

Reaction and disruption for Fe/La_{1.85}Sr_{0.15}CuO₄: Interface formation for high-temperature superconductors

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Inverse photoemission studies of the interface formed when Fe is deposited onto the high- T_c superconductor La_{1.85}Sr_{0.15}CuO₄ show that Fe leaches oxygen from the near-surface region to form insulating Fe-O. This reduces the number of Cu 3d-O 2p antibonding electronic states straddling the Fermi level. The Fe-induced depletion continues until the nominal Fe coverage reaches $\approx 8 \text{ \AA}$, at which point reaction is kinetically limited and a metallic Fe overlayer grows. Insight into the evolving near-surface environment of La is obtained through chemical shifts observed for the empty La 4f levels. Line-shape decompositions for these atomiclike empty states provide information analogous to that obtained with core-level photoemission.

The elucidation of the properties of high-temperature superconductors^{1,2} of the form La_{2-x}Sr_xCuO₄ and YBa₂Cu₃O_{7-x} has been extraordinarily rapid since their recent discovery. Measurements of the bulk crystal structures, the role of oxygen defects, and the electric and magnetic properties have contributed to the understanding of the high- T_c phenomenon.³ Probes of the electronic states using photoemission⁴⁻⁸ and inverse photoemission^{9,10} have generated insight into the band structures.¹¹⁻¹⁴ The surface stability of high- T_c materials under oxygen exposure and electron bombardment has also been addressed.^{9,10} On the other hand, the physics and chemistry of interfaces involving metals and high- T_c materials have not been studied. These interfaces are of critical importance if contacts are to be made to the superconductor, passivating layers are to be developed, and the promises of high- T_c technology are to be realized through integration with existing technologies.

In this paper we report the results of the first microscopic study of the interface between a metal and a high-temperature superconductor. We have used inverse photoemission to follow the evolving electronic structure and atomic distribution for Fe overlayers deposited in ultra-high vacuum onto cleaved polycrystalline La_{1.85}Sr_{0.15}CuO₄. This study is unique for several reasons. It is the first study that focuses on the stability and adatom-induced degradation of metal-superconductor interfaces involving the class of high- T_c ceramics. As we will show, substantial interface disruption and intermixing is observed so that the effect of reactive metal overlayers will be suppression of superconductivity in thin films. Second, we show that chemical state information can be obtained by investigating *empty* localized, atomiclike levels, in our case the La 4f levels 8.7 eV above the Fermi level E_F for the cleaved surface. These novel results are analogous to core-level characterization of reacting interfaces, but the technique of inverse photoemission has never before been used in this way. Iron was chosen for these interface stud-

ies because of the strong Fe-O affinity and because Fe impurities adversely affect superconductivity.

In our inverse photoemission experiments, we directed a highly collimated, monoenergetic beam of electrons at clean or Fe-covered La_{1.85}Sr_{0.15}CuO₄ surfaces. The distribution of emitted photons of energy $h\nu$ (the photon distribution curve or PDC) was measured. These photons resulted from the radiative decay of the incoming electrons from initial-state energies E_i of the solid to final, lower-lying empty states at energy E_f with conservation of energy so that $h\nu = E_i - E_f$. The experimental system allowed us to perform inverse photoemission experiments in both the ultraviolet (12–48 eV) and x-ray (1486.6 eV) regions. The latter is generally termed bremsstrahlung isochromat spectroscopy (BIS)¹⁵ while the former is momentum or k -resolved inverse photoemission (KRIPES).¹⁶ These are the time-reversed analogs of uv and x-ray photoemission.

The uv spectrometer consists of an $f/3.5$ grating and a position-sensitive detector which collects photons dispersed by the grating in a wavelength window determined by the grating setting. The x-ray spectrometer is an 0.5-m Rowland circle monochromator with a quartz grating and a microchannel plate detector. Only photons of energy 1486.6 eV are transmitted by this monochromator, and discrimination is enhanced by a self-supporting Al filter. The final-state energies were scanned by ramping the accelerating voltage of the electron gun. The electron gun is a custom-designed Pierce-type gun which produces a highly collimated electron beam of dimension 1 mm \times 5 mm.^{9,17} The combined energy resolution (electrons plus photons) was determined by analysis of the Fermi-level cutoff of a Au standard. It was 0.7 eV for BIS and 0.3–0.6 eV for KRIPES, depending on the photon energy. The combination of uv and x-ray spectroscopies enabled us to vary the probe depth of the measurements via the electron mean free path. It also made it possible to identify the orbital character of particular empty-state structures through variations in their cross sections.⁹

The $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ sample was high density, polycrystalline, and single phase with a superconducting transition temperature of ≈ 35 K (Ref. 18). The sample was cleaved *in situ* at better than 1×10^{-10} Torr. The Fe overlayers were evaporated at pressures less than 1.6×10^{-10} Torr at a rate of ~ 0.6 Å/min as monitored with a quartz thickness monitor. A series of KRIPES experiments with two different electron energies typically took ≈ 3 h to complete; the lower count rate of BIS increased the time per coverage to ≈ 5 h. The electron beam current was 15 μA for KRIPES and 100 μA for BIS. All measurements were conducted at room temperature.

In Fig. 1 we show KRIPES photon distribution curves for $\text{Fe}/\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ for incident energy $E_i = 26.25$ eV relative to E_F and for Fe coverages Θ between 0.25 to 30 Å. The topmost curve is for the as-cleaved surface. As can be seen, the density of states is very low within ~ 3.5 eV of E_F . The dominant structure at 8.7 eV has been identified with the La 4*f* empty states and the shoulder at 5.8 eV has been associated with the empty La 5*d* states. These results for the clean surface have been discussed in detail elsewhere.⁹ We now find that the effects of Fe adatoms are profound both near E_F and in the range of the

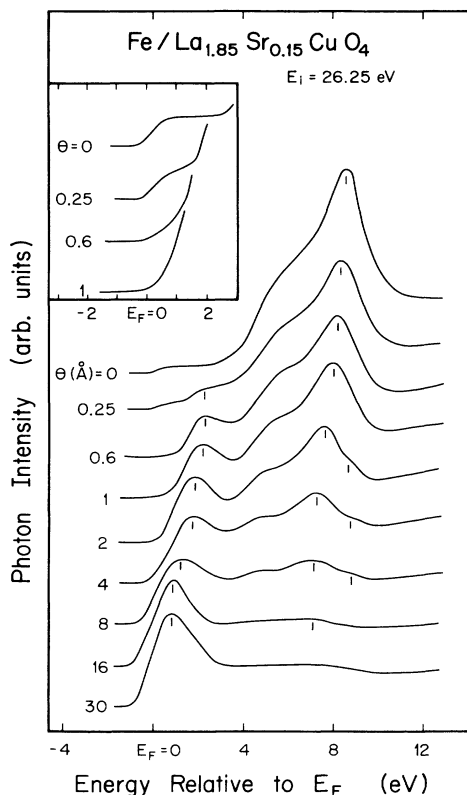


FIG. 1. Inverse photoemission spectra with $E_i = 26.25$ eV for the evolving $\text{Fe}/\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ interface showing the shift to lower energy of the La 4*f* and La 5*d* states. Fe 3*d* states initially appear well above E_F but shift toward E_F as they grow; a metallic Fermi-level cutoff becomes obvious after 8 Å of Fe. In the inset we expand fivefold the portion of the PDC's for low coverage to show the loss of emission from the hybrid Cu *d*-O *p* states within 2 eV of E_F .

La 5*d* and 4*f* states.

For the La states, there is a broadening and a shift to lower energy with increasing Fe coverage. This rather rigid shift reflects changes in chemical environment for the emitting La atoms. In the upper panel of Fig. 2 we summarize the energy position of the La 4*f* feature, using the KRIPES results of Fig. 1 for coverages below 30 Å and the more bulk sensitive BIS results for coverages between 30 and 80 Å. As shown, this shift is rapid at low coverage but there is saturation to 7.2 eV by ~ 8 Å. The BIS results show a slightly reduced shift because they probe a greater thickness and average over a range of states. Comparison of the final La 4*f* position with the corresponding energy position in La metal (at 5.3 eV) provides clear evidence that the local bonds of La in the perovskite crystal have been altered by the addition of Fe and the depletion of oxygen, rendering the environment of La more like that of the metal.

Careful analysis of the high-resolution KRIPES results of Fig. 1 shows that the 4*f* feature for the reacting interface for $\Theta = 2$ Å appears as a doublet with a small shoulder on the higher-energy side of the dominant 4*f* peak. This doublet structure persists to higher coverage. At lower coverage it is obscured because of the overlap with the shifting La 4*f* emission, but its presence can be detect-

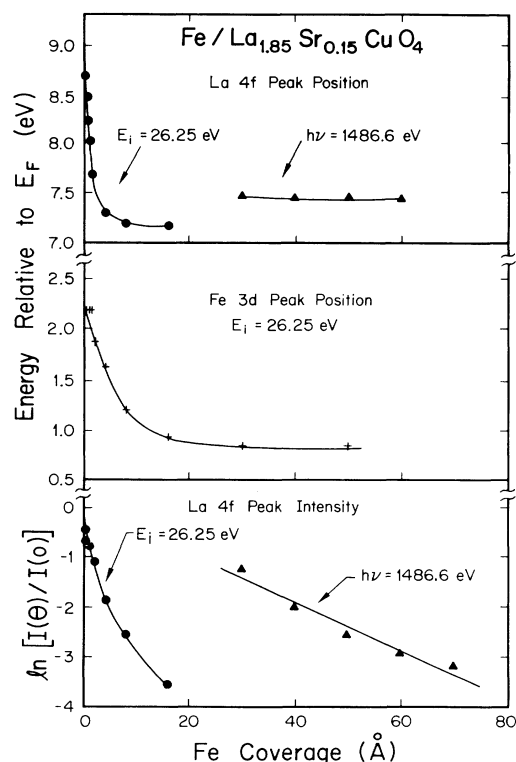


FIG. 2. Peak positions for the La 4*f* emission (top panel) and the Fe 3*d* emission (center panel) as a function of coverage for both KRIPES and BIS results showing the evolving energy position of the respective features. Attenuation curves for the La 4*f* emission are shown in the bottom panel. These results all demonstrate chemical interaction followed by the growth of an Fe overlayer.

ed through the broadening of the overall $4f$ feature. In Fig. 3 we show the results of line-shape decomposition for the PDC at 2 \AA , following the subtraction of a smooth background. The contributions from ≈ 3.5 to $\approx 7 \text{ eV}$ correspond to the reacted and unreacted La $5d$ component, and the line shape is complicated compared to the simpler Gaussian shape of the $5d$ emission spectra for the clean surface.⁹ The fits to the prominent higher-energy structure reveals that the shifted or reacted structure has an energy position of 7.7 eV . This corresponds to La atoms whose oxygen neighbors have been removed by Fe-O surface and near-surface reaction. The weaker peak at 8.7 eV reflects La from the unreacted portion of the superconductor. For La, the full width at half maximum (FWHM) for the reacted and unreacted $4f$ components was 1.4 and 1.0 eV , respectively, and the broadening of the reacted peak indicates that there are slightly inequivalent La chemical environments. Comparison of the emission intensity for unreacted La indicates that it is $\approx 7\%$ of that of the clean surface. The relative intensities of the two components are consistent with the $\approx 4 \text{ \AA}$ mean free path of incident electrons of energy $\approx 26 \text{ eV}$ relative to E_F . We therefore conclude that the outermost $\approx 8 \text{ \AA}$ of the nominal $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ surface is modified by the deposition of 2 \AA of Fe as it disrupts the $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ structure and breaks the chemical bonds between La and O.

Additional insight into the destruction of the $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ surface by the Fe overlayer, and the production of a nonsuperconducting skin, can be gained by examining changes in the PDC's near E_F . The results of Fig. 1 demonstrate that the Fe $3d$ states appear $\approx 2 \text{ eV}$ above E_F , whereas we would have expected them to grow at E_F if metallic Fe were forming. They then shift toward E_F and this shift in Fe $3d$ energy is summarized in the central panel of Fig. 2. By the time that the Fe coverage has reached 16 \AA , the peak has stabilized, but the PDC's

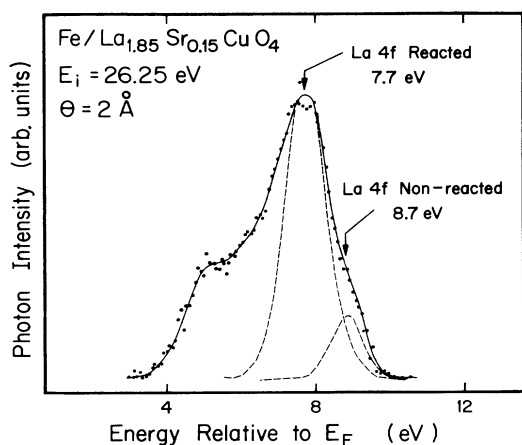


FIG. 3. Line-shape deconvolution of La $4f$ and La $5d$ structure for a nominal Fe coverage of 2 \AA following the subtraction of a smooth background. The $4f$ structure at 8.7 eV is the remnant of the unreacted substrate while the dominant feature at 7.7 eV reflects the La chemical environment after the scavenging of oxygen by Fe.

of Fig. 1 indicate that metallic Fe with a Fermi-level cutoff was forming by $\approx 8 \text{ \AA}$. The convergence to metallic Fe indicates that the chemical destruction of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ is limited at room temperature. The higher-energy position of the Fe $3d$ states at the lowest coverage indicates the formation of a large band-gap form of Fe-O.¹⁹ Analogous emission $\approx 4 \text{ eV}$ above E_F has been observed in nickel oxide formation.²⁰ This implies that there is an insulating phase at the Fe/ $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ interface. At the same time, the results of Fig. 1 indicate a dynamic evolution of Fe-O bonding configurations as the number of Fe atoms increases.

Another extremely important observation that can be made from Fig. 1 is that the reacting Fe overlayer directly modifies the Cu $3d_{x^2-y^2}-\text{O } 2p_{x,y}$ states near E_F . This is significant because the Cu $3d_{x^2-y^2}-\text{O } 2p_{x,y}$ states appear to play an important role in superconductivity, even though the density of these states is very low near E_F because of the single band character;^{11,12} as shown in the inset of Fig. 1, the density of these states is decreased by the deposition of 0.25 \AA of Fe. (The inset highlights the changes near E_F by enhancing the spectra fivefold for coverages to 1 \AA .) Deposition of Fe to 0.6 \AA diminishes these states further. For coverages of 0.6 and 1 \AA , there is hardly any emission, and this continues to be the case until the Fe $3d$ states of the growing metallic overlayer disperse to E_F and dominate. This can be understood in terms of dissociation of the Cu—O bonds and provides further evidence that the highly reactive metal Fe depletes the near-surface oxygen content as it forms an Fe-O phase. The loss of Cu-O antibonding states, the chemical shift of La, and the energy of the Fe $3d$ states all indicate the formation of a complex, multicomponent interface region. It appears likely that superconductivity in this region will be suppressed and that the scale of interaction will be enhanced by thermal activation. Indeed, the limited extent of the Fe-O interaction indicates kinetic limitations, not thermodynamics, and the metal/superconductor interface is then metastable.

In order to determine whether there is further chemical interdiffusion following the initial strong chemical interaction revealed by KRIPES, we conducted BIS studies for Fe coverages $30\text{--}80 \text{ \AA}$. For these measurements, the probing depth was substantially larger ($\lambda \approx 20 \text{ \AA}$) and the sensitivity to the La $4f$ states was much greater because of cross-section effects.^{9,21} These BIS spectra showed a saturated $4f$ chemical shift, as discussed above and shown in Fig. 2. Moreover, the BIS spectra showed the attenuation of the reacted La $4f$ peaks, indicating the termination of chemical reaction by the time the nominal Fe coverage reached $\sim 8 \text{ \AA}$. We estimate that this corresponds to disruption of $\sim 20 \text{ \AA}$ of the superconductor.

A more quantitative assessment of the rate at which the La $4f$ emission is attenuated by the growing Fe overlayer is shown in the bottom panel of Fig. 2 where we plot $\ln[I(\Theta)/I(0)]$ vs Θ , where $I(\Theta)$ is the total $4f$ emission at a coverage Θ . These intensities were obtained by subtracting a smooth background from the structure in the PDC's shown in Fig. 1. For brevity, the BIS data are not shown here but will be presented in a longer paper. In these attenuation curves, a straight-line behavior would

signal layer by layer growth and the slope would be a measure of the (incident) electron mean free path. The attenuation curves again demonstrate that there is extensive chemical reaction at low coverage since the La intensity decreases rapidly with a $1/e$ value which is smaller than the expected mean free path. This behavior is analogous to what is often observed for reactive metal/semiconductor interfaces and reflects outdiffusion of O to form the Fe-O layer. This layer is then thicker than that indicated by the nominal Fe coverage. For coverages exceeding about 4 Å, this rate is sharply reduced as the diffusion of O is curtailed. We estimate the mean free path from this behavior to be ≈ 4 Å at $E_i = 26.25$ eV. The BIS results for higher coverage further support a model in which the substrate and the thin reacted skin are covered by a thickening Fe layer, and we estimate the $1/e$ length to be 20 Å, consistent with high-energy electron scattering lengths (Fig. 2, bottom panel). Significantly, these results indicate that there is little, if any, La outdiffusion and that the Fe layer covers the surface uniformly without substantial amounts of exposed substrate. This latter characteristic is essential for the growth of a protective or passivating

film for high- T_c surfaces, even though the reaction-induced modification of the buried interface is not desirable.

In conclusion, we have studied the interface properties of Fe/La_{1.85}Sr_{0.15}CuO₄ with inverse photoemission with both uv and x-ray techniques. The results demonstrate that localized empty levels can be monitored to provide clear information about interface reaction and morphology. We have found Fe-O formation at the expense of La-O and Cu-O bonds. The interaction penetrated ≈ 20 Å into the La_{1.85}Sr_{0.15}CuO₄ surface, forming what are probably nonsuperconducting La-Cu metallic regions and insulating Fe-O regions. These chemical interactions were limited by diffusion, and a metallic Fe layer ultimately formed.

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- ¹J. G. Bednorz and K. A. Müller, *Z. Phys. B* **64**, 189 (1986).
- ²C. W. Chu, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, and Y. Q. Wang, *Phys. Rev. Lett.* **58**, 405 (1987).
- ³A listing of recent papers related to high-temperature superconductors appears in *Phys. Rev. Lett.* **58**, No. 20 (1987) and *Jpn. J. Appl. Phys.* **26**, No. 4 (1987).
- ⁴S. C. Moss, K. Forster, J. D. Axe, H. You, D. Hohlwein, D. E. Cox, P. H. Hor, R. L. Meng, and C. W. Chu, *Phys. Rev. B* **35**, 7195 (1987).
- ⁵A. Fujimori, E. Takayama-Muromachi, Y. Uchida, and B. Okai, *Phys. Rev. B* **35**, 8814 (1987).
- ⁶M. Onellion, Y. Chang, D. W. Niles, Robert Joynt, G. Margaritondo, N. G. Stoffel, and J. M. Tarascon *Phys. Rev. B* **36**, 819 (1987).
- ⁷P. D. Johnson, S. L. Qiu, L. Jiang, M. W. Ruckman, M. Strongin, S. L. Hulbert, R. F. Garrett, B. Sinkovic, N. V. Smith, R. J. Cava, C. S. Jee, D. Nichols, E. Kaczanowicz, R. E. Salomon, and J. E. Crow, *Phys. Rev. B* **35**, 8811 (1987).
- ⁸R. L. Kurtz, R. L. Stockauer, D. Mueller, A. Shih, L. E. Toth, M. Osofsky, and S. A. Wolf, *Phys. Rev. B* **35**, 8818 (1987).
- ⁹Y. Gao, T. J. Wagener, J. H. Weaver, A. J. Arko, B. Flandermayer, and D. W. Capone II, this issue, *Phys. Rev. B* **36**, 3971 (1987).
- ¹⁰T. J. Wagener, Y. Gao, J. H. Weaver, A. J. Arko, B. Flandermayer, and D. W. Capone II, this issue, *Phys. Rev. B* **36**, 3899 (1987).
- ¹¹L. F. Mattheiss, *Phys. Rev. Lett.* **58**, 1028 (1987).
- ¹²Jaejun Yu, A. J. Freeman, and J.-H. Xu, *Phys. Rev. Lett.* **58**, 1035 (1987).
- ¹³W. E. Pickett, H. Krakauer, D. A. Papaconstantopoulos, and L. L. Boyer, *Phys. Rev. B* **35**, 7252 (1987).
- ¹⁴Werner Weber, *Phys. Rev. Lett.* **58**, 1371 (1987); **58**, 2154 (E) (1987).
- ¹⁵J. K. Lang and Y. Baer, *Rev. Sci. Instrum.* **50**, 221 (1979).
- ¹⁶F. J. Himpsel and Th. Fauster, *J. Vac. Sci. Technol. A* **2**, 815 (1984); P. D. Johnson and N. V. Smith, *Phys. Rev. B* **27**, 2527 (1983).
- ¹⁷Y. Gao, M. Grioni, B. Smandek, J. H. Weaver, and T. Tyrie (unpublished).
- ¹⁸J. D. Jorgensen, H. B. Schuttler, D. G. Hinks, D. W. Capone II, K. Zhang, M. B. Brodsky, and D. J. Scalapino, *Phys. Rev. Lett.* **58**, 1024 (1987).
- ¹⁹L. F. Mattheiss, *Phys. Rev. B* **5**, 290 (1972).
- ²⁰F. J. Himpsel and Th. Fauster, *Phys. Rev. Lett.* **49**, 1583 (1982).
- ²¹Th. Fauster and F. J. Himpsel, *Phys. Rev. B* **30**, 1874 (1984).