



ELSEVIER

Journal of Physics and Chemistry of Solids 63 (2002) 1069–1072

JOURNAL OF  
PHYSICS AND CHEMISTRY  
OF SOLIDS

www.elsevier.com/locate/jpcs

# Zn-substitution effects on the low-energy quasiparticles in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ studied by angle-resolved photoemission spectroscopy

S. Nishina<sup>a</sup>, T. Sato<sup>a</sup>, T. Takahashi<sup>a,\*</sup>, S.-C. Wang<sup>b</sup>,  
H.-B. Yang<sup>b</sup>, H. Ding<sup>b</sup>, K. Kadowaki<sup>c</sup>

<sup>a</sup>Department of Physics, Tohoku University, 980-8578 Sendai, Japan

<sup>b</sup>Department of Physics, Boston College, Chestnut Hill, MA 02467, USA

<sup>c</sup>Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305-3573, Japan

## Abstract

We have performed high-resolution angle-resolved photoemission spectroscopy on  $\text{Bi}_2\text{Sr}_2\text{Ca}(\text{Cu}_{1-x}\text{Zn}_x)_2\text{O}_{8+\delta}$  ( $x = 0.0, 0.05$ ) to study the Zn-substitution effects on the low-energy quasiparticles. We found that the Zn substitution causes the reduction of the quasiparticle intensity and the superconducting gap, while it does not affect the normal-state band dispersion, the Fermi surface, or the quasiparticle lifetime. This indicates that the Zn substitution locally destroys or hinders the superconducting pairing and as a result decreases the superfluid density, but does not affect the long-range coherence among quasiparticles. © 2002 Elsevier Science Ltd. All rights reserved.

**Keywords:** A. Oxides; C. Photoelectron spectroscopy; D. Superconductivity

## 1. Introduction

It is well known but surprising that only a few percent Zn impurity in the cuprate high-temperature superconductors (HTSCs) drastically suppresses the superconductivity, while such a non-magnetic impurity does not so strongly affect the superconductivity in the conventional BCS superconductors. The role of the non-magnetic impurity in the cuprate HTSCs has been intensively studied in relation to the origin of the high-temperature superconductivity. The transport and microwave studies on the Zn substitution in  $\text{CuO}_2$  planes show that Zn acts as a very strong scatterer of carriers, thereby increasing the in-plane residual resistivity [1,2] and drastically modifies the low-energy charge dynamics [3]. A remarkable suppression of the superfluid density by the Zn substitution has been also observed by the  $\mu\text{SR}$  experiment [4]. All these experimental results suggest that the low-energy electron dynamics, namely the

quasiparticle, is strongly influenced by the Zn substitution. In return, the Zn substitution may serve as a useful tool to study the quasiparticle behavior and consequently the superconducting mechanism in HTSCs. Angle-resolved photoemission spectroscopy (ARPES) is a unique and powerful experimental technique to study the momentum-resolved electronic structure of materials. A recent remarkable improvement in the energy and momentum resolution enables a direct observation of quasiparticles in HTSCs [5,6] and ARPES results are now intensively discussed in comparison with the superfluid density [7,8], the in-plane resistivity [5], and the optical conductivity [6] to study the low-energy electron dynamics.

In this paper, we report a comparative ARPES study on Zn-substituted  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  ( $\text{Bi}2212$ ) to address the microscopic mechanism of Zn substitution in suppressing the superconductivity. We have studied the Zn-substitution effects on the normal-state electronic structure (band dispersion and Fermi surface) as well as the superconducting properties such as the superconducting gap and the superconducting quasiparticles. We discuss the ARPES results in comparison with the in-plane resistivity [1,2], the superfluid density [4], and the scanning tunneling spectroscopy (STS) results [9].

\* Corresponding author. Tel.: +81-22-217-6417; fax: +81-22-217-6419.

E-mail address: t.takahashi@msp.phys.tohoku.ac.jp (T. Takahashi).

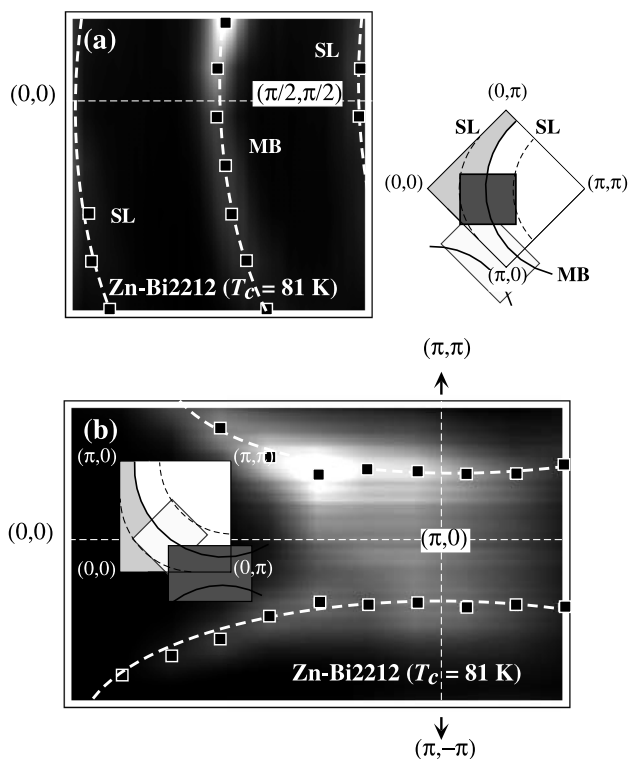


Fig. 1. ARPES intensity plot near  $E_F$  for Zn-substituted  $\text{Bi}_2\text{Sr}_2\text{Ca}(\text{Cu}_{1-x}\text{Zn}_x)_2\text{O}_{8+\delta}$  around (a)  $(\pi/2, \pi/2)$  and (b)  $(\pi, 0)$  points in the Brillouin zone. The ARPES spectral intensity was integrated in the binding-energy range of  $\pm 20$  and  $\pm 50$  meV with respect to  $E_F$  for (a) and (b), respectively. The  $k_F$  points (Fermi surface) obtained by the minimum gap locus method [10] as well as by the MDC curves are shown with filled squares. MB and SL represent the main-band and the super-lattice band, respectively.

## 2. Experimental

High-quality single crystals of  $\text{Bi}_2\text{Sr}_2\text{Ca}(\text{Cu}_{1-x}\text{Zn}_x)_2\text{O}_{8+\delta}$  ( $x = 0.0$  and  $0.05$ ) were grown by the traveling solvent floating zone method. The Zn concentration is the nominal value in the starting composition of single-crystal growth. The superconducting transition temperature determined by SQUID is 91 and 81 K for  $x = 0.0$  and  $0.05$ , respectively. The steep superconducting transition ( $\Delta T < 2$  K) confirms the high-quality of the crystals.

ARPES measurements were performed using a SCIENTA SES-200 spectrometer with a high-flux discharge lamp and a toroidal grating monochromator. We used the He I $\alpha$  resonance line (21.218 eV) to excite photoelectrons. The energy and angular (momentum) resolutions were set at 11–15 meV and  $0.2^\circ$  ( $0.007 \text{ \AA}^{-1}$ ), respectively. The Fermi level ( $E_F$ ) of the sample was referenced to a gold film evaporated onto the sample substrate.

## 3. Results and discussion

Fig. 1 shows the Fermi surface of  $\text{Bi}_2\text{Sr}_2\text{Ca}(\text{Cu}_{1-x}\text{Zn}_x)_2\text{O}_{8+\delta}$  ( $x = 0.05$ ) around the  $(\pi/2, \pi/2)$  and  $(\pi, 0)$  points in

the Brillouin zone, derived from the present ARPES measurements. The ARPES intensity near  $E_F$  is plotted as a function of momentum in Fig. 1, where the bright areas (lines) correspond to the Fermi surface. In Fig. 1(a), we find a strong bright line almost perpendicular to the  $(0,0)$ – $(\pi, \pi)$  line together with two weak lines; the strong bright line corresponds to the main-band Fermi surface and the weak lines are the super-lattice replicas. It is clear in Fig. 1(b) that two main-band Fermi surfaces, which smoothly connect to the main-band Fermi surface around  $(\pi/2, \pi/2)$  point (Fig. 1(a)), do not touch each other even around the  $(\pi, 0)$  point with keeping a finite distance between the two. This definitely indicates that the Fermi surface is hole-like as in the Zn-free Bi2212 [11,12]. Furthermore, the  $k_F$  values on the two high-symmetry lines,  $(0,0)$ – $(\pi, \pi)$  and  $(\pi, 0)$ – $(\pi, \pi)$ , are the same as those of the Zn-free Bi2212 within the experimental accuracy ( $\pm 0.01\pi$ ). All these clearly indicate that the Zn substitution does not alter the Fermi surface topology or the Fermi surface volume. In other words, Zn does not add additional holes or electrons in the system [13]. In the following, we discuss the present ARPES results based on this experimental fact that the doping level is the same between the Zn-free and the Zn-substituted Bi2212 samples.

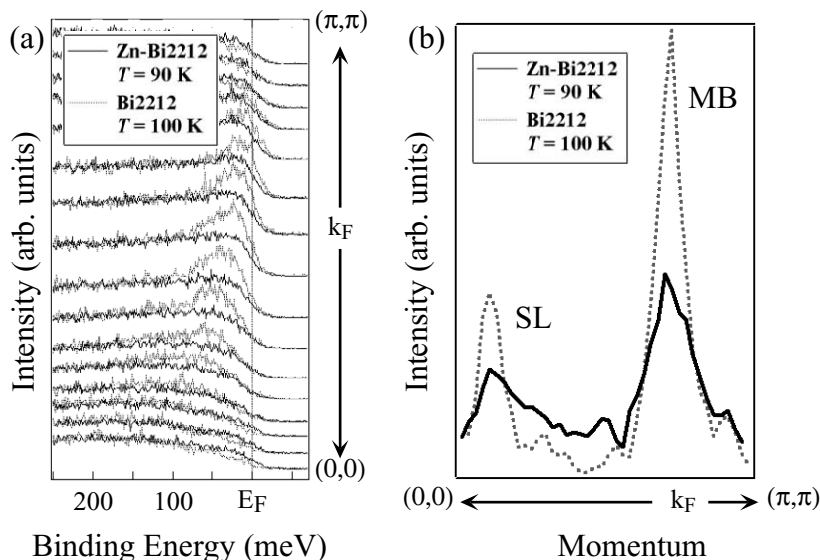


Fig. 2. Comparison of (a) the normal-state ARPES spectra along the  $(0,0)$ – $(\pi,\pi)$  cut and (b) the MDC curve at  $E_F$  between the Zn-free and the Zn-substituted Bi2212.

Fig. 2(a) shows comparison of the normal-state ARPES spectra near  $E_F$  along the  $(0,0)$ – $(\pi,\pi)$  cut between the Zn-free and Zn-substituted Bi2212 samples. We find that the spectral intensity near  $E_F$  is remarkably reduced in the Zn-substituted Bi2212, although the gross dispersive feature as well as the  $E_F$ -crossing point ( $k_F$ ) looks the same between the two. It is also noted that the change in the spectral intensity by the Zn substitution is remarkable near  $E_F$  ( $E_F$ –150 meV binding energy) in the energy range and also near the  $k_F$  point in the momentum range. This suggests that Zn affects more effectively the superconducting quasiparticles. Fig. 2(b) shows comparison of the momentum distribution curve (MDC) spectra at  $E_F$  between the Zn-free and Zn-substituted Bi2212. A MDC spectrum is defined as an ARPES spectral intensity curve as a function of momentum at a fixed binding energy and is complementary to a usual ARPES spectrum, which is defined as an ARPES intensity curve as a function of binding energy at a fixed momentum. As clearly seen in Fig. 2(b), the MDC spectrum at  $E_F$  is slightly broader in the Zn-substituted sample. This suggests that the scattering rate  $\Gamma$ , which is inversely proportional to the lifetime of quasiparticle, is larger in the Zn-substituted sample. Since the in-plane transport is dominated by the low-energy excitation along the nodal direction, the increase of the  $\Gamma$  value as well as the remarkable suppression of the spectral intensity by the Zn substitution shows a good correspondence to the reported increase of the in-plane residual resistivity by the Zn substitution [1,2].

Next we discuss the effect of the Zn substitution on the electronic structure in the superconducting state. In Fig. 3, we plot the ARPES intensity as a function of binding energy and momentum for the Zn-substituted Bi2212, measured

along the  $(0,0)$ – $(\pi,\pi)$  cut at 40 K and the  $(\pi,0)$ – $(\pi,\pi)$  cut at 13.5 K. Fig. 3 also shows comparison of the ARPES spectra near  $E_F$  measured at two Fermi momenta ( $k_F$ ) along the  $(0,0)$ – $(\pi,\pi)$  and  $(\pi,0)$ – $(\pi,\pi)$  cuts between the Zn-free and Zn-substituted samples in the superconducting state. In the  $(0,0)$ – $(\pi,\pi)$  cut a ‘kink’ structure at 70–80 meV is clearly seen in the band dispersion, while the band is almost dispersionless in the  $(\pi,0)$ – $(\pi,\pi)$  direction, showing a large superconducting gap of about 40 meV. These overall features are essentially the same as in the Zn-free Bi2212. However, the direct comparison of the ARPES spectra at  $k_F$  (Fig. 3(c)) reveals several definite Zn-substitution effects on the ARPES spectra in the superconducting state. Firstly, the intensity of the superconducting quasiparticle peak at/near  $E_F$  is remarkably reduced by the Zn substitution, while the spectral features at the higher binding energy look unchanged.<sup>1</sup> This suggests that Zn in Bi2212 destroys or hinders the superconducting pairing and as a result reduces the superfluid density [7,8]. In fact, the observed reduction of quasiparticle weight by the Zn substitution (about 40%) is quantitatively consistent with the  $\mu$ SR measurement for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  [4], which has reported a 25–40% reduction in the  $c$ -axis superfluid density by the Zn substitution. Secondly, we find in Fig. 3(c) that the superconducting quasiparticle peak at the  $(\pi,0)$ – $(\pi,\pi)$  crossing is slightly shifted toward  $E_F$  by the Zn substitution. Numerical fittings to the ARPES spectra showed that the superconducting gap ( $\Delta$ ) decreases from 37 meV in the Zn-free Bi2212 to 34 meV in the Zn-substituted Bi2212. However, it is noted

<sup>1</sup> Similar kink and dip energy (70–80 meV) between Zn-free and Zn-substituted Bi2212 suggest that mode energy interacting with electrons [14,15] does not alter by Zn substitution.

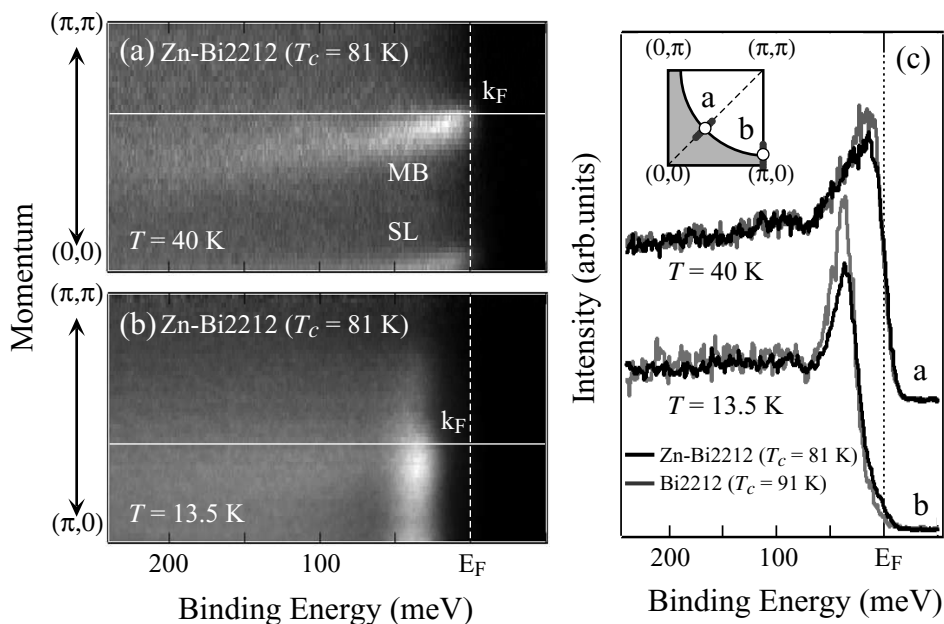


Fig. 3. ARPES intensity plot as a function of binding energy and momentum along (a)  $(0,0)$ – $(\pi,\pi)$  and (b)  $(\pi,0)$ – $(\pi,\pi)$  cuts. (c) Comparison of ARPES spectra at two  $k_F$ -points along the  $(0,0)$ – $(\pi,\pi)$  and  $(\pi,0)$ – $(\pi,\pi)$  cuts in the superconducting state.

that the  $2\Delta/k_B T_c$  value ( $= 9.6$ – $9.9$ ) is unchanged by the Zn substitution. This means that the reduction of the superconducting gap with the Zn substitution is understood simply in terms of the reduction of  $T_c$ . Thirdly, it is found in Fig. 3(c) that a small but finite ARPES intensity emerges at  $E_F$  at the  $(\pi,0)$ – $(\pi,\pi)$  crossing with the Zn substitution. This residual density of states in the superconducting gap may correspond to a sharp ‘intra-gap’ peak at the Zn site observed by the STS for Zn-substituted Bi2212 [9]. In contrast to these changes caused by the Zn substitution, the width of the superconducting coherent peak looks unchanged as seen in Fig. 3(c). This suggests that the lifetime of the superconducting quasiparticles (Cooper pairs) is not so strongly affected by the Zn substitution. Taking into account the experimental fact that the weight of the quasiparticle peak is significantly reduced by the Zn substitution, the present experimental result suggests that Zn atoms locally destroy the superconducting pairs but not the long range coherence among them.

#### 4. Conclusion

We have performed high-resolution ARPES on  $\text{Bi}_2\text{Sr}_2\text{Ca}(\text{Cu}_{1-x}\text{Zn}_x)_2\text{O}_{8+\delta}$  ( $x = 0.0, 0.05$ ) to study the Zn-substitution effects on the electronic structure at both the normal and superconducting states. We found that the normal-state electronic structure such as the band dispersions and the Fermi surface are essentially unchanged by the Zn substitution. In contrast, we observed several definite Zn-substitution effects in the superconducting state: (1) the strong suppres-

sion of the quasiparticle weight (namely the superfluid density), (2) the slight reduction of the superconducting energy gap, and (3) the emergence of the intra-gap state at/near  $E_F$ . All these suggest that Zn atoms in Bi2212 locally destroy the superconducting pairs but not the long range coherence.

#### Acknowledgements

This work was supported by a grant from the MEXT of Japan. TS thanks the Japan Society for the Promotion of Science for financial support.

#### References

- [1] Y. Fukuzumi, et al., Phys. Rev. Lett. 76 (1996) 684.
- [2] T.R. Chien, et al., Phys. Rev. Lett. 67 (1991) 2088.
- [3] D.A. Bonn, et al., Phys. Rev. B 50 (1994) 4051.
- [4] C. Bernhard, et al., Phys. Rev. Lett. 77 (1996) 2304.
- [5] T. Valla, et al., Science 285 (1999) 2110.
- [6] A. Kaminski, et al., Phys. Rev. Lett. 84 (2000) 1788.
- [7] D.L. Feng, et al., Science 289 (2000) 277.
- [8] H. Ding et al., Phys. Rev. Lett. 87 (2001) 227001.
- [9] S.H. Pan, et al., Nature (London) 403 (2000) 746.
- [10] M.R. Norman, et al., Nature (London) 392 (1998) 157.
- [11] H.M. Fretwell, et al., Phys. Rev. Lett. 84 (2000) 4449.
- [12] S.V. Borisenko, et al., Phys. Rev. Lett. 84 (2000) 4453.
- [13] H. Alloul, et al., Phys. Rev. Lett. 67 (1991) 3140.
- [14] A. Lanzara, et al., Nature (London) 412 (2001) 510.
- [15] J.C. Campuzano, et al., Phys. Rev. Lett. 83 (1999) 3709.