RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 44, NUMBER 21 1 DECEMBER 1991-I

Evidence of chemical-potential shift with hole doping in $Bi_2Sr_2CaCu_2O_{8+\delta}$

Z.-X. Shen, D. S. Dessau, and B. O. Wells
Stanford Electronics Laboratory, Stanford University, Stanford, California 94305

C. G. Olson
Ames Laboratory, Iowa State University, Ames, Iowa 50011

D. B. Mitzi* and Lou Lombado
Department of Applied Physics, Stanford University, Stanford, California 94305

R. S. List† and A. J. Arko
Los Alamos National Laboratory, Los Alamos, New Mexico 87545

(Received 30 May 1991; revised manuscript received 30 September 1991)

We have performed photoemission studies on high-quality $Bi_2Sr_2CaCu_2O_{8+\delta}$ samples with various δ. Our results show a clear chemical-potential shift (0.15–0.2 eV) as a function of doping. This result and the existing angle-resolved-photoemission data give a rather standard doping behavior of this compound in its highly doped regime.

Among the many interesting physical properties of the high-temperature superconductors is their doping mechanism: the superconductors are made by doping antiferromagnetic Mott insulators.[1] Much theoretical and experimental work has been carried out to understand this problem.[2–14] This includes recent spectroscopic experiments which suggest that different states develop inside the charge-transfer gap when the material is doped from an insulator to a metal.[2–8] In a conventional material where the one-electron picture works well, an important aspect of doping is a chemical-potential shift. For the high-temperature superconductors where the simple one-electron band theory is thought to have serious difficulties, it is not obvious whether one should see a chemical-potential shift as a function of doping. Experimentally, no clear evidence has been found that suggests a chemical-potential shift as a function of doping.

In this paper, we present results of our recent angle-integrated- and angle-resolved-photoemission studies of $Bi_2Sr_2CaCu_2O_{8+\delta}$ crystals with different oxygen content. Referenced to the Fermi level, both the valence band and the shallow core levels shift about 0.15–0.2 eV with the oxygen content change. Except for this shift, the line shape of the valence band, the shallow core levels, and even the background were remarkably similar. This result can be best interpreted as a chemical-potential shift of about 0.15–0.2 eV with doping. If this interpretation is true, then this result is the first clear evidence for a chemical-potential shift in the cuprate superconductors as a function of doping.

A series of high-quality single crystals of $Bi_2Sr_2CaCu_2O_{8+\delta}$ were prepared for the photoemission experiments. The uniform hole doping of the sample is achieved by annealing the sample at different oxygen partial pressures. The high quality of the doping process is reflected by the fact that neither the width nor the strength of the Meissner transition was adversely affected (2 K for 10%–90%).[15] The samples which yield the data in Fig. 1 were annealed in Ar atmosphere ($T_c = 89$ K) and 12 atm O_2 ($T_c = 77$ K), while the samples which yield the data in Fig. 2 were as-grown ($T_c = 89$ K) and annealed in 12 atm O_2 ($T_c = 81$ K).

The photoemission experiments were performed at the Stanford Synchrotron Radiation Laboratory (SSRL) and the Synchrotron Radiation Center (SRC). The angle-integrated-photoemission experiments were performed on the new 4° grasshopper beamline at SSRL in a Varian chamber with a cylindrical mirror analyzer (CMA). The base pressure of the chamber was 1×10^{-10} torr, and total-energy resolution of the setup was about 350 meV at 120-eV photon energy. The single crystals were cleaved and kept at 80 K for the experiment. The angle-resolved-photoemission experimental setup was the same as those reported elsewhere.[16] The total system resolution was 100 meV for the full valence-band scans. The crystals were cleaved at low temperature (20 K) at a base pressure of 5×10^{-11} torr. Samples were warmed up to ~ 100 K in order to do the experiments in the normal state. The Fermi level of the spectrometer was periodically determined by the Pt metal reference spectra.

Figure 1 presents 120-eV photon energy distribution curves of the valence band and some shallow core levels for two $Bi_2Sr_2CaCu_2O_{8+\delta}$ samples with different oxygen contents. The spectra taken from the two samples are almost identical except for $a \sim 0.15$–0.2 eV shift. Referenced to the Fermi level, the valence-band and core-level features of the high oxygen (hole) content sample shift to lower binding energy with respect to the low oxygen content sample. The Fermi levels of the two samples are the same since they are grounded to the photoelectron spectrometer. The best explanation for this observation is that the chemical potential of the more hole doped sample is lower, just as one would intuitively expect. If this interpretation of the data is correct, then the result in Fig. 1 is the first clear evidence for a chemical-potential shift in the cuprate superconductors as a function of doping. The fact

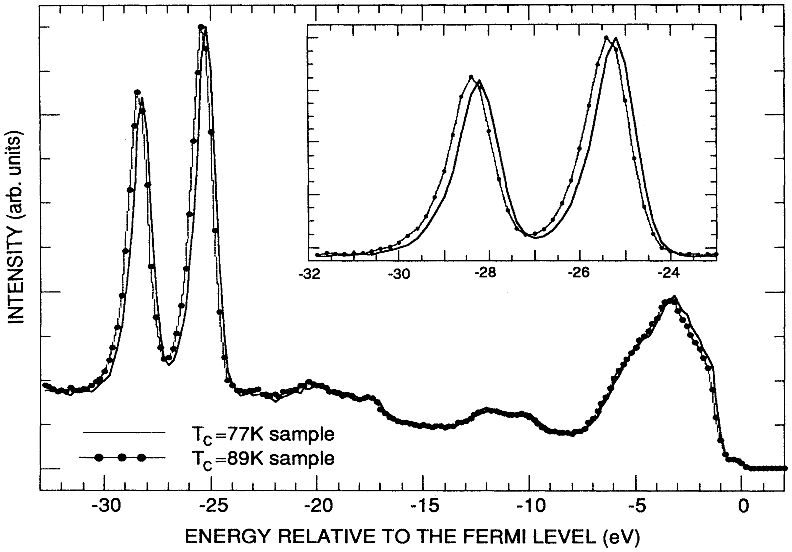

FIG. 1. Angle-integrated-photoemission data from an Ar-annealed sample (dots) and a 12 atm O_2-annealed sample (line) at photon energy of 120 eV. Referenced to the Fermi level, the core levels, the valence band, and even the background of the two samples were remarkably well reproduced except an approximately 0.15–0.2 eV shift. These data clearly indicate a chemical-potential shift as a function of doping: for the oxygen-annealed (hole doped) sample, the chemical potential is lowered.

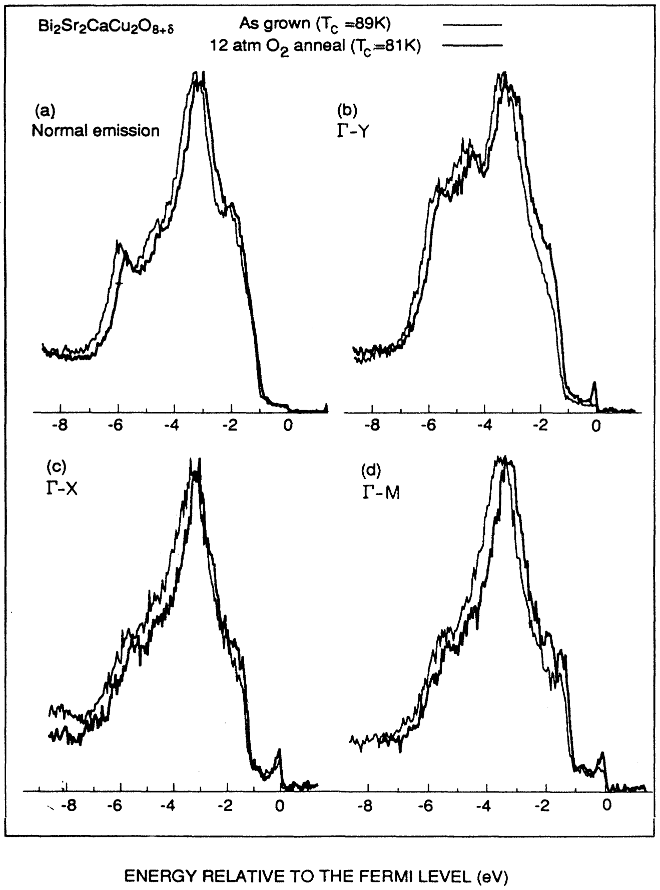

FIG. 2. Angle-resolved-photoemission data from an as-grown (light line) and a 12 atm O_2-annealed $Bi_2Sr_2CaCu_2O_{8+\delta}$ single crystal at different parts of the Brillouin zone. The photon energy used here is 19 eV.

that the spectra from the two samples are so similar and the shift is seen in all the features gives us confidence about our interpretation. From these data, we estimate that the chemical potentials of the two samples are shifted by approximately 0.15–0.2 eV as is seen more clearly in the inset of Fig. 1. Although the shift of the valence band might be larger than that of the core level by a very small amount, it is fair to say that the core-level and the valence-band data give the same amount of Fermi-level shift (~0.15–0.2 eV) within our experimental uncertainty.

We have also observed similar results in our angle-resolved-photoemission data. Figure 2 shows results of our angle-resolved-photoemission spectra for the as-grown (thin line) and 12 atm O_2-annealed (thick line) samples. The four sets of data spectra are taken at different parts of the Brillouin zone: normal emission, near where the first band (with the lowest binding energy) crosses E_F along Γ-Y, near where the first band crosses E_F along Γ-X, and near where the first band crosses E_F along Γ-M. Besides some small line-shape changes, the main valence-band features of the 12 atm oxygen-annealed sample shift about 0.2 eV towards the Fermi level. The fact that the shift shows up for all directions sampled is important, as we cannot resolve individual bands in the mixture of bands which comprise the main valence band. Such changes for any particular direction may be explained by matrix element effects or energy dispersion. However, the fact we see such a shift in all sampled directions and the fact that the line shapes of the spectra of the two samples are so similar makes the chemical-potential shift the only sensible explanation of the experimental data. Furthermore, the fact we can reproduce the same result in different experimental setups is also very suggestive that the chemical-potential shift is the correct interpretation of our data.

This amount of chemical-potential shift with doping by annealing our samples in oxygen is also consistent with the estimations from the oxygen content change. The change of oxygen content from as-grown Ar-annealed samples to 12 atm oxygen-annealed samples is about 0.06 per cell.[15] Assuming the oxygen has a valence of 2− and using 2.88 $\text{eV}^{-1}\text{cell}^{-1}$ total density of states at the Fermi level from a band calculation,[17] we anticipate about 0.1-eV chemical-potential shift. If we use the density of states, which is at most half the value of the band calculation as measured by angle-integrated photoemission,[18] we expect at least a 0.2-eV chemical-potential shift. On the other hand, if we use the density of states which is two times the value of the band calculation as indicated by the magnetic-susceptibility measurement or the effective band mass from angle-resolved photoemission,[15,19] we anticipate a 0.05-eV chemical-potential shift. Given the crudeness of these estimations, we think the results of these estimations are consistent with the observed of about 0.15–0.2-eV chemical-potential shift.

In addition to the chemical-potential shift, the $Bi_2Sr_2CaCu_2O_{8+\delta}$ compound also exhibits other interesting behavior with doping. First of all, we notice in Fig. 2 that the spectral intensity near E_F increases as the hole doping increases (O_2 partial pressure increases). However, one should be cautious in drawing conclusions about the density of states from angle-resolved-photoemission data. In the angle-integrated-photoemission data, we do not see such a spectral weight increase near E_F with hole doping. The problem with our angle-integrated-photoemission data might be the relatively poor energy resolution so that we do not really know what happens very close to the Fermi level. It is also possible that the photon energy we used for the angle-integrated data has a very small photoionization cross section for the states affected by doping. Therefore, our photoemission data do not provide definitive information about the density of states near E_F as a function of doping. From other measurements, there are reasons to believe that the density of states near E_F increases as a function of hole doping in this system: (i) From Pauli susceptibility and Hall-effect measurements on the samples (see Table I), we found that the density of states at E_F increases with doping;[15] (ii) from earlier angle-integrated-photoemission and x-ray-absorption work on the $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+\delta}$ system where the doping range is larger, it was found that states develop at E_F with an increase of hole-doping.[8] (iii) A similar trend was also observed in other hole-doped cuprates.[3,4]

We have also made efforts to investigate the possible Fermi-surface changes as a function of doping. Our data are inconclusive about whether there is a change of Fermi surface accompanying the chemical-potential shift as a function of doping. This uncertainty is likely to be caused by the relatively poor momentum resolution (about 10%). Earlier high-resolution studies showed that the bands at E_F in various samples have a Fermi surface, which is consistent with the band Fermi surface.[19,20] We were able to provide information about the atomic origins of the bands at different parts of the Brillouin zone.[16] We demonstrated that, for the 12 atm annealed sample, the band crossing the Fermi level along Γ-Y has mainly Cu-O character, while the band crossing the Fermi level along Γ-M has more Bi-O character. These findings are consistent with the Fermi-surface predicted by the band calculation, implying that the Luttinger theorem is obeyed.

TABLE I. Results of magnetization and Hall effects measurements for the samples used in the photoemission experiments (Ref. 15). χ_{Pauli} is the Pauli susceptibility (units of 10^{-7} cm^3/g). $g(E_F)$ is obtained from χ_{Pauli} by $\chi_{\text{Pauli}}=\mu_b^2 g(E_F)$ (units of states per eV Cu site). n_H is the carrier density measured by Hall-effect measurement.

Sample	χ_{Pauli}	$g(E_F)$	n_H (207 K)
No anneal	4.3	6.1	$3.1\times10^{21}\ \text{cm}^{-3}$
N atm	4.9	6.9	$3.7\times10^{21}\ \text{cm}^{-3}$
12 atm	5.2	7.2	$4.6\times10^{21}\ \text{cm}^{-3}$

Therefore, we now have the following picture of doping for metallic $Bi_2Sr_2CaCu_2O_{8+\delta}$: (i) The chemical-potential shifts with hole doping; (ii) the spectral weight at E_F increases with hole doping; (iii) the Fermi-surface obeys the Luttinger theorem. This rather normal doping behavior in the metallic $Bi_2Sr_2CaCu_2O_{8+\delta}$ can be quite well accounted for by the renormalized band approaches,[9–14] and is significantly different from an earlier result nearer the insulating regime where a very minimal chemical-potential shift was observed as opposed to what one would intuitively expect.[21] We are not sure what the mechanism is that causes the difference between the results of the insulating regime and the metallic regime. However, we speculate that the following scenarios are possible explanations. First, it is generally accepted that the undoped parent compound in the insulating regime is not a Fermi liquid while the system will eventually become a Fermi liquid when it is sufficiently doped. The fact that the superconducting-transition temperature T_c drops with the increase of the hole doping in our samples indicates that we are in a high-doping regime. The normal doping behavior from our photoemission data seems to suggest that the $Bi_2Sr_2CaCu_2O_{8+\delta}$ samples are in a doping regime where some aspects of the Fermi-liquid description have been recovered. Second, the earlier result was obtained by comparing photoemission spectra from $La_{2-x}Sr_xCuO_4$ (p type) and $Nd_{2-x}Ce_xCuO_4$ (n type) materials. The electronic-structure difference in these two compounds may not be a necessary equivalent to that of a single compound doped (hypothetically) from p type to n type.

To summarize, we found that the chemical-potential shifts with doping in metallic $Bi_2Sr_2CaCu_2O_{8+\delta}$. This result is very different from the earlier result in the insulating regime.

We thank D. King, D. Marshall, and E. Ratner for experimental help. We would like to thank Professor W. E. Spicer, Professor A. Kapitulnik, Professor R. M. Martin, Professor S. Doniach, and Professor J. W. Allen for helpful discussions. Experiments were performed at SSRL and SRC, which are funded by DOE under Contracts No. DE-AC03082 and No. ER-13000, and by NSF under Contract No. DMR-86-01349. The Stanford work is funded by NSF Grant No. DMR89-13478, NSF Grant No. DMR-21735-A2 through the Center for Material Research at Stanford, and JSEP Contract No. DAAL-0338-C0011. The Ames Laboratory is operated for the U.S. DOE by Iowa State University under Contract No. W-7405-ENG-82. The Los Alamos National Laboratory is operated for DOE by the University of California.

---

[*] Present address: IBM Thomas J. Watson Research Center, Yorktown Heights, NY 10598.

[†] Present address: Texas Instruments Central Research Laboratory, Mail Stop 154, P. O. Box 655936, Dallas, TX 75265.

[1] J. B. Torrance *et al.*, Phys. Rev. Lett. **61**, 1127 (1988); Phys. Rev. B **40**, 8872 (1989), and references therein.

[2] *High Temperature Superconductors—Electronic Structure,* edited by A. Bianconi and A. Marceli (Pergamon, New York, 1989).

[3] N. Nücker *et al.*, Phys. Rev. B **37**, 5158 (1988).

[4] A. J. Arko *et al.*, Phys. Rev. B **40**, 2268 (1989); B. W. Veal *et al.* (unpublished).

[5] H. Matsuyama *et al.*, Physica C **161**, 567 (1989).

[6] G. A. Tomas *et al.*, Phys. Rev. Lett. **61**, 1313 (1988).

[7] R. T. Collins *et al.*, Phys. Rev. B **39**, 6571 (1989).

[8] T. Takahashi, in *Correlation and Superconductivity,* edited by H. Fukuyama, S. Maekawa, and A. P. Alexis, Springer Series in Solid-State Sciences Vol. 89 (Springer-Verlag, Berlin, 1989), p. 311.

[9] M. Tachiki, in *Correlation and Superconductivity* (Ref. 8), p. 138; and (unpublished).

[10] D. M. Newns, M. Rasolt, and P. C. Pattnaik, Phys. Rev. B **38**, 6650 (1988).

[11] C. A. R. Sáde Melo and S. Doniach, Phys. Rev. B **41**, 6633 (1989).

[12] B. H. Brandow, Solid State Commun. **69**, 915 (1989); but with the relative energy positions is very different from those in Ref. 2.

[13] Qimiao Si, Jian Ping Lu, and K. Levin, Physica C **162–164**, 1467 (1989).

[14] J. Zannan and Olle Gunnarsson, Physica C **162–164**, 821 (1989).

[15] D. B. Mitzi *et al.*, Phys. Rev. B **41**, 6564 (1990).

[16] B. O. Wells, Z.-X. Shen, D. S. Dessau, W. E. Spicer, C. G. Olson, D. B. Mitzi, A. Kapitulnik, R. S. List, and A. J. Arko, Phys. Rev. Lett. **65**, 3056 (1990).

[17] H. Krakauer and W. E. Pickett, Phys. Rev. Lett. **60**, 1665 (1988).

[18] Z.-X. Shen, P. A. P. Lindberg, I. Lindau, W. E. Spicer, C. B. Eom, and T. H. Geballe, Phys. Rev. B **38**, 7152 (1988).

[19] C. G. Olson *et al.*, Science **245**, 731 (1989).

[20] R. Manzke *et al.*, Europhys. Lett. **9**, 477 (1989).

[21] J. W. Allen *et al.*, Phys. Rev. Lett. **64**, 595 (1990).