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Absence of an energy gap in measurements of Cu-O superconductors with high-resolution electron-energy-loss spectroscopy

R. B. Phelps,* P. Akavoor, and L. L. Kesmodel
Physics Department and Materials Research Institute, Indiana University, Bloomington, Indiana 47405

A. L. Barr and J. T. Markert
Department of Physics, University of Texas, Austin, Texas 78712

J. Ma, R. J. Kelley, and M. Onellion
Department of Physics, University of Wisconsin, Madison, Wisconsin 53706
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We report extensive measurements of $Bi_2Sr_2CaCu_2O_8$ (Bi 2:2:1:2) and $YBa_2Cu_3O_7$ (Y 1:2:3) single crystals with high-resolution electron-energy-loss spectroscopy (HREELS). Both as-grown and oxygen-annealed Bi 2:2:1:2 samples were studied. In all cases, peaks due to surface optical phonons were observed at loss energies from 24 to 80 meV. We see no evidence for the weak feature near 60 meV which has been previously reported and attributed to the superconducting energy gap. Our results demonstrate that the optical conductivity of high-temperature superconductors deduced from HREELS, like that deduced from infrared spectroscopy, does not exhibit the gaplike structure expected for a BCS superconductor.

The energy gap of high-temperature (high-T_c) superconductors has been the subject of intense investigation, with most studies focusing on the symmetry, size, and temperature dependence of the gap. Despite the large number of studies devoted to this topic, key properties of the gap remain highly controversial. In the case of infrared (IR) spectroscopy, for example, debate over a fundamental question—whether or not the gap is detected with IR—has persisted for years. This profound lack of consensus underscores the need for close scrutiny of all experimental reports concerning the gap, and for careful examination of the gap with a wide variety of experimental techniques.

In recent studies of high-T_c cuprates with high-resolution electron-energy-loss spectroscopy (HREELS), Demuth and co-workers[1,2] and Lieber and co-workers[3,4] have reported a weak feature at a loss energy of ~60 meV and have attributed this feature to the energy gap.[1–4] Such measurements are of particular interest because HREELS is a surface-sensitive probe which, when operated under dipole scattering conditions, resembles IR in its interaction with phonons and electronic excitations. In the work of Demuth and co-workers,[1,2] single crystals of both $YBa_2Cu_3O_7$ (Y 1:2:3) and $Bi_2Sr_2CaCu_2O_8$ (Bi 2:2:1:2) were examined. The HREELS spectrum was reported to exhibit qualitative variations in measurements on different regions of the sample surface. For $T<T_c$, some regions exhibited the 60 meV feature attributed to the gap superimposed on a low-intensity background. The peak was largely (but not completely) suppressed as T approached T_c from below. Regions exhibiting such behavior were designated as "metallic" or "high conductivity" regions. Other regions exhibited stronger, sharper peaks at ~50 and 80 meV superimposed on a higher background. These peaks were largely independent of temperature and were attributed to surface optical phonons. Regions exhibiting this second type of behavior were designated as "low conductivity" regions.

Subsequently, Li and co-workers measured Bi 2:2:1:2 single crystals annealed in O_2 at pressures from 0.2 to 50 bars for five days at 540 °C. These authors reported a weak feature at 60 meV similar to that reported by Demuth and co-workers. In this study, however, the peak was reported to disappear completely at T_c. Both Demuth and co-workers and Li and co-workers interpreted their 60 meV peaks as the response of a highly conducting layer near the surface of the sample which screens the response of dielectric regions beneath the layer. Persson and Demuth[2] have argued that, for a highly conducting surface layer, the dipole scattering cross section of HREELS is proportional to the resistivity of the layer. On this basis, the 60 meV feature has been interpreted as arising from a resistivity onset at $\omega \approx 2\Delta$ predicted by the model of Mattis and Bardeen for BCS superconductors in the dirty limit.

In this paper, we report extensive measurements of Bi 2:2:1:2 and Y 1:2:3 with HREELS. Some of our preliminary measurements of phonons on Bi 2:2:1:2 have recently been reported.[5] In marked contrast to the results of the earlier studies discussed above, we observe no sign of the 60 meV feature which has been attributed to the energy gap. We observe only peaks due to surface optical phonons. Our results strongly suggest that the HREELS spectra which have been attributed to the gap arose from experimental artifacts. Furthermore, our results are in agreement with recent IR studies which report that the ac conductivity of the high-T_c cuprates does not exhibit the gap expected for BCS superconductors.

The details of our experimental methods are described elsewhere.[5] The measurements were made in a conventional ultrahigh vacuum (UHV) chamber with a base pressure of $\sim 5 \times 10^{-11}$ Torr. The design of the HREELS spectrometer is based on that of the 127° cylindrical deflection analyzer and includes a double-pass monochromator.[6] The size of the beam at the sample is approximately 1×0.2 mm^2. The angles of both the incident and scattered electron beams were

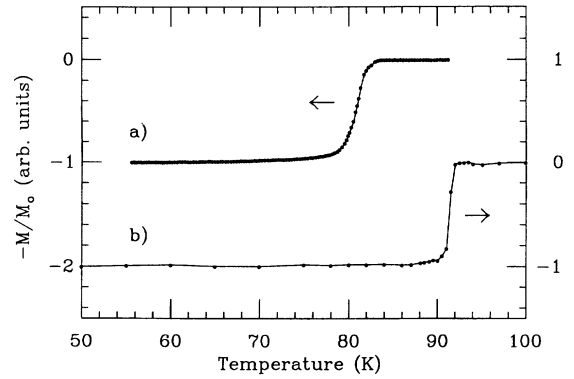

FIG. 1. The points show magnetization data typical of two types of samples used in this study, scaled by the magnetization M_0 at the lowest temperature measured. Curve (a) corresponds to Bi 2:2:1:2 annealed in 1 atm of O_2, measured with a magnetic field of 1 Oe. Curve (b) corresponds to Y 1:2:3, measured with a field of 10 Oe. The lines serve as a guide to the eye. The transition temperatures and widths deduced from these data are discussed in the text.

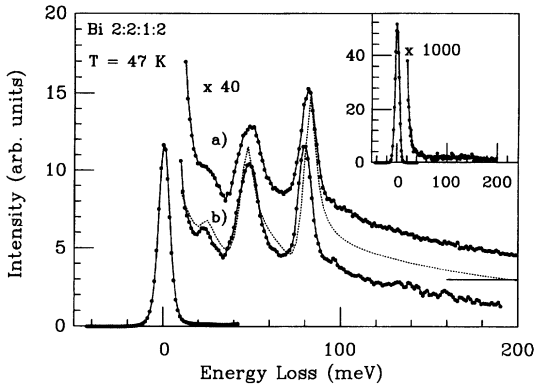

FIG. 2. The points show HREELS data for (a) as-grown Bi 2:2:1:2 and (b) Bi 2:2:1:2 annealed in 1 atm O_2. The peaks near 25, 50, and 80 meV are due to surface optical phonons and are not significantly affected by the O_2 annealing. Spectrum (a) has been shifted vertically for clarity. The dashed line shows the spectrum expected for the model high-T_c system described in the text and is to be compared with experimental spectrum (b). The inset shows the spurious spectrum obtained from a charged surface, characterized by a very low background intensity and an absence of features. The lines connecting the data points serve as a guide to the eye.

65° relative to the surface normal. The kinetic energy of the electrons incident on the sample was 3 eV for the Bi 2:2:1:2 samples and 10 eV for the Y 1:2:3 samples, and the pass energy was 1.5 eV. The resolution was typically 7–8 meV. All measurements reported here were made at a temperature of 47 K.

The Bi 2:2:1:2 samples were grown using a flux growth method based on standard techniques described elsewhere.[7] Samples subjected to various O_2 annealing treatments were studied. Typical magnetization data for crystals annealed in 1 atm of O_2 at 540 °C for 6 days, are shown in Fig. 1(a). The 10%-to-90% transition width (δT) and the transition temperature (T_c) determined from this magnetization curve are ~3 and 83 K, respectively. The Y 1:2:3 single crystals were grown in yttria-stabilized zirconia crucibles from a flux with composition $YBa_4Cu_{10}O_x$. The flux was cooled from ~1000 °C at about 4–5 °C/h. The crystals were mechanically separated, annealed in flowing O_2 for 4 weeks at 425 °C, and cooled to room temperature over 2 weeks. Typical magnetization data for these samples are shown in Fig. 1(b). For these samples, $\delta T \sim 1$ K, and T_c is 92 K.

The samples were mounted with silver-filled, conductive epoxy on Mo stubs, and a metal post was epoxied to the top surface of the sample. The stubs were transferred into the UHV system by means of a load lock and attached to the end of a cold finger cooled with liquid helium. The post was pulled off to cleave the sample at a temperature of 47 K. Special procedures for mounting the stub-sample-post sandwich, discussed elsewhere in detail,[8] were necessary to avoid exposure of epoxy upon cleavage. These procedures were especially important for Y 1:2:3, which cleaves less easily than Bi 2:2:1:2. Whenever epoxy was exposed by the cleave, electron beam-induced charging occurred and spurious spectra were observed, as discussed below. Sharp (1×5) and (1×1) low-energy electron diffraction patterns were observed for Bi 2:2:1:2 and Y 1:2:3, respectively, in agreement with previously published results.[9]

Typical HREELS data for two types of Bi 2:2:1:2 crystals, as-grown and 1 atm-O_2-annealed, are shown in Fig. 2. The peaks at approximately 25, 50, and 80 meV are caused by surface optical phonons, as discussed elsewhere in greater detail.[5,18] Similar data are observed for Y 1:2:3, as shown in Fig. 3. It is evident from Fig. 2 that the phonon peaks observed for annealed samples are not significantly different from those observed for as-grown samples. We have observed similar spectra for Bi 2:2:1:2 samples annealed in O_2 pressures as high as 8 atm. We note that Demuth and co-workers reported observation of surface optical phonons on ~30% of the surface of their Bi 2:2:1:2 samples. Li and co-workers have also made note of this type of spectrum on unannealed samples[3] and annealed samples with broad transitions.[4] The difference between the present work and these previous studies is that we *always* observe the type of spectra shown in Fig. 2, independent of the position of the

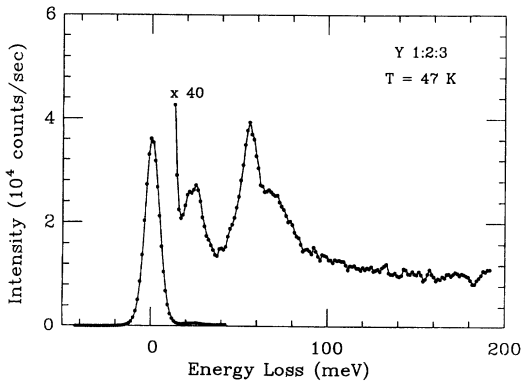

FIG. 3. The points show HREELS data for Y 1:2:3. The peaks near 24, 56, and 69 meV are due to surface optical phonons. The data are qualitatively similar to those for Bi 2:2:1:2 shown in Fig. 2. The lines serve as a guide to the eye.

sample and the annealing procedures used to prepare the sample.

The only measurements in which we have not observed the phonon peaks shown in Figs. 2 and 3 are those which were demonstrably affected by charging of the sample or its surroundings. As shown in the inset to the figure, our measurements of charged surfaces resulted in spurious spectra which were characterized by an absence of features and a background with very low intensity. When samples exhibiting such spectra were dosed with an adsorbate, no sign of the adsorbate's vibrational spectrum was observed. This result and other evidence which confirms our interpretation of the spectrum shown in the inset are discussed elsewhere.[8] We note that the background level of the spectrum shown in the inset (0.004% of the elastic peak at 100 meV) is comparable in intensity to the background in the spectra which Demuth and co-workers and Li and co-workers have associated with the energy gap. This observation, together with recent theoretical results (see below), strongly suggests that the spectra which have been attributed to the gap were caused by charging.

The significant differences between the present results and those of previous authors cannot be attributed to differences in the quality of the samples used. The transition widths for the samples we have used are comparable to or better than those reported in the previous studies.[10] Samples similar to those studied in the present work have been shown to exhibit an energy gap in photoemission (Bi 2:2:1:2) (Refs. 11 and 12) and tunneling (Y 1:2:3) (Ref. 13) measurements. Nor can these differences be attributed to special O_2 annealing procedures. The 1 atm-O_2-annealed samples which we used were annealed with parameters essentially identical to those used by Li, Liu, and Lieber.[4] Furthermore, we observe little or no change in the intensity of the phonon peaks for samples annealed at O_2 pressures as high as 8 atm.

A possible explanation for the difference in results is inhomogeneity of high-T_c samples parallel to the c axis. Such inhomogeneity could result in exposure of surfaces with different structure or composition upon cleavage. We regard such effects as extremely unlikely in the present study. In all, we have examined approximately 32 Bi 2:2:1:2 samples grown in three separate laboratories[14] and 8 Y 1:2:3 samples. Many samples were cleaved more than once; some were cleaved as many as four times. In all measurements, except for those affected by charging, peaks attributable to surface phonons were observed. The intensity of these peaks and the background levels in the spectra were highly reproducible. This high degree of reproducibility provides strong evidence that the behavior we observe is intrinsic to the high-T_c superconductors we have studied.

A second possible, but unlikely, explanation for the contrast between our results and those of previous studies is the difference in the size of the electron beam. Demuth and co-workers and Li and co-workers employed the same spectrometer in their respective studies. The size of the beam in this spectrometer (estimated to be $\sim 50 \times 70\ \mu m^2$) was significantly smaller than that of our spectrometer. However, Li and co-workers have reported that their O_2-annealed Bi 2:2:1:2 samples are quite homogeneous. They reported observation of phonons only on unannealed samples[3] and annealed samples with broad transitions.[4] Since we observe phonons even on annealed samples with narrow transitions, it is unlikely that the size of our electron beam can account for the difference between our results and those of Li and co-workers.

These new results provide compelling experimental evidence that HREELS spectra for the high-T_c superconductors are intrinsically dominated by surface optical phonons ("phononlike"), rather than the largely featureless, "gaplike" spectra reported earlier. In the remainder of this paper, we turn to theoretical considerations which lend strong support to our data.

We first consider qualitative arguments to show that one expects *a priori* that vibrations of the topmost atomic layers should be observable with HREELS. It has been established[15] that the topmost layer of cleaved Bi 2:2:1:2 is Bi-O, followed by Sr-O and Cu-O. In the case of Y 1:2:3, cleaved surfaces exhibit both Cu-O and Ba-O terminations, due to the existence of two equivalent cleavage planes.[13] Hence, it is clear that the response of these terminal layers cannot be screened since they lie above the topmost Cu-O layer. That is, normal modes with symmetry consistent with the dipole selection rule will be observable. It is instructive to consider the analogy of a monolayer of a dipole-active adsorbate such as CO on a metal surface. If we assume that the Bi-O vibrations are analogous to those of the adsorbate, we would expect their dipolar loss intensity to be at least in the range of 0.1–1.0 %.[16] As a second example, we note that Al_2O_3 films with a thickness of only 2–4 monolayers on metallic substrates such as Pd or Al yield surface optical phonons which are approximately eight times more intense than those observed in the present work.[17] Therefore, the experimental relative loss intensity we observe ($\sim 1\%$) for surface optical phonons is in line with these qualitative arguments, allowing for differences in oscillator strengths and layer thicknesses. These same arguments do not support the gaplike spectra reported earlier since these spectra show no evidence of phonon losses even at *very high magnification* (i.e., $\times 2000$) and even *above* the superconducting transition temperature.

We now consider quantitative models which incorporate both the bulk phonons and the conductivity of the Cu-O layers. We first note that Persson and Demuth[2] have considered the properties of a model high-T_c system consisting of dielectric layers separated by two-dimensional conducting sheets. However, these authors generally treated the case of the conducting sheet as the topmost layer and did not present explicit calculations for the experimentally relevant case of a dielectric, vibrationally active surface termination.

Mills *et al.* have recently undertaken new calculations of the electron-energy-loss spectrum for Bi 2:2:1:2.[18] The model system used in these calculations is based on an earlier model developed for semiconductor superlattices.[19] It consists of a semi-infinite superlattice with two components, A and B. The dielectric function of the A layers includes Lorentzian oscillators corresponding to the bulk phonon modes. The B layers, which represent the Cu-O layers in the physical system, are given a Drude conductivity with a frequency-dependent relaxation time and a dc resistivity ρ_0 of 106 $\mu\Omega$ cm. The use of such an ac conductivity lacking gaplike structure (even at temperatures below T_c) is consistent with recent infrared studies which report gapless optical

conductivities for Bi 2:2:1:2 and Y 1:2:3.[20,21] In this model, the layer thicknesses of the dielectric and conducting layers can be explicitly included and the terminal cleavage layer can have a different thickness. This model therefore encompasses the relevant system consisting of a Bi-O and Sr-O terminal A layer with a thickness of 4.6 Å , followed by Cu-O layers (with a thickness of 3.1 Å) which alternate with dielectric layers (with a thickness of 12.3 Å).

The results of a calculation using the model of Mills *et al.* are shown as a dashed line in Fig. 2. Salient features of the results are as follows.

(i) The model gives a good fit to the experimental data both in terms of the phonon intensities as well as the background level. The fit to the experimental background implies a *surface* resistivity parallel to the ab plane of $\sim 500\ \mu\Omega$ cm when spatially averaged over the conducting and dielectric layers.

(ii) The same model and parameters yield a good fit to the infrared reflectance data for Bi 2:2:1:2 (not shown).[22]

(iii) The model predicts effective screening for phonons in the dielectric layers *beneath* the first conducting layer, so that 50–75 % of the phonon intensity can be attributed to the terminal layer for the parameters for the Fig. 2 calculation.

(iv) The model predicts a background level which scales roughly as $\rho_0^{1/2}$ for $10\ \mu\Omega\ \text{cm} \leq \rho_0 \leq 10^3\ \mu\Omega$ cm. Hence, the extremely low background levels which Demuth and co-workers and Li and co-workers have attributed to "metallic" surface terminations are, in our view, incompatible with realistic values for the dc resistivity of these materials. This incompatibility, together with our own observation of comparably low background levels in the presence of charging, strongly suggests that the spectra which have been attributed to the gap arose from charging.

In conclusion, on both Bi 2:2:1:2 and Y 1:2:3 samples for which a superconducting energy gap has been observed by other methods, our HREELS data exhibit no feature attributable to the gap. The data exhibit surface optical phonons, unless affected by charging. Our results are in direct contradistinction to those of Demuth and co-workers and Li and co-workers and strongly suggest that the spectra which these authors have attributed to the gap arose from experimental artifacts. Our results for Bi 2:2:1:2 are in good agreement with theoretical results for a model system with a Drude-like ac conductivity, and are fully consistent with the results of several recent infrared studies. Hence, our results demonstrate that the optical conductivity of high-T_c superconductors derived from HREELS, like that derived from infrared, does not exhibit the gap observed for BCS superconductors.

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*Present address: Department of Physics, Grinnell College, Grinnell, IA 50112.

[1] J. E. Demuth, B. N. J. Persson, F. Holtzberg, and C. V. Chandrasekhar, Phys. Rev. Lett. **64**, 603 (1990).

[2] B. N. J. Persson and J. E. Demuth, Phys. Rev. B **42**, 8057 (1990).

[3] Y. Li, J. L. Huang, and C. M. Lieber, Phys. Rev. Lett. **68**, 3240 (1992).

[4] Y. Li, J. Liu, and C. M. Lieber, Phys. Rev. Lett. **70**, 3494 (1993).

[5] R. B. Phelps, P. Akavoor, L. L. Kesmodel, J. E. Demuth, and D. B. Mitzi, Phys. Rev. B **48**, 12 936 (1993).

[6] L. L. Kesmodel, J. Vac. Sci. Technol. A **1**, 1456 (1983).

[7] P. D. Han and D. A. Payne, J. Cryst. Growth **104**, 201 (1990); D. B. Mitzi *et al.*, Phys. Rev. B **41**, 6564 (1990).

[8] P. Akavoor, R. B. Phelps, and L. L. Kesmodel, J. Vac. Sci. Technol. A **12**, 587 (1994).

[9] P. A. P. Lindberg *et al.*, Appl. Phys. Lett. **53**, 2563 (1988); N. G. Stoffel *et al.*, Phys. Rev. B **37**, 7952 (1988).

[10] In the text of Ref. 4, Li, Liu, and Lieber reported transition widths of ~2 K. However, when we apply the same 10%-to-90% criterion used to determine δT for our samples to the magnetization data shown in Ref. 4, we obtain widths of at least 6 K.

[11] Y. Hwu *et al.*, Phys. Rev. Lett. **67**, 2573 (1991).

[12] R. J. Kelley, J. Ma, G. Margaritondo, and M. Onellion, Phys. Rev. Lett. **71**, 4051 (1993).

[13] H. L. Edwards, J. T. Markert, and A. L. de Lozanne, Phys. Rev. Lett. **69**, 2967 (1992).

[14] The total number of Bi 2:2:1:2 samples examined includes approximately 15 crystals used for the work reported in Ref. 5, supplied by J. E. Demuth, D. B. Mitzi, W. C. Lee, and D. M. Ginsberg.

[15] M. Tanaka *et al.*, Nature (London) **339**, 691 (1989); P. A. P. Lindberg *et al.*, Phys. Rev. B **39**, 2890 (1989).

[16] H. Ibach and D. L. Mills, *Electron Energy Loss Spectroscopy and Surface Vibrations* (Academic, New York, 1982), Chap. 6.

[17] D. A. Hensley and L. L. Kesmodel, J. Phys. Chem. **95**, 1368 (1991); Surf. Sci. **231**, 361 (1990).

[18] D. L. Mills, R. B. Phelps, and L. L. Kesmodel, this issue, Phys. Rev. B **50**, 6394 (1994).

[19] R. E. Camley and D. L. Mills, Phys. Rev. B **29**, 1695 (1984); S. R. Streight and D. L. Mills, *ibid.* **35**, 6337 (1987).

[20] D. Mandrus *et al.*, Phys. Rev. Lett. **70**, 2629 (1993)

[21] M. J. Sumner, J.-T. Kim, and T. R. Lemberger, Phys. Rev. B **47**, 12248 (1993).

[22] A. Zibold *et al.*, Physica C **193**, 171 (1992).