Low-energy excitations in Cu-O–based superconductors with electron-energy-loss spectroscopy

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We have investigated the ability of high-resolution electron-energy-loss spectroscopy to contribute to the understanding of the Cu-O superconductors. Our results do not show temperature dependence attributable to the superconducting transition, perhaps in part due to high surface sensitivity. A strong loss feature at 50 meV appears to be due to phonon modes, involving oxygen in the Cu-O planes, that have a strong dipole moment.

Much of the effort to understand the electronic properties of the new high-temperature superconducting materials has been directed towards the low-energy (<1-eV) excitations. From these excitations, information may be gained about the nature of the carriers, interactions of phonons and electronic excitations with these carriers that may be responsible for superconductivity, and the existence and magnitude of the superconducting gap. The techniques of tunneling, infrared reflectivity, Raman spectroscopy, and valence-band photoemission have all been applied to this study. As the quality and understanding of these materials has improved, these results have become more consistent. Nonetheless, the transport properties are not yet understood.

With the availability of moderate-size single crystals, and the increased understanding of successful surface preparation, it has become possible to use another technique, high-resolution electron-energy-loss spectroscopy (HREELS). While this technique is more susceptible to surface effects than the optical techniques, it has the advantage of sensitivity to longitudinal-optical modes and to small differences from unity reflectance. The latter difference is important to spectroscopic detection of the gap. We report here the results of a study of single-crystal $Bi_2Sr_2CaCu_2O_8$ and $YBa_2Cu_3O_{7-x}$. These results have considerable variation, apparently due primarily to surface conductivity variation, but show some interesting features which we will discuss in the context of studies by other techniques. In particular, a strong vibrational feature is observed and attributed to optical phonons, involving oxygen in the Cu-O planes, that show strong dipole moment. No consistent temperature dependence associated with superconductivity was observed.

The experiments were performed on single-crystal samples of $Bi_2Sr_2CaCu_2O_8$ and $YBa_2Cu_3O_{7-x}$,[1] which were cleaved in vacuum. The surfaces of the $Bi_2Sr_2CaCu_2O_8$ samples were characterized using low-energy electron diffraction (LEED) and spectroscopic ellipsometry. The LEED results indicated good crystalline character, including the long-range modulation that exists in these materials,[2] similar to LEED results previously reported.[3] The optical measurements gave results similar to those of bulk ceramic samples, and showed no indication of a loss of surface conductivity.[4] These $Bi_2Sr_2CaCu_2O_8$ samples have also been used in photoemission studies of the temperature dependence of the valence band at the Fermi level,[5] giving results that have been confirmed by other groups.[6,7] These characterizations thus support the existence of superconducting material at or near the surface in these samples. Our optical characterization of the $YBa_2Cu_3O_{7-x}$ crystals revealed that the cleaved surfaces were oxygen deficient, even when cleaved in air, due to lower oxygen content inside the crystal than at the surface.[4] The optical spectra correspond to a value $x\sim0.7$, which is a nonsuperconducting composition; even though the uncleaved surfaces showed high oxygen composition and high critical temperature. These samples therefore give us the opportunity to contrast the energy-loss-spectroscopy (ELS) spectra of superconducting and nonsuperconducting compositions.

The samples were attached to a copper sample holder with conducting epoxy. The samples were mounted on narrow sample holders to minimize background signal, due to the small size of the samples, ~1 mm^2. The holder and samples were then painted with acquadag to minimize problems with contact potentials. Measurements were

made with a Leybold-Heraeus ELS-22 spectrometer, using primary energies of 4–20 eV. Most spectra were taken with 8-eV electrons, where reflectivity seemed relatively high, as suggested from higher energy-loss spectra.[8] The resolution was better than 15-meV full width at half maximum (FWHM). Spectra were obtained from three $Bi_2Sr_2CaCu_2O_8$ samples and three $YBa_2Cu_3O_{7-x}$ samples.

The results of a room-temperature cleave on $Bi_2Sr_2CaCu_2O_8$ are shown in Fig. 1. Features include sharp peaks at 50 and 75 meV, and a broad tail extending to 500 meV with possible structure at 150 meV. A broad peak centered near 800 meV was observed immediately after the cleave. This may correspond to the plasmon loss observed by transmission electron-energy-loss measurements.[8] This peak was not observed in later spectra, however, suggesting a change in the surface conductivity. However, we also did not observe the structure on later low-temperature cleaves, so the feature may have been due to some other surface variation. No clear dependence of the lower-energy features on primary energy was observed, and attempts to take spectra in off-specular geometries were frustrated by the small surfaces, which permitted significant off-specular signal to come from the sample holder. After about 10 h, the feature at 75 meV and much of the strength in the tail were gone, suggesting that they are surface excitations that are removed by contamination. By contrast, the 50-meV peak remained, indicating that it is more intrinsic to the bulk structure of the material.

We cleaved the second and third samples at 35 K; see Fig. 2. No sharp features were initially observed on the cold surface spectra, which only showed a broad foot on the elastic peak. After the second sample had been brought above 100 K, the 50-meV peak was observed. This intriguing temperature dependence was reversible, but not with good consistency, so we believe it to be due to temperature-dependent changes in sample position. This is particularly critical for the small surfaces. Our results on both the second and third samples, as well as the $YBa_2Cu_3O_{7-x}$ samples, did not show the 50-meV feature until the initial cleave had been heated above 100 K, so it is possible that the appearance of this feature is related to an irreversible change in the surface. The feature was still present the following day after warming to room temperature, again indicating a lack of sensitivity to contamination.

We must also consider the possibility that the feature is due to contamination. The fact that the most likely contaminant to show a vibration in this energy range is oxygen makes such a distinction quite difficult. The immediate appearance of the feature on room-temperature cleaves suggests that if it is due to surface oxygen, the oxygen probably comes from the material, either as evolved oxygen or as the original surface atoms with modified surface bonds.

At higher energies, two broad features centered around 150 and 370 meV are observed. Since the signal for these features is very weak, we compared the spectrum due to nonspecular reflection from the acquadag-coated holder and found that it shows similar structure. Therefore, we are unable to draw conclusions from this part of the spectra.

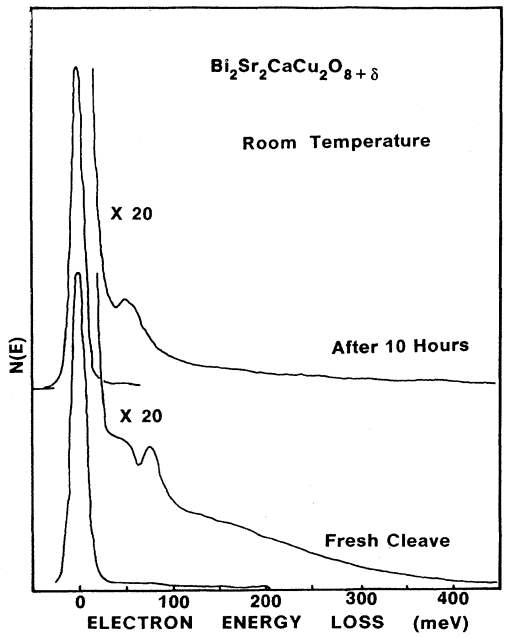

FIG. 1. Electron energy-loss spectra of $Bi_2Sr_2CaCu_2O_8$ cleaved at room temperature, immediately after cleaving and 10 h later. The primary energy was 8 eV and the electrons were incident at 60° from the surface normal.

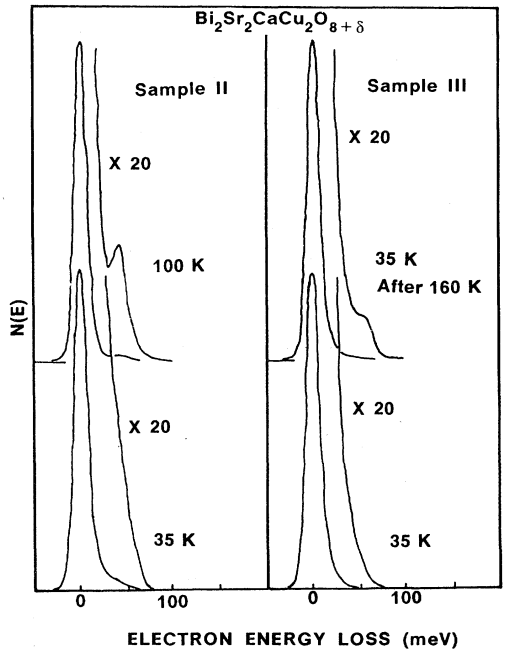

FIG. 2. Electron energy-loss spectra from $Bi_2Sr_2CaCu_2O_8$ cleaved at 35 K, and after warming above 110 K. These spectra are representative, but the intensities of the features showed significant variation in the course of our experiments.

Finally, the third surface gave somewhat different spectra. Again, the initial 35-K surface gave a broad foot and no sharp structure. However, even after the sample had been heated to 160 K, there was only a weak feature near 55 meV, which was often obscured by the loss tail. The temperature dependence of this tail and peak was again inconsistent, suggesting that it was dependent on small changes in sample position. The most interesting point seems to be the change in the position of the sharp loss peak. This sample was also the only one not to show the feature at 50 meV at room temperature after being allowed to warm up overnight.

Considering the sensitivity of energy-loss data to small differences from unity reflectance, we searched for evidence of the opening of the superconducting gap in our spectra. No evidence was found. More subtle evidence might be revealed by subtracting the background due to the elastic peak, but unfortunately our results still show too much variation in peak width and shape, apparently due to surface variation and the small irregular facets which complicate focus. We cannot exclude the possibility of observing the gap on larger surfaces of extremely high quality.

In our spectra, the only clearly identifiable feature that seems intrinsic to the material is the 50-meV peak. The existence of such a feature for both the $Bi_2Sr_2CaCu_2O_8$ surfaces and the low-oxygen $YBa_2Cu_3O_{7-x}$ surfaces suggests that it is not directly related to carrier concentration, as with a plasmon. We thus compare the spectra obtained by infrared reflectivity and Raman spectroscopy in order to consider a vibrational origin for the figure.

The vibrational features of $Bi_2Sr_2CaCu_2O_8$ have received the most study by Raman spectroscopy.[9-11] These results show that the 50-meV feature is within the energy range of several vibrational excitations. The excitations in this energy range have been associated with modes that are dominated by motion of oxygen atoms along the crystal c axis. While this technique probes non-dipole-active modes, the spatial separation of the oxygen atoms across the Ca atom at the inversion center suggests that the dipole-active Davydov partners to these modes should have similar energies.[11]

Most of the effort to study $Bi_2Sr_2CaCu_2O_8$ by infrared spectroscopy has involved reflectance from crystals with the light polarized in the a-b plane.[12] Such reflectivity is dominated by the free carriers which cause heavy screening of the phonons. Some ir results on polycrystalline, less-oriented samples show weak features due to vibrations, including one near 50 meV (400 cm^{-1}).[13] Recent results on highly oriented $YBa_2Cu_3O_{6.4}$ allowed studies with polarization both perpendicular and parallel to the c axis.[14] The low-oxygen content reduced the conductivity so that screening was also reduced. These results revealed a transverse-optical mode near 45 meV. Calculations of the loss function $(1/\epsilon)$ from these data indicated a substantial splitting between the longitudinal and transverse modes, consistent with a strong dipole moment.

Considering these results, and calculations of vibrational modes for $Bi_2Sr_2CaCu_2O_8$,[11] we attribute the 50-meV feature to vibrations of oxygen atoms. Because of the similarities in the spectra for the two types of samples, it seems likely that the mode involving the oxygen in the CuO_2 planes is very important. The calculations also show substantial energy splitting between the LO and TO modes, suggesting high oscillator strength. The energy of such a feature in the HREELS spectrum is expected to be between the LO and TO modes due to the $1/(\epsilon+1)$ dependence of the surface loss. The strength of this excitation may also be enhanced relative to the ir measurements due to lower conductivity and screening at the surface. This is consistent with the fact that the feature seems to be stronger after the sample has been heated somewhat, a treatment that has been shown to result in lower-conductivity surfaces in $YBa_2Cu_3O_{7-x}$.[15]

The difference between the third $Bi_2Sr_2CaCu_2O_8$ sample and the others may suggest a difference due to the orientation of the sample. The spectra that showed the strongest 50-meV feature were obtained by scattering the electrons along the direction of the long-range modulation of the crystal. This was not the case for the third sample.

In conclusion, we have used HREELS to study the low-energy excitations of the Cu-O superconductors. We are unable to see a temperature dependence related to superconductivity, although this may be possible with better surfaces. No new excitations suggest themselves as causes of the superconductivity. Vibrational structure near 50 meV is consistent with optical spectroscopy, and is associated with movements of oxygen atoms in the Cu-O planes. The intensity of this structure appears to vary with surface conductivity, due to screening. Our results indicate that the phonon mode has a substantial long-range dipole interaction.

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[1]P. A. Morris, W. A. Bonner, B. G. Bagley, G. W. Hull, N. G. Stoffel, L. H. Greene, and M. Giroud, Appl. Phys. Lett. **53**, 249 (1988).

[2]J.-M. Tarascon, Y. Le Page, P. Barboux, B. G. Bagley, L. H. Greene, W. R. McKinnon, G. W. Hull, M. Giroud, and D. M. Hwang, Phys. Rev. B **37**, 9382 (1988).

[3]P. A. P. Lindberg, Z.-X. Shen, B. O. Wells, D. B. Mitzi, I. Lindau, W. E. Spicer, and A. Kapitulnik, Appl. Phys. Lett. **53**, 2563 (1988).

[4]M. K. Kelly, P. Barboux, J.-M. Tarascon, and D. E. Aspnes, Phys. Rev. B **40**, 6797 (1989).

[5]Y. Chang, Ming Tang, R. Zanoni, M. Onellion, Robert Joynt, D. L. Huber, G. Margaritondo, P. A. Morris, W. A. Bonner, J. M. Tarascon, and N. G. Stoffel, Phys. Rev. B **39**, 4740 (1989).

[6]J.-M. Imer, F. Patthey, B. Darbel, W. D. Schneider, Y. Baer, Y. Petroff, and A. Zettl, Phys. Rev. Lett. **62**, 336 (1989).

[7]C. G. Olson *et al.* (unpublished).

[8]N. Nücker, H. Romberg, S. Nakai, B. Scheerer, J. Fink, Y. F. Yan, and Z. X. Zhao, Phys. Rev. B **39**, 12379 (1989).

[9]L. A. Farrow, L. H. Greene, J. M. Tarascon, P. A. Morris, W. A. Bonner, and G. W. Hull, Phys. Rev. B **38**, 752 (1988).
[10]D. Kirillov, I. Bozovic, T. H. Geballe, A. Kapitulnik, and D. B. Mitzi, Phys. Rev. B **38**, 11955 (1988).
[11]J. Prade, A. D. Kulkarni, F. W. de Wette, U. Schroeder, and W. Kress, Phys. Rev. B **39**, 2771 (1989).
[12]M. Reedyk, D. A. Bonn, J. D. Garrett, J. E. Greedan, C. V. Stager, T. Timusk, K. Kamaras, and D. B. Tanner, Phys. Rev. B **38**, 11981 (1988).
[13]Z. V. Popovic, C. Thomsen, M. Cardona, R. Liu, G. Stanisic, R. Kremer, and W. Koenig, Solid State Commun. **66**, 965 (1988).
[14]Patrick Echegut, Francois Gervais, Krystof Dembinsky, Monique Gervais, and Philippe Odier, Solid State Commun. **69**, 359 (1989).
[15]R. List, A. J. Arko, Z. Fisk, S.-W. Cheong, S. D. Conradson, J. D. Thompson, C. B. Pierce, D. E. Peterson, R. J. Bartlett, N. D. Shinn, J. E. Schirber, B. W. Veal, A. P. Paulikas, and J. C. Campuzano, Phys. Rev. B **38**, 11966 (1988).