Ultraviolet photoemission study of single-crystal BaPb$_{1-x}$Bi$_x$O$_3$

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An ultraviolet photoemission study on single-crystal BaPb$_{1-x}$Bi$_x$O$_3$ with $x = 0.15$ (superconductor) and $x = 1.0$ (semiconductor) has been presented. A clear Fermi-edge structure was observed for the first time for the superconducting compound. A rigid shift of the valence band by 0.3–0.4 eV between the superconductor and the semiconductor was observed although the shift is much smaller than predicted from the band-structure calculation. The "mysterious 9-eV peak," whose origin has been controversial in cuprate superconductors, was found also for degraded crystal surfaces of BaPb$_{1-x}$Bi$_x$O$_3$. Its origin was discussed in connection with the difference and similarity in the high-T_c mechanism between cuprate and noncuprate superconductors.

The perovskite-type BaPb$_{1-x}$Bi$_x$O$_3$ is the "high-transition temperature (T_c) superconductor" in the compositional range of $0.05 \leq x \leq 0.3$ with the highest $T_c \sim 13$ K at $x = 0.25$.[1] The most striking feature of BaPb$_{1-x}$Bi$_x$O$_3$ distinct from other high-T_c superconductors such as YBa$_2$Cu$_3$O$_7$ is the absence of copper atoms or CuO$_2$ sheets in the crystal structure. Because of the relatively lower T_c than those of cuprate superconductors, it has been generally accepted that the mechanism of superconductivity is different from that emerging in the cuprate compounds. However, the discovery of noncuprate Ba$_{1-x}$K$_x$BiO$_3$ with the T_c as high as 31 K (Ref. 2) comparable to that of La$_{2-x}$Sr$_x$CuO$_4$ (Ref. 3) has raised a serious question to the so far believed classification between the cuprate and the noncuprate superconductors. In order to elucidate the mechanism of high-T_c superconductivity, including the role of copper atoms and CuO$_2$ sheets, it would be crucial to clarify the difference and similarity between the two types of superconductors.

The electronic structure of the cuprate high-T_c superconductors has been intensively studied by electron spectroscopies such as photoemission and inverse photoemission, but very few such studies have been reported for the noncuprate high-T_c superconductors. In this Rapid Communication, we report the first ultraviolet photoemission study of single-crystal BaPb$_{1-x}$Bi$_x$O$_3$ ($x = 0.15$ and 1.0). We found a clear Fermi-edge structure, which was absent in the previous photoemission studies,[4,5] for the superconducting compound ($x = 0.15$), as well as a rigid shift of the valence band between the superconductor and the semiconductor ($x = 1.0$) though the shift is much smaller than predicted from the band-structure calculation.[6,7] We also found degradation of the crystal surface under ultrahigh vacuum; an unknown peak at 9 eV in binding energy emerged in the spectrum of a degraded surface. This peak is quite similar to the longstanding controversial peak observed at 9 eV in the photoemission spectra of cuprate superconductors.[8–10] We discuss the origin of the "mysterious peak" in connection with the mechanism of high-T_c superconductivity.

The single crystals were grown from PbO-rich melt for $x = 0.15$ and from stoichiometric melt for $x = 1.0$.[11] Resistivity and magnetic susceptibility measurements showed that the crystal of the composition $x = 0.15$ becomes superconducting at 7 K with a substantial amount of Meissner signal, more than 10% of the ideal value in the field-cooling run measurement, while that of $x = 1.0$ (BaBiO$_3$) is a semiconductor in the entire temperature range.

Photoemission measurements were performed using an ultraviolet photoemission spectrometer constructed at our laboratory. The spectra were recorded with the He I (21.2 eV) and He II (40.8 eV) resonance lines. The total-energy resolution of the spectrometer was 0.15 eV. A clean surface of the sample for photoemission measurement was prepared by scraping the surface with a diamond file. Scraping was repeated several times until almost no change was detected in the spectrum. Photoemission measurements were done at room temperature and also at low temperature (~ 180 K) to study the effect of possible desorption of oxygen atoms and resulting compositional change at the surface. The Fermi level of the sample was referred to that of a silver film deposited on the crystal.

Figure 1 shows the photoemission spectra of BaPb$_{0.85}$Bi$_{0.15}$O$_3$ and BaBiO$_3$ measured with the He I resonance line. Both spectra were recorded at room temperature within 30 min after scraping. As shown later, the spectra are identical to those recorded at low temperature. The inset of Fig. 1 is an enlargement of the spectra in the vicinity of the Fermi level. The spectrum of BaPb$_{0.85}$Bi$_{0.15}$O$_3$ has a clear Fermi-edge structure characteristic of normal metal while it is completely absent in BaBiO$_3$. This is the first direct observation of the Fermi-edge structure in BaPb$_{1-x}$Bi$_x$O$_3$, suggesting that the superconductivity would be driven by Cooper pairing of electrons in the Fermi-liquid states. Features of the whole valence-band photoemission spectra are essentially the same as those reported previously,[4,5] showing band A at 3 eV and band B at 8.5 eV, which have been ascribed mainly to the O $2p$ and the Bi and Pb $6s$ states,[4,5] respectively. The as-
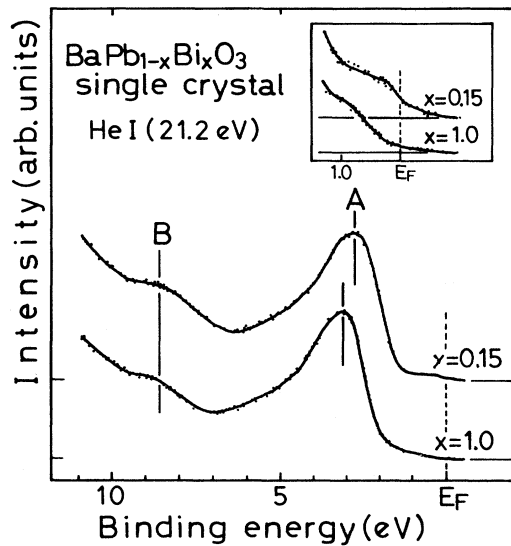
FIG. 1. He I photoemission spectra of $BaPb_{1-x}Bi_xO_3$ ($x = 0.15$ and 1.0). The inset is an enlargement of the vicinity of the Fermi level. Note a clear Fermi edge for the superconductor ($x = 0.15$) and its absence for the semiconductor ($x = 1.0$) as well as a shift of band A by 0.3–0.4 eV between the two compounds.

signment of band B, however, may be changed because it was found in this study that the intensity of band B increased remarkably upon degradation of the sample surface in a quite similar manner to the mysterious peak at 9 eV for $La_{2-x}Sr_xCuO_4$ (Ref. 12) and $EuBa_2Cu_3O_7$.[13] This point will be discussed in detail later.

As shown in Fig. 1, band A of the semiconductor ($x = 1.0$) is apparently shifted by 0.3–0.4 eV toward the high-binding-energy side with respect to that of the superconductor ($x = 0.15$), while the energy shift is not clear for band B owing to the large background in the spectra. The observed shift of band A by 0.3–0.4 eV coincides well with the shift of the spectral feature in the vicinity of the Fermi level, suggesting a rigid shift of the whole valence band. The band-structure calculations[6,7] have presented a rough estimation of rigid shift of the valence band by about 2 eV between $BaPbO_3$ and metallic $BaBiO_3$. This calculated value is much larger than the presently observed one although the shift itself is in the same direction. However, when we take account of the opening of a charge-density-wave (CDW) gap of about 2 eV (Ref. 14) in $BaBiO_3$ and its p-type semiconducting behavior with the activation energy of 0.2 eV,[15] the discrepancy between the experiment and the calculation may be reduced by about 1 eV (half of the CDW gap), leading to a fair agreement between the experiment and the calculation. A band bending in the near-surface region may take place in semiconducting $BaBiO_3$. But the band bending would rather enlarge the difference between the experiment and the calculation, because $BaBiO_3$ is a p-type semiconductor and surface states causing the band bending would move the Fermi level toward the center of the CDW gap.

An alternative explanation for the relatively small shift with respect to the simple rigid-band picture is that new

electronic states are created by "doping" in the vicinity of the Fermi level and pin the Fermi level there. Actually, Nücker et al.[16] have found new electronic states emerging at the Fermi level with "doping of holes" by the electron-energy-loss study of $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{7-y}$. A similar result has been obtained by an x-ray absorption study of $YBa_2Cu_3O_{7-y}$.[17] If this is the case with $BaPb_{1-x}Bi_xO_3$, the shift of the valence band could be greatly reduced with respect to the rigid-band model. Whether or not, or how much the rigid-band picture is valid, in the $BaPb_{1-x}Bi_xO_3$ system would be resolved by a systematic study with combination of photoemission and electron-energy-loss (or x-ray absorption) measurements.

Next we proceed to the study of degradation of the crystal surface under ultrahigh vacuum. Figure 2 shows the photoemission spectra measured immediately after scraping the crystal surface at low temperature, compared with those recorded after keeping it at room temperature for about one day. An insertion enlarges the photoemission spectra in the vicinity of the Fermi level. We find some remarkable changes in the photoemission spectra upon degradation: (1) Intensity near the Fermi level is reduced, (2) band A is shifted toward the high-binding energy, (3) intensity of band B considerably increases, (4) a new band C appears, and (5) band E becomes prominent and is shifted slightly toward the high-binding energy. All these spectral changes were found to be irreversible with respect to the cycle of temperature of measurement. The spectral changes look more pronounced in the He II measurement than in the He I. This indicates that the degradation causing the irreversible spectral change is confined
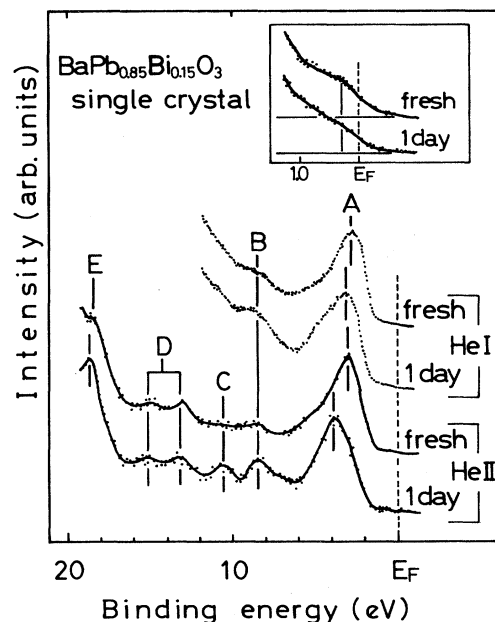

FIG. 2. Photoemission spectra of $BaPb_{0.85}Bi_{0.15}O_3$ measured for a fresh surface scraped at ~ 180 K compared with those recorded after keeping it at room temperature for one day. The inset is an enlargement of the vicinity of the Fermi level. These spectral changes were irreversible.

to a very thin region at the surface since the He II measurement is very surface sensitive and probes a few atomic layers at the surface.

Band D with doublet structure is ascribed to the Ba $5p$ states and shows little change even after one day. Bands B, C, and E may be due to the Pb $6s$, the Bi $6s$, and the Pb $5d_{5/2}$ states, respectively.[4,5] However, we observed a distinct photoemission peak at 9 eV for $BaBiO_3$ which contains no Pb atoms as shown in Fig. 1 and its progressive growth upon degradation of the sample surface (spectrum not shown) like band B of $BaPb_{0.85}Bi_{0.15}O_3$ in Fig. 2. Hence, the present experimental result indicates that a large portion of band B, especially for a deteriorated surface, is not ascribable to the Pb $6s$ state. It is noteworthy that a quite similar unknown peak at 9 eV was also reported for cuprate superconductors and has been a focus of longstanding controversy in connection with the mechanism of high-T_c superconductivity.[8-10] The 9-eV peak observed in both $La_{1-x}Sr_xCuO_4$ (Ref. 18) and YBa_2-Cu_3O_7 (Ref. 19) was at first ascribed to carbon atoms as impurity since carbonate compounds were used as starting materials. However, later it was reported that the 9-eV peak is still present for a carbon-free surface[20] as well as for a single-crystal surface,[8] giving a negative confirmation for carbon atom as an origin of the 9-eV peak. Petroff *et al.*[21] proposed the 9-eV peak as a two-hole bound state on the same oxygen site. But this interpretation leads to too small on-site correlation energy of O $2p$ holes, inconsistent with the x-ray photoemission spectroscopy and Auger data.[22] Recently, List *et al.*[13] reported that the mysterious 9-eV peak disappeared completely when they cleaved a single crystal of $EuBa_2Cu_3O_7$ at 20 K and measured the photoemission spectrum while keeping it at the low temperature. They also found a substantial density of states at the Fermi level for the surface. A similar result has also been observed for $La_{1-x}Sr_x$-CuO_4,[12,23] though the temperature was not so low as in the case of $EuBa_2Cu_3O_7$.[13] As for $Bi_2Sr_2CaCu_2O_8$,[24,25] a substantial density of states at the Fermi level was found by photoemission spectroscopy, but no such mysterious peak nor surface degradation under ultrahigh vacuum has been observed even for the room-temperature measurement. According to these studies, it seems that the appearance of 9-eV peak coincides with the reduction of density of electronic states at the Fermi level as well as the disappearance of superconductivity.

Ramaker[9] and Kurtz *et al.*[10] have ascribed the 9-eV peak to a state with two holes localized on nearest-neighbor oxygen atoms and successfully explained the coincidence of the appearance of the 9-eV peak and the disappearance of superconductivity. Their interpretation is based on the strong correlation of Cu $3d$ electrons and could be applicable to $BaPb_{1-x}Bi_xO_3$ with no copper atoms since the Bi $6s$ has a relatively large correlation energy due to the relativistic effect,[26] although it is not so strong to create a local moment.[27] If this is the case, the mechanism of superconductivity would be essentially the same between the cuprate and noncuprate high-T_c superconductors since both superconductors become almost equivalent from the viewpoint of the electronic structure. However, a substantial isotope effect[28] and a diamagnetic behavior of susceptibility[29] observed in $BaPb_{1-x}Bi_xO_3$ seem to indicate that different mechanisms drive superconductivity in the two families of compounds. Thus, the appearance of the mysterious 9-eV peak in $BaPb_{1-x}$-Bi_xO_3 has again brought about an essential question of whether the mechanism of high-T_c superconductivity is identical or not between the cuprate and the noncuprate superconductors. In order to understand the mechanism of high-T_c superconductivity, further studies to clarify the difference and similarity between the two types of superconductors as well as to elucidate the origin of the mysterious 9-eV peak are required.

In conclusion, we have performed an ultraviolet photoemission study on single-crystal $BaPb_{1-x}Bi_xO_3$ ($x =0.15$ and 1.0). We found for the first time a clear Fermi-edge structure for the superconductor ($x =0.15$), which suggests that the superconductivity would be driven by Cooper pairing of electrons in the Fermi-liquid states. We also found a rigid shift of the valence band between the superconductor and the semiconductor ($x =1.0$) by 0.3–0.4 eV. We discussed the origin of the mysterious 9-eV peak observed also for $BaPb_{1-x}Bi_xO_3$ in connection with the mechanism of high-T_c superconductivity.

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