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X-ray Absorption Studies of $YBa_2Cu_3O_{6+x}$, $La_{2-x}Sr_xCuO_4$, and $Nd_{2-x}Ce_xCuO_4$

C.L. Lin, S.L. Qiu, Jie Chen,* and Myron Strongin
Brookhaven National Laboratory
Physics Department
Upton, NY 11973-5000

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J.E. Crow
Physics Department
Temple University
Philadelphia, PA 19122

C.W. Chu
Physics Department
University of Houston
Houston, TX 77204

ABSTRACT

O K-edge absorption studies show that the density of O 2p empty states near the Fermi level increases with increasing oxygen content for $YBa_2Cu_3O_{6+x}$, and Sr concentration in $La_{2-x}Sr_xCuO_4$. With Zn substitution for Cu in $YBa_2Cu_3O_7$, T_c does not correlate with the density of O 2p empty states. In this case Tc dramatically decreases with Zn substitution while the pre-edge feature remains unchanged. The O K-edge spectrum of $Nd_{2-x}Ce_xCuO_4$ barely changes from the undoped, insulating, to the Ce doped superconducting sample. The lack of unoccupied O 2p states near the Fermi level in this case is consistent with naive expectations for electron-doping.

INTRODUCTION

It is generally believed that undoped La_2CuO_4 is a charge-transfer insulator and that the metallic conductivity is achieved by substituting divalent Sr for trivalent La which yields extra hole doping. For $YBa_2Cu_3O_{6+x}$, "doped holes" are created by added oxygen atoms which modify the electronic structure. In addition, T_c increases with increasing oxygen content as $x>0.50$. The transition from the insulating ($x<0.5$) to the superconducting phase ($x>0.5$) is also accompanied by a transition from tetragonal to orthorhombic crystal structure. The latter contains both CuO_2 planes and Cu-O chains. Photoemission,[1] electron energy loss,[2] and x-ray absorption[3,4] measurements on $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{6+x}$ have revealed that there is very little evidence of the Cu 3+ valence state and

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* Also at Hunter College, CUNY, NY 10021.

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the doped holes have dominantly oxygen 2p character. In addition, Hall effect measurements[5] indicate that holes are the charge. However, the nature and symmetry of the O 2p orbitals, which are thought to be the hole sites, are not yet firmly established.

Another interesting subject is the study of the effect of substitutions on high T_c superconductivity. For $YBa_2Cu_3O_7$, it is known that the substitution of rare earth elements for Y, except Ce, Pr and Tb, does not affect the superconductivity. This has been interpreted as showing that the rare earth site is not involved in the mechanism for superconductivity. Transition metal substitution for Cu has been investigated by both thermodynamic and magnetic measurements.[6,7] Surprisingly, Zn substitution for Cu exhibits a more dramatic depression rate for T_c than that for magnetic ions, e.g., Fe and Ni. To understand this significant change in T_c, it is crucial to study the change in the density of unoccupied O 2p states with Zn substitution.

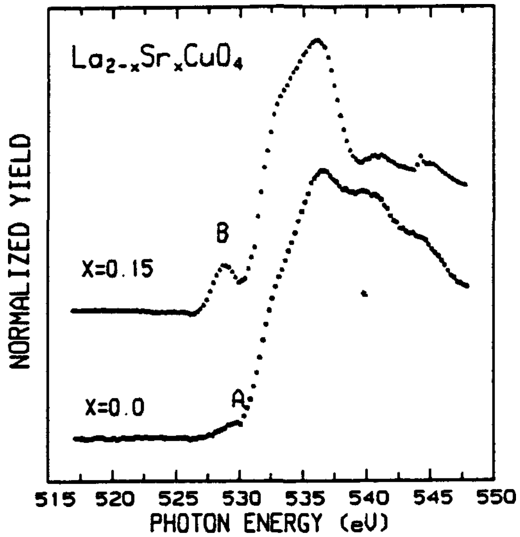
Recently, new superconducting cuprates, $Nd_{2-x}Ce_xCuO_4$, have been discovered,[8] and Hall effect and seeback coefficient measurements[9] have confirmed that the charge carriers are electrons, which is naively predicted by simple valence counting. This simple picture naturally raises the interesting question of whether or not hole doping is a prerequisite for high T_c superconductivity.

EXPERIMENTAL

In the work reported here, O K-edge absorption measurements using total electron yield were performed on the U7A beamline at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. The photon energies were calibrated by comparing the oxygen 1s --> $1\pi_g$ absorption peak of condensed molecular oxygen with that of reported[6] gas phase data which yields the π_g feature at 530.8 eV. Polycrystalline samples were scraped in situ with a stainless steel grinder under UHV conditions. Scraping was continued until the carbon 1s peak due to surface contamination could no longer be observed.

RESULTS AND DISCUSSION

The oxygen K-edge absorption spectra of $La_{2-x}Sr_xCuO_4$ with x=0.0 and x=0.15 are shown in figure 1. The pre-edge peak marked A at about 530 eV for undoped La_2CuO_4 is similar to that observed for simple transition metal oxides, e.g., CuO and NiO.[10] It has been suggested that this feature is due to filling a hybridized Cu 3d state which has some oxygen component because of the strong hybridization between the Cu 3d and O 2p orbitals. For the Sr doped superconducting material, a new feature marked B appears at about 528.5 eV, which was also observed in the electron energy loss[2] and fluorescence emission[11] measurements. It should be pointed out that the reported data for the XPS O 1s core level still remain controversial, and the position of this feature is very important for the interpretation of O K-edge absorption studies. The earlier published results[1,12,13] for cleaved single crystal and scraped polycrystal $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_7$ showed that the XPS O 1s core level was at 529 eV. However, a dominant O 1s feature at 528 eV for cleaved single crystal $YBa_2Cu_3O_7$ was reported very recently[14] and must be



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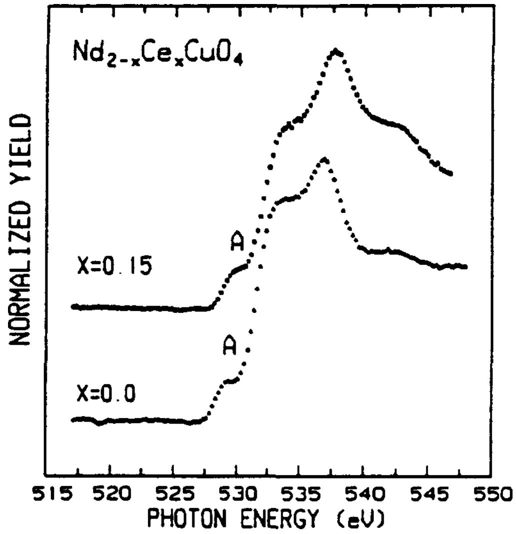
Shown in figure 2 are oxygen K-edge absorption spectra of $Nd_{2-x}Ce_xCuO_4$ with x=0.0 and x=0.15. The spectrum does not change on going from the undoped insulating to doped metallic state except for a small shift to higher photon energies. It should be noted that before scraping, the pre-edge peak marked A of the Ce doped sample did not shift as compared with that of undoped Nd_2CuO_4. The same set



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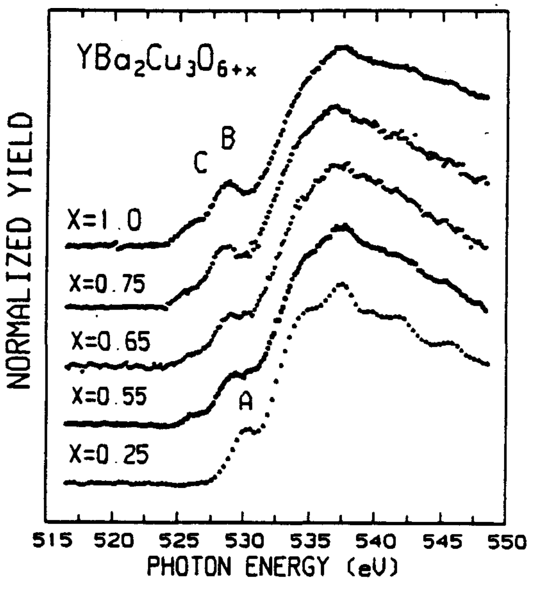

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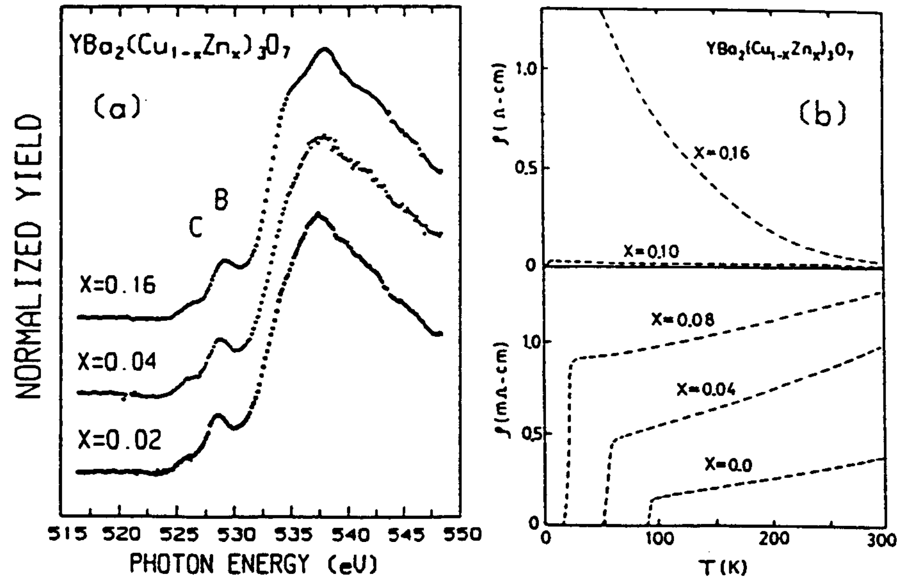
Figure 4(a) shows the O K-edge absorption spectra of $YBa_2(Cu_{1-x}Zn_x)_3O_7$ with x=0.02, 0.04 and 0.16. Surprisingly, the intensity of peaks B and C is not significantly reduced as the Zn concentration increases to 16%; while T_c is suppressed entirely at about 10% Zn substitution which can be seen in figure 4(b). In other words, T_c



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does not correlate with the density of O 2p holes and this is in contrast to the case of $YBa_2Cu_3O_{6+x}$ with different oxygen content. This behavior is in good agreement with that of $EuBa_2Cu_3O_7$ and $EuBa_2(Cu_{1-x}Zn_x)_3O_7$ which has been reported previously.[19]

At $x=0.10$, the critical concentration for the complete suppression of superconductivity, there is a dramatic increase of the resistivity and a switch from metallic to semiconducting-like behavior. For $x>0.10$, the resistivity data cannot be fit to a simple thermally activated behavior with one characteristic energy scale.[20] Anderson localization can lead to a variable range hopping expression for the resistivity given by $R(T)=A\exp[(B/T)^{1/4}]$, and which fits the experimental data in a crude way. This may suggest that the conduction is due to phonon-assisted variable range hopping and the electronic states are localized at the Fermi level by disorder in this system, and thus superconductivity is suppressed dramatically.

From the viewpoint of chemical bonding,[21] it has been known for some years that Cu with a 2+ valence state forms fourfold coordinated bonds with a sp^2d configuration. This type of bond configuration forms the square planar lattice found in the high T_c superconductors. Zn however would have no d involvement in the bonding and this would change the local symmetry and could lower T_c dramatically. For the case of Ni, which is magnetic, similarly to the Cu case, sp^2d fourfold coordinated bonds with oxygen are formed and thereby the bonding symmetry is not seriously affected. This would explain why Ni doping in $YBa_2Cu_3O_7$ has less effect on T_c, when compared to Zn.

CONCLUSION

We show that the pre-edge features of Sr doped La_2CuO_4 and $YBa_2Cu_3O_7$ are different from those for undoped La2CuO4 and $YBa_2Cu_3O_{6.5}$. However, the O K-edge spectra of $Nd_{2-x}Ce_xCuO_4$ barely change from the undoped to the Ce doped superconductor. So far there is no well accepted mechanism to explain the significant depression of T_c by Zn substitution for Cu in $YBa_2Cu_3O_7$. The absence of changes in the density of O 2p empty states near the Fermi level, along with drastic changes in the resistivity implies that the states probed in the near edge measurement become localized with Zn substitution.

ACKNOWLEDGMENTS

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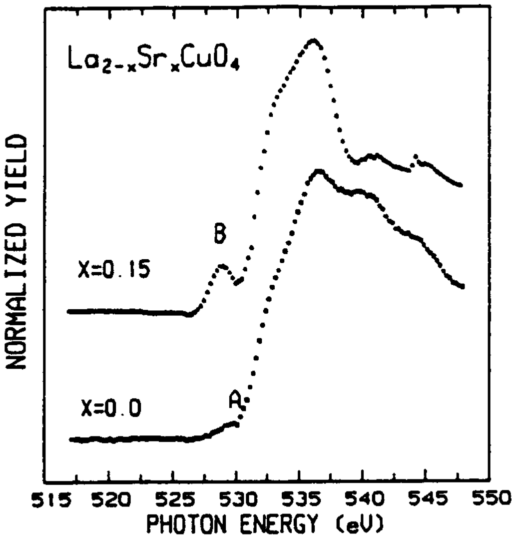
REFERENCES

1. See for example, K. C. Hass, Solid State Physics, vol. 42, 213(1989) and references therein.

2. N. Nucker, J. Fink, J. C. Fuggle, P. J. Durham, and W. M. Temmerman, Phys. Rev. B 37, 5158 (1988); N. Nucker, H. Romberg, X. X. Xi, J. Fink, B. Gegenheimer, and Z. X. Zhao, Phys. Rev. B 39, 6619 (1989).
3. J.M. Tranquada, S. M. Heald, A. R. Moodenbaugh, and M. Suenaga, Phys. Rev. B 35, 7187 (1987); P. Steiner, V. Kinsigner, I. Sander, B. Siegment, S. Hufuer, C. Politis, R. Hoppe, and H. P. Muller, Z. Phys. B 67, 487 (1987).
4. P. Kuiper, G. Kruizinga, J. Ghijsen, M. Grioni, P. J. M. Weijs, F. M. deGroot, G. A. Sawatzky, H. Verwij, L. F. Feiner, and H. Petersen, Phys. Rev. B 38, 6483 (1988).
5. M. F. Hundly, Z. Zettl, A. Stacy, and M. L. Cohen, Phys. Rev. B 35, 8800 (1987); N. P. Ong, Z. Z. Wang, J. Clayhold, J. M. Tarascon, L. H. Greene, and W. R. McKinnon, Phys. Rev. B 35, 8807 (1987).
6. C. S. Jee, D. Nichols, A. Kebede, S. Rahman, J. E. Crow, A. M. Ponte Goncalves, T. Mihalisin, G. H. Myer, I. Perez, P. E. Salomon, P. Schlottmann, S. H. Bloom, M. V. Kunc, Y. S. Yao, and R. P. Gurtin, J. Super. 1, 63 (1988).
7. Thomas J. Kistenmacher, Phys. Rev. B 38, 8862 (1988).
8. Y. Tokura, H. Takagi, and S. Uchida, Nature, 337, 345 (1989).
9. H. Takagi, S. Uchida, and Y. Tokura, Phys. Rev. Lett. 62, 1197 (1989).
10. P. Kuiper, G. Kruizinga, J. Ghijsen, G. A. Sawatzko, and H. Verwij, Phys. Rev. Lett. 62, 221 (1989).
11. A. Krol C. S. Lin, Z. H. Ming, C. J. Sher, Y. H. Kao, C. L. Lin, S. L. Qiu, J. Chen, J. M. Tranquada, Myron Strongin, G. C. Smith, C. T. Chen, F. Sette, Y. Ma, C. W. Chu, Gang Cao, and J. E. Crow, submitted to Phys. Rev. B.
12. J. H. Weaver, H. M. Meyer III, P. J. Wagner, D. H. Hill, Y. Gao, D. Peterson, Z. Fisk, and A. J. Arko, Phys. Rev. B 38, 4668 (1988).
13. S. L. Qiu, C. L. Lin, M. W. Ruckman, J. Chen, D. H. Chen, Y. Xu, A. R. Moodenbaugh, Myron Strongin, D. Nichols, and J. E. Crow, AIP Proc. #182, p. 365 (1989).
14. D. E. Fowler, C. R. Brundle, J. Lerczak, and F. Holtzberg, to be published.
15. N. Nucker, P. Adelmann, M. Alexander, H. Romberg, S. Nakai, J. Fink, H. Rietschel, G. Roth, H. Schmidt, and H. Spille, Z. Phys. B 75, 421 (1989).
16. J. M. Tranquada, S. M. Heald, A. R. Moodenbaugh, G. Liang, and M. Croft, Nature, 337, 720 (1989).
17. E. E. Alp, S. M. Mini, M. Ramanathan, B. Dabrowski, D. R. Richards, and D. G. Hinks, Phys. Rev. B 40, 2617 (1989).
18. The previous report by our group showed that two features were at 528 eV and 529 eV which are due to different photon energy calibration.
19. M. L. denBoer, C. L. Chang, H. Petersen, M. Schaible, K. Reilly, and S. Horn, Phys. Rev. B 38, 6588 (1988).
20. See for example, Myron Strongin, R. S. Thompson, O.F. Kammerer, and J. E. Crow, Phys. Rev. B 1, 1078 (1970).
21. "The Nature of the Chemical Bond," 3rd ed., Linus Pauling, Cornell University Press, 1960.



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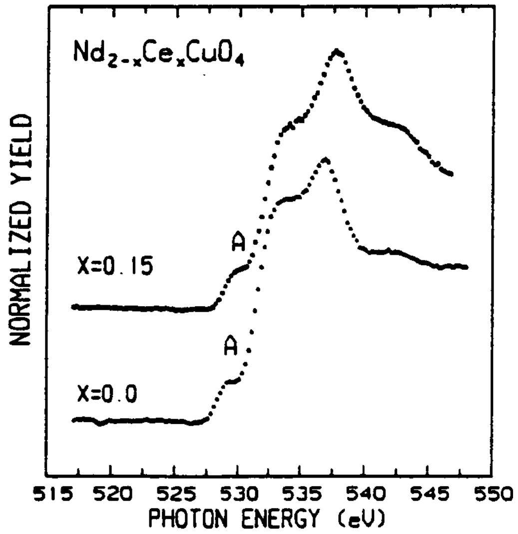

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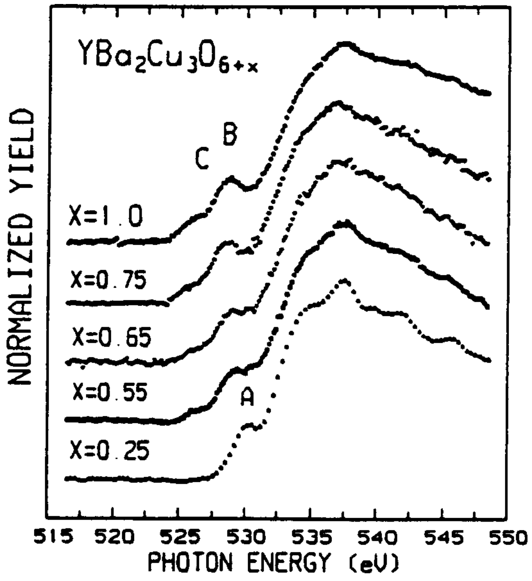

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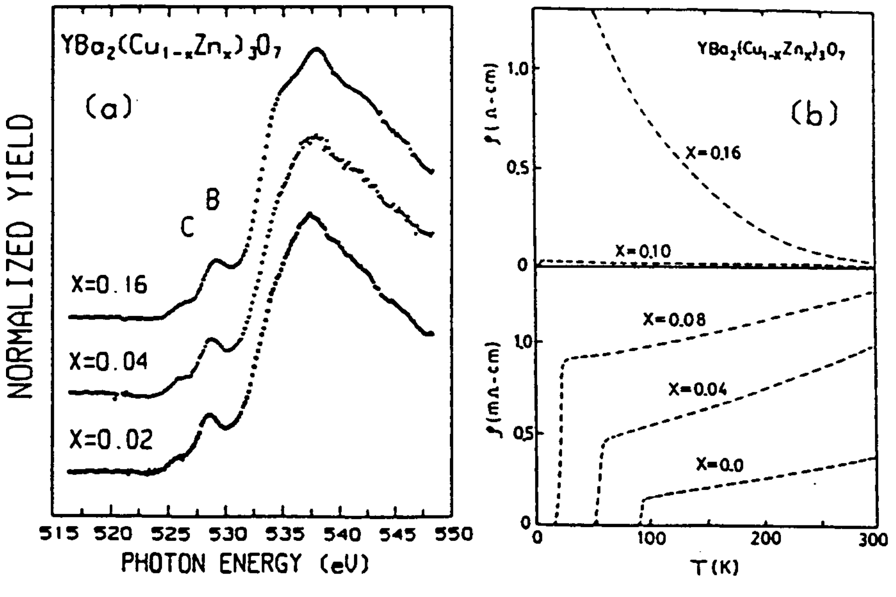

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We show that the pre-edge features of Sr doped La_2CuO_4 and $YBa_2Cu_3O_7$ are different from those for undoped La2CuO4 and $YBa_2Cu_3O_{6.5}$. However, the O K-edge spectra of $Nd_{2-x}Ce_xCuO_4$ barely change from the undoped to the Ce doped superconductor. So far there is no well accepted mechanism to explain the significant depression of T_c by Zn substitution for Cu in $YBa_2Cu_3O_7$. The absence of changes in the density of O 2p empty states near the Fermi level, along with drastic changes in the resistivity implies that the states probed in the near edge measurement become localized with Zn substitution.

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REFERENCES

1. See for example, K. C. Hass, Solid State Physics, vol. 42, 213(1989) and references therein.

2. N. Nucker, J. Fink, J. C. Fuggle, P. J. Durham, and W. M. Temmerman, Phys. Rev. B 37, 5158 (1988); N. Nucker, H. Romberg, X. X. Xi, J. Fink, B. Gegenheimer, and Z. X. Zhao, Phys. Rev. B 39, 6619 (1989).
3. J.M. Tranquada, S. M. Heald, A. R. Moodenbaugh, and M. Suenaga, Phys. Rev. B 35, 7187 (1987); P. Steiner, V. Kinsigner, I. Sander, B. Siegment, S. Hufuer, C. Politis, R. Hoppe, and H. P. Muller, Z. Phys. B 67, 487 (1987).
4. P. Kuiper, G. Kruizinga, J. Ghijsen, M. Grioni, P. J. M. Weijs, F. M. deGroot, G. A. Sawatzky, H. Verwij, L. F. Feiner, and H. Petersen, Phys. Rev. B 38, 6483 (1988).
5. M. F. Hundly, Z. Zettl, A. Stacy, and M. L. Cohen, Phys. Rev. B 35, 8800 (1987); N. P. Ong, Z. Z. Wang, J. Clayhold, J. M. Tarascon, L. H. Greene, and W. R. McKinnon, Phys. Rev. B 35, 8807 (1987).
6. C. S. Jee, D. Nichols, A. Kebede, S. Rahman, J. E. Crow, A. M. Ponte Goncalves, T. Mihalisin, G. H. Myer, I. Perez, P. E. Salomon, P. Schlottmann, S. H. Bloom, M. V. Kunc, Y. S. Yao, and R. P. Gurtin, J. Super. 1, 63 (1988).
7. Thomas J. Kistenmacher, Phys. Rev. B 38, 8862 (1988).
8. Y. Tokura, H. Takagi, and S. Uchida, Nature, 337, 345 (1989).
9. H. Takagi, S. Uchida, and Y. Tokura, Phys. Rev. Lett. 62, 1197 (1989).
10. P. Kuiper, G. Kruizinga, J. Ghijsen, G. A. Sawatzko, and H. Verwij, Phys. Rev. Lett. 62, 221 (1989).
11. A. Krol C. S. Lin, Z. H. Ming, C. J. Sher, Y. H. Kao, C. L. Lin, S. L. Qiu, J. Chen, J. M. Tranquada, Myron Strongin, G. C. Smith, C. T. Chen, F. Sette, Y. Ma, C. W. Chu, Gang Cao, and J. E. Crow, submitted to Phys. Rev. B.
12. J. H. Weaver, H. M. Meyer III, P. J. Wagner, D. H. Hill, Y. Gao, D. Peterson, Z. Fisk, and A. J. Arko, Phys. Rev. B 38, 4668 (1988).
13. S. L. Qiu, C. L. Lin, M. W. Ruckman, J. Chen, D. H. Chen, Y. Xu, A. R. Moodenbaugh, Myron Strongin, D. Nichols, and J. E. Crow, AIP Proc. #182, p. 365 (1989).
14. D. E. Fowler, C. R. Brundle, J. Lerczak, and F. Holtzberg, to be published.
15. N. Nucker, P. Adelmann, M. Alexander, H. Romberg, S. Nakai, J. Fink, H. Rietschel, G. Roth, H. Schmidt, and H. Spille, Z. Phys. B 75, 421 (1989).
16. J. M. Tranquada, S. M. Heald, A. R. Moodenbaugh, G. Liang, and M. Croft, Nature, 337, 720 (1989).
17. E. E. Alp, S. M. Mini, M. Ramanathan, B. Dabrowski, D. R. Richards, and D. G. Hinks, Phys. Rev. B 40, 2617 (1989).
18. The previous report by our group showed that two features were at 528 eV and 529 eV which are due to different photon energy calibration.
19. M. L. denBoer, C. L. Chang, H. Petersen, M. Schaible, K. Reilly, and S. Horn, Phys. Rev. B 38, 6588 (1988).
20. See for example, Myron Strongin, R. S. Thompson, O.F. Kammerer, and J. E. Crow, Phys. Rev. B 1, 1078 (1970).
21. "The Nature of the Chemical Bond," 3rd ed., Linus Pauling, Cornell University Press, 1960.