Electronic correlations in $YBa_2Cu_3O_{7-\delta}$ from Auger spectroscopy

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Cu L_3VV Auger spectra of the superconducting compound $YBa_2Cu_3O_{7-\delta}$ have been measured above and below the critical temperature $T_c = 90$ K and compared with those of CuO. In the superconductor a localized peak whose intensity increases with temperature is found. Such a structure, lacking in copper oxide, is attributed to electronic correlations in the Cu $3d^8$ configuration.

The recent discovery of superconductivity at 30 K in the Ba-La-Cu-O system by Bednorz and Müller[1] has been followed by an impressive amount of experimental and theoretical work to understand the mechanism of superconductivity in these layered perovskites. The $YBa_2Cu_3O_{7-\delta}$ oxide is of particular interest because its transition temperature occurs at 90 K, well above the liquid-nitrogen temperature. Increasing experimental evidence has outlined the relevance of strong electronic correlation effects which are likely to play an important role in the mechanism leading to high-temperature superconductivity. Up to now, sizeable electron collective interactions have been reported for $YBa_2Cu_3O_{7-\delta}$ using photoemission spectroscopy.[2-6] These correlation effects cause the appearance of Cu $3d^8$ final-state satellites in the valence band and shift the portion of the Cu—O band states close to the Fermi level (E_F) by ≈ 1 eV toward higher binding energies. As a consequence the density of states at E_F is overestimated in one-electron density-of-states calculations.[7]

In this paper we provide experimental evidence that remarkable temperature effects are present in the Cu L_3VV Auger spectra of $YBa_2Cu_3O_{7-\delta}$. Lowering the temperature to 85 K, we find that an extra feature develops on the low kinetic side of the main L_3VV Auger peak. We suggest two possible explanations for this new structure. The first is based on the presence of unequivalent Cu atoms in the unit cell with different coupling to the neighbor oxygens and/or different oxidation state (Cu^{2+}, Cu^{1+}) and thus a different hole-hole correlation energy. The second assumes that the increase of the correlation is due to the modifications of the $3d$-like density of states at the Cu site with decreasing temperature found in photoemission studies.[4,5]

The measurements have been carried out on $YBa_2Cu_3O_{7-\delta}$ pellets prepared from Y_2O_3, $BaCO_3$, and CuO powders repeatedly ground and sintered at 950 °C in air or O_2 following currently used procedures to obtain this class of compound. The x-ray analysis showed that the samples were single phase. The superconducting transition was checked by the four-point method and the onset temperature occurred at 92 K. Additional magnetic characterization is reported elsewhere.[8]

Auger spectra at different temperatures were collected in UHV conditions ($p < 5 \times 10^{-10}$ Torr) using the Al $K\alpha$ line as an excitation source and a vacuum generator CLAM 100 electron analyzer. The overall energy resolu-

tion was 1.15 eV. Special care was adopted to minimize Cu reduction which is well-known to occur in copper oxides upon x-ray and/or uv irradiation under vacuum conditions.[9] A reducing agent has been identified in atomic hydrogen which progressively reduces the surface of the irradiated cupric oxide (CuO) to cuprous oxide (Cu_2O) and metallic Cu.[10] The presence of Cu in different oxidation states can be unambiguously inferred by an analysis of the Cu-$2p$ emission and Cu L_3VV Auger line shape.[9,10] For this purpose we have measured CuO pellets prepared from high-purity CuO powder obtained by controlled thermal decomposition of malachite $Cu_2CO_3(OH)_2$. The method of preparation and characterization is described in Ref. 11. It was found that the incorporation of water, which inevitably occurs whenever the sample is exposed to air, leads to a fast degradation of the surface. This effect can be avoided when the sample is heated up to 120 °C for 2 h and scraped to regenerate the surface.[12] The spectra at low temperature are not further modified by scraping. The same treatment was applied to $YBa_2Cu_3O_{7-\delta}$ samples. Auger spectra of $YBa_2Cu_3O_{7-\delta}$ taken at $T = 85$, 185, and 245 K are reported in Fig. 1 and compared with the room-temperature spectrum (solid line). For each temperature the difference spectrum is shown as well. The main structure of the L_3VV Auger spectrum peaks at 918.0 ± 0.2 eV and does not shift with temperature. Its energy position coincides, within the experimental uncertainty, with that of CuO (see below), indicating the copper is *predominantly* in the Cu^{2+} formal valence state. Lowering the temperature, a subsidiary peak grows at ≈ 3 eV below the main peak and slightly shifts to lower kinetic energies as better described in Fig. 2.[13] The temperature changes are reproducible and fully reversible. The L_3VV Auger spectrum of Cu in CuO measured at $T = 300$ and 85 K is reported in Fig. 3. The overall spectral shape is the same as in $YBa_2Cu_3O_{7-\delta}$ but no temperature effects are observable: this rules out contamination effects as the cause of the observed changes. Hence we infer that the thermal effect is peculiar to the superconducting oxide.

In the L_3VV Auger transition, we observe a valence-band (V) electron which fills a previously created core (L_3) hole. Its excess energy causes ionization of a second valence-band (V) electron called an Auger electron. The energy distribution of the latter gives information about the valence-band density of states spatially localized around the atom containing the core hole. The kinetic en-
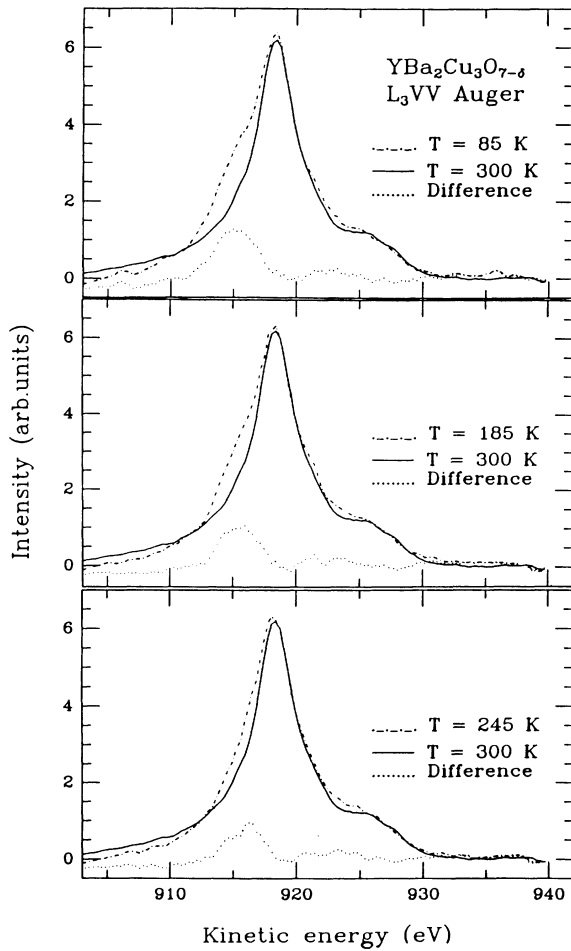
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FIG. 1. L_3VV Auger spectrum of Cu in $YBa_2Cu_3O_{7-\delta}$ measured at temperatures 85, 185, and 245 K (broken curve) compared with the one measured at room temperature (solid curve). For each temperature the difference spectrum is also shown (dotted curve).
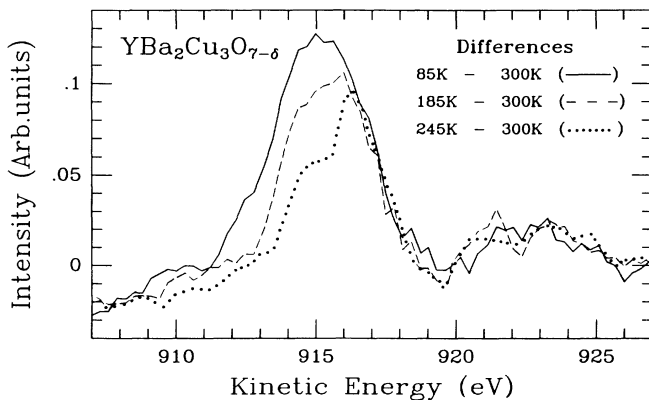

FIG. 2. Cu L_3VV Auger difference spectra for $T=85$ K (solid), 185 K (dashed), and 245 K (dotted) and room-temperature spectrum for $YBa_2Cu_3O_{7-\delta}$.
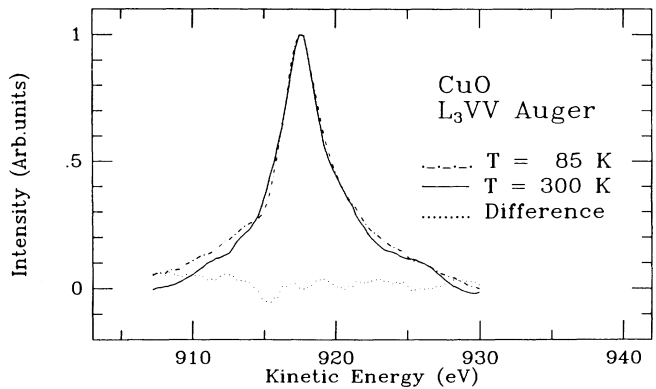

FIG. 3. Cu L_3VV Auger spectrum at $T=85$ K (dashed line) and room temperature (solid line) in CuO. The difference spectrum (dotted line) is also reported.

ergy $E(L_3VV)$ of the Auger line is

$$E(L_3VV)=E(L_3)-2E(V)-U , \qquad (1)$$

where $E(L_3)$ and $E(V)$ are the core level and the centroid energy of the valence band, respectively. The Coulomb interaction term U describes many-body interactions such as hole-hole interaction, relaxation effects, etc. For filled, nondegenerate bands, and neglecting the nonlocal contribution, the two-hole Auger profile is described by the well-known expression[14]

$$D(E) = \frac{D^0(E)}{[1-F(E)U]^2+\pi^2U^2[D^0(E)]^2} , \qquad (2)$$

where $D^0(E)$ is the self-convolution of the one-particle density of states and $F(E)$ is the Hilbert transformation of $D^0(E)$. For unfilled bands, the closed-band expression (2) can still be used,[15] provided the number of holes per valence state is much smaller than one and U is not too large. By increasing the U/W value, where W is the occupied bandwidth, one fulfills the condition leading to quasi-atomic spectra as in the case of filled bands. We have computed the Auger profile of $YBa_2Cu_3O_{7-\delta}$ for which the above-mentioned restrictions apply, using the muffin-tin valence-band projected densities of states at the copper sites calculated by Mattheiss and Hamann.[7] The resulting spectrum is shown in Fig. 4. The U value has been adjusted to bring the energy position of the ^1G term of the $3d^8$ configuration, responsible for the main Auger peak, close to the experimental value. The calculated profile has a bandlike behavior which reproduces satisfactorily the experimental spectrum with $U \approx 2$ eV and a $U/W \approx 0.5$. It is remarkable that these figures are closer to those found for Ni and its alloys,[16] where the average number of holes per atom is ≈ 0.6, than in Cu metal which has a filled valence band and a correlation energy of about 8 eV. The other multiplet terms of the $3d^8$ configuration, i.e., ^1D, ^1S, ^3P, and ^3F, contribute to the Auger line shape with different weights and U values. The ^1S singlet component adds intensity at the low kinetic energy side of the split-off peak, but its weight is generally small and cannot
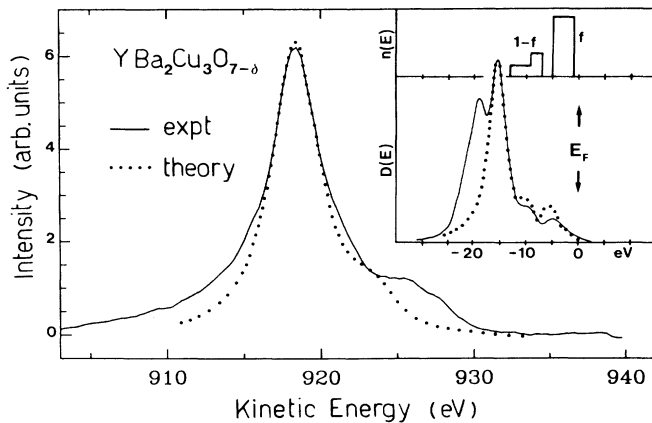
FIG. 4. Cu L_3VV experimental Auger spectrum of $YBa_2Cu_3O_{7-\delta}$ at room temperature (solid line). The theoretical spectrum (dotted line) is obtained from the Eq. (2) using the local density of states of Mattheiss and Hamann (Ref. 7) and a Gaussian broadening of 3 eV full width at half maximum which takes into account the core-hole lifetime. The inset shows a simple two-band density-of-states model and the corresponding Auger profile calculated with $f=0.8$ (dotted line), $f=0.5$ (solid line), and a correlation energy $U=2$ eV.

explain the feature around 915 eV. The enhanced Auger cross section between 925 and 930 eV is reminiscent of the Cu $2p^53d^9$ satellite structure measured both in $YBa_2Cu_3O_{7-\delta}$ and CuO $2p$ core emission.[17] The above analysis applies equally well to the Auger spectrum of CuO of Fig. 3, which also displays satellites in the photoemission spectrum similar to those of $YBa_2Cu_3O_{7-\delta}$.[18]

The origin of the temperature-dependent structure therefore remains unexplained. One can think that atomic double ionization processes[16] which are known to occur at the high-binding energy side of the main Auger peak are important in correlated systems but in this case the temperature behavior is hard to understand. A more plausible speculation is that the apparently higher correlation energy may reflect a smaller relaxation of screening in the final two-hole state for the Cu atoms in the Cu—O linear chains with respect to those having square planar coordination. In this case one should find a double peak for the L_3VV Auger line shape whose low-kinetic energy component has the larger U value. On the other hand, the experimental Auger behavior is qualitatively reproduced by a simple model for the Cu local density of states consisting of two bands[19] of relative intensities f and $1-f$. According to the uv photoemission measurements,[5] f depends on temperature. Room temperature and $T=85$ K experimental spectra are reproduced using $f=0.8$ and $f=0.5$, respectively (inset of Fig. 4).

The present results emphasize the importance of the electronic interactions at low temperature in the high-T_c superconducting oxide. The relationship to the mechanism of the superconductivity remains, however, to be determined.

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