

Angle-resolved photoemission study of untwinned $\text{PrBa}_2\text{Cu}_3\text{O}_7$: Undoped CuO_2 plane and doped CuO_3 chain

T. Mizokawa

Department of Complexity Science and Engineering and Department of Physics, University of Tokyo, Bunkyo-ku, Tokyo 113-0033, Japan

C. Kim and Z.-X. Shen

Department of Applied Physics and Stanford Synchrotron Radiation Laboratory, Stanford University, Stanford, California 94305

A. Ino and A. Fujimori

Department of Complexity Science and Engineering and Department of Physics, University of Tokyo, Bunkyo-ku, Tokyo 113-0033, Japan

M. Goto, H. Eisaki, and S. Uchida

Department of Superconductivity, University of Tokyo, Bunkyo-ku, Tokyo 113-0033, Japan

M. Tagami, K. Yoshida, A. I. Rykov, Y. Siohara, K. Tomimoto, and S. Tajima

Superconductivity Research Laboratory, International Superconductivity Technology Center, Koto-ku, Tokyo 135-0062, Japan

(Received 14 May 1999)

We have performed an angle-resolved photoemission study on untwinned $\text{PrBa}_2\text{Cu}_3\text{O}_7$, which has low resistivity but does not show superconductivity. We have observed a dispersive feature with a band maximum around $(\pi/2, \pi/2)$, indicating that this band is derived from the undoped CuO_2 plane. We have observed another dispersive band exhibiting one-dimensional character, which we attribute to signals from the doped CuO_3 chain. The overall band dispersion of the one-dimensional band agrees with the prediction of the t - J model calculation with parameters relevant to cuprates except that the intensity near the Fermi level is considerably suppressed in the experiment. [S0163-1829(99)04541-5]

I. INTRODUCTION

In the study of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (YBCO) and its family cuprates, the physical properties of the CuO_3 chain itself have been a subject of interest as well as those of the CuO_2 plane. In particular, evidence for charge instability has been observed in the hole-doped CuO_3 chain of YBCO and its relation with superconductivity has been discussed.¹ Among the YBCO family compounds, $\text{PrBa}_2\text{Cu}_3\text{O}_7$ (PBCO) is unique in that it does not show superconductivity, while the other rare-earth substituted YBCO compounds are superconducting.² Optical studies³ have revealed that the CuO_2 plane is not doped with holes and consequently that the superconductivity is suppressed in PBCO. In order to explain the hole depletion in the CuO_2 plane, several models have been proposed. Among them, the model proposed by Fehrenbacher and Rice (FR),⁴ in which the $\text{Pr } 4f$ - $\text{O } 2p_\pi$ states trap holes from the $\text{Cu } 3d$ - $\text{O } 2p_\sigma$ band, has been most successful. It was also argued that hole transfer between the CuO_2 plane and the CuO_3 chain may play an important role.⁵ Experimental studies of the band structure of the CuO_2 plane, the CuO_3 chain, and the $\text{Pr } 4f$ state should further reveal the difference between the superconducting YBCO and nonsuperconducting PBCO.⁶ Another important and potentially even more interesting point is that, if the CuO_2 plane is undoped and the CuO_3 chain is doped as suggested by the various experimental and theoretical studies, PBCO may give us an opportunity to study a hole-doped CuO_3 chain with good one dimensionality compared to YBCO. Recently, an angle-resolved photoemission spectroscopy (ARPES) study of SrCuO_2 by Kim *et al.*⁷ has shown the spinon and holon bands of the undoped CuO_3 chain, which is a manifestation of spin-charge separation in the one-dimensional system, and has attracted much interest. However, no ARPES study of a hole-doped CuO_3 chain has been made so far. Although YBCO has been studied by ARPES,⁸ the band dispersion from the CuO_3 chain is far from being one dimensional because of the strong interaction between the chain and the plane.

In this paper, we report an ARPES study of untwinned PBCO samples that have relatively low resistivity but is not superconducting. As we show below, we observe at least two kinds of dispersive features: one from the undoped antiferromagnetic CuO_2 plane and the other, which is a highly one-dimensional band, from the doped CuO_3 chain.

II. EXPERIMENT

Single crystals of PBCO were grown in a MgO crucible by a pulling technique. The composition was determined to be $\text{Pr}_{1.02}\text{Ba}_{1.98}\text{Cu}_{2.92}\text{Mg}_{0.08}\text{O}_7$ by inductively coupled plasma analysis.⁹ Because a small amount of Mg impurities originating from the crucible are substituted preferentially for the plane Cu sites,¹⁰ it is expected that the CuO_3 chain is not affected by these impurities. Rectangular shaped samples were cut out from the as-grown crystal and annealed at 500 °C in oxygen atmosphere under uniaxial pressure. The resistivity parallel to the chain direction increases with cooling from 8 mΩ cm at 300 K up to 10 Ω cm at 10 K and that perpendicular to the chain direction increases from

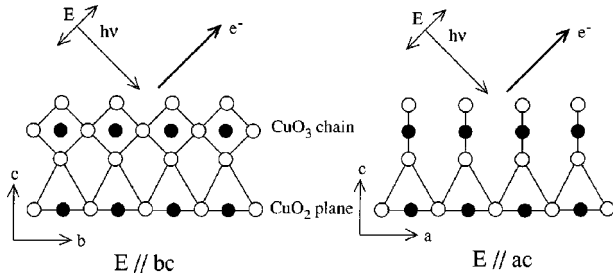


FIG. 1. $E\parallel bc$ and $E\parallel ac$ arrangements in which ARPES measurements were performed. The chains are along the b axis.

400 m Ω cm at 300 K to 70 Ω cm at 10 K. The ARPES measurements were performed using the Vacuum Science Workshop chamber attached to the undulator beamline 5-3 of Stanford Synchrotron Radiation Laboratory (SSRL). Incident photons were linearly polarized and had energy of 29 eV. The total energy resolution including the monochromator and the analyzer was approximately 40 meV. The angular resolution was $\pm 1^\circ$, which gives the momentum resolution of $\pm 0.05\pi$ at $h\nu=29$ eV. [In the text, momenta along the a and b axes are given in units of $1/a$ and $1/b$, respectively. Here, a ($=3.87$ Å) and b ($=3.93$ Å) are the lattice constants of PBCO perpendicular and parallel to the chain direction, respectively.] The chamber pressure during the measurements was less than 5×10^{-11} Torr. The samples were cooled to 10 K and cleaved *in situ*. The cleaved surface was the ab plane. Orientation of the a and b axes was done by Laue diffraction before and after the measurement. The cleanliness of the surfaces was checked by the absence of a hump at energy ~ -9.5 eV.⁸ All the spectra presented here were taken within 30 h of cleaving. We cleaved the samples three times and checked the reproducibility. As shown in Fig. 1, ARPES data were taken in two arrangements: an $E\parallel ac$ arrangement, in which the photon polarization E is in the ac plane and is perpendicular to the chain, and an $E\parallel bc$ arrangement, in which E is in the bc plane and has a component parallel to the chain. The position of the Fermi level (E_F) was calibrated with gold spectra for every measurement.

III. RESULTS AND DISCUSSION

The entire valence-band data measured at $(k_a, k_b) = (0,0)$ are shown in Fig. 2. Here, k_a and k_b are momenta along the a and b axes, respectively. The Ba 5p core levels are split into surface and bulk components as observed in YBCO,⁸ indicating that the cleaved surface is as good as that of YBCO. The peak labeled as A is intense for $E\parallel bc$, while it loses its weight for $E\parallel ac$. This strong polarization dependence indicates that peak A is derived from the CuO_3 chain and that the CuO_3 chain is well aligned at the surface. Peak A can be attributed to the nonbonding O 2p states of the CuO_3 chain.⁷ On the other hand, the intensity of peak B is insensitive to the photon polarization, indicating that it is derived from the CuO_2 plane. Peak B has energy of ~ -2.3 eV and is similar to that found in $\text{Sr}_2\text{CuO}_2\text{Cl}_2$.¹¹ As pointed out by Pothuizen *et al.*,¹¹ peak B corresponds to the nonbonding O 2p states of the CuO_2 plane.

Figure 3 shows ARPES spectra along the $(0,0)\rightarrow(\pi,\pi)$

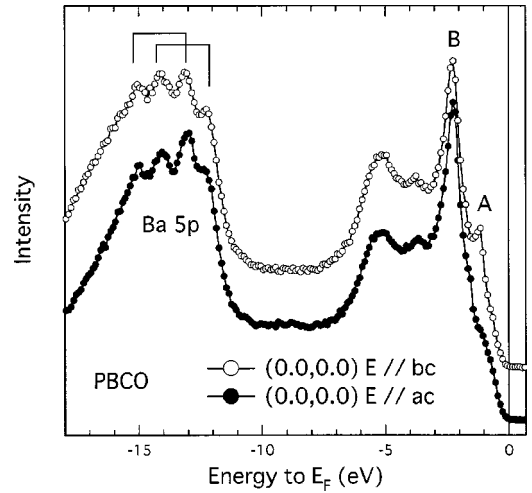


FIG. 2. Valence-band spectra taken at $(0,0)$ with $E\parallel bc$ (open circles) and with $E\parallel ac$ (closed circles).

direction and those along the $(0,\pi/2)\rightarrow(\pi,\pi/2)$ direction taken with $E\parallel ac$. The uppermost and second uppermost spectra in the left panel were taken at $(0,0)$ and $(\pi/4,\pi/4)$, respectively. The intensity from -0.2 to -0.4 eV is enhanced at $(\pi/4,\pi/4)$ compared to that at $(0,0)$. Let us denote this feature as α and discuss it in the following paragraphs. The spectra taken at $(\pi/2,\pi/2)$ are shown by the thicker solid curves and marked by the closed circles in the two panels of Fig. 3. Figure 4 shows ARPES spectra nearly along the $(0,0)\rightarrow(\pi,\pi)$ direction for $E\parallel bc$. In Fig. 4, the spectrum taken at $(\pi/2,\pi/2)$ is shown by the thicker solid curve and marked by the closed circle. In these spectra taken around $(\pi/2,\pi/2)$, a dispersive feature with a band maximum at ~ -0.4 eV is clearly seen and is labeled as β . This structure β is very similar to that found at $(\pi/2,\pi/2)$ in $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ and can be interpreted as the Zhang-Rice (ZR)

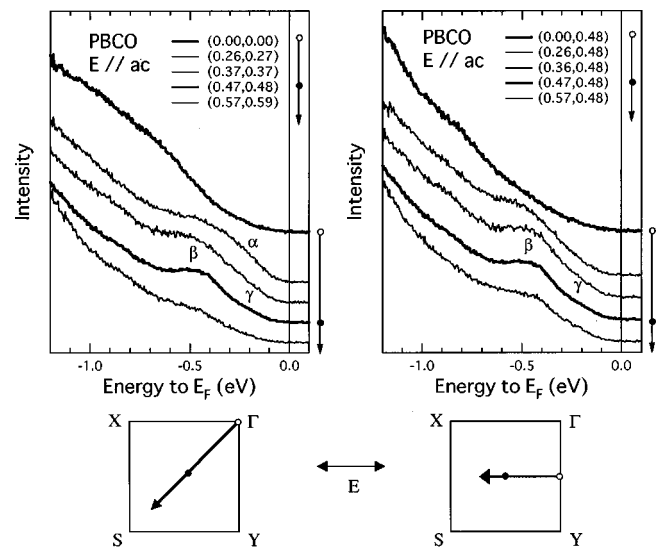


FIG. 3. Left panel: ARPES spectra along the $(0,0)\rightarrow(1,1)$ direction for $E\parallel ac$. Right panel: ARPES spectra along the $(0,1/2)\rightarrow(1/2,1/2)$ direction for $E\parallel ac$. Lower panel shows some measured points (open and closed circles) and directions in the momentum space and the in-plane component of the photon polarization (arrows). ΓY is the chain direction.

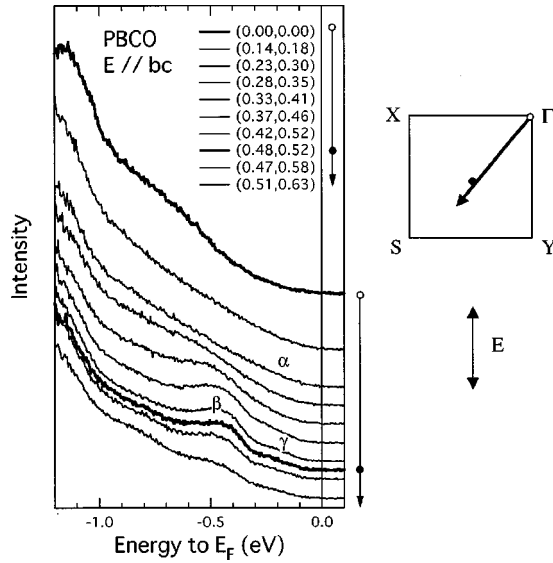


FIG. 4. ARPES spectra approximately along the $(0,0) \rightarrow (1,1)$ direction for $E \parallel bc$. The arrows indicate the measured directions. The momenta along the a and b axes are given in units of π/a and π/b . Right panel shows some measured points (open and closed circles) and directions in the momentum space and the in-plane component of the photon polarization (arrows). ΓY is the chain direction.

singlet state of the undoped antiferromagnetic CuO_2 plane.¹¹ The energy difference between the ZR state at $(\pi/2, \pi/2)$ (structure β) and the nonbonding O $2p$ state at $(0,0)$ (peak B) is ~ 2 eV in PBCO, in agreement with the observation in $\text{Sr}_2\text{CuO}_2\text{Cl}_2$.¹¹ In addition to the ZR state, a weak structure γ at -0.2 eV was observed around $(\pi/2, \pi/2)$.

By comparing Figs. 3 and 4, one can notice that the intensity of structure α at $(\pi/4, \pi/4)$ is weak for $E \parallel bc$ compared to that for $E \parallel ac$. In addition, while the relative intensity of structure α to structure β has strong polarization dependence, that of structure γ to structure β has only small polarization dependence. This suggests that these two structures α and γ have different origins. As discussed in the next paragraph, structure α at $(\pi/4, \pi/4)$, which shows strong polarization dependence, is part of a one-dimensional band from the CuO_3 chain. On the other hand, since structure γ shows weak polarization dependence and probably has two-dimensional character, it is tempting to interpret structure γ as a Pr $4f$ -O $2p_\pi$ hybridized state or a so-called FR state. If this is the FR state, the present spectra are consistent with the FR scenario because the FR state is closer to E_F than the ZR state of the CuO_2 plane.¹² The situation that the FR state is partially occupied and is observable in photoemission spectroscopy is consistent with the optical result, which has shown that the formal valence of the Pr ion is $+3.5$ and the FR state is occupied by 0.5 electrons on average if it exists.³ This argument on structure γ should be confirmed by using Pr $4d$ - $4f$ resonant photoemission in the future.

In Figs. 5 and 6, we have plotted ARPES data along the chain direction taken with $E \parallel ac$. In the spectra taken at $(k_a, 0)$ (k_a is 0, $\pi/10$, $\pi/5$, $3\pi/10$, or π), which are shown at the uppermost position in each panel, the broad feature labeled as α' is located at -0.7 ± 0.2 eV. This feature moves toward E_F as k_b increases and reaches a band maxi-

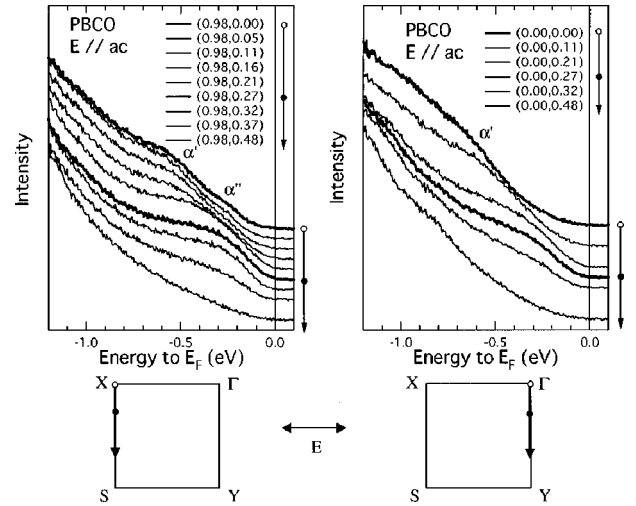


FIG. 5. Left panel: ARPES spectra along the $(0,0) \rightarrow (0,1/2)$ direction or the chain direction for $E \parallel ac$. Right panel: ARPES spectra along the $(1,0) \rightarrow (1,1/2)$ direction or the chain direction for $E \parallel ac$. Lower panel shows some measured points (open and closed circles) and directions in the momentum space and the in-plane component of the photon polarization (arrows). ΓY is the chain direction.

um with energy of ~ -0.2 eV around $(k_a, \pi/4)$. The spectra taken at $(k_a, \pi/4)$ are shown by the thicker solid curves and marked by the closed circles in each panel of Figs. 5 and 6. This feature loses its weight for $k_b > \pi/4$ and the spectrum at $(k_a, \pi/2)$ is almost featureless. This behavior does not depend on k_a , i.e., the momentum perpendicular to the chain, meaning that this dispersive feature is highly one dimensional. In order to demonstrate the dispersion more clearly, the contour plots of the difference spectra, which are obtained by subtracting the featureless spectrum at $(\pi, \pi/2)$ from the spectra at each k point, are shown for $k_a = 0, 3\pi/10$, and π in Fig. 7. Indeed, the overall dispersion of structure α' does not depend on k_a so much. Therefore, we can conclude that the band is derived from the CuO_3 chain. Structure α at $(\pi/4, \pi/4)$ (see Fig. 3) is also part of this one-dimensional band. The fact that the one-dimensional band reaches a band maximum at $k_b \sim \pi/4$ and disappears for $k_b > \pi/4$ indicates that the filling of the Cu $3d_{x^2-y^2}$ -O $2p_\sigma$ band in the CuO_3 chain is close to $1/4$, namely, the formal valence of Cu in the chain is $\sim +2.5$. This is consistent with the optical study.³

There are two interesting points in this one-dimensional band. The first point is that the other structure (α''), which has higher energy than structure α' , is observed around $(\pi, 0)$ (compare the uppermost spectra shown by the thicker solid curves in the two panels of Fig. 5). In order to show the dispersion clearly, the density plots of the second derivatives of the ARPES spectra along the chain direction are displayed for $k_a = 0, 3\pi/10$, and π in Fig. 8. The dispersion of α'' is visible in the spectra for $k_a = \pi$, which is shown in the right panel of Fig. 8. It is possible to attribute α' and α'' to the holon and spinon bands of the Tomonaga-Luttinger (TL) liquid.¹³ While the total width of the holon band is predicted to be $\sim 4t$, that of the spinon band has an energy scale of J .¹⁴ In Figs. 7 and 8, model holon and spinon dispersions of $-2t \cos(k_b + \pi/4)$ and $-\pi J/2 \cos(2k_b)$ (Refs. 13 and 14) are

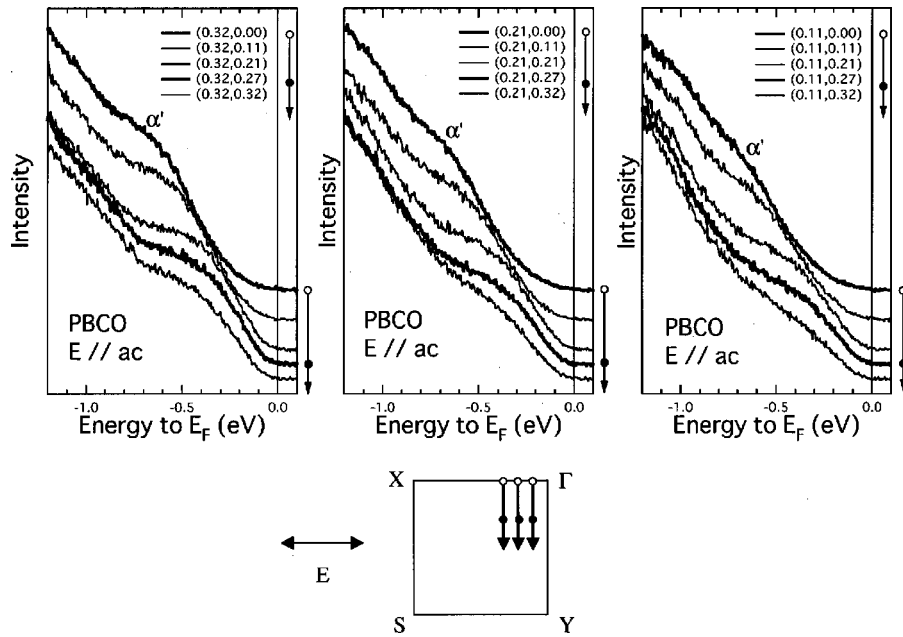


FIG. 6. ARPES spectra along the chain direction taken in the arrangement of $E \parallel ac$. k_a is the momentum perpendicular to the chain. Lower panel shows some measured points (open and closed circles) and directions in the momentum space and the in-plane component of the photon polarization (arrows). ΓY is the chain direction.

shown by solid curves. The two curves with t of 0.5 eV and J of 0.16 eV, which are reasonable values for the cuprates,¹⁴ roughly follow the dispersions in Fig. 8. Here, it should be noted that the two structures are very broad compared to the prediction by t - J model¹⁴ and that the agreement between theory and experiment is not perfect. The second point is that

the spectral weight near E_F , is considerably suppressed in the experimental data in disagreement with the theoretical prediction on the TL liquid.^{13,14} Although the lengths of the CuO_3 chain at the surface are finite because of the surface termination,⁸ the observation of the nice dispersive behavior indicates that the lengths of the CuO_3 chains are long enough

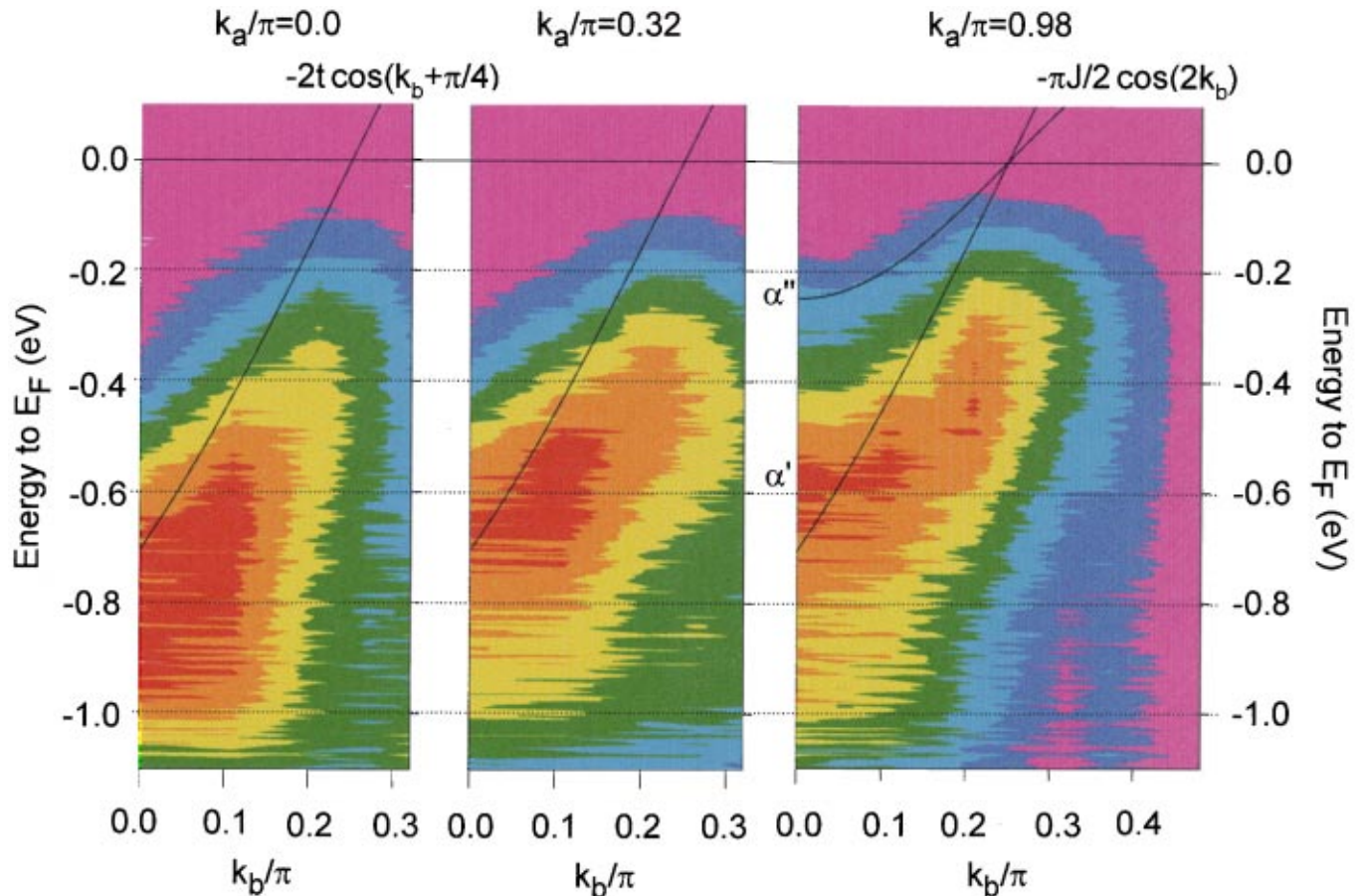


FIG. 7. (Color) Contour plots of the ARPES spectra along the chain direction for $E \parallel ac$. Intensity increases in going from blue to yellow to red regions.

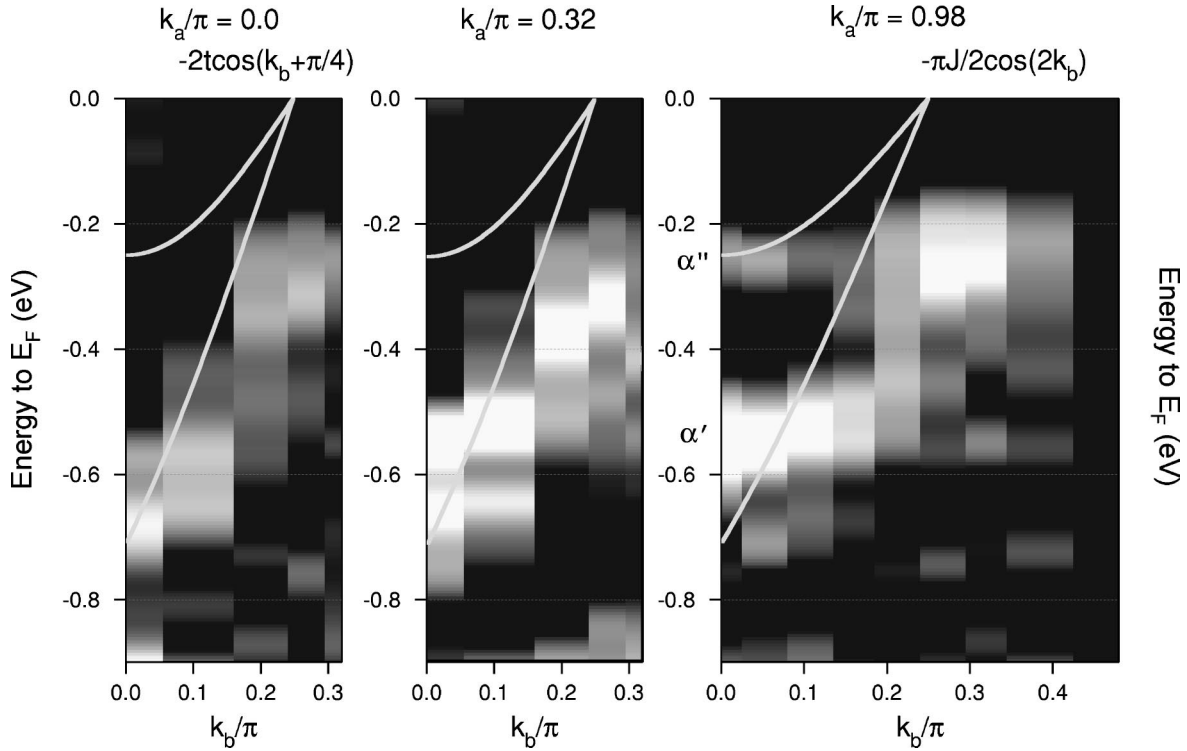


FIG. 8. Second derivatives of the ARPES spectra along the chain direction for $E||ac$. In the right panel, two dispersive features are visible as two bright belts. The solid curves are model holon and spinon dispersions given by $-2t \cos(k_b + \pi/4)$ and $-J \cos(2k_b)$ with $J = 0.5$ eV and $t = 0.16$ eV.

to allow us to compare the data with the theory for the doped CuO_3 chain. A possible origin of the intensity suppression near E_F is the instability of the nearly-1/4-filled CuO_3 chain leading to charge density waves (CDW's).¹⁵ Actually, charge instability in the hole-doped CuO_3 chain of PBCO has been observed by NMR and nuclear quadrupole resonance measurements.¹⁶ In addition, it has recently been pointed out that the spectral function of one-dimensional CDW insulators can have the holon and spinon dispersions.¹⁷

Here, it should be remarked how we would observe the feature with $E||ac$. In PBCO, the CuO_4 square plane of the CuO_3 chain is perpendicular to the ab plane, i.e., the sample surface. Therefore, the photon polarization has a component perpendicular to the sample surface, namely, parallel to the CuO_4 square plane of the CuO_3 chain as shown in Fig. 1. It is this additional component of the polarization that gives a finite transition matrix element to the ZR state in the CuO_3 chain.

With $E||bc$, the contribution from the chain is very weak when k_a is small. As k_a becomes larger, the intensity of the one-dimensional band for $E||bc$ becomes larger and, at $k_a = \pi$, is comparable to that for $E||ac$. Figure 9 shows ARPES spectra along the $(\pi, \pi/2) \rightarrow (\pi, -\pi/2)$ direction, namely, along the chain direction taken with $E||bc$. The two dispersive features, which can be interpreted as the holon and spinon dispersions, are also observed for $E||bc$. In order to show the dispersion obtained for $E||bc$ clearly, the density plot of the second derivatives of the ARPES spectra is dis-

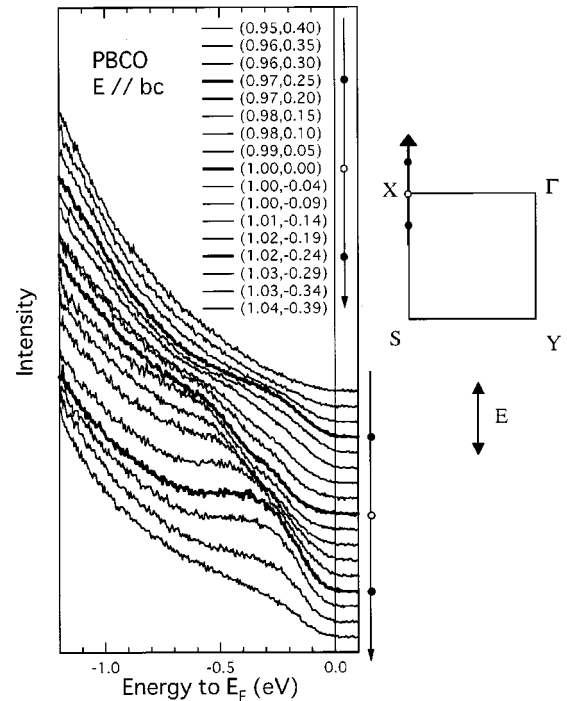


FIG. 9. ARPES spectra along the $(1, -1/2) \rightarrow (1, 1/2)$ direction or the chain direction for $E||bc$. Right panel shows some measured points (open and closed circles) and directions in the momentum space and the in-plane component of the photon polarization (arrows). ΓY is the chain direction.

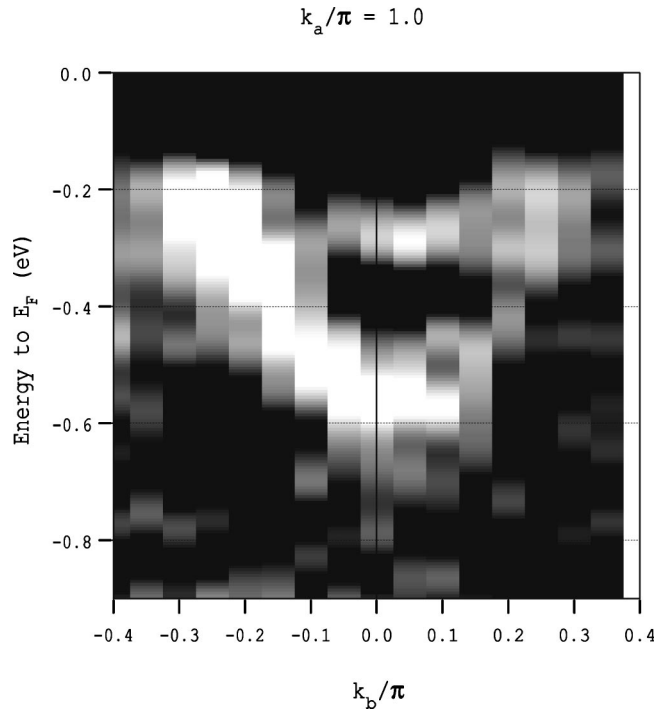


FIG. 10. Second derivatives of the ARPES spectra along the chain direction for $E||bc$. Two dispersive features are visible as two bright belts.

played in Fig. 10. The dispersions of the holon and spinon bands are almost symmetric with respect to $k_b=0$ and reach maxima around $k_b = \pi/4$ and $-\pi/4$. These dispersions obtained for $E||bc$ are consistent with those obtained for $E||ac$.

In the present ARPES data taken with $E||ac$ and $E||bc$, the relative intensity of the spinon band to the holon band strongly depends on k_a . The spinon band becomes more

intense as k_a becomes larger. The same behavior was found in the undoped CuO_3 chain by Kim *et al.*⁷ Further experimental and theoretical investigation is required to reveal this peculiar k_a dependence of the spectral function.

IV. CONCLUSION

In conclusion, we have observed the band dispersions from the CuO_2 plane and the hole-doped CuO_3 chain of non-superconducting PBCO. The band dispersion from the CuO_2 plane clearly shows that PBCO has an undoped insulating CuO_2 plane. On the other hand, the one-dimensional dispersive feature from the doped CuO_3 chain consists of two structures that can be interpreted as holon and spinon bands. These bands lose intensity beyond $k_b \sim \pi/4$, indicating that the CuO_3 chain is nearly 1/4 filled. Further experimental and theoretical studies are desirable to reveal the nature of the one-dimensional band including its momentum and polarization dependence.

ACKNOWLEDGMENTS

We would like to thank M. Schabel, I. Terasaki, T. Thoyama, S. Maekawa, D. D. Sarma, and K. Penc for valuable comments. We are grateful to P. J. White, A. Y. Matsuura, and the staff of SSRL for technical support. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture of Japan, Special Coordination Funds of the Science and Technology Agency of Japan, the New Energy and Industrial Technology Development Organization (NEDO), the U.S. DOE, Office of Basic Energy Science and Division of Material Science. SSRL is operated by the U.S. DOE, Office of Basic Energy Sciences, Division of Chemical Sciences.

¹H. A. Mook, P. Dai, K. Salama, D. Lee, F. Dogan, G. Aeppli, A. Boothroyd, and M. E. Mostoller, *Phys. Rev. Lett.* **77**, 370 (1996); H. L. Edwards, A. L. Barr, J. T. Markert, and A. L. de Lozanne, *ibid.* **73**, 1154 (1994).

²H. B. Radousky, *J. Mater. Res.* **7**, 1917 (1992).

³K. Takenaka, Y. Imanaka, K. Tamasaku, T. Ito, and S. Uchida, *Phys. Rev. B* **46**, 5833 (1992).

⁴R. Fehrenbacher and T. M. Rice, *Phys. Rev. Lett.* **70**, 3471 (1993); A. I. Liechtenstein and I. I. Mazin, *ibid.* **74**, 1000 (1995).

⁵D. Khomskii, *J. Supercond.* **6**, 69 (1993).

⁶Very recently, it has been reported that PBCO synthesized by the traveling-solvent floating-zone method has a longer c -axis lattice parameter than the usual nonsuperconducting PBCO and shows superconductivity. [Z. Zou, J. Ye, K. Oka, and Y. Nishihara, *Phys. Rev. Lett.* **80**, 1074 (1998).] The essential difference between the superconducting and nonsuperconducting PBCO samples remains controversial.

⁷C. Kim, A. Y. Matsuura, Z.-X. Shen, N. Motoyama, H. Eisaki, S. Uchida, T. Tohyama, and S. Maekawa, *Phys. Rev. Lett.* **74**, 964 (1996); *Phys. Rev. B* **56**, 15 589 (1997).

⁸M. Schabel, C.-H. Park, A. Matsuura, Z.-X. Shen, D. A. Bonn,

Ruixing Liang, and W. N. Hardy, *Phys. Rev. B* **55**, 2796 (1997); **57**, 6090 (1997); **57**, 6107 (1997).

⁹Inductively coupled plasma analysis is widely used to determine cation ratios. For example, see A. Longmore, A. T. Boothroyd, Chen Changkang, Hu Yongle, M. P. Nutley, N. H. Andersen, H. Casalta, P. Schlegler, and A. N. Christensen, *Phys. Rev. B* **53**, 9382 (1996).

¹⁰J. T. Marherth *et al.*, *MRS Bull.* **41**, 37 (1989).

¹¹B. O. Wells, Z.-X. Shen, A. Matsuura, D. M. King, M. A. Kastner, M. Greven, and R. J. Birgeneau, *Phys. Rev. Lett.* **74**, 964 (1995); J. J. M. Pothuizen, R. Eder, N. T. Hien, M. Matoba, A. A. Menovsky, and G. A. Sawatzky, *ibid.* **78**, 717 (1997); C. Kim, P. J. White, Z.-X. Shen, T. Tohyama, Y. Shibata, S. Maekawa, B. O. Wells, Y. J. Kim, R. J. Birgeneau, and M. A. Kastner, *ibid.* **80**, 4245 (1998).

¹²Recently, the unoccupied part of the FR state has been observed by x-ray absorption spectroscopy. [M. Merz, N. Nücker, E. Pellegrin, P. Schweiss, S. Schuppler, M. Kielwein, M. Knupter, M. S. Golden, J. Fink, C. T. Chen, V. Chakarian, Y. U. Idzerda, and A. Erb, *Phys. Rev. B* **55**, 9160 (1997).]

¹³J. Solyom, *Adv. Phys.* **28**, 201 (1979); V. Meden and K. Schönhammer, *Phys. Rev. B* **46**, 15 753 (1992); J. Voit, *ibid.* **47**, 6740

- (1993); K. Penc, K. Hallberg, F. Mila, and H. Shiba, *Phys. Rev. Lett.* **77**, 1390 (1996).
- ¹⁴S. Maekawa, T. Thoyama, and S. Yunoki, *Physica C* **263**, 61 (1996).
- ¹⁵B. Dardel, D. Malterre, M. Gioni, P. Weibel, Y. Baer, and F. Lévy, *Phys. Rev. Lett.* **67**, 3144 (1991); P. A. Lee, T. M. Rice, and P. W. Anderson, *ibid.* **31**, 462 (1973).
- ¹⁶B. Grévin, Y. Berthier, G. Collin, and P. Mendels, *Phys. Rev. Lett.* **80**, 2405 (1998).
- ¹⁷J. Voit, in *Proceedings of the Ninth International Conference on Recent Progress in Many-Body Theories*, edited by D. Neilson (World Scientific, Singapore, 1998).