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Core-level shifts on cleaved $YBa_2Cu_3O_{7-x}$ (001) surfaces observed in angle-resolved photoemission

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We have performed synchrotron-radiation photoemission on the (001) surfaces of superconducting $YBa_2Cu_3O_{7-x}$ crystals which were prepared by *in situ* cleaving. The Ba 4*d* and Ba 5*p* core-level line shapes differed substantially when the photoelectrons were collected at normal or grazing emission angles. The normal-emission core-level spectra appear to be composed of two components shifted relative to one another by about 0.9 eV. The more tightly bound component dominates the grazing-emission spectrum. This is interpreted as a surface core-level shift of the Ba atoms to larger binding energies, since the photoelectrons detected at grazing angles are predominantly emitted from the outermost atomic planes. The nature of the shift is discussed.

INTRODUCTION

Electron spectroscopies have been used extensively to study the electronic structure of the new oxide superconductors, particularly, of $YBa_2Cu_3O_{7-x}$ and related compounds.[1] Kurtz has recently reviewed the use of photoemission to examine valence structure,[2] while Wendin has produced an overview of the application of photoemission and other spectroscopies to the valence and core electrons in these materials.[3] Two factors have complicated the interpretation of these spectroscopic results. One is the difficulty of preparing surfaces of the ceramics which are characteristic of the bulk material, and the other is the extensive effects of electron-electron correlation on the photoelectron spectra.

A number of workers have performed photoemission studies of sintered polycrystalline samples of the high-temperature superconductor $YBa_2Cu_3O_{7-x}$ in the vacuum ultraviolet and soft-x-ray regime.[4-18] The most commonly used method of surface preparation, mechanical abrasion of ceramic samples with some type of file, has lead to a set of experimental spectra which are qualitatively in agreement with each other, but differ in some important details. The most controversial results have involved reports of core-level binding-energy shifts or temperature-dependent effects. Some of these results are possibly due to contaminants in the starting materials or to residual gases condensed on the surfaces at low temperatures. Progress is being made to identify and to eliminate these problems.

Recently, Schrott *et al.*[19] have used x-ray photoemission spectroscopy (XPS) and scanning electron microscopy (SEM) to characterize the surfaces obtained by either fracturing or filing the sintered materials. They conclude that filing (or scraping) produces the best surface, but that a significant fraction of the surface area is composed of intergranular fractures. These grain boundaries contain varying amounts of extrinsic material, such as $BaCO_3$, depending upon the density, purity, and preparation technique of the sintered material. The SEM results also show that the filing procedure leaves loose granular material on the surface. It is our experience that these grains, if not removed completely, can be charged positively by the photocurrent. This can lead to spurious photoemission features on the high binding-energy side of the real electronic features.

In light of these problems, the principal advantage of using cleaved single-crystal samples[20] is obvious—residues at the grain boundaries and loose grains are avoided entirely. A second advantage is that the ordered surfaces produced by cleaving can be effectively probed by angle-resolved photoemission for signs of energy-band dispersion. A final benefit from the use of cleaved crystal samples is the ability to create surfaces which are locally flat over most of the exposed surface. This allows us to collect photoelectrons at well-defined grazing-emission angles from our single-crystal samples. Such spectra are intrinsically very surface sensitive, and differ markedly from the normal-emission spectra. We interpret these results as indicative of surface shifts in the Ba core binding energies. Implications of these shifts for the interpretation of earlier results from sintered materials are discussed.

EXPERIMENTAL PROCEDURES

The $YBa_2Cu_3O_{7-x}$ single crystals were grown by partially melting a mixture of Y_2O_3, $BaCO_3$, and CuO in an alumina crucible, with excess CuO used as a growth flux.[21] Rutherford backscattering spectroscopy (RBS) on dozens of crystals confirmed that the cation stoichiometry was always 1:2:3 within the sensitivity of RBS. Ion channeeling[22] and x-ray diffraction were used to confirm the crystal structure. Polarized light microscopy revealed relatively few oxygen-ordering domain walls in our crystals. We speculate that the (110) twinning observed in ceramic materials[23] is promoted largely by geometric constraints during the oxygen intercalation. We note that our crystals are almost free growing, and do not need to form twins to accommodate the tetragonal-to-orthorhombic distortion.[24]

The superconducting transition, as determined by ac susceptibility measurements, has an onset at 90 K and finishes above 50 K.[25] A comparison of the as-grown crystals and cleaved surfaces using spectroellipsometry[26] suggests that the centers of the crystals used in this experiment may have a lower O content than the surfaces. Evidence relating to the O stoichiometry at the actual cleaved surfaces is discussed later.

Crystal platelets of at least 1.5 mm along *a* and *b* axes were used in these experiments. The thickness varied from 0.1–0.3 mm along the *c* axis. The samples were bonded flat to a copper holder by one face, and metal cleaving tabs were fastened to the other face using ultrahigh vacuum (UHV) compatible epoxy. In order to provide a sample ground and prevent charging effects, the copper holder, the exposed epoxy surfaces, and the exposed edges of the crystals were painted with a conductive paste, also UHV compatible. This paste (Ohmex) has a low and featureless photoyield. The sample holder was mounted on a cryostat in a UHV photoelectron spectrometer system, and the chamber was baked at 150 °C. The base pressure was 2.5×10^{-10} Torr.

The crystals were cleaved by gently pulling on the cleaving tabs in UHV. Visual inspections of both the crystal and the spot produced by the reflection of a He-Ne laser beam were used to judge the quality of the cleaves *in situ*. A microscopic examination was conducted *ex situ* after the experiment to verify that the samples were cleaved across their entire width. The surfaces of the acceptable cleaves exhibited many visible steps separating smooth (001) facets.

The surface normal was determined from the reflection angle of the laser beam. The effectiveness of this procedure in determining the ⟨001⟩ direction was confirmed by low-energy electron diffraction in our earlier study of cleaved crystals.[20] The angle-resolved spectra were obtained with a hemispherical electron energy analyzer operated with 0.25 eV resolution. The input lens defined a source area on the sample less than 1 mm in diameter. For this experiment, we used photons from the three-meter torroidal-grating monochromator at the University of Wisconsin Synchrotron Radiation Center.

RESULTS

A. Valence-band spectra

The valence-band spectra from the cleaved surfaces agree with our earlier results on cleaved crystals,[20] which were restricted to photon energies below 40 eV. Since the quality of the cleaved surface and its oxygen stoichiometry are critical issues in the interpretation of our core-level results, we have looked carefully at the valence spectra of each of the three cleaved crystals used in this study. Representative spectra are shown in Fig. 1. We call attention to the following results.

First, we observe significant intensity in the shoulder found at -2.5 eV for low photon energies. This feature has been associated with higher oxygen stoichiometry in earlier studies.[13] The cleaving procedure and photoemission measurements were performed on one of the crystals at a nominal temperature of 77 K in order to minimize possible oxygen loss. The room-temperature and low-temperature results did not differ in any significant way.

Second, spectra taken at photon energies near the Cu 3*p* threshold, 76 eV, show the resonant Cu d^8 satellite at -12.5 eV, an energy characteristic of Cu^{2+} ions. There is no similar resonance at -15 eV, associated with Cu^{1+} ions, which has been found to accompany severe oxygen depletion at the cleaved surface.[13] We note that this is not a precise indication of surface oxygen stoichiometry, since Cu^{1+} would only be expected to be present for an O content below $YBa_2Cu_3O_{6.5}$ ($x=0.5$). By performing measurements on reference samples of known stoichiometry, Kelly[26] has shown that spectroellipsometry can provide a useful measure of the oxygen content in these materials. The application of this technique to our cleaved surfaces suggests a decreasing oxygen-concentration gradient toward the center of these crystals, apparently due to the

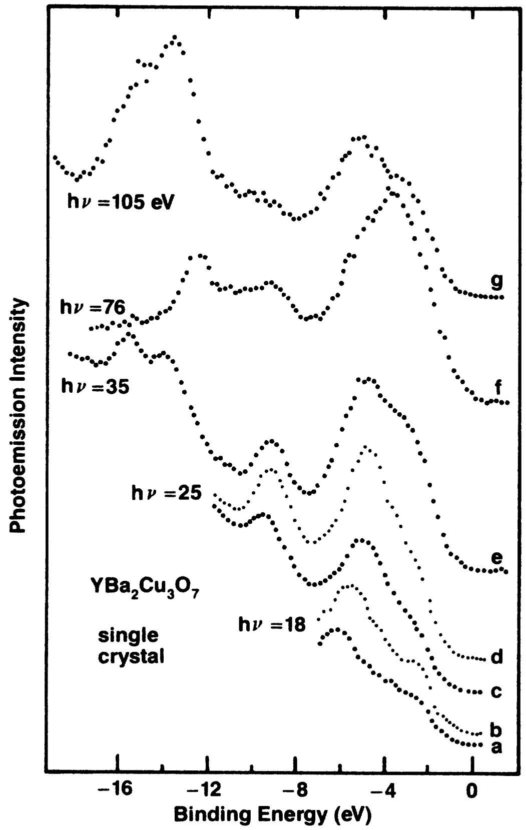

FIG. 1. A comparison of valence-band spectra from *in situ* cleaved $YBa_2Cu_3O_{7-x}$ obtained with the indicated photon energies. Spectra (b) and (d) were taken at a photoemission angle $\theta=60°$. The other spectra were taken in the normal emission, $\theta=0°$.

slow diffusivity of oxygen in the crystals relative to the ceramic materials. Measurements on crystals from the same batch as used in this study suggest that at the as-grown surface x is about 0.2, but that x is near 0.5 in the interior regions of the thickest crystals.

Third, we find a sharp peak near −9.5 eV from the Fermi energy. This feature has no explanation in one-electron band theory,[27,28] and many authors have attributed this peak to contamination by carbonates or water. Recent experiments have shown that both of these potential contaminants yield some photoemission intensity near this energy.[19,29] However, we have seen this feature on all of our cleaved surfaces immediately after cleaving, even at low temperature, and on sintered samples synthesized without carbonates. We will argue in a separate paper,[30] based on cross section effects, that this is an intrinsic electronic feature related to oxygen multihole states.

Fourth, the energies and intensities of the valence-band features were almost independent of the emission angle in both the (010) and (110) planes. Compare curves (a) and (b) or (c) and (d) in Fig. 1. We did not observe apparent angular dispersion of more than 0.25 eV. This may reflect a localized and highly correlated electronic structure in this oxide. However, there is still considerable debate over the proper theoretical framework in which to interpret the angle-resolved photoemission results.[5,27,28,31]

B. Core-level shifts

The position and line shape of the Ba core levels in $YBa_2Cu_3O_{7-x}$ have differed in reports by various groups. Miller[32] has reviewed the experimental results for the Ba 5*p* levels, and there are significant variations in the reported Ba 4*d* spectra as well. Some of the discrepancies have been attributed to contaminants, principally unreacted $BaCO_3$, or to oxygen deficiencies. However, we note that the position and shape of the Ba 5*p* doublet and its apparent spin-orbit splitting seem to differ consistently in published studies for the two photon energy ranges where it has an appreciable cross section—near 35 eV and near 105 eV.

We have taken Ba 5*p* spectra at low and high photon energies on the same cleaved surfaces of several crystals, and we also find this discrepancy. The Ba 5*p* doublet is better resolved in the low photon energy regime, and the spin-orbit splitting and intensity ratios are closer to the atomic values. At higher photon energies, the Ba 5*p* doublet is unresolved, even when the system resolution is the same. This effect is seen in the top and bottom curves of Fig. 2, where Ba 5*p* spectra taken near the normal-emission direction are compared for photon energies of 40 and 100 eV. We attribute the more narrow line shape at the latter energy to the shorter electron escape depth at the resultant electron kinetic energies. The low cross section for Ba 5*p* emission at intermediate energies prevents us from following the evolution of the spectra from the low-energy to the high-energy line shape. However, we can use the emission angle to control the probing depth in a similar and more continuous manner. The middle spectrum in Fig. 2, taken at an angle of 73° from the surface normal in the (100) plane, has a line shape very similar to the low-energy result.

We found that the 5*p* spectrum at 100 eV can be approximated by shifting the 40 eV line shape (or the grazing angle line shape) to lower binding energy by 0.9 eV and superimposing it upon the unshifted spectrum. The most straightforward explanation for the broadened Ba 5*p* line shape is, therefore, the overlap of the surface Ba core level with the bulk core level shifted to lower binding energy. The 5*p* levels appear at a kinetic energy of 20 and 80 eV for the low- and high-energy spectra, respectively. Considering the typical energy dependence of the primary-electron escape depth,[33] we expect that the 40 eV spectrum is quite surface sensitive, possibly probing only the outermost Ba layer. Apparently, the 100 eV spectrum samples deeper Ba layers than the 40 eV data.

An identical trend with emission angle is seen for the Ba 4*d* core levels as seen in Fig. 3. The spin-orbit splitting is larger for the Ba 4*d* levels (2.6 eV) than for the 5*p* doublet (2.0 eV), so the splitting can be clearly resolved at both angles. However, the normal-emission line shape is clearly broader than the grazing-emission spectrum, apparently due to the superposition of an additional component at lower binding energy. Again, we can fit the normal-emission line shape by a superposition of two doublets, one at the energy of the grazing-emission spec-

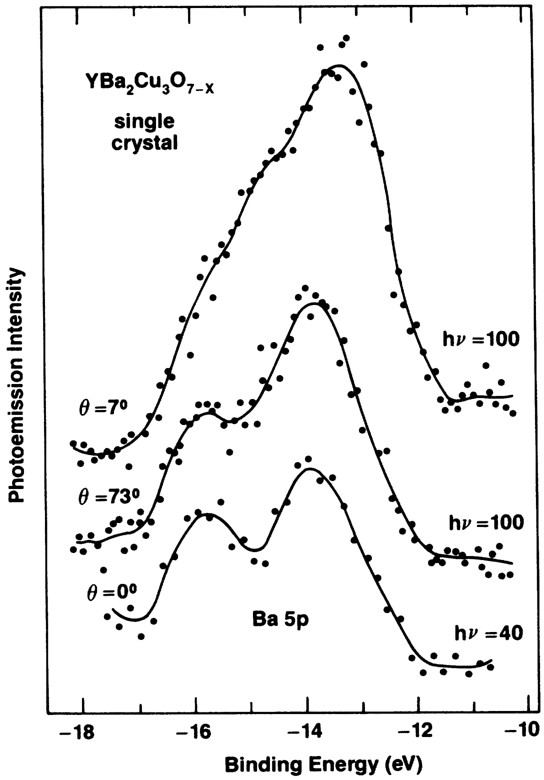

FIG. 2. A comparison of the line shape of the Ba 5*p* core level at photon energies $h\nu = 40$ and 100 eV, taken at room temperature. A sloping background has been subtracted from the 40 eV spectrum. Emission angles θ are as indicated. The spin-orbit doublet of the Ba 5*p* core level is unresolved for $\theta = 7^\circ$ and $h\nu = 100$ eV, because photoemission is less surface sensitive under these conditions and both surface and bulk core levels contribute to the spectrum.

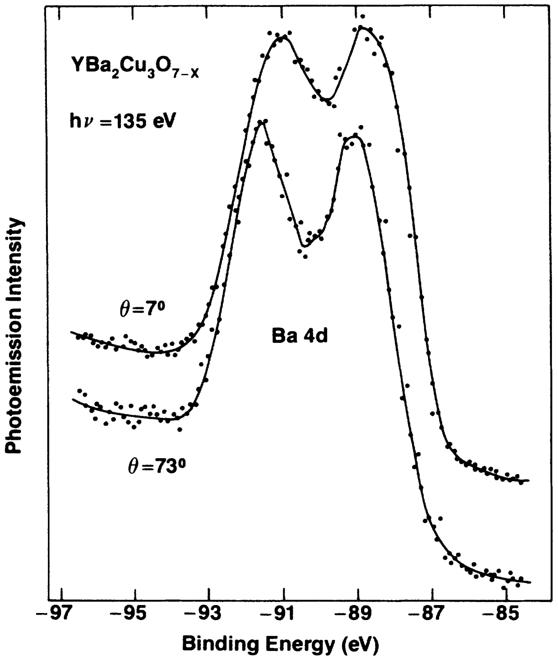

FIG. 3. The Ba $4d$ core level exhibits the same qualitative angular behavior as the Ba $5p$ levels in Fig. 2. The more surface sensitive spectrum ($\theta=73°$) is well resolved, while the near-normal-emission spectrum appears to be composed of two doublets shifted relative to one another by about 0.9 eV.

trum and a second, bulk doublet of comparable intensity shifted 0.9 eV to lower binding energy. We estimate the uncertainty of this shift to be less than 0.1 eV. Thus, the surface shift of the Ba $4d$ and Ba $5p$ doublets are equal, although the latter is less precisely determined. Core-level spectra at intermediate angles show a smooth transition from one type of spectra to the other, with the low binding-energy component gradually diminishing with increasing angle.

C. Origin of the core-level shifts

We note that both Ba atoms in the unit cell occupy equivalent positions in the bulk crystal structure, and should have identical bulk binding energies. The higher binding-energy feature is then almost certainly due to Ba atoms in an altered surface environment. Surface core-level shifts of both signs with magnitudes up to 1 eV have been reported in many metals and semiconductors,[34] but there have been relatively few studies of core shifts on oxides. A number of effects leading to surface core-level shifts have been identified. Among these are charge transfer away from the surface atoms, reduced core-hole screening of the final state, or effects of the altered surface Madelung potential. The interpretation of the surface shift in the present case is complicated by the possible occurrence of surface reconstructions or of changes in Ba oxygen coordination.

The model of Citrin and Wertheim[34] attributes most previously observed surface shifts to redistribution of charge in the initial state due to reduced coordination and a concomitant narrowing of the surface electronic bands. Since the Ba valence states lie mostly above the Fermi energy, narrowing of the bands should reduce the effective charge on the Ba site, leading to the proper sign of the core-level shift. The surface shift of Ba to higher binding energies would also be consistent with the observed shift of the cation core levels in numerous compound semiconductors. However, realistic estimates of the surface shift are complicated by our lack of knowledge of the surface atomic structure.

We discount the possibility that the shift is induced by the adsorption of residual gases in the UHV chamber. Although some authors have claimed that the freshly prepared surfaces are highly reactive, we have no evidence for changes in our spectra between 0.1 and 20 h after cleaving. Changes occurring at longer times are first noticeable in the valence-band spectra, not in the core levels.

Not much is known about the local oxygen coordination at the surface following cleaving in vacuum. This is a separate issue from the possibility of spontaneous oxygen deintercalation in the near-surface region, which may also be occurring. It may prove very difficult to determine the actual oxygen-site occupancy at the cleaved surface. Our surface-sensitive spectra may be probing only 0.5 nm into the surface, less than the thickness of a unit cell (1.17 nm).

Furthermore, it is not known whether our cleaving technique exposes a particular plane among the several atomic planes parallel to the (001) direction in $YBa_2Cu_3O_{7-x}$. From the symmetry of the unit cell, there can be no unique cleavage plane which lies between planes of atoms. The surface, therefore, is likely to have domains where the cleave shifts between equivalent planes. However, it seems reasonable that the Ba atoms might have reduced oxygen coordination due to the cleaving process, and possibly due to O desorption. This may result in reduced screening of the surface core hole and, thereby, to a less energetic core photoelectron, in agreement with our result. However, given our current understanding of the cleavage plane and possible surface atomic reconstructions, the relative contribution of final-state effects to the surface core shift cannot be determined.

CONCLUSIONS

Our photoemission results show a significant shift in the binding energies of the Ba core levels at the (001) surface of $YBa_2Cu_3O_{7-x}$. This is not unexpected, since such shifts are a ubiquitous feature of high-resolution core-level photoemission studies of clean surfaces. These shifts may indicate an altered electronic structure at the surface of this high-T_c material. Most core-level shifts have their origin is surface rearrangements of valence electrons, which may, in principle, be observed in valence-band photoemission spectra. However, our limited search for such effects has failed to reveal any profound differences in the surface and bulk valence structure. This supports the conclusion that the photoemission results, although they are surface sensitive, are probing electronic states similar to the bulk valence bands.

The Ba core-level shifts would be affected by reconstruction of the cleaved surface, particularly, by changes in the coordination of barium by oxygen. Our results on the low-temperature and room-temperature cleaves suggest that the surface oxygen content is not significantly depressed by thermal desorption at room temperature. We also note that the surface-sensitive spectra do not reveal the characteristic satellite feature associated with Cu in the Cu^{1+} valence state. The (001) surface is apparently more stable with respect to oxygen loss than the randomly fractured surfaces. Nonetheless, we still do not have a quantitative measure of the oxygen stoichiometry in the critical region within a few atomic layers of the surface. Some techniques which are commonly used to measure chemical composition might themselves affect the surface oxygen content. Photoemission measurements on crystals which have been prepared in the tetragonal, semiconducting phase would help answer the remaining questions.

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[1] M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu, Phys. Rev. Lett. **58**, 908 (1987).

[2] R. L. Kurtz, in *Thin Film Processing and Characterization of High-Temperature Superconductors,* edited by J. M. E. Harper, R. J. Colton, and L. C. Feldman, AIP Conf. Proc. No. 165 (AIP, New York, 1988), p. 222.

[3] G. Wendin, in *Fourteenth International Conference on X-ray and Inner-shell Processes* [J. Phys. (Paris) (to be published)].

[4] P. D. Johnson, S. L. Qiu, L. Jiang, M. W. Ruckman, M. Strongin, S. L. Hulbert, R. F. Garret, B. Sinkovic, N. V. Smith, R. J. Cava, C. S. Lee, D. Nichols, E. Kaczanowicz, R. E. Salomon, and J. E. Crow, Phys. Rev. B **35**, 8811 (1987).

[5] A. Fujimori, E. Takayama-Muromachi, Y. Uchida, and B. Okai, Phys. Rev. B **35**, 8814 (1987).

[6] R. L. Kurtz, R. L. Stockbauer, D. Mueller, A. Shih, L. E. Toth, M. Osofsky, and S. A. Wolf, Phys. Rev. B **35**, 8818 (1987).

[7] P. Steiner, V. Kinsinger, I. Sander, B. Siegwart, S. Hufner, and C. Politis, Z. Phys. B **35**, 19 (1987).

[8] F. C. Brown, T. C. Chiang, T. A. Friedman, D. M. Ginsberg, G. N. Kwawer, T. Miller, and M. G. Mason, J. Low Temp. Phys. **69**, 151 (1987).

[9] M. Onellion, Y. Chang, D. W. Niles, R. Joynt, G. Margaritondo, N. G. Stoffel, and J. M. Tarascon, Phys. Rev. B **36**, 819 (1987).

[10] J. A. Yarmoff, D. R. Clarke, W. Drube, U. O. Karlsson, A. Taleb-Ibrahimi, and F. J. Himpsel, Phys. Rev. B **36**, 3967 (1987).

[11] E. R. Moog, S. D. Bader, A. J. Arko, and B. K. Flandermeyer, Phys. Rev. B **36**, 5583 (1987).

[12] A. Fujimori, E. Takayama-Muromachi, and Y. Uchida, Solid State Commun. **63**, 857 (1987).

[13] N. G. Stoffel, J. M. Tarascon, Y. Chang, M. Onellion, D. W. Niles, and G. Margaritondo, Phys. Rev. B **36**, 3986 (1987).

[14] P. Thiry, G. Rossi, Y. Petroff, A. Revcolevschi, and J. Jegoudez, in Proceedings of the Workshop on Scientific and Technological Applications of Synchrotron Radiation, Trieste, Italy, 1987 (unpublished).

[15] T. Takahashi, F. Maeda, A. Arai, H. Katayama-Yoshida, Y. Okabe, T. Suzuki, S. Hosoya, A. Fujimori, T. Shidara, T. Koide, T. Miyahara, M. Onoda, S. Shamoto, and M. Sato, Phys. Rev. B **36**, 5686 (1987).

[16] H. M. Meyer III, D. M. Hill, T. J. Wagener, Y. Gao, J. H. Weaver, D. W. Capone, and K. C. Goretta (unpublished).

[17] Zhi-xun Shen, J. W. Allen, J. J. Yeh, J. S. Kang, W. Ellis, W. Spicer, I. Lindau, M. B. Maple, Y. D. Dalichaouch, M. S. Torikachvili, J. Z. Sun, and T. H. Geballe, Phys. Rev. B **36**, 8414 (1987).

[18] A. Samsavar, T. Miller, T. C. Chiang, B. G. Pazol, T. A. Friedmann, D. Ginzberg, and M. Ginzberg, Phys. Rev. B **37**, 5164 (1988).

[19] A. G. Schrott, S. L. Cohen, I. K. Dinger, F. J. Himpsel, J. A. Yarmoff, K. G. Frase, S. I. Park, and R. Purtell (unpublished).

[20] N. G. Stoffel, Y. Chang, M. K. Kelly, L. Dottl, M. Onellion, P. A. Morris, W. A. Bonner, and G. Margaritondo, Phys. Rev. B **37**, 7952 (1988).

[21] P. A. Morris, W. A. Bonner, G. W. Hull, B. Meagher, and N. G. Stoffel, in *Proceedings of the Symposium on High Temperature Superconductors II,* edited by D. W. Capone, W. H. Butler, B. Batlogg, and C. W. Chu (Materials Research Society, Pittsburgh, 1988), Vol. EA-14, p. 43.

[22] N. G. Stoffel, P. A. Morris, W. A. Bonner, and B. J. Wilkens, Phys. Rev. **37**, 2297 (1988).

[23] Y. Syono, M. Kikuchi, K. Oh-Ishi, K. Hiraga, H. Arai, Y. Matsui, N. Kobayashi, T. Sasaoka, and Y. Muto, Jpn. J. Appl. Phys. **26**, L498 (1987).

[24] J. M. Tarascon, W. R. McKinnon, L. H. Greene, G. W. Hull, and E. M. Vogel, Phys. Rev. B **36**, 226 (1987).

[25] This broad transition is probably due to Al doping from the crucible [see T. Siegrist, L. F. Schneemeyer, J. V. Waszczak, N. P. Singh, R. L. Opila, B. Batlogg, L. W. Rupp, and D. W. Murphy, Phys. Rev. B **36**, 8365 (1987)] and to inhomogeneities in the O content. We currently obtain transition widths of less than 3 K from as-grown crystals prepared in an oxygen ambient in platinum crucibles.

[26] M. K. Kelly, P. Barboux, J. M. Tarascon, D. E. Aspnes, W. A. Bonner, and P. A. Morris (unpublished).

[27] S. Massidda, J. Yu, A. J. Freeman, and D. D. Koelling, Phys. Lett. A **122**, 198 (1987).

[28] L. F. Mattheiss and D. R. Hamann, Solid State Commun. **63**, 395 (1987).

[29] S. L. Qiu, M. W. Ruckman, N. Brookes, P. D. Johnson, J. Chen, C. L. Lin, M. Strongin, B. Sinkovic, J. E. Crow, and Cham-Soo Jee, Phys. Rev. B **37**, 3747 (1988).

[30] Ming Tang, N. G. Stoffel, Qi Biao Chen, David LaGraffe, P. A. Morris, W. A. Bonner, G. Margaritondo, and M. Onellion (unpublished).

[31] J. C. Fuggle, P. J. W. Weijs, R. Schoorl, G. A. Sawatzky, J. Fink, N. Nucker, P. J. Durham, and W. M. Temmerman, Phys. Rev. B **37**, 123 (1988).

[32] D. C. Miller, D. E. Fowler, C. R. Brundle, and W. Y. Lee, in Ref. 2, p. 336.

[33] C. R. Brundle, J. Vac. Sci. Technol. **11**, 212 (1974).

[34] P. H. Citrin and G. K. Wertheim, Phys. Rev. B **27**, 3176 (1983).