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ab-plane optical properties of $Tl_2Ba_2CuO_{6+\delta}$

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We report on absolute *ab*-plane reflectivity measurements of the single-layer high-T_c superconductor $Tl_2Ba_2CuO_{6+\delta}$ in both the normal and superconducting states. The reflectivity has been measured from 40 to 40 000 cm^{-1} and the optical conductivity has been calculated from Kramers-Kronig analysis. The unusual form of the low-frequency reflectivity leads to an intense low-frequency feature in the optical conductivity. In the superconducting state, the spectral weight is strongly suppressed at frequencies below ~ 800 cm^{-1} due to the formation of a superfluid fraction. The value of the London penetration depth has been estimated to be 2400 ± 200 Å, larger than that from muon-spin-resonance (μSR) experiments.

The $Tl_2Ba_2CuO_{6+\delta}$ (Tl2201) system provides an opportunity to study high-temperature superconductivity in the overdoped regime. The whole overdoped region, from the highest T_c superconductor to the nonsuperconducting normal metal, is accessible by means of changes to the oxygen level. Another important advantage of this material is that it has a relatively simple single-layer structure without complications arising from chainlike structural units.[1] Finally, despite its being a single-layer material, Tl2201 is among the highest-T_c superconductors. As a result, Tl2201 has attracted much interest during the past few years. However, to our knowledge, there have been no reports on the far-infrared optical properties, except for early work on ceramic samples.[2]

In this paper, we report on the optical properties of nearly optimally doped Tl2201 in the normal and superconducting states in the frequency region from the far infrared to the near ultraviolet. An unusual low-frequency optical conductivity has been observed with a pseudogaplike feature at ~ 70 cm^{-1}. In the superconducting state, a redistribution of the spectral weight occurs due to the formation of a superconducting condensate. The London penetration depth has been estimated to be $\lambda_L = 2400 \pm 200$ Å.

The experiments were done on the Tl2201 single crystals prepared by a solid-state self-flux method as reported elsewhere.[3] The crystals were platelike with natural mirrorlike *ab* surfaces and typical dimensions of $0.5 \times 0.7 \times 0.04$ mm^3. As-grown crystals were used without any annealing. The superconducting transition temperatures were obtained by means of ac magnetization measurements. Two crystals were measured optically and gave similar results. Therefore, we will focus on one of them in this report. The onset T_c value for this crystal was found to be 88 K with $\Delta T_c = 8$K. It may be possible that the superconducting transition was somewhat broadened by the relatively high (2.5 G) value of the magnetic field used.[4] Results of x-ray measurements performed on similar samples indicated a tetragonal structure. In agreement with this, no anisotropy of the *ab*-plane reflectivity has been observed. As well, the positions of the phonon modes in the Raman spectra measured on the crystals used in this study suggest a tetragonal structure.[5]

The experimentally measured reflectivity is shown in Fig. 1 at several temperatures above and below the T_c. The very high absolute values of the low-frequency reflectivity are somewhat surprising given that this material, at optimal doping, is a rather poor conductor: $\rho_{dc}(300\ K) \simeq 500-600$ $\mu\Omega$ cm.[6] As an example, the dotted curves in Fig. 1 show the reflectivity calculated in the free-electron approximation using ρ_{dc} values from transport measurements performed on similar crystals.[6] The lower curve corresponds to $\rho_{dc}(300\ K) = 525$ $\mu\Omega$ cm and the upper one to $\rho_{dc}(90\ K) = 200$ $\mu\Omega$ cm. One can see that the low-frequency reflectivity of

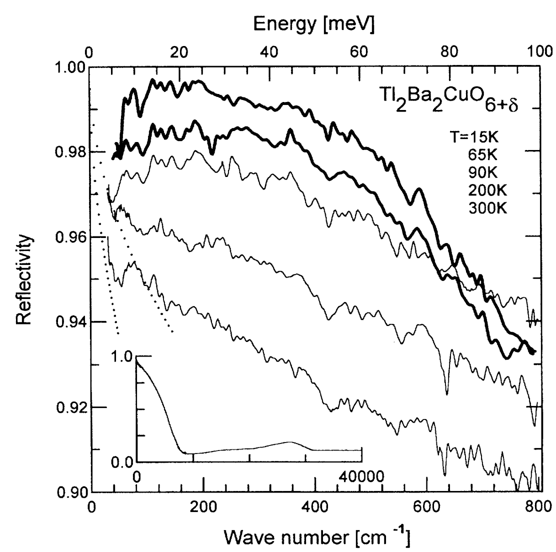

FIG. 1. Experimentally measured low-frequency reflectivity spectra at different temperatures. The bold curves show the reflectivity at superconducting temperatures. The dotted curves show free-electron behavior expected for a conductor with $\rho_{dc} = 525$ Ω cm (lower curve) and $\rho_{dc} = 200$ Ω cm (upper curve). Inset: reflectivity in the whole measured frequency range at room temperature.

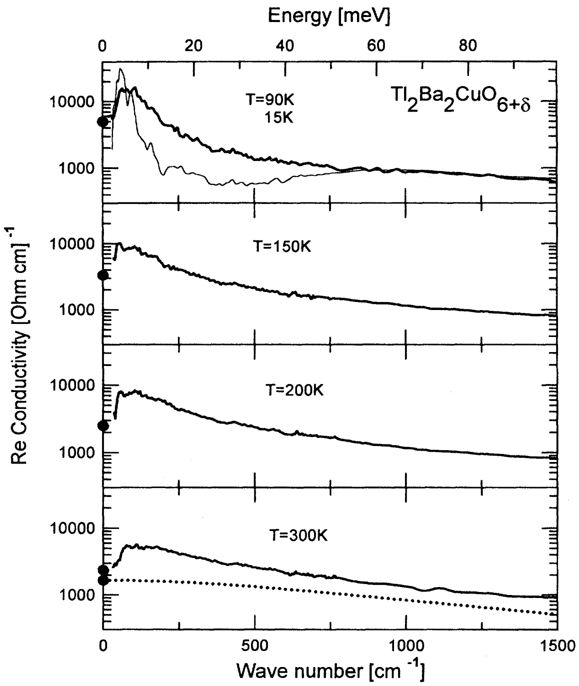

FIG. 2. The real part of the optical conductivity calculated through Kramers-Kronig analysis of the reflectivity spectra presented in Fig. 1. The conductivity at $T=15$ K is shown by the narrow line in the upper panel. The symbols on the vertical axes show the dc conductivity reported for crystals similar to ours in Ref. 6. The second symbol on the vertical axis of the $T=300$ K panel shows the dc conductivity value obtained by Manako *et al.* on crystals grown by this group. The dotted curve on this panel shows an example of the Drude contribution which could be responsible for the dc temperature dependence as discussed in the text. The rest of the optical conductivity in this case belongs to the MIR contribution.

such a relatively bad conductor would normally be expected to be much lower than that observed experimentally for the Tl2201 single crystals. Furthermore, the reflectivity does not increase monotonically towards unity at zero frequency as expected for the free-electron model. Instead, with decreasing temperature it develops a maximum at about 200 cm^{-1}. All of the above observations point to a mechanism, different from the free-electron model, that is responsible for the high reflectance. Other features worth noting are the weak minima at 429 and 632 cm^{-1}. Similar to other high-T_c superconductors,[7] these frequencies correspond to the frequencies of the LO phonon modes along the c axis.[8] The inset of Fig. 1 shows reflectivity in the complete measured frequency range up to ~5 eV. A plasma minimum has been observed at about 1.1 eV and the rest of the reflectivity is relatively featureless except for a broad peak at 28 000 cm^{-1} (3.47 eV) and a broad knee at 16 000 cm^{-1} (1.98 eV) which may be a manifestation of an interband transition processes.

The real part of the optical conductivity [$\sigma_1(\omega)$], calculated through Kramers-Kronig (KK) analysis of the reflectivity, is presented in Fig. 2 for several temperatures. As expected from the peculiar reflectivity behavior, its frequency dependence is quite different from free-electron behavior: the low-frequency optical conductivity is strongly suppressed below 70 cm^{-1}. For example, at room temperature, $\sigma_1(\omega)$ at ~70 cm^{-1} is approximately twice the dc value. With decreasing temperature, the spectral weight shifts to lower frequencies, which may be a result of a decrease in the scattering rate. However, the low-frequency feature does not disappear. Instead, it seems to increase in magnitude as additional spectral weight piles up above 70 cm^{-1}. As a result a pseudogaplike feature is present throughout the whole measured temperature range.

Reliable results, reproducible from sample to sample ($\Delta R \leq 0.5\%$), have been obtained above 40 cm^{-1}. Therefore, to perform KK analysis at normal temperatures, we have used a low-frequency reflectivity approximation, obtained from the dc conductivity measured on similar crystals at corresponding temperatures.[6] For example, the reflectivities at $T=300$ and 90 K have been approximated, below 35 cm^{-1}, by the dotted curves on Fig. 1. At temperatures $T<T_c$ unit reflectivity has been assumed below ~30 cm^{-1}. Above 100 cm^{-1} the optical conductivity was found not to be sensitive to the choice of low-frequency approximation. However, due to high absolute values of the reflectivity, this choice was found to be more important at lower frequencies, especially at superconducting temperatures. We estimate the uncertainty in the absolute value of $\sigma_1(\omega)$ at 50 cm^{-1} to be about 20% for the $T=15$ K spectrum. Nevertheless, we emphasize that the pseudogaplike feature itself is *not* an artifact created by an arbitrary choice of the reflectivity below 40 cm^{-1}, nor is it due to behavior of the reflectivity below 100 cm^{-1} alone. In fact, even joining the measured reflectivity smoothly with a Drude-like reflectivity function at 100 cm^{-1}, thereby neglecting completely the *experimental* data below this frequency, does not change the result qualitatively: additional non-Drude absorption still exists as a hump on the slope of the artificially created low-frequency Drude peak. To give an impression of the spread of absolute values in the dc conductivity reported for this material with a similar T_c we have included, on the vertical axis of the $T=300$ K panel of Fig. 2, the value obtained by Manako *et al.*[9] on crystals grown by another group. This value is essentially the same as the one obtained on our crystals which suggests that it is not artificially reduced by sample inhomogeneity, losses in contacts, or other reasons. Finally, we must note that qualitatively similar behavior has been observed for other high-temperature superconducting materials, such as $Pb_2Sr_2(Y/Ca)Cu_3O_8$ (Ref. 10) and $Tl_2Ba_2CaCu_2O_8$.[11] Considering all of the above, we believe that the observed pseudogaplike feature in the optical conductivity is an intrinsic property of the Tl2201 system.

The superconducting reflectivity is qualitatively different from the normal one. Already at $T=65$ K reflectivity rises sharply above the normal $T=90$ K curve crossing it at about 600 cm^{-1}. As can be seen in Fig. 2, these changes lead to a characteristic reduction of a spectral weight under $\sigma_1(\omega)$ which is a signature of a formation of a superconducting condensate. Indeed, a superconducting condensate, responsible for the infinite dc conductivity, may be described by a δ function centered at zero frequency in a real part of optical conductivity. However, the sum rule for $\sigma_1(\omega)$ requires the total spectral weight to be conserved, therefore, in order for the δ function to appear, an equal part of the spectral weight

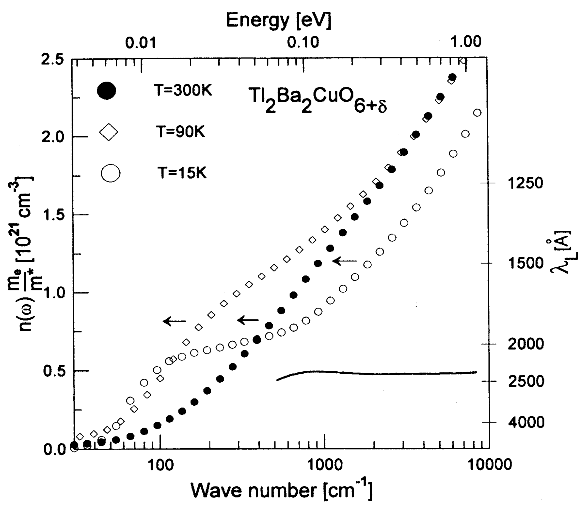

FIG. 3. The effective number of carriers obtained by integration of $\sigma_1(\omega)$ up to a certain frequency, as described in the text, is plotted against this frequency for different temperatures. Lowering the temperature from $T=300$ K to $T=90$ K induces a transfer of the spectral weight to lower frequencies, leaving the total spectral weight unchanged. The reduction in the total spectral weight at $T=15$ K reflects the formation of the δ peak at zero frequency, not included in our integration. On the right-hand vertical axis the London penetration depth $\lambda_L^2=c^2m^*/4\pi n_s e^2$ is plotted for $n_s=n(\omega)$ from the left-hand axis. The difference in the spectral weight between $T=90$ K and $T=15$ K, shown by the solid curve, corresponds to $n_s=4.7\times10^{20}$ cm^{-3} or $\lambda_L=2400$ Å.

should be taken from finite frequencies.[12] We note that the large frequency region directly affected by the superconducting transition $\omega_c\simeq 13kT_c$ is much larger than $3.5kT_c$ expected for a BCS-like model. A kneelike structure, similar to what is seen in $YBa_2Cu_3O_{7-\delta}$, develops in the optical conductivity at low temperatures, although in our case it occurs at a higher frequency of about 600 cm^{-1}. It was shown previously that similar structure may occur due to interaction of an electron continuum with LO phonons along the c axis.[7] Indeed, there exists an intense phonon feature at 632 cm^{-1} in the c axis loss function.[8]

Integrating the spectral weight under $\sigma_1(\omega)$ from zero to a certain frequency ω_0 one can obtain the effective density of free carriers $n(\omega_0)$, participating in the electronic processes at an energy scale of $\hbar\omega\leq\hbar\omega_0$, multiplied by the ratio of the free-electron mass m_e to the effective carrier mass m^*. Using this procedure we calculated $n(\omega)(m_e/m^*)$ for three temperatures ($T=15$, 90, and 300 K) and the results are presented in Fig. 3. One can see that although the decreasing temperature from $T=300$ K to $T=90$ K produces redistribution of the effective carrier density, with part of the spectral weight shifting towards the low-energy part of the spectrum, the total carrier density $n_{\rm tot}$ below $\sim$9000 cm^{-1} remains unchanged. The value of $n_{\rm tot}\simeq 2.5\times10^{21}(m^*/m_e)$ cm^{-3} represents the total density of free carriers in this material and corresponds to about $0.37(m^*/m_e)$ holes per one planar Cu atom. The number of the normal carriers missing in the superconducting state gives a number of superconducting carriers n_s. The difference between the $T=90$ K and the $T=15$ K curves above 500 cm^{-1} is shown by the solid line on Fig. 3 and corresponds to $n_s\simeq 4.7\times10^{20}(m^*/m_e)$ cm^{-3}. The right-hand vertical axis is scaled in units of penetration depth and is related to the left-hand one by the equation $\lambda_L{}^2=c^2m^*/4\pi n_s e^2$ with $n_s=n(\omega)$. The density of superconducting carriers given by the solid line corresponds to $\lambda_L=2400\pm200$ Å. The uncertainty comes mainly from the uncertainty in the low-frequency $\sigma_1(\omega)$ behavior resulting from the unknown low-frequency reflectivity behavior as discussed above. Many possible approximations were tried and the range of λ's found is contained in the error limits of λ_L. The temperature $T=15$ K can be considered low enough compared to the T_c to assume that $\lambda_L(0)=\lambda_L(15\text{ K})=2400\pm200$ Å.

The value of n_s obtained above is less than half the one obtained in the muon resonance spectroscopy (μSR) experiments.[13] However, we believe that our result is more reliable because of the following: (1) Our calculation is completely model independent and based only on the sum rule for $\sigma_1(\omega)$. (2) In order to obtain $n_s\simeq10^{21}(m^*/m_e)$ cm^{-3} as in Ref. 13 almost half of the carriers located below the plasma minimum at 1.1 eV [including the mid-infrared (MIR) contribution] or *all* carriers below 300 cm^{-1} have to condense. This was not observed in our study on Tl2201 nor has it been observed for any other cuprate material. (3) Our experiment has been performed on high-quality single crystals, while only ceramic Tl2201 samples have been studied by the μSR method so far. Intrinsic inhomogeneity of ceramic samples (grain boundaries, random orientation of the grains) as well as increased pinning of the magnetic vortexes may lead to strong distortions of the vortex lattice, leading to a reduced value of λ_L.[14]

The London penetration depth value of 2400 Å found in this work is rather large compared to other nearly optimally doped high-T_c cuprates. For example, λ_L along the chain-free direction was found to be 1600 Å in $YBa_2Cu_3O_{6.95}$ (Y123) and 2000 Å in $YBa_2Cu_4O_8$ (Y124).[15] This means that the total density of the in-plane superconducting carriers in Y124 is about 1.44 times larger and in Y123 is approximately 2.25 times larger compared to that in Tl2201, if a constant effective mass is assumed. However, the number of superconducting carriers per planar Cu atom, normalized to the effective mass, is almost the same in all these materials: $0.08(m^*/m_e)$ in Tl2201, $0.09(m^*/m_e)$ in Y123, and 0.07 (m^*/m_e) in Y124.[16] The difference of 20% between Y123 and Tl2201 may be due to a slightly nonoptimal doping in Tl2201. It has been suggested that the normal-state hole density per planar Cu atom is similar for all optimally doped cuprate materials.[17] In this case, similarity in the density of superconducting carriers would mean that a similar fraction (about 50%) of these holes condense into a superfluid below the T_c or, in other words, that the in-plane superconducting-state behavior is similar for all these materials.

A similar discrepancy between $\sigma_1(\omega)$ and $\sigma_{\rm dc}$ observed in $Tl_2Ba_2CaCu_2O_8$ thin films has been attributed to zone-centered optical phonons.[11] However, the large amount of spectral weight involved, compared to that expected for phonons, puts this explanation in question. Another possible way to account for the anomalous low-frequency pseudogaplike feature is to assume that a low-energy pseudogap exists in the density of states of electronic excitations. In this case the optical conductivity at frequencies below the pseudogap will be reduced and will be Drude-like only at much higher frequencies.[18] The pseudogap may originate from a certain degree of disorder associated with, for example, intrinsic local disordered octahedral distortions in the TlO layers reported for this and other Tl-based materials.[19] If these distortions may be regarded as a source of random potential for the CuO_2 layers, then free carriers in these layers may be partially localized. In the $Pb_2Sr_2(Y/Ca)Cu_3O_8$ material a similar localization may occur due to the randomness of distribution of the Ca atoms on Y sites.[10] In fact, single crystals of $YBa_2Cu_3O_{6.95}$ irradiated with low-energy He ions demonstrated a similar decreasing optical conductivity at low frequencies. Although the irradiation dose was found to be too low to change the chemical composition of the samples, local structural damage was expected to occur.[20] We should note, however, that the dose of irradiation at which the peak appeared caused a drop of about 13 K in the transition temperature. The transition temperature of our sample was 88 K, which is about the upper limit found for this material. Another question that should be clarified is why the dc conductivity has a metallic temperature dependence despite the presence of a pseudogap. An alternative way is to assume that the dc temperature dependence is dominated by a Drude-like free carrier part of the optical conductivity as shown by the dotted line on Fig. 2 for $T=300$ K. The rest of the spectral weight in this case would be formed by the MIR component, which does not contribute to the dc properties but is responsible for the anomalous feature in the low-frequency part of $\sigma_1(\omega)$. Finally, we believe that more exotic mechanisms for the opening of the pseudogap, resulting from spin- or charge-density dynamics, for example, cannot be ruled out at this stage. Evidence for opening of a spin gap have been obtained in NMR measurements on a $T_c=85$ K Tl2201 sample at a characteristic temperature of $T_0=120$ K$=83$ cm^{-1},[21] which corresponds roughly to the onset energy of the pseudogap feature in the optical spectra. It should be noted, however, that indications on the opening of the spin gap, for example, in Y123, have been obtained previously only along the *c* axis.[22]

In conclusion, we report on absolute *ab*-plane reflectivity measurements performed in the frequency range of 30–40 000 cm^{-1} on Tl2201 single crystals in the normal and the superconducting states. The optical conductivity was calculated and unusual behavior was found in the low-frequency part of the spectra. In the superconducting state the London penetration depth $\lambda_L(0)$ was found to be 2400 ± 200 Å, which is larger than the μSR result.

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