Spectroscopic Observation of Bipolaronic Point Defects in $Ba_{1-x}K_xBiO_3$

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An infrared-absorption band centered at 0.85 eV, which is below the big optical absorption at the charge-density-wave (CDW) gap energy of 1.85 eV, has been observed for semiconducting single crystalline $Ba_{1-x}K_xBiO_3$. With substituting K for Ba, the spectral weight of the new band increases with x, while that of the CDW-gap excitation decreases. Since the impurity state with the K substitution is known to be nonmagnetic at low temperatures, the Bi^{3+} state with $6s^2$ electrons surrounded by the six Bi^{5+} ions forms a small bipolaron by losing a pair of electrons in the Rice-Sneddon model. The new band is assigned to a transition from the lower-Peierls band to a state of the bipolaronic point defect.

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For a three-dimensional Peierls semiconductor, $BaBiO_3$ (BBO), a big optical response, has been found at 1.85 eV, which corresponds to the Peierls gap formed by the presence of the short-range order of Bi charge disproportionation [1]. Band-structure calculations [2,3] indicate that BBO, taking a cubic lattice symmetry, would potentially be a high T_c superconductor with high density of states at the Fermi energy and presumable strong electron-phonon interaction, as the band of the Bi $6s$–O $2p$ antibonding state is half filled. The energy gap in the real system possessing monoclinic lattice symmetry arises from the breathing-mode distortion of oxygen octahedra and also the tilting one accompanied by a slight charge disproportionation of Bi atoms. Theoretical calculation [4] by using an extended Peierls-Hubbard model exhibits that direct-exciton excitations on the W-L lines on the boundary surface of the Brillouin zone reproduce the big optical response at 1.85 eV.

When holes are doped, the system should immediately undergo the semiconductor-metal (SM) transition, but a wide range of the semiconductive region is found for $BaPb_xBi_{1-x}O_3$ (BPBO) or $Ba_{1-x}K_xBiO_3$ (BKBO). For BPBO, which is semiconductive for $x < 0.65$, the electron-empty Pb^{4+} band is centered in the upper-Peierls band [1,5]. Because of the increased bandwidth with the considerable Pb doping, the bottom of the Pb band touches the lower-Peierls Bi^{3+} band, thereby inducing the SM transition of the overlapping-band type. Rice and Sneddon [6] have made a model in which Bi $6s$ electrons couple with the breathing-mode distortion of oxygen octahedra to form Bi^{3+} and Bi^{5+} ions. Using a magnetic analog, they have inferred that dilution by the substitution of Pb for Bi causes the SM transition for BPBO.

For BKBO, however, there is no definite interpretation of the wide semiconducting region for $x < 0.3$, although the reflection spectra have been found to exhibit behavior similar to the one in the case of BPBO [7–9]. Recently, using the Rice-Sneddon model in slightly hole-doped BBO, Bischofs, Kostur, and Allen [10] have estimated energy of small polarons or bipolarons, which are self-organized point defects and trap carriers in bound states inside the Peierls gap. They have predicted the bipolaronic point defect which is the state of missing pair of electrons on the nominal Bi^{3+} sublattice. Formation of the small bipolaron may be the mechanism of the insulating state persisting over such a wide range in BKBO.

Here we note that, in optical absorption experiments for BBO, a small indirect energy gap has been found to correspond to the activation energy of the resistivity [11]. Narrowing of the indirect gap has been observed with increase of the substitution in BPBO [12] and also in BKBO [13].

In this Letter, we find a mid-infrared-absorption band centered at 0.85 eV, the spectral weight of which increases with x, while that of the direct transition between the Peierls gap decreases. These indicate that the K-doping destroys locally electron pairs to form the bipolaronic defect states in the charge-density wave (CDW). The result reported here supersedes previous interpretations in optical studies for the semiconducting region of BKBO [7–9,14], in which the new band at 0.85 eV has not been perceived.

For BBO, a single crystal was prepared by slow cooling a stoichiometric mixture of BaO_2 and Bi_2O_3 that was melted in an Al_2O_3 crucible at 1333 K. For BKBO, single crystals were synthesized by an electrochemical method [15]. The K concentrations x of these single crystals were determined by an electron-probe microanalysis (EPMA). A calibration curve between x and the pseudocubic lattice parameter, which is given in Ref. [16], differs from the one for the ceramic samples [17]. All the samples were cut into a form of a flat plate of dimensions $5 \times 4 \times 2$ mm^3 with a large (100) surface that was polished by using Al_2O_3 powder of 0.05 μm in size for the optical measurements. The reflectivity spectra in a frequency range 0.005–0.7 eV were measured on the large surface at ~11° incidence by using a Fourier transform spectrometer and those in a frequency range 0.7–4 eV were obtained by a grating spectrometer. All the measurements were carried out at room temperature. The absolute value of the reflectivity was determined as compared with that of an evaporated Au or Al film, which was measured with the same optical alignment. The dielectric function was obtained by a Kramers-Kronig (KK) transformation of the reflectivity. The experimental data were extrapolated by a curve with the frequency dependence of ω^{-4} from 4 to 17 eV, which was effective for the compensation in the high-frequency ranges.

In Fig. 1 we display the imaginary part of the dielectric function ϵ_2 from the KK analysis. For $x = 0.13$, and 0.16, we clearly find an additional new absorption band *B* below a primary peak *A*. The new peak is more conspicuous in the ϵ_2 spectrum than in the conductivity one. The electronic part of the spectrum can be discussed phenomenologically in terms of a Lorentz-oscillator model in which the dielectric function is given by

$$\epsilon(\omega) = \epsilon_{uv} + \sum_j \frac{\omega_j^2 S_j}{\omega_j^2 - \omega^2 - i\omega\gamma_j}, \tag{1}$$

where ω_j, S_j, and γ_j are the frequency, strength, and damping factor of the *j*th Lorentz optical excitation, respectively, and ϵ_{uv} is the high-frequency ultraviolet dielectric constant.

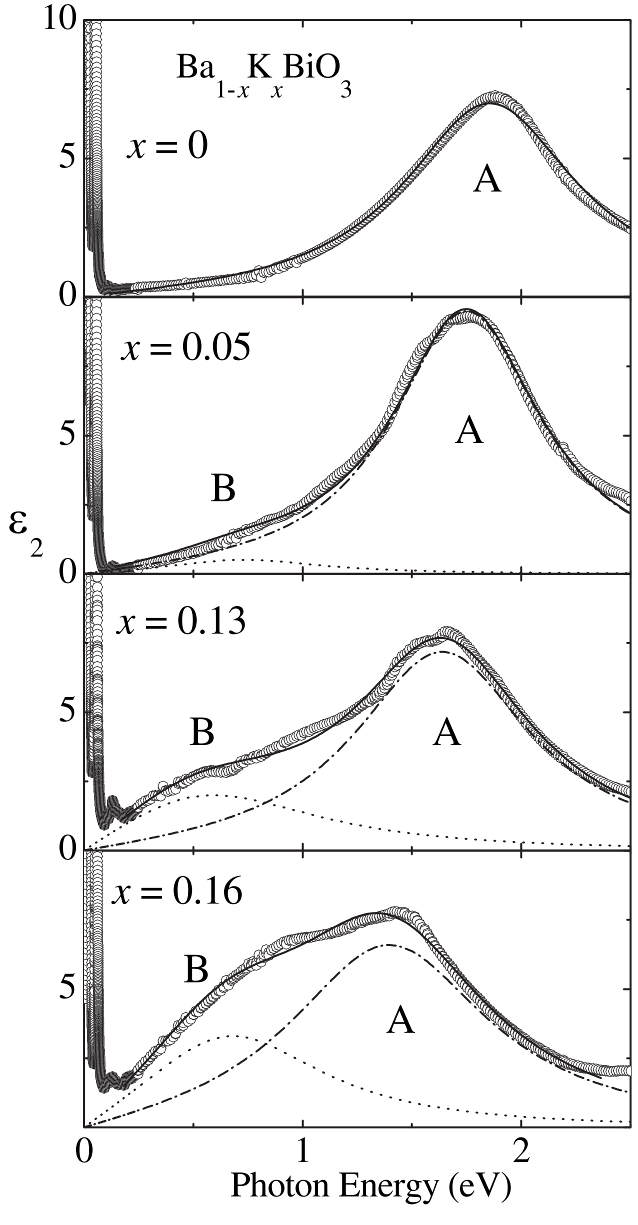

FIG. 1. Imaginary part of dielectric function for semiconductive BKBO. The spectra are decomposed into two Lorentzians of the peak *A* and *B* by fitting. The peak *B* corresponds to an excitation from the lower-Peierls band to the bipolaron- defect state, which increases the intensity with doping. The peak *A* shifts the position to the lower energy with *x*.

In fitting ϵ_2 for $x = 0.13$ and 0.16, we find a sharp feature centered at 1.71 eV, and 1.5 eV (peak *A*) and another one at 0.85 eV and 0.85 eV (peak *B*), respectively. For the spectrum of $x = 0.05$, the new band *B*, also located at 0.85 eV, is weak and difficult to distinguish from the intense peak *A* at 1.8 eV. In Fig. 2 we show the compositional changes of ω_1 and ω_2 with previous results for single crystals [8,9] or ceramic samples [7] where the peaks *A* and *B* were not well resolved. Here, the *x* values for the single crystals are recalculated by using the calibration curve of the *x* versus the lattice parameters [16], and the frequencies ω_{MAX} for the optical conductivity spectra are plotted. Since synthesis of ceramic samples in a semiconductive region is known difficult [18], the frequency in the metallic region is plotted. The position of the peak *A* is found to decrease with *x* but remain finite in the beginning of the metallic region, which indicates the pseudogap as in the case of BPBO [1]. The peak *A* width does

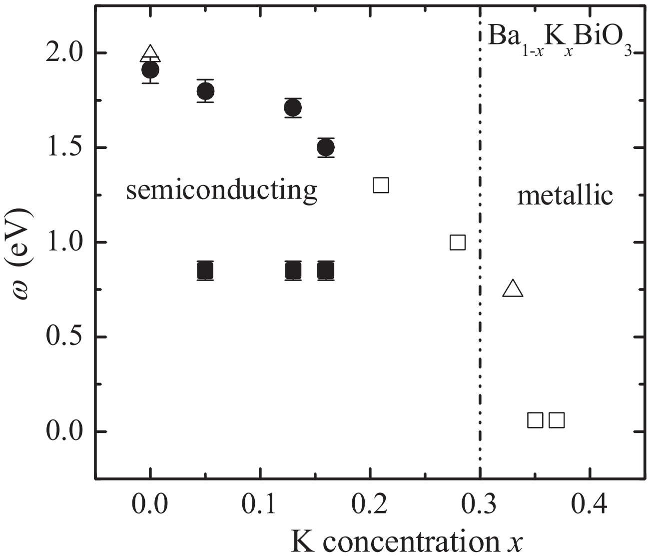

FIG. 2. The peak positions ω_j for the peak *A* (full circles) and *B* (full squares). Previous results for single crystals [8,9] (open squares) and ceramic samples [7] (open triangles) are also plotted for the spectra with an apparently single peak.

not change significantly with increasing x (i.e., $\gamma_1 \sim 1.0$ eV). The peak B keeps a nearly constant position of 0.85 eV with doping and has a nearly equal width to the peak A, $\gamma_2 \sim \gamma_1$. With increasing x, we expect that the peak B with a larger width overlaps the peak A with the decreasing position, resulting in a single broad peak in the spectrum.

In Fig. 3, we estimate and plot the effective number of electrons per a Bi atom, N_{eff}, involved in the optical excitations for each absorption band by the following integration,

$$N_{\text{eff}} = \frac{m_0 V_c}{2\pi^2 e^2} \int_0^{\omega_0} \omega' \epsilon_2(\omega') d\omega', \tag{2}$$

where m_0 and V_c are the bare-electron mass and the crystal volume per a Bi atom [19], respectively. For the upper limit of the integral ω_0, the cutoff frequency should be used, since the Lorentzian function is known to have a long tail. We use the frequency giving the minimum of the optical conductivity spectrum in accordance with the definition of Ref. [9]. In Fig. 3, it is found that N_{eff} at $x = 0$ is 0.5 by a factor of $1/2$ smaller than 1 electron per Bi, which should be involved in the excitation across the CDW gap assuming no transition to the higher levels, as Puchkov *et al.* [9] have pointed out as the missing spectral weight.

For the peak B component, we find that the N_{eff} increases with doping and approaches the substantial part of the reported values for the overdamped midinfrared component in the metallic region [9,20]. On the other hand, that of the peak A increases once and decreases with x.

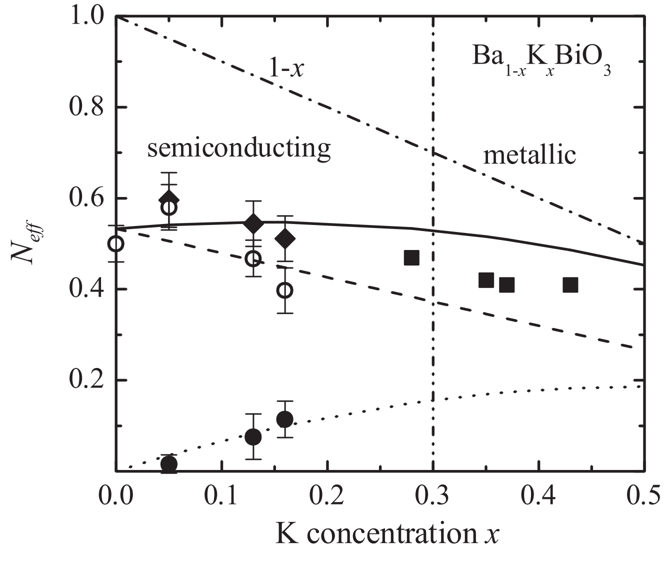

FIG. 3. Spectral weight for the peak A (open circles), B (full circles), the sum (full diamonds), and the previous results (full squares) [8,9]. The broken, dotted, and solid lines are fits to the spectral weights of $a(1-x)/4$, $b(1-x)x/4$, and the sum, respectively, in which the expressions take account of the bipolaron concentration with the doping. The chain line is $N_{\text{eff}} = 1 - x$.

In the Rice-Sneddon model, in which the strong interaction is taken into consideration between electrons and the breathing-mode distortion in BKBO, the doped holes are shown to be self-trapped to result in small polarons or small bipolarons [10,21]. The small bipolaron is predicted more stable than the small polarons and amounts to a point defect. Absence of local-intrinsic-moment behavior in doping systems [22,23] is consistent with the small-bipolaron picture. The predicted energy level of the small bipolaron in the Peierls gap of 2Δ is located at $0.7\Delta = 0.7$ eV above the lower-Peierls band compatible with the experimental observation of 0.85 eV.

The number of the bipolaron states per a Bi atom is $x/2$, and that of the lower band, i.e., Bi^{3+} states, decreases as a function of $(1-x)/2$. Thus, the weight of the transition from the lower band to the small-bipolaron state changes as $bx(1-x)/4$; on the other hand, that from the lower to higher Peierls band should decrease as $a(1-x)/4$. We note that a and b would be constants as long as x is small and the transition matrix elements between the states remain constant with x. In Fig. 3, we plot the fits to the spectral weights for the peaks A and B, where $a = 2.13$ and $b = 2.98$. The total spectral weight of A and B is close to the previous data even in the more concentrated region [9]. Therefore, the optical spectrum below 1.85 eV in the metallic region seems to be comprised of the peaks A, B and the Drude component from the free carriers, in accordance with the experimental observation [20] that the optical conductivity for $x = 0.4$ consists of two contributions; one is a Drude-like component (about 6% of the midinfrared one) and another is an overdamped Lorentz component centered at $\sim$0 eV.

Since the electronic wave function compatible with the CDW would be expressed as $\cos\frac{\pi}{2}x\cos\frac{\pi}{2}y\cos\frac{\pi}{2}z$ and the wave function at the bipolaron point defect is the s state at the origin, the optical transition is forbidden [10]. In the realistic band calculation [3] for BBO, the top of the lower band is predicted to be the W-point state, though the optical transition to the bipolaronic point defect would still be forbidden. In BBO, however, LO phonons are found both infrared and Raman active, which indicates that BBO lacks inversion symmetry [24]. Although a compatible local or uniform crystal structure is unknown, the local structure seems different from the mean crystal structure measured by the neutron or x-ray diffraction method, and the observed peak B transition is optically allowed, since the N_{eff} is close to the K content or the doped-hole one. For the peak A, the reason for the first increase of N_{eff} at $x = 0.05$ may possibly be due to the increase of the local distortion around Bi^{5+} ions adjacent to the bipolaron defects which appear with the doping.

According to Bischofs, Kostur, and Allen [10], as a result of the hole doping, the Bi^{5+} bipolaron state occurs at the Bi^{3+} site, and a single bipolaron distortion changes six adjacent Bi^{5+} states to six localized ones for electrons below the bottom of the unoccupied upper-Peierls band. With increasing doping, these localized states will have width just like the impurity band, since the electronic wave functions become to overlap each other between the localized states. Therefore, the width of the upper-Peierls band increases and the peak position of the spectrum A decreases with the doping. Furthermore, two bipolarons adjacent to a Bi^{5+} upper-Peierls state will appear with doping and make the localized state with further lowering its energy. Since the peak B position keeps constant in the semiconducting region, the system is inferred to undergo the SM transition, when the bottom of the upper-Peierls band crosses the top of the lower-Peierls band on lowering the energy with the interaction between the Bi^{5+} site and the adjacent several bipolaron defects.

For the semiconducting sample near the SM transition, the bipolaron transport is claimed from the optical conductivity spectrum [14], which seems, however, to be assigned as the merged feature of the peak A and B, as has been discussed above for Figs. 2 and 3. Observed peak of the bipolaron is due to the interband transition, not the intraband one. Since the indirect gap was found in the optical absorption spectrum [13], the electrons and holes are thermally excited across the gap, so that small electron polarons and hole ones rather than small bipolarons seem to play important role in the transport phenomena as a result of the strong electron-phonon interaction. The bipolaron which appears with the K substitution for Ba will reside near the K site because of the Coulomb interaction. At high temperatures up to 400 K, a new excitation [25,26] appears below the peak B, and at low temperatures the behavior of the finite optical conductivity was found at the far-infrared region [27], which indicates the small-polaron excitation.

In summary, in the system of BKBO, there are two components in the optical spectra below 1.85 eV; one corresponds to the CDW-gap excitation from the lower to upper-Peierls band, and another to the transition from the lower-Peierls band to the bipolaron local defects in the semiconducting region, and both remain even in the metallic region.

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