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Surface phonons on $Bi_2Sr_2CaCu_2O_{8+\delta}$

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We report measurements of surface optical phonons on $Bi_2Sr_2CaCu_2O_{8+\delta}$ with high-resolution electron-energy-loss spectroscopy (HREELS). In addition to peaks near 50 and 80 meV (403 and 645 cm^{-1}), which have been previously observed, our loss spectra exhibit a peak at 26 meV (210 cm^{-1}). Loss spectra were measured at temperatures from 45 to 146 K, and the temperature dependence of the peaks was found to be weak. The 50 and 80 meV peaks shift to lower frequency by $\sim$1.5 meV over this temperature range. All three peaks are attributed to surface optical phonons. The identification of particular bulk modes corresponding to the surface modes observed with HREELS is discussed.

I. INTRODUCTION

In a recent study, Demuth *et al.*[1,2] reported measurements of the superconducting energy gap of high-temperature superconductors with high-resolution electron-energy-loss spectroscopy (HREELS). The samples studied included $YBa_2Cu_3O_7$ (Y 1:2:3) and $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi 2:2:1:2). Although single-crystal samples were used, qualitatively different spectra were obtained for measurements on different regions of the surface. In some areas, a broad asymmetric feature with a maximum near 55 meV was observed at low temperatures. This feature was observed on (5–10)% of the sample surface on Bi 2:2:1:2 samples and $\sim$ 33% of the surface on Y 1:2:3 samples, on average. In the case of Y 1:2:3 samples, the feature was observed to disappear almost completely above the transition temperature T_c and was associated with the superconducting energy gap.

A second type of loss spectrum with two prominent loss peaks was observed on $\sim$30% of the area of the Bi 2:2:1:2 samples. At a temperature of 22 K, the peaks were found to be at 55 and 82 meV. The peaks were attributed to surface analogs of bulk optical phonons. According to Persson and Demuth,[2] the different spectra on Bi 2:2:1:2 reflect variations in the surface resistivity with position. In areas where the gap is observed, the conductivity of the surface is high, and the surface screens the interactions of the incident electron with the rest of the sample. In areas where phonons are observed, the conductivity of the surface is lower, and the electric field of the incident electron penetrates 100–1000 Å into the crystal. The authors suggest that these variations in the surface resistivity are due to small differences in the local oxygen concentration.

Several other investigations of the Cu-O superconductors have been performed with HREELS.[3–6] Three early studies[3–5] detected excitations in the range of loss energies from 50 to 80 meV and attributed these excitations to vibrational modes involving oxygen atoms. Subsequent to the work of Demuth *et al.*, Li *et al.*[6] reported observation of the energy gap on Bi 2:2:1:2 samples which had been annealed in oxygen for several days at a pressure of 12 atm. In contrast to the work of Demuth *et al.*, the feature associated with the gap was observed to disappear completely above T_c. As-grown samples were found to exhibit weak features at 85–90 meV which persisted above T_c.

We have measured approximately 15 high-quality Bi 2:2:1:2 single crystals with HREELS, including several samples annealed in oxygen. For the samples we have studied, no sign of the gaplike features reported by Demuth *et al.* and Li *et al.* was observed. Instead, we observe only the second type of behavior discussed by Demuth *et al.*: peaks attributable to surface analogs of bulk optical phonons. In addition to the two peaks seen by Demuth *et al.*, we observe a third peak at 26 meV. The temperature dependence of these peaks was measured at temperatures between 45 and 146 K and was found to be weak. The assignment of the surface phonon peaks to particular bulk phonons is discussed in the light of recent measurements of bulk phonons in Bi 2:2:1:2 with infrared and Raman spectroscopy.

II. EXPERIMENT

Loss spectra were measured in a conventional ultrahigh vacuum (UHV) chamber with a base pressure of $\sim 5 \times 10^{-11}$ Torr. The HREELS spectrometer used includes a dual-pass monochromator and a 127° cylindrical deflection analyzer.[7] The size of the beam at the sample is approximately 1 mm × 0.2 mm. The analyzer is rotatable, allowing measurements as a function of the two-dimensional wave vector parallel to the surface $q_{\parallel}$. The measurements reported here were made at $q_{\parallel} = 0$ with both the incident and scattered angles at 60°. The ki-

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netic energy of the electrons incident on the sample was 3 eV, and the pass energy of the monochromator was 1.5 eV.

The measurements presented here were performed on two types of Bi 2:2:1:2 single crystals. No difference between the two types of samples was detected in the loss spectra. One group of crystals was grown from near stoichiometric melts using a directional solidification technique described elsewhere.[8] These samples were unannealed and had transition temperatures between 88 and 91 K. The approximate cation composition was $Bi_{2.1}Sr_{1.9}Ca_{0.9}Cu_{2.0}O_{8+\delta}$. The other group of samples[9] was grown using a flux method from a mixture of Bi_2O_3, $SrCO_3$, $CaCO_3$, and CuO in the ratio 2:2:1:4. The mixture was heated to 1050 °C in a Pt crucible in air and held at this temperature for 4 h. The melt was first cooled to 850 °C at a rate of 3 °C/h, then furnace cooled to room temperature. The crystals were annealed in O_2 at 650 °C at a pressure of approximately 1 atm for 3 days. These samples had transition temperatures of ~83 K.

The samples were mounted on Mo stubs with a conductive, silver-filled epoxy.[10] They were introduced into the chamber by means of a load-lock system which allowed samples to be changed without venting the chamber. The stubs were mounted with spring clips on a Cu block which was soldered to the end of a thin-walled stainless steel tube. The Cu block was cooled by a continuous-flow APD liquid helium transfer line. The temperature of the Cu block was routinely monitored with a chromel-alumel thermocouple. The temperatures reported in this work are those of the Mo stubs, which were determined through tests which compared the thermocouple attached to the Cu block with a second thermocouple attached directly to a stub.

The samples were cleaved *in vacuo* by pulling off a stainless steel post epoxied to the top of the sample. In all, approximately 15 samples were examined. Cleaving was performed at a temperature of 45 K. Initially, many of our freshly cleaved samples yielded spectra characterized by a narrow, intense elastic peak, and a featureless background with little or no intensity in the inelastic region of the spectrum. Some spectra measured on the day of cleaving and nearly all spectra measured on subsequent days exhibited inelastic peaks and a nonzero, temperature-dependent background intensity. As discussed elsewhere in greater detail,[11] it was later determined that the featureless spectra were artifacts caused by a buildup of electric charge either on the sample or on nearby surfaces. Samples which were mounted carefully to avoid exposure of epoxy to the incident electron beam always exhibited a nonzero background intensity and inelastic peaks, suggesting that the (nominally conductive) epoxy was the origin of the charging effects. After the completion of measurements with HREELS on the day of cleaving, samples were examined using low-energy electron diffraction. Sharp diffraction patterns similar to those which others[12] have reported for Bi 2:2:1:2 were observed.

Data for two samples, which we shall call A and B, are presented below. The data for each sample were collected the day after that on which the sample had been cleaved. The samples were left in the UHV chamber during this time. Similar data have been observed for freshly cleaved samples which have been mounted so as to avoid the charging problems mentioned above. The data have been smoothed using a five-point smoothing routine, and the positions of the peaks were determined by fitting the data with Gaussian peaks added to a linear baseline.

III. RESULTS

Data for Bi 2:2:1:2 samples A and B are shown as points in Figs. 1 and 2, respectively. The line connecting the points serves as a guide to the eye. Figure 1 includes data at three temperatures from 45 to 146 K. Figure 2 shows a spectrum measured at 45 K in which somewhat better resolution was achieved. The spectra exhibit two prominent peaks near 50 and 80 meV. A third, smaller peak is evident near 26 meV. With increasing temperature, the intensity of the background increases relative to that of the peaks. The resolution, as measured by the full width of the elastic peak at half-maximum intensity, degrades from 8.3 meV at 45 K to 10.3 meV at 146 K for the spectra in Fig. 1. The resolution for the spectrum in Fig. 2 is 7.4 meV.

In addition to the three clear peaks, the data provide evidence which suggests the presence of two other features. The first of these is a shoulder on the low-energy side of the 50 meV peak, seen most clearly in Fig. 2. The strength of this shoulder varies considerably from sample to sample, and as a function of temperature on a given sample, as is evident in Figs. 1 and 2. This variability could be caused primarily by differences in resolution, since the shoulder is clearest in the spectra with the best resolution. Nearly all of our spectra show some sign of this shoulder. In most spectra, the shoulder is similar in

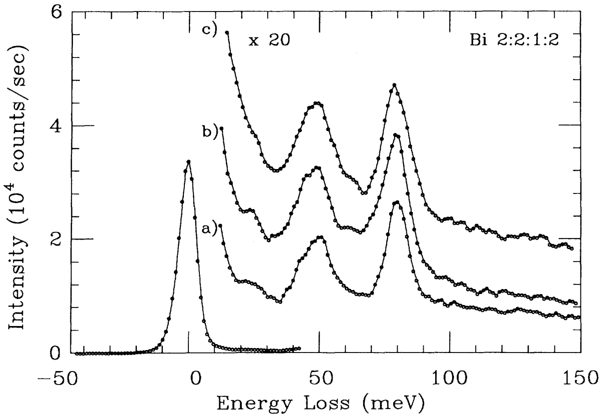

FIG. 1. The points show electron-energy-loss spectra for the Bi 2:2:1:2 sample A at (a) 45 K, (b) 83 K, and (c) 146 K. Peaks near 26, 50, and 80 meV (210, 403, and 645 cm^{-1}) are evident. A weak shoulder on the low-energy side of the peak at 50 meV is also apparent in spectra (a) and (b). Spectra (b) and (c) have been displaced vertically for clarity. The lines between the points serve as a guide to the eye.

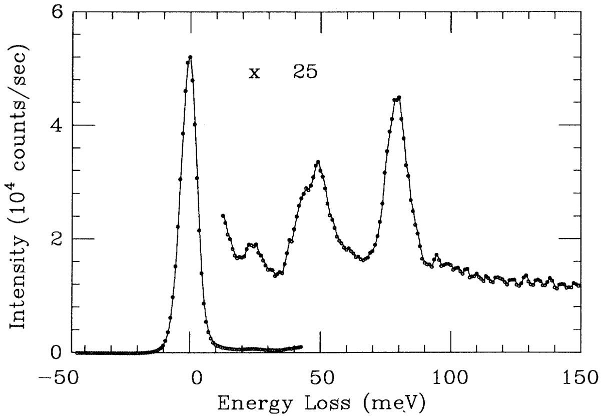

FIG. 2. Electron-energy-loss spectrum for sample B measured under conditions similar to those of Fig. 1 but with improved resolution. The peak at 26 meV and the shoulder on the peak at 50 meV are more prominent than in Fig. 1.

strength to those seen in spectra (a) and (b) in Fig. 1. Thus, there is considerable evidence for a shoulder on the 50 meV peak.

The second possible feature is suggested by the structure near 63 meV seen in spectra (b) and (c) of Fig. 1. This structure is not apparent in the spectra measured at 45 K. The structure is also not apparent in data measured in the temperature range between 65 and 85 K on other samples. Thus, the evidence for this feature is considerably weaker than that for the low-energy shoulder on the 50 meV peak. Additional data with improved resolution over the entire temperature range shown in Fig. 1 would be of interest to investigate the possible structure near 63 meV and to study the shoulder on the 50 meV peak.

The 50 and 80 meV peaks are sufficiently high in energy relative to the tail of the elastic peak that a single linear baseline allows a good fit to both these peaks and the region of the spectrum above 90 meV. By picking an appropriate linear baseline for each temperature, we have accounted for the change in the slope of the background with temperature. The positions of the peaks are 49.8 and 80.8 meV (402 and 652 cm^{-1}) at 45 K, shifting to 48.3 and 79.0 meV (390 and 637 cm^{-1}) at 146 K. The uncertainty in these positions is ± 0.5 meV. Thus, both peaks shift to lower energy by approximately 1.5 meV.

Because of the presence of the tail of the elastic peak, the linear baseline used to fit the 50 and 80 meV peaks did not provide a good fit for the low-energy peak near 26 meV. A baseline with a steeper slope was used to fit this peak, and its position was found to be 26 ± 2 meV. The larger uncertainty in the position of this peak reflects the uncertainty in the choice of the baseline. Within this larger uncertainty, the position of the 26 meV peak was found to be independent of temperature. The fact that the 26 meV peak becomes less clear at higher temperatures may indicate that the intensity of the peak decreases with temperature. However, in view of the decrease in resolution of the spectra measured at temperatures above 45 K, it is more likely that the 26 meV peak becomes obscured by the tail of the elastic peak. Spectra with better resolution at temperatures above 45 K are needed to clarify the nature of the temperature dependence which we observe.

IV. DISCUSSION

As mentioned earlier, the peaks we observe near 50 and 80 meV have been observed in a previous HREELS study.[1,2] Persson and Demuth (PD) attributed these peaks to surface analogs of bulk optical phonons. The terminology chosen by PD to describe these modes reflects the results of their analysis, which linked the surface modes observed with HREELS to bulk modes predicted by the lattice dynamic calculations of Prade *et al.*[13] Other materials, such as ZnO, are known to exhibit surface optical phonons which are closely related to bulk modes.[14] Such surface modes are sometimes called Fuchs-Kliewer modes. In ionic crystals, the penetration depth of these surface modes depends on the magnitude of the two-dimensional wave vector $q_{\parallel}$. Near the edge of the Brillouin zone, the atomic displacements associated with the mode are localized in the outermost few atomic layers. For the conditions of the present study, in which $q_{\parallel} \rightarrow 0$, the phonon may penetrate deeply into the crystal. In keeping with the terminology used by Ibach and Mills, we will refer to these modes as surface optical phonons. We agree with PD's conclusion that the modes observed with HREELS are surface optical modes. However, we have reevaluated the correspondence between these surface modes and particular bulk modes in the light of recent optical data on the bulk phonon spectrum of Bi 2:2:1:2. As we discuss below, our assignments differ somewhat from those of PD.

The simple models for surface optical modes devised for materials like ZnO are difficult to apply to Bi 2:2:1:2 because of two factors: the anisotropic structure of the bismuth compound and the high conductivity of its $\mathrm{CuO_2}$ planes. To address these complicating factors, PD modeled the superconductor as a semi-infinite sequence of conducting layers separated by dielectric slabs. The dielectric function for the slabs included optical phonons which were assumed to have dynamic dipole moments oriented perpendicular to the conducting sheets (c-axis phonons). Phonons with dipole moments oriented parallel to the conducting sheets (ab-plane phonons) were excluded since it was found that in this case, given the screening of the sheets, unphysically large dipole moments would be necessary to fit the data. PD used this model to fit their data for Bi 2:2:1:2 at room temperature, a spectrum which included peaks at 51 and 81 meV. The fit yielded transverse optical (TO) phonon frequencies of 37 and 66 meV.

PD found good agreement between the results of their analysis and the frequencies of bulk optical phonons predicted by the lattice-dynamical calculations of Prade *et al.*[13] Prade *et al.* based their calculations on the use of short-range repulsive potentials and Coulomb potentials in the framework of the shell model. Using a body-centered tetragonal (bct) structure for Bi 2:2:1:2, they predicted a total of 14 infrared-active modes for bulk Bi

2:2:1:2. Of these, seven modes consist of vibrations perpendicular to the CuO_2 planes. Six of these have A_{2u} symmetry and one has B_{2u} symmetry. The transverse optical and longitudinal optical (LO) frequencies of the A_{2u} modes, listed as TO(LO), are 17.0(17.5), 21.0(21.0), 34.4(34.5), 41.4(59.1), 60.4(61.6), and 63.7(65.7) meV. We will refer to these modes as $\omega_1, \omega_2, \ldots, \omega_6$, respectively. The modes with higher frequencies correspond to vibrations primarily of the oxygen atoms, while those with lower frequencies correspond to motion primarily of the heavier, metallic cations. These modes may be grouped into three pairs, where the separation of each pair is less than the 8 meV resolution of typical HREELS measurements on Bi 2:2:1:2 samples. PD attribute their 81 meV peak to ω_5 and ω_6, and their 51 meV peak to ω_3 and ω_4. No feature corresponding to ω_1 and ω_2 was observed in PD's measurements, presumably because it was obscured by the tail of the elastic peak.

The analytical framework developed by PD provides one way of explaining both their data and the new features reported here. In this interpretation, the new peak at 26 meV could be attributed to ω_1 and ω_2. The shoulder on the low-energy side of the 50 meV peak could be attributed to ω_3, which is now partially resolved since the resolution of the measurement (7.4 meV for Fig. 2) is close to the 7.0 meV separation of ω_3 and ω_4. However, two considerations argue against this line of interpretation.

The first difficulty with PD's interpretation is that surface optical phonons are constrained to lie between the TO and LO frequencies of the bulk modes to which they correspond.[17] Comparison of the present HREELS data with the predictions of Prade *et al.* shows that only the peak at 50 meV obeys this constraint, lying between the TO and LO frequencies of of ω_4. The 80 meV peak lies well above the LO frequency predicted for ω_6, and the 26 meV peak lies above the LO frequency of ω_2 but below the TO frequency of ω_3.

The second difficulty is that the bulk phonon spectrum measured for Bi 2:2:1:2 is significantly different from that predicted by Prade *et al.* Zibold *et al.*[18] and Liu *et al.*[15] have measured the bulk vibrational spectrum with infrared (IR) and Raman spectroscopy, respectively. Both these groups found bulk modes at frequencies substantially different from those predicted by Prade *et al.* Liu *et al.* also found several modes not predicted by Prade *et al.* These extra modes were attributed to two well-known distortions of the bct lattice, the orthorhombic distortion and the superstructural modulation.[15]

An alternative set of assignments for the surface modes observed with HREELS is suggested by the IR data of Zibold *et al.* These authors measured the reflectance of Bi 2:2:1:2 single crystals with the electric field of the incident radiation polarized parallel to each of the principal crystallographic axes. The range of photon energies studied was 30 meV to 6 eV. The conductivity was obtained from a Kramers-Kronig analysis of the reflectance data. For incident radiation polarized parallel to the *a* and *b* axes, the conductivity was a smoothly varying function of frequency, but for radiation polarized parallel to the *c* axis, several sharp peaks attributed to phonons were observed.[16] Zibold *et al.* fit the conductivity parallel to the *c* axis with a Fano-resonance model which included Lorentzian oscillators for the phonons and an electronic oscillator representing broadband electronic excitations. This analysis yielded four prominent phonon modes at 36, 39, 47, and 76 meV. A very weak mode at 59 meV was also detected. Zibold *et al.* assigned the mode at 76 meV to vibrations of the "apex" oxygens (i.e., those oxygens located between the Bi-O and Cu-O planes) parallel to the *c* axis. Hence, the IR mode at 76 meV appears to correspond to the mode ω_6 predicted by Prade *et al.*, which is dominated by motion of the apical oxygens. Although Zibold *et al.* did not assign the other four modes which they observed, it is reasonable to assign these modes to four of the five modes ω_1–ω_5 predicted by Prade *et al.*, suggesting that one of these modes was not observed in the IR measurements.

At least two of the modes observed with HREELS can be assigned according to their proximity to the corresponding IR modes. The modes we observe at 50 and 80 meV can be associated with the modes observed at 47 and 76 meV in the IR data, respectively. Since the IR data extend downward in frequency only to 30 meV, it is unclear whether the IR spectrum includes a mode near our 26 meV peak. However, noting that one of the modes predicted by Prade *et al.* is absent from the spectra of Zibold *et al.*, we propose that mode ω_1 lies below 30 meV. We can then tentatively associate our 26 meV peak with ω_1, which primarily involves motion of the Bi atoms. If the remaining IR modes are matched in order of increasing frequency to the modes ω_2–ω_5, our 50 meV peak would be associated with ω_4. This mode primarily involves motion of the oxygens in the Bi-O plane. No features corresponding to the IR modes at 36, 39, or 59 meV are observed in the present data, but the presence of weak features at these energies cannot be excluded. Table I summarizes the frequencies of the modes observed with HREELS and our proposed assignments. We emphasize that the assignments we propose are tentative: Zibold *et al.* assigned only one of the modes they observed, and we observe only two surface modes with HREELS over the range of frequency in which they saw four prominent IR modes.

The nature of the low-energy shoulder on the 50 meV

TABLE I. Frequency and proposed assignment of surface optical modes observed with HREELS on Bi 2:2:1:2. The infrared frequencies for the corresponding bulk modes from the work of Zibold *et al.* are shown for comparison. The mode designations ν_1–ν_3 are used here solely for the purpose of enumerating the modes observed in the present work.

Mode	HREELS Frequency (meV)	HREELS Frequency (cm^{-1})	IR Frequency (meV)	Assignment
ν_1	26	210	Not observed[a]	Bi
ν_2	50	403	47	O in Bi-O plane
ν_3	80	645	76	Apical O

[a] The infrared measurements did not include frequencies below 30 meV.

peak observed with HREELS remains unclear, since the IR data show only one peak near 50 meV. It is possible that our HREELS measurements have detected a feature which is either inactive or very weak in the infrared, but further work is necessary to understand this feature. In this regard, HREELS measurements with improved resolution would be of interest. The work by Zibold *et al.* is, to our knowledge, the first IR study of *c*-axis phonons in single crystals of Bi 2:2:1:2. Therefore, it would be helpful to have additional IR data, including data at frequencies below 30 meV. An extension of the lattice dynamic calculations of Prade *et al.* to include the orthorhombic distortion and the superstructural modulation would be of great interest and would help clarify the relationship between the IR-active and Raman-active modes. The fact that we do not observe surface modes corresponding to the IR bulk modes at 36, 39, and 59 meV suggests that these surface modes are either weak or inactive. Calculations of the number and relative intensity of the surface optical modes on Bi 2:2:1:2 would therefore also be of interest.

The weak temperature dependence of the peaks in our HREELS data is in qualitative agreement with the results of other measurements, including the HREELS measurements of PD and the IR data of Kamarás *et al.*[19] Resonant neutron absorption spectroscopy has been used to observe softening of *a*-*b* plane phonons in Bi 2:2:1:2, but no such softening was observed for *c*-axis phonons.[20]

V. CONCLUSIONS

We have made measurements of Bi 2:2:1:2 using HREELS. No sign of gaplike features was observed. Three peaks were observed and attributed to surface optical phonons. Two of these peaks correspond to those observed previously by Demuth *et al.*, and one at lower energy has not been previously observed. The present data are in good agreement with measurements of the bulk phonon spectrum with infrared spectroscopy. The temperature dependence of the peaks is weak in the range of temperatures studied.

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[16] It should be noted that some workers have reported observation of *ab*-plane phonons in Bi 2:2:1:2 with infrared spectroscopy. See, for example, M. Shimada *et al.*, Physica C **193**, 353 (1992). The fact that Zibold *et al.* were able to observe *c*-axis modes clearly yet were unable to observe *ab*-plane modes suggests that the latter are much weaker. These observations can be qualitatively explained by noting that the high conductivity of the CuO_2 planes is expected to screen the *ab*-plane modes.

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