Review of lightly doped BaBiO$_3$

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1 Motivation

Insulating BaBiO$_3$ can be a metal (in fact, superconductor) by hole-doping with substitutional K or Pb such as $(\text{Ba}_{1-x}\text{K}_x)\text{BiO}_3$ or $\text{Ba}(\text{Bi}_{1-x}\text{Pb}_x)\text{O}_3$. The insulator-metal transition, however, occurs at remarkably high critical dopant concentration (0.65 for Pb or 0.35 for K). Besides, the metal, which becomes a superconductor, has a high superconducting critical temperature ($T_c \approx 30$ K). It can be compatible with a conventional electron-phonon mechanism, but has not been understood obviously by either theory or spectroscopy.

2 Model

The research by Allen et al.[1, 2, 3] is based on the Rice-Sneddon model[4] considering a cubic structure which occurs at $T \approx 800$K. In the model, BaBiO$_3$ is viewed as a valence configuration of $\text{Ba}_2(\text{Bi}^{3+}\text{Bi}^{5+})\text{O}_6$, which is stabilized by polarizing the O octahedron. When nearest neighbor oxygens move away from the Bi atom, electrons are accumulated, i.e. the Bi ions become Bi$^{3+}$ ($5d^{10}6s^2$), because of lowering the potential energy of electrons. When the oxygens move in the opposite direction, the Bi ions become Bi$^{5+}$ ($5d^{10}6s^0$). So Bi atom has an electronic degree of freedom, the amplitude of 6s electron orbital ($C_i^+$). Neglecting the influence of vibrations perpendicular to bond directions, “a local dilation or breathing amplitude $e(l)$” can be defined such as

$$e(l) = \sum_{\alpha=x,y,z} [u(l^+,\alpha) - u(l^-,\alpha)]$$

(1)

$$= \sum_{\alpha=x,y,z} [u(l^+\alpha) - u(l^-\hat{\alpha},\alpha)]$$

(2)

where $u(l^\pm,\alpha)$ is the displacement of oxygen atoms at $a\hat{l} \pm (a/2)\hat{\alpha}$. $a$ is a lattice constant 4.28 Å.
Using the Raman spectroscopy result of $\hbar \omega=70$ meV for the O breathing mode, the O displacement $u(\vec{l}, \alpha)$ is 0.087 Å. Then the elastic constant $K$ is 19 eV/Å² because each O displacement costs elastic energy $(K/2)u(\vec{l}, \alpha)^2$.

The resulting Hamiltonian is

$$H = -t \sum_{<l,l'>} c_{l'}^+ c_l - g \sum_l e(\vec{l}) c_{l'}^+ c_l + \frac{1}{2} K \sum_{\vec{l}, \alpha} u(\vec{l}, \alpha)^2$$

where $t$ is a nearest neighbor $< l, l'>$ hopping integral and $g$ is the deformation potential. Using the adiabatic approximation treating O mass as infinite (i.e. without oxygen displacement), within the tight banding model the energy dispersion is given by

$$E(\vec{k}) = -2t[\cos(k_x) + \cos(k_y) + \cos(k_z)]$$

By comparison with band calculation, the hopping integral $t$ is 0.35 eV, which is appropriate for the bandwidth $\omega = 12t \approx 4$ eV.

The dimensionless coupling constant $\sqrt{\Gamma}$, $\Gamma = g^2/Kt$, is introduced so that the energies are measured in units of $t$ and the lattice displacement in units $\sqrt{t/K}$. If the deformation potential, $g=1.39$ eV/Å, is chosen for a Peierls band gap $2\Delta$ to be agreed with optical measurement $\approx 2$ eV, the coupling constant $\Gamma$ is 0.30 for the undoped BaBiO₃ which is intermediate between weak ($\Gamma \ll 1$) and strong coupling ($\Gamma \gg 1$).

3 Polaron and bipolaron

Allen et al. treat the problem in the extreme atomic limit ($\Gamma \to \infty$) to neglect the hopping term because of mathematically greatly simplification.

3.1 Bipolaron crystal

Within the extreme limit of a Peierls charge density wave (CDW) for half-filled Bi $s$ level, the strong-coupling solution consists of Bi$^{3+}$ ($6s^2$) on sublattice A and Bi$^{5+}$ ($6s^9$) on sublattice B. The paired electrons are called as “bipolarons” or “negative U centers”.

Let us define the Peierls order parameter (amplitude of CDW) $\rho_0$ by

$$\Sigma_{\sigma} < c_{l'}^+ c_l >= 1 + (-1)^L \rho_0$$

where $(-1)^L$ is 1 for the sublattice A and -1 for the sublattice B. While the undistorted cubic structure has $\rho_0=0$, the strong coupling limit does $\rho_0=1$. An oxygen between a Bi ion on A site and a Bi ion on B site experiences two forces, $2g\rho_0$ toward B site and restoring force $Ku$ in the opposite direction, so that the optimum displacement $u_0$ is $2g\rho_0/K$ or breathing amplitude $12g\rho_0/K$. For strong coupling ($\rho_0 \to 1$) and zero hopping integral, the lowest energy excitation
is an electron transfer from site A to site B with energy cost (Peierls gap) \(2\Delta_0 = 24g^2/K = 24\Gamma t\).

The total energy is \(-6\Gamma t (-12g/K^2\) per electron of on-site orbital energy and \(6g/K^2\) per atom of elastic energy) in the strong coupling limit, but hopping energy \(-2t\) for the weak coupling limit. Thus, the critical value \(\Gamma_c\) for crossover between strong and weak limit is 1/3.

### 3.2 One hole in the atomic limit

Keeping the Peierls distortion fixed, the energy cost to remove an electron is \(12g^2/K\). If the hopping integral is zero, the hole is on A site, and then the oxygen local Peierls displacement is \(u_1 = g\rho_0/K = u_0/2\). In a result, the reduced elastic energy is \(6 \times K(u_0^2 - u_1^2)/2 = 9g^2/K\) and the energy of the s orbital on A site is raised by \(-6g^2/K\). Therefore, the net energy saved by this local distortion is \(3g^2/K\). Considering a N Bi atoms system, the isolated polaron is the system having \(N - 1\) electrons. The energy of the polaron is \(E[P] = E_{gs}(N - 1) - E_{gs}(N) = 9g^2/K\). The energy difference between \(E[P]\) and the electron removal energy without Peierls distortion is the polaron trapping energy \(E_t[P] = 3g^2/K\).

### 3.3 Two holes in the atomic limit

The bipolaron trapping energy is given by \(E_t[B] = 12g^2/K\). When two polarons bind into a singlet bipolaron, the released energy is \(E_b = 6g^2/K\), but the on-site Coulomb repulsion interaction \(U\) should be subtracted. The Coulomb repulsion is the energy difference between \(E(Bi^{3+}) + E(Bi^{5+})\) and \(2E(Bi^{4+})\). But, in a single band model, the effective \(U\) is about 0.6 \pm 0.4 eV, very close to the activation energy \(6g^2/K \approx 0.6\) eV. Even if hopping is turned on, \(U\) is less effective since the attractive energy is decreased and the bipolaron is spread out. Therefore, \(U\) is small enough to permit bipolarons to exist.

For small hopping \(t\), however, the Peierls gap can be expanded by

\[
\Delta = \Delta_0(1 - \frac{1}{48\Gamma^2} + ...) \quad (6)
\]

Since the energy state is \(\lambda(k) = \pm \sqrt{\Delta^2 + E(k)^2}\), the energy cost to delocalize hole is diminished. As a result, the competing bipolaron state cannot be completely localized on a site.

### 3.4 Numerical study of polaron

Bischofs et al.[1] used about 200 atoms to study doping by one or two holes per supercell for \(\Gamma > 0.22\).

The results show that \(\Gamma\) should be greater than 0.18 for polaron to be stable and 0.15 for bipolaron to be stable. At low \(\Gamma\), an inserted hole just stays at the top of the valence band due to the Peierls gap.
In the $\Gamma \to \infty$ limit, the polaron trapping energy is $E_t[P] = 12\Gamma t - 9\Gamma t$. Only correlated by the vacuum term (half-filled ground state), the energy is $E_t[P]/t \approx 3\Gamma - (1/4)\Gamma$. For the bipolaron, however, $E_t[B]/t \approx 12\Gamma - (1/2)\Gamma$.

For the realistic value $\Gamma = 0.3$, the depleted electrons from the central A site are 0.84 electrons for the polaron and 1.74 electrons for the bipolaron. For the polaron, 0.16 electrons are taken from some site. (Actually, neighboring A is more depleted electrons, while neighboring B gains electrons.)

The perturbation by the polaron defect is strong enough to create 6 new localized states at the bottom of the conduction band. In the strong coupling limit, when the hopping $t$ is turned on, the six states are split into a s-like, d-like doublet, and p-like triplet. The s-like state is bound only for $\Gamma$ above 0.30 for a polaron and 0.28 for a bipolaron.

3.5 Mobility of bipolarons

At T=0K, the band formation occurs with bandwidth exponentially reduced by Huang-Rhys factors $e^{-S}$ [5] from the vibrational overlap integrals. In the strong coupling limit, the factor S is given by

$$S = \frac{12 M w (u_0 - u_1)^2}{\hbar}$$

(7)

$$= \frac{\Delta \Delta 1}{\hbar w t 48\Gamma} \approx 2.8$$

(8)

The polaron band width is of order 0.06 eV, thus Anderson localized polaron is expected since the disorder caused by the dopant atoms should be larger. For the bipolaron, the Huang-Rhys factor is smaller by $2 \times 10^{-4}$ than for polaron, so it will be completely immobile.

At high temperature ($k_B T \approx \hbar w$), the bipolaron mobility is $w \times \exp(-E_s/k_B T)$. For the realistic value $\Gamma = 0.3$, the activation energy $E_s \approx \Delta/3 \approx 0.3$ eV, experimentally 0.17 to 0.27 eV.

4 Self-trapped exciton

4.1 Atomic limit $t = 0$

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$^{5+}$. If the electron and the hole are spatially separated, each energy is lowered by lattice relaxation. The elastic energy of both the electron and the hole is lowered by $3\Delta/4$, but the on-site energy of each unpaired electron on a Bi$^{4+}$ ion is raised by $\Delta/2$. The net energy cost is $3\Delta/2$ to create the isolated pair of polarons.

The self-trapped exciton, an electron polaron weakly bound to a hole polaron, costs $\epsilon_{exc} = 17\Delta/12$ to create. The total energy gain from lattice relaxation is the exciton binding energy $E_{exc} = 7g^2/K + U$, considering the on-site Coulomb repulsion.
4.2 Numerical results

Numerical method[2] was used for $t \neq 0$. In this case, localizing and delocalizing terms compete. So there is a critical value $\Gamma_c$ to exist self-trapped exciton. $\Gamma_c \approx 0.175$ is very close to $\Gamma_c(P) = 0.18$. Using a vacuum correction, $E_{exc}/t \approx 7\Gamma - 1/2\Gamma$.

Comment: Mereglli et al.[6], which is not explained extremely in this paper, suggest LDA±U approach for further understanding of the physics. Besides, they say ”negative U”. But, what’s the negative U? Is there no symmetry between positive and negative U?

References


