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High-resolution electron-energy-loss spectroscopy of $YBa_2Cu_3O_7$

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High-resolution electron-energy-loss spectroscopy has been performed for a polycrystalline sample of $YBa_2Cu_3O_{7-\delta}$ in the temperature range between 300 and 45 K. A pronounced surface-conductivity transition is observed between 100 and 200 K both via the inelastically and elastically scattered electrons.

Since the discovery of high-T_c superconductivity in copper oxide–based systems,[1,2] a considerable number of theoretical models have been proposed to account for the unexpectedly high transition temperatures (T_c) in these systems. These models range from the weak-coupling to the strong-coupling limit, with several proposals lying well outside the Bardeen-Cooper-Schrieffer theory.[3] One common point of all these models is to start from the known bulk properties of the high-T_c compounds. This *a priori* eliminates the surface of the sample (as well as grain and twinning boundaries) from playing any role in the discussion of possible mechanisms for high-T_c superconductivity. In particular, the grain and twinning boundaries have been considered to be insulating or normal metallic barriers between the otherwise superconducting bulk.[4]

On the basis of electron spectroscopic results,[5] it appeared desirable to explicitly probe the nature of the surface conductivity of these materials. This has not been attempted before since there are few ways of carrying out such an experiment. In the present work we show that an access to this problem is provided by the interaction of a beam of low-energy electrons with the surface of such a material. Specifically, the inelastic scattering of electrons from a surface is governed by the imaginary part of the dielectric function and therefore also related to the frequency-dependent conductivity $\sigma(\omega)$. We have applied for the first time high-resolution electron-energy-loss spectroscopy (HREELS) to study the surface conductivity of $YBa_2Cu_3O_{7-\delta}$. Our results show the existence of a pronounced surface conductivity transition at temperatures well above the bulk T_c.

The $YBa_2Cu_3O_{7-\delta}$ sample was prepared in the usual ceramic route starting from a mixture of CuO, $BaCO_3$, and Y_2O_3, which—after sintering at 950 °C—was oxygen annealed at 450 °C for 12 h. The resulting material was checked with powder x-ray diffraction to be single phase. Occurrence of superconductivity in the sample was established by standard four-probe resistance measurements before and after the HREELS experiments. The resistance-versus-temperature curves from these two runs were the same exhibiting zero resistance for temperatures below 83 K.

The HREELS experiments were performed in an ultrahigh-vacuum (UHV) chamber described elsewhere.[6] In order to avoid loss of oxygen from the sample, the system was baked out at only 380 K for 20 h. During the room-temperature measurements, the pressure in the chamber was 1×10^{-9} mbar dropping to 4×10^{-10} mbar in the low-temperature experiments. The energy resolution of the spectrometer was about 6 meV for the reflected beam from a single-crystal surface. In the present measurements on the polycrystalline sample, the full width at half maximum (FWHM) of the elastic peak was found to be 15 meV at a primary-beam energy of 2.5 eV.

The sample in the form of a cylinder (3 mm height and 13 mm diameter) was clamped by Ta braces onto a Ta support, which was screwed onto the Cu cold finger of the cryosample holder. The temperature was measured by a NiCr-CuNi thermocouple spot-welded to the Ta support next to the sample (see inset in Fig. 1); it was calibrated against a carbon resistor. It should be noted that in this configuration, the temperature of the sample surface can only be higher than that measured by the thermocouple. Sample cleaning was performed by *in situ* scraping with a razor blade prior to recording the spectra.

In order to take spectra at different temperatures, the sample along with the Cu cold finger was first cooled to the lowest temperature (45 K) and then only the sample was heated up to about 320 K by radiation heating. Spectra at different temperatures were recorded on the subsequent cooling of the sample. This procedure was applied in order to reduce the chance of contaminating the sample surface by condensation of residual gases from the UHV chamber.

In Fig. 1 we show the loss-region spectra recorded at

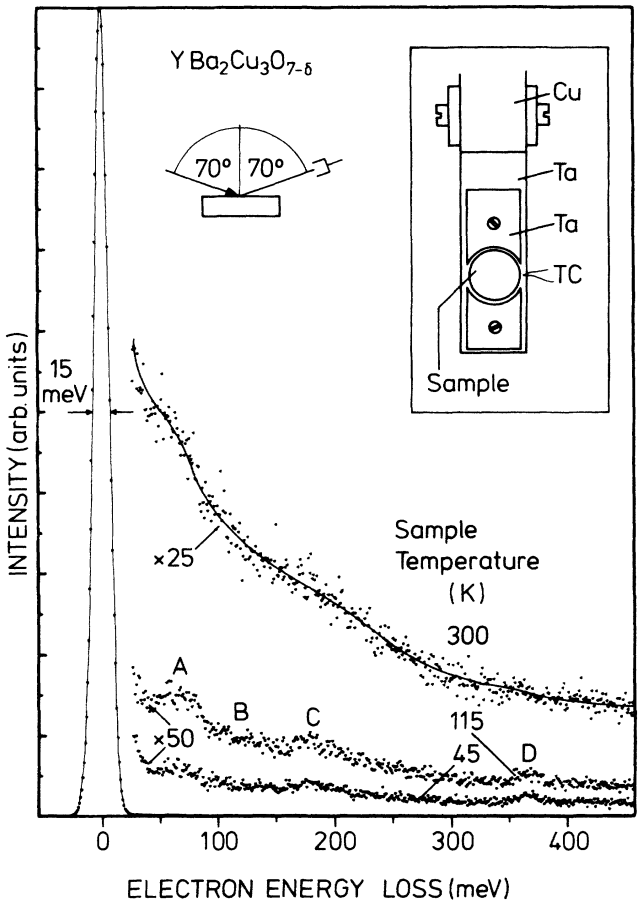

FIG. 1. High resolution electron-energy-loss spectra of polycrystalline $YBa_2Cu_3O_{7-\delta}$ at three different temperatures. The lower temperatures were attained by cooling with liquid N_2 or liquid He. Energy of the primary electrons was 2.5 eV. The beam geometry is indicated. The inset shows the sample holder including the position of the thermocouple (TC).

temperatures of 300, 115, and 45 K, normalized to the intensity of the elastic peak. Within statistical accuracy, the 300-K spectrum is without distinct loss features. This is possibly due to the fact that a large number of overlapping loss peaks gives rise to a very broad distribution, which is further superimposed on signals arising from interband transitions due to the free-carrier Drude term. As the temperature is lowered to 115 K, the contribution from the free carriers decreases significantly. Simultaneously, we observe the emergence of distinct loss features at energies of 50–70 meV (*A*), 100–150 meV (*B*), 170 meV (*C*), and 360 meV (*D*) below the elastic peak. The appearance of distinct loss peaks at low temperatures is unexpected on the basis of the 300-K spectrum, since one would anticipate all the loss features to change uniformly in intensity with decreasing temperature. It should be noted here that several Raman and infrared studies did not show any pronounced temperature dependence.[7] While HREELS probes essentially a few monolayers at the surface,[8] Raman and infrared spectroscopies are bulk sensitive. Loss feature *D* at 360 meV is probably due to OH vibrations from sample contamination, while the other features with smaller energy losses appear to be intrinsic. The apparently double-peaked structure *A* can be attributed to metal-oxygen stretching modes, arising possibly from two inequivalent Cu–O bonds; the energy position of weak feature *B* compares well with oxygen-oxygen vibrations in bulk peroxides.[9] The origin of peak *C* is not yet clear. Lowering the temperature further to 45 K did not significantly change the spectrum from that at 115 K.

From Fig. 1 it is clear that there is a strong reduction of loss intensities at all energies with decreasing temperature. The temperature variation of loss intensity at a loss energy of 50 meV, normalized at 300 K, is shown in Fig. 2(a) for the two sets of measurements. In Fig. 2(b) we present the corresponding temperature variation of the elastic-peak intensity. For comparison, we also measured the variation of the loss intensity as a function of temperatures from *in situ* heavily oxidized Cu (as a typical metal oxide); this measurement hardly showed any temperature dependence. We also did not find any strong temperature dependence for a $La_{2-x}Sr_xCuO_4$ sample which lost its superconductivity during baking in the UHV chamber. It is also known that normal metals (e.g., Ni) exhibit only minor and approximately linear decreases in their loss intensities with temperature.[8] The behavior of the loss peaks observed for the superconducting sample is therefore fundamentally different from either a normal metal

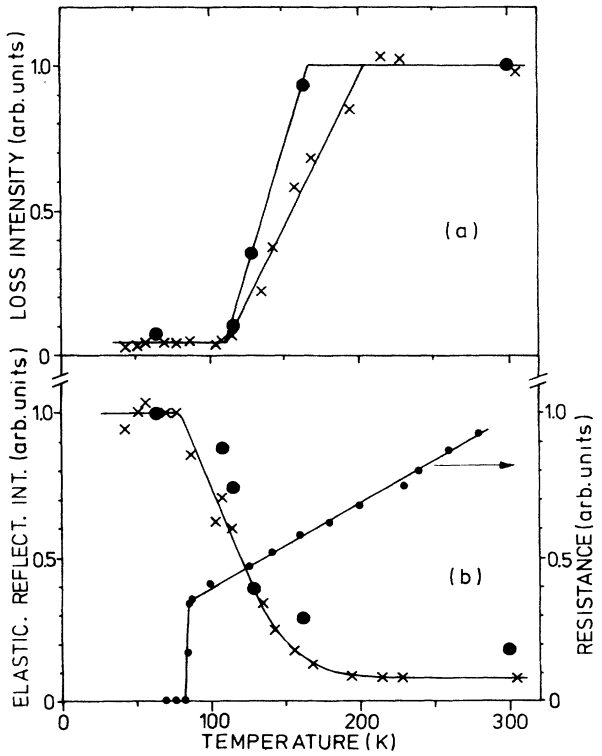

FIG. 2. (a) Loss intensity at a loss energy of 50 meV normalized to the elastically reflected electron intensity as a function of temperature for a 2.5-eV electron beam impinging onto the $YBa_2Cu_3O_{7-\delta}$ sample. (b) Temperature dependences of elastically reflected electron intensity and bulk electrical resistance. Crosses and dots are for two independent HREELS runs.

or a metal oxide, with dramatic changes occurring in the temperature range between 100 and 200 K.

The loss intensity at a particular energy in a metallic sample is related to the imaginary part of the dielectric constant and—under simplifying assumptions—may be shown to be inversely proportional to the frequency-dependent conductivity $\sigma(\omega)$.[8] Thus, the drastic reduction in loss intensity is related to a rapid increase in the surface conductivity of the sample starting just below 200 K and being completed at about 110 K. The intensity of the elastic peak exhibits a related temperature variation [Fig. 2(b)]. While the loss intensity is inversely proportional to $\sigma(\omega)$, the elastic peak integrates over all frequencies and is expected to increase monotonically with $\sigma(\omega)$. Because of its dependence on a wide range of frequencies the elastic peak intensity is likely to be a more sensitive (though less direct) monitor of variations in surface conductivity. This may then be the reason why we find that the intensity variation of the elastic peak, though starting at the same temperature as that of the loss peak variation, continues down to the bulk-superconducting transition [shown in Fig. 2(b) for comparison].

Keeping in mind that the studied sample exhibits superconductivity at 83 K in a bulk-resistivity measurement [Fig. 2(b)] and that the intensity variations of both loss and elastic peaks are small in the vicinity of 83 K as compared to changes above 90 K, we are tempted to attribute the large changes in the 200–90-K region to a superconducting transition at the surface. This surface-superconducting transition would then precede and in fact induce the bulk-superconducting transition at 83 K. The apparently large width of the surface transition may either be intrinsic or due to inherent inhomogeneities of the surface composition causing different T_c's. The latter possibility seems more likely, since the two sets of experiments, while leaving the lower temperature end of the transition unaffected, resulted in different starting temperatures for the transition. It should be noted that the second set of data (crosses) was obtained after further scraping the sample, thereby presumably exposing surface regions with still higher transition temperatures.

Almost all proposed theoretical models for high-T_c superconductivity are based solely on bulk properties,[3] with no consideration given to the surface. Only recently is an awareness growing that low-dimensional regions, like surface, grain, and twinning boundaries may play some role in the superconductivity mechanism.

In conclusion, applying for the first time HREELS to the study of superconductors, we establish a very pronounced transition in surface conductivity in $YBa_2Cu_3O_{7-\delta}$. This transition, which we tentatively associate with a surface superconducting transition, has a onset around 200 K, far above the bulk, and is virtually completed at temperatures where the bulk transition sets in. We are aware of the fact that the explanation of our experiment is rather preliminary, since too little is known about the electronic changes at the surface during the superconducting transition.

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