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Electronic excitations of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ superconductor: A study by transmission electron-energy-loss spectroscopy with an electron microprobe

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Electronic excitations of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ superconductor: A study by transmission electron-energy-loss spectroscopy with an electron microprobe

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Interband and core-level transitions and plasmon resonance in the high-temperature oxide superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ were studied by transmission electron-energy-loss spectroscopy using an electron microprobe $\sim 5\text{--}10 \text{ \AA}$ in size. Both single-crystal and polycrystalline ceramic samples have been examined. No significant change in electronic structure was observed at the grain boundaries. A 13.5-eV interband-transition peak was found to be sensitive to damages created by ion-beam bombardment.

The recent discovery of the 90-K Y-Ba-Cu-O superconductor¹ has spurred intensive research activities. Detailed knowledge of electronic structure is a vital first step in understanding the superconducting mechanism responsible for such a high T_c . The theoretical band structure has been calculated^{2,3} and strongly shows two-dimensional and one-dimensional features in the energy bands. Experimentally, the electronic structure has been studied by many workers using surface-sensitive spectroscopies.⁴⁻⁷ Since the discovery of the high- T_c oxide superconductor, the ubiquitous presence of grain and twin boundaries has raised questions regarding the possible roles they play in the superconductivity. Studies of electronic-structure changes at the boundaries, if any, compared with the bulk of the grains are therefore of great importance. Experiments carried out with the large probe sizes required by many conventional spectroscopies cannot answer these questions.

In this paper, we report transmission electron-energy-loss spectroscopy on both single-crystalline and polycrystalline $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ superconductor samples using a 5-10 \AA electron microprobe generated by a scanning transmission electron microscope. We have observed many features in the energy-loss spectra which can be attributed either to single-particle excitations such as interband and core-level transitions, or to a collective plasmon excitation. We found no significant changes of the electronic excitation spectra at the grain boundaries or the twin boundaries. However, sensitive changes due to ion-beam radiation damage are observed. Some small differences between the single-crystal and polycrystalline samples are also seen.

In this experiment, we used both single-crystal and polycrystalline $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ samples. Preparations of single-crystal and polycrystalline ceramic bulk samples have been described elsewhere.^{8,9} This samples for the transmission electron-energy-loss spectroscopy were prepared by mechanical polishing followed by ion milling with 5 kV Ar^+ . The electron-energy-loss spectra were obtained from a V.G. scanning transmission electron microscope operating at 100 kV with a probe size $\sim 5\text{--}10 \text{ \AA}$. A Gatan 607 magnetic electron spectrometer was also used. The overall energy resolution of the system is $\sim 0.75 \text{ eV}$.

We will first present our observation for the single-

crystal sample. Examination of the single-crystal $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ sample in a transmission electron microscope shows the presence of twinned domains $\sim 500\text{--}1000 \text{ \AA}$ in size, which is considerably smaller than those found in the polycrystalline ceramics.⁷ An edge-on view of the twin boundaries in the single-crystal sample is shown in Fig. 1(a). By placing the fine electron probe at point A

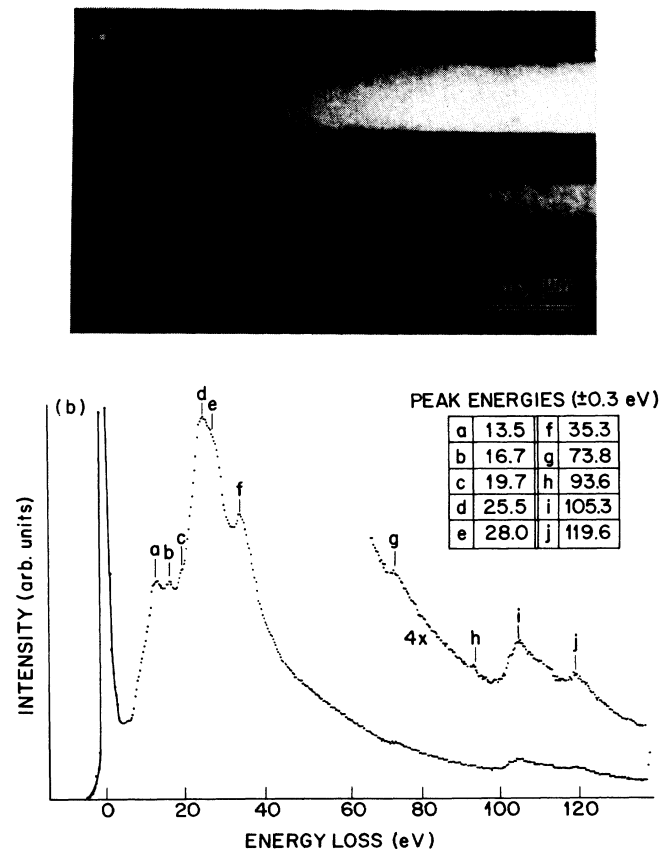


FIG. 1. (a) Electron micrograph showing an edge-on view of twin boundaries appearing in single crystals, (b) electron-energy-loss spectrum obtained from point A inside a twin domain of single crystal. Inset table lists the energy positions of the main features in the spectrum.

within a domain we have obtained energy-loss spectra in the energy range $0 < \hbar\omega < 140$ eV shown in Fig. 1(b). Similar spectra were observed at point *B* at the twin boundary. This shows that the electronic structure within 10 Å of the twin boundary is essentially the same as the domain interior. Figure 1(b) exhibits many features above 10 eV labeled as peaks *a* through *j*, although several poorly defined or resolved excitations are also present at energies below 8 eV. The slight asymmetry of the elastic zero-loss peak is, in fact, due to the presence of these low-energy excitations. We shall ignore the low-energy excitations at the moment and focus our attention to the higher energy excitations. Their peak positions are listed in table inset in Fig. 1(b). It is a nontrivial task to identify all these features in the absence of band-structure information extending over 20 eV above and below Fermi level E_F . In our measurement, we are measuring transition cross sections and energy differences between the initial and final states. The energy conservation law alone cannot determine if a particular interband transition is more favorable than others. The transition probability associated with a interband transition is therefore important for identification of electronic excitations. The excitation involving core levels are usually easy to identify due to the appearance of their characteristic peak energies. In Fig. 1(b), we can thus identify peaks *h*, *i*, and *j* as the excitations associated with Ba 4*d* core levels and the small kink at 73.8 eV as Cu 3*p* core excitation. Collective plasmon excitations are also easy to identify due to their large excitation cross section for fast electrons. The predominant peak *d* at 25.5 eV is therefore identified as plasmon excitation. Surface reflection energy-loss spectroscopy using low-energy electrons yielded a bulk plasmon peak ~ 1 eV lower than our observed value. Our experiment in transmission represents a cleaner and more accurate measurement of the bulk excitations. Identification of other features in Fig. 1(b) require further consideration. It is clear that these features are most likely interband transitions. Since the states near E_F are derived from Cu 3*d* and O 2*p* orbitals and the states with energy 10–30 eV below E_F are localized Ba or Y core states, the interband transition probability between the deep localized states to the extended states just above E_F is very small and we therefore should ignore them. Instead, we consider two most probable cases: first, the transition from the deep localized Ba or Y core states to the states derived from the same atom far above E_F ; second, the transition from non-localized Cu 3*d*-O 2*p* states just below E_F to conduction-band states more than 10 eV above E_F . Since Ba 5*p* and Y 4*p* are ~ 12 eV and ~ 25 eV below E_F , respectively, and Ba 4*d* and Y 4*d* conduction band is some 10 eV above E_F , we identify the 35 eV peak as Y 4*p* \rightarrow Y 4*d* core transitions and the shoulder at 28 eV as Ba 5*p* \rightarrow Ba 4*d* transition. Peaks *a*, *b* are then assigned to transitions from extended Cu 3*d*-O 2*p* states just below E_F to states some 10 eV above E_F . Peak *c* is a core transition of O 2*s* which is ~ 20 eV below E_F to O 2*p* states just above E_F .

By placing the electron probe in various spots on the sample we found that only the strength of the 13.5 eV peak tends to show variations. Other features appear to be insensitive to the probe location. In the course of this

study we have found that the 13.5 eV peak is also very sensitive to radiation damage induced by the Ar⁺ ion during sample preparation. For samples prepared by Ar⁺ ion milling, thin areas (~ 500 Å) near the edge of the pinhole have become amorphous. Electron-energy-loss spectra obtained from the damaged area reveal a very strong 13.5 eV peak. In Fig. 2 we show three electron-energy-loss spectra obtained from three different spots near the thin edge of a pinhole. Spectrum (a) obtained from a spot 1500 Å from the edge shows a normal height for the 13.5 eV peak. However, as the probe was moved closer to the edge, the intensity of the 13.5 eV peak increases rapidly, as shown in spectra (b) and (c), which were obtained from spots 1000 Å and 500 Å from the edge, respectively. Therefore the strength of the 13.5 eV peak is directly related to the level of ion-beam damage. Since the 13.5 eV peak is due to interband transition from Cu 3*d*-O 2*p* states at E_F , we expect ion-beam damage would have the most effect on this peak. The most probable damages created by 5 kV ion beam are lattice disorder and some loss of oxygen. At this time, we do not fully understand the effect of this damage relative to changes in the band structure. Another complication could arise due to still unknown chemical changes near the thin edge when the sample was left in air for an undetermined length of time. Moisture pickup conceivably might be possible. If this is the case, then the 13.5 eV peak enhancement near the thin edges can be attributed to the presence of hydrogen atoms which have an ionization energy very close to the observed value. At this moment, we do not have any hard evidence to support this argument.

We now turn to the measurements carried out on polycrystalline YBa₂Cu₃O_{7-x} ceramics. Electron-energy-loss

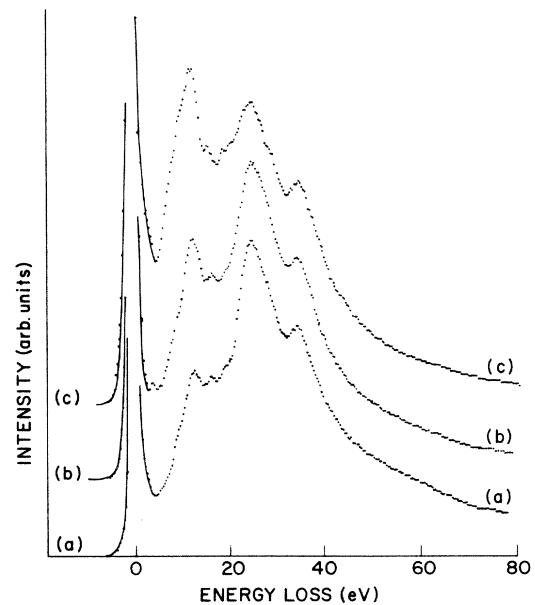


FIG. 2. (a), (b), and (c) are electron-energy-loss spectra obtained from three spots 1500, 1000, and 500 Å from a thin edge of a pinhole. Note the increase of the 13.5 eV intensity toward the edge of the pinhole.

spectra obtained from various spots in the polycrystalline ceramics sample show more variations than the single-crystal sample, suggesting that the ceramic is less homogeneous. Figure 3 shows an energy-loss spectrum obtained from a single grain. In addition to those structures observed in the single-crystal samples, features at 2.5, 4.4, and 5.6 eV are now clearly seen. In single crystals, the 2.5 eV hump is less pronounced and the double peaks at 4.6 and 5.6 eV are not well resolved. An expanded view of these lower energy excitations is also shown in the inset of Fig. 3. The 2.5 eV feature can be assigned to transitions from E_F to the top of Cu $3d-O 2p_{x,y}$ conduction bands. The 4.4 eV is the transition from Cu $3d-O 2p$ valence bands to Cu $3d-O 2p_z$ conduction bands near E_F and the 5.6 eV peak is due to transition from E_F to Ba $5d$ states. The visibility of these new features at lower energies varies from grain to grain, and we believe that the grains which exhibit distinct excitations of these features represent what the best crystal should be. Clearly, the local variation of oxygen concentration and lattice disorder would have the most direct effect on these lower energy interband transitions. The 13.5 eV peak, again, is found to be sensitive to radiation damage induced by Ar^+ ion bombardment during sample preparation, similar to what we observed in single crystals. We note that the spectrum shown in Fig. 3 was obtained from a thicker area and, as a result, a pronounced hump ~ 50 eV is evident due to double scattering of the bulk plasmons.

Placing the electron microprobe at a grain boundary between two grains with twin boundaries in different orientations, we observed essentially the same spectrum as that obtained with the grain. This shows that, within the resolution (~ 0.75 eV) of our measurement, the electronic structure at grain boundaries is not significantly different from the bulk. However, our observation does not exclude the possibility that differences in the electronic structure exist in the energy range below 1 eV. These low-energy excitations, which involve an electronic state near the Fermi surface, would play a more crucial role in superconductivity. Within the grain of superconducting phase, we

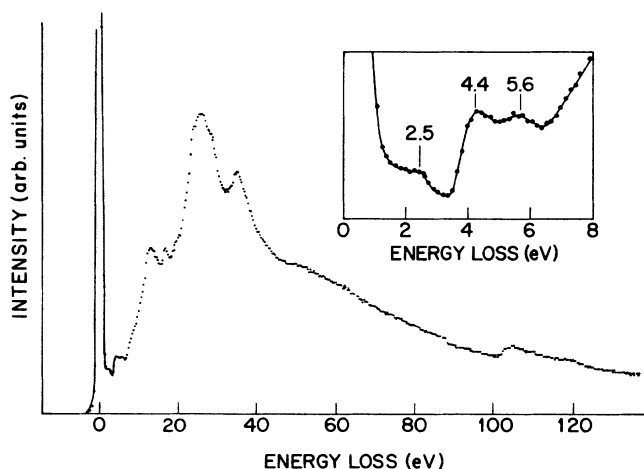


FIG. 3. Electron-energy-loss spectrum obtained from a point inside a grain of polycrystalline ceramics. Inset shows an expanded view of the spectrum below 8 eV.

found rather homogeneous excitation spectra. Most of the inhomogeneities in the polycrystalline ceramics take place from one grain to another and not within a grain. In a so-called pure-phase polycrystalline sample, there are always trace amounts of second phases present. Microprobe electron-energy-loss spectra can easily identify these phases. An example is shown in Fig. 4, which was obtained from a Y_2O_3 grain present in the ceramics sample. The excitation spectra in this case is totally different from that of the superconducting phase.

As we mentioned earlier, $YBa_2Cu_3O_{7-x}$ superconductors are sensitive to ion-beam bombardment. Recently, it has been shown that superconducting states in $YBa_2Cu_3O_{7-x}$ thin films are very sensitive to defects created by high-energy (MeV) ion bombardment.^{10,11} It was found that the superconducting onset temperatures do not change significantly with the ion fluence but the width of the transition broadens gradually until the resistance no longer reaches zero. The ion-milling process for the sample preparation, in which 5 kV Ar^+ ions were impinging at the sample surface with a small angle $\sim 22^\circ$, is not expected to produce defects that could affect the bulk superconductivity significantly. Ion milling typically produces a damaged surface layer less than 50-Å thick, which is considerably smaller than the total thickness of the thin area (~ 1000 Å). Our experiment, which is carried out with transmission of high-energy electrons through the sample, should be dominated by the bulk and not the surface effects. During the course of our study, we have not noticed any significant damage induced by the incident electron beam. The sample is reasonably stable under the illumination with such a high brightness beam (~ 1 nA confined within 10-Å probe size). The 100 kV electrons used in our measurement are not energetic enough to produce defects by nuclear collisions.

In conclusion, we have studied the homogeneity of the electronic structure in both single-crystalline and polycrystalline $YBa_2Cu_3O_{7-x}$ by electron-energy-loss spectroscopy with a 5-10-Å microprobe. Single-crystal samples are found to be slightly more homogeneous than the ceramics. Homogeneity may be important to high critical

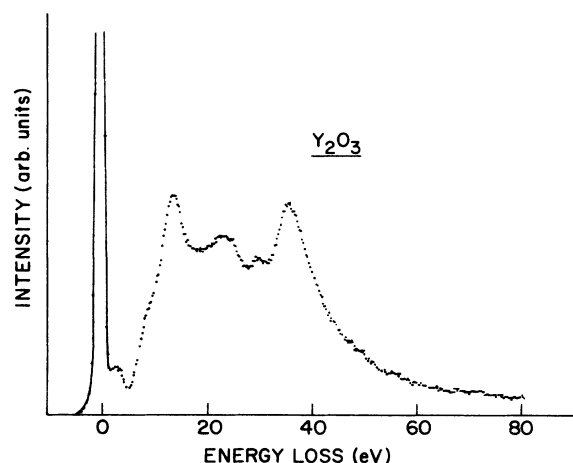


FIG. 4. Excitation spectrum obtained from a Y_2O_3 grain in the ceramics sample.

current density in the oxide superconductors. Spectra obtained at grain or twin boundaries did not reveal any significant changes from the interior of the grains or twinned domains. The 13.5 eV interband transition peak originating from Cu $3d$ -O $2p$ valence bands is found to be

very sensitive to radiation damage induced by the ion beam.

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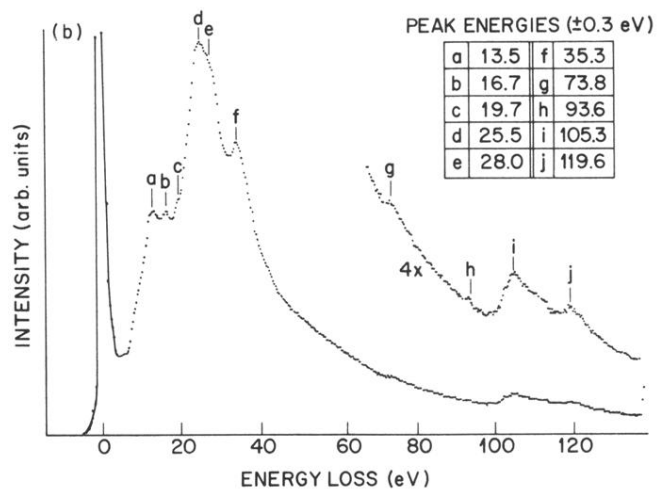
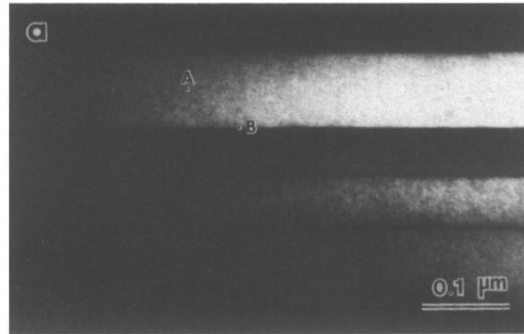


FIG. 1. (a) Electron micrograph showing an edge-on view of twin boundaries appearing in single crystals, (b) electron-energy-loss spectrum obtained from point *A* inside a twin domain of single crystal. Inset table lists the energy positions of the main features in the spectrum.