

Electronic structure of the system $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+\delta}$

H. Romberg, M. Alexander, N. Nücker, P. Adelman, and J. Fink
*Kernforschungszentrum Karlsruhe, Institut für Nukleare Festkörperphysik,
 P.O. Box 3640, D-7500 Karlsruhe, Federal Republic of Germany*

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The electronic structure of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+\delta}$ has been studied by measuring O 1s absorption edges using high-energy electron-energy-loss spectroscopy in transmission. Upon doping the insulating compound the conduction-band states are reduced and states in the gap are formed. When going from insulating to conducting compounds there is a continuous increase of states at the Fermi level, which is at the bottom of the gap. The insulator-metal transition is probably driven by delocalization of these states.

Among the cuprates showing high- T_c superconductivity, the system $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ ($M=\text{Ba},\text{Sr}$), first discovered by Bednorz and Müller,¹ is one of the most suitable to study the electronic structure of high- T_c superconductors. The undoped parent compound La_2CuO_4 is an antiferromagnetic insulator. This is due to strong electronic correlation effects on the Cu sites which force the otherwise metallic compound with a half-filled band to become a charge-transfer insulator.² A charge-transfer gap appears between the valence band (ligand band) with mainly O 2p character and the conduction band (upper Hubbard band) with mainly Cu 3d character. Upon p -type doping with Sr, antiferromagnetism disappears and an insulator-metal transition occurs near $x=0.06$.³ For $0.06 \leq x \leq 0.30$ superconductivity is observed with a maximum T_c near $x=0.15$. Though numerous experimental and theoretical studies have been carried out on this system, the electronic structure as a function of dopant concentration, the mechanism of high- T_c superconductivity, and even the nature of the normal state for $x \sim 0.15$ still remain unclear.

In this Rapid Communication we report on changes of the electronic structure of La_2CuO_4 upon doping with Sr, which are probably essential to understand the normal-state properties of high- T_c superconductors. With increasing dopant concentration there is a continuous increase of the density of states at the Fermi level, which is located at the bottom of the gap between the ligand band and the upper Hubbard band. No discontinuity is observed close to the insulator-metal transition. This points out that this transition is driven by delocalization. The present results probably can be generalized to other cuprate systems showing high- T_c superconductivity.

O 1s absorption edges of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+\delta}$ have been measured in the concentration range $0 \leq x \leq 0.30$ by electron-energy-loss spectroscopy (EELS) in transmission. These edges probe the local unoccupied density of states with p symmetry at the O sites provided the interaction of the excited electron with the core hole is small. The latter assumption is supported, at least for metallic cuprates, by the strong similarity of O 1s absorption edges and resonant bremsstrahlung isochromat spectroscopy (BIS) spectra on $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$,⁴ and by the rather good agreement between experimental C and N 1s core-level absorption spectra with the calculated total density of

states in transition-metal carbides and nitrides.⁵ Ceramic samples were prepared as described previously.⁶ From these samples about 1000-Å-thick films were cut with an ultramicrotome using a diamond knife. The EELS measurements were performed in transmission using a dedicated 170-keV spectrometer⁷ operated with an energy resolution of 0.4 eV. We emphasize that our probing depth is the sample thickness and, therefore, our results are not influenced by surface degradations.

In Fig. 1 we show O 1s edges of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+\delta}$ close to the threshold energy for $0 \leq x \leq 0.3$. The lowest spectrum is from an undoped sample annealed at 250°C under ultrahigh vacuum conditions. The strong rise of spectral weight above ~ 531 eV is mainly related to O 2p states hybridized with La 5d and 4f states, i.e., excitations in the LaO layers (see Ref. 6). This rise remains unchanged upon doping; only a slight shift towards lower energies is observed in some annealed samples. For the annealed La_2CuO_4 sample a prepeak (labeled with C) at ~ 530.2 eV with a threshold at 529.7 eV is observed. For the nontreated undoped $\text{La}_2\text{CuO}_{4+\delta}$ sample there is some spectral weight at lower energies starting at ~ 528.2 eV. Upon doping with Sr, peak C decreases, broadens, and slightly moves towards higher energies. The spectral weight below the threshold of peak C increases forming a well-pronounced peak V near 528.7 eV for $x \geq 0.05$. In Fig. 2 we show the intensity of peak V and the decrease of intensity of peak C as a function of dopant concentration. These intensities were obtained by integrating the spectral weight up to 529.7 eV (peak V) and by integrating the difference between the $x=0$ spectrum and that with finite x between 529.7 and 531 eV. For both, an almost linear relationship is observed. Deviations are caused by excess O and O deficiency of the samples for low ($x \leq 0.05$) and high ($x=0.30$) dopant concentration, respectively. The slope for peak V is about five times larger than that for peak C.

The prepeak C is assigned to transitions into unoccupied O 2p states admixed to the conduction band. The wave function of this band in the ground state can be written in the form $|\Psi\rangle = \alpha|d^9\rangle + \beta|d^{10}\underline{L}\rangle$, where $|\alpha|^2$ determines the number of 3d holes and $|\beta|^2$ the admixture of empty O 2p states (ligand holes are denoted by \underline{L}). The intensity of peak C is therefore a measure of covalency of the Cu-O bond. Assuming that peak V is due to hole

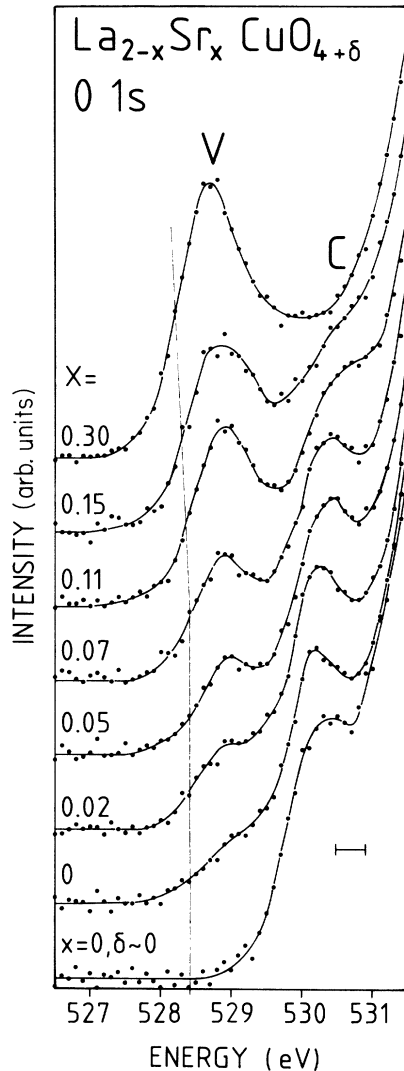


FIG. 1. O 1s absorption edges of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+\delta}$ for $0 \leq x \leq 0.3$ measured by electron-energy-loss spectroscopy. For $x=0$, spectra for $\delta \sim 0$ and 0.015 are shown. The energy resolution (0.4 eV) is shown in the right-hand-side lower corner.

states produced by p -type doping⁶ and that one Sr atom induces about one hole having predominantly O 2p character, from the slope of intensity V vs x and from the intensity in the energy range from 529.7 to 531 eV (peak C) for $x=0$ one may estimate the admixture of O 2p states to the upper Hubbard band. Since considerable spectral weight of this band may be hidden below the spectral weight due to the LaO layers ($E > 531$ eV), we can only estimate lower limits of 10% for the O 2p admixture, and 1 eV for the width of the conduction band, respectively. The width may be close to a value estimated from the relation⁸ $W \sim 4t_{pd}^2/\Delta \sim 2.5$ eV, where $t_{pd} \sim 1.5$ eV is the hopping integral between Cu and O and $\Delta \sim 3.5$ eV is the charge-transfer energy.⁹ We mention that prepeak C has been observed in other insulating cuprates such as CuO , $\text{YBa}_2\text{Cu}_3\text{O}_6$, Nd_2CuO_4 , $\text{Ca}_{0.86}\text{Sr}_{0.14}\text{CuO}_2$, and $\text{La}_2\text{SrCu}_2\text{O}_6$, as well.¹⁰ There is a systematic variation of the threshold energy as a function of the Cu-O distance, i.e.,

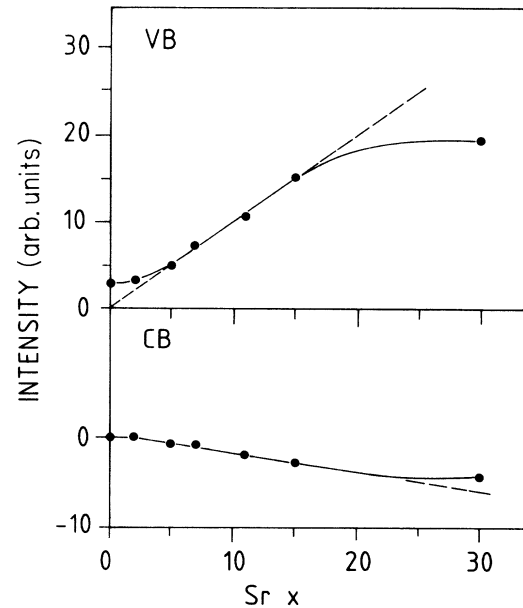


FIG. 2. Intensity of peak V and peak C of Fig. 1 as a function of dopant concentration x .

on the covalency of the Cu-O bond.¹¹

The spectral shape of prepeak V , and in particular the observed edge (for $x > 0$) with a width of about 0.8 eV (bottom to top), can be explained in a first approximation by a convolution of the experimental resolution (0.4 eV) and the lifetime broadening of ~ 0.2 eV of the O 1s state with an edge followed by a decreasing or increasing density of states for high or low doping concentration, respectively. The position of the edge, which is indicated by a dashed line in Fig. 1, is close to 528.4 eV for $x \leq 0.11$ and then slightly moves by 0.3 eV towards lower energy for $x = 0.30$. This threshold value is close to the O 1s binding energy relative to the Fermi level $E_F = 528.5$ eV measured by x-ray-induced photoemission spectroscopy,¹² as expected for a metal. The threshold of peak V is about 1.5 eV lower than the threshold of peak C , a value close to the gap measured by optical spectroscopy ($E_g \sim 1.7$ eV).¹³ This indicates that the Fermi level for the doped samples is at the bottom of the gap close to the valence band. The observation of states in the gap for the untreated $x=0$ compound is explained by the fact that this sample has some excess O ($\delta \sim 0.015$) leading to a finite p -type doping. As mentioned in Ref. 3, this excess oxygen can be removed by vacuum annealing leading to an increase of the Néel temperature. This is consistent with our observation of a strong reduction of states in the gap upon vacuum annealing (see Fig. 1, lowest spectrum). It is interesting to note that upon vacuum annealing a sample with $x=0.05$, the intensity of peak V decreases, the spectrum being identical to that observed for untreated $x=0.02$ samples. This demonstrates the equivalence of p -type doping by excess O or replacement of La by Sr. The present measurements clearly show that already in the insulating range ($x \leq 0.06$) there is a broad distribution of states in the gap. With increasing dopant concentration the density of states at the Fermi level increases continuously. There is

no discontinuity between $x=0.05$ and 0.07 at the insulator-metal transition. With the present energy resolution of 0.4 eV, which is much larger than thermal energies, no first-order transition at the insulator-metal transition near $x=0.06$ could be detected. Probably for $x \leq 0.05$ the states at E_F are localized, e.g., by the potential of the disordered Sr ions, and for higher concentrations the insulator-metal transition is driven by delocalization of these states. They do not belong to a narrow impurity band. Rather, the valence states merge more and more across the Fermi level (which remains almost at constant energy) into the gap, thus forming hole states. This is confirmed by photoemission experiments¹⁴ which measure the occupied states. In the present data the Fermi level slightly moves into the valence band (ligand band) only at the highest doping concentrations $x \geq 0.15$. For $x=0.3$ there is no clear evidence for a further existence of peak *C*. This may indicate a transition from a highly correlated system for $x \leq 0.15$ to a less-correlated system for $x \geq 0.30$. The width of the unoccupied part of the valence band is about 2 eV. This value is close to that derived from band-structure calculations in the local-density approximation,¹⁵ however, the experimental spectral shape is quite different from the calculated one.

In addition, we mention that the situation in the system $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+\delta}$ is quite different from Li-doped NiO, although similar O $1s$ absorption spectra have been observed.¹⁶ In the latter system localized unoccupied impurity states were observed which have no overlap with the valence band thus exhibiting no insulator-metal transition upon doping.

The simplest explanation for the states in the gap formed upon doping would be a shift of valence-band states into the gap by the potential of neighboring Sr atoms. Then, however, narrow impurity states or bands would be expected for low doping concentration which are not observed in the present experiments. Therefore, this explanation for gap states is very unlikely.

There are various theoretical models for CuO_2 planes predicting the formation of states upon doping in the gap. In particular, we mention cluster calculations in the Emery model¹⁷ and the Anderson lattice model using a slave boson representation.^{18,19} These calculations indicate that the Fermi level is at the bottom and at the top of the gap upon p - or n -type doping, respectively. Furthermore, these models show a reduction of conduction- (and/or valence-) band states upon doping which is clearly seen in the present measurements. There may be other explanations for the intensity reduction of peak *C*, e.g., a reduction of excitonic effects in the insulating compound upon

doping which would lead to a broadening and a shift towards higher energies. Furthermore, final-state effects hybridizing the conduction-band states with the ligand band may explain the reduction of peak *C*.^{16,20} As mentioned above, for the p -type doped system $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+\delta}$ we realized a pinning of the Fermi level close to the top of the valence band. It is remarkable that for the n -type doped systems O $1s$ absorption spectra^{10,11} indicate a pinning of the Fermi level close to the bottom of the conduction band and no formation of a narrow, partially filled impurity band. From this impurity band an additional prepeak at lower energy is expected in the O $1s$ absorption edges of n -type doped systems. The spectral weight of this prepeak should have at least 15% of that of peak *C* when assuming the same O $2p$ admixture for the upper Hubbard band and the impurity band. The measured spectra show no intensity in the relevant energy range within a limit of 2% of peak *C*, thus strongly arguing against the formation of a partially filled impurity band upon n -type doping. This is further supported by x-ray photoemission spectroscopy (XPS) measurements of the O $1s$ binding energy E_B relative to E_F in n -type doped systems.^{21,22} For the "undoped" (but probably slightly n -type doped) system and for the n -type doped system, the same O $1s$ binding energy $E_B \sim 528.9$ eV and the same O $1s$ threshold energy $E_{th} \sim 528.6$ eV have been observed. This indicates that for n -type doping the Fermi level is pinned close to the bottom of the conduction band. These findings on the difference of the position of the Fermi level between p - and n -type doped systems are at variance with recent photoemission data¹⁴ which postulate that there is no shift of the Fermi level when going from p - to n -type doping. However, Ref. 14 is in line with our observation that the shift of E_F on the amount of either p - or n -type doping is small.

Finally, we mention recent optical measurements¹³ on the system $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ yielding upon doping transitions in the gap and a reduction of charge-transfer transitions. However, these data are less conclusive for the formation of gap states. The gap transitions may also be explained by intraband transitions into the holes of the valence band, formed upon doping. In addition, using an oscillator strength sum rule both intraband transitions into hole states and transitions into gap states should reduce charge-transfer excitations.

In this contribution we focused on the evolution of the electronic structure of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+\delta}$ as a function of dopant concentration. It would be interesting to extend these investigations to higher doping levels where Hall effect measurements indicate n -type conductivity.

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