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Far-infrared transmission of $Ba_{1-x}K_xBiO_3$ thin films

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The far-infrared transmission of $Ba_{1-x}K_xBiO_3$ thin films, grown on MgO substrates, was measured in the frequency range from 15 to 200 cm^{-1}, and temperature range from 9 to 100 K. There is a BCS-like peak in the transmission spectrum. The strong-coupling Eliashberg theory gives a better description of the optical data than the weak-coupling Mattis-Bardeen theory. For a $T_c=18$ K sample the Eliashberg fits give a London penetration depth of 5500±100 Å and an energy gap $2\Delta(0)=4.0\pm0.1kT_c$ (6.2 meV).

Since its discovery in 1988 there has been considerable interest in $Ba_{1-x}K_xBiO_3$ (BKBO). Because it has a high critical temperature compared to other known s-wave BCS-like superconductors it has been conjectured that the pairing mechanism in BKBO may be related to that in the high-T_c cuprates. Also, it has been shown that BKBO/BKBO junctions have ideal Josephson behavior, making BKBO important for applications in superconducting electronics.[1] In addition, its cubic symmetry gives it an advantage in some applications where the high anisotropy of the cuprates is undesirable.

The bismuthates and the cuprates have several properties in common. They both have a very high ratio of T_c to the density of states at the Fermi level $N(0)$, suggestive of unusual pairing mechanisms.[2] They both have asymmetric-linear background in tunneling conductance,[3] and in the insulating parent materials these systems have collective states which, for the cuprates, are an antiferromagnetic insulator, and for $BaBiO_3$, are a Peierls charge-density-wave (CDW) ground state.[4] The interactions which give rise to the CDW lattice distortions in the insulating materials are thought to be responsible for the superconductivity in the metallically doped materials.[5]

In other respects, the bismuthates and the cuprates are quite different. The bismuthates are cubic crystals, while cuprates are planar, with a highly anisotropic effective mass. Another difference is that a prominent gap feature has been seen in the reflectivity[6,7] and absorptivity[8] of BKBO and, in this paper, in transmission. The infrared gap has been markedly controversial in the cuprates. Also the bismuthates show a clean BCS-like gap feature in tunneling measurements,[9–11] as well as a large isotope effect, unlike the cuprates.[2]

We report here on infrared transmission measurements of two samples, a 1200 Å $Ba_{1-x}K_xBiO_3$ ($x=0.4$), with $T_c=18\pm0.5$ K and a 1400 Å thick ($x=0.53$) sample with $T_c=14\pm1$ K. These samples were grown by molecular-beam epitaxy on MgO substrates as described in detail elsewhere.[12] The critical temperatures were respectively determined by ac susceptibility and resistivity measurements and the transition widths correspond to the 90% and 10% points on the susceptibility (resistivity) curves. The far-infrared transmission was measured using a rapid scan Fourier transform spectrometer with a Ge bolometer detector, cooled to 1.5 K. The sample and a MgO reference were cooled to $T\geqslant9$ K in a separate optical transmission Dewar where they could be switched *in situ* into and out of the path of the IR beam. The transmission of the sample was ratioed to that of the reference. Both sample substrate and reference were wedged 4° in order to avoid interference fringes from multiple internal reflections. The transmission measurements were made for a series of temperatures between 9 and 100 K.

For these measurements the transmission is well described by a Fresnel formula modified to include the effects of multiple internal reflections, absorption in the substrate and the optical properties of the superconducting film in the thin-film limit, $d\ll\lambda_L\ll\lambda$ (where d is the BKBO film thickness, λ_L is the London penetration depth, and λ is the wavelength):

$$T=\frac{4n}{|N+1+y|^2}\left[\frac{T_s\exp(-\alpha x)}{1-R_sR_f\exp(-2\alpha x)}\right], \quad (1)$$

where $N=n+ik$ is the refractive index of the MgO substrate,[13] and the term in square brackets is the correction factor (of order unity) for multiple reflections and absorption in the substrate. $\alpha=4\pi\omega k$ is the substrate absorption coefficient, with ω the frequency. $T_s=4n/|N+1|^2$ and $R_s=|N-1|^2/|N+1|^2$ are the transmission and reflectivity of the substrate-vacuum boundary and $R_f=|N-1+y|^2/|N+1+y|^2$ is the reflectivity of the BKBO film, with $y=4\pi\sigma d/c$, where σ is the frequency-dependent complex conductivity of the BKBO film.

In Fig. 1, we show the transmission ratio $T_r=T_{\rm sample}/T_{\rm substrate}$ versus frequency ω for the two BKBO films at their lowest temperatures. The low-frequency behavior of the transmission spectra is dominated by the superfluid screening which leads to a rapid reduction of the transmission below the gap. At high frequencies the transmission approaches the normal-state result. The peak in the transmission around 50 cm^{-1} for the $T_c=18$ K sample and 38

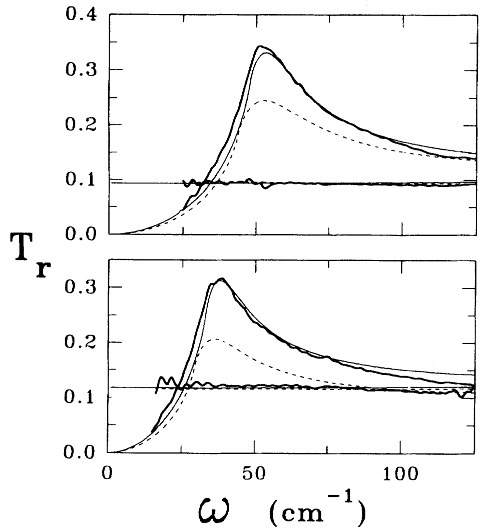

FIG. 1. In the top panel the transmission ratio T_r versus frequency ω (1 cm^{-1}=8.0655 meV) of the T_c=18 K sample at 9.2 K is plotted as the heavy solid line. For comparison the transmission as calculated using the conductivities from the Eliashberg strong-coupling model (light solid line) and from the Mattis-Bardeen dirty limit BCS theory (in the light dotted line) are shown. Also shown is the normal-state transmission data at 18.1 K (heavy solid line) along with its Eliashberg model calculation (light solid line). At the bottom is a similar plot for the 8.9 K data of the T_c=14 K sample.

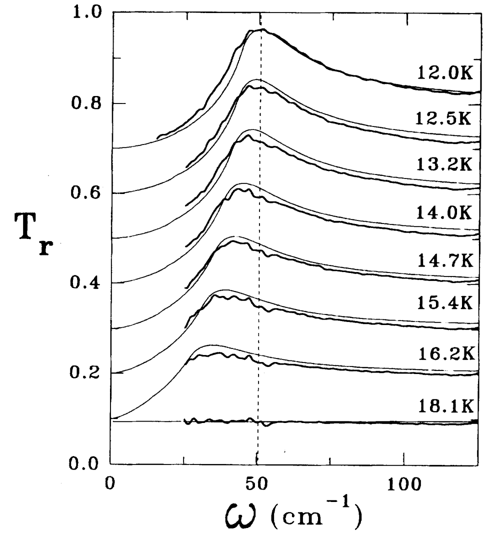

FIG. 2. The transmission ratio spectra for the T_c=18 K sample are plotted for several temperatures with the vertical origins shifted for clarity. The heavy curves are the experimental data and the light curves are the calculations from Eliashberg theory, as described in the text. In order from top to bottom are the curves for the data taken from 12.0 to 18.1 K$\cong T_c$. There is a quartz window absorption peak at 130 cm^{-1}, where the data are cut off. Beyond that frequency, the transmission ratio changes by less than 10%. The vertical dashed line shows the position of the zero-temperature gap.

cm^{-1} for the T_c=14 K sample corresponds closely to twice the energy gap (2Δ) according to BCS theory. The normal-state transmission for both samples is practically independent of frequency, which implies a nearly constant normal-state conductivity over the frequency range of the figure. Therefore we can conclude that $\omega\tau \ll 1$ for the normal state, where τ is the quasiparticle relaxation time, and that $1/\tau$ is frequency independent over our measurement range to within our measurement error $\cong 5\%$. Also, $\omega\tau \ll 1$ implies that the superconducting electrodynamics is in the dirty limit since $\Delta\tau \ll 1$ also holds. The fact that the samples are in the dirty limit is also implied by the prominence of the gap related peak,[14] since in the clean limit, there is little oscillator strength in the conductivity for transitions across the gap. The normal-state conductivity σ_N was obtained by fitting the normal-state transmission data at T_c to Eq. (1) with $\sigma = \sigma_N$.

The conductivity in the normal state extrapolated to zero frequency is equal to the dc conductivity. From our measurements of σ_N we get $\rho_N = 5\times10^{-4}\,\Omega$ cm for the T_c=18 K film and $7\times10^{-4}\,\Omega$ cm for the T_c=14 K. This compares well with typical values for BKBO films at T_c.[15]

In Fig. 2 we show the transmission ratio spectra for the T_c=18 K sample at several temperatures. As the temperature increases, the peak decreases in magnitude and shifts to lower frequency. The frequency position of the peak feature decreases slowly at low temperatures and then rapidly at $T \to T_c$, similarly to the behavior of the BCS energy gap.

We have analyzed the superconducting transmission data in terms of both weak-coupling and strong-coupling models. The first model is the Mattis-Bardeen (MB) theory, based on the dirty limit, weak-coupling BCS superconductivity. To calculate the Mattis-Bardeen curves for each temperature, σ_N was determined from the normal-state data, then for each temperature, numerical integrations were made of the Mattis-Bardeen equations for σ_1/σ_N and σ_2/σ_N.[16] The absolute transmission was calculated with the energy gap scaled so that the peak position matches that of the data. For both samples the magnitude of the peak feature in the MB calculation is significantly smaller than that of the data, as can be seen in Fig. 1.

We have also repeated the BCS calculation in the limit intermediate to the *clean limit* ($\Delta\tau \gg 1$) and the *dirty limit* ($\Delta\tau \ll 1$).[17] The transmission was calculated by using the measured normal-state conductivity σ_N and calculating a finite value of τ from it. The details of this τ estimation will be discussed shortly. Then the gap was freely varied so the peak position of the calculated transmission and data matched. The result of this calculation is that the transmission peak can be enhanced above the result in Fig. 1 but it still falls far short of the experimental result. We conclude that the experiments are not compatible with the weak-coupling BCS theory.

For the strong-coupling analysis we use the conductivity based on the Eliashberg theory.[18,19] The input parameters are the normal-state scattering rate $1/\tau$, T_c, and the $\alpha^2F(\omega)$ spectrum and residual Coulomb repulsion μ^*. For the latter two we have used the results obtained from tunneling data on a multifaceted crystal pellet of similar stoichiometry with T_c =25 K, grown by a melt processing technique.[10,20] Due to the difference in the T_c and stoichiometry of our samples, we have scaled the amplitude of the $\alpha^2F(\omega)$ by a constant factor, chosen to fit the experimentally determined T_c. The electron-phonon mass renormalization parameter was then found to be $\lambda_{ep}=1$ for the $T_c=18$ K sample. One could equivalently vary μ^* to fit T_c. This is a standard procedure for Eliashberg calculations.[21] The normal-state scattering rate was estimated from the Drude conductivity in the $\omega\tau \ll 1$ limit: $\sigma_N=\omega_D^2\tau/4\pi$, where $\omega_D=4\pi ne^2/m_e$ is the effective Drude plasma frequency. Estimating the carrier density from the potassium concentration x using $n=x/a^3$, where $a=4.29$ Å is the BKBO cubic unit cell dimension, we obtain ω_D=2.6 eV and $1/\tau$=3600±1000 cm^{-1} for the T_c =18 K sample and ω_D=3.05 eV and $1/\tau$=6800±1500 cm^{-1} for the T_c=14 K sample. These are in rough agreement with previous measurements of the scattering rate for BKBO thin films.[12,22,23] Using these input parameters and no other free parameters the Eliashberg complex conductivity function $4\pi\sigma(\omega)/\omega_D^2$ was calculated at each temperature. A close fit to the data was obtained for both samples, especially for the lowest-temperature spectra in the superconducting state as can be seen in Fig. 2. The Eliashberg theory also properly describes the normal-state transmission. Therefore, although ω_D is not known with certainty and this leads to uncertainties in $1/\tau$, very good representations for the superconducting transmission data were obtained.

In order to assess the sensitivity of the analysis to the input parameters we have made another estimate of the normal-state scattering rate from the measured σ_N by using the ω_D deduced from room-temperature broadband optical reflectance measurements on samples of similar stoichiometry. The conductivity function from these reflectance measurements has a mid-infrared absorption band in the conductivity in addition to the Drude response.[24] This mid-infrared band in the metallic state is thought to be a remnant of the Peierls charge-density-wave gap which is found in the insulating state. The mid-infrared band has a negligible contribution in our spectral range, as can be deduced from a calculation based on the Lorentz-Drude model with parameters from the optical reflectance measurements.[24] From the reported optical data the strength of the Drude component is found to correspond to ω_D=1.98 eV for $x=0.4$. Thus the low-frequency conductivity can be adequately described by a simple Drude model, with a scattering rate $1/\tau$=2000 cm^{-1} as derived from σ_N and ω_D. For the T_c=14 K sample, with $x=0.53$, ω_D=2.4 eV according to optical reflectance data, which implies a scattering rate of 4300 cm^{-1}. Using these normal-state parameters in the Eliashberg calculation does not change the fits appreciably, the main effect being a slight ($\cong$5%) increase in the height of the peak. Therefore, we find that the curves are mainly sensitive to ω_D and τ through the combination $\omega_D^2\tau$. Also, these different parameters do not affect the values of the energy gaps deduced for these samples.

We have also examined the effect of variations in the value of T_c on the transmission calculations. Reducing T_c by 0.5 K has the effect of pushing the curves toward lower frequencies. This improves the low-frequency fits at some expense to the high-frequency part. Since ΔT_c=0.5 K is outside the error expected from thermometry, this result may indicate an inhomogeneity in the T_c of the sample or gap anisotropy. A 0.5 K spatial inhomogeneity in T_c for these films is not unreasonable.

We have also calculated the transmission with Eliashberg theory replacing the tunneling $\alpha^2F(\omega)$ spectrum with a single δ function positioned at the Allen-Dynes frequency ω_{ln} deduced from the $\alpha^2F(\omega)$ spectrum.[21,25] The result is essentially the same as the transmission spectrum with the full $\alpha^2F(\omega)$. This result demonstrates that, in the dirty limit, because the Holstein structure is negligible, the optical properties are sensitive to the strong coupling only through single parameter T_c/ω_{ln}. In the weak-coupling BCS limit, T_c/ω_{ln} would be zero. For the tunneling $\alpha^2F(\omega)$ of BKBO, ω_{ln}=20.1 meV and so for the T_c=18 K sample T_c/ω_{ln}=0.077. For comparison, the strong-coupling superconductor Pb has T_c/ω_{ln}=0.128.

Therefore, we can characterize how the input parameters affect the transmission spectrum in the dirty limit of the Eliashberg calculation. The ratio of T_c to ω_{ln} determines the shift of the energy gap relative to the weak-coupling value and hence the peak position. The parameters ω_D and τ enter essentially in the combination of $\omega_D^2\tau$, which is proportional to the normal-state conductivity and hence determines the high-frequency transmission background. Therefore the Eliashberg conductivity function is nearly proportional to σ_N as in Mattis-Bardeen theory. The height of the peak relative to this background is increased by increasing T_c/ω_{ln} and/or τ. The dependence on the peak height on τ is weak.

At the top of Fig. 1 the 9.2 K data are shown in comparison with the best Mattis-Bardeen curve and the transmission calculated from Eliashberg theory. In the Eliashberg calculation the transmission peak height much better represents that of the data. The differences between the two theory curves are significantly larger than the experimental errors, which are less than ±5% in the vicinity of the peak of the transmission ratio spectrum. The data of 9.2 K (at the top of Fig. 1) were taken several months after the data in Fig. 2. During that time it can be inferred that the sample developed a surface dead layer of about 100 Å,[26] decreasing d, and therefore slightly increasing the height of the peak since $T_r \propto 1/d^2$. However, the bulk of the sample was apparently quite well preserved since the peak position and T_c did not change. In the calculated curves, both MB and Eliashberg, this decrease in d was included.

The 12 K data curve was measured with more signal averaging to improve the signal-to-noise ratio at low frequency where the Hg lamp source intensity is low. This low-frequency data (at 15 to 20 cm^{-1}) were used to estimate the London penetration depth using the London model for the transmission, which is expected to be valid in the $\hbar\omega \ll 2\Delta$ regime. Including the effects of multiple reflections, for $\omega \ll \Delta$, we can write approximately, T_r $=1.22\omega^2/(\omega^2+\Omega^2)$, where $\Omega=cd/(n+1)\lambda_L^2$. Therefore, since $\omega \ll \Omega$ we can see that $\lambda_L \propto d^{1/2}T_r^{1/4}$ in this regime. Because of the fourth root dependence of λ_L on T_r, large errors in T_r lead to only small errors in λ_L. If the uncertainty in T_r in this spectral range is conservatively estimated to be ±50%, with a ±5% uncertainty in d_f, this leads to an uncertainty in λ_L of less than ±15%. Using this method λ_L =5500±700 Å at T=12 K for the T_c=18 K sample. We can extrapolate this value to zero temperature using Eliashberg theory or BCS theory to obtain $\lambda_L(0)$=4500±700 Å. For the T_c=14 K sample the London penetration depth is $\lambda_L(0)$=5900±800 Å, obtained with somewhat greater uncertainty because the energy gap is lower for this sample, and the frequency region for which the London model is valid is in the regime where the S/N begins to deteriorate. These λ_L values are somewhat greater than those obtained by microwave methods for similarly grown thicker films ($d=3600$ Å) of similar T_c.[27] These differences can be attributed to the shorter electron mean free path found in the thinner films used in the infrared measurements.

From the Eliashberg theory the zero-temperature London penetration depth was calculated from the weight of the zero-frequency δ function of σ_1. The $\lambda_L(0)$ values for the $T_c=18$ K and 14 K samples were 5500 ± 100 Å and 7500 ±100 Å, respectively, where the uncertainties result from the uncertainties in $1/\tau$. These values are larger than those estimated from the London model, but not far outside of the error estimate.

With the Eliashberg calculation we find, for the $T_c=18$ K sample, $2\Delta(0)=50.1$ cm^{-1} (6.2 meV)$=4.0\pm0.1kT_c$ and, for the $T_c=14$ K sample, $2\Delta(0)=38$ cm^{-1} (4.7 meV) $=3.9\pm0.3kT_c$. Estimating the energy gap from the Mattis-Bardeen fits and extrapolating the values to $T=0$ we find $2\Delta(0)=3.9\pm0.1kT_c$ and $2\Delta(0)=3.9\pm0.3kT_c$, respectively. The uncertainties are from the uncertainty in the measured T_c's. From these results, we can conclude that these BKBO samples are not in the weak-coupled limit characterized by $2\Delta(0)/kT_c=3.52$. While some previous tunneling[9] and reflectivity[6] measurements have determined a weak-coupling value of the gap ratio of 3.5, the uncertainty quoted was large enough to overlap with our value of 4.0. In more recent tunneling[28,29] and reflectivity[7] experiments on single crystals a value of about 4 is found.

In summary, we have measured the far-infrared transmission of BKBO films and found a peak that can be associated with a superconducting energy gap of $2\Delta(0)/kT_c=4.0$. The transmission spectrum is much better represented by an Eliashberg strong-coupling calculation for the conductivity as compared with weak-coupling BCS theory. From these results we conclude that BKBO is in the moderate-coupling regime. Because the BKBO films are in the dirty limit, the optical properties do not reflect the fine structure of the $\alpha^2F(\omega)$ spectrum (Holstein structure). The effects of the strong coupling on the optical properties is found to be completely specified by the Allen-Dynes parameter together with T_c. The infrared transmission is used to determine the London penetration depth of the films.

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