

Photoemission study of single-crystalline $(\text{La}_{1-x}\text{Sr}_x)_2\text{CuO}_4$

T. Takahashi, F. Maeda, H. Katayama-Yoshida, Y. Okabe, and T. Suzuki
Department of Physics, Tohoku University, Sendai 980, Japan

A. Fujimori
National Institute for Research in Inorganic Materials, Tsukuba, Ibaraki 305, Japan

S. Hosoya
Institute for Materials Research, Tohoku University, Sendai 980, Japan

S. Shamoto and M. Sato
Institute for Molecular Science, Myodaiji, Okazaki 444, Japan
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Ultraviolet and x-ray photoemission measurements have been performed on single-crystal $(\text{La}_{1-x}\text{Sr}_x)_2\text{CuO}_4$ with $x=0.0$ and 0.04 . Considerable differences are found in the photoemission spectra when compared with the results for sintered samples: a single-peak structure for the O $1s$ level and the absence of the peak at 9 eV of unknown origin reported for sintered samples, etc. Comparison is also made with band-structure calculations.

The electronic structure of the oxide superconductors^{1,2} is of considerable interest with respect to understanding the mechanism giving rise to such high transition temperatures. Photoemission spectroscopy³⁻¹⁸ has provided fundamental knowledge about the electronic structure which forms a basis for studies of the high- T_c mechanism. Ultraviolet photoemission spectroscopy has shown that (i) the density of states at the Fermi level is very small compared with that of band calculations^{19,20} and (ii) the valence-band spectrum is shifted by 1–2 eV relative to the calculations while x-ray photoemission studies have found a satellite of the Cu $2p$ level, indicating a divalent state for the copper atoms. Photoemission studies with synchrotron radiation have reported a remarkable resonance for the satellite peak of the Cu $3d$ level. These results have been interpreted as an indication of strong electron correlation in favor of the theoretical proposals of a high- T_c mechanism based on strong electron correlation.²¹ Although photoemission spectroscopy has thus provided valuable information on the electronic structure, the spectra reported by different researchers do not necessarily agree with each other. Notable discrepancies are found in the valence band, a band emission of unknown origin at about 9 eV, and the O $1s$ core level. These discrepancies may be ascribed to sintered samples which consist of many small grains and possess boundaries of differing compositions from that of the bulk superconducting phase. It is also known that the oxide superconductors absorb and desorb oxygen very easily, implying that the concentration of oxygen atoms at the sample surface may change rapidly under ultrahigh vacuum. These two effects may have brought about the confusion in the photoemission spectra, especially in the oxygen-related region. Since it has been suggested by various experiments that oxygen plays a key role in the occurrence of the high- T_c superconductivity, the discrepancy in the O $1s$ photoemission spectrum has

become a great obstacle to understanding the high- T_c mechanism.

In this paper, we report the results of photoemission measurements on a single crystal of the high- T_c superconductor $(\text{La}_{1-x}\text{Sr}_x)_2\text{CuO}_4$ ($x=0.04$) together with the undoped one ($x=0.0$). We took utmost care to prevent compositional change at the sample surface. We found remarkable differences in the photoemission spectra in the valence-band region and the O $1s$ core level compared with the previous studies on sintered samples. We discuss the electronic structure and the chemical states of constituent atoms in the high- T_c superconductors using the present experimental results.

Single crystals were prepared by slowly cooling the non-stoichiometric melt with excess CuO.²² Typical crystal size was $10 \times 10 \times 5$ mm³. Their single crystallinity was checked by Laue diffraction measurement and their composition was determined by electron-probe microanalysis (EPMA), which also showed that Sr atoms were distributed uniformly in the crystal. The resistivity and Meissner-effect measurements showed that La_2CuO_4 is an insulator while $(\text{La}_{0.96}\text{Sr}_{0.04})_2\text{CuO}_4$ becomes superconductive at about 20 K.

Photoemission measurements were performed with He II (40.8 eV) and Mg $K\alpha$ (1253.6 eV) lines with the energy resolution of 0.2 and 1.0 eV, respectively. The Mg $K\alpha$ spectra have been corrected for the satellites of the x-ray source. The single crystals were scraped with a diamond file under ultrahigh vacuum (2×10^{-10} Torr) in the spectrometer to obtain a fresh surface for the photoemission measurements. The sample was kept at low temperature (80–150 K) or at room temperature during the measurements. Photoemission spectra changed rapidly at room temperature, especially in the He II measurement, while the changes were reduced when the sample was cooled.

Figure 1 shows valence-band photoemission spectra of $(\text{La}_{1-x}\text{Sr}_x)_2\text{CuO}_4$ excited by the He II line. Spectra denoted by low temperature (LT) were measured at low temperature (about 150 K) within 30 min after scraping while the spectrum denoted by room temperature (RT) was obtained at room temperature for the same sample surface after warming it to room temperature. This spectral change was irreversible. When the sample was scraped and kept at room temperature, the spectrum changed very fast, giving finally a spectrum similar to that denoted by RT in Fig. 1. Spectral features of the undoped (LT and $x=0.0$) and doped (LT and $x=0.04$) samples are almost the same; low density of states at the Fermi level and two main structures at about 4 and 17 eV (bands A and C). Band A is due to the heavily hybridized states of the Cu 3d and O 2p orbitals^{19,20} and band C to the La 5p state. The photoemission spectrum in the band-A region shows a fair agreement with the density of states calculated by Redinger, Yu, Freeman, and Weinberger²⁰ except for a rigid shift of about 1.5 eV, as reported in previous studies on sintered samples.⁴⁻⁷ When going from LT to RT, drastic changes take place: (i) subband A_1 is considerably reduced while subband A_2 is slightly enhanced, (ii) a new feature, band B, appears at about 9 eV, and (iii) band C is shifted by about 1 eV toward the high binding energy.

In the early photoemission studies^{5,16,18} on sintered samples of the La system (superconductors based on

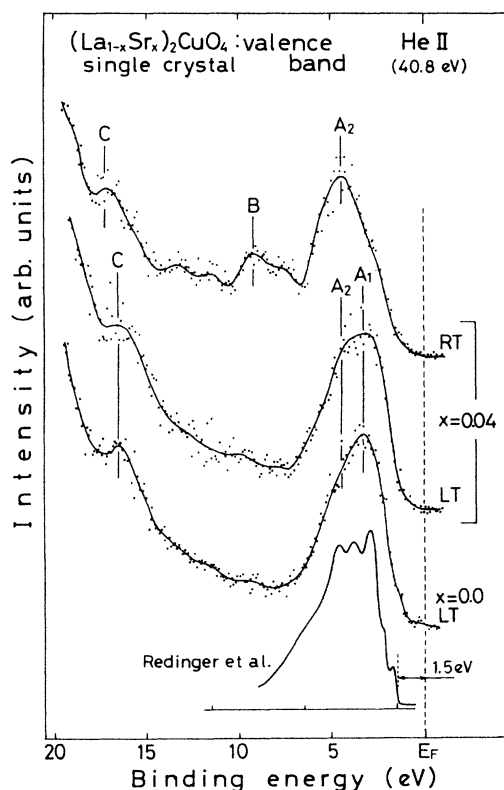


FIG. 1. He II photoemission spectra of valence band in $(\text{La}_{1-x}\text{Sr}_x)_2\text{CuO}_4$ ($x=0.0$ and 0.04) single crystals. Calculated He II spectrum by Redinger *et al.* (Ref. 20) is also shown with an energy shift of 1.5 eV.

La_2CuO_4), a band similar to band B was clearly resolved. A similar and more pronounced structure has been also observed in the Y system (superconductors based on $\text{YBa}_2\text{Cu}_3\text{O}_7$).^{9,10,12,14,15,17,18} Various proposals have been presented as the origin of band B: extrinsic effects such as carbon atom as an impurity^{5,10,15,17,18} and intrinsic ones such as the multielectron feature of Y,⁹ two-hole bound state of the O 2p level,¹⁴ 3d⁸ final state,¹⁶ etc. Petroff *et al.*¹⁴ reported a resonant enhancement of band B at the O 2s core threshold in the Y system and interpreted it as an indication of existence of empty O 2p state and a strong correlation between O 2p electrons. However, it is obvious from Fig. 1 that at least in the La system band B is extrinsic and is not related to the electronic structure of the superconducting phase. We tentatively ascribe band B to some different oxides formed at the surface since we observed a drastic change of the O 1s spectrum for the same sample surface (discussed below).

In the valence-band spectrum of sintered high- T_c superconductors, two main structures have been found at about 3 and 5 eV, although their intensity ratio differs for different reports. As shown in Fig. 1, the intensity ratio between subbands A_1 and A_2 changes drastically according to the preparation method and history of the sample. The wide variation of the spectral shape of band A reported in early studies may be due to possible inhomogeneity and/or deterioration of the sintered-sample surfaces. The point of controversy in band A is which subband has more weight of the O 2p character and which one has more Cu 3d weight. Since the surface deterioration is certainly due to changes of the chemical state of oxygen atoms rather than those of Cu atoms as revealed by the core-level photoemission study (shown later), subband A_1 would have a larger weight of the O 2p state.

Figure 2 shows the O 1s core-level spectra obtained under various conditions. Each spectrum is roughly normalized to the number of incident photons. Spectra denoted by LT were obtained at low temperature (about 80 K) and the spectrum denoted by RT1 was measured at room temperature within 15 min after scraping while the same sample gave spectrum RT2 a few hours later. In the earlier photoemission studies of the La system, Steiner *et al.*³ and Nücker *et al.*⁶ presented a two-peak structure for the O 1s level while Sarma and Rao¹⁶ reported the third peak, ascribing it to monovalent oxygen (O^{1-}). The confusion in the O 1s photoemission result seems greater in the Y system. In the present study with single crystals, we found a single peak for the O 1s level at about 529 eV in both the superconductor ($x=0.04$) and insulator ($x=0.0$). But the O 1s peak transforms into a double peak structure upon deterioration of the surface as shown in Fig. 2. The single-peak behavior of the O 1s photoemission spectra seems in good agreement with the theoretical prediction by Redinger *et al.*²⁰ which calculates the energy difference between two nonequivalent O atoms in La_2CuO_4 as 0.66 eV, which is within the resolution of x-ray photoemission measurement. A small shoulder at the higher energy observed in the spectra of the doped sample (middle two spectra in Fig. 2) may be due to a slight deterioration of the surface: it was found in the He II measurement that the deterioration is faster in the

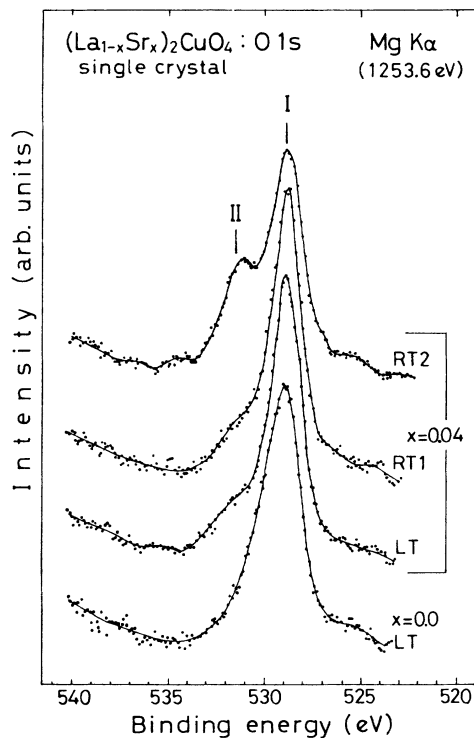


FIG. 2. O $1s$ core-level photoemission spectra of $(\text{La}_{1-x}\text{Sr}_x)_2\text{CuO}_4$ single crystals obtained under various conditions. LT and RT mean measurements at low and room temperatures. The irregular background of the spectra may be due to the La NMM Auger transitions.

doped crystal. We could not resolve the third O $1s$ peak at about 533 eV which has been reported and interpreted by Sarma and Rao¹⁶ as an indication of the existence of monovalent oxygen. As found in Fig. 2, the total intensity of the O $1s$ photoemission peak does not change significantly even after deterioration, which suggests that the deterioration may not be due to removal of oxygen atoms but is rather ascribed to transformation of the high- T_c oxide into other types of oxides. It is noted that Meyer *et al.*²³ reported recently a single-peak feature for the O $1s$ level in a dense sintered sample as in the present result, although an unknown peak at 9 eV still exists in their spectrum.

Thus, the valence-band and the O $1s$ spectra show rapid and drastic changes due to the degradation of the sample surface. However, it is surprising that the Cu $2p$ spectrum does not show any changes as shown in Fig. 3: the spectrum denoted by RT was obtained under nearly the same conditions as spectrum RT2 in Fig. 2. This insensitivity of the Cu $2p$ level suggests that copper atoms may not be involved in the surface deterioration, or at least, that the chemical bonding of copper atoms to neighboring oxygens does not change even after the degradation. The appearance of satellite structures denoted

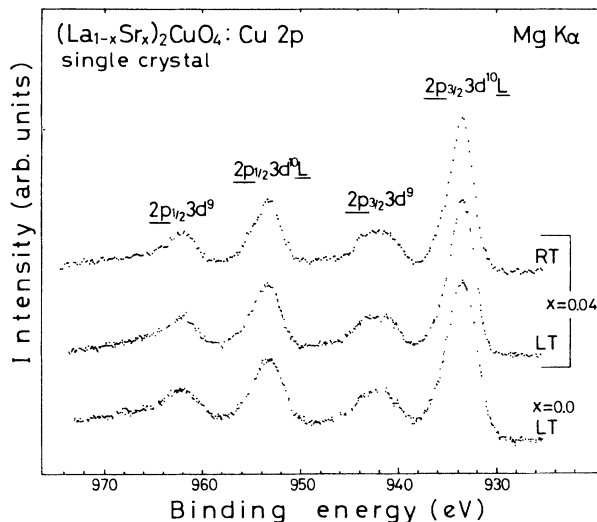


FIG. 3. Cu $2p$ core-level photoemission spectra of $(\text{La}_{1-x}\text{Sr}_x)_2\text{CuO}_4$ single crystals obtained at room temperature (RT) and low temperature (LT).

by $2p3d^9$ in Fig. 3 indicates that copper atoms in both $(\text{La}_{1-x}\text{Sr}_x)_2\text{CuO}_4$ ($x=0.0$ and 0.04) take divalent state (Cu^{2+}) as reported in the previous studies.^{3,6,7,18}

In conclusion, we have performed ultraviolet and x-ray photoemission studies on single-crystalline $(\text{La}_{1-x}\text{Sr}_x)_2\text{CuO}_4$ ($x=0.0$ and 0.04) samples in order to obtain reliable photoemission data to serve as a basis for understanding the high- T_c mechanism. Remarkable differences have been found in comparison with the previous photoemission results with a sintered sample; (i) the O $1s$ core level shows a single-peak structure in both the undoped and Sr-doped crystals, but it transforms into a double-peak structure upon degradation of the crystal surface; (ii) the Cu $2p$ core-level spectrum exhibits a clear satellite structure indicating the divalent state of copper atoms; (iii) valence-band photoemission spectra of undoped and doped crystals are almost the same, having a very low density of states at the Fermi level and a broad band at about 4 eV which shows an energy shift by about 1.5 eV relative to the band calculation;²⁰ (iv) a photoemission band at 9 eV of unknown origin reported for sintered samples is completely absent in a clean surface but appears as a prominent structure as the surface deterioration, indicating that the band at 9 eV is extrinsic, probably due to some other oxides formed at the surface. A similar photoemission study with a single crystal is urgently desired also for the Y system.

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