Self-Trapped Exciton Defects in a Charge Density Wave: Electronic Excitations of BaBiO₃

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I. INTRODUCTION

The previous paper on BaBiO₃resents a simple and yet sufficiently realistic model which gives a microscopic description of the Peierls distortion, and makes unambiguous predictions about the low-energy behavior. The previous paper looks carefully at the small polarons created by doping or photoemission. These were noticed already by Yu, Chen, and Su. Here we examine what happens when an electron-hole pair is inserted, and discover a self-trapped exciton which has not previously been discussed. This exciton gives a natural explanation for the Urbach tail seen in optical absorption and for the multi-phonon spectrum of the “breathing mode” seen in Raman scattering. These two phenomena occur because of the Franck-Condon effect associated with oxygen displacement in the excited state.

71.38+i, 71.45.Lr

II. ATOMIC LIMIT $T = 0$

As in the previous paper, the zero bandwidth ($t = 0$, $\Gamma \to \infty$) case provides a soluble limit which gives good insight into the more complete theory. If a hole is created in the lower Peierls or occupied valence band, and an electron in the upper Peierls or empty conduction band, without allowing any lattice relaxation, the energy cost is $2\Delta = 24g^2/K$. The hole is a Bi$^{4+}$ ion on a site normally occupied by Bi$^{3+}$, and the electron is a Bi$^{4+}$ ion on a site normally occupied by Bi$^{3+}$.

Because of the simple Hamiltonian, the problem has particle-hole symmetry. This is true at all values of parameters, not just $t = 0$. Upper and lower Peierls bands have energies $\pm \lambda(\vec{k})$ where $\lambda(\vec{k}) = \sqrt{\Delta^2 + \epsilon(\vec{k})^2}$, and $\epsilon(\vec{k})$ is the nearest neighbor “cosine” band dispersion. Thus particle and hole bands are symmetrical.

If the electron and hole are spatially separated, each will lower its energy by lattice relaxation. Both electron and hole save $3\Delta/4$ in elastic energy by moving surrounding oxygens half way back to their cubic perovskite positions. However, each unpaired electron on a Bi$^{4+}$ ion has its on-site energy increased by $\Delta/2$, for a net lowering of energy by $\Delta/4$ for each, or a cost of $3\Delta/2$ to create the isolated pair of polarons.

As shown in Fig. 1, there is an advantage to having the electron and hole polarons form on adjacent Bi ions. The oxygen between the two Bi$^{4+}$ ions can further relax to the undistorted perovskite position. Rather than 12, now only 10 oxygens are half displaced, saving an additional $\Delta/12 = g^2/K$ in elastic energy. This bound pair of polarons, called a “self-trapped exciton,” costs $E_{\text{exc}} = 17\Delta/12$ rather than $2\Delta$ to create. The total energy gain from lattice relaxation is the exciton binding energy $\epsilon_{\text{exc}} = 7g^2/K$. Taking the on-site Coulomb interaction into account, the break-up of the Bi$^{3+}$ paired electrons into separated electron-hole pairs will reduce the excited state energy further, to $\epsilon_{\text{exc}} = 7g^2/K + U$ where $U$ is the Hubbard on-site Coulomb repulsion.
FIG. 1. Schematic structure of the self-trapped exciton. The electron is in the left-central cell (“exciton-electron”), the hole (“exciton-hole”) in the right-central cell. Filled circles are Bi$^{3+}$ ions with two $s$ electrons, shaded circles are Bi$^{4+}$ ions with one $s$ electron, and open circles are Bi$^{5+}$ ions with no $s$ electrons. X’s denote oxygen ions. The central oxygen ion is undisplaced, which lowers the energy relative to separated electron and hole polarons.

The energy of the ground and excited state depend on the amount of lattice distortion. The configuration coordinate $\alpha$ smoothly connects the optimal oxygen configurations of the ground state at $\alpha = 0$ and the self-trapped exciton state at $\alpha = 1$, as shown in Fig. 2. The energy depends quadratically on $\alpha$, separating ground and excited state by the gap $2\Delta$ at $\alpha = 0$.

III. NUMERICAL RESULTS

For $t \neq 0$ we are not able to solve analytically, and rely on numerical studies. We find that the excited state has zero slope $dE/d\alpha = 0$ at $\alpha = 0$, and downward curvature. No potential barrier separates the excited state at $\alpha = 0$ and the self-trapped exciton at $\alpha = 1$. This is contrary to most self-trapped exciton theories [6], where a metastable free excited state and a self-trapped exciton state can coexist, separated by a potential barrier.

For $t \neq 0$, localizing and delocalizing terms in the Hamiltonian compete against each other, yielding a critical coupling constant $\Gamma_c(\text{exc})$ above which self-trapped exciton states exist. To obtain the lowest excited state numerically, oxygen positions are varied using the algorithm described in the preceding paper, under the constraint that an electron was removed from the highest-lying valence band state and inserted in the lowest-lying conduction band state. We find $\Gamma_c(\text{exc}) \approx 0.175$, close to the polaron stability limit $\Gamma_c(P) = 0.18$ of the previous paper. Since the self-trapped exciton is an electron-polaron weakly bound to a hole-polaron, it is not surprising that the polaron and the self-trapped exciton have similar threshold coupling constants. The first correction to strong coupling for $\epsilon_{\text{exc}}$ can be approximated using a “vacuum correction” of order $1/\Gamma^2$ discussed in Sect.III.A of the preceding paper: $\epsilon_{\text{exc}}/t \approx 7\Gamma - 1/2\Gamma$ and approaches asymptotically the $t = 0$ limit $\epsilon_{\text{exc}} = 7g^2/K$.

FIG. 2. Excited state and ground state energy versus configuration coordinate $\alpha$ for $t = 0$. At $\alpha = 0$, the ground and excited state are separated by the gap $2\Delta$. The self-trapped exciton at $\alpha = 1$ has its energy lowered by the maximal amount – the exciton binding energy $\epsilon_{\text{exc}}$. Including on-site Coulomb repulsion, the energy curve of the excited state will be shifted down by the Hubbard $U$.

FIG. 3. Exciton binding energy $\epsilon_{\text{exc}}$ for $t \neq 0$ computed numerically. The bold solid line is the $t = 0$ prediction. The dashed line is an approximate $1/\Gamma^2$ correction.

The behavior of self-trapped exciton states and their evolution with $\Gamma$ is very similar that of polarons [1]. The local change in the oxygen environment leads to the appearance of localized gap states (Fig. 4) in addition to the states which constitute the exciton.
cated by the diverging radius. The self-trapped exciton

\Gamma

The particles are confined approximately to one site for

the two states comprising the exciton is shown in Fig. 5.

\textit{\textbf{FIG. 5.}} Radius \langle r \rangle of the exciton-hole and exciton-electron.

A radius of 0 corresponds to complete localization of the

wave-function at one site. The radius diverges as \Gamma \to \Gamma_c(E).

The finite value at \Gamma_c(E) is caused by the finite system size of

the numerical calculations. Inset: IPR-values of the gap

states, indicating their degree of localization. They approach

their asymptotic (symmetry determined) IPR values of 1, \frac{1}{3},

\frac{1}{7} (doubly degenerate), \frac{11}{27} and 1 for \Gamma \to \infty.

\section*{IV. OPTICAL PROPERTIES}

In this section we discuss the observability of self-

trapped excitons in experiment \textit{via} an Urbach tail in opt-

ical absorption experiments and a multi-phonon spec-

trum of the “breathing mode” in phonon experiments,

both governed by the Franck-Condon effect. Zheng and

Nasu have also obtained theoretically a tail in the optical

conductivity. Their theory includes quantum lattice

fluctuations (as does ours) and bears some relation to our

theory.

As a first step we neglect both Coulomb and lattice polar-

ization effects. Then the imaginary part of the dielec-

tric constant can be computed exactly in electric dipole

approximation. The dipole matrix element between an

s state on a Bi atom at \vec{R} and one on the neighboring

Bi atom at \vec{R} + a \hat{x} is \text{-} int \partial \vec{E} / \partial \vec{k}. This gives the correct

intraband \textless \vec{E} \text{|} \vec{p} \text{|} \vec{k} \text{>} = (m/\hbar) \partial \vec{E} / \partial \vec{k} relation between mo-

mentum matrix element and group velocity. Then for for

unpolarized light we get

\begin{equation}
\epsilon_2(\omega) = \frac{4e^2 t^2}{m^2 \omega_0^2 \pi \hbar^2} \int_{BZ} d^3 \vec{k} \left( \sin^2(k_x a) + \sin^2(k_y a) + \sin^2(k_z a) \right) \times \delta(2\sqrt{\epsilon_k^2 + \Delta^2} - \hbar \omega).
\end{equation}

This was evaluated numerically using a tetrahedron code

\cite{8,9}, and is shown as the dashed line in Fig. 5. The

behavior of \epsilon_2 is dominated by the divergence of the

the charge-density wave, before disappearing into a band

electron-hole pair at \Gamma_c(E), just as \text{\textit{\textbf{FIG. 3.}}} the small polaron

evolves through a large CDW-like polaron state before

becoming a band hole at \Gamma_c(P).
joint-density of states at photon energy $\hbar \omega = 2\Delta$, corresponding to transitions from states at the top of the lower Peierls band into those at the bottom of the upper band. These states are mainly responsible for the charge disproportion and have vanishing amplitude on the $B$ and $A$ sites respectively. These are also the states from which localized polaron and self-trapped exciton states form. Since transitions between these states are highest in optical density, we may expect the line shape to be dominated by the signature of self-trapped excitons.

Materials with self-trapped excitons show Franck-Condon broadening of electronic transitions, a concept well known to molecular spectroscopists, since molecular excited electronic states generally have altered nuclear coordinates. The process involves simultaneous creation of electronic excitation and nuclear vibrations, causing the appearance of vibrational sidebands in the electronic spectra [10]. In simple solids, excitations are usually delocalized which eliminates this effect [11]. However, in case of self-localized states, because of their significant lattice relaxation, Franck-Condon broadening of the electronic transitions must reappear. $\epsilon_2(\omega)$ in Franck-Condon approximation is given by:

$$\epsilon_2(\omega) \propto |P_{\lambda\lambda'}|^2 \sum_n \sum_{n'} w_{\lambda n} |\langle \lambda n | \lambda' n' \rangle|^2 \delta(h\omega + E_{\lambda n} - E_{\lambda' n'},$$

where $P_{\lambda\lambda'}$ is the electronic dipole matrix element between the electronic ground state $\lambda$ and excited state $\lambda'$, $w_{\lambda n}$ the probability to find $n$ vibrational quanta in the electronic ground state and $|\langle \lambda n | \lambda' n' \rangle|$ the overlap integral between the vibrational wave functions $\chi_{\lambda n}$. This integral can be large even when the vibrational quantum numbers $n, n'$ are quite different from each other, because the vibrational wave-functions $\chi_{\lambda n}$, $\chi_{\lambda' n'}$ have origins which are off-set from each other.

At zero temperature, the broadening of the electronic transition derives from the overlap of zero point motion of the oxygens with excited vibrations in the electronic excited state. The sum over $n$ in Eq.(3) then has only one term, $w_{\lambda n} = \delta_{n,0}$ . We lift the adiabatic approximation applied so far by adding quantized vibrations, but treat the problem in the atomic limit ($t=0$), i.e. in single site approximation. The excited electron states couple to eleven oxygens, which are treated as independent Einstein oscillators with frequency $\omega_0$ and oxygen mass $M$ in our model. They move in harmonic potentials and thus the Franck-Condon factor [12] is a product of eleven vibrational overlap integrals of the form $|\langle 0 | n \rangle|^2$ with:

$$|\langle 0 | n \rangle|^2 = \left( \frac{\alpha^2}{2} \right)^n \frac{(R - R')^n}{\sqrt{n!}} \exp\left( -\frac{\alpha^2}{4} (R - R')^2 \right),$$

where $\alpha = \sqrt{M \omega_0 / \hbar}$ and $R$ and $R'$ are the oxygen equilibrium positions of the ground and excited state respectively. The total absorption at a frequency $\hbar \omega = E_{\text{exc}} + n\hbar \omega_0$, requires a sum over all different ways to distribute $n$ quanta over the eleven oxygens. The result is

$$\epsilon_2(\omega) = \frac{4\pi^2 e^2}{m^2 \omega^2} \sum_n \frac{1}{n!} \left( \frac{7\Delta}{12\hbar \omega_0} \right)^n \exp\left( -\frac{7\Delta}{12\hbar \omega_0} \right) \times \delta(h\omega - \frac{17}{12} \Delta + n\hbar \omega_0).$$

In our simplified Einstein model, absorption occurs at discrete frequencies corresponding to different numbers of vibrations created in the absorption process. In reality these peaks are broadened by phonon dispersion, and discreteness of the individual peaks should only be seen for one or two vibrational quanta. The line shape should look similar to the envelope function of Fig.6 with maximal absorption at $\omega = 2\Delta$ and significant absorption below the gap at $2\Delta = 2\hbar\omega_0$.

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FIG. 6. Imaginary part of dielectric constant versus frequency. The dashed line shows Eq.(2), where the integral was evaluated with a tetrahedron code [8,9]. Taking lattice relaxation into account the absorption spectra will be dominated by the Franck-Condon effect Eq.(3), leading to significant peak broadening and absorption in the gap, known as an Urbach tail.

The absorption spectra of self-trapped excitons will change with temperature due to the temperature-dependent occupation of vibrational states in the electronic ground state given by $w_{\lambda n} = \exp(\beta n\hbar \omega_0) / Z$, where the partition function $Z = (1 - \exp(\beta \hbar \omega_0))^{-1}$ and $\beta = 1/k_B T$. Temperature enhances the absorption in the low energy regime and shifts the on-set of absorption to smaller energies. The temperature effect up to room temperature is very weak. At $T = 300K$ the probability to find a phonon on one of the eleven oxygens is less than 6%. The analytical calculations for temperature corrections become increasingly tedious and Fig.6 shows a first temperature correction obtained numerically.
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FIG. 7. Imaginary part of dielectric constant (logarithmic scale) versus frequency at $T=0$, and the first temperature correction to the Franck-Condon spectra at 300K.

The clearest evidence for self-trapped excitons is normally observation of weak sub-gap features in optical absorption $\alpha(\omega) \propto \epsilon_2(\omega)$ and a large Stokes shift in the luminescence spectrum. We are not aware of luminescence measurements. Transient absorption measurements have been interpreted as indicating that interband excitations relax rapidly to a state shifted down by 0.7 eV. Transmission measurements through thin single crystals were reported by Kozlov et al. These have been interpreted as showing an indirect band gap at 0.5 eV with anomalous temperature dependence. We believe that the measured absorption can be re-interpreted as an Urbach tail arising from the self-trapped exciton, with binding energy $\epsilon_{\text{exc}}$ enhanced beyond our values by the on-site Coulomb $U$.

Clear experimental support for the existence of self-trapped excitons in BaBiO$_3$ comes from harmonics of the Peierls breathing mode phonon seen both in Raman experiments and in the infrared. These spectra are dominated by a strong peak at 570 cm$^{-1}$, assigned to the breathing mode $Q = 0 A_{1g}$ phonon. Unlike in ordinary semi-conductors, a series of higher harmonics is observed. The simplest explanation for the Raman process is that the incoming photon creates a virtual self-trapped exciton, except that because of the Franck-Condon principle, the lattice coordinates stay at their ground state rather than their excited state values, which means that a cloud of virtual local vibrations is also created. When this virtual excitation re-radiates the scattered photon, not all the virtual vibrational quanta need to disappear. The test of this mechanism is that this process is resonant when the laser photon energy coincides with the Peierls gap. This resonance was seen by Tajima et al. Similar behavior occurs in the Raman spectrum of LaMnO$_3$ where a somewhat different species of self-trapped exciton is predicted to occur. In the infrared spectrum of BaBiO$_3$, the selection rule against Raman phonons appearing in infrared must be violated by local loss of inversion symmetry due to static or dynamic lattice fluctuations. Multiples of the breathing phonon are as easily excited as a single phonon because of the vibrational overlap factors.

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[1] I. Bischofs, V. Kostur, and P. B. Allen, preceding paper.
[2] T. M. Rice and L. Sneddon, Phys. Rev. Letters 47, 689 (1982); P. Prelovsek, T. M. Rice, and F. C. Zhang, J. Phys. C 20, L229 (1987).
[3] J. Yu, X.-Y. Chen, and W. P. Su, Phys. Rev. B 41, 344 (1990).
[4] M. E. Kozlov, X. Ji, H. Minami, and H. Uwe, Phys. Rev. B 56, 12211 (1997).
[5] S. Tajima, S. Uchida, A. Masaki, H. Takagi, K. Kitazawa, S. Tanaka, and S. Sugai, Phys. Rev. B 35, 696 (1987).
[6] K. S. Song and R. T. Williams, Self-Trapped Excitons, 2nd Ed., (Springer, Berlin, 1996).
[7] H. Zheng and K. Nasu, Physica B 292, 344 (2000).
[8] G. Lehmann and M. Taut, Phys. Stat. Sol. (b) 54, 469 (1972); 57, 815 (1973).
[9] O. Jepsen and O. K. Andersen, Sol. State Commun. 9, 1763 (1971).
[10] G.Herzberg, Spectra of Diatomic Molecules, (Van Nostrand, 1950).
[11] E.I. Rashba, Opt. Spektrosk. 2, p.75 (1957).
[12] K. Huang and A. Rhys, Proc. R. Soc (London), Ser. A 204, 406 (1950).
[13] J. F. Federici, B. I. Greene, E. H. Hartford, and E. S. Hellman, Phys. Rev. B 42, 923 (1990).
[14] V. Perebeinos and P. B. Allen, cond-mat/0007302 and Phys. Rev. B (in press).
[15] P. B. Allen and V. Perebeinos, Phys. Rev. Letters 83, 4828-31 (1999).