and by optical methods are not important. τ may actually be smaller at infrared frequencies and cannot be determined to better than 10%. The fact that our values of τ do not increase monotonically as N decreases, contrary to expectation for ionized impurity scattering when only one type of impurity is present, is probably due to considerable compensation in our samples.

We can obtain values of m^*/m_e from the values of ω_p that fit the reflection spectra. For samples 1–3 at 78°K we find that m^*/m_e is 0.0668, 0.0726, and 0.0770, respectively. To compare these with the values of DeMeis and Paul[13] and of Spitzer and Whelan[12] one must increase them by about 4% to correct for the change in m^* due to increasing the temperature from 78 to 300°K.[13] To put our values on the same basis as those of Refs. 12 and 13 we must use $A=1$. The values of N in Table I must then be multiplied by $(1.08)^{-1}$ and the values of m^*/m_e listed above must be multiplied by $(1.08)^{-1/2}$, just cancelling the temperature correction. Our values of m^*/m_e thus "corrected" fall about 0.03 units below the data of Ref. 12, obtained by a method similar to ours, and range from 0.03 units below the data of Ref. 13 (sample 1) to about 0.05 units above them (sample 3). Agreement is "satisfactory," except for the unusually large dependence of m^*/m_e on N that we seem to have. This cannot be considered significant, however, because only three samples were used.

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Two-Quantum Excitations in Alkali Halides*

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Optical excitations involving the simultaneous production of two or more excitons by a single photon in alkali halides are considered. The electron-electron interaction is approximated by a term derived from Toyozawa's theory of the electronic polaron. Using a Lee-Low-Pines transformation for the c.m. motion and the Hartree approximation for the internal motion of an exciton, dipole matrix elements are calculated for many-exciton transitions. Specifically, for typical alkali halides we find the oscillator strength ratio $f^{(2)}/f^{(1)}\sim 10^{-2}$, in disagreement with the ratio 1.5 obtained by Miyakawa for LiF. Ultraviolet and x-ray data in the two-exciton region are briefly discussed.

I. INTRODUCTION

The optical properties of insulating solids (e.g., alkali halides[1,2] and rare-gas solids[3] have been extensively studied, both experimentally and theoretically, near the fundamental absorption edge.[4] For large-gap systems, the spectra are dominated by exciton absorption bands[5] above and below threshold. Structure at high energies has been identified with (1) Frenkel excitations[6] and charge transfer states,[7] (2) interband edges above the energy gap,[8] (3) metastable or "kinematic" exciton resonances,[9] (4) plasmon creation,[10] (5) core excitations,[11] and (6) two-exciton transitions[11,12] caused by electronic correlation. In this paper we present a calculation of contribution (6) to high-energy absorption in typical alkali halides, where the effects are expected to be most prominent.

Calculations of two-electron transitions have been

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[*] Research supported in part by the Advanced Research Projects Agency under Contract No. SD-131.

[1] J. E. Eby, K. J. Teegarden, and D. B. Dutton, Phys. Rev. **116**, 1099 (1959); F. Fischer and R. Hilsch, Z. Angew. Math. Phys. **8**, 241 (1959); K. J. Teegarden and G. Baldini, Phys. Rev. **155**, 896 (1967); G. Baldini and B. Bosachi, *ibid.* **166**, 863 (1968); D. M. Roessler and W. C. Walker, J. Opt. Soc. Am. **57**, 677 (1967); Phys. Rev. **166**, 599 (1968); T. Miyata and T. Tomiki, J. Phys. Soc. Japan **22**, 209 (1967); **22**, 463 (1967).

[2] H. R. Phillipp and H. Ehrenreich, Phys. Rev. **131**, 2016 (1963).

[3] O. Schnepp and K. Dressler, J. Chem. Phys. **33**, 49 (1960); G. Baldini, Phys. Rev. **128**, 1562 (1962); D. Beaglehole, Phys. Rev. Letters **15**, 551 (1965); J. F. O'Brien and K. J. Teegarden, *ibid.* **17**, 991 (1966).

[4] For a comprehensive review of the optical properties of solids, see J. C. Phillips, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1966), Vol. 18.

[5] Exciton theory has been reviewed by R. S. Knox, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963), Suppl. 5.

[6] D. L. Dexter, Phys. Rev. **83**, 435 (1951); **108**, 707 (1957); T. Muto, Y. Oyama, and H. Okuno, Progr. Theoret. Phys. (Kyoto) **20**, 804 (1958).

[7] R. Hilsch and R. W. Pohl, Z. Physik **57**, 145 (1929); **59**, 812 (1930); A. von Hippel, *ibid.* **101**, 1702 (1956); F. Bassani and N. Inchauspé, Phys. Rev. **105**, 819 (1957); B. Goodman and O. S. Oen, J. Phys. Chem. Solids **8**, 291 (1959); R. S. Knox and N. Inchauspé, Phys. Rev. **116**, 1093 (1959).

[8] J. C. Phillips, Phys. Rev. **136**, A1705 (1964); **136**, A1714 (1964); **136**, A1721 (1964).

[9] M. Cardona and G. Harbeke, Phys. Rev. Letters **8**, 90 (1962); J. C. Phillips, *ibid.* **10**, 329 (1963); K. P. Jain, Phys. Rev. **139**, A544 (1965); J. Hermanson, Phys. Rev. Letters **18**, 170 (1967); Phys. Rev. **166**, 893 (1968).

[10] D. W. Lynch, Solid State Commun. **4**, 159 (1966).

[11] T. Miyakawa, J. Phys. Soc. Japan **17**, 1898 (1962).

[12] T. Sagawa *et al.*, J. Phys. Soc. Japan **21**, 2587 (1966).

previously reported by several authors[13–16] for molecular crystals. For these systems, characterized by negligible intermolecular overlap, two-electron transitions take place in two steps: (1) An intermediate state is reached from the ground state by (a) photon absorption or (b) two-electron transition due to intermolecular correlation and (2) the final state is created by (a) intermolecular correlation or (b) photon absorption; the amplitudes A_1 and A_2 for steps 1 and 2 are additive, according to second-order time-dependent perturbation theory. The basic result is that two-electron transitions are two orders of magnitude weaker than are the familiar one-electron transitions; however, strong evidence for the higher-order process has been found by Varsanyi and Dieke for $PrCl_3$,[17] in a spectral region where one-electron excitations are not expected to occur.

In alkali halides the Frenkel model is not valid. Thus intermolecular correlation, the effects of which were studied by the above authors, must be replaced by the long-range electron-electron interaction, suitably screened by valence shell polarization. An earlier calculation, that of Miyakawa,[11] treated Wannier 1*s* excitons in LiF, omitting polarization and approximating the second-order matrix element for two-exciton production by a term derived from Toyozawa's theory of the electronic polaron (i.e., an electron clothed by a cloud of virtual excitons).[18] The result, that double excitations are about as favorable as single excitations, seems unphysical in the context of the results cited above for molecular crystals. In particular, Miyakawa's result would imply a matrix element of the correlation potential with the magnitude of the energy gap and the electron-electron self-energy would also be comparable to the energy gap, so that a consideration of renormalization effects would be essential. In addition, to satisfy the oscillator-strength sum rule[19] the amplitude of one-electron transitions would have to be decreased substantially relative to the result expected without correlation. Using Huang-Rhys theory[20] as a guide (but substituting longitudinal excitons for LO phonons) the Debye-Waller factor e^{-S}, where S is the Huang-Rhys factor (≈ 1.5 in Ref. 11) should multiply the zero-exciton line strength (i.e., for one-electron transitions). Since e^{-S} contains all powers of the electron-exciton coupling, a nonperturbative approach is necessary.

The approach of the present paper is based upon the canonical transformation introduced by Lee, Low, and Pines[21] for the lattice polaron. In this connection we note that the coupling constant α appropriate to the electron-exciton interaction in alkali halides is about unity, so that intermediate coupling theory is valid. The theory is outlined in Sec. II. Many-electron matrix elements of the electric dipole operator are determined in Sec. III, and a brief discussion of relevant optical data is given in Sec. IV.

II. APPROXIMATE MANY-ELECTRON WAVE FUNCTION

As is well known, the basic excitation of an insulating solid is the electron-hole pair or exciton.[5] The interaction of this quasiparticle with the polarization field of the crystal has been treated in various ways to derive self-energies[18,21–23] and r-dependent dielectric constants[22–25] which screen the electron-hole Coulomb interaction. A simple approach, due to Toyozawa,[18] is to replace the many-electron field of valence charges (ionic screening may be neglected for tightly bound excitons) by a single dispersionless boson field consisting of longitudinal excitons, and renormalizing the coupling constants to reproduce the electrostatic polarization potential of a point charge.[26] The effective electron-exciton interaction which results is

$$H_I=\sum_{\kappa} V_\kappa(a_\kappa^\dagger e^{-i\boldsymbol{\kappa}\cdot\mathbf{r}_1}-a_\kappa e^{+i\boldsymbol{\kappa}\cdot\mathbf{r}_1}), \tag{2.1}$$

where r_1 is the electron coordinate and $a_\kappa^\dagger$ (a_κ) is the boson creation (annihilation) operator for the longitudinal exciton field. The scattering amplitude V_κ for momentum transfer $\hbar_\kappa$ to the electron and production of an exciton with wave vector $\boldsymbol{\kappa}$ is given by

$$V_\kappa=i\frac{E_0}{|\boldsymbol{\kappa}|}\left(\frac{4\pi R\alpha}{V}\right)^{1/2},$$

$$R=\left(\frac{\hbar^2}{2m_eE_0}\right)^{1/2}, \quad \alpha=\frac{1}{2}\left(1-\frac{1}{\epsilon_\infty}\right)\frac{e^2}{R}\frac{1}{E_0}, \tag{2.2}$$

in terms of the (longitudinal) exciton energy E_0, the electron-exciton coupling constant α, and R, the semiclassical "radius" of the electronic polaron; V is the crystal volume and $\epsilon_\infty=n^2$ is the optical dielectric constant.

We emphasize that the electronic polaron model is deficient in the treatment of screening at long wave-

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[13] D. L. Dexter, Phys. Rev. **126**, 1962 (1962).

[14] L. N. Ovander, Fiz. Tverd. Tela 4, 294 (1962) [English transl.: Soviet Phys.—Solid State 4, 212 (1962)].

[15] J. Jortner and S. A. Rice, J. Chem. Phys. **44**, 3364 (1966).

[16] G. F. Kventsel', Fiz. Tverd. Tela 8, 1819 (1966) [English transl.: Soviet Phys.—Solid State 8, 1445 (1966)].

[17] F. Varsanyi and G. H. Dieke, Phys. Rev. Letters 7, 442 (1961).

[18] Y. Toyozawa, Progr. Theoret. Phys. (Kyoto) 12, 421 (1954).

[19] D. Pines, in *Elementary Excitations in Solids*, edited by J. P. Jackson and D. Pines (W. A. Benjamin, Inc., New York, 1963), Chap. 4.

[20] K. Huang and A. Rhys, Proc. Roy. Soc. (London) **A204**, 406 (1950); M. Lax, J. Chem. Phys. **20**, 1752 (1952).

[21] T. D. Lee, F. Low, and D. Pines, Phys. Rev. **90**, 297 (1953); T. D. Lee and D. Pines, *ibid.* **92**, 883 (1953); W. Klemm, Z. Physik **82**, 529 (1933); N. F. Mott and M. J. Littleton, Trans. Faraday Soc. **34**, 485 (1938).

[22] H. Haken and W. Schottky, Z. Physik Chem. (Frankfurt) **16**, 218 (1958).

[23] W. Weller, Z. Naturforsch. **16a**, 401 (1961); G. Hanisch, Physik Kondensierten Materie 4, 297 (1965).

[24] J. Hermanson and J. C. Phillips, Phys. Rev. **150**, 652 (1966); J. Hermanson, *ibid.* **150**, 660 (1966).

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

[26] H. Frohlich, H. Pelzer, and S. Zienau, Phil. Mag. **41**, 221 (1950).

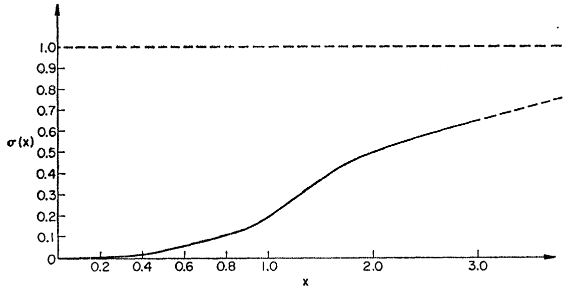

FIG. 1. Electronic factor $\sigma(x)$ for hydrogenic 1s states. Here $x=\frac{1}{2}s_1K_0r_0$ in terms of the excitonic Bohr radius r_0 and the usual momentum-space cutoff $K_0=2\pi/a$; s_1 is a kinematic factor slightly less than unity for narrow valence bands. For large x, $\sigma(x)$ approaches unity asymptotically.

lengths $k\rightarrow 0$, where plasmon effects are important, since the electron-hole continuum is not properly included. Thus many-body effects such as two-quantum excitations are overestimated in this model, particularly in the case of shallow excitons, where the Bohr radius is large compared with the lattice parameter. Plasmon corrections are probably unimportant in molecular crystals, where most of the oscillator strength of the electronic polarization field is contained in deep exciton states. At the other extreme are the semiconductors, whose many-body effects can safely be calculated neglecting electron-hole attraction in the treatment of screening; transformation to collective plasmon coordinates would be convenient for this case. Alkali halides are intermediate to these limits, and so are very difficult to treat accurately. However, since we are mainly interested in finding an upper bound to two-quantum transition rates, and especially since our computed rates are small compared with typical one-quantum rates, we omit plasmon corrections in this paper. Qualitatively, we expect that as the exciton radius increases the two-quantum rate decreases, in opposition to the calculated trend shown in Fig. 1.

The many-electron interaction H_I has three important effects: (1) It contributes a sizable self-energy $\Sigma\sim 2$–3 eV to band states (the imaginary part of Σ is zero below $E_0+(E_0-\Delta)$ by energy conservation, where Δ is the transverse-longitudinal exciton splitting at $\boldsymbol{\kappa}=0$), (2) the effective mass of electrons or holes is slightly increased ($\lesssim 10\%$), and (3) it makes possible many-electron excitations through optical absorption above $2E_0-\Delta$. To study these effects we assume, as did Haken and Schottky,[22] that the effective Hamiltonian for an electron-hole pair interacting with the polarization field according to H_I can be written within the effective-mass approximation as

$$H=E_G+\frac{\mathbf{p}_1^2}{2m_1}+\frac{\mathbf{p}_2^2}{2m_2}-\frac{e^2}{|\mathbf{r}_1-\mathbf{r}_2|^\dagger}+\sum_{\mathbf{k}} a_{\mathbf{k}}^\dagger a_{\mathbf{k}}E_0$$
$$+\sum_{\mathbf{k}} V_{\mathbf{k}}[a_{\mathbf{k}}^\dagger(e^{-i\mathbf{k}\cdot\mathbf{r}_1}-e^{-i\mathbf{k}\cdot\mathbf{r}_2})-a_{\mathbf{k}}(e^{i\mathbf{k}\cdot\mathbf{r}_1}-e^{i\mathbf{k}\cdot\mathbf{r}_2})], \quad (2.3)$$

in terms of the effective mass m_1 (m_2) and radial coordinate $\mathbf{r}_1$ ($\mathbf{r}_2$) for the electron (hole); here $\mathbf{p}_i$ is the momentum operator for particle i and E_G is the one-electron energy gap.

The Hamiltonian (2.3) is harder to treat than is the usual polaron problem because of the strong coupling between electron and hole. The approach of Haken and Schottky was to expand the wave function in polaron pairs, using intermediate coupling wave functions[21] for the electron and (separately) the hole. However, this product form is appropriate only when the exciton Bohr radius $r_0\gg R$. Table I shows that this condition is not well met in typical alkali halides. Moreover, since the boson field responds instantaneously to the coordinate $\mathbf{r}_1$ (or $\mathbf{r}_2$) in the intermediate coupling wave function, the exciton emission amplitudes for electron and hole cancel as $|\mathbf{r}_1-\mathbf{r}_2|\rightarrow 0$ and hence many-electron optical transitions are forbidden in this model. To treat the case where the Bohr radius is comparable with the radius of the electronic polaron and especially the limit $\mathbf{r}_1\rightarrow\mathbf{r}_2$ (where the polarization field cannot follow the very rapid internal motion of the exciton) we adopt the Hartree approximation for polarization effects due to the relative motion of the electron and hole. We begin by transforming to c.m. coordinates in (2.3);

$$\mathbf{R}=\frac{m_1\mathbf{r}_1+m_2\mathbf{r}_2}{m_1+m_2},$$
$$\mathbf{r}=\mathbf{r}_1-\mathbf{r}_2. \quad (2.4)$$

Thus we have the separable form

$$H=E_G+\frac{\mathbf{P}^2}{2M}+\frac{\mathbf{p}^2}{2\mu}-\frac{e^2}{r}+\sum_{\mathbf{k}} E_0a_{\mathbf{k}}^\dagger a_{\mathbf{k}}$$
$$+\sum_{\mathbf{k}} V_{\mathbf{k}}[a_{\mathbf{k}}^\dagger e^{-i\mathbf{k}\cdot\mathbf{R}}(e^{-is_1\mathbf{k}\cdot\mathbf{r}}-e^{is_2\mathbf{k}\cdot\mathbf{r}})$$
$$-a_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{R}}(e^{is_1\mathbf{k}\cdot\mathbf{r}}-e^{-is_2\mathbf{k}\cdot\mathbf{r}})], \quad (2.5)$$

where $\mu=(m_1^{-1}+m_2^{-1})^{-1}$ is the reduced mass, $M=m_1+m_2$ is the total mass of the exciton, and $s_i=\mu m_i^{-1}<1$. Here the momentum of the c.m. is represented by the operator $\mathbf{P}=-i\hbar\partial/\partial\mathbf{R}$ and the relative momentum operator $\mathbf{p}=-i\hbar\partial/\partial\mathbf{r}$. Since the coordinate $\mathbf{R}$ does not appear in the electron-hole interaction, it can be eliminated from (2.5) by the unitary

TABLE I. Exciton parameters for typical alkali halides. The effective Bohr radius r_0 for 1s states is calculated neglecting screening. The optical dielectric constant $\epsilon_\infty=n^2$; α and R are given in Eq. (2.2).

	ϵ_∞	α	r_0(a.u.)	R(a.u.)
RbCl	2.19	0.53	2.14	1.88
KCl	2.13	0.49	2.22	1.88
KBr	2.33	0.54	2.57	2.17
KI	2.69	0.614	2.76	2.42

transformation

$$H\to H_{\mathrm{new}}=U_1^{-1}HU_1,\quad U_1=\exp\Big[-i\sum_{\mathbf{k}}a_{\mathbf{k}}^{\dagger}a_{\mathbf{k}}\mathbf{k}\cdot\mathbf{R}\Big]. \tag{2.6}$$

We find easily

$$H_{\mathrm{new}}=\frac{\hbar^2}{2M}\Big(-i\frac{\partial}{\partial\mathbf{R}}-\sum_{\mathbf{k}}\mathbf{k}a_{\mathbf{k}}^{\dagger}a_{\mathbf{k}}\Big)^2+\sum E_0a_{\mathbf{k}}^{\dagger}a_{\mathbf{k}}+E_G+\sum_{\mathbf{k}}\big[V_{\mathbf{k}}a_{\mathbf{k}}^{\dagger}(e^{-is_1\mathbf{k}\cdot\mathbf{r}}-e^{is_2\mathbf{k}\cdot\mathbf{r}})+\text{c.c.}\big]. \tag{2.7}$$

The eigenfunctions of H have the form

$$\Phi=e^{i\mathbf{q}\cdot\mathbf{R}}\exp\Big(+i\sum_{\mathbf{k}}a_{\mathbf{k}}^{\dagger}a_{\mathbf{k}}\mathbf{k}\cdot\mathbf{R}\Big)\Phi_{\mathbf{q}}(r,a), \tag{2.8}$$

where $\Phi_{\mathbf{q}}$ is the eigenvector of the transformed Hamiltonian

$$H_{\mathbf{q}}=\frac{\hbar^2}{2M}\Big(\mathbf{q}-\sum_{\mathbf{k}}a_{\mathbf{k}}^{\dagger}a_{\mathbf{k}}\mathbf{k}\Big)^2+\sum_{\mathbf{k}}E_0a_{\mathbf{k}}^{\dagger}a_{\mathbf{k}}+E_G+\mathbf{p}^2/2\mu-e^2/r+\sum_{\mathbf{k}}V_{\mathbf{k}}\big[a_{\mathbf{k}}^{\dagger}(e^{-is_1\mathbf{k}\cdot\mathbf{r}}-e^{is_2\mathbf{k}\cdot\mathbf{r}})-a_{\mathbf{k}}(e^{is_1\mathbf{k}\cdot\mathbf{r}}-e^{-is_2\mathbf{k}\cdot\mathbf{r}})\big]. \tag{2.9}$$

The total momentum $\mathbf{q}$ of the system is a constant of the motion due to the commutation of the operator

$$\mathbf{P}=-i\hbar\frac{\partial}{\partial\mathbf{R}}+\sum_{\mathbf{k}}\hbar\mathbf{k}a_{\mathbf{k}}^{\dagger}a_{\mathbf{k}} \tag{2.10}$$

and the full Hamiltonian H; the second term on the right side of (2.10) is the exciton recoil momentum operator. The Hamiltonian for the bound (electronic) polaron is obtained from $H_{\mathbf{q}}$ by neglecting the kinetic energy of the c.m. in (2.9) ($M\to\infty$); in alkali halides $M\sim 10m_e$.

We now make the Hartree approximation for the electron-hole internal motion. This approximation assumes that the valence charge polarization field responds to the static charge distribution of the exciton; i.e., $\Phi_{\mathbf{q}}$ in (2.8) has the product form

$$\Phi_{\nu\mathbf{q}}(r,a)=\psi_\nu(r)\varphi_{\nu\mathbf{q}}(a), \tag{2.11}$$

where ν is the principle quantum number and a refers to all boson coordinates $a_{\mathbf{k}}$ and $a_{\mathbf{k}}^{\dagger}$. The Hartree wave function (2.11) makes it possible to separate the coordinate $\mathbf{r}$ from the boson coordinate, resulting in two effective wave equations coupled together by the requirement that $\psi(\mathbf{r})$ and $\varphi(a)$ be determined self-consistently in both equations. Applying the variational principle we find the equations satisfied by ψ and φ:

$$[\mathbf{p}^2/2\mu-e^2/r+V_{\mathrm{pol}}(\mathbf{r})]\psi_\nu(\mathbf{r})=E_{\nu\mathbf{q}}\psi_\nu(\mathbf{r}), \tag{2.12a}$$

$$\frac{\hbar^2}{2M}\Big(\mathbf{q}-\sum_{\mathbf{k}}a_{\mathbf{k}}^{\dagger}a_{\mathbf{k}}\mathbf{k}\Big)^2+E_0\sum_{\mathbf{k}}a_{\mathbf{k}}^{\dagger}a_{\mathbf{k}}+\sum_{\mathbf{k}}V_{\mathbf{k}}(a_{\mathbf{k}}^{\dagger}\rho_{n\mathbf{k}}-a_{\mathbf{k}}\rho_{n\mathbf{k}}^{*})\varphi_{\nu\mathbf{q}}(a)=\epsilon_{\nu\mathbf{q}}\varphi_{\nu\mathbf{q}}(a). \tag{2.12b}$$

Both the polarization potential

$$V_{\mathrm{pol}}(\mathbf{r})=\sum_{\mathbf{k}}V_{\mathbf{k}}\big[\Phi_{\mathbf{k}}^{*}(e^{-is_1\mathbf{k}\cdot\mathbf{r}}-e^{is_2\mathbf{k}\cdot\mathbf{r}})-\Phi_{\mathbf{k}}(e^{is_1\mathbf{k}\cdot\mathbf{r}}-e^{-is_2\mathbf{k}\cdot\mathbf{r}})\big] \tag{2.13a}$$

and the intraband scattering term for the c.m.

$$V_\nu(a)=\sum_{\mathbf{k}}V_{\mathbf{k}}(a_{\mathbf{k}}^{\dagger}\rho_{\nu\mathbf{k}}-a_{\mathbf{k}}\rho_{\nu\mathbf{k}}^{*}) \tag{2.13b}$$

must be determined self-consistently. Here

$$\Phi_{\mathbf{k}}=\langle\varphi_{\nu\mathbf{q}}(a)|a_{\mathbf{k}}|\varphi_{\nu\mathbf{q}}(a)\rangle \tag{2.14a}$$

and

$$\rho_{\nu\mathbf{k}}=\int d^3r\,|\psi_\nu(\mathbf{r})|^2(e^{-is_1\mathbf{k}\cdot\mathbf{r}}-e^{is_2\mathbf{k}\cdot\mathbf{r}}) \tag{2.14b}$$

are the charge density form factors for the boson field and the internal exciton motion, respectively.

The equation of motion (2.12b) is equivalent to the equation for free polarons[21] with $V_{\mathbf{k}}$ replaced by the more complicated term $V_{\mathbf{k}}\rho_{\nu\mathbf{k}}$ which approaches zero as $|\mathbf{k}|$ at long wavelengths (unlike $V_{\mathbf{k}}$ which diverges as $|\mathbf{k}|^{-1}$) and decreases more rapidly than $|\mathbf{k}|^{-1}$ for large $|\mathbf{k}|$. This behavior is a direct consequence of the fact that an exciton is electrically neutral and is characterized by a Bohr radius that is comparable to a lattice spacing for alkali halides. Equation (2.12b) describes *intraband* scattering of the exciton due to valence shell polarization; *interband* scattering has been included within the Hartree approximation (i.e., static screening of the electron-hole interaction).

To solve (2.12b) we note that the coupling constant $\alpha\lesssim 1$, so that we may employ the Lee-Low-Pines transformation.[21]

$$\varphi_{\nu\mathbf{q}}(a)=\exp\Big[\sum_{\mathbf{k}}g_{\mathbf{k}}(a_{\mathbf{k}}^{\dagger}+a_{\mathbf{k}})\Big]|\{n_{\mathbf{k}}\}\rangle,\quad |\{n_{\mathbf{k}}\}\rangle=\prod_{\mathbf{k}}\frac{(a_{\mathbf{k}}^{\dagger})^{n_{\mathbf{k}}}}{(n_{\mathbf{k}}!)^{1/2}}|0\rangle, \tag{2.15}$$

where $|0\rangle$ is the vacuum or ground state of the crystal and $g_{\mathbf{k}}$ is the variational displacement of the $\mathbf{k}$th oscillator. Substituting $\varphi_{\nu\mathbf{q}}$ into (2.12b) we find

$$\epsilon_{\nu\mathbf{q}}(\{n_{\mathbf{k}}\})=\frac{\hbar^2}{2M}\Big(\mathbf{q}-\sum_{\mathbf{k}}\mathbf{k}n_{\mathbf{k}}\Big)^2-\sum_{\mathbf{k}}(V_{\mathbf{k}}\rho_{\nu\mathbf{k}}g_{\mathbf{k}}+\text{c.c.})+\frac{\hbar^2}{2M}\Big(\sum_{\mathbf{k}}|g_{\mathbf{k}}|^2\mathbf{k}\Big)^2+\sum_{\mathbf{k}}|g_{\mathbf{k}}|^2\Big(E_0-\frac{\hbar^2\mathbf{k}\cdot\mathbf{q}}{M}+\frac{\hbar^2}{2M}k^2\Big)+\sum_{\mathbf{k}}n_{\mathbf{k}}\mathbf{k}\cdot\frac{1}{M}\sum_{\mathbf{k}'}|g_{\mathbf{k}'}|^2\mathbf{k}'. \tag{2.16}$$

As usual the nondiagonal terms (corrections to intermediate coupling theory) have been omitted in (2.16). Applying the variational principle, the oscillator displacement for the electronic state ψ_ν is

$$g_{\mathbf{k}}=\frac{-V_{\mathbf{k}}\rho_{\nu\mathbf{k}}}{E_0+\hbar^2\mathbf{k}^2/2M-(\hbar^2\mathbf{k}/M)\cdot(\mathbf{q}-\sum_{\mathbf{k}'}n_{\mathbf{k}'}\mathbf{k}')(1-\eta)},$$

$$\eta\mathbf{q}=\sum_{\mathbf{k}}\frac{|V_{\mathbf{k}}|^2|\rho_{\nu\mathbf{k}}|^2\mathbf{k}}{E_0+\hbar^2\mathbf{k}^2/2M-(\hbar^2\mathbf{k}/M)\cdot(\mathbf{q}-\sum_{\mathbf{k}'}n_{\mathbf{k}'}\mathbf{k}')(1-\eta)}. \tag{2.17}$$

The approximate orthogonality of excited states $\varphi_{\nu\mathbf{q}}$ corresponding to different free boson states $|\{n_{\mathbf{k}}\}\rangle$ can be shown if the exciton bandwidth $W\ll E_G$. Since W is roughly given by the valence bandwidth, the assumption is valid for alkali halides. We may therefore neglect the recoil terms in (2.17) and replace the energy denominator by E_0. In turn, the mass enhancement $(M^*/M-1)\lesssim 1\%$ of the c.m. is neglected in the following discussion. Within these approximations the total energy of the system is found from Eqs. (2.9), (2.15), and (2.17):

$$E_{\nu q}(\{n_k\})=E_G+\frac{\hbar^2}{2M}(\mathbf{q}-\sum_{\mathbf{k}}n_{\mathbf{k}}\mathbf{k})^2+E_0\sum_{\mathbf{k}}n_{\mathbf{k}} +E_\nu-\Sigma_\nu. \tag{2.18}$$

The first two terms give the kinetic energy of the (transverse) exciton relative to the valence band edge ($\hbar\mathbf{q}$ is the total momentum), the third term is the total energy of the free bosons (later we specialize to the case $\sum_{\mathbf{k}}n_{\mathbf{k}}=1$), E_ν the (negative) Coulomb energy of the electron-hole pair in the state ψ_ν,

$$E_\nu=\int d^3r\,\psi_\nu^*(\mathbf{r})\left(\frac{\mathbf{p}^2}{2\mu}-\frac{e^2}{r}\right)\psi_\nu(\mathbf{r}), \tag{2.19}$$

and Σ_ν is the exciton-exciton self-energy due to H_I,

$$\Sigma_\nu=\sum_{\mathbf{k}}\frac{|V_{\mathbf{k}}|^2|\rho_{\nu\mathbf{k}}|^2}{E_0}, \tag{2.20}$$

neglecting the exciton band width compared to E_0.

Calculations of the internal energy $E_\nu-\Sigma_\nu$ were carried out for variational 1s states

$$\psi_{1s}(r)=[1/(\pi r_0^3)^{1/2}]e^{-r/r_0}, \tag{2.21}$$

using the Hartree formula as well as the Haken-Schottky self-energy[22]

$$\Sigma_\nu^{\mathrm{HS}}=2\sum_{\mathbf{k}}\frac{|V_{\mathbf{k}}|^2}{E_0}(1-\rho_{\nu\mathbf{k}}^{(1)}). \tag{2.22}$$

Here the electronic form factor

$$\rho_{\nu\mathbf{k}}^{(1)}=\int d^3r\,e^{i\mathbf{k}\cdot\mathbf{r}}|\psi_\nu(r)|^2 \tag{2.23}$$

approaches 1 as $\mathbf{k}\to 0$ by normalization of ψ_ν; $\rho_{\nu\mathbf{k}}^{(1)}$ should be compared with Eq. (2.14b), and the valence and conduction bandwidth have been neglected compared to E_0. For typical alkali halides we find $\Sigma_\nu^{\mathrm{HS}}>\Sigma_\nu$, suggesting that the Haken-Schottky variational ansatz for the exciton is better, on the average, than is our Hartree approximation. As emphasized above, however, the former theory is not accurate near the origin, and predicts zero amplitude for many-electron excitations. Our theory, which gives an exciton binding energy some 20% less than does the Haken-Schottky theory, is more accurate near the origin; this theory will be applied in Sec. III in a calculation of two-excition optical transitions. Both self-energy theories lead to an effective Bohr radius r_0 that is only slightly larger ($\sim$10%) than the unscreened value μ^{-1} (a.u.).

As is well known, central cell corrections for deep exciton states are large.[24] In particular, (1) the nonparabolicity of the conduction band and (2) the orthogonality requirement each leads to sizeable corrections to the hydrogenic result for the binding energy of 1s states. However, as demonstrated explicitly for rare-gas solids in Ref. 24, the quantum defects due to (1) and (2) substantially cancel one another; for this reason, and because we are primarily interested in calculating the order of magnitude of many-body effects, we omit the difficult numerical computation of the microscopic corrections (1) and (2). In addition we do not attempt to calculate local field corrections (umklapp processes) not included in the Toyozawa model.

III. MULTIEXCITON OSCILLATOR STRENGTHS

In this section the approximate wave functions derived above are used to calculate dipole matrix elements for multiexciton transitions in optical absorption. The electron-photon interaction $\mathbf{p}\cdot\mathbf{A}$ is proportional to the transition operator

$$T=\sum_{\mathbf{k}}b_{\alpha\mathbf{k}+\kappa}{}^{\dagger}b_{\beta\mathbf{k}}\langle\alpha\boldsymbol{\kappa}+\boldsymbol{\kappa}|(\boldsymbol{\varepsilon}\cdot\mathbf{p})e^{i\kappa\cdot\mathbf{r}}|\beta\mathbf{k}\rangle \tag{3.1}$$

acting between the valence band β and the conduction band α, where $b^\dagger$ (b) is the creation (annihilation) operator for Bloch electrons, $\mathbf{k}$ is the photon wave number, and $\boldsymbol{\varepsilon}$ is the polarization vector perpendicular to $\boldsymbol{\kappa}$. The $\mathbf{k}$ dependence of the dipole matrix element,

$$P_\kappa=\langle\alpha\mathbf{k}+\boldsymbol{\kappa}|(\boldsymbol{\varepsilon}\cdot\mathbf{p})e^{i\kappa\cdot\mathbf{r}}|\beta\mathbf{k}\rangle, \tag{3.2}$$

is neglected in the following.

Optical absorption is given according to the Born approximation by a sum over excited states $|\nu\mathbf{q}\rangle$[19]:

$$\alpha(\omega)=A(\hbar\omega)^{-1}\sum_{\{n_{\mathbf{k}}\}\nu\mathbf{q}}|\langle\nu\mathbf{q}|T|0\rangle|^2\delta(E_{\nu\mathbf{q}}-\hbar\omega), \tag{3.3}$$

where A is a constant, $|0\rangle$ denotes the ground state of the solid, and $E_{\nu\mathbf{q}}$ is the energy of the excited state relative to the ground state. From Eqs. (2.8), (2.11), and (2.15) we have, in the Bloch representation, the result

$$|\nu\mathbf{q}\rangle=\sum_{\mathbf{k}_1\mathbf{k}_2} C_{\mathbf{k}_1\mathbf{k}_2}{}^{(\nu\mathbf{q})} b_{\alpha\mathbf{k}_1}{}^{\dagger} b_{\beta\mathbf{k}_2}|0\rangle\,, \tag{3.4a}$$

where $C_{\mathbf{k}_1\mathbf{k}_2}$ is the Fourier transform of the "envelope function" (2.8):

$$\begin{aligned} &e^{i\mathbf{q}\cdot\mathbf{R}}\exp(+i\sum_{\mathbf{k}} a_{\mathbf{k}}{}^{\dagger}a_{\mathbf{k}}\mathbf{k}\cdot\mathbf{R})\psi_\nu(\mathbf{r}) \\ &\qquad\times\exp[\sum_{\mathbf{k}} g_{\mathbf{k}}(a_{\mathbf{k}}{}^{\dagger}+a_{\mathbf{k}})]|\{n_{\mathbf{k}}\}\rangle \\ &\qquad=N^{-2}\sum_{\mathbf{k}_1\mathbf{k}_2} e^{i(\mathbf{k}_1\cdot\mathbf{r}-\mathbf{k}_2\cdot\mathbf{r}_2)} C_{\mathbf{k}_1\mathbf{k}_2}{}^{(\nu\mathbf{q})}|0\rangle\,. \end{aligned} \tag{3.4b}$$

Using the orthonomality of Bloch functions and assuming momentum-independent matrix elements (3.2), the transition amplitude for optical excitation of the state $|\nu\mathbf{q}\rangle$ is calculated from Eqs. (3.1) and (3.4):

$$\langle\nu\mathbf{q}|T|0\rangle=P_\kappa\psi_\nu(0)\langle\{n_{\mathbf{k}}\}|\exp(-\hat{S}_\nu)|0\rangle\delta(\boldsymbol{\kappa}-\mathbf{q})\,, \tag{3.5}$$

where

$$\hat{S}_\nu=\sum_{\mathbf{k}} g_{\mathbf{k}}(a_{\mathbf{k}}{}^{\dagger}+a_{\mathbf{k}}) \tag{3.6}$$

is an operator which depends on the internal quantum state ψ_ν through the form factor $\rho_{\nu\mathbf{k}}$, and the δ function expresses momentum conservation. The usual result of effective-mass theory,[27,28] $\alpha\sim|\psi_\nu(0)|^2$, is obtained by replacing the boson matrix element by unity (i.e., by neglecting corrections to Hartree-Fock theory). Note that the transition probability for one-exciton absorption ($n_{\mathbf{k}}=0$ for all $\mathbf{k}$) is reduced from Elliott's result by the factor

$$\begin{aligned}\gamma&=|\langle 0|\exp(-\hat{S}_\nu)|0\rangle|^2\\ &=\exp(-S_\nu)<1\,,\end{aligned} \tag{3.7}$$

where

$$\begin{aligned} S_\nu&=\sum_{\mathbf{k}}|g_{\mathbf{k}}|^2 \\ &=\frac{1}{4\pi^2}\left(1-\frac{1}{\epsilon_\infty}\right)\left(\frac{e^2}{E_0}\right)\int\frac{d^3k}{k^2}|\rho_{\nu\mathbf{k}}|^3 \end{aligned} \tag{3.8}$$

using Eqs. (2.17) and (2.2), and neglecting the exciton bandwidth compared to E_0. As usual, the $\mathbf{k}$-space integration in (3.8) is restricted to the central Brillouin zone. The quantity γ is a kind of Debye-Waller factor for the electron-exciton interaction, giving the reduction of oscillator strength in the main exciton peak due to the zero-point motion of the electronic polarization field (for the solids of interest $kT\ll E_0$). Physically, this reduction is necessary in order to satisfy the optical-absorption sum rule, which is obeyed in the presence of electron-electron interactions. The analogous reduction of intensity on the zero-phonon line associated with impurity excitations is well known.

Oscillator strengths $f_\nu{}^{(m+1)}$ for $(m+1)$-exciton transitions (m longitudinal, one transverse exciton with quantum number ν) can be calculated from the definition (we omit trivial factors)

$$f_\nu{}^{(m+1)}=\int_0^{+\infty}dE\sum_{\nu\mathbf{q}\{n\mathbf{k}\}}|\langle\nu\mathbf{q}|T|0\rangle|^2\delta(E_{\nu\mathbf{q}}-\hbar\omega)\,, \tag{3.9}$$

where $\Sigma_{\mathbf{k}}n_{\mathbf{k}}=m$ for each set $\{n_{\mathbf{k}}\}$.

Using Feynman operator techniques[29] and Eqs. (3.3) and (3.5), we have the result

$$f_\nu{}^{(m+1)}=f_\nu{}^{(0)}e^{-S_\nu}(S_\nu)^m/m!, \tag{3.10}$$

where $f_\nu{}^{(0)}=|P_\kappa|^2|\psi_\nu(0)|^2$ is the one-exciton line strength according to Elliott's theory, apart from unimportant factors. The quantity S_ν is a kind of Huang-Rhys factor[20] for the electron-exciton coupling, specifying the relative probabilities for the mth sideband corresponding to the emission of m longitudinal excitons during the optical excitation of the νth (transverse) Wannier state. In particular, the ratio of transition probabilities for the two- and one-exciton processes is simply

$$f_\nu{}^{(2)}/f_\nu{}^{(1)}=S_\nu\,, \tag{3.11}$$

whereas the absolute rate for the two-quantum excitation is

$$f_\nu{}^{(2)}=f^{(0)}e^{-S_\nu}S_\nu\,. \tag{3.12}$$

As required by the sum rule[19] the total absorption is unchanged by correlation effects:

$$\sum_{m=0}^{\infty}f_\nu{}^{(m+1)}=f_\nu{}^{(0)}\,. \tag{3.13}$$

The emission factor S_ν can be written, using Eq. (3.8), as a product of two factors

$$S_\nu=S_0\sigma_\nu\,, \tag{3.14}$$

where

$$S_0=4\alpha R/a \tag{3.15}$$

depends only on parameters of the polarization field [see Eq. (2.2)] and a, the lattice parameter, and σ_ν is an electronic factor which depends upon the form factor $\rho_{\nu\mathbf{k}}$. For hydrogenic 1s states (2.21) σ has the form

$$\begin{aligned}\sigma_{1s}=1+\frac{1}{6(1+x_0{}^2)^3}+\frac{5}{24(1+x_0{}^2)^2}\\ -\frac{11}{16}\left(\frac{1}{1+x_0{}^2}+\frac{\tan^{-1}x_0}{x_0}\right),\end{aligned} \tag{3.16}$$

where $x_0=\frac{1}{2}s_1K_0r_0$ is a dimensionless parameter with $s_1=\mu/m_1\lesssim 1$, and $K_0=2\pi/a$ is the average "radius" of the Brillouin zone for the fcc structure. The k-space cutoff K_0 is the one used in the usual polaron problem.[21] The "bare" factor S_0 is listed in Table II for typical alkali halides: RbCl, KCl, KBr, and KI, substances for which conduction-band masses have been inferred,[30] using Feynman's theory of the lattice polaron,[31] from

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[27] R. J. Elliott, Phys. Rev. **108**, 1384 (1957).

[28] C. Kittel, *Quantum Theory of Solids* (John Wiley & Sons, Inc., New York, 1963), p. 302.

[29] R. P. Feynman, Phys. Rev. **80**, 440 (1950).

[30] J. W. Hodby, J. A. Borders, F. C. Brown, and S. Foner, Phys. Rev. Letters **19**, 952 (1967).

[31] R. P. Feynman, Phys. Rev. **97**, 660 (1955); D. C. Langreth, *ibid.* **159**, 717 (1967).

TABLE II. Multiexciton parameters for typical alkali halides. The relative amplitude S for two-quantum excitation is the product of a bare polarization factor S_0 and a term $\sigma(x_0)$ related to the charge density form factor of the exciton.

	a(a.u.)	S_0	x_0	$\sigma(x_0)$	S
RbCl	12.36	0.323	0.495	0.03	0.009
KCl	11.86	0.310	0.535	0.045	0.014
KBr	12.44	0.376	0.591	0.055	0.021
KI	13.36	0.436	0.591	0.055	0.024

cyclotron resonance experiments.[30,32] Note that S_0 increases monotonically with Z, the halide atomic number, since valence shell polarizability, and with it the electron-exciton coupling strength, increases along this direction in the periodic table.

The electronic factor σ, shown in Fig. 1, has the property that (1) as $x \rightarrow \infty$, $\sigma(x) \rightarrow 1$ and (2) as $x \rightarrow 0$, $\sigma(x) \rightarrow 0$; also, the slope of σ has a maximum near $x=1$ ($K_0 r_0 \sim 1$). Thus, small-radius exciton states have smaller emission probabilities S_ν than do large-radius states (indeed, as $x \rightarrow 0$ the multipole fields of the exciton vanish and so cannot polarize the background). The saturation behavior of σ for large x is due to the momentum-space cutoff K_0.

The Huang-Rhys factors S are listed in Table II for Wannier 1*s* states in RbCl, KCl, KBr, and KI. These numbers were calculated assuming $m_2 \approx 10m$, ($s_1 \approx 0.9$) and the effective Bohr radius

$$r_0 = \mu^{-1}(\text{a.u.}) \tag{3.17}$$

(given in Table I) since screening corrections were found small for these tightly bound excitons. As noted above for S_0, the exciton emission probability S_ν increases with electron-exciton interaction strength α (or Z).

IV. DISCUSSION

We have merged two well-known theories in this work: (1) Toyozawa's theory of the electronic polaron[18] and (2) intermediate coupling theory based on the Lee-Low-Pines variational wave function.[21] This permitted the calculation of multiexciton optical transition rates for Wannier excitons in insulating solids. Like the earlier result for molecular crystals,[13–17] we find that two-exciton absorption is nearly two orders of magnitude weaker than is the familiar one-exciton process discussed by Elliott.[27] We emphasize that our theory leads to an upper limit for the double excitation rate in the Toyozawa model, since the valence charge polarization field has been "renormalized" into a single longitudinal exciton branch, In reality, in alkali halides the oscillator strength below threshold is an order of magnitude less than that above threshold, for excitations of the valence shells. In other words, the coupling constant α used in the calculations is too large, and the rate of double excitations has been overestimated.

As a first application of these results, the strong peak near 15 eV in LiF discussed by Miyakawa[11] probably cannot be attributed to the production of two excitons by a single photon.[33] In addition, anomalies in recent x-ray data on alkali halides[12] involving core excitations are not explicible in terms of this process; as shown by Muto and Okuno,[34] Wannier states associated with core excitations have Bohr radii, and hence S factors in our theory, only slightly different (smaller) than the radii of valence excitations. Of course, the approximate theory presented here does not accurately describe microscopic details of the polarization potential in the core region, since it is based on Toyozawa's dipole approximation. It is possible that core excitations are more strongly coupled to the polarization field than our theory allows, since the hole charge density is localized near the origin. However, an increase of S by several orders of magnitude, which would be required to explain the data of Ref. 12, seems unlikely.

The one-electron background near $2E_G$ in the absorption spectra of large-gap insulators is weak, due to exhaustion of the oscillator strength by exciton effects near E_G. Thus two-quantum excitations, though weak compared to optical transitions below the gap, may be observable in the spectra of alkali halides. Unfortunately, the complexities of structure near $2E_G$,[35] together with the availability of several theoretical mechanisms, prevent explicit identifications at present. We emphasize that since the exciton bands have dispersion the two-exciton peaks are expected to be broader than peaks below threshold (the total momentum $\mathbf{K}_1+\mathbf{K}_2 \approx 0$ for the two excitons). Auto-ionization broadens the bands still further.

Photoemission data can perhaps be used to distinguish double excitations from one-electron transitions (to high-energy excitons). Since the vacuum level lies above the energy gap, photoemissive yield drops sharply at the two-exciton threshold (neither electron has enough energy to leave the solid) and increases sharply beyond the two-exciton region, whose width in energy is determined by spin-orbit splitting of the 1*s* state (we assume higher states of the Rydberg series make negligible contribution since $f_\nu^{(0)} \alpha \nu^{-3}$), excitonic densities of state, lifetime broadening,[36] and auto-ionization.[37] Strong evidence for a two-exciton process can be said to exist when the yield has a significant dip in the energy region where the absorption coefficient has a peak (or peaks). When a dip occurs without corresponding absorption structure, it is possible that Auger excitation of an electron-hole pair (by a single photoelectron near $2E_G$) is primarily responsible for the dip. Even when two-exciton absorption is important, the Auger process must be considered as a possible contributor. Indeed the probability for the latter process, like the former, increases with valence polarizability in an electronic polaron model, since the same coupling constant governs both phenomena. We do not calculate Auger lifetime

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[32] M. Mikkor, K. Kanazawa, and F. C. Brown, Phys. Rev. Letters **15**, 489 (1965); J. Borders and J. Hodby (to be published).

[33] Although the conduction band mass in LiF is unknown, a reasonable guess is one-half the free-electron mass. This leads to (the upper limit) $S=0.032$.

[34] T. Muto and H. Okuno, J. Phys. Soc. Japan **11**, 633 (1956).

[35] P. H. Metzger, J. Phys. Chem. Solids **26**, 1879 (1965).

[36] Y. Toyozawa, Progr. Theoret. Phys. (Kyoto) **20**, 53 (1958).

[37] U. Fano, Phys. Rev. **124**, 1866 (1961).

effects because intermediate coupling theory is not valid near $2E_G$ (the variational displacement g_K of the Kth oscillator diverges due to a vanishing energy denominator). However, it is highly plausible that the trends in photoemissive yield predicted by our theory would be unchanged by these effects.

The main feature of the calculated two-quantum rates is that their ratio with one-exciton absorption increases with valence shell polarizabilities; i.e., $f^{(2)}/f^{(1)}$ increases in the sequence KCl, KBr, KI. Turning to Metzger's data,[35] we see that these qualitative predictions are consistent with the trends observed. The dip near $2E_G$ becomes more prominent towards the iodides, for all alkalis, and is nearly indistinguishable in RbF and CsF, which solids are characterized by large gaps and weak electron-exciton coupling.

The two-exciton process in solid rare gases is also weak. These crystals have very small Bohr radii and small coupling constants due to their large energy gaps and small dielectric constants. On the other hand, semiconductors correspond to values of x much larger than unity in Fig. 1. Our theory might well predict $f^{(2)}/f^{(1)} \approx 1$ for some systems characterized by small energy gaps. However, as noted above, the Toyozawa model breaks down for these crystals because the oscillator strength for the (longitudinal) exciton field is spread over a wide energy range compared to E_G,[38] and so cannot properly be renormalized into a single exciton band below threshold. Moreover, the one-exciton line is often difficult to resolve in semiconductors, and the much broader two-exciton structure will likely elude identification.

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[38] H. R. Phillipp and H. Fhrenreich, Phys. Rev. **129**, 1550 (1962).

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Vacancy Production and Volume Expansion in KBr and KBr-KCl Mixed Crystals*

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The generation of Frenkel defects in KBr and KBr–KCl mixed crystals after x irradiation at 66°K has been investigated. The growth of the optical absorption bands induced by the defects was studied, and the volume expansion was measured with the photoelastic technique. The relative defect production rate at 66 and 87°K can be explained simply in terms of the thermal stability of the vacancy-interstitial pairs. The energy required to produce a Frenkel defect pair at 66°K does not depend upon the quality of the x rays used to irradiate the crystals. The variation in the α/F ratio indicates that recombination luminescence is not an important factor in determining this ratio at 66°K. The volume expansion associated with the F-center Frenkel pair in pure KBr agrees with the results due to Lüty *et al.* for KBr–KH, indicating that the interstitial Br^0 atom causes little expansion. No volume expansion could be attributed to the V_4 center; thus, it cannot be the exact antimorph of the F center, but must involve a localized hole as in Kanzig's V_F center or Itoh's model of the V_4 center. Analysis of the α-center expansion data yielded an expansion at 66°K caused by the interstitial bromine ions which was smaller than that produced at 5°K. The expansion caused by F-center Frenkel pairs was larger in KBr–KCl crystals than in pure KBr. This indicates that the F-center production process involves the displacement of Cl^- ions from their substitutional sites. The expansion induced by α-center Frenkel pairs in the mixed crystals was half that observed in KBr. Possible explanations for this anomalous result would appear to be aggregates of α centers which are not additive in their effect and overlap to change the bulk compressibility of the crystal in their vicinity, or a similar change produced by the vacancy-interstitial pairs.

I. INTRODUCTION

It is now well established that the coloration induced in alkali halide crystals exposed to ionizing radiation at low temperatures arises from the creation of Frenkel defects and self-trapped holes in the perfect lattice.[1–4] In this process halide ions are displaced from their

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[1] J. M. Schulman and W. D. Compton, *Color Centers in Solids* (Pergamon Press, Inc., London, 1962).

[2] W. Känzig and T. Woodruff, J. Phys. Chem. Solids **9**, 70 (1958).

[3] H. Rabin and C. C. Klick, Phys. Rev. **117**, 1005 (1960).

[4] M. N. Kabler, Phys. Rev. **136**, A1296 (1964).