

# Electronic structure of the compound $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

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We have investigated the electronic structure of ceramic  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  using photoelectron spectroscopy and characteristic-electron energy-loss spectroscopy at liquid-nitrogen temperatures. In these experiments we have observed changes in the spectra of freshly-cleaned surfaces with time, indicating a rearrangement of the surface electronic structure due to loss of oxygen from the surface layers. The characteristic time for this change is 5 minutes; spectra obtained after times larger than this characteristic time essentially coincide with those given in the experimental literature. There is reason to assume that the electronic structure of the surface in the first seconds after cleaning is close to that calculated in the one-electron approximation.

In order to understand the mechanism for superconductivity in the recently-discovered superconductors with high critical temperatures,<sup>1–3</sup> it is extremely important to study their electronic structure in detail. According to band-structure calculations of the electronic spectrum,<sup>4–8</sup> the valence band of the compound  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  consists primarily of hybridized Cu  $3d$ - and  $2p$ -states and has a rather large density of states  $N(E)$  at the Fermi level  $E_F$ . However, experimental studies of the density of occupied states using the method of photoelectron spectroscopy (PES) show an unusually low value of  $N(E_F)$ .<sup>9–12</sup> Furthermore, the experimental peaks in the density of states are found to be shifted in the direction of large binding energies by 1.5 to 2.0 eV. This result casts doubt on the validity of band-structure calculations of the electronic structure of these high-temperature superconductors.

However, we have observed<sup>13</sup> that when the surfaces of ceramic  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  samples are cleaned in ultrahigh vacuum, substantial changes appear in the characteristic electron energy-loss spectrum (CEELS) during the first 3–5 minutes immediately after cleaning for energies corresponding to excitation of electronic states in the valence band. This circumstance led us to doubt the correctness of commonly used methods of obtaining photoelectron spectroscopy data on similar samples of high-temperature ceramics, and motivated us to undertake a study of the dynamics of this time-dependent variation of the PES and CEELS spectra. The form of the CEELS spectrum is determined by the imaginary part of the inverse dielectric permittivity function, and to first approximation by interband electronic transitions from occupied electronic states to unoccupied ones and by plasma oscillations. The methods of PES and CEELS complement one another; their juxtaposition allows us to obtain representations both of the occupied bands and of the bands of unoccupied electron states. Our investigations of the PES and CEELS spectra were carried out using the apparatus described in Ref. 14. In order to excite photoelectron emission we used monochromatized synchrotron radiation from the specialized "Sibir'-1" storage ring with energies from 10 to 25 eV. In order to obtain the CEELS spectra in reflection we used an electron beam having a nonmonochromaticity of the primary beam of  $\sim 0.65$  eV in energy. In order to measure the energy spectrum of the electrons, we used an electron analyzer of cylindrical-mirror type with second-order focusing of the axis-axis type. The resolution of the analyzer came

to 0.5% of the energy  $E$  being analyzed. Electrons traversing the electron analyzer were detected using a VEU-6 electronic amplifier, whose single-electron pulses were amplified, filtered and processed. Operation of the apparatus was automated within a CAMAC standard based on an "Elektronika-60" computer linked to a CM-4 computer.

For our samples of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  ceramic  $T_K$  ranged from 90 to 92 K, with transition widths of  $\sim 2$  K. Their surfaces were cleaned using mechanical *in situ* scraping within the spectrometer chamber. It should be noted that in order to obtain a truly "clean" surface (by a "clean" surface we mean the surface of a cleaved crystal) it would be necessary to cleave each of the crystallites at the surfaces of the ceramic sample. In practice, a portion of these crystallites remain whole during the scribing, uncovering the surface of underlying crystallites whose structure and properties may differ from the bulk (in what follows we will call these surfaces "uncleaned"). Therefore in the course of investigating ceramic samples using PES and CEELS we expect that a rather large contribution to the spectrum comes from these uncleaned surfaces. This contribution can be significant; furthermore, it will fluctuate over wide limits as a function of the sample cleaning conditions, which are determined by the

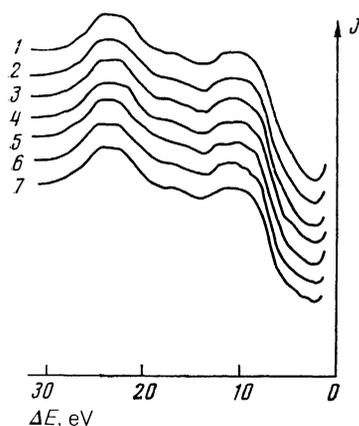


FIG. 1. Characteristic electron energy loss (CEELS) spectra for a sample of ceramic  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (the energy of the primary electron beam was 100 eV), measured 60 (1), 130 (2), 240 (3), 350 (4), 430 (5), 555 (6), and 740 seconds (7) after the end of surface cleaning. Cleaning of the sample was carried out at liquid nitrogen temperatures in an ultrahigh vacuum.

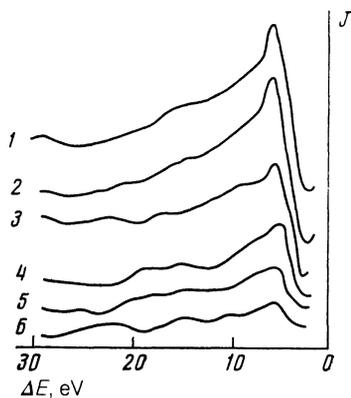


FIG. 2. CEELS difference spectra of a ceramic sample of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , i.e. spectra obtained by subtracting from the CEELS spectra measured after 60 (1), 130 (2), 240 (3), 350 (4), 430 (5), 555 seconds (6) the CEELS spectrum measured after 740 seconds (7); times are measured from the end of the sample cleaning.

temperature, heating, and mechanical properties of the sample.

In Fig. 1 we show samples of CEELS for a sample of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  ceramic at a primary-beam electron energy of 100 eV. Spectra 1, 2, 3, 4, 5, 6, and 7 were taken 60, 130, 240, 350, 430, 555, and 740 seconds after the end of sample cleaning, respectively. The measurements were carried out at liquid-nitrogen temperatures in a vacuum of  $2 \cdot 10^{-10}$  Torr. The overall shape of these spectra is close to the spectra published in Refs. 15, 16; however, in the energy region 0–13 eV we find noticeable distortions in their shape as time passes, indicating a significant rearrangement of the sample's electronic valence-band structure.

By subtracting spectrum 7 from spectra 1, 2, 3, 4, 5, and 6, we obtained the difference spectra 1, 2, 3, 4, 5, and 6 respectively (Fig. 2). These difference spectra reflect that part of the contribution from the clean surfaces which corresponds to changes in the electronic structure with time. It is clear from Fig. 2 that the difference spectra are almost unchanged in shape with time: only their intensity changes. In Fig. 3 we show the time dependence of the intensity of a characteristic feature of the difference spectra observed at an energy of 5.8 eV, starting from the end of the surface cleaning. The characteristic time for the spectra (and correspondingly the electronic structure) of the sample to change is found to be 300 seconds.

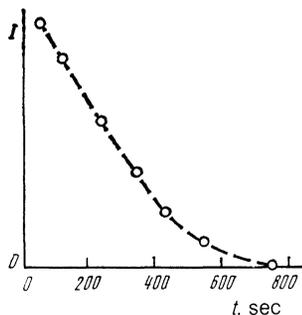


FIG. 3. Time dependence of the intensity of the characteristic feature at  $E \approx 5.8$  eV in the difference spectra (see Fig. 2). The time origin corresponds to the instant that the surface cleaning of the ceramic  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  sample is complete.

Previously, using the method of Auger spectroscopy, we observed a decrease in oxygen content with time at the surface of the yttrium ceramics, which correlated with the change in the CEELS spectra described above. Apparently, the change in the CEELS spectrum is connected with the change in the partial density of occupied and unoccupied electron states at the oxygen atoms. Qualitatively, the spectrum of a sample whose surface has already undergone this change (Fig. 1, curve 7), and also the results of Refs. 15, 16, can be explained by starting with the densities of occupied and unoccupied states determined experimentally by the methods of photoelectron spectroscopy and inverse photoemission.<sup>17</sup> In this case features in the CEELS spectrum should be observed which are connected with transitions from states with energies of  $-2.3$  and  $-4.5$  eV in the valence band to a state with energy 7 eV in the unoccupied band of states<sup>17</sup>; these features are also apparent in the spectra given in Ref. 15, in the form of features at energies of 8.7 and 11.5 eV. The results of Refs. 9–12 and 15–17 should be understood in terms of surface reconstruction, because they obviously were obtained over a period of time which exceeded the characteristic time for the electronic structure to change. The nature of these features in the electronic spectrum of the surface immediately after cleaning can be explained in sufficient detail if we assume that the electronic spectrum of the sample is close to the one calculated in Refs. 5, 6.

According to Ref. 5, the valence band of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  has a width of  $\sim 6$  eV, and its dominant features are peaks in the density of states at energies  $-4.7$ ,  $-3.5$ ,  $-2.3$ ,  $-1.5$ ,  $-0.8$ , and  $-0.5$  eV. The primary contribution to the majority of these peaks comes from the Cu  $d$ -states, while the peaks with the largest relative partial contribution of oxygen  $2p$  states are at  $-0.8$ , and  $-0.5$  eV. In the band of unoccupied states there is a characteristic peak with energy 1.5 eV (Ref. 4) which is essentially due to  $\text{O}2p$  states. The loss of oxygen from the bulk of the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  should give rise to a decrease in the density of states at these peaks, and also to a shift in the Fermi level (the "almost rigid" band model); if this is so, the photoelectron spectra will exhibit a shift in the dominant features of the valence-band density of states at  $-3.5$ ,  $-2.3$ , and  $-1.5$  eV toward the side of larger binding energies. The density of states at the Fermi level will be very small in this case. The experimental photoelectron spectra correspond to exactly this case.<sup>9–12</sup> We have also obtained analogous data for photoelectron spectra which were recorded 10 minutes after the end of the sample cleaning.

In Fig. 4 we show photoelectron spectra of a sample of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  at liquid-nitrogen temperatures. The excitation energy  $\hbar\omega = 10.6$  eV; the period for collecting the statistics of spectrum 1 was from 20 to 300 seconds, for spectrum 2, 500 to 900 seconds (these times were measured from the instant the cleaning of the sample was complete). It is clear from Fig. 3 that spectrum 1 (Fig. 4) was recorded during the time interval when the changes in the CEELS spectrum were observed, while for spectrum 2 the CEELS spectrum had essentially ceased to change.

The values of  $N(E_F)$  we obtained for freshly-cleaned surfaces exceed the values of  $N(E_F)$  obtained in Refs. 9–12. There are several features visible in spectra 1 and 2; some of these features remain unchanged in their energy locations ( $-1.5$  eV and  $-2$  eV), while some of the features in spec-

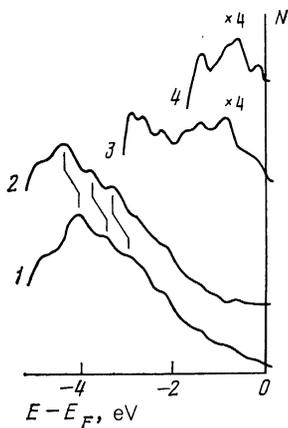


FIG. 4. Photoelectron spectra of ceramic samples of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  measured at  $\hbar\omega = 10.6$  eV and at liquid-nitrogen temperatures. The beginning of measurement of spectrum 1 was at 20 seconds, the end was at 300 seconds after the end of sample cleaning; for spectrum 2, at 500 and 900 seconds, respectively. Curve 3 is the difference of spectra 1 and 2. Curve 4 is the difference of spectra 1 and 2 where the latter is shifted on the energy scale by 0.3 eV.

trum 2 (in the region of binding energies  $-2.7$  to  $-4.3$  eV) are shifted relative to spectrum 1 by 0.3 eV toward the side of larger binding energies. This could indicate a time-dependent shift of the Fermi level (in the "almost rigid" band model) toward the unoccupied state energy region. The fact that the time-dependent change in the CEELS spectra is small argues in favor of the applicability of this model.

Useful information about  $N(E_F)$  for clean unreconstructed portions of the surface can be obtained by investigating the difference spectra. In Fig. 4 we show difference spectrum 3, obtained by subtracting spectrum 2 from spectrum 1, and difference spectrum 4, also obtained by subtracting spectrum 2 from spectrum 1 and shifting the energy scale by 0.3 eV, i.e., by the value of the shift in the Fermi level assumed in this experiment. We note that the contribution to  $N(E)$  from the uncleaned surfaces in the energy region 0 to  $-1.5$  eV is insignificant, and in practice does not affect the shape of the difference spectrum in this region of energies. Apparently, spectrum 3 reflects a real dependence of the density of electron states on energy in the region of binding energies 0 to  $-1.5$  eV for an unreconstructed clean surface, and has a strong resemblance to  $N(E)$  for the compound  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  calculated in Refs. 5,6. The positions of the peaks with energies  $-0.8$  and  $-1.5$  eV practically coincide with the data in Refs. 5,6. The low intensity of spectrum 3 is related to the fact that within the measurement time the surface undergoes a very significant reconstruction. Furthermore, a certain rearrangement of the surface can also take place within the time interval from the end of the sample cleaning to the beginning of the measurements. If we assume that during the surface reconstruction the electronic structure changes according to the almost-rigid band model, then spectrum 4 should reflect that part of  $N(E)$  which disappears when the surface reconstructs. Spectrum 4 in the region 0 to  $-1$  eV is very close to the sum of the partial densities of states of the copper atoms in the positions Cu(1) and those of the oxygen atoms in positions O(1) and O(4) (Ref. 5). This indicates that during the surface reconstruction there is a significant change in the structure of the planar chains Cu(1)-O(1)-O(4) which accompanies the loss of oxygen on these chains.

The statements made above give us reason to assume that the changes in the CEELS spectra with time are connected with a decrease in the partial electron density of states at the Cu(1)-O(1)-O(4) chains; thus, the peak with energy 5.8 eV in the difference CEELS spectra (Fig. 2) corresponds to transitions from states with energies  $-0.2$ ,  $-0.8$ , and  $-1.5$  eV (Fig. 4, spectrum 3) to an unoccupied state with an energy of 5 eV (from the data from Ref. 6).

Taken as a whole, the data presented here clearly show that the surface of the compound  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  is rapidly reconstructed and loses oxygen after cleaning. The electronic structure of the reconstructed surface differs considerably from that of the bulk for this compound. Despite the difficulty of making quantitative comparisons between theory and experiment, we can assert that during the first seconds after cleaning the electronic structure of freshly-cleaned surfaces of yttrium ceramics is close to their bulk electronic structure as calculated theoretically in Refs. 4, 8. The closest agreement is observed when we compare our experiments in the low-energy region with the data from Refs. 5,6.

After our article had already been presented for printing, a communication appeared (Ref. 18) reporting the investigation of single-crystal samples of  $\text{EuBa}_2\text{Cu}_3\text{O}_{7-\delta}$  by the PES method. The results obtained there also indicated that oxygen is lost from the near-surface layer of the sample, and that the PES spectra change as a function of time and temperature. The authors are in agreement with our conclusions about the close correspondence between spectra of unreconstructed surfaces and the results of band structure calculations presented in Ref. 5.

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