Study of the 3*d* band of copper in $Y_1Ba_2Cu_3O_{7-x}$

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(Submitted 29 December 1988)
Pis'ma Zh. Eksp. Teor. Fiz. **49**, No. 3, 163–166 (10 February 1989)

The results of an experimental study of the structure of a 3*d* band of copper in a superconducting film at two temperatures (300 K and 80 K) are presented. A smaller overlap of the orbitals of the Cu–O bonds and the effective repulsion potential of holes has been observed at a low temperature.

A characteristic feature of the new high-T_c superconductors is their proximity to the metal-insulator transition. Studies of complex oxides with a perovskite structure have made it possible to construct a generalized phase diagram which suggests that there are critical values of the metal-oxide overlap integral at which there is an abrupt transition from the insulating state to the antiferromagnetic state and then to a metallic state or a superconducting state. These transitions are the result of intensification of the spin-spin coupling, which is described by the constant $j = 4t^2/U$, and also the increase in the degree of delocalization of the *d*-shell electrons. These tendencies play a decisive role in the theory of resonance valence bonds[2] and spin-spin pairing.[3]

In the transition *d*-metals a resonance is known to occur in the Auger spectrum because of a strong hole-hole interaction. The state density in this case is taken into account in a complex way in the Auger spectrum and the Auger line profile is described by the expression[4]

$$A(E) = \frac{N(E)}{(1 - UI(E))^2 + (\pi N(E))^2}, \qquad (1)$$

 0021-3640/89/030191-05$01.00

where $N(E)$ is the self-convolution of the state density, U is the effective interaction potential of the holes, and $I(E)\int[N(E')dE'/(E-E')]$. The self-convolution of the state density can be determined from the Auger spectrum by representing Eq. (1) in the form

$$F(E) = U\pi A(E) = \mathrm{Im}\left(\frac{1}{1-G(E)}\right), \tag{2}$$

where $G(E) = UI(E) + iU\pi N(\mathrm{E})$. Making use of the relationship between the real and imaginary parts of the function $1/[1-G(E)]$, we find

$$F'(E) = \mathrm{Re}\left(\frac{1}{1-G(E)}\right) = 1 - \frac{1}{\pi}\int \frac{F(E')dE'}{E-E'}.$$

Since $F(E)$ and $F'(E)$ are known, we can easily calculate the self-convolution of the state density

$$U\pi N(E) = \mathrm{Im}\, G(E) = \frac{F(E)}{F(E)^2 + F'(E)^2}.$$

Since the value of $F(E)$ has been determined experimentally within a constant which is determined by the apparatus, we normalized the original Auger spectrum in such a way that the value of $N(E)$ obtained would give, upon its substitution in Eq. (1), an exact value of the function $F(E)$ for any value of E.

The experiments were carried out with an "ESCALAB-5" spectrometer with a

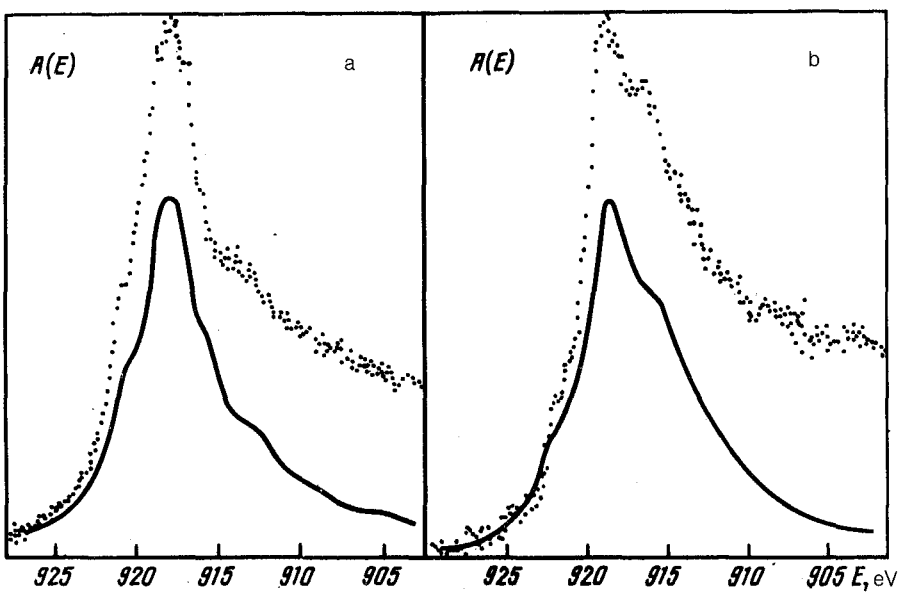

FIG. 1. Auger line profiles of copper at 300 K (a) and 80 K (b).

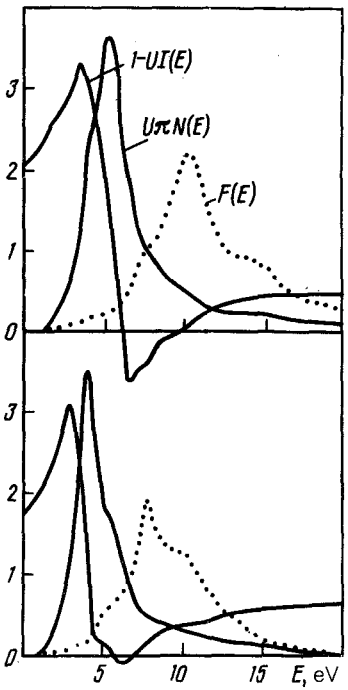

FIG. 2. The functions $U\pi N(E)$ and $1—UI(E)$ calculated from the Auger spectra.

semispherical analyzer with an absolute resolution of 0.2 eV. As the sample we used a superconducting film with $T_c = 82$ K. To reduce the effect of x-ray emission on the film surface, we carried out measurements only at two temperatures.

Figure 1 shows the experimental L_3VV Auger spectra of copper obtained at 300 K (a) and 80 K (b). The points represent the original spectra and the solid line shows the spectra after the removal of the background of inelastic losses. We see that at various temperatures the line profiles differ dramatically from each other. At 80 K the maximum of the spectrum undergoes a 2.4-eV shift up the energy scale. The solid lines in Fig. 2 show the results of calculations, based on these spectra, of the self-convolution of the state density $U\pi N(E)$ and of the function $1 - UI(E)$. The points represent the spectra which were reconstructed from Eq. (1) and which coincide with the experimental spectra within 2%, suggesting that the normalization is correct. Here and elsewhere in the text, the energy is reckoned from the Fermi level. The calculated values of $U\pi N(E)$ and $1 - UI(E)$ at $T = 80$ K suggest that the $3d$ band of copper changes abruptly. The resonance point [the point at which $1 - UI(E) = 0$] shifts down the energy scale, reducing the value of the peak energy of the Auger spectrum.

The solid line in Fig. 3 represents the results of the self-convolution of the state density at 300 K (a) and 80 K (b). For comparison we also show in this figure the theoretical curves for the local state density at the copper atoms in a $2D$ layer of CuO_2 (the dashed line) and in the chains directed along the c axis (the points).[5] We see that the main state-density peak is situated at 2.5 eV. All the singularities on the experimental curve (Fig. 3a) coincide in the energy position with the given theoretical data.

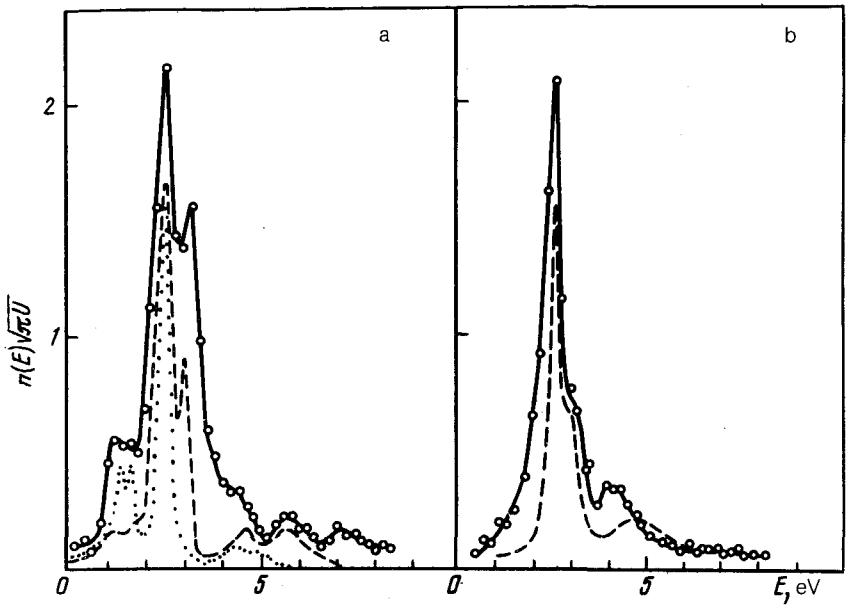

FIG. 3. The solid curves represent the experimental state density of copper in $Y_1Ba_2Cu_3O_{7-x}$; theoretical data on the local state density[5]—dashed curve and dotted curve (a); experimental state density of pure copper[6]—dashed curve (b).

It follows from the calculations of the local state density of $Y_1Ba_2Cu_3O_7$ (Ref. 5) and the experimental data for pure copper[6] that the main peak (2.5 eV) corresponds to twice the degenerate $3d_\pi$ orbitals of copper which slightly overlap the $2p$ orbitals of oxygen, while the remaining singularities of the state-density spectrum correspond to the hybrid $3d_\sigma$ Cu–$2p$O orbitals.

At low temperatures the state density has only one peak at 2.5 eV and a bump at 4.5 eV. The state-density curve in this case is similar to the state-density curve for pure copper (the dashed line), obtained by the photoelectron-spectroscopy method,[6] in which the $3d$ band is localized. The presence of a broad band at 300 K suggests that the overlap of the Cu–O orbitals, which leads to a delocalization of the $3d$ electrons in $Y_1Ba_2Cu_3O_{7-x}$ and to a metallic conductivity, is sufficiently strong. The narrowing of the $3d$ band observed at low temperatures indicates that the structural distortion in the CuO_2 plane is such that it causes the Cu–O coupling to weaken. The $3d$ electrons thus tend to become localized, with the formation of a narrow band with a Coulomb correlation interaction. Such an effect has been observed in Ti-, V-, and Cr-based perovskites in which a sharp narrowing of the d zone occurs because of a smaller overlap of the d orbitals of these metals with the $2p$ orbitals of the oxygen.[1] At a certain critical value of the overlap integral this situation leads to a transition to the antiferromagnetic state. The structural distortion of the CuO_2 plane in $Y_1Ba_2Cu_3O_7$ can be explained in terms of the displacement of oxygen atoms because of their pairwise attraction and repulsion in mutually perpendicular directions[2] or because of dimerization of the Cu–O–Cu chains in the same plane.[7]

Integrating the curve of $\sqrt{U\pi n(E)}$ in Fig. 3 and normalizing $\int n(E)dE = 1$, we can estimate the value of the potential U_{eff}. At 300 K, U_{eff} is 4.5 eV. This value is approximately equal to the known value for copper (5 eV). At a low temperature we have $U_{\text{eff}} = 2.5$ eV. This result is of considerable interest since U_{eff} appears in the denominator of the constant j which is directly related to the critical temperature of the superconductor.

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Translated by S. J. Amoretty