_e$ and the static dielectric constant is 13.1.]

COMPARISON WITH EXPERIMENT

With our choice of parameters, good agreement is obtained with absorption and emission data for the

[29] S. R. Tibbs, Trans. Faraday Soc. **35**, 1471 (1939).
[30] Z. Ya. Evseev and K. B. Tolpygo, Fiz. Tverd. Tela 4, 3644 (1962) [English transl.: Soviet Phys.—Solid State 4, 2665 (1963)].
[31] Z. Ya. Evseev, Fiz. Tverd. Tela **5**, 2345 (1963) [English transl.: Soviet Phys.—Solid State 5, 1705 (1964)].
[32] J. E. Eby, K. J. Teegarden, and D. B. Dutton, Phys. Rev. **116**, 1099 (1959).
[33] T. Kojima, J. Phys. Soc. Japan **12**, 918 (1957).
[34] T. E. Feuchtwang, Phys. Rev. **126**, 1616 (1962).
[35] N. N. Kristofel', Fiz. Tverd. Tela **5**, 2367 (1963) [English transl.: Soviet Phys.—Solid State 5, 1722 (1964)].

[35a] V. M. Buimistrov, Fiz. Tverd. Tela 5, 3264 (1963) [English transl.: Soviet Phys.—Solid State 5, 2387 (1964)].
[35b] V. M. Buimistrov and S. I. Pekar, Zh. Eksperim. i Teor. Fiz. **32**, 1193 (1957) [English transl.: Soviet Phys.—JETP **5**, 970 (1957)].

NaCl F center. The calculated absorption energy is 2.80 eV and the emission energy is 1.24 eV, as compared with the experimental values at 77°K of[36] 2.7 and 1.08 eV.[37,38] According to the calculation, the excited state after relaxation is 0.12 eV below the conduction band, as compared with Swank and Brown's experimental value of 0.07 eV.[5] Our calculated ratio of $|\langle z \rangle|^2_{abs}$ to $|\langle z \rangle|^2_{emis}$ is 7.5. In order to compare this with experiment we consider Eq. (19) of Ref. 9, which in our case reduces to

$$\frac{\Sigma_{mk}}{\tau_{km}^{-1}} = \left[\frac{\mathscr{E}_{eff}(E_{mk})}{\mathscr{E}_{eff}(E_{km})}\right]^2 \frac{\pi^2 \hbar^3 c^2}{n(E_{mk})n(E_{km})} \frac{E_{mk}}{E_{km}^3} \frac{|\langle z \rangle|^2_{abs}}{|\langle z \rangle|^2_{emis}} \cdot 3. \quad (16)$$

In Eq. (16), m represents the ground state and k the excited level, Σ_{mk} is the absorption cross section, τ_{km}^{-1} the reciprocal decay time, and $\mathscr{E}_{eff}$ is the effective field at the absorption or emission center; it is to be evaluated at the peak energy of absorption (E_{mk}) or emission (E_{km}), as is the index of refraction n. Using Silsbee's experimental value[39] of 0.91×10^{-16} cm^2 eV for the F-center absorption cross section in NaCl, and observed energies and dielectric constants, we find that

$$\tau_{km} = 8.95 \times 10^{-8} \left[\frac{\mathscr{E}_{eff}(E_{mk})}{\mathscr{E}_{eff}(E_{km})}\right]^2 \frac{|\langle z \rangle|^2_{abs}}{|\langle z \rangle|^2_{emis}} \text{sec} \quad (17)$$

for NaCl. $\mathscr{E}_{eff}$ for emission will be somewhat smaller than that for absorption[9,40] (if the excited state in emission is diffuse), so that the squared effective-field ratio will be $\lesssim 2$. Using this value and the calculated value for the squared dipole-matrix-element ratio, it is found that $\tau \lesssim 134 \times 10^{-8}$ sec, in agreement with Swank and Brown's observed value of 100×10^{-8} sec.

There are a number of other experimental results which seem at least qualitatively consistent with our result. These include the absence of an Ivey law for emission and the fact that the emission energy varies more rapidly with temperature than the absorption energy.[7] Both of these observations are consistent with the picture of a system with one state (the excited state) whose energy is insensitive to variations in lattice parameter, and one state (the ground state) whose energy is sensitive to variations in the lattice parameter. In the case of absorption, of course, both states are strongly dependent on lattice parameter and weakly dependent on anything else (such as dielectric constant).

The observed effective frequency for lattice vibration associated with emission is ≈ 1.5 times that for absorption,[7] and is thus closer to the longitudinal optical

frequency. This is consistent with the picture of a large-orbit state, which should interact to some extent with the optical modes.

In connection with the lattice interaction problem, certain aspects of the emission situation may differ even qualitatively from the absorption problem. With a very diffuse excited state and a very compact ground state, one would expect that the excited-state energy level would not be strongly affected by localized vibrations which would affect the ground state significantly, while the converse would be true with respect to the normal optical vibrations of the lattice. If the localized and optical modes were largely uncoupled one would have the ground- and excited-state energies varying independently, whereas in the usual configuration coordinate picture these energies are correlated since both states are affected by the same vibrational mode. Thus, not only would it be improper to attempt to describe absorption and emission data with one configuration coordinate, it would be improper to attempt to describe emission data alone on the basis of only one configuration coordinate.

Data on F_A-center emission furnish more persuasive arguments for the picture suggested here. It is observed[6] that for a number of F_A centers the emission lifetimes are within 10% of those of the F center, the emission energies are slightly lower than for the F center, and the bandwidths are about the same. Spinolo and Brown[6] have discussed these results and have pointed out that it is difficult to explain them on the basis of either Fowler and Dexter's suggestion that the Jahn-Teller effect changes the symmetries of the wave functions, or Swank and Brown's[9] suggestion that the "$2s$" state is important in emission. These results do seem consistent with the present considerations, however, as Spinolo and Brown point out. Assuming that the F_A center is not too badly distorted, the large-orbit excited state should be about the same as for the F center. The localized ground state would also not change greatly, although its energy would change slightly due to the local perturbation.

We believe that the "anomalous" case reported by Gramm[41] is also consistent with our picture. Gramm finds that the KCl:Li F_A center has a lifetime *shorter* than predicted by absorption strengths, has an emission energy of only 0.46 eV and a bandwidth of only 0.045 eV,[42] as contrasted with the KCl F center's low-temperature width of 0.248 eV.[7] The position of the maximum of the emission band is almost independent of temperature in a range from 20 to 204°K,[42] and emission appears to be associated with an excited-state wave function whose dipole lies along the vacancy-Li$^+$ axis.[42]

We suggest that for this case there is so much local

[36] E. Mollwo, Z. Physik 85, 56 (1933).
[37] P. J. Botden, C. Z. van Doorn, and Y. Haven, Philips Res. Rept. 9, 469 (1954).
[38] C. Z. van Doorn and Y. Haven, Philips Res. Rept. 11, 479 (1956).
[39] R. H. Silsbee, Phys. Rev. 103, 1675 (1956).
[40] R. F. Guertin and F. Stern, Phys. Rev. 134, A427 (1964).

[41] G. Gramm, Phys. Letters 8, 157 (1964).
[42] B. Fritz and F. Lüty, Z. Physik (to be published).

distortion[43] that the $1s$ wave function does not remain localized after lattice relaxation but becomes diffuse along with the $2p$ wave function. This can lead to larger dipole matrix elements for emission than for absorption,[9] and a small transition energy. This picture is also consistent with the temperature independence of the emission-band peak. The narrow bandwidth may perhaps also be understood. Huang and Rhys[11] calculated the absorption bandwidth of the F center due to interactions with optical modes. They found that, using Simpson's F-center wave functions,[14] the predicted width was 2–3 times smaller than that observed. Although several interpretations of their results are possible, one of the more obvious is that Huang and Rhys calculated correctly the interaction with optical modes, that it is indeed small, and that in the absorption problem there are quasilocalized acoustic modes which are much more important. If this be the case, we argue that KCl:Li in the relaxed excited state may be a system in which both states, being diffuse, do interact with optical modes, that the Huang-Rhys result applies to this system, and that the narrow width is therefore understandable. The apparent absence of polarized emission in most F_A centers, and its apparent presence in KCl:Li,[42] seems qualitatively consistent with the picture of a diffuse excited state whose degeneracy is substantially removed only in the case of a large asymmetric perturbation such as that characteristic of KCl:Li.

There are a number of other properties of the F center which should be investigated in terms of our model. These include questions regarding the formation and destruction of color centers, concentration quenching of F-center luminescence, phonon scattering associated with F centers, and the effect of electric[44] and magnetic fields on the excited F center.

SUMMARY AND CONCLUSIONS

We have examined the suggestion that the excited F center relaxes in such a way that the $2p$ state before emission is very diffuse, while the $1s$ state remains rather compact. It has been shown that, given certain reasonable choices of parameters, this suggestion is borne out in a model calculation. Finally, we have argued that a number of experimental observations regarding F- and F_A-center emission seem to be consistent with this theory. Although these points are not conclusive, they are persuasive, and we feel that our theory is a good working hypothesis upon which to base further investigations.

[43] Mieher has found, using electron nuclear double resonance techniques, that there is a large lattice distortion associated with the KCl:Li F_A center in its ground state [Robert Lee Mieher, Phys. Rev. Letters 8, 362 (1962)].

[44] R. N. Euwema and R. Smoluchowski, Phys. Rev. 133, A1724 (1964).

APPENDIX

According to Haken,[20] the interaction between electron and hole via ionic polarization may be expressed as

$$H_I = \frac{1}{2}\sum_k |\gamma_k|^2 \left\{ \frac{e^{i k \cdot r}}{(\hbar^2 k^2/2m_1^*) + \hbar\omega} + \frac{e^{i k \cdot r}}{(\hbar^2 k^2/2m_2^*) + \hbar\omega} + \text{c.c.} \right\} + H_{s.e.}, \quad (A1)$$

where k is the phonon wave vector, ω the longitudinal optical frequency, r the electron-hole separation, and m_1^* and m_2^* are the effective masses of the two particles. c.c. stands for complex conjugate.

$|\gamma_k|^2$ is given by

$$|\gamma_k|^2 = (\hbar\omega)^2 (4\pi/Vk^2)(\alpha/u), \quad (A2)$$

where V is the crystal volume and α/u is given by

$$\alpha/u = (e^2/2\hbar\omega)(1/\epsilon^*), \quad (A3)$$

where

$$1/\epsilon^* = 1/K_0 - 1/K.$$

$H_{s.e.}$ represents the self-energies of the electron and of the hole with respect to the lattice polarization.

According to Haken, the part of H_I associated with m_1^*, where m_1^* is of the order of m_e, or smaller, is given by

$$H_I(m_1^*) = (e^2/2r)(1/\epsilon^*)(1 - e^{-vr}) - (e^2 v/2\epsilon^*), \quad (A4)$$

where v is defined in Eq. (9). We now evaluate the part of H_I associated with m_2^*, letting $m_2^* \to \infty$ to represent an immobile vacancy.

$$H_I(m_2^*) = \frac{2\pi}{V}\frac{e^2}{2\epsilon^*}\sum_k \frac{1}{k^2}\{e^{i k \cdot r} + e^{-i k \cdot r}\} - \frac{e^2}{e^* a}. \quad (A5)$$

We convert $(1/V)\sum_k$ into $(1/(2\pi)^3)\int d^3k$, and integrate to $k = \pi/a$, where a is the nearest-neighbor separation. Then

$$H_I(m_2^*) = \frac{e^2}{2\epsilon^*}\frac{1}{\pi r}\int_{-r\pi/a}^{r\pi/a}\frac{\sin\mu}{\mu}d\mu - \frac{e^2}{e^* a}. \quad (A6)$$

For $r/a > 1$, $H_I(m_2^*) \to e^2/2\epsilon^* r - e^2/\epsilon^* a$, while for r/a small $H_I(m_2^*) \to 0$. This behavior is reasonable. For

small r, $H_I(m_2{}^*)$ goes to zero, the self-energy of the vacancy being canceled, while as $r \to \infty$ the only energy is the vacancy-lattice self-energy.

To continue in the spirit of Haken we fit $H_I(m_2{}^*)$ to an exponential such that it behaves properly for large and small r, the result being

$$H_I(m_2{}^*) \approx (e^2/2\epsilon^* r)[1 - e^{-2r/a}] - (e^2/\epsilon^* a) . \quad \text{(A7)}$$

The exponential fit is not too good for $r \lesssim a$ but in the region of interest is sufficiently accurate.

The last terms in Eqs. (A4) and (A7) are the self-energies of the electron and vacancy due to the polariza-tion of the lattice. These negative terms outside the potential well are equivalent to a change in the zero of energy inside, and in fact these terms derived from polaron theory are analogous to the last term in W, Eq. (5). Thus to be perfectly consistent one should, when using the Haken dielectric constant, replace the last term in W by the quantity $(e^2/\epsilon^*)[(v/2)+(1/a)]$. This we have not done. For the large-orbit state the terms in question are approximately equal, since $v/2 \ll 1/a$ and $e^2/\epsilon^* a \approx e^2/\epsilon^* R$. However, in treating a smaller-radius excited state one should use the Haken self-energy.

Coupled-Optical-Phonon-Mode Theory of the Infrared Dispersion in BaTiO₃, SrTiO₃, and KTaO₃*

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The independent-oscillator model fails to predict the dielectric behavior of the high-dielectric-constant materials BaTiO₃, SrTiO₃, and KTaO₃ in certain infrared-frequency regions near the three infrared-active modes. A more general classical model is proposed with mode coupling. The model has one additional param-eter for each pair of modes that are coupled, and gives decreased (or increased) dielectric loss in certain regions between the modes, compared with the independent oscillator model. Very satisfactory fits to re-flectivity data for the above materials are obtained using the coupled-mode theory. In a mechanical analog of the model, the coupling element may be either a spring or a dashpot, since the two cases are shown to be equivalent. For the above materials, however, there is a physically interesting simplification in the spring-coupling form, since two of the otherwise arbitrary parameters are zero. The result suggests that the damp-ing is best viewed as applying to the total polarization rather than to the individual normal modes.

INTRODUCTION

IN an insulating crystal with more than one infrared active mode, the reflectivity in the *restrahlen* region is often quite well reproduced by a formula involving the sum of contributions from independent classical oscillators.[1] There are notable exceptions, however. The high dielectric constant materials BaTiO₃, SrTiO₃, and KTaO₃ provide a striking example. In fitting independent classical oscillator expressions one is immediately faced with compromises when choosing the damping constants for some modes. For example, near 21-μ wavelength in the case of SrTiO₃, the reflectiv-ity shows a dip to a value of less than 1%. The low damping indicated by this dip is inconsistent with the large damping nearby.[2] Figure 1 shows SrTiO₃ reflectiv-ity data and the best over-all classical oscillator fit.[3] The fit can be improved near 21 μ by decreasing the damping constant of the highest frequency mode. This effect is shown in the figure—there is an improved fit near the minimum but a poorer fit elsewhere. The fit can also be improved by decreasing the damping constant of the lowest frequency mode. Again there is improvement only over a small wavelength interval. Similarly, the rather square reflectivity shoulder extend-ing from 22 to 26 μ cannot be reproduced at all by the classical oscillator formula without choices of damping constants which spoil the fit elsewhere.

There are two separate difficulties involved in attempting to go beyond the classical independent oscillator model. One problem is to correctly describe

* Work supported in part by the National Science Foundation.
[1] W. G. Spitzer and D. A. Kleinman, Phys. Rev. **121**, 1324 (1961).
[2] In general, such dips occur at the frequency where ϵ', the real part of the dielectric constant, is passing through the value $\epsilon'=1$

on the high-frequency side of a mode. If ϵ'', the imaginary part of the dielectric constant, is zero here, the reflectivity will dip to zero. The dip then provides a sensitive measure of ϵ'' which, in turn, depends directly on γ, the damping constant.

[3] W. G. Spitzer, R. C. Miller, D. A. Kleinman, and L. E. Howarth, Phys. Rev. **126**, 1710 (1962).