Superconducting energy gap and a normal-state excitation in $Ba_{0.6}K_{0.4}BiO_3$

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We report the first measurement of the energy gap of the high-temperature bismuth oxide superconductor $Ba_{0.6}K_{0.4}BiO_3$ ($T_c \simeq 30$ K). With temperature- and magnetic-field-dependent infrared reflectivity measurements, we obtain a reduced energy gap of $2\Delta/kT_c \simeq 3.5 \pm 0.5$, consistent with a BCS-type mechanism with moderate or weak coupling. In the normal state a broad peak in the infrared conductivity is observed near 5000 cm^{-1}. This unusual infrared behavior is common to both the $BaPb_{1-x}Bi_xO_3$ and the $Ba_{1-x}K_xBiO_3$ systems and may provide a fundamental clue to the mechanism of superconductivity in the cubic bismuth oxides.

The discovery of high-temperature superconductivity in layered copper oxide compounds[1] has generated renewed interest in the cubic bismuth oxide superconductors.[2,3] Recently superconducting transition temperatures up to $T_c \simeq 30$ K have been demonstrated in cubic $Ba_{1-x}K_xBiO_3$,[4-6] which is a variant of the previously studied $BaPb_{1-x}Bi_xO_3$ system ($T_c \lesssim 12$ K).[2,7-10] This transition temperature (30 K) is high enough to raise serious doubts about the applicability of a conventional phonon pairing theory to the bismuth oxide superconductors, but not so high as to rule it out, especially in view of recent experiments showing a substantial oxygen isotope effect in these compounds.[5,6] Both the superconducting mechanism in $Ba_{1-x}K_xBiO_3$ and the closely related question of the nature of the relationship between the bismuth and copper oxide superconductors are of great interest.

In this paper we report infrared measurements of normal- and superconducting-state properties of $Ba_{0.6}K_{0.4}BiO_3$. Using both temperature and magnetic field dependence we obtain a reduced energy gap of $2\Delta/kT_c \simeq 3.5 \pm 0.5$, consistent with a BCS-type mechanism with moderate or weak coupling. This conventional gap ratio contrasts with the unusually large reduced energy gap, $2\Delta_{a\text{-}b} \simeq 8kT_c$, obtained from similar infrared measurements of the a-b plane reflectivity of $Y_1Ba_2Cu_3O_7$.[11] In the normal state of $Ba_{0.6}K_{0.4}BiO_3$ we observe a broad peak in the real part of the conductivity near 5000 cm^{-1}. This normal-state infrared behavior is very similar to that of $BaPb_{0.8}Bi_{0.2}O_3$, in which Tajima *et al.*[8,9] related the presence of a peak in $\sigma_1(\omega)$ to the persistence of local charge-density-wave (CDW) order in the metallic regime of the $BaPb_{1-x}Bi_xO_3$ alloy system.

Two synthesis methods were used to prepare the $Ba_{1-x}K_xBiO_3$ samples. In the first method low-density pellets were prepared as described previously.[12,13] Because of the low firing temperatures (700 °C in nitrogen followed by 450 °C in oxygen) the density obtained with this type of sample is limited to about 80%. In a second method, developed to give higher densities, a stoichiometric mixture of the oxides is melted and rapidly cooled in a mold. The resulting, nearly 100% dense, pellets are then heat treated using the same temperatures and gas sequences as used for the low-density pellets. In our infrared experiments we studied a low-density sample with $T_c \simeq 29$ K with a transition width of about 1 K, and a high-density sample with $T_c \simeq 26$ K with a width of about 4 K. Far-infrared measurements were performed using a Michelson interferometer to measure reflectivity at roughly 45° incidence, as a function of temperature and magnetic field (up to 12 T) in the region of the superconducting transition. Reflectivities at higher frequencies were measured using a scanning interferometer (50–12 000 cm^{-1}) and a grating monochromator (4000–40 000 cm^{-1}) at near normal incidence.

In Fig. 1 the reflectivity of a high-density $Ba_{0.6}K_{0.4}BiO_3$ sample (solid line) is shown from 75–15 000 cm^{-1}, along with the real part of the conductivity, $\sigma_1(\omega)$, and dielectric function, $\epsilon_1(\omega)$ obtained from a Kramers-Kronig transformation of the reflectivity. The conductivity, $\sigma_1(\omega)$, exhibits a broad peak centered at approximately 5000 cm^{-1} and a sharper peak at the origin, while $\epsilon_1(\omega)$ has a zero crossing (plasma edge) at $\simeq 10\,000$ cm^{-1} and a near-zero crossing at $\simeq 1500$ cm^{-1}. In the inset to Fig. 1(a), reflectivity data extending to 40 000

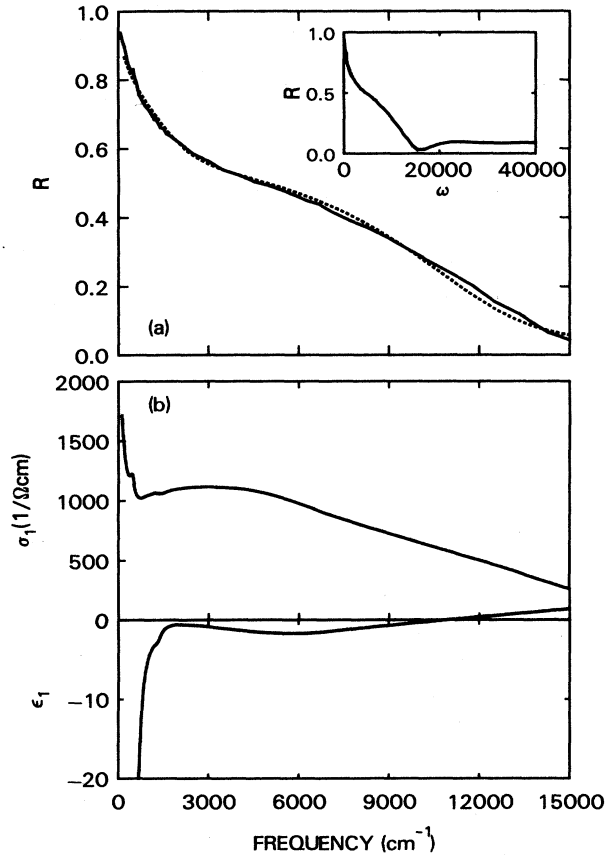

FIG. 1. The normal-state reflectivity of $Ba_{0.6}K_{0.4}BiO_3$ and the conductivity and dielectric function obtained from a Kramers-Kronig transform of the reflectivity are shown. The broad peak in $\sigma_1(\omega)$ at ~ 5000 cm^{-1} was also seen in $BaPb_{1-x}Bi_xO_3$. The dotted curve is a two-oscillator fit to the data. The inset shows the reflectivity up to 40 000 cm^{-1}, including the minimum near 17 000 cm^{-1} (orange) associated with the bluish hue of this material.

cm^{-1} show the minimum in the red-yellow part of the visible spectrum that is responsible for the bluish color of this compound.

The Kramers-Kronig transform was terminated with a Hagen-Rubens form at low frequency, and with a $1/\omega^4$ termination at high frequency ($\gtrsim 300\,000$ cm^{-1}). This corresponds to the limit in which no additional high-frequency excitations contribute to the transform in the range of interest. Decreasing the termination frequency tends to reduce the strength of the mid-infrared mode somewhat and drive $\epsilon_1(\omega)$ even more negative in the frequency range of the near-zero crossing and below, but does not alter the essential features of either $\sigma_1(\omega)$ or $\epsilon_1(\omega)$.

The reflectivity spectrum shown in Fig. 1 is reminiscent of $BaPb_{0.8}Bi_{0.2}O_3$, where the bump in $\sigma_1(\omega)$ at ~ 5000 cm^{-1} has been interpreted both as an exciton, with the potential for direct pair mediation, and as evidence for a pseudogap associated with short-range CDW order in metallic $BaPb_{1-x}Bi_xO_3$.[9,14–16] (To make the association between the mid-infrared peak in $\sigma(\omega)$ and CDW order, Tajima *et al.*[8,9] identified a peak in the infrared conductivity of $BaBiO_3$ with excitations across a Peierls gap, and followed the evolution of that peak through the $BaPb_{1-x}Bi_xO_3$ alloy system.) The observation that this feature is also present in $Ba_{0.6}K_{0.4}BiO_3$ is potentially significant for understanding both the normal-state metal-insulator transition and the superconducting mechanism in the cubic bismuth oxides. The end member compound for both alloy series, $BaBiO_3$, has a half-filled band and exhibits a Peierls-type instability in which a commensurate CDW is accompanied by lattice distortions characteristic of zone-boundary Bi—O bond stretching modes. The persistence of local CDW order, and the accompanying lattice distortions, into the metallic regime has been related to coupling between the carriers and these breathing-mode-type phonons.[14–16]

To facilitate the evaluation of sum rules and the comparison of our results with those from $BaPb_{0.8}Bi_{0.2}O_3$,[8] we have fit our data using the combination of a Drude term and a mid-infared oscillator. We use a Drude term with $n/m = 1.7\times10^{21}$ cm$^{-3}/m_e$, and a scattering rate of 2000 cm^{-1}; augmented by an oscillator centered at 4800 cm^{-1} with a strength of 22 500 cm^{-1} and a width of 9000 cm^{-1}; and a high-frequency dielectric constant of 4 (see Ref. 9). The total oscillator strength in these two terms corresponds to a reduced carrier density of 7.4×10^{21} cm$^{-3}/m_e$, which is roughly 1.5 times larger than the corresponding quantity in $BaPb_{0.8}Bi_{0.2}O_3$, and approximately the contribution to the conductivity sum rule one expects if each Ba atom contributes one electron to the sum rule (7.6×10^{21} cm$^{-3}/m_e$). The strength of the Drude term relative to the mid-ir oscillator, however, is about the same in $Ba_{0.6}K_{0.4}BiO_3$ and $BaPb_{0.8}Bi_{0.2}O_3$, although the former is much closer to half-filling of the Bi-O conduction band. This observation supports the view that doping on the perovskite *A* site (Ba) allows the metallic region to extend closer to half-filling than was previously attainable in $BaPb_{1-x}Bi_xO_3$ where the doping occurs at the perovskite *B* (Bi) site.[17]

The measured reflectivity rises above the fit below about 500 cm^{-1} indicating the presence of additional non-Drude behavior not directly associated with the mid-infrared peak. Similar observations in $Y_1Ba_2Cu_3O_7$ have been associated with the presence of inelastic scattering. We have made reflectivity measurements at temperatures from 30 to 300 K to determine whether the temperature dependence which is characteristic of frequency-dependent scattering is present.[18] We do observe small changes in the absolute reflectivity at low frequency, but these are difficult to quantify as they are close to the detection limit ($\simeq 1\%$) of these measurements. Below 200 cm^{-1} the reflectivity is consistent with a dc conductivity of $\sim 2000/(\Omega$ cm). At the present time this provides the only estimate of the dc conductivity in $Ba_{0.6}K_{0.4}BiO_3$, since direct measurements of the intrinsic dc resistivity have not yet been successful. Our infrared estimate is comparable to dc conductivities reported for $BaPb_{0.8}Bi_{0.2}O_3$.[7]

Focusing now on the changes in the reflectivity associated with the transition to the superconducting state, in Fig. 2 we show temperature- and magnetic-field-dependent reflectivity ratios taken with the lower T_c sam-

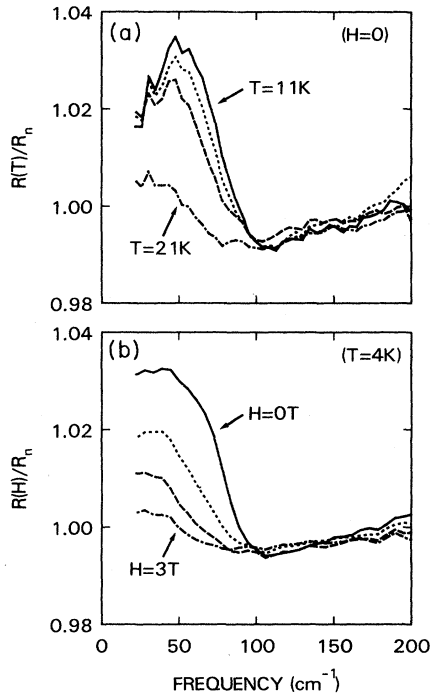

FIG. 2. (a) The reflectivity in the superconducting state at $T=11$, 14, 17, and 21 K, divided by a normal-state reference at $T=30$ K is shown for a high-density sample. This low-frequency reflectivity enhancement is associated with the superconducting energy gap. (b) The suppression of the low-frequency reflectivity enhancement by an applied magnetic field is demonstrated. Reflectivity spectra at $T=4$ K are shown for fields of 0, 1, 2, and 3 T divided by a 6-T reference spectrum (also at 4 K).

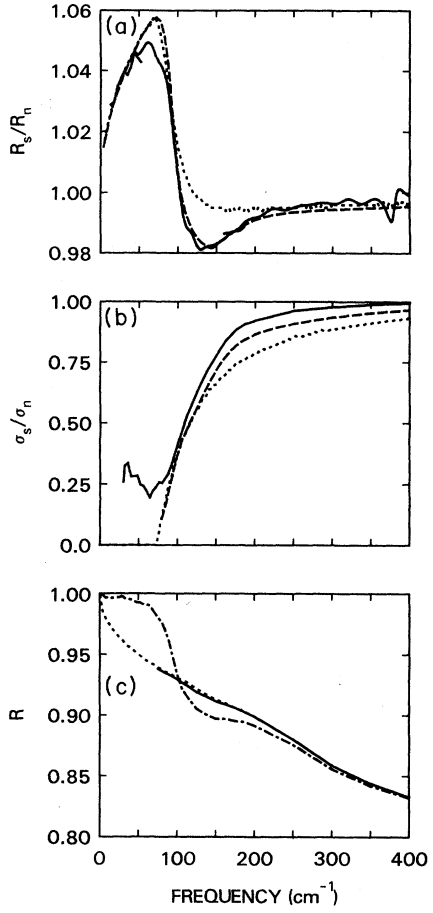

FIG. 3. (a) The reflectivity in the superconducting state divided by that in the normal state is shown (solid line). (b) The real part of the conductivity in the superconducting state divided by that in the normal state is shown (solid line). An estimate of the energy gap can be obtained either from the frequency of the peak in R_s/R_n, or from the extrapolated cutoff of σ_s/σ_n. The dotted and dashed curves are the results of Mattis-Bardeen and Eliashberg calculations, respectively, both with $2\Delta \simeq 70$ cm^{-1}. (c) The reflectivity in the normal state (solid curve) and its Hagen-Rubens extrapolation to dc (dotted curve) are shown. The reflectivity in the superconducting state (dot-dashed curve) is obtained from the product of this normal-state reflectivity and R_s/R_n from Fig. 3(a).

ple (26 K) positioned in a large solenoidal magnet. These spectra show the enhancement of the low-frequency reflectivity as the temperature is reduced below T_c, and the dependence of this reflectivity enhancement on an applied magnetic field (H). In Fig. 2(a) the position of the maximum in the reflectivity ratio shifts to higher frequency as temperature is reduced. The reflectivity spectra in Fig. 2(b) demonstrate the suppression of this reflectivity enhancement by a magnetic field. These observations are consistent with the expected behavior of a superconducting energy gap.

In Fig. 3(a) we show the reflectivity in the superconducting state divided by that in the normal state for our higher T_c sample, along with two calculated reflectivity ratios. Reflectivity calculations are reasonably straightforward for $Ba_{1-x}K_xBiO_3$ because its electrodynamic response is nearly isotropic and close to the classical (London) limit. The dotted curve shows a calculation using the standard Mattis-Bardeen conductivity[19] with an energy gap of about 70 cm^{-1}, and using normal-state parameters, $n/m = 1.7\times10^{21}$ cm^{-3}/m_e and $\rho_{dc} = 0.5$ $m\Omega$ cm, based on our reflectivity measurements (Fig. 1). The Mattis-Bardeen form for σ_s/σ_n is valid only in the zero (or infinite) mean free path and extreme weak-coupling limits. The dashed curve shows the results of a more general Eliashberg calculation[20] (with $\lambda \simeq 1$), which is not restricted to these limits. This calculation provides a better fit to the data above 2Δ, although with either approach an estimate for the energy gap of about 70 cm^{-1} is obtained for this sample ($T_c \simeq 29$ K). For our lower T_c sample (26 K) an energy gap of about 60 cm^{-1} was estimated.

Following the approach of Tinkham and Glover,[21] the energy gap can also be obtained from the extrapolated cutoff of the real part of the conductivity in the superconducting state divided by that in the normal state, which is shown in Fig. 3(b). To obtain this conductivity ratio we use the measured reflectivity ratio shown in Fig. 3(a), and the measured normal-state reflectivity extrapolated to

low frequency with a Hagen-Rubens form as shown in Fig. 3(c). An estimate for the reflectivity in the superconducting state, also shown in Fig. 3(c), is obtained by multiplying this normal-state curve (R_n) by R_s/R_n from Fig. 3(a). From the frequency at which σ_s/σ_n extrapolates to zero, an estimate for the energy gap of about 70 cm^{-1} is obtained, consistent with the value obtained by fitting R_s/R_n.

It has been suggested that the existence of a mid-infrared mode, as we find in the normal state (Fig. 1), may effect the measurement of the superconducting energy gap. In order to investigate this possibility we have performed parametrized calculations with and without that mode included, using both the Mattis-Bardeen and Eliashberg conductivities. We find that the effect of the mid-infrared mode is insignificant in the region of the superconducting energy gap. (R_s/R_n is about 0.1% lower at 150 cm^{-1} when the mode is included.) The negligible effect of the mid-infrared mode on the gap region is related to the fact that the plasma edge(s) lie well above the gap region. Although the ability of plasma edge to obscure an energy gap has been discussed recently[22] its relevance to any system, with the possible exception of polycrystalline $La_{2-x}Sr_xCuO_4$,[23,24] has never been demonstrated. Polycrystalline $La_{2-x}Sr_xCuO_4$ is a rather pathological system due to the combination of a low c-axis conductivity and a strong c-axis phonon,[24,25] which lead to a very low-frequency zero crossing of $\epsilon_1(\omega)$. In the present system there is no zero crossing of $\epsilon_1(\omega)$ near 2Δ, and $\epsilon_1(\omega)$ is quite negative below ~ 1000 cm^{-1} regardless of whether there is a near-zero crossing or actual zero crossing of $\epsilon_1(\omega)$ at ~ 1500 cm^{-1}. This underscores a point that we have tried to make previously,[24,26] namely that it is anisotropy that complicates the analysis of data from polycrystalline samples of $La_{2-x}Sr_xCuO_4$ and $Y_1Ba_2Cu_3O_7$, rather than the behavior of the conductivity in the mid-infrared region.

In the conventional theory of superconductivity the magnitude of $2\Delta/kT_c$ is related to the coupling strength.[27] Using $2\Delta \simeq 70$ cm^{-1} with $T_c \simeq 29$ K, and $2\Delta \simeq 60$ cm^{-1} with $T_c \simeq 26$ K, we estimate that $2\Delta/kT_c \simeq 3.5 \pm 0.5$. In Eliashberg theory,[28] an upper bound of 4.0 on $2\Delta/kT_c$ places an approximate upper bound on the coupling strength of $\lambda \simeq 1$, and a corresponding lower bound on the energy of the pair mediating excitation of about 40 meV ($\sim 15kT_c$). This lower bound lies well within the optical phonon spectrum of $BaBiO_3$ and thus does not rule out a phonon pairing mechanism for the cubic bismuth oxides.

In conclusion, we have used infrared measurements to study the high-T_c (30 K) cubic superconductor $Ba_{0.6}K_{0.4}BiO_3$. Using temperature- and magnetic-field-dependent measurements an energy gap of $2\Delta/kT_c \simeq 3.5 \pm 0.5$ is obtained, consistent with a BCS-type mechanism with moderate or weak coupling. This conventional reduced energy gap contrasts with the unconventionally large value, $2\Delta_{a-b} \approx 8$ kT_c, inferred from similar infrared measurements of $Y_1Ba_2Cu_3O_7$.[11,29] In the normal state a broad peak in the infrared conductivity is observed near 5000 cm^{-1}, demonstrating an unusual infrared behavior common to both the $BaPb_{1-x}Bi_xO_3$ and the $Ba_{1-x}K_xBiO_3$ systems.

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