Optical study of $Ba_{0.6}K_{0.4}BiO_3$ single crystals: Normal and superconducting properties

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We report absolute reflectivity measurements on $Ba_{0.6}K_{0.4}BiO_3$ in both normal and superconducting states. The superconducting-gap value was determined to be $2\Delta=90\pm10$ cm^{-1}, which gives $2\Delta/k_BT_c=4.2\pm0.5$, consistent with previous experiments. However, finite absorption below 2Δ frequency was found. No Holstein shift of the phonon-related spectrum was observed. Optical conductivity below 2 eV consists of two contributions: a narrow ($\leq$350 cm^{-1}) Drude-like part (Drude component) and an overdamped midinfrared component. We suggest that while the carriers responsible for the Drude contribution form the superfluid at $T<T_c$, the carriers responsible for the midinfrared one remain normal and account for the finite absorption inside the superconducting gap. The value of the London penetration depth λ_L was determined to be (4550$\pm$300) Å. Anomalous temperature dependence of reflectivity at temperatures above ~120–150 K was observed.

I. INTRODUCTION

$Ba_{1-x}K_xBiO_3$ or BKBO (as well as $BaPb_xBi_{1-x}O_3$ or BPBO) is a family of superconductors based on the perovskite $BaBiO_3$. Superconductivity in this compound was discovered by Mattheiss, Gyorgy, and Johnson[1] in 1988 and since then BKBO has attracted a great deal of attention because of a combination of a high T_c with relatively simple isotropic structure (cubic perovskite in the superconducting phase[2]) and lack of Cu. Nevertheless, just as in the copper-based materials, its normal state properties, their doping dependence, and mechanism of superconductivity are far from being understood.

Despite its relatively low (31 K) superconducting-transition temperature, there are several reasons to place BKBO in the same group as the cuprates: (1) As first pointed out by Batlogg,[3] the value of T_c is exceptionally high in relation to an extremely low density of states $N(0)$ at the Fermi level. This is an extremely unfavorable situation for the phonon-mediated BCS mechanism and yet BKBO has a higher T_c than any other known copper-free material, except for C_{60}. This puts into question the application of the BCS mechanism with electron-phonon coupling for BKBO but is in agreement with the general trend in all high-T_c superconductors: large T_c despite of low $N(0)$. (2) The maximum T_c was observed near the semiconductor-metal (SM) transition followed by a decrease in T_c with "overdoping"—another signature of high-temperature superconductors. (3) Two contributions to the optical conductivity below ~2 eV were observed in BKBO,[4–6] as well as in the cuprates.[7] (4) Other similarities have been observed in tunneling, muon spin resonance (μSR), and optical experiments.[8]

There are some differences as well. We will list only the main ones: (1) The undoped component $BaBiO_3$ is diamagnetic.[9] (2) The charge carriers are electrons[10,11] while in all copper oxide superconductors [except for $(Nd,Ce)_2CuO_4$] they are holes. (3) There is a well-defined onset of a superconducting gap in BKBO,[4,12–16] while in the cuprates this issue is still an open one.[7,17] (4) The isotope shift was reported to be 0.2–0.4 (Refs. 18–20) in contrast with much smaller values for the cuprates.

Previous optical measurements on this material have been done mainly on thin films.[4,5,16] Recently, optical work on BKBO single crystals with different potassium doping was reported by Karlow *et al.*,[6] but only at room temperature. Although ratios of reflectivities in superconducting and normal states have been obtained for the thin films,[4,16] in none of the above experiments were absolute low-temperature reflectivity measurements performed. As a result, detailed behavior of $\sigma_1(\omega)$ at low temperature above and below the superconducting transition still needs to be clarified.

In this paper we present the absolute reflectance of $Ba_{0.6}K_{0.4}BiO_3$ at different temperatures in the range from 10 K to 300 K. Single crystals of BKBO have been chosen for this study as they usually demonstrate higher T_c values than thin films. Our data cover a wide frequency range, 30–40 000 cm^{-1}, which permits more accurate calculations of the optical conductivity than was possible in previous experiments, especially at low frequencies. As a result, we were able to resolve a finite absorption inside the superconducting gap and find an anomalous temperature dependence of reflectivity in the normal state. A low noise level enabled us to estimate value of the electron-phonon interaction strength in this material.

II. EXPERIMENT AND SAMPLE PREPARATION

Single crystals of $Ba_{0.6}K_{0.4}BiO_3$ were grown electrochemically using a technique described elsewhere.[21] As-

grown crystals were annealed for 2 h in flowing oxygen in order to reduce the number of possible oxygen vacancies, followed by slow cooling. Crystals treated this way have a higher T_c and lower width of the superconducting transition. All crystals had a brilliant blue hue, which indicates metallic $Ba_{1-x}K_xBiO_3$.

The crystals were characterized in two ways. Energy dispersive x-ray (EDX) analysis, when compared to stoichiometric polycrystalline samples, shows that x=0.4±0.03. Single-crystal x-ray analysis was performed as well, and after the absorption correction routine, the value of x was determined to be 0.415(10) (parentheses represent error in last digit). The superconducting transition temperatures were obtained from results of magnetization measurements shown in Fig. 1 for a typical sample. Onset of superconductivity occurred at ~30.8 K with a transition width $\Delta T_c \simeq 5$ K. The crystals show a single-step transition which indicates that they behave, at least from a macroscopic point of view, as a single-phase material. Resistivity measurements give a lower $\Delta T_c \simeq 3$ K.

For the optical measurements, one of the large (~1.5×1.5 mm^2) sample faces was mechanically polished using a 1 μm abrasive. The far-infrared reflectance measurements were carried out using a rapid scan interferometer with focused optics on a sample mounted in a continuous flow cryostat. For near-infrared and visible measurements, a grating spectrometer with appropriate detector-filter combinations with overlapping frequency ranges was used. To obtain the absolute value of the reflectance, geometrical scattering losses were accounted for by *in situ* evaporation of a metallic film (Au or Al) onto the surface of the sample. The coated sample was then remeasured and the absolute value of R is then given by the ratio of spectra before and after plating, corrected for the absolute reflectance of the metallic film.[22]

Measurements in the frequency range 30–9000 cm^{-1} were repeated on four different crystals from the same batch. The sample-to-sample reflectance variation was in the range $\Delta R = \pm 0.5\%$ below ~1000 cm^{-1}, although above 2000 cm^{-1} it was substantially larger (ΔR = 3–5 % at 9000 cm^{-1}). All measurements above 9000 cm^{-1} were performed on one crystal, but each detector-filter combination used for the various frequency bands was repeated at least twice. In the regions of overlap, adjacent bands differed by less than $\Delta R = 1\%$ from each other.

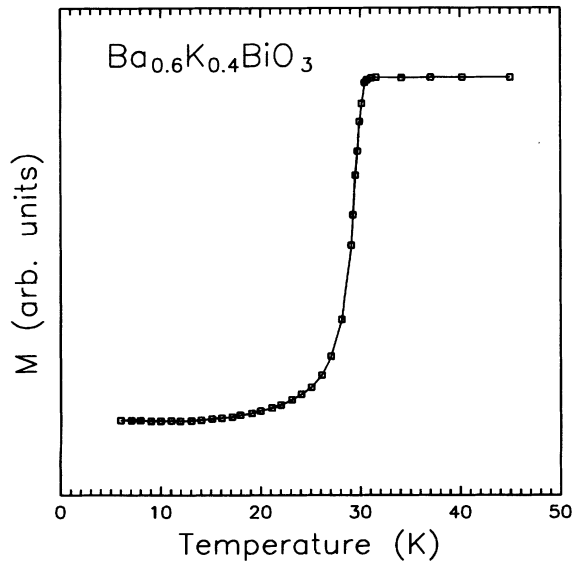

FIG. 1. Magnetization versus temperature for a typical sample of BKBO used in this study.

III. RESULTS AND ANALYSIS

Figure 2 shows the frequency dependence of the reflectivity at different temperatures for a typical crystal in the whole measured frequency range. Our data covered the spectral region from 30 to 40 000 cm^{-1} for 300 and 180 K and from 30 to ~9000 cm^{-1} for the lower temperatures. Although all spectra have characteristic metallic behavior (reflectance is increasing towards unity at low frequency), an unusual temperature dependence above ~1000 cm^{-1} was observed: The reflectance below ~15 000 cm^{-1} is rapidly decreasing with decreasing temperature from 300 to ~120 K while increasing above the plasma edge, in the same temperature range. Changes with temperature below ~120 K are much less prominent and are near the accuracy limit of our experiment.

Conductivity curves, obtained by Kramers-Kronig (KK) analysis of the reflectivity spectra, are shown in Fig. 3. For the spectra at 300 and 180 K the KK transform was terminated above the range of our measurements (40 000 cm^{-1}) by extending R as a constant to 1 000 000 cm^{-1} and then letting it decrease as $1/\omega^4$. The exact value of the upper frequency is not important — any choice above ~200 000 cm^{-1} leads to the same $\sigma_1(\omega)$ in the frequency range of our actual measurements. In order to perform KK analysis at lower temperatures the spectra were first extended towards the plasma edge as shown by the dashed line in Fig. 2 and then were assumed to be equal to the reflectivity spectrum at 180 K. Although such a procedure may be questioned, all reasonable extensions lead to the same $\sigma_1(\omega)$ at frequencies below ~7000 cm^{-1}. Below 30 cm^{-1} various approximations were tried. All of them lead to the same $\sigma_1(\omega)$ above ~50 cm^{-1}.

The temperature dependence of the midinfrared reflectivity leads to the corresponding changes in $\sigma_1(\omega)$: The spectral weight below ~15 000 cm^{-1} decreases rapidly with temperature in the range 300–120 K with the missing spectral weight piling up above the plasma edge. This behavior is surprising given the basic principle of temperature-frequency equivalency. Usually one would expect temperature dependence (if any) of an optical conductivity in a frequency range of order of experimental temperature. Contrary to this we found significant changes up to 5 eV. Below ~120 K no temperature dependence of the optical conductivity was observed.

Reflectivity data at different temperatures are shown in Fig. 4 on a lower-frequency scale. Spectra at temperatures above 10 K were offset by $\Delta R = -1\%$ for

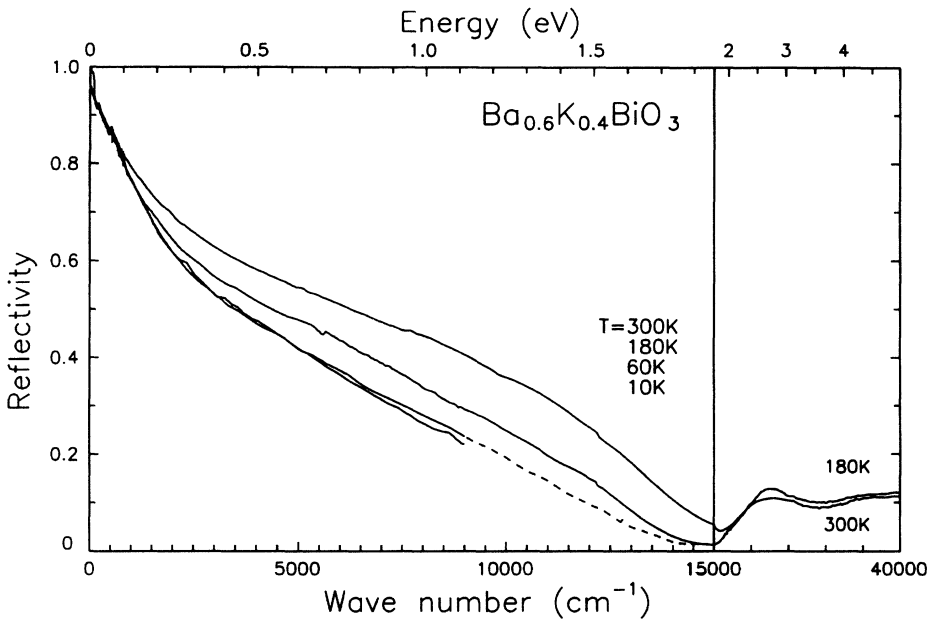

FIG. 2. Reflectivity as a function of frequency at different temperatures (please note a change of the x-axis scale at 15 000 cm^{-1}). The high-frequency approximation for the spectra at T<180 K is shown (dashed line).

each spectrum in order of increasing temperature. At temperatures below the superconducting transition reflectivity increases sharply below ~100 cm^{-1} — feature that can be associated with opening of a superconducting gap. Within our noise level, the reflectivity spectrum at $T = 15$ K was found to be identical to that at $T = 10$ K and is therefore not shown.

The calculated optical conductivity below T_c is shown on the low-frequency scale in Fig. 5 for several temperatures below the superconducting transition, along with $\sigma_1(\omega)$ just above T_c. As temperature is lowered below T_c, the spectra show a decrease of spectral weight below ~100 cm^{-1} resulting in an apparent opening of a superconducting gap. As a result of the finite absorption below the gap frequency (Fig. 4), the optical conductivity remains finite even at lowest measured temperature of 10 K, resembling in this respect the copper-oxide-based superconductors. It seems unlikely that this result can be attributed to experimental errors in our measurement of reflectivities very close to unity for the following reasons: (1) All (four) samples in the study gave similar results, e.g., finite absorption below the superconducting gap. (2) Although at frequencies below ~60 cm^{-1} the value of the absorption $(1 - R)$ was found to be comparable with experimental error, the absorption of 1.5% at 80 cm^{-1} is substantially above our uncertainty. (3) It also seems to be unlikely that this effect is caused by errors in the temperature determination: The spectrum at

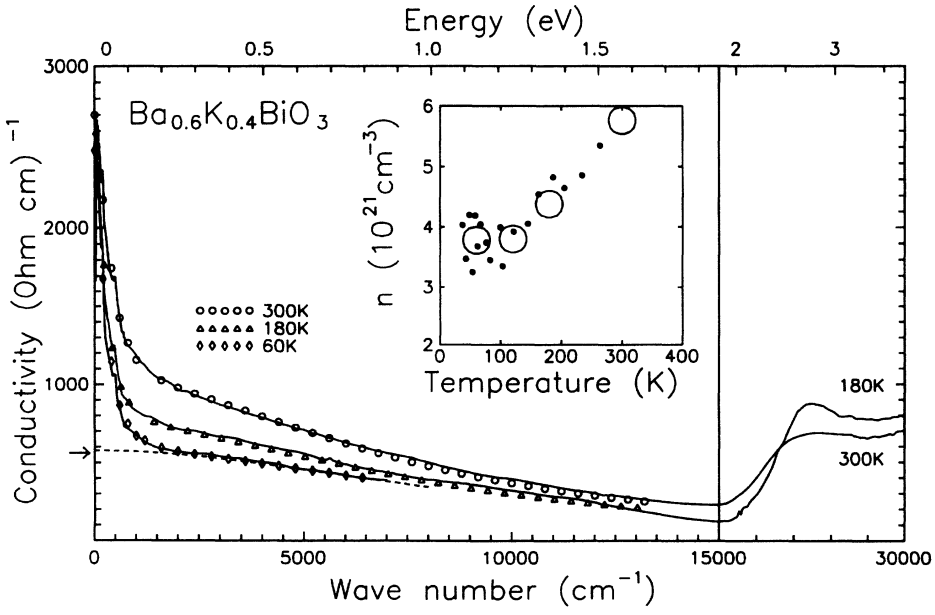

FIG. 3. Real part of the optical conductivity obtained from KK analysis of the experimental data (solid lines). At lower temperatures high-frequency optical conductivity curves are identical to the one at 60 K. Result of fit to Eq. (1) is shown with open symbols. The dashed line represents the MIR continuum obtained in the fit for T=60 K, while the arrow on the vertical axis shows a value of residual conductivity inside of the superconducting gap at T=10 K. The inset: $n(T)/m^*$, calculated with the assumption of m^*=1 (open symbols) in comparison with $n(T)$ from the single-crystal Hall measurements (points) reported in Ref. 11.

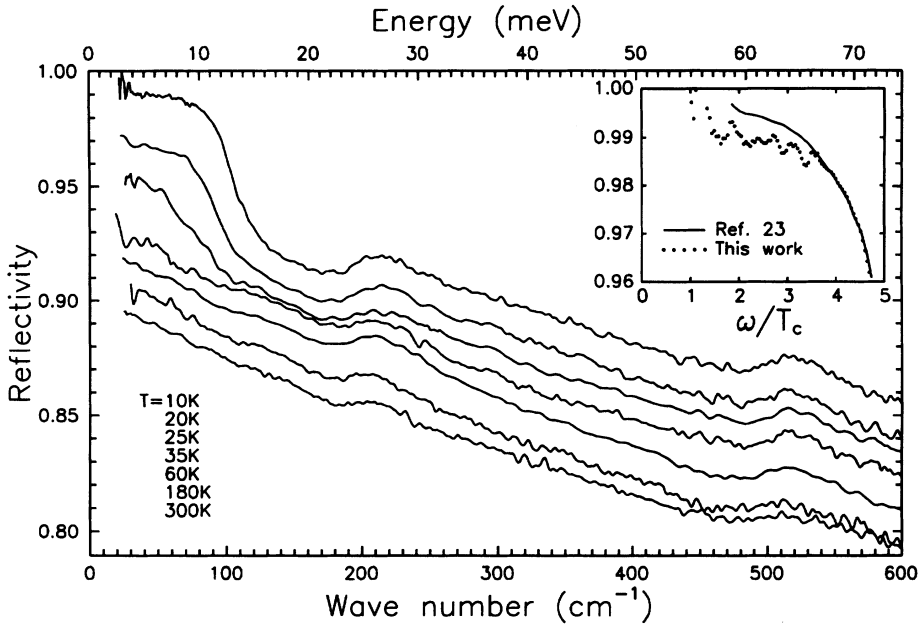

FIG. 4. Reflectivity spectra obtained at different temperatures. For all temperatures except for 10 K the spectra were offset downwards for clarity by $\Delta R = 1\%$ for the each spectrum in order of increasing temperature. The inset: absorption inside the superconducting gap obtained in our study at 10 K (symbols) and by Miller *et al.* (Ref. 23) at liquid helium temperature (solid line). Frequency was normalized to actual T_c for each sample to account for the differences in the gap value.

25 K already shows specific superconducting behavior, indicating that the uncertainty in the temperature determination is less than 5 K in this temperature region. (4) Our reflectivity data are in good agreement with results of the more sensitive (in this frequency range) absolute absorption measurements on BKBO thin films at liquid He temperatures[23] (inset of Fig. 4).

The value of 2Δ can be roughly estimated from position of the gap feature to be 90 ± 10 cm^{-1} which gives value of $2\Delta/k_BT_c=4.2\pm0.5$. This value is somewhat higher, although close, to the one reported previously.

The spectral weight under the conductivity curves at all temperatures can be clearly divided into two major contributions: a very broad continuum extending up to 16 000 cm^{-1} [adopting language accepted for the cuprates it will be referred as a midinfrared (MIR) contribution] and a narrow Drude-like peak (hereafter "Drude"). These two contributions can be formally associated with two types of carriers and it is of interest to investigate them separately. The only way of separation is to fit the measured data below the plasma edge using some model of dielectric response. The simplest two-component model of $\sigma_1(\omega)$, used for BKBO before,[4,6] can be written as

$$\sigma_1(\omega) = \frac{1}{4\pi}\frac{\omega_{pD}^2\tau_D}{(\omega\tau_D)^2+1} + \frac{1}{4\pi}\frac{\omega_{pO}^2\tau_O}{\frac{[(\omega_O^2-\omega^2)\tau_O]^2}{\omega^2}+1}. \quad (1)$$

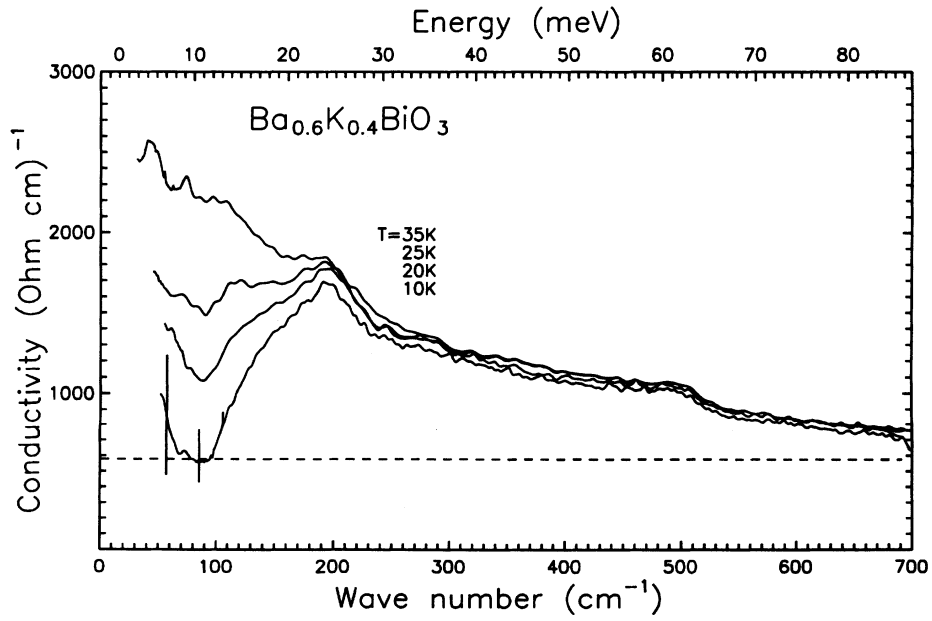

FIG. 5. Optical conductivity, calculated from the reflectivity spectra, below the superconducting transition and just above it (solid lines). The MIR continuum, obtained from the fit at 60 K, is shown (dashed line).

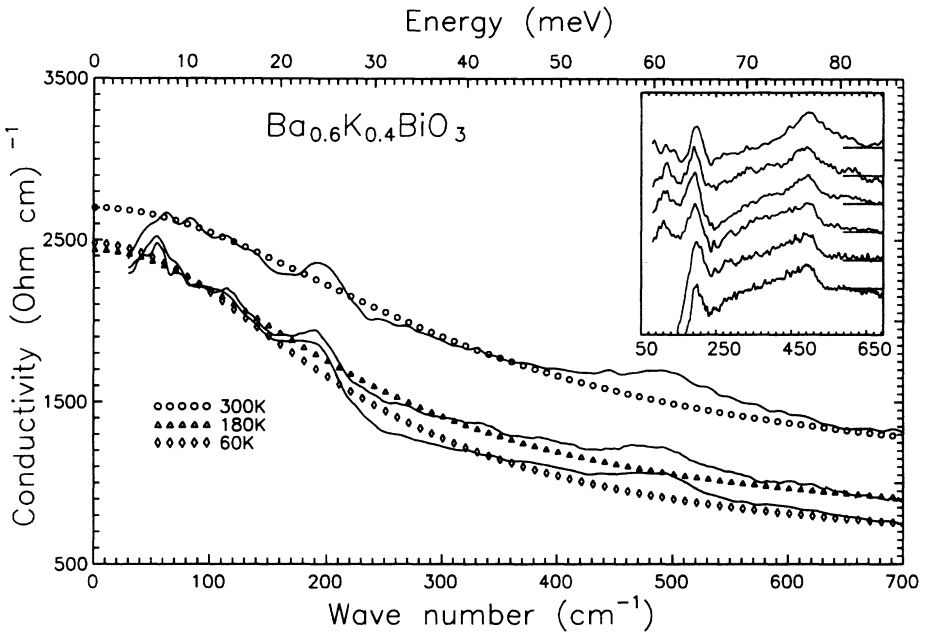

FIG. 6. $\sigma_1(\omega)$ dependence, calculated from experimental data at three normal temperatures, is shown (solid lines). The same fit as in Fig. 3 is shown with open symbols. The inset: phonon spectra at different temperatures obtained by subtracting of the fitted results from the experimental data. Temperatures are, in order from top to bottom, 300 K, 180 K, 60 K, 35 K, 20 K, 10 K. The broad peak at 500 cm^{-1} is getting more asymmetric with decreasing temperature.

The first term is the standard Drude free carrier response with strength ω_{pD} and scattering rate $1/\tau_D$. The second term is a Lorentz oscillator with strength ω_{pO} and width $1/\tau_O$, centered at a finite frequency ω_O to account for the MIR absorption band. However, this model is oversimplified which can be seen from the doping dependence studies.[5,6] The MIR component is not well described by a single oscillator. While at doping level $x \simeq 0.33$ the MIR component has its maximum at finite frequency, it seems to contribute already to the dc conductivity (i.e., a SM transition has taken place). The whole feature looks like the optical response of a free charge carrier system with a pseudogap in a density of states. The optical response of such a system is Drude-like ($\omega_O=0$) at frequencies well above the pseudogap but deviates downwards below it.[24] It is natural to assume that at our doping level the MIR component has the same shape although the pseudogap, if still exists, is smaller. Therefore we have chosen the model with $\omega_O=0$ expecting, however, low-frequency deviations of the fitted results from the experimental data. The fit appeared to be reasonably good from the plasma minimum down to ~60–80 cm^{-1} (Fig. 3 and Fig. 6) where the measured curves start to deviate downwards from the fitted results, possible evidence of a low-lying pseudogap. The lack of accuracy of our KK analysis in this frequency range prevents us from making a firm conclusion. Table I presents the numerical parameters used in the fit.

The inset of Fig. 6 shows the phonon spectra at different temperatures, obtained by subtracting of the fitted results from the experimental data. Two peaks are prominent: one at about 200 cm^{-1} and another one at 500 cm^{-1}. A third mode of much lower intensity can be seen at about 120 cm^{-1}. With decreasing temperature the shape of the 500 cm^{-1} peak becomes increasingly asymmetric. Similar results have been reported previously in Raman scattering experiments on this material.[25] In this Raman experiment this peak was shown to consist actually of several phonon modes with intensity redistributing in favor of the lower-lying ones upon cooling. No explanation of this phenomenon has been proposed so far. However, it should be noted that, overall, the phonon lines are not anomalous as they are in the copper oxides where prominent antiresonances in the *ab* plane response can be seen at frequencies corresponding to longitudinal phonons polarized in the *c* direction.[7,26] Here the phonon lines are due to TO optical phonons and, to a first approximation, have the same central positions as in the undoped $BaBiO_3$.[27] Nevertheless, there are some differences: While in $BaBiO_3$ all phonon modes, except for the lowest one, have almost the same intensity, in $Ba_{0.6}K_{0.4}BiO_3$ only 200 cm^{-1} and 500 cm^{-1} lines are prominent.

With a $v_F=10^8$ cm/sec,[28] we can estimate the superconducting coherence length $\xi_0=v_F h/2\pi^2\Delta=380$ Å and the mean free path l from width of the Drude component of 230 cm^{-1} to be 230 Å. The mean free path for the MIR component will be 30–40 times smaller. Thus

TABLE I. The parameters used to fit the optical conductivity using Eq. (1). ω_{pD} and $1/\tau_D$ are the plasma frequency and scattering rate of the Drude part and $1/\tau_O$, ω_{pO} are the width and strength of the MIR oscillator (central position of which was assumed to be equal to zero). Approximate error is represented in the brackets. Note that its relative value is much smaller for the latter component.

T (K)	ω_{pD} (cm^{-1})	$1/\tau_D$ (cm^{-1})	ω_{pO} (cm^{-1})	$1/\tau_O$ (cm^{-1})
300	5600 (±150)	350 (±20)	21150 (±200)	7500 (±200)
180	5300 (±150)	255 (±20)	19100 (±200)	8325 (±200)
60	5300 (±150)	230 (±20)	18350 (±200)	9700 (±200)

with $l<\xi_0$ the samples are dirty and the gap is expected to be observable.

IV. DISCUSSION

As noted above, two major contributions to the optical conductivity below the plasma minimum were observed. Similar results were reported previously.[4–6] For the reader's convenience we compared our results with those published previously for the samples of approximately the same composition in Fig. 7. The Drude component appeared to be reasonably similar for all conductivity curves except the one by Karlow *et al.*[6] where the relatively high low-frequency limit of the actual measurements (800 cm^{-1} compared to 25 cm^{-1} in our experiment) made it difficult to resolve this relatively narrow component and could, in principle, seriously affect the calculation of the overall low-frequency optical conductivity. At the same time shape and spectral weight under the MIR contribution are substantially different in different measurements performed on different samples. While in both thin film measurements this contribution has a maximum at about 3000–4000 cm^{-1}, neither single-crystal curve shows it. Spectral weights under the conductivity curves vary by up to 30–40% at frequencies above 1000 cm^{-1}. Thus, the optical conductivity, especially in the MIR range, is varying from sample to sample even for the same nominal stoichiometric composition. Possible reasons for this phenomenon will be discussed later in this section.

The detailed origin of these two contributions is still not clear. This problem has its roots in a more general one: What mechanism is making undoped $BaBiO_3$ semiconducting despite the expected half filling[28] of the conduction band? The most popular explanation includes the formation of commensurate charge density wave (CDW) order, which splits the conduction band into two parts, separated by a gap.[27,28] However, it should be noted that the gap value of 2 eV determined for this material[27] is rather large compared to the conduction band width of ~4 eV. Other proposed mechanisms of semiconductivity of $BaBiO_3$ include, for example, semiconducting domain walls[29] and localization due to formation of small bipolarons.[30] The optical conductivity of $BaBiO_3$ shows a roughly Lorentzian shape feature which gradually broadens and shifts downwards with increasing doping level, forming the MIR contribution in the metallic phase.[5,6] Meanwhile, the Drude component develops at some value of the doping level between $x = 0.3$ and $x = 0.4$. While the Drude component is new (it does not exist in $BaBiO_3$) the existence of the MIR one suggests that the metallic phase of BKBO still retains some of the characteristics of the mechanism that makes the undoped $BaBiO_3$ semiconducting. For example, (local) CDW order extending into the metallic phase of BKBO was suggested by Blanton *et al.*[5] and Karlow *et al.*[6]

The CDW scenario and other suggested mechanisms require deviations (at least local) from the cubic perovskite structure in the metallic phase of BKBO. A number of experimental observations support this hypothesis. For example, noncubic symmetry is particularly evident from the phonon-rich Raman spectra[25,30] (a perfect cubic lattice has no Raman-allowed modes). Structural studies[2] (and characterization procedure performed on our samples) revealed no phase separation in $Ba_{0.6}K_{0.4}BiO_3$ so that any structural imperfections can occur on local scale only, making "macroscopic" techniques, such as usual Rietveld refinement of neutron data, insensitive to them. Indeed, recent observations of Rosenfeld and Egami of a noncubic local distribution of equilibrium atomic positions on the scale of several tens of Å in $Ba_{0.6}K_{0.4}BiO_3$ (Ref. 31) gives direct experimental evidence for this.

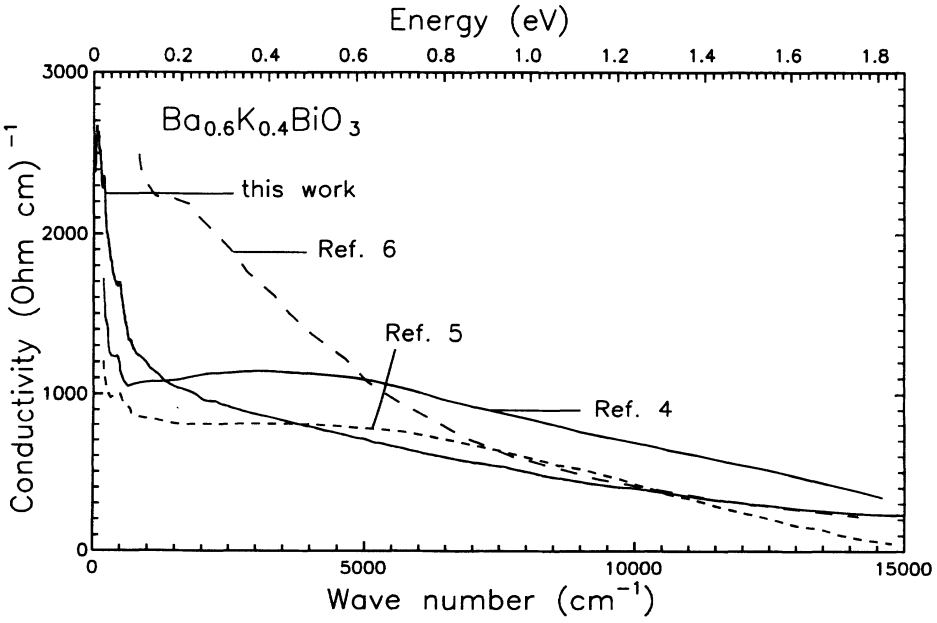

FIG. 7. Comparison of results of the optical conductivity of $Ba_{1-x}K_xBiO_3$ with $x \simeq 0.4$ obtained by different groups on different samples. Work in Ref. 6 was done on a single crystal with $x = 0.41$, in Refs. 4,5 thin films with $x = 0.4$ were used. While the narrow Drude contribution looks reasonably similar for at least three of the conductivity curves, the MIR component is remarkably different. All of the data were taken at 300 K.

It is interesting to note that the SM transition in BKBO occurs at $x \simeq 0.3$,[5,6] which is a percolation threshold x_c for the site problem in a simple cubic lattice formed of Ba/K ions.[32] (In the case of BPBO the transition occurs at $x \simeq 0.7$, corresponding to $1 - x_c$ for the same problem.[27]) This suggests a percolation scenario where lattice regions with relatively low doping level (these microscopic regions are inevitable due to randomness of the potassium doping) form a continuous "semiconducting" network, retaining the characteristic peculiarities, such as the local lattice distortions, of the undoped component. At the same time doped sites gradually dilute it, forming metallic clusters, leading at $x = x_c$ to formation on an infinite one and the SM transition. It would be natural to assume that the MIR carriers are associated with the semiconducting network, as this component exists throughout the whole doping range, while the Drude ones belong to the metallic cluster. Due to the disappearance of long-range order, the semiconducting network should be affected by doping as well, resulting in smoothing of the semiconducting gap boundaries, its lowering followed by transformation into a pseudogap, and, possibly, final disappearance. In this scenario, the semiconducting or MIR carriers should be particularly sensitive to changes in noncubic local structure, screening it at the same time from the metallic ones. Percolation-type models in relation to the BKBO system were discussed at different times by Phillips,[29] Sugai *et al.*,[30] Hellman and Hartford.[33]

In Fig. 5, the low-temperature MIR contribution, obtained from our fit to Eq. (1), is plotted with a dashed line in comparison with the optical conductivity in the superconducting state. Although the experimental error in calculating $\sigma_1(\omega)$ (shown by vertical bars on the 10 K curve) is quite large below the gap frequency, due to almost perfect reflectance, it is noteworthy that the magnitude of the nonzero conductivity below 2Δ at $T = 10$ K corresponds fairly accurately to the value of the MIR contribution. This can be seen especially clearly in Fig. 3, where the approximate value of the residual conductivity is shown by an arrow on the vertical axis while fitted at 60 K MIR continuum is shown by the dashed line. In BCS theory, at $T = 10$ K $\simeq T_c/3$ all carriers should be already condensed. Indeed, lowering temperature from $T = 15$ K to $T = 10$ K does not produce any changes of reflectivity and, therefore, changes in the optical conductivity. Results of absolute absorption measurements show that finite absorption of similar magnitude still exists even at $T = 4.2$ K.[23] Therefore, it is unlikely that lowering the temperature below 10 K will move the finite optical conductivity in the gap region any lower. All of the above suggests that, while the metallic Drude carriers undergo a superconducting transition at $T_c \simeq 30$ K with a gap at $2\Delta \sim 90$ cm^{-1}, the MIR carriers remain normal, accounting for the finite absorption below 2Δ frequency. The normal MIR contribution may be accounting for a finite zero-bias conductance that can be seen in tunneling data.[13–15]

The hypothesis that only the Drude carriers form the superfluid below $T_c \simeq 30$ K is strongly supported by results of dc resistivity measurements, made by different groups.[16,33] Although the overall dc resistivity value and temperature dependence vary dramatically from sample to sample (of the same stoichiometric composition), T_c value and width of the superconducting transition remain largely unchanged. Even samples with a resistivity as large as 0.016 (Ω cm) at low temperature, which is near or below minimum Mott's conductivity, were found to be superconducting with T_c of about 30 K. This behavior looks puzzling unless one will adopt point of view that there are two separate contributions to the dc resistivity: One is responsible for the superconducting phenomenon and another one gives the resistivity variations observed. This issue will be discussed later in this section.

The spectral weight, missing under the conductivity curves at temperatures below T_c, goes to a δ-function peak, centered at zero frequency. From the missing spectral weight one can determine a plasma frequency of the superconducting carriers ω_{ps}. This value can be used to determine the London penetration depth $\lambda_L = c/\omega_{ps}$. Using this method we have obtained $\lambda_L(10\text{ K}) = (4550 \pm 300)$ Å. The uncertainty comes mainly from the uncertainty in the exact determination of the spectral weight missed at frequencies below ~ 35 cm^{-1}. The temperature of 10 K, compared to T_c of our samples, is low enough to assume that $\lambda_L(0) \simeq \lambda_L(10\text{ K})$. The value of $\lambda_L(0) = (4550 \pm 300)$ Å is in good agreement with the one obtained recently in transmission measurements.[12]

The role of phonons in superconducting pairing in BKBO is an important issue. A number of groups have suggested that this material is an electron-phonon superconductor[5,13,34] while results of other experiments[14,18] do not lead to this conclusion. The conventional phonon mechanism is predicted to be accompanied by a Holstein process where a charge carrier absorbs a photon and emits a phonon. As a result, a sideband starting with a threshold at the phonon energy appears in the optical conductivity. Its spectral weight, normalized to the free carrier contribution, is equal to the electron-phonon coupling constant λ_{tr},[35] appropriate for transport, but thought to be closely related to the Eliashberg λ. The signature of the Holstein effect is a shift, upwards by 2Δ, of the sideband when temperature is reduced below T_c, reflecting the fact that now a photon needs additional energy to break a Cooper pair. This effect is well known for conventional strong coupling superconductors, such as Pb.[36] Given that a $\lambda \geq 1$ is required to explain the high T_c in BKBO,[37] the Holstein structure was expected to be particularly strong in this material. Nevertheless, no 2Δ shift of the phonon-related spectrum in the optical conductivity when temperatures crosses T_c can be seen (Fig. 5). This result indicates an absence (at least on scale of our signal-to-noise ratio) of the Holstein structure. Its magnitude was expected to be around $\sim 5\%$ for $\alpha^2 F(\omega)$ reported by Huang *et al.*,[34] $\lambda = 1.4$, and a scattering rate $1/\tau_D$ from our fit.[23,38] Our signal-to-noise ratio is about $\pm 0.5\%$; therefore we can put a rough upper limit on the electron-phonon coupling constant $\lambda_{tr} \leq 0.3$–0.4 (for the superconducting carriers), which is consistent with earlier work on specific heat and magnetization.[18,39] We would like to note that our result does not rule out the possibility of a stronger electron-

phonon coupling for the MIR carriers. First of all, their large scattering rate can lead to an overall smoothing of the Holstein structure in optical spectra.[23] Second, there should be no shift of this structure at temperatures below T_c for nonsuperconducting MIR carriers. Stronger coupling of phonons to the MIR continuum may account for a doping-induced softening of phonon modes observed in inelastic neutron scattering experiments.[40]

We can estimate the strength of the electron-phonon interaction for the Drude carriers in a different way, using the fitted parameters for this contribution (listed in Table I) and the formula[41]

$$1/\tau = 2\pi\lambda_{\rm tr}k_BT, \qquad (2)$$

where $1/\tau = 1/\tau_D$ is the scattering rate determined from the width of the Drude peak. Taking into account all the uncertainties of our fit we find $\lambda_{\rm tr}$=0.2±0.1.

Both our estimates give a value of $\lambda_{\rm tr}$ which is much smaller than that required for the explanation of the high T_c in this material by the conventional electron-phonon mechanism and therefore this result can be interpreted as an argument in favor of nonphonon superconductivity. Large phonon frequencies do not always lead to high T_c values. In fact, due to small value of Fermi energy in BKBO, too large a phonon frequency (as well as too high a value of λ) can actually lead to a *reduction* in T_c instead an increase.[42] Another check on the relation of phonons to superconductivity in this compound could be provided by tunneling measurements. Unfortunately, there is still no consensus in this area.[14,16,34] Finally, it should be emphasized that although our result can be interpreted as an evidence against phonon-mediated pairing in BKBO, it is *not* evidence for a non-BCS mechanism of superconductivity in this material. The BCS mechanism itself can include any attractive interaction and was demonstrated to be working well in tunneling experiments.

The temperature dependence of the high-frequency optical conductivity, found in our study, may be related to the recently reported[31] temperature-induced variations in a local atomic structure, including a distribution of equilibrium positions.[43] Although the microscopic reasons for this behavior are not clear, it is possible that it can modify the energy spectrum of electronic excitations and, therefore, the optical conductivity, in a much wider frequency range than that allowed by conventional electronic models. As can be seen from Table I, it is the temperature behavior of the MIR contribution that is unusual: The scattering rate increases with decreasing temperature (note that slightly decreasing ω_{pD} is almost inside the possible error range). This observation is in accord with the suggestion made above, that the MIR carriers are influenced by the local noncubic structure.

It is interesting to compare our spectra with those from optical studies of the doping dependence.[5,6] The spectra are unusual in a parallel way: Even a relatively minor increase of potassium concentration from, for example, 0.38 to 0.41 was found to alter $\sigma_1(\omega)$ appreciably up to 6 eV,[6] instead of the expected small changes below the plasma minimum. Therefore doping not only provides carriers, but induces additional system modifications. Furthermore, anomalous reflectivity changes with relatively small applied pressure were reported in $Ba_{0.6}K_{0.4}BiO_3$.[44] Finally, as shown in Fig. 7, in different optical studies different $\sigma_1(\omega)$ spectra were obtained even for samples with nominally the same stoichiometric composition. All of the above experimental facts may have their origin in variations of a noncubic local distribution of equilibrium atomic positions, if these variations can be induced by doping, pressure, or particular sample preparation conditions as well as by temperature. Further structural studies are needed in order to clarify this question.

Despite numerous attempts to determine the transport properties of the BKBO system,[11,16,33,45] these are still not clear: The temperature behavior of $\rho_{\rm dc}(T)$ and the absolute values of a Hall coefficient $R_H(T)$ vary dramatically from sample to sample, depending on slight variations in the sample preparation routine, even for samples of nominally the same stoichiometric composition. Nevertheless, there is one feature in common to all transport measurements results: $\rho_{\rm dc}(T)$ as well as $R_H(T)$ seem to show a crossover from one regime to another around 120–150 K for a majority of samples with $x\sim0.4$. In a recently published work, Hellman and Hartford[33] were able to fit many experimental data assuming two parallel channels conductivity: one metallic and one semiconducting with an activation energy of 46 meV (371 $\rm cm^{-1}$). The relative mixture of the two channels was assumed to vary from sample to sample to account for the resistivity variations. This model is in a qualitative agreement with the existence of two components in optical conductivity, both contributing to the dc resistivity. In particular, the metallic channel can be naturally associated with the Drude contribution leaving the MIR carriers to account for the semiconducting one. However, our spectra do not show any evidence of the semiconducting gap at 46 meV, predicted by this model. A conventional semiconducting mechanism can also be ruled out by the nature of the temperature dependence of optical conductivity. Therefore, the simple description used for the "semiconducting" channel of the dc conductivity may not be appropriate. However, it may work qualitatively which can be seen from the results of our experiment. The overall optical conductivity of the MIR carriers decreases with decreasing temperature from 300 K down to ~120–150 K while below 120 K it is "frozen." Although we do not know the exact behavior of the dc conductivity for the MIR carriers because of the possibility of the pseudogap, it may reflect the overall conductivity reduction and, in combination with the Drude carriers, give a $\rho_{\rm dc}(T)$ in agreement with the experimental data in the same way as the model by Hellman and Hartford does. It has been suggested[33] that the metallic channel is fairly similar for a majority of samples. Indeed, the dc resistivity parameters, which can be obtained for the metallic Drude channel from our results, fall quite nicely on the $[\rho_m(300\ {\rm K})-\rho_0]$ vs ρ_0 plot in Ref. 33. In the same reference the semiconducting channel was found to be vastly different from sample to sample, in good agreement with the variations of the MIR component in optical measurements, performed on different samples.

In order to compare our results with Hall measure-

ments we calculated the total electronic density n at different temperatures using a plasma frequencies ω_{pD}^2 and ω_{pO}^2 from our fit and the equation

$$n = n_D + n_O = \frac{1}{4\pi e^2}(m_D^* \omega_{pD}^2 + m_O^* \omega_{pO}^2) \simeq \frac{m_O^* \omega_{pO}^2}{4\pi e^2}, \tag{3}$$

where m^* is an effective carrier mass and the subscripts D and O refer to the Drude and MIR components, respectively. The effective mass m_O^* was assumed to be equal to the bare electron mass. A comparison with $n(T)$ from single-crystal Hall measurements[11] is shown in the inset of Fig. 3. The agreement is surprisingly good indicating that the same mechanism that causes the temperature dependence of reflectivity may be responsible for the temperature dependence of the Hall coefficient.

Knowing the exact value of the plasma frequency ω_{pD} for the metallic channel we can redo the calculations of λ_{tr} made in Ref. 33. Hellman and Hartford estimated λ_{tr}=2.0 from the temperature dependence of the dc resistivity assuming the plasma energy to be 3.4 eV. But, as we have suggested, the metallic channel is formed by the Drude carriers and has a plasma energy of only 0.7 eV. If the authors would use this value of $\hbar\omega_p$, they would obtain $\lambda_{tr}=2.0\times(0.7/3.4)^2=0.085$ consistent with our estimate made above.

V. SUMMARY

We have used reflectivity measurements in a frequency region from the far infrared to the near ultraviolet to study single crystals of the high-T_c superconductor $Ba_{0.6}K_{0.4}BiO_3$. In agreement with previous observations, our results indicate that the spectral weight below 16 000 cm^{-1} is formed by two contributions: a relatively narrow ($\leq$350 cm^{-1}) Drude-like feature (Drude component) and an overdamped continuum formed by the MIR carriers. At frequencies above 60–80 cm^{-1} the MIR contribution was found to be well described by a Drude form with large scattering rate ~7500–9500 cm^{-1}. The same as in the Cu-based materials, a finite absorption below the gap frequency was observed. We speculate that below T_c=30 K the Drude carriers form the superfluid while the MIR carriers remain normal, accounting thus for the finite conductivity below the superconducting gap. The London penetration depth was found to be λ_L = (4550±300) Å. With weak coupling of the Drude carriers to the phonons, $\lambda_{tr}<0.4$, we are unable to confirm that this material is an electron-phonon superconductor. Finally, it was shown that transport properties of BKBO may be consistent with our optical results.

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