of the Brillouin zone where they could undergo direct recombination with holes in the valence band. A direct-recombination model such as this could also explain the temperature variation of the recombination time if one assumes that the activation energy corresponds to the depth of the valley minima of the lowest conduction band. If this were the situation, at very high temperatures one should measure the direct recombination time while at very low temperatures one could (ideally) measure the indirect recombination time, because all the electrons would be at the edges of the Brillouin zone. The estimates of valley depth given by Kahn and Leyendecker[5] were between 0.02 and 0.05 eV, which is considerably lower than our activation energy of 0.105 eV. However, recent experimental determination of electronic effective mass by Parker and Yahia[8] indicate a greater curvature of the valley minima than was estimated by Kahn and Leyendecker, suggesting that the valley depth may be larger than what was estimated.

A somewhat more straightforward interpretation of the temperature dependence of the results would be to assume that there are impurity states at about 0.105 eV below the conduction band which trap a larger percentage of the electrons as the temperature is lowered. One problem with this interpretation is the fact that experimental results showed no significant change in the induced absorption at 6328 Å as the temperature was lowered from room temperature to 145°K. Since, at the lower temperature, a great majority of the electrons would have to be in the traps, this interpretation would require that the absorption cross section of the electron in the trap and that of the free carrier be the same. This is possible although it would seem to be an unlikely coincidence.

Other explanations for the observed recombination behavior are also conceivable at this stage and more thorough photoconductivity and fluorescence measurements will be required to further clarify the choice of models.

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## EXCITON-PHONON BOUND STATE: A NEW QUASIPARTICLE*

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We point out that an exciton and an optical phonon may form a bound state which moves through the crystal. Calculated binding energies and oscillator strengths for this new quasiparticle lend support to recent suggestions that strong exciton-phonon mixing is present in the optical spectra of some ionic crystals.

In the optical spectra of some ionic crystals such as ZnO,[1] MgO and BeO,[2] and TlCl and TlBr,[3] the separation of the first exciton peak and a higher energy companion is less than the energy $\omega_0$ of the LO phonon by a fraction $\Delta \sim 10\%$. Also, spectral lines associated with the bound exciton in AgBr:I,[4] although observed at energy separations close to $\omega_0$ in emission, occur at separations nearly 30% smaller than $\omega_0$ in absorption. These facts suggest that (1) the companion structure may be associated with phonon sidebands and (2) final-state interaction between the exciton and phonon leads to a negative energy shift of this structure. To help clarify the situation, we present model calculations which demonstrate the possibility of bound states of the ex-

citon-phonon system, which are free to move through the crystal. The attractive force is ascribed to virtual transitions among internal states of the exciton.

A phonon sideband corresponds to simultaneous excitation of an exciton and a phonon with respective energies $E_0(\vec{k})$ and $\omega_0(-\vec{k})$ and momenta $\vec{k}$ and $-\vec{k}$ (the incident photon momentum may be neglected). We omit LO-phonon dispersion in comparison with that of the exciton, and assume that $E_0(\vec{k})$ has a minimum at $\vec{k}=0$. A second-order perturbation calculation of sideband shape predicts a continuum which starts at $E_0(0)+\omega_0$, rising with the three halves power of the energy, and extends over the energy range of a few times $\omega_0$. The peak is at $E_0(0)+(1+\nu)\omega_0$, where $\nu$ depends upon coupling constants and effective masses and is of order unity. The real discrepancy between lowest order perturbation theory and the observations cited above is therefore $(\Delta+\nu)\omega_0$ rather than the nominal shift $\Delta\omega_0$.

As long as perturbation theory converges, calculated exciton but not phonon energies are renormalized.[5] However, the observed energy shift may be associated with a bound state of the exciton-phonon system, in which case the perturbation expansion diverges. We now derive, from first principles, an attractive force which leads to splitoff bound states consistent with the interpretation of existing optical data.

Consider an electron and a hole with effective masses $m_e$ and $m_h$, interacting with each other by Coulomb's law and with the LO-phonon field according to the Fröhlich interaction. By introducing the exciton center-of-mass coordinate $\vec{R}$ and relative coordinate $\vec{r}$, and $\vec{K}$, the total momentum (a constant of motion) of the exciton-phonon system, the wave function can be written as $\Psi(b,\vec{r},\vec{R})=\exp[i(\vec{K}-\sum_{\vec{q}}\vec{q}b_{\vec{q}}^{\dagger}b_{\vec{q}})\cdot\vec{R}]\Phi(b,\vec{r})\equiv S\Phi$, in terms of creation and annihilation operators $b_{\vec{q}}^{\dagger}$ and $b_{\vec{q}}$ for phonons of wave vector $\vec{q}$. This unitary operator $S$, which was first introduced by Lee, Low, and Pines[6] in the polaron problem, leads to the transformed Hamiltonian[7]

$$S^{-1}HS=(\vec{K}-\sum_{\vec{q}}\vec{q}b_{\vec{q}}^{\dagger}b_{\vec{q}})^2/2M+\sum_{\vec{q}}\omega_0 b_{\vec{q}}^{\dagger}b_{\vec{q}}+E_g+p^2/2\mu-1/\kappa_o r+\sum_{\vec{q}}\{iV_q\rho_{\vec{q}}(\vec{r})b_{\vec{q}}+\text{H.c.}\},\tag{1}$$

where $E_g$ is the energy gap and $M$ and $\mu$ are exciton translational and reduced masses respectively. The electron-phonon coupling coefficient $V_q\equiv[2\pi\omega_0(\kappa_o^{-1}-\kappa_s^{-1})]^{1/2}q^{-1}$, $\kappa_o$ and $\kappa_s$ are the optical and static dielectric constants, and $\rho_{\vec{q}}(\vec{r})\equiv\exp(is_e\vec{q}\cdot\vec{r})-\exp(-is_h\vec{q}\cdot\vec{r})$ with $s_{e,h}\equiv m_{h,e}/(m_e+m_h)$.

We begin with the Hartree ground state[8] $\Phi(b,\vec{r})=\varphi(\vec{r})U(b)|0\rangle$, where $|0\rangle$ denotes the vacuum. Using the Lee-Low-Pines canonical transformation[6] $U(b)=\exp\{\sum_{\vec{q}}(d_{\vec{q}}b_{\vec{q}}^{\dagger}-d_{\vec{q}}^{*}b_{\vec{q}})\}$, where $d_{\vec{q}}$ is the displacement of the $q$th oscillator, we minimize the system energy with respect to $\varphi(\vec{r})$ and $d_{\vec{q}}$. As in Ref. 7, the result is a set of self-consistent equations; the lowest energy solution $[d_{\vec{q}}^{(0)},\varphi_0(\vec{r})]$ has energy $\tilde{E}_0(\vec{K})$. A complete set of internal exciton states $\varphi_\lambda$ (one of which is $\varphi_0$) with energies $\tilde{E}_\lambda(\vec{K})$ are determined[9] in the static field $d_{\vec{q}}^{(0)}$. Upon introducing creation-annihilation operators $a_\lambda^{\dagger}$ and $a_\lambda$ for these zero-order states, the effective Hamiltonian may be written as

$$\begin{aligned}H_{\text{eff}}\equiv U^{-1}S^{-1}HSU=&\sum_\lambda\tilde{E}_\lambda(\vec{K})a_\lambda^{\dagger}a_\lambda+\sum_{\vec{q}}[\omega_0-(1-\eta)\vec{K}\cdot\vec{q}/M+q^2/2M]b_{\vec{q}}^{\dagger}b_{\vec{q}}\\&+\sum_{\lambda\lambda'}\{iV_q(\rho_{\vec{q}\lambda\lambda'}-\delta_{\lambda\lambda'}\rho_{\vec{q}00})a_\lambda^{\dagger}a_{\lambda'}b_{\vec{q}}+\text{H.c.}\},\end{aligned}\tag{2}$$

where $\eta\equiv\sum_{\vec{q}}|d_{\vec{q}}^{(0)}|^2\vec{q}/\vec{K}$ and $\rho_{\vec{q}\lambda\lambda'}$ is the electron-hole density matrix in the $\varphi_\lambda$ representation. The omitted terms make no contribution to the energy within the approximation used below. As a result of eliminating $\vec{R}$ the exciton recoil energy appears in the phonon term.

Intraband scattering $\lambda=\lambda'$ vanishes for the exciton ground state $\lambda=0$ due to our self-consistent renormalization. Consequently, the second-order energy for this state has the energy denominator $\omega_0+\epsilon_\lambda$ $(\lambda\neq0)$, where $\epsilon_\lambda=\tilde{E}_\lambda(\vec{K})-\tilde{E}_\lambda(\vec{K})$ is the excitation energy of the exciton internal motion. For the one-phonon state, the second-order energy consists of the same term, corresponding to phonon emission, and an additional term due to phonon absorption with the energy denominator $-\omega_0+\epsilon_\lambda$. Although the second term is of order $N^{-1/2}$ for each plane-wave phonon state, it is possible to construct a coherent state with finite negative energy shift due to this term. The effect will be appreciable if the electron-hole binding energy $\epsilon_B$ is as small as $\omega_0$, for then a host of exciton states $\lambda\neq0$ are nearly degenerate with the one-phonon state.

To treat this near-resonant situation $\epsilon_B/\omega_0\sim1$ we use the following Ansatz for the next excited state

above the exciton ground state $\tilde{E}_0$:

$$\chi=(\sum_{\vec{q}} s_{\vec{q}} b_{\vec{q}}^{\dagger}) a_0^{\dagger}|0\rangle+\sum_{\lambda\neq 0} t_\lambda a_\lambda^{\dagger}|0\rangle. \tag{3}$$

Eliminating the zero-phonon amplitude $t_\lambda$ from the simultaneous Schrödinger equations for $s$ and $t$, we get the eigenvalue equation for the one-phonon amplitude $s$:

$$[\omega_0-(1-\eta)\vec{K}\cdot\vec{q}/M+q^2/2M-\omega]s_{\vec{q}}+\sum_{\vec{q}\vec{q}'}(\vec{q}\cdot\vec{q}'/M)d_{\vec{q}}^{(0)}d_{\vec{q}'}^{(0)*}s_{\vec{q}'}$$
$$-\sum_{\lambda\neq 0,\vec{q}'}(\epsilon_\lambda-\omega)^{-1}V_q V_{q'}\rho_{\vec{q}0\lambda}{}^{*}\rho_{\vec{q}'\lambda 0}s_{\vec{q}'}=0, \tag{4}$$

where we have measured the energy $\omega$ from $\tilde{E}_0$.

We confine ourselves to $\vec{K}=0$, and study only $s$-like solutions of Eq. (4). Then the second term vanishes because $d_{\vec{q}}^{(0)}$ is also $s$-like for $\vec{K}=0$. The third term is a nonlocal interaction between the exciton and phonon, due to virtual transitions among internal exciton states; at energies $\omega<\epsilon_\lambda$, for all $\lambda\neq 0$, the potential is attractive. Since LO-phonon dispersion has been neglected, the kinetic energy of relative motion is simply $q^2/2M$. Competition between the potential and kinetic energy terms in Eq. (4) determines whether a bound solution $\omega<\omega_0$ exists.

Three approaches were used to study the solutions of Eq. (4). In each case we took as $\varphi_0$ a $1s$ hydrogenic orbital with "Bohr" radius $a=\kappa'/\mu$ in terms of an effective dielectric constant $\kappa'$. The two-level model (I), in which only the $1s$ and $2s$ exciton states are taken into account, allows us to solve Eq. (4) exactly, since the integral kernel is separable. In general this model underestimates exciton-phonon binding energy since it limits internal degrees of freedom; however, it is quite useful for studying resonance effects between two nearly degenerate states. To estimate contributions from the higher excited states of the exciton we have employed a second model (II), based on the closure relation

$$\sum_{\lambda\neq 0}{}' \rho_{\vec{q}0\lambda}\rho_{\vec{q}'\lambda 0}=(\rho_{\vec{q}}\rho_{\vec{q}'})_{00}-\rho_{\vec{q}00}\rho_{\vec{q}'00},$$

after replacing the energy $\epsilon_\lambda$ in the denominator of (4) by a suitable average value $\bar{\epsilon}$. The lowest eigenstate was calculated by the variational method with a trial function $s_{\vec{q}}=q/(u^2+q^2)^2$. By putting $\epsilon=\epsilon_{2s}$ we clearly overestimate the strength of exciton-phonon attraction and can calculate (within the limitations imposed by our choice of trial function) an upper bound for the binding energy. Finally (III), we can replace the intractable sum $\sum_{\lambda\neq 0}t_\lambda\varphi_\lambda$ in (3) by a single trial function $\psi(\vec{r})$, assuming an effective Coulomb potential $-1/\kappa' r$. Choosing $\psi(\vec{r})=c[3-(1+\beta)r/a]\times\exp(-\beta r/a)$ which is orthogonal to the $1s$ exciton ground state irrespective of the variational parameter $\beta$, we have calculated the lowest eigenvalue of (4). Model I is obtained by putting $\beta=\frac{1}{2}$; minimization of $\omega$ occurs for $\beta>\frac{1}{2}$, or more localized orbitals $\psi$ which increase the potential energy. Throughout the calculations, we have put $\rho_{\vec{q}}(\vec{r})=\exp(i\vec{q}\cdot\vec{r})-1$, assuming $m_h\gg m_e$.

The bound-state solutions $\omega<\omega_0$ are shown in Fig. 1(a) as a function of $\epsilon_B/\omega_0$ for various values of the coupling parameter $\gamma\equiv\kappa'(\kappa_0^{-1}-\kappa_s^{-1})$ and the effective-mass parameter $\eta\equiv 4\mu/M$. For each pair of parameter values $(\gamma,\eta)$ three curves show the variation of our theoretical energies among the models described in the last paragraph. Comparison of I and II illustrates the contribution of higher exciton states; since I underestimates and II overestimates this contribution, the real situation should be somewhere between. Method III includes some of the effects of higher states but does not require the approximation of energy denominators. We expect this method to be most satisfactory; however, the variational calculations have been carried out only for the special cases $\eta=0$ $(M\to\infty)$ and $\omega=\omega_0$. The results for the latter, shown in Fig. 1(b), determine the existence criterion of the bound state.

The oscillator strength of the transition between the ground state of the crystal and the exciton-phonon bound state has been calculated also for models I and III. The dipole operator $P=P_0\sum_\lambda\varphi_\lambda(0)[a_\lambda^{\dagger}+a_\lambda]$ has transition-matrix elements

$$\langle 0|P|\Psi\rangle=\{\varphi_0(0)\sum_{\vec{q}}(-d_{\vec{q}}^{(0)*}s_{\vec{q}})+\sum_{\lambda\neq 0}t_\lambda\varphi_\lambda(0)\}\exp(-\sum_{\vec{q}}\tfrac{1}{2}|d_{\vec{q}}^{(0)}|^2), \tag{5}$$

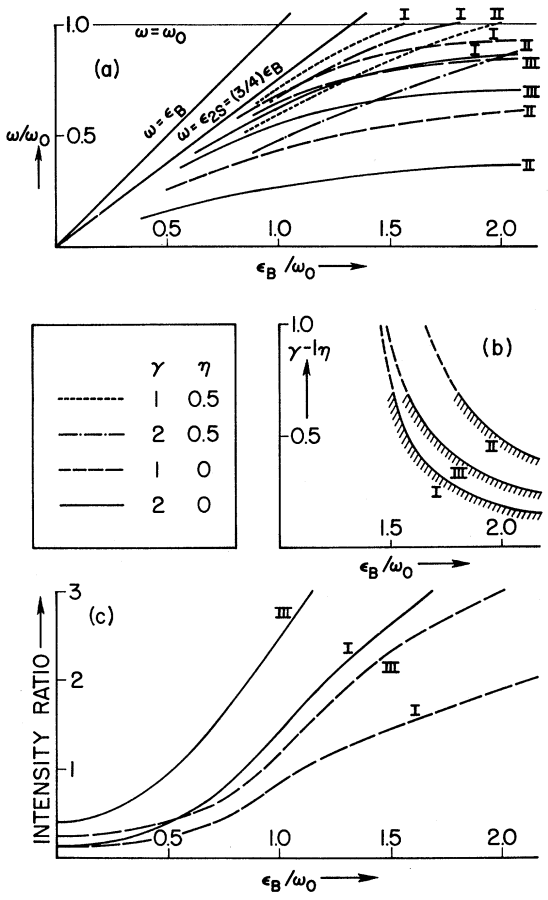


FIG. 1. (a) The energy of the exciton-phonon bound state, calculated by methods I, II, and III, as a function of $\epsilon_B/\omega_0$ for various values of $\gamma$ and $\eta$. (b) Existence criterion for the bound state. (c) Intensity ratio of the bound state and zero-phonon state for the case $\eta=0$.

where $\Psi=SU\chi$. Since $d_{\vec{q}}^{(0)}$ is spherically symmetric for $\vec{K}=0$, only $s$-like states are optically active. The oscillator strength, proportional to $|\langle 0|P|\Psi\rangle|^2$, contains a one-phonon part due to the first term in (5), a zero-phonon part from the second term, and an interference term. The quantity $\sum_{\vec{q}}|d_{\vec{q}}^{(0)}|^2$ in the exponent of the Debye-Waller factor gives the relative transition rate of the one- and zero-phonon lines in the absence of interband scattering $\lambda\neq\lambda'$. Calculated intensity ratios of the bound state and zero-phonon line are given in Fig. 1(c) as a function of $\epsilon_B/\omega_0$ and $\gamma$, for the simplest case $\eta=0$. Preliminary calculations for mobile states $\eta>0$ yield smaller oscillator strengths consistent with the weaker binding of these states. For large $\epsilon_B/\omega_0\gg1$ our results are not accurate, since the exciton Bohr radius is comparable with the lattice parameter and phase-space integrals for the oscillator strength (and binding energy) are overestimated. We note that the results for methods I and III are qualitatively similar but differ in magnitude due to the more localized excited state used in III, which leads to stronger exciton-phonon binding. Also, the binding energies and oscillator strengths increase monotonically with coupling strength $\gamma$.

It should be noted that even at absolute zero temperature the exciton-phonon bound state (with $K=0$) has a finite probability of decaying into an ordinary exciton state by emitting an acoustic phonon with wave vector $K=(2M\omega)^{1/2}$. The lifetime broadening due to this decay is estimated to be of the order of $E_d^2MK^2/2\pi\rho u\hbar$, where $E_d$ is the deformation potential for the exciton, $u$ the sound velocity, and $\rho$ the density of the crystal. It is smaller than $\omega_0$ by one order of magnitude. This means that at low temperatures the exciton-phonon bound state can be observed as a distinct peak in the absorption spectra.

As seen in Fig. 1(b) the exciton-phonon bound state exists for $\gamma\sim1$ if the effective-mass ratio $m_h/m_e$ (or $m_e/m_h$) is large or $\epsilon_B$ is near $\omega_0$. For $\epsilon_B$ appreciably less than $\omega_0$ our solution corresponds to an excited state of the exciton, renormalized by virtual emission and reabsorption of LO phonons. This is evident in Fig. 1(c), where the intensity ratio decreases rapidly as $\epsilon_B$ decreases, tending to a small value characteristic of the higher exciton state. The question whether there is, above $\epsilon_B$, a quasibound state of predominantly one-phonon character requires further study. It should also be noted that apart from minor modifications to be made, we can describe the exciton bound to an imperfection, by putting $\eta=0$ in our theory, since there is no exciton recoil.

In connection with the optical data cited[1-4] in the introduction, our approximate calculations are consistent with the following observations: (i) Negative energy shifts have been reported for higher energy peaks only in those crystals for which $\epsilon_B$ and $\omega_0$ are not very different; (ii) the shift is around 10% for intrinsic (mobile) excitons but somewhat larger for bound excitons; (iii) the intensity ratio with the first exciton line is larger for bound excitons; (iv) the oscillator strength of the higher energy peak is larger than expected for pure electronic excited states of the exciton. Consequently, our results lend support to the suggestions of Refs. 1-3 that strong exciton-phonon mixing may be present in the spectra of several ionic crystals with shallow excitons. The broad sideband corresponding to the creation

of a free pair of an exciton and an LO phonon seems to be obscured in these crystals because of its overlap with the continuum of interband transitions which has larger intensity.

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## GENERATION OF 100 WATTS OF COHERENT OPTICAL PHONONS IN QUARTZ

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By simultaneously sending through a quartz sample two coherent light beams having a beat frequency equal to the frequency of the 207-$cm^{-1}$ optical mode of the quartz, we have been able to generate coherent optical phonons with an estimated power of 100 W.

The emission of Stokes light by Raman and Brillouin scattering can be described as[1]

$$\text{photon } 1 \rightarrow \text{phonon} + \text{photon } 2. \quad (1)$$

When a low-power laser beam of photons 1 (frequency $\nu_1$) is propagating in a material medium, incoherent photons 2 ($\nu_2$) and incoherent phonons ($\nu = \nu_1 - \nu_2$) are generated. The higher the pumping power, the greater the number of spontaneous photons 2 created will be. Finally, a threshold is reached and the phenomenon becomes stimulated at a still higher pumping power. At this state, both photons 2 and phonons then become coherent.

If relation (1) is written as

$$\text{photon } 1 - \text{photon } 2 \rightarrow \text{phonon}, \quad (2)$$

we see that a very efficient way to produce coherent phonons without threshold is to send simultaneously two coherent light beams with frequencies $\nu_1$ and $\nu_2$ through a Raman-active crystal; if phonons having a frequency $\nu = \nu_1 - \nu_2$ can be propagated, a beat will be driven in the crystal. The effect is then immediately stimulated.

An energy $P_1$ is thus transferred from the light beam of higher frequency to the elastic wave and the secondary light beam, which receive, respectively, powers $p$ and $P_2$, where $P_1$, $P_2$, and $p$ are related by the Manley-Rowe equations $P_1/\nu_1 = P_2/\nu_2 = p/\nu$. As $\nu_1$ and $\nu_2$ are higher than $\nu$ by several orders of magnitude, an easy way for measuring the intensity of the produced phonons is to measure $P_1$ or $P_2$.

For the Brillouin effect, this two-beam method has been theoretically studied by Kastler[1] and Kroll[2]; Caddes and co-workers[3] have produced acoustical phonons in this way. On the other hand Papoular and Chartier[4,5] have suggested generalizing this method to the Raman effect, and we think we are the first to have produced coherent optical phonons in this way, viz., by beating two light beams of appropriate frequencies.

The experimental setup is given in Fig. 1.