Gap in the infrared response of $HgBa_2Ca_2Cu_3O_{8+\delta}$

J. J. McGuire, M. Windt, T. Startseva, and T. Timusk
Department of Physics and Astronomy, McMaster University, Hamilton, Ontario, Canada L8S 4M1

D. Colson and V. Viallet-Guillen*
Physique de l'Etat Condensé, DRECAM/SPEC, CEA, Saclay, 91191 Gif sur Yvette, France
(Received 12 June 2000)

The ab-plane optical spectra of one underdoped and one nearly optimally doped single crystal of $HgBa_2Ca_2Cu_3O_{8+\delta}$ were investigated in the frequency range from 40 to 40 000 cm^{-1}. The frequency-dependent scattering rate was obtained by Kramers Kronig analysis of the reflectance. Both crystals have a gap in the scattering rate of about 1000 cm^{-1} which is much larger than the 700-cm^{-1} gap seen in optical studies of several cuprates with maximum T_c around 93 K. There appears to be a universal scaling between gap size and maximum T_c for the cuprate superconductors.

Although high-temperature superconductivity in the copper oxides was discovered over a decade ago, an understanding of the mechanism that gives rise to the high transition temperature T_c is still elusive. Most of the research has been directed towards the one- and two-layer systems which have a maximum T_c in the 93-K range. Recently, however, high quality single crystals of the three-layer Hg based materials with a maximum $T_c \approx 135$ K have become available[1] making it possible to examine, spectroscopically, oxide superconductors that have significantly higher T_c.

Of particular interest is the gap, or partial suppression of the density of low-energy excitations, which is seen in all high-temperature superconductors. In underdoped materials this gap seems to persist even in the normal state where it is referred to as the pseudogap. A pseudogap has been seen with a variety of techniques such as angle-resolved photoemission (ARPES), tunneling spectroscopy, specific heat, dc resistivity, nuclear magnetic resonance and optical spectroscopy.[2] It is not clear whether a true distinction exists between the normal-state pseudogap and the superconducting state gap since in most experiments no discontinuity in gap properties is seen at T_c. However, specific-heat experiments[3] have been interpreted to suggest that the gaps do have separate origins.

The size of the gaps in the one- and two-layer materials are of the order of $9.5k_BT_c$ at optimal doping and essentially independent of temperature. As T_c is reduced below optimal doping the gaps increase in size.[3–5] This, however, is not true in the ab-plane infrared response. A comparison[6] of infrared spectra of $YBa_2Cu_3O_x$ (Y-123), $YBa_2Cu_4O_8$ (Y-124), $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi-2212) and $Tl_2Sr_2CuO_{6+\delta}$ (Tl-2201) showed no dependence of gap size on doping level or even on which system was being measured. All samples showed a gap of ≈ 700 cm^{-1}.

One explanation for this difference between the doping dependence of the gap in infrared measurements and that seen using other techniques may be that for reflectance in the clean limit, where $1/\tau(\omega) \ll 2\Delta$, onset of absorption does not occur until $\hbar\omega > (2\Delta + \hbar\Omega)$ where $\hbar\Omega$ is the frequency of a momentum conserving inelastic excitation. Gaps in the infrared response will therefore be larger by $\hbar\Omega$ than those seen in tunneling and Raman spectra and may in fact have a different doping dependence depending on the doping dependence of $\hbar\Omega$.[7]

While Puchkov *et al.*[6] show that the infrared gap has no doping dependence and that its magnitude is the same for several materials, a relationship between gap size and maximum T_c cannot be ruled out since all of these materials have T_c near 93 K at optimal doping. In this work the ab-plane infrared reflectance of single crystal $HgBa_2Ca_2Cu_3O_{8+\delta}$ (Hg-1223) is measured in order to study the gap in the superconducting state of a material with a maximum T_c significantly higher than those of the other systems that have been studied previously.[8]

The measurements were carried out on two single crystals grown in gold foil by a single step synthesis.[1] The crystals were characterized by x-ray diffraction and wavelength dispersive spectrometry.[9] The nearly optimally doped crystal had a T_c of 130 K and dimensions $0.4\times0.3\times0.03$ mm^3. The underdoped sample had a T_c of 121 K and dimensions $0.6\times0.5\times0.04$ mm^3. The smallest dimension is the c axis or [001] direction with the [100] direction 45° from the two larger edges. In both crystals the width of the transition was about 6 K. Reflectance measurements between 40 and 8000 cm^{-1} were performed on as-grown ab-plane faces with a Michelson interferometer using three different detectors. A grating spectrometer with three additional detectors was used for the rest of the range up to 40 000 cm^{-1} (5 eV).

The ab-plane reflectance of the optimally doped crystal is shown in Fig. 1. At low temperature there is a striking temperature-dependent feature below 1000 cm^{-1}. In the optimally doped sample this is seen only in the three spectra below T_c. The inset of the figure shows a similar feature in the reflectance of the underdoped sample also at 1000 cm^{-1}. The presence of the feature in the 125-K data, which is now above the 121-K T_c, shows that it persists in the normal state, although at a somewhat lower frequency. Similar behavior in reflectance has been observed in other high-T_c materials, for example, Bi-2212,[6] where a feature appears in the region of 700 cm^{-1} well above T_c and shifts to slightly higher frequency in the superconducting state. Detailed analysis shows that the 700-cm^{-1} feature in the reflectance

0163-1829/2000/62(13)/8711(4)/$15.00

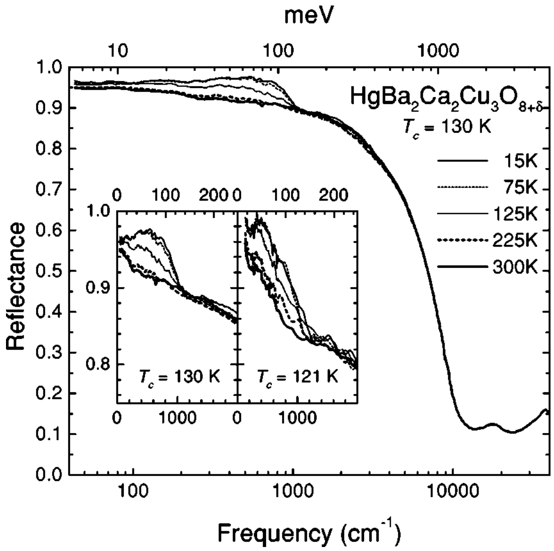

FIG. 1. *ab*-plane reflectance of the optimally doped crystal of Hg-1223 with $T_c = 130$ K. The inset compares this to the reflectance of the underdoped sample with $T_c = 121$ K. The temperature dependence below 1000 cm^{-1} corresponds to a gap in the scattering rate.

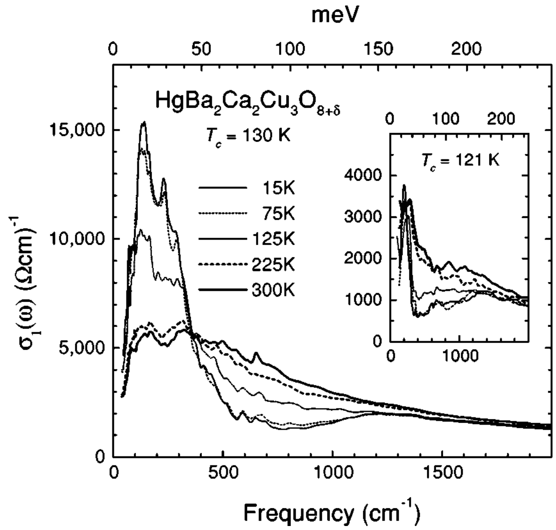

FIG. 2. The real part of the optical conductivity of the optimally doped crystal of Hg-1223. There is a marked transfer of spectral weight from $\omega < 1200$ to a peak centered at 184 cm^{-1}. This peak is much narrower and weaker in the spectra shown in the inset for the underdoped sample.

spectrum is the result of depressed quasiparticle scattering below this frequency at low temperature, a gap in the scattering rate spectrum. Our observation of the feature at 1000 cm^{-1} in Hg-1223 suggests that in this material, as in other high-temperature superconductors, there is a gap in the scattering rate but at a substantially higher energy.

The calculation of the optical conductivity and frequency-dependent scattering rate requires extrapolation of the reflectance to all frequencies for the Kramers-Kronig analysis. The spectra were extrapolated to high frequencies using the Bi-2212 data of Terasaki *et al.*[10] above 5 eV, and using power-law extrapolations: ω^{-1} above 25 eV and ω^{-4} above 124 eV. Below our lowest measured point at 43 cm^{-1} we assumed a Drude conductivity in the normal state and $1-\omega^2$ reflectance in the superconducting state. We estimate our experimental uncertainty of the reflectance to be ± 0.005. Combined with uncertainties due to the extrapolations, this gives an uncertainty in our optical conductivity of $\pm 8\%$ above 200 cm^{-1}. At low frequencies the uncertainty rises, reaching $\pm 40\%$ at 43 cm^{-1}. The resolution of the spectra is 20 cm^{-1} up to 680 cm^{-1} and 30 cm^{-1} up to 8000 cm^{-1}.

The real part of the optical conductivity of the optimally doped sample is shown in Fig. 2. As the temperature is lowered there is a transfer of spectral weight from a region between 360 and 1200 cm^{-1} to a peak centered at 184 cm^{-1}. There is an isosbestic point in the conductivity spectra at 360 cm^{-1} where the curves taken at different temperatures cross suggesting that there is a transfer of spectral weight from one component to another without an attendant change in the lineshape of either component. In this case one component is a Drude-like continuum, and the other is the peak at 184 cm^{-1}.

Such a peak is often seen in high-temperature superconductors where there is oxygen disorder[11,12] which, in Hg-1223, is expected more in optimally doped samples than in underdoped ones.[13] In agreement with this, the peak in the optical conductivity spectra of the underdoped sample, shown in the inset of Fig. 2, is narrower and weaker. It should also be noted that Hg-1223 crystals are prone to surface deterioration with exposure to air.[14] The underdoped sample was measured soon after growth, and it is possible that some of the absorption in the optimally doped sample, measured a year later, could be attributed to the influence of parasitic phases.[14] It is unlikely that the peak is due to diffraction from the small sample. Diffraction effects should nearly cancel out with our technique of evaporating gold onto the sample to create a reference.

The overall infrared spectral weight up to 8000 cm^{-1}, expressed as a squared plasma frequency from the conductivity partial sum rule, is $I(8000) = \int_0^{8000} \sigma_1(\omega) d\omega = 4.3 \times 10^8$ cm^{-2}. This is a factor of 1.3 higher than the comparable figure for the *a*-axis spectral weight of the two-layer Y-123 at optimal doping and a factor of 2.2 higher than that for Bi-2212.[6] In terms of spectral weight per plane copper, the Hg-1223 value is higher by factors of 1.33 and 1.53, respectively.

The frequency-dependent scattering rate was calculated using the extended Drude model and is shown in Fig. 3 for the optimally doped sample. Here the gap is clearly seen as a temperature-dependent suppression of the scattering rate below 1000 cm^{-1}. There is a substantial residual scattering of 300 cm^{-1} at low frequencies which is consistent with the 300 cm^{-1} width of the low-frequency peak in the optical conductivity at low temperature. The scattering rate of the underdoped sample is shown in the inset of Fig. 3. It shows no residual scattering, and is about 300 cm^{-1} lower than that of the optimally doped sample over the entire range shown.

The two samples also show different gap onset temperatures T^*. For the underdoped sample $T^* > 300$ K, while for the optimally doped sample $125 < T^* < 225$ K. These values are consistent with measurements of dc resistivity[15] and NMR ^{63}Cu T_1 (Ref. 16) that give T^* values of 320 and 230 K, respectively. The doping dependence is similar to that of other high-temperature superconductors.[6]

The gap feature at 1000 cm^{-1} in Hg-1223 is at a consid-

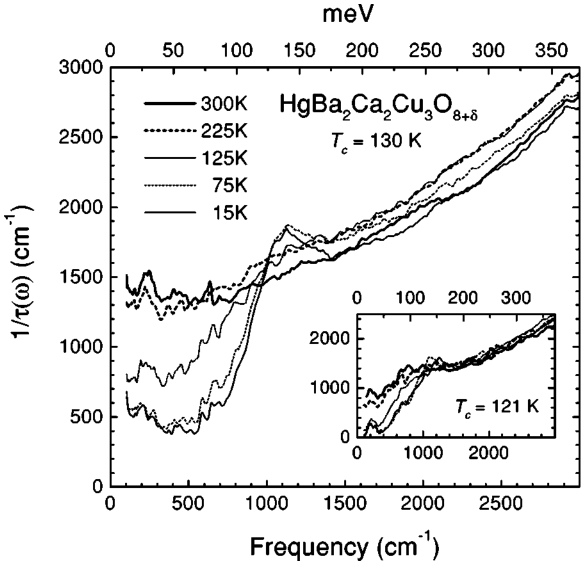

FIG. 3. The frequency-dependent scattering rate of the optimally doped crystal of Hg-1223. There is a gap, or suppression of scattering, below 1000 cm^{-1}. The inset shows the spectra for the underdoped sample.

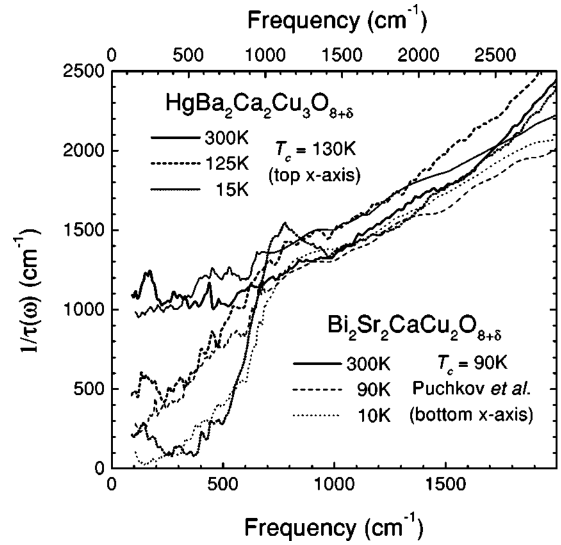

FIG. 4. A comparison of the frequency-dependent scattering rate of Hg-1223 with that of Bi-2212 from Puchkov *et al.* The frequency scales differ by a factor of 135/93=1.45, and a frequency-independent scattering rate of 300 cm^{-1} has been subtracted from the Hg-1223 data.

erably higher frequency than the corresponding features in Y-123, Y-124, Bi-2212, and Tl-2201 which are all at about 700 cm^{-1}.[6] Since these superconductors also have similar values of $T_c \approx 93$ K, the gaps are in the same ratio (1000/700=1.43) as the transition temperatures (135/93 =1.45).

Julien *et al.* analyzing hyperfine NMR shift data find a much higher transferred hyperfine coupling constant B in Hg-1223 than in Y-123, suggesting a higher in-plane superexchange J between the copper spins.[16] With our finding of a larger gap in the Hg-1223 material these results support the idea of a superconducting mechanism closely tied to the antiferromagnetism of the copper oxygen planes.

Figure 4 shows a comparison of the scattering rate of Hg-1223 with that of Bi-2212 from Puchkov *et al.*[6] The frequency scales differ by the ratio of the values of maximum T_c, 135/93, and a frequency-independent scattering rate of 300 cm^{-1} has been subtracted from the Hg-1223 data to take the residual scattering into account. The similarity of the scattering rate spectra of the two-layer Bi based superconductor with those of the three-layer Hg material is striking. A slight overshoot like the one seen in the 1200 cm^{-1} region for Hg-1223 is also seen in several other optimally doped materials.[6]

$La_{2-x}Sr_xCuO_4$ is the only material for which ab-plane reflectance measurements show a gap that does not scale with maximum T_c. It has a gap of about 700 cm^{-1} and a maximum T_c of only 40 K. Many of its other properties, however, are also inconsistent with the gap properties observed in other cuprate superconductors, and it has been suggested that this may be due to the presence of paramagnetic centers intrinsic to the random alloy.[2] It is reasonable to conclude that $La_{2-x}Sr_xCuO_4$ should be treated as a special case.

Because the gap seen in reflectance measurements includes a momentum conserving inelastic excitation of energy $\hbar\Omega$, it is difficult to make direct comparisons to gap sizes measured using other techniques. Nevertheless, these other measurements also show evidence for a universal scaling between gap size and T_c. This is demonstrated in an interpretation by Williams *et al.*[17] of NMR data on several high-temperature superconductors. In an ARPES measurement Harris *et al.*[18] find that the gap in $Bi_2Sr_{2-x}La_xCuO_{6-\delta}$, which has a maximum T_c of 29 K, is roughly three times smaller than the gap in Bi-2212 and hence seems to scale with maximum T_c. A similar scaling can be seen in B_{1g} Raman spectra. Figure 5 is a comparison of the B_{1g} Raman intensity of nearly optimally doped Hg-1223 measured by Sacuto *et al.*[13] with that of Bi-2212 measured by Hackl *et al.*[19] Again the frequency scales differ by a factor of 135/93=1.45. The positions of the maxima at 500 and 780 cm^{-1} are proportional to the superconducting gaps.

A universal scaling between gap size and maximum T_c is far from trivial. For example, in conventional electron-

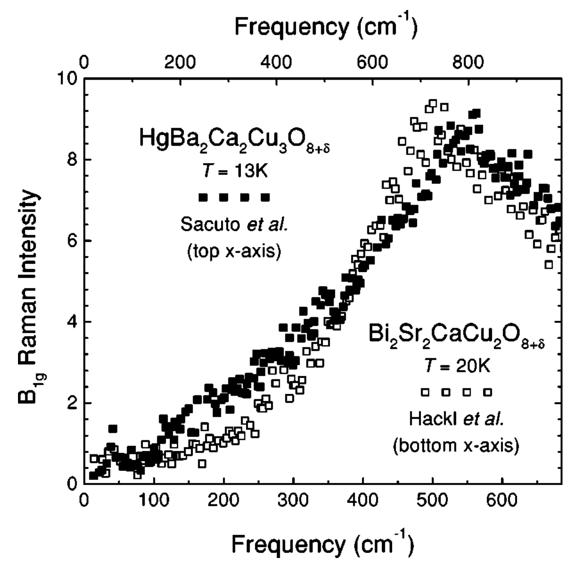

FIG. 5. A comparison of the B_{1g} Raman Intensity of Hg-1223 measured by Sacuto *et al.* with that of Bi-2212 measure by Hackl *et al.* The frequency scales differ by a factor of 135/93=1.45.

phonon mediated superconductors, $2\Delta/k_b T_c = 3.5$ for the lowest T_c materials, but *rises* with T_c to as high as 5.2.[20] We see no change in the gap ratio as maximum T_c is enhanced by 40%. In addition, this scaling is seen despite the presence of a momentum conserving inelastic excitation which therefore may also scale with maximum T_c. In order to further investigate this remarkable behavior of the cuprate superconductors, estimates of gap size need to be obtained for more systems with T_c significantly different from 93 K, particularly the two-layer Hg compound, Hg-1212, and the two- and three-layer Tl compounds, Tl-2212 and Tl-2223.

We are grateful to A. Sacuto for helpful discussions. The work at McMaster University was supported by the Natural Sciences and Engineering Research Council of Canada.

*Present address: Laboratoire d'Etude des Matériaux Hors d'Equilibre, Bât. 415, Université Paris-Sud, 91405 Orsay Cedex, France.

[1] D. Colson, A. Bertinotti, J. Hammann, J. F. Marucco, and A. Pinatel, Physica C **233**, 231 (1994); A. Bertinotti, D. Colson, J. Hammann, J.-F. Marucco, D. Luzet, A. Pinatel, and V. Viallet, *ibid.* **250**, 213 (1995).

[2] T. Timusk and B. Statt, Rep. Prog. Phys. **62**, 61 (1999).

[3] J. W. Loram, K. A. Mirza, J. R. Cooper, and J. L. Tallon, Physica C **282-287**, 1405 (1997).

[4] Ch. Renner, B. Revaz, J.-Y. Genoud, K. Kadowaki, and Ø. Fischer, Phys. Rev. Lett. **80**, 149 (1998).

[5] Y. DeWilde, N. Miyakawa, P. Guptasarma, M. Iavarone, L. Ozyuzer, J. F. Zasadzinski, P. Romano, D. G. Hinks, C. Kendziora, G. W. Crabtree, and K. E. Gray, Phys. Rev. Lett. **80**, 153 (1998).

[6] A. V. Puchkov, D. N. Basov, and T. Timusk, J. Phys.: Condens. Matter **8**, 10 049 (1996).

[7] J. P. Carbotte, Nature (London) **401**, 354 (1999).

[8] There is a short report of a reflectance ratio on thin films of a three-layer mercury material by E. J. Choi, J. Korean Phys. Soc. **31**, 815 (1997). These reflectivity data are dominated by a prominent structure around 500 cm^{-1}, possibly due to substrate phonons since this structure is absent in our single-crystal data.

[9] A. Bertinotti, D. Colson, J.-F. Marucco, V. Viallet, J. Le Bras, L. Fruchter, C. Marcenat, A. Carrington, and J. Hammann, in *Studies of High Temperature Superconductors*, edited by A. Narlikar (Nova Science, New York, 1997).

[10] I. Terasaki, S. Tajima, H. Eisaki, H. Takagi, K. Uchinokura, and S. Uchida, Phys. Rev. B **41**, 865 (1990).

[11] T. Timusk, D. N. Basov, C. C. Homes, A. V. Puchkov, and M. Reedyk, J. Supercond. **8**, 437 (1995).

[12] D. N. Basov, B. Dabrowski, and T. Timusk, Phys. Rev. Lett. **81**, 2132 (1998).

[13] A. Sacuto, R. Combescot, N. Bontemps, C. A. Müller, V. Vialet, and D. Colson, Phys. Rev. B **58**, 11 721 (1998).

[14] A. Sacuto (private communication).

[15] A. Carrington, D. Colson, Y. Dumont, C. Ayache, A. Bertinotti, and J. F. Marucco, Physica C **234**, 1 (1994).

[16] M.-H. Julien, P. Carretta, M. Horvatić, C. Berthier, Y. Berthier, P. Ségransan, A. Carrington, and D. Colson, Phys. Rev. Lett. **76**, 4238 (1996).

[17] G. V. M. Williams, J. L. Tallon, E. M. Haines, R. Michalak, and R. Dupree, Phys. Rev. Lett. **78**, 721 (1997).

[18] J. M. Harris, P. J. White, Z.-X. Shen, H. Ikeda, R. Yoshizaki, H. Eisaki, S. Uchida, W. D. Si, J. W. Xiong, Z.-X. Zhao, and D. S. Dessau, Phys. Rev. Lett. **79**, 143 (1997).

[19] R. Hackl, G. Krug, R. Nemetshcek, M. Opel, and B. Stadlober, Proc. SPIE **2696**, 194 (1996).

[20] J. P. Carbotte, Rev. Mod. Phys. **62**, 1027 (1990).