Characteristic-electron-energy-loss spectroscopy of an $YBa_2Cu_3O_{7-\delta}$ superconducting ceramic

I. V. Kireev, M. N. Mikheeva, V. G. Nazin, and A. V. Svishchev
I. V. Kurchatov Institute of Atomic Energy, Moscow

(Submitted 15 November 1988)
Pis'ma Zh. Eksp. Teor. Fiz. **48**, No. 11, 633–634 (10 December 1988)

Spectra of the reflection characteristic electron energy losses have been measured for an $YBa_2Cu_3O_{7-\delta}$ sample. The results show that during the first 3 min after the surface of the sample is cleaned the shape of the spectra changes significantly. These changes are evidence of a change in the electronic structure of the sample over time.

We have carried out a study of the time evolution of the properties of the surface of an $YBa_2Cu_3O_{7-\delta}$ superconducting ceramic by the method of spectroscopy of the reflection characteristic electron energy loss (inelastic electron scattering). The shape of the loss spectrum is determined by the imaginary part of the reciprocal of the dielectric constant and, in a first approximation, by interband transitions of electrons from filled states of the solid to vacant states and also by plasma oscillations. The dominant spectral features in the energy interval 0–13 eV should be features associated with transitions to the final state with an energy of 7 eV. When we work from the theoretical prediction of the state density,[1] we conclude that the spectrum should have peaks at energies of 7.5 and 9.5 eV (case a). If we instead work from the experimental state density,[2] found by photoelectron spectroscopy and inverse photoemission, we conclude that features should be observed at energies of 9.3 and 11.5 eV (case b). The loss spectra measured in Refs. 3 and 4 for an yttrium ceramic correspond to the second case.

We have carried out time-resolved measurements of the characteristic-electron-energy-loss spectra of an yttrium ceramic immediately after mechanical cleaning of its surface with a scraper in ultrahigh vacuum, 3×10^{-10} Torr. The measurements were carried out on the apparatus of Ref. 5; the energy of the primary electron beam was 100 eV, the temperature was 65 K, and the resolution was 0.8 eV. The spectra were normalized in terms of the intensity of the peak of elastically reflected electrons. The samples had a superconducting transition temperature $T_c = 92$ K. After a sample was cleaned, a large number of shiny grains—small crystals—were visible on the surface of the sample. Figure 1 shows energy-loss spectra of an yttrium ceramic measured 120, 280, and 800 s after the end of the cleaning (lines 1–3, respectively). In this figure we see pronounced changes in the spectra with time in the regions 20–27 eV and 3–13 eV. The freshly cleaned surface of a sample undergoes substantial changes over a fairly short time, $\sim$3 min. Spectra 1 and 2 differ significantly from those given in Refs. 3 and 4. A spectrum similar to that reported in Refs. 3 and 4 was found after the sample was exposed for approximately half an hour under the specified conditions. The same spectrum was found after oxygen was admitted into the chamber (for 30 s at a pressure of 5×10^{-6} Torr) (line 4). When the oxygen was admitted, the peaks at 12.5 and

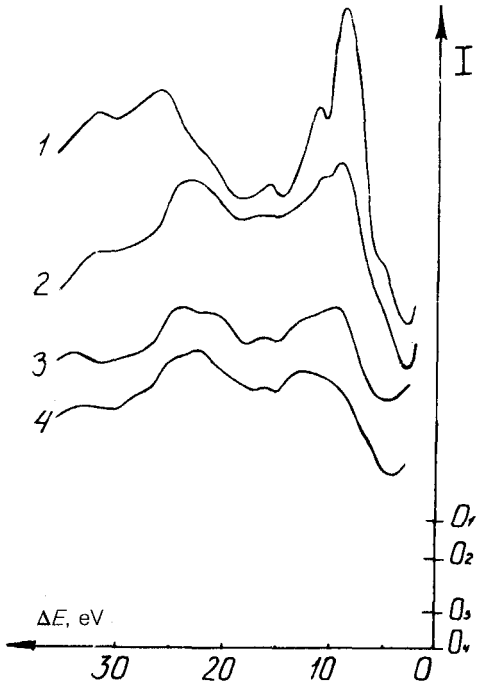

FIG. 1. Intensity of inelastically scattered electrons for an $YBa_2Cu_3O_{7-\delta}$ sample versus the energy. The origin for the energy scale is the peak corresponding to elastically reflected electrons. Spectra 1, 2, and 3 were measured 120, 280 and 800 s, respectively, after the cleaning of the sample was terminated; spectrum 4 was measured after the adsorption of oxygen on the surface of the sample.

22.5 eV intensified significantly. It is reasonable to suggest that these peaks correspond to the excitation of adsorbed molecular oxygen. Comparison of spectra 1 and 4 in the region 3–13 eV reveals that spectrum 4 corresponds primarily to case b; i.e., this spectrum can be explained on the basis of experimental data on the state density. Spectrum 1 corresponds better to case a; the features in this spectrum have positions along the energy scale which are close to those of features found through the use of the theoretical state densities. In our opinion, the peak at 25.5 eV (spectrum 1) corresponds to the excitation of a bulk plasma oscillation of the freshly cleaned surface of the compound $YBa_2Cu_3O_{7-\delta}$. Since the literature reveals no data from calculations of the characteristic energy-loss spectra, we cannot make a closer comparison of the theory with our experimental results. We can assert, however, that the electron state density of the freshly cleaned surface $YBa_2Cu_3O_{7-\delta}$ undergoes significant changes over a time scale ~ 3 min, and after these changes the electron spectrum seen experimentally ceases to reflect the bulk properties of $YBa_2Cu_3O_{7-\delta}$. The apparent explanation is that immediately after it is cleaned the surface begins to undergo structural changes through a displacement of atoms in the surface layers of the lattice to new equilibrium positions. It is possible that this process is accompanied by a loss of some of the oxygen atoms from the lattice.

We would like to call attention to the following circumstances: In a study of the electron state density of the compound $YBa_2Cu_3O_{7-\delta}$ by photoelectron spectroscopy and inverse photoemission, the times required to record the experimental spectra after

the sample was cleaned were usually 10 min or more. It would clearly be incorrect to compare the experimental data with theoretical predictions in this case.

[1]W. Y. Ching, Guang-Lin Zhao *et al.*, Phys. Rev. Lett. **59**, 1333 (1987).
[2]A. J. Viescas, J. M. Tranquada, A. R Moodenbaugh, and P. D. Johnson, Phys. Rev. **B37**, 3738 (1988).
[3]Y. Chang, M. Onellion, D. W. Niles *et al.*, Solid State Commun. **63**, 717 (1987).
[4]A. Ando, K. Saiki, K. Ueno, and A. Koma, Jpn. J. Appl. Phys. **27**, L304 (1988).
[5]M. N. Mikheeva, V. G. Nazin, A. V. Svishchev, and A. Yu. Stogov, in: Proceedings of the International Conference on Low-Temperature Physics 87, Daĭdzhest, Budapest (F), 1987, p. 59.

Translated by Dave Parsons