Effect of polarization of the exciting light on resonant photoelectron emission from $La_2CuO_{4+\delta}$ single crystals

M. N. Mikheeva, V. G. Nazin, A. V. Svishchev, and M. B. Tsetlin

Kurchatov Institute Russian Science Center, 123182 Moscow, Russia

D. S.-L. Law

SERC Daresbury Laboratory, Daresbury, Warrington, WA4 4AD, UK

A resonant increase in the emission from electron states with a binding energy ≈ 6 eV at an exciting-photon energy ≈ 17 eV has been observed in photoelectron spectra of the valence band of $La_2CuO_{4+\delta}$ single crystals. The intensity of the resonant-emission peak is comparable to the maximum of the valence band. An effect of the polarization of the exciting light on the nature of the resonance has been observed for the first time: As the orientation of the polarization vector with respect to the crystallographic axes is varied, changes occur in the binding energy of the resonant peak and in the resonant emission frequency. The effect, with very slight differences, is observed for both insulating and superconducting samples. The experimental data are discussed within the framework of the theory of resonant photoemission. © *1994 American Institute of Physics.*

This letter reports the first use of resonant photoemission to study the effect of oxygen doping on the electronic structure of the valence band of $La_2CuO_{4+\delta}$ single crystals for various directions of the polarization vector of the exciting light with respect to the crystallographic axes.

The method of resonant photoelectron spectroscopy, which was developed because of the use of synchrotron radiation, makes it possible to distinguish the contributions of electron states of a certain type[1] and, through the use of linearly polarized exciting light, to determine the orientation of these electron states with respect to the crystallographic axes.

The measurements were carried out at the synchrotron radiation source of Daresbury Laboratory, in the UK, on high-quality $La_2CuO_{4+\delta}$ single crystals grown at the Institute of Solid State Physics and Semiconductors in Minsk, Belarus.[2] Evidence that the crystals were of high quality comes from the high Néel temperature (up to 320 K after annealing in vacuum), the absence of additional x-ray diffraction peaks, and other experimental results, e.g., on the electrical resistance, the electric susceptibility, and optical properties.[3–5] As we showed in Ref. 6, the surfaces of freshly cleaved $La_2CuO_{4+\delta}$ single crystals retain their properties for several hours in a vacuum $\sim 10^{-10}$ torr at ~ 30 K. The $La_2CuO_{4+\delta}$ single crystals with a high oxygen content δ were prepared by annealing La_2CuO single crystals with an approximately stoichiometric oxygen content in oxygen
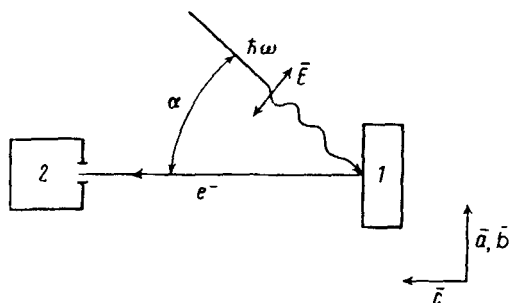
FIG. 1. Experimental layout. 1—Sample; 2—analyzer. The direction of the linear polarization of the light and the directions of the crystallographic axes of the sample are shown.

at a pressure of 3 kbar and a temperature of 450 °C. The doping level was estimated from the orthorhombicity parameter $(a-b)/(a+b)$, where a and b are the lattice constants in the Cu–O plane. This estimate of the oxygen concentration δ yielded $0 \leqslant \delta \leqslant 0.01$ for the undoped samples (we will call these the samples of group A), $0.014 \leqslant \delta \leqslant 0.019$ for the samples with an intermediate oxygen concentration (group B), and $0.024 \leqslant \delta \leqslant 0.029$ for the samples with the highest oxygen concentration (group C). The samples of group C were superconductors. The transition temperature $T_c = 25$ K was determined from the magnetic susceptibility by an ac method. As in Ref. 6, the sample temperature did not exceed 70 °C during the outgassing of the apparatus. A clean surface was prepared by cleaving the samples in ultrahigh vacuum at about 30 K before the measurement of the photoelectron spectra. The cleavage plane was perpendicular to the c crystallographic axis (Fig. 1). The photoelectron emission was detected with a VG ADES400 spherical-deflector energy analyzer. The entrance aperture of the analyzer was 4°. Electrons emitted along the normal to the surface of the sample were analyzed. We studied the polarization dependence of the photoelectron spectra by working in two experimental layouts, in which the angle (α) at which the photons were incident was either 20° or 70 °C (Fig. 1). The synchrotron radiation was polarized predominantly in the plane of the figure. The fraction of the exciting light with $E \perp c$ was about 80% in the $\alpha = 20°$ case and about 20% in the $\alpha = 70°$ case. The spectrometer was calibrated with the help of a gold sample placed beside the test samples.

Figure 2 shows photoelectron spectra of the valence band found at various energies of the incident photons, $\hbar\omega$, for one of the group-A samples (the binding energy is reckoned from the Fermi level). It can be seen from Fig. 2a that in the $\alpha = 20°$ case there is a peak in the density of states which has a resonant dependence on the energy of the exciting light, $\hbar\omega$, in the valence-band spectrum at a binding energy $E_B = 6.2$ eV. This peak arises at energies $\hbar\omega = 16$ eV, reaches a maximum at $\hbar\omega = 17$ eV, and fades away at $\hbar\omega \geqslant 18$ eV. Its intensity is comparable to the valence-band intensity or even slightly greater. In the spectra obtained in the $\alpha = 70°$ arrangement (Fig. 2b), we again see this peak, but it is much less intense. An unexpected result was the observation of a second structural feature (Fig. 2b), at $E_B = 5.4$ eV, which reached its maximum intensity at $\hbar\omega = 16.5$ eV. We believe that the two structural features in the spectra in Fig. 2b correspond to resonances involving electron states which are identical in nature, aside from having different spatial orientations. For the samples with other values of δ, the overall spectra are essentially the same, except for slight changes in the amplitudes and widths of the resonance. It can be seen from Fig. 3 that the amplitude of the resonance at
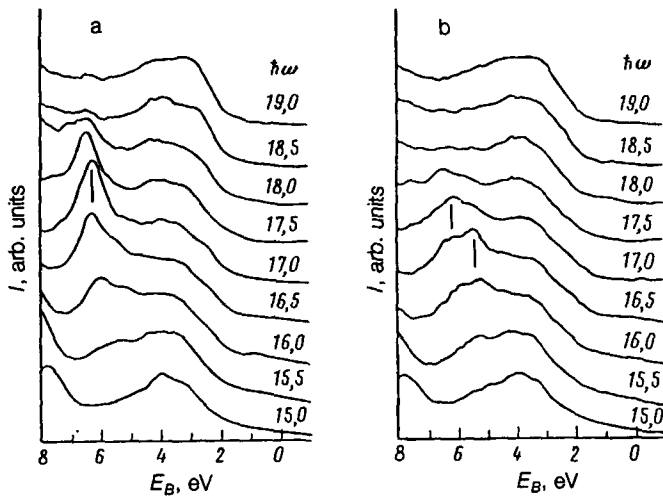
FIG. 2. Valence-band photoelectron spectra for various energies of the exciting light, $\hbar\omega$. a—The photons are incident in a direction close to the normal ($\alpha = 20°$); b—the photons are incident near a grazing angle ($\alpha = 70°$). The spectra have been normalized in terms of emission intensity and have been shifted along the vertical axis. A constant background has been subtracted. The vertical line segments mark resonant features.

$E_B = 6.2$ eV is essentially the same for the samples of groups B and C, while it is slightly higher for the insulating samples (group A).

The picture we are seeing here is typical of resonant photoemission. According to the present understanding,[7] resonant photoemission is a two-stage process. First, a photon is absorbed, and an electron undergoes a transition from a deep level (level I in Fig. 4) to a free state near the Fermi level (level II in Fig. 4). The energy of the photon here is $\hbar\omega = E_{II} - E_I$. This intermediate excited state is regarded as a virtual state. The second stage is an Auger process, which causes an electron to undergo a transition from an excited state to the ground state, and the energy is expended on exciting an electron from the valence band (level III) into an empty state above the Fermi level. Experimentally, one observes a resonant increase in the emission of electrons with a binding energy E_{III} in this case. If resonant photoemission is to be seen clearly, the electron states must be localized in one spatial region. Since level I has a large binding energy and corresponds to a state with a pronounced localization at a certain atom, states II and III should
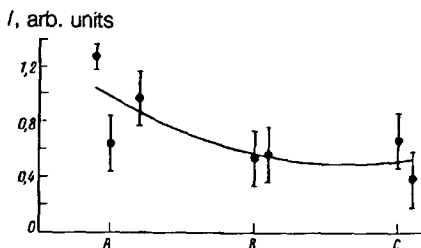

FIG. 3. Amplitude of the resonant feature in the $\alpha = 20°$ case for the three groups of samples. The amplitude has been normalized to the maximum of the valence band.
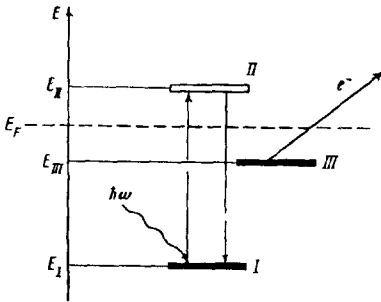
FIG. 4. Energy-level diagram used to explain the resonant photoelectron emission.

also have a large density at this atom. The polarization of the incident light affects only the first stage of the process, in which the selection rules for optical absorption determine the symmetry of the initial and final states involved in the process.

Two possibilities can be offered in the way of an identification of the levels partici-pating in the resonance. We know[8] that the binding energies of the La5p doublet are 16.5 and 18.5 eV. Peaks corresponding to these states have been observed[6] in our experiments at $\hbar\omega > 30$ eV. The first possible explanation assumes that lower level I corresponds to the La5p state with $E_B = 16.5$ eV. Level II then lies $\sim (0.5-1)$ eV above the Fermi level, and level III corresponds to $E_B = 6.2$ eV (for $\alpha = 20°$). One might suggest that levels II and III correspond to La5d states which are hybridized with O2p states. This suggestion agrees with cluster calculations for lanthanide oxides.[9] This explanation looks completely plau-sible to us, but it contradicts the results of Ref. 10. In that study, the density of free electron states in La$_{1.85}$Sr$_{0.15}$CuO$_4$ was determined by inverse photoemission. It was found that the density of states is small and that there are no distinguishable features at energies up to 3 eV above the Fermi level. However, it is possible that all the valence electron states of lanthanum undergo a restructuring in the course of the excitation of the La5p state. A similar effect is observed near the threshold for excitation of the La4d shell for La atoms in the gas phase,[11] in which case one sees a "collapse" of f electrons: The presence of a hole in a core level (this situation corresponds to an increase of $+1$ in the effective charge) leads to a cerium-like valence shell containing f electrons. One might expect that a similar collapse would occur in our case also, and that La5d states would appear near the Fermi level. The La5p electron would be excited into these virtual states. One might suggest that a similar effect near the threshold for La5p excitations would be observed for any compound of lanthanum. Unfortunately, we know of no calculations on this complex effect.

In the second possible explanation, oxygen states play a decisive role at resonance. One might suggest that lower level I corresponds to an O2s state hybridized with La5p (Ref. 9), while levels II and III correspond to O2p states hybridized with La5p and Cu3d. The suggestion that there are oxygen states above the Fermi level agrees with data on x-ray absorption near the O1s threshold.[12] The discrepancy with Ref. 10 may be due to a low sensitivity of the inverse-photoemission method to oxygen states.

We are unable to determine which of these possibilities is realized, since at the moment there is no theory for resonant photoemission involving hybridized levels. Nev-ertheless, the first explanation looks more likely to us. Indirect evidence in favor of this

first explanation comes from the narrowness of the band of resonant states, since in the case of the second version we would logically expect resonant excitation of other oxygen states in the valence band.

The effect of the polarization on the resonant photoemission can be explained in terms of transitions between electron states with different spatial orientations.[13] In the first version, with $E\perp c$, the transitions $La5p_{x,y}\rightarrow La5d_{x^2-y^2}$ and $La5p_{x,y}\rightarrow La5d_{3z^2-r^2}$ should play a role, while in the $E\perp c$ case the transitions $La5p_z\rightarrow La5d_{3z^2-r^2}$ should play a role. In the second version, with $E\perp c$, the $O2s\rightarrow O2p_x$ and $O2\rightarrow O2p_y$ transitions would be important, while for $E\|c$ the $O2s\rightarrow O2p_z$ transitions would be important. If we adopt the model of a resonance involving oxygen states, then La–O bonds with different oxygen atoms should participate in the resonance for different polarizations: For the $E\|c$ case, the bond oriented along the c axis should be involved, while for $E\perp c$ it should be the bond lying in the ab plane. Regardless of which of these excitation processes actually occurs, there is still the interesting fact that there is a difference between the energies of the La–O hybridized states in the valence band which are at resonance for the different polarizations. Here we are apparently seeing a correlation between the two stages of the resonant photoemission: the absorption of the photon and the emission of the electron from the valence band.

The basic result of this study is the observation that the polarization of the exciting light affects the resonant photoemission: In $La_2CuO_{4+\delta}$ crystals in the $E\perp c$ configuration, the resonant peak has its maximum intensity at a photon energy $\hbar\omega = 17$ eV and at a binding energy $E_B = 6.2$ eV. For the $E\|c$ case, the corresponding figures are $\hbar\omega = 16.5$ eV and $E_B = 5.4$ eV.

[1] O. Gunnarson et al., Phys. Rev. B **41**, 4811 (1990).
[2] S. N. Barilo et al., Sverkhprovodimost' (KIAE) **2**(8), 138 (1989) [Superconductivity **2**(8), 158 (1989)].
[3] A. A. Zakharov et al., Sverkhprovodimost' (KIAE) **5**(2), 198 (1992) [Superconductivity **5**(2), 207 (1992)].
[4] S. V. Varyukhin et al., JETP Lett. **56**, 469 (1992).
[5] A. V. Bazhenov et al., Physica C **214**, 45 (1993).
[6] M. N. Mikheeva et al. Surf. Sci. **287/288**, 662 (1993).
[7] O. Gunnarson and T. C. Li, Phys. Rev. B **36**, 9488 (1987).
[8] J. Kirz et al., X-Ray Data Booklet (Berkeley, 1986).
[9] M. V. Ryzkov et al., Z. Phys. B **59**, 7 (1985).
[10] B. Reihl et al., Phys. Rev. B **35**, 8804 (1987).
[11] M. Richter et al., Phys. Rev. A **39**, 5666 (1989).
[12] E. Pellegrin et al., Phys. Rev. B **47**, 3354 (1993).
[13] D. D. Vvedensky, in Unoccupied Electronic States, ed. by J. C. Fuggle and J. E. Inglesfield (Berlin, 1992).

Translated by D. Parsons