Electronic states of BaPb$_{1-x}$Bi$_x$O$_3$ in the semiconducting phase investigated by optical measurements

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The semiconducting BaPb$_{1-x}$Bi$_x$O$_3$ $(0.35 < x \leq 1)$ is investigated in detail by optical measurements. The optical spectrum shows that BaPb$_{1-x}$Bi$_x$O$_3$ has a clear optical gap over the whole semiconducting compositional range. It is clearly shown by resonant Raman scattering measurements that the origin of this gap is a charge-density wave (CDW) accompanied by the breathing-mode distortion. No apparent effect of Pb substitution can be observed in the reflectivity spectra for the sample with $x > 0.7$. For $x \leq 0.7$, the CDW gap decreases with x and simultaneously the absorption tail extends into the gap. This spectral behavior can be well interpreted in terms of the recently proposed theoretical model with emphasis on a local CDW and/or a substantial energy difference between Pb and Bi sites arising from the strong electron-phonon interaction. Thus it can be concluded that the strong electron-phonon interaction plays an essential role in the semiconducting phase of this material as well as in the metallic phase.

I. INTRODUCTION

The alloy system BaPb$_{1-x}$Bi$_x$O$_3$ has been very attractive because it exhibits superconductivity with a high transition temperature T_c near the Bi composition $x = 0.25$,[1] in spite of the low carrier density,[2] followed by the abrupt metal-semiconductor (M-S) transition at $x = 0.35$.[1,2] Most experimental investigations reported to date have been concerned mainly with the properties of the metallic phase $(x < 0.35)$, especially near the high-T_c composition.[3] However, even in the metallic phase various unusual properties have been found which could be ascribed to the precursory effects towards the M-S transition.[4] Thus it is of essential importance to investigate the electronic states in the semiconducting phase in order to understand properly the origin of the high-T_c superconductivity and the interrelationship between the superconductivity and the M-S transition.

There have been few experimental reports on the semiconducting properties of BaPb$_{1-x}$Bi$_x$O$_3$ except for some structural investigations.[5,6] Only for BaBiO$_3$ have several reports been published, e.g., extended x-ray-absorption fine structure (EXAFS),[7] neutron diffraction,[8,9] optical absorption of phonons,[10] etc., of which the primary concern was whether the inequivalent Bi sites exist or not. Our recent optical study[11] has shown that the breathing-mode phonon—alternating contraction and expansion of oxygen octahedra surrounding Bi atoms—is frozen out in BaBiO$_3$, so that inequivalent Bi sites are present, although the magnitude of the charge disproportionation remains open to question.

On the other hand, in the theoretical respect it is an interesting problem why the semiconducting properties persist over such a wide compositional range as $1.0 \geq x > 0.35$. There have been proposed a few theoretical models which try to explain the problem described above.[12–16] Although they stand on the common recognition that the semiconducting gap of BaBiO$_3$ is introduced by the charge-density-wave (CDW) instability corresponding to the charge disproportionation of the Bi site, different approaches were taken to explain the persistent semiconductivity over the wide compositional range of the alloy. These models give a fairly good insight into the essential properties of this material but are still far from providing a complete understanding.

In our previous publication[17] we reported mainly the properties of BaPb$_{1-x}$Bi$_x$O$_3$ in the metallic phase and near the M-S transition, especially the anomalous behavior of the reflectivity spectra in the metallic side of the compositions. We interpreted it as a precursor effect of the M-S transition, assuming that the semiconducting gap of BaBiO$_3$ is introduced by the CDW instability.

The present work focuses on the semiconducting phase of this material. Our purpose is to clarify the electronic structure of this material experimentally through the optical reflectivity and the Raman scattering measurements. We examine the compositional change in greater detail, covering the wide spectral range from far infrared to near ultraviolet.

II. EXPERIMENTAL RESULTS AND ANALYSIS

A. Electrical resistivity

The samples used in the present measurements are single crystals with a composition from 0.4 to 1.0 by a 0.1 step. The samples with $x < 0.7$ were grown by the flux method using PbO$_2$ + Bi$_2$O$_3$ as a solvent,[18] while the sam-
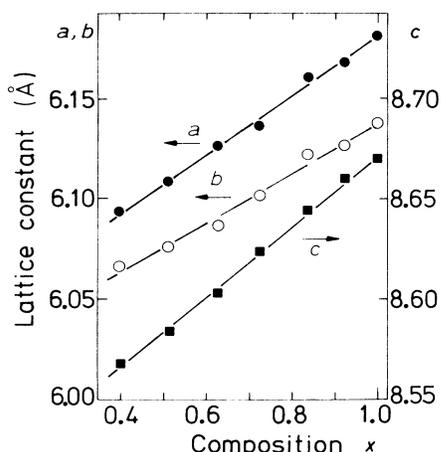
FIG. 1. Composition (x) dependence of the lattice constants in the range $0.4 \le x \le 1$ obtained by x-ray diffraction measurement. The parameters a, b, and c are related to the simple-cubic lattice parameter a_0 by the approximate relations $a \approx b \approx \sqrt{2}a_0$ and $c \approx 2a_0$.

ples with $x > 0.7$ were directly grown from the melt of BaCO$_3$, PbO$_2$, and Bi$_2$O$_3$. The Bi composition of the samples was determined by an electron-probe microanalyzer. The lattice constants measured by using an x-ray diffractometer are plotted in Fig. 1. As shown in this figure, the lattice constant changes continuously with x, indicating that a series of our specimens forms homogeneous solid solutions.

Electrical resistivity was measured by a conventional four-probe method in the temperature range 300—1000 K. The results are shown in Fig. 2.

The resistivity is plotted in a logarithmic scale against the inverse of temperature for the samples with various compositions x employed. The resistivity increased with a decrease of temperature for all the samples, confirming that they are all semiconductors.

Each curve shows an activation process with a single activation energy E_A in a wide temperature range. The deviation from the linear line at the higher temperature is considered to be an evidence for the precursor effect of

the semiconductor-to-metal phase transition. A detailed discussion about this will be reported in a separate paper. As plotted in Fig. 6, the value of E_A decreases with decreasing the Bi composition x. Although, as mentioned in the following sections, this result cannot be simply interpreted as the obtained activation energy being equal to the band-gap energy, it certainly reflects some changes in the band structure.

B. Reflectivity spectra

Reflectivity spectra were measured in a wide wavelength range using a Perkin-Elmer grating-type spectrometer for $\lambda = 0.4$—2.5 μm and a Fourier-type spectrometer

FIG. 2. Electrical resistivity plotted against the inverse of temperature for the samples in the semiconducting phase with various composition x.
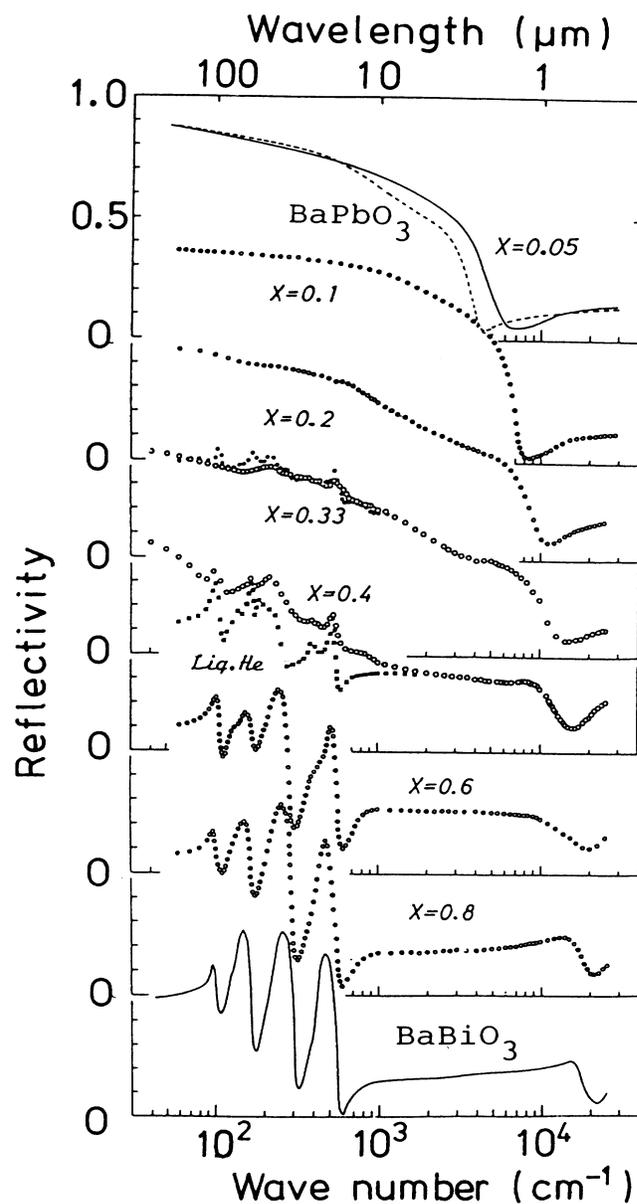
FIG. 3. Reflectivity spectra of BaPb$_{1-x}$Bi$_x$O$_3$ in the whole compositional range. At the composition $x \simeq 0.35$ the phase transition takes place from metal to semiconductor.

for 2.5—500 μm. The sample surfaces to be measured were mirror polished using Al_2O_3 powder of 0.06 μm in size.

Figure 3 shows the reflectivity results for the semiconducting samples with various x, together with the spectra in the metallic phase. In the present work the wide energy range is covered from 20 to 25 000 cm^{-1} and the composition x is also covered in greater detail than in the previous work,[17] which enables us to examine the electronic structure of this system more comprehensively.

As clearly seen in Fig. 3, the spectrum for the sample with x larger than 0.35 is typical of a semiconductor. Comparing the spectrum in the semiconducting phase with that in the metallic phase, representatively, $BaBiO_3$ with $BaPbO_3$, we can see the characteristic of the semiconducting-phase spectra. In the lower-energy region below 600 cm^{-1} the four phonon peaks are dominant in $BaBiO_3$, while in the metallic phase such a phonon structure disappears in the spectrum because of the strong absorption of the plasma excitation. Although the plasma reflection is observed in the spectrum of the semiconducting $BaPb_{0.6}Bi_{0.4}O_3$ at the room temperature, it disappears when the specimen is cooled down. In the higher-energy region (> 1000 cm^{-1}) the reflectivity in relatively small and the spectrum is featureless except for a reflectivity edge observed at $\hbar\omega = 15\,000$—$20\,000$ cm^{-1}. This reflectivity edge indicates an optical absorption corresponding to some electronic excitation.

Now we see the effect of Pb substitution for Bi. In the compositional range from $x = 1.0$ to 0.8 no remarkable change can be observed in the energy region higher than 1000 cm^{-1}, while a small amount of change is seen in the lower-energy phonon spectrum. When the amount of Pb substitution exceeds 30 at. %, i.e., $x \leq 0.7$, a spectral change can be observed also in the higher-energy region. The reflectivity edge shifts towards the lower energy and the reflectivity value at the plateau part in the spectrum is increased with decreasing x. The reflectivity edge seems to be evolved from the plasma edge in the metallic phase. Moreover, observing the spectra carefully, we notice that the gradient of this part is negative, i.e., $dR/d\omega < 0$ for the sample with $x < 0.7$, while it is positive for $x > 0.7$. The negative gradient indicated the existence of some absorption extending over the range 1000 cm$^{-1} < \hbar\omega < 10\,000$ cm^{-1}.

C. Analysis of the reflectivity spectra

Since the study of the far-infrared phonons in this system was reported previously,[11] we focus here mainly on the electronic excitation in the higher-energy regions.

As seen in Fig. 3 the plasma edge in the metallic phase is preserved as a reflectivity edge in the semiconducting phase, so it is naturally supposed that these edges have the same origin. In Fig. 4 we plotted the frequency at the reflectivity edge as a function of composition x. Its value was strictly determined by the usual oscillator-fit procedure, in which the edge frequency is assumed to be a longitudinal collective mode frequency of the corresponding oscillator and is represented by ω_p. As shown in Fig. 4, the value of ω_p changes continuously over the whole compositional range, which confirms our conclusion in the previous paper[17] that the electrons supplied by the Bi atoms are involved in this collective excitation, though the energy gap is formed at the Fermi surface. In Fig. 4 ω_p calculated by a simple tight-binding model are plotted on the assumption that one free electron per Bi atom is supplied in the conduction band. The agreement between the results of experiment and of calculation is excellent. The value of ω_p varies almost linearly with x up to $x \simeq 0.6$, but tends to saturate near $x = 1.0$ because the band shape near E_F deviates from a parabolic one as x approaches 1—the exactly half-filled case. Another important consequence of the continuous change of ω_p is that the present system forms a complete solid solution or at least our samples are homogeneous as long as they are observed in the wavelength scale, ~ 0.5 μm.

To clarify the origin of the excitation associated with this oscillator, we have performed the Kramers-Kronig transformation to evaluate the dielectric function $\epsilon(\omega)$ from the reflectivity spectra $R(\omega)$. The real part of the conductivity $\sigma = \sigma_1 + i\sigma_2$ can be obtained from the imaginary part of the dielectric function $\epsilon = \epsilon_1 + i\epsilon_2$ by the relation $4\pi\sigma_1(\omega) = \omega\epsilon_2(\omega)$. The σ_1 spectra of $BaPb_{1-x}Bi_xO_3$ in the semiconducting phase are shown in Fig. 5. We have checked the accuracy of the calculation in the same way as described in the previous publication,[17] adopting the same extrapolation scheme in the energy region below 20 cm^{-1} and above 25 000 cm^{-1}. In the present work, grading up the accuracy of the integration calculation enabled us to discuss the line shape of the conductivity spectrum in more detail than in our previous publication.[17]

Starting from the spectrum for $BaBiO_3$ ($x = 1.0$), the relatively small peaks below 1000 cm^{-1} correspond to optical phonons. The strong peak centered at about 15 000 cm^{-1} is presumably assigned to the interband excitations beyond a gap which makes this material a semiconductor.

Next we follow the spectral change accompanied with the Pb substitution. In the compositional range $x = 1.0$—0.8, no appreciable change can be observed in the higher-energy peak position except that the peak height becomes a little bit smaller with decreasing x. It should be noted that there can be seen no significant change at around $x \simeq 0.95$ where the structural change from monoclinic to orthorhombic takes place.[5] A qualitative change is seen rather at $x \lesssim 0.7$. For $x = 0.7$ the peak postion is
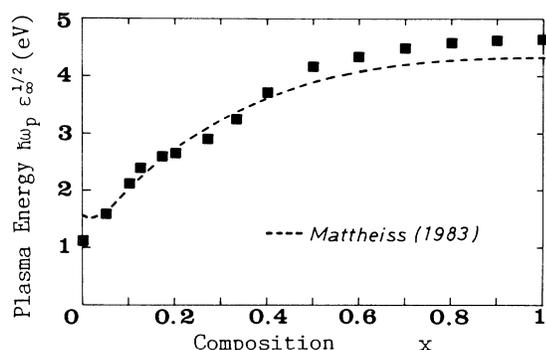
FIG. 4. Composition (x) dependence of the plasma energy. The dashed line is the result calculated by Mattheiss, using a simple tight-binding model (Ref. 12).
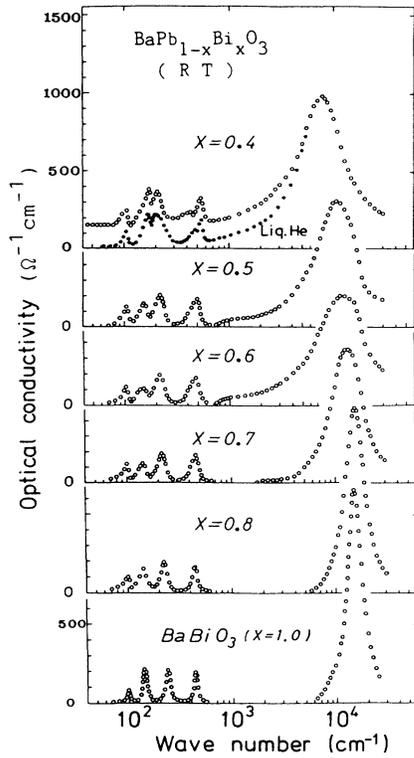
FIG. 5. Optical conductivity spectrum for the samples in the semiconducting phase. The data, plotted in a linear scale, were obtained from the spectrum measured at room temperature. For $x = 0.4$, the data at liquid-He temperature are also shown by the solid circles.

located at lower-energy as compared with BaBiO$_3$ and the low-energy tail dominates extending down to about 2000 cm^{-1}. When the Bi composition x is decreased further, the peak shifts its position towards lower energy and the peak tail extends further to lower energy. Consequently the spectral weight seems to be transferred from the higher-energy peak to the lower-energy tail. At $x = 0.5$ the lower end of the tail reaches the highest peak of the
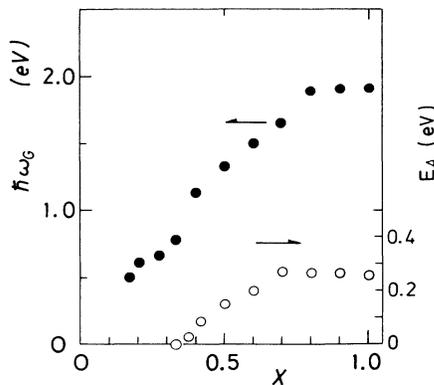
phonons and overlaps them at $x = 0.4$, where the energy gap is assumed to be considerably small, although there exists the finite gap, as clearly shown from the difference between the spectra at room temperature and at the liquid-He temperature. From these results it might be said that the Pb substitution decreases the semiconducting gap energy by deforming the bands rapidly below $x = 0.7$. It should be noticed that the edge energy of the band tail is of the same order as the activation energy estimated from the resistivity measurement.

In Fig. 6 the energy of the peak position in the conductivity spectrum, denoted by $\hbar\omega_G$, is plotted against the Bi composition. It is nearly constant in the range $x = 1.0-0.8$ and then decreases almost linearly with a decrease of x. The activation energy E_A plotted in the same figure was calculated from the temperature dependence of the resistivity. Although its value is one order of magnitude smaller than that of the optical gap energy, the dependency of E_A on the composition x is similar to the case of $\hbar\omega_G$ as far as $x > 0.4$. This suggests that these two quantities characterize the specific electronic structure in the semiconducting phase and thus substantial change in the electronic band structure at about $x = 0.7$, i.e., from Pb-insensitive to Pb-sensitive electronic structure.

D. Raman spectra

We performed measurements of a Raman spectrum of BaBiO$_3$ in a backscattering configuration using a longitudinal single-mode Ar ion laser (5145 Å) as an excitation.

The Raman spectrum of BaBiO$_3$ is shown in Fig. 7. Following the strongest peak at 570 cm^{-1}, which was assigned to the breathing mode in the previous work,[19] a series of peaks was observed with the energy shift, $\hbar\omega_n = n\hbar\omega_0$, with $\hbar\omega_0 = 570$ cm^{-1}, and its scattering intensity was decreased as n was increased. The peaks are thus the higher harmonics of the breathing mode, which indicates that the breathing-mode phonon is in resonance with the 2.4-eV excitations corresponding to 5145-Å incident laser beam. The energy 2.4 eV is near the peak position of the $\sigma(\omega)$ spectrum associated with the interband transitions across the fundamental optical energy gap.

FIG. 6. Composition dependence of the energy ($\hbar\omega_G$) corresponding to the peak position in the conductivity spectrum, including the data in the metallic phase and the activation energy (E_A) determined from the resistivity measurements plotted (right-hand scale) for composition.
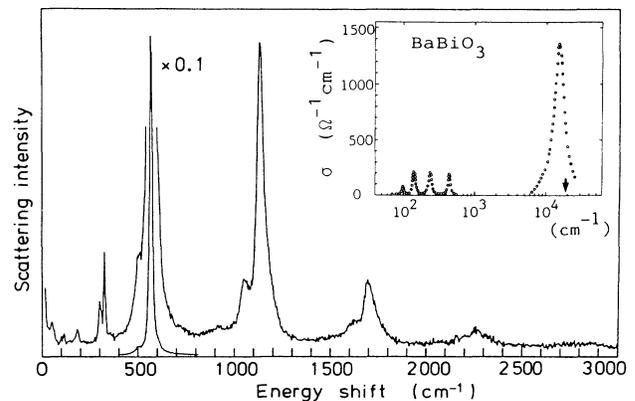
FIG. 7. Raman spectrum of BaBiO$_3$ extended to higher frequency up to 3000 cm^{-1}. The absorption spectrum taken on the same sample is shown in the inset. The 5145-Å argon-laser excitation indicated by the arrow is resonant with the 570-cm^{-1} phonon mode, producing higher harmonics.
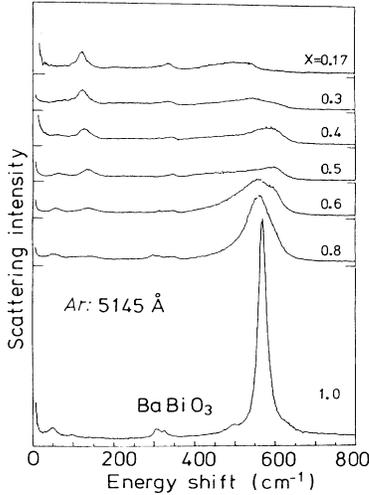
FIG. 8. Raman spectra for various compositions. The spectra were measured at 273 K with a 5145-Å Ar-laser excitation.

Thus the result provides direct evidence that the breathing mode distortion is primarily responsible for the gap formation; that is, this gap should be a CDW gap.

When the Bi composition x is decreased, the Raman spectrum changes as shown in Fig. 8. The peak height of the 570-cm^{-1} line decreases with increasing Pb composition possibly due to the alloy smearing and/or due to the fact that the incident beam energy (~ 2.4 eV) is more and more distant from the peak of the interband transitions. However, this mode maintains a substantial intensity in the whole semiconducting region as compared with the intensities of other optical phonon modes, demonstrating that the breathing-mode phonon is resonant with the interband transitions across a CDW gap also in the alloy compositions.

III. DISCUSSION

A. Origin of the semiconducting energy gap in BaBiO₃

From our optical study we have described in the previous publication[17] the speculation on the mechanism of the gap formation in BaBiO₃ as follows: Two Bi sites with different valences form the NaCl-type lattice with the oxygen octahedra around them expanding and contracting alternatively—the breathing-mode distortions. These lattice distortions coupled strongly with the conduction electrons lead to an electronic instability at the Fermi surface and create an energy gap—a CDW instability.

The existence of the different Bi sites has been proposed experimentally by neutron diffraction[8] and EXAFS (Ref. 7) measurements, although negative results were also reported in the x-ray photoemission spectroscopy (XPS) experiment.[20] A recent study of the optical phonons by the authors[11] proposed the presence of the breathing-mode distortion: The spectrum of the infrared reflectivity showed the presence of a new optical phonon which was expected to be ir active due to the breathing-mode distortion, an acoustic phonon branch being folded onto the Γ point. In the Raman spectrum an extraordinarily strong peak was observed at 570 cm^{-1}, which was assigned to a breathing-mode phonon because it has a large deforma-
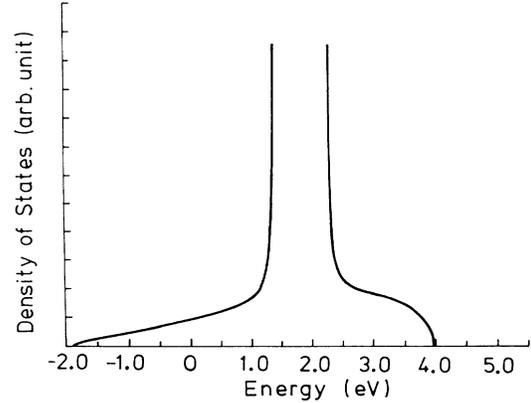
FIG. 9. Density of states near the Fermi level of BaBiO₃ calculated by Kondo and Hanamura by using a tight-binding model (Ref. 16). In their calculation they adopt the parameters used by Mattheiss and Hamann (Ref. 21).

tion potential as calculated by Mattheiss and Hamann.[21]

The present results have assured our speculation described above. Mattheiss has pointed out another interpretation of our reflectivity results[12] that the conductivity peak at 1.9 eV may be due to the interband transitions between the flat nonbonding O_{2p} bands and the conduction band just above E_F. If this were the case, another transition across the semiconducting gap should have also been observed, whereas we could not detect any other absorption peak in the range covered, $\lambda = 0.4$—400 μm. Therefore, it is unlikely that the conductivity peak shown in Fig. 5 is attributable to such an electronic excitation as pointed out by Mattheiss.

The results of the resonant Raman scattering indicate directly that the lattice distortion of the breathing-mode type causes the formation of the gap about 2 eV. The x dependence of the Raman spectrum in Fig. 8 supports this interpretation. The spectral shape of the optical conductivity shown in Fig. 5 is also suggestive of this CDW picture. The sharp peak at 1.9 eV in the spectrum of BaBiO₃ is not like a typical absorption edge of an ordinary semiconductor such as GaAs but rather resembles the interband excitation across the gap in a one-dimensional CDW
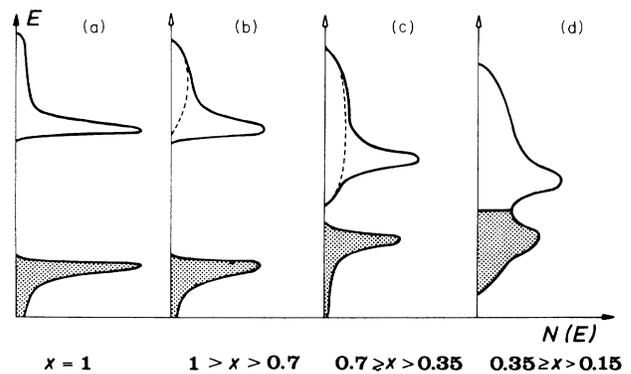
FIG. 10. Schematic representation of the change in the electronic density of states with the composition in the semiconducting phase and near the M-S transition.

system such as K$_2$Pt(CN)$_4$Br$_{0.3}$·3H$_2$O (KCP) (Ref. 22) and K$_{0.3}$MoO$_3$ (Ref. 23). In an ideal one-dimensional CDW system the perfect nesting of the Fermi surface leads to the split "divergent" density of states. Figure 9 shows the results of the simple tight-binding calculation for BaBiO$_3$ by Kondo and Hanamura (K-H),[16] which demonstrates that the half-filled Bi 6s conduction band of "three-dimensional" arrays of NaCl type can bring about similar CDW instability to the one-dimensional case due to the perfect nesting of the Fermi surface. Therefore we can schematically depict the band structure, as shown in Fig. 10(a), with the nearly divergent density of states. Here, it should be noticed that the gap energy is almost equal to the optical gap energy observed, as the peak in the optical conductivity spectrum which is larger, by one order, than the activation energy estimated from the resistivity. This fact is suggestive of the existence of some midgap states. We briefly discuss its possibility in the following section.

B. Alloying effect on the electronic structure

Concerning the origin of the semiconductivity in the compositional range $0.35 < x < 1.0$, several possibilities have been proposed. One of them is that oxygen vacancies cause the Anderson localization in the electronic system of this material which makes the system semiconducting.[24] Certainly there is an experimental report[25] which shows that many oxygen atoms are lost in BaBiO$_3$ depending on the oxygen pressure and the heat-treatment temperature and these vacancies can stabilize the valence fluctuation of Bi; for example, Bi^{3+} — Bi^{5+}. However, a mechanism originated from oxygen loss which strongly depends on the history of the crystal growth cannot be an essential cause for semiconductivity, because specimens of variable oxygen content can be prepared which all show semiconductivity. It may, However, affect the metal-semiconductor phase boundary.

Another possibility is that a phase separation takes place and there exist two phases in the crystal[26,27]—the metallic phase and the semiconducting phase, presumably BaBiO$_3$. This is also unlikely because the lattice constant measured by x-ray changes linearly with the composition x and the activation energy and the optical parameters such as ω_p and ω_G also change continuously with x. Thus we should attribute the semiconductivity of alloys to the intrinsic origin. The most plausible one would be the CDW instability, as in the case of BaBiO$_3$. The theoretical models by Yoshioka and Fukuyama[15] (Y-F) and by Jurczek and Rice[14] (J-R) have recently been proposed to explain the semiconductivity of this material up to 65 at. % of Pb composition in terms of the CDW, the latter assuming strong electron-phonon coupling that favors a local CDW and the former taking explicit account of the energy difference between Bi and Pb sites. As far as we know, no attempt has been made to detect the breathing-mode distortions directly by the neutron diffraction experiment in the alloy. However, our recent optical data on the infrared phonons[11] have shown that the lattice distortion, presumably the breathing-mode one, persists in the whole semiconducting range. In the following we show that the present experimental results on the alloy composi-

tions can also be explained based on the CDW picture.

Up to about 20 at. % of Pb composition we can see no apparent effect of Pb substitution on the reflectivity spectra as shown in Figs. 3 or 5. This implies that in this compositional range there is no substantial change in the split Bi-subband structure. Moreover, considering the results of the resistivity measurement in Figs. 2 or 6, it can be concluded that the Pb states are not in the split Bi band gap. According to the Y-F model[15] the effective energy difference between the Pb and Bi site can be enhanced by introducing on-site attractive interaction—the Anderson's negative U derived from the electron-phonon coupling. Thus, our experimental results can be interpreted such that the states associated with the substituted Pb occupy the position higher than the upper Bi subband, as shown in Fig. 10(b), perhaps because of the large energy difference between the Pb and Bi site. In other words, it is evidence that the on-site attractive interaction between electrons is strong enough to push the Pb states out of the gap. Very strong electron-phonon interaction also favors a local CDW state proposed by Jurczek and Rice.[14]

Another indication for the local CDW is the fact that the magnitude of the gap is fairly large ($2\Delta \simeq 2$ eV). Estimating the CDW coherence length ξ by using the equation $\xi = \hbar v_F / \pi \Delta \simeq (E_F / 2\Delta) a_0$, it turns out to be very short (~ 10 Å), the same order as the lattice constant a_0.

For the composition about $x = 0.7$ the optical absorption spectrum shows a low-energy tail below the main absorption peak, which indicates that some states come into the gap. With further substitution by Pb the tailing becomes more significant and the low-energy end of the tail approaches the optical phonon region. Therefore it is reasonable to suppose that these states correspond to the Pb-derived band which goes down as x is decreased and extends in the gap energy region for $x < 0.7$. (It is also suggestive for the local picture that the composition $x = 0.7$ is near the percolation limit for Pb atoms distributed in the Bi simple-cubic lattice.[28]) This interpretation is consistent with the theoretical model of Yoshioka and Fukuyama. The reduction of the on-site attractive interaction due to the Pb substitution leads to the decrease in the energy difference between Pb and Bi sites, thus lowering the Pb band with respect to the Bi band.

Here it should be noted that the threshold energy for the interband optical transitions corresponding to the low-energy end of the absorption tail may be assigned to the energy difference between the edge of the lower Bi subband and that of the Pb band invading the gap between the split Bi subbands. Indeed, for $x < 0.7$ the end energy of the absorption tail is nearly identical to the activation energy observed in the resistivity measurement in Fig. 6. This energy appears to become zero at the M-S transition point $x = 0.35$. On the other hand, the energy corresponding to the peak in Fig. 5 can be assigned to the peak-to-peak gap between the two split Bi subbands. A rather sharp spectral shape indicates that the singular structure in the density of states, as shown in Fig. 10(a) for BaBiO$_3$, is still preserved in this alloy composition region. On decreasing x, this "optical gap" is also decreased, reflecting the reduction in the strength of the attractive interaction, but possesses a substantial magnitude

even at the M-S transition point.

Based on these considerations we can depict a schematic energy band structure in the semiconducting phase, as shown in Fig. 10(c). This picture is similar to the one theoretically calculated by Jurczek and Rice[14] with emphasis on the local CDW. However, the results of our optical study clearly show the existence of a real gap as seen in Fig. 5, whereas the calculated density of states in their model has only a pseudogap and it requires the localization of the midgap states to explain the semiconductivity of this alloy. This difficulty may be avoided if the energy difference between the Pb and Bi sites is treated by the coherent-potential approximation (CPA) as in the K-H model or in the Y-F model. In view of the present experimental results the CPA leads to a successful explanation for the semiconducting phase of this alloy system.

Below the composition $x = 0.35$ where the M-S transition takes place, the optical conductivity extrapolated at zero frequency becomes finite as seen in the spectrum for $x = 0.33$ (see Fig. 5 in Ref. 17) and the electrically detected activation energy becomes almost zero. As Yoshioka and Fukuyama proposed, this may be interpreted in terms of extending the Pb band into the lower Bi subband. On the other hand, the interband transitions between the surviving Bi subbands which were detected optically still show up as a pseudogap, corresponding to the peak in the conductivity spectrum, as shown in our previous work.[17]

C. Possibility of the midgap states in BaBiO₃

As is clearly seen in the results of Fig. 6, the optical-gap energy and the electrical activation energy are different by an order of magnitude. Considering the band tailing derived from the Pb state, this difference is acceptable in the compositional range $x < 0.7$. However, in the range $x > 0.7$, or at least at $x = 1.0$, no optical transitions to any state within the gap could be detected by the reflectivity measurement. We attempted some other optical measurements—photoacoustic spectroscopy (PAS) and bolometric measurement. These measurements[29] also failed to detect any apparent structure at the energy $\hbar\omega \sim 0.24$ eV in the spectra, which is the activation energy not only of the resistivity but also of the Seebeck and Hall effects.[29]

All these results are suggestive of the presence of some midgap states which cannot be detected easily by optical measurements but contributes to the transport properties. One of the possibilities is a two-particle excitation in the bipolaronic array. In the present system a pair of inequivalent Bi sites—in the limiting case (Bi^{3+}, Bi^{5+})—can be regarded as a bipolaronic ensemble. In such a bipolaronic system two types of electronic excitations are expected: single-particle excitations and two-particle ones. The former destroy the bipolaronic array transforming (Bi^{3+}, Bi^{5+}) to (Bi^{4+}, Bi^{4+}) and cost energy corresponding to the CDW gap. This is easily excited by an optical absorption and should correspond to the optical conductivity peak at 1.9 eV in BaBiO₃. The latter is such that two electrons (holes) are simultaneously excited, i.e., (Bi^{3+}, Bi^{5+}) to (Bi^{5+}, Bi^{3+}), which corresponds to a higher-order optical process; consequently, it may be hardly observable in a normal reflectivity process. On the other hand, our transport measurements indicate that the activation energy of this process is $E_A = 0.24$ eV in BaBiO₃. Hence, we may imagine the presence of the midgap states associated with the two-particle excitation in the CDW state which can be created thermally and contribute to the transport properties. For optical observation of the latter process an experiment using a laser may be promising.

In the model described above there remain a few problems: whether such a small value of the activation energy as 0.24 eV is reasonable or not, whether the excited two particles can easily move or not, etc. These problems will be discussed in a separated paper.[29]

IV. CONCLUSION

The optical spectra, including Raman scattering, have been investigated in greater detail for $BaPb_{1-x}Bi_xO_3$ in the semiconducting phase. Resistivity measurements have confirmed that the semiconducting property persists in the wide compositional range $0.4 \le x \le 1.0$, exhibiting the temperature dependence of an activation type over a wide temperature range. The optical spectrum is also typical of semiconductors: The spectrum in the higher-energy region is characterized by one large absorption peak, while several phonon peaks are observed in the lower-energy region(< 1000 cm^{-1}). These results are contrary to the proposal that this alloy series owes its semiconductivity to the electronic localization. Some of the properties are known to be sensitive to the conditions of sample preparation, particularly to the degree of oxidation. However, the systematic change of the optical properties with composition has confirmed that some basic features which are independent of sample history bring about the M-S transition and stabilize the semiconducting phase.

The spectra of the optical phonons and the Raman scattering have given evidence for a CDW instability accompanied by the breathing-mode distortions. The fundamental absorption peak observed in the optical spectrum can be assigned to the transitions across a CDW gap which were found to be in resonance with breathing-mode phonons in the Raman scattering.

In general, a CDW is formed in the lower-dimensional system where the nesting condition is more easily fulfilled over a large portion of the Fermi surface than in the three-dimensional system. In this respect BaBiO₃ is quite unique in that the Fermi surface of an exactly half-filled s band nests perfectly in spite of three dimensions. However, this nesting condition can be easily destroyed by alloying. As proposed theoretically, the persistency of the semiconductivity in the alloys requires electron-phonon interaction strong enough to favor a local CDW as well as a substantial energy difference between Pb and Bi sites. The present experimental results are consistent in many aspects with this theoretical proposal. Based on the experimental results and discussions we can imagine the electronic states near Fermi level in the semiconducting alloys as summarized below.

The Pb substitution for Bi is expected to form states within the gap and simultaneously weaken the strength of the electron-phonon coupling, which leads to a decrease in the Bi-band splitting. We cannot see any trace of these ef-

fects of Pb substitution in both optical and electrical mea-
surements in the compositional range $0.7 < x \leq 1.0$, except
the lattice constants varying continuously with increase of
Pb substitution. This could be interpreted as showing that
the electron-phonon interaction via the breathing-mode
phonon is so strong that the CDW in this system cannot
be destroyed easily by the Pb substitution. This, as well as
the fact that the magnitude of the CDW gap is large (~ 2
eV), seems to favor the picture of the CDW localized at
Bi sites.

The apparent effect of the Pb substitution on the elec-
tronic state is seen in the composition $x < 0.7$. From the
optical spectrum we deduce a decrease of the Bi band
splitting and an invasion of the Pb band into the gap be-
tween the split Bi subbands. Here the minimum energy
gap is no longer defined between the split Bi subbands but
between the Pb band and the lower Bi subband.

At the composition where the M-S transition takes
place, the Pb band attaches the lower Bi band and thus
the gap vanishes. Even in the metallic phase the Bi-band
splitting remains as was shown in our previous paper.
This suggests the presence of substantial attractive in-
teraction in the metallic phase which would bring about
the high-T_c superconductivity.

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