Correction

PHYSICS

The authors note that due to a printer’s error, the figure legends for Figs. 5, 6, and 7 do not correspond to the proper figure. The figures and their corrected legends appear below.

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**Fig. 5.** 2D electron density (ED) profiles along (100) and (110) atomic planes of the M-I bilayer system. The EDs were determined from the experimentally measured diffraction intensities using the COBRA technique. Cold colors represent low ED while warmer colors represent higher ED. Schematic cross-sections of the complete tetragonal unit cell along each atomic plane are illustrated near the sides of the two respective panels. (Left) In (100) plane, the white lines highlight the projected shapes of the CuO$_6$ octahedra, in particular the elongation near the surface. (Right) In (110) plane, the white lines highlight the projected profiles of the La-apical O planes, in particular the corrugation near the surface.

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**Fig. 6.** Variation of the interatomic distances in single-phase metallic films. (A) The measured Cu(Al)–apical O distance, $c_A$, varies as a function of the nominal position of Cu(Al) atoms inside the refined structure. The data from four single-phase metallic films and the average over the four are presented. The lower and upper arrows represent the bulk values of $c_A$ for the LSAO substrate and for La$_2$CuO$_4$ insulator (I), respectively. (B) The comparison of $c_A$, $c_1$, and $c_2$, averaged for each unit cell, as a function of Z position from metallic single-phase samples. (Inset) the lattice constant $c_0$ as a function of Z. The dotted line represents the bulk substrate value. The horizontal dashed line is the average value of $c_0$ in bilayers extracted from the electron density, as described in the text. In A, B and the Inset, the vertical dashed lines represent the nominal substrate/metal interface.

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**Fig. 7.** The comparison of the averaged $c_A$ over measured single-phase metallic (M) and superconducting (S) films and M+I bilayers. The lower and upper arrows represent the bulk values of $c_A$ for the substrate and for the insulator, respectively. The vertical dashed lines and the dotted line represent the nominal substrate/metal interface and metal/insulator interface, respectively.

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Anomalous expansion of the copper-apical-oxygen distance in superconducting cuprate bilayers

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We have introduced an improved x-ray phase-retrieval method with unprecedented speed of convergence and precision, and used it to determine with sub-Angstrom resolution the complete atomic structure of epitaxial \( La_{2-x}Sr_xCuO_4 \) ultrathin films. We focus on superconducting heterostructures built from constituent materials that are not superconducting in bulk samples. Single-phase metallic or superconducting films are also studied for comparison. The results show that this phase-retrieval diffraction method enables accurate measurement of structural modifications in near-surface layers, which may be critically important for elucidation of the change in \( c_A \), the distance between copper and the nearest apical-oxygen site charge (17). This structural feature makes apical oxygen prone to very large displacements—e.g., in HgBa\(_2\)CuO\(_4\) one finds \( c_A \approx 2.8 \) Å, longer by 0.9 Å than the in-plane Cu-O bond; coincidentally, this compound has the highest \( T_c \) among all single-CuO\(_2\)-layer cuprates (18). It is also known that epitaxial strain strongly affects \( T_c \) in thin \( La_{2-x}Sr_xCuO_4 \) films (2, 19–21). It is generally agreed that tensile strain (e.g., on SrTiO\(_3\) substrates) tends to reduce \( T_c \) while compressive strain (e.g., on LaSrMIO\(_4\) like in the present study) tends to increase \( T_c \), although there has been some controversy about the precise enhancement mechanism and possible incorporation of interstitial oxygen (2, 19–21).

It is thus important to find out what happens to the apical oxygen in \( M - 1 \) bilayers. Since in ultrathin films the atomic positions can vary from one unit-cell layer to another, the standard x-ray diffraction analysis algorithms are no longer applicable. For this, the most suitable technique is the Coherent Bragg Rod Analysis (COBRA) method (22–24). COBRA is most effective for epitaxial films that are just a few unit cells (UCs) thick, but fabrication of ultrathin HTS films has been extremely challenging. Fortunately, we have a technical solution at hand—a unique atomic layer-by-layer molecular beam epitaxy (ALL-MBE) system with proven capability of fabricating ultrathin HTS layers (25 and 26).

For this study we have synthesized by ALL-MBE a number of \( La \)-capped ultrathin films including \( i \) single-phase films of optimally-doped \( La_{1.84}Sr_{0.16}CuO_4 \) superconductor \( S \), \( ii \) overdoped metal \( M \), and \( iii \) \((n \times M + m \times 1)\) bilayers, where \((n,m)\) determine the thickness of the respective layers expressed as the number of UCs. In this article, we show the COBRA results for all of these but with the focus on \( M + 1 \) bilayer samples. The films were deposited at \( T = 650^\circ C \) and \( p = 9 \times 10^{-6} \) Torr of ozone and subsequently cooled down under high vacuum to drive out all the interstitial oxygen. We used \( 10 \times 10 \times 1 \) mm\(^2\) single-crystal LaSrMIO\(_4\) (LSAO) substrates polished with the large surface perpendicular to the (001) direction. The substrate lattice constants are \( a_0 = b_0 = 3.755 \) Å, \( c_0 = 12.636 \) Å. The films are under compressive strain induced by the LSAO substrate and “pseudo-morphic” with it, meaning that the in-plane lattice constants in the film are almost equal to those of the substrate. The crystal structure of \( La_2CuO_4 \) is illustrated in Fig. 1A. Atomic force microscopy scans over a large \((10 \times 10)\)\( \mu m^2\) area showed rms surface roughness of 0.25 nm in the (2, 3) and 0.11 nm in the (2.5, 2.5) bilayer sample; this is significantly less than the 0.5 UC step height which is 0.66 nm. Magnetic susceptibility correlates with the maximal \( T_c \)—the longer \( c_A \), the higher \( T_c \). The first fact can be understood: \( c_A \) is “soft” because apical oxygen has no hard contact with the nearest copper ion; rather, it “levitates” on the electrostatic potential—a structural feature peculiar to certain layered oxides with alternating ionic planes of opposite charge (17). This structural feature makes apical oxygen prone to very large displacements—e.g., in HgBa\(_2\)CuO\(_4\) one finds \( c_A \approx 2.8 \) Å, longer by 0.9 Å than the in-plane Cu-O bond; coincidentally, this compound has the highest \( T_c \) among all single-CuO\(_2\)-layer cuprates (18). It is also known that epitaxial strain strongly affects \( T_c \) in thin \( La_{2-x}Sr_xCuO_4 \) films (2, 19–21). It is generally agreed that tensile strain (e.g., on SrTiO\(_3\) substrates) tends to reduce \( T_c \) while compressive strain (e.g., on LaSrMIO\(_4\) like in the present study) tends to increase \( T_c \), although there has been some controversy about the precise enhancement mechanism and possible incorporation of interstitial oxygen (2, 19–21).

Another recent discovery of interface superconductivity in complex oxides (1–5) has also generated some excitement and triggered a debate about its origin and the possibility to enhance \( T_c \) further (6–9). The interfacial enhancement (3) of \( T_c \) is influenced by the crystal structure. The Z-axis lattice constant \( (c_A) \) of epitaxial films varies significantly among undoped \( La_2CuO_4 \), an insulator \((I)\), \( La_{1.84}Sr_{0.16}CuO_4 \), an overdoped metal \((M)\), and bilayer \( M + I \) or \( M + M \) films, depending on the deposition sequence, and it affects superconductivity: \( T_c \) scales linearly with \( c_0 \) (10). In \( La_{2-x}Sr_xCuO_4 \) the change in \( c_0 \) goes together with the change in \( c_A \), the distance between copper and the nearest apical-oxygen, which some believe to play a key role in the HTS phenomenon (11–16). It is known that \((i)\) from one cuprate to another, \( c_A \) varies more than any other bond length, and \((ii)\) at least in simple cuprates with a single CuO\(_2\) layer in the unit cell it
was measured via two-coil mutual inductance technique and revealed sharp superconducting transitions at $T_c = 34$ K in the (2, 3), and $T_c = 36$ K in the (2.5, 2.5) bilayer, which is remarkable given that the films studied here are only 5 UC thick. This transition temperature was also confirmed by measuring the electric resistance (see Fig. 1B) after the x-ray scattering experiments were completed.

The atomic structure of the cuprate ultrathin films was investigated at beamline ID-33 of the Advanced Photon Source by measuring the diffraction intensities along the substrate-defined Bragg rods. The sample and a pixel array area detector (Dectris PILATUS 100 K model, see ref. 27) were mounted on a six-circle goniometer in the Kappa geometry. The experimental procedures are described in previous publications (23 and 24). Ten symmetry-invariant Bragg rods were recorded with the maximum value for the vertical reciprocal space coordinate $L_{\text{max}} = 10.5$ r.l.u. (reciprocal lattice units) and the sampling density of 50 points per r.l.u. The x-ray flux was $3 \times 10^{15}$ photons/sec at the wavelength $\lambda = 0.8266$ Å. The x-ray beam was focused to 0.1 mm (vertical) $\times$ 0.2 mm (horizontal) at the fixed incidence angle of 3.5°. The background and diffuse x-ray scattering contributions were removed accurately using the area detector images. The final results were normalized by taking into account the beam polarization and Lorentz factors and then analyzed using the COBRA method (22–24). In general, COBRA uses the measured diffraction intensities and the fact that the complex structure factors (CSFs) vary continuously along the substrate-defined Bragg rods to determine the diffraction phases and the CSFs. The CSFs are then Fourier transformed into real space to obtain the three-dimensional electron density of the film and of the substrate with sub-Angstrom resolution.

**Results and Discussions**

The experimental data of representative Bragg rods of a metal-insulator ($M + I$) bilayer sample are shown in Fig. 2. Notice that the diffraction intensity along the rods (excluding the Bragg peaks) varies by more than four orders of magnitude with excellent signal-to-noise ratio. The reference structures chosen as the starting point for the COBRA analysis were the bulk LSAO substrate structure and the tetragonal $M + I$ bilayer with the nominal (bulk) atomic positions. In our numerical simulations, the topmost four unit cells of the substrate were allowed to deform, however the resulting deformations turned out to be very small. The COBRA method uses the approximation that at two adjacent points along the Bragg rod the change in the complex structure factors (CSFs) contributed by the unknown part of electron density is negligible compared to the change in CSFs contributed from the reference structure (23). The use of this approximation allows COBRA to converge very quickly to approximately the right solution but not to the exact one. To overcome this limitation we further refined the CSFs using the Difference-Map algorithm introduced by Elser (28) and recently applied to thin films (29). Using the COBRA solution as the starting point for the Difference-Map algorithm and using a proper filter program that takes advantage of the fact that the CSFs vary continuously along the Bragg rods, the Difference-Map algorithm converges after about 20 iterations - an acceleration in convergence by about two orders of magnitude. As seen in Fig. 2, the final calculated and measured intensities are in very good agreement. Similar agreement was found for all other Bragg rods and the overall x-ray reliability factor is $R = \frac{\sum |F_o - F_c|}{\sum F_o} = 0.02$; here, $|F_o|$ and $|F_c|$ are the observed and the calculated diffraction amplitudes, respectively. To the best of our knowledge, so far there has been only one published determination of the structure of an ultrathin film using the Difference-Map method (29). In that study, over 2,000 iterations were needed to achieve convergence. The present study shows that the combined COBRA/Difference-Map method unites the best features of both methods and ensures rapid convergence to the correct solution.

The CSFs were Fourier transformed into real space yielding the three-dimensional electron density (ED). As an example, we show in Fig. 3 the ED of a (2, 3) bilayer sample along the (0, 0, Z) and (0.5, 0.5, Z) lines that go through the La(Sr), O, and Cu(Al) atoms. As seen, the ED has almost no negative parts. Together with the excellent agreement between the calculated and measured diffraction intensities, this suggests that the ED is very close to the correct one. All the atoms including oxygen can be clearly identified and their positions determined with sub-Angstrom resolution. The small ED intensity fluctuation below -53 Å provides a measure of the inaccuracy in the ED and it is small even compared to the oxygen ED. The occupancy of the last half UC is significantly reduced; this may be due to growth-induced terraces and island structures as observed also by atomic force microscopy, but also possibly due to some surface reconstruction or chemical modification due to exposure to atmosphere, with concomitant loss of epitaxial registry in that particular layer. The occupancy of the next-to-last half UC is also reduced but to a lesser extent, so that the atomic positions in this half UC are still well defined and are therefore included in our analysis.
The atomic positions in the Z direction were determined by fitting a Gaussian to each peak. We determined the size of the UC in the Z direction by measuring the distance between consecutive pairs of La(Sr) and Cu atoms. The results are shown in Fig. 4B inset. Each point corresponds to an average of four La-La distances and two Cu-Cu distances. The measured lattice constant of the bilayer film is 13.304 ± 0.016 Å and is larger by 0.148 Å than that of the bulk La$_2$CuO$_4$ ($c_0 = 13.156$ Å).

While the changes observed in the UC size are as expected from the strain and the elastic parameters (30), the variations in the Cu-apical-O and La-apical-O distances are quite unexpected. The distances $c_{A}$, $c_{I}$, and $c_2$ are defined in Fig. 1A; the distances labeled $c_{A}'$, $c_{I}'$, and $c_2'$ would be their symmetry-equivalents in bulk samples, but in thin films they could differ in principle. For our samples, the measured values for the primed and unprimed distances were in fact equal within the experimental error, except at the $M/II$ interface. The measured values averaged over $c_{A}$ and $c_{A}'$ are shown in Fig. 4A. The square, circular, and diamond dots represent the distances measured in one (2, 3) and two (2.5, 2.5) bilayer samples, respectively; the triangular dots are averages over the three samples. Every pair of triangular dots corresponds to one UC. The dashed and dotted vertical lines represent the nominal substrate/M interface and $M/II$ interface. The arrows on the right indicate $c_{A}$ as measured in the bulk samples. The results show that, within the experimental error (the error bar determination is described in the Methods section), the values of $c_{A}$ in the substrate are equal to those in the bulk but they are very different in the film. In both I and M bulk crystals (17), $c_{A}$ is equal to 2.41 Å. In the metal layer closest to the substrate $c_{A} = 2.3$ Å, and it then rises steadily all the way to $c_{A} = 2.75$ Å—a change of 0.45 Å. This anomalous expansion of the Cu-apical-O distance is clearly seen in the ED profiles of planes that contain the apical-O. These ED profiles were obtained by COBRA from the experimental diffraction intensities. The (100) ED profile in Fig. 5 (left) shows the elongation of the Cu-O$_6$ octahedra while the (110) ED profile in Fig. 5 (right) shows the striking enhanced corrugation of the La(Sr)-apical-O planes as the surface is approached. One point to stress is that no significant lateral displacement of the apical-O from the bulk positions can be resolved unambiguously from the analysis of our x-ray data.

In Fig. 4B we display $c_{A}$ together with the La-apical-O distance, $c_{2}$, and the distance between La and the nearest CuO$_2$ plane, $c_1$. Each point represents an average over the two bulk-symmetry-equivalent distances and over the three measured samples. Notice that $c_1$ changes by about 0.1 Å, while $c_{A}$ increases by about 0.45 Å, and $c_2$ decreases by about 0.25 Å. Close to the film surface, the apical-oxygen atoms are displaced away from the nearest Cu atoms. The La atoms are displaced towards the closest CuO$_2$ plane, but by a smaller amount, while the separation between two adjacent CuO$_2$ planes remains constant.

A critical question regarding the apical-O expansion in $M + I$ bilayer samples is whether it is a surface effect or associated with the $M – I$ interface, and whether it is also present in optimally-doped S films. With this motivation, x-ray measurements and COBRA analyses were also performed on single-phase $M$ and $S$ films of similar thickness. The determined values of $c_{A}$ for four single-phase $M$ films and the average over them are shown in Fig. 6A. The results show that, within the experimental error, the values of $c_{A}$ in the substrate are equal to those in the bulk and they are almost constant in the film but slightly smaller than the bulk $M$ value, as marked by the red arrow. The sample-to-sample variations show a comparably larger uncertainty of the $c_{A}$ values for the UCs near the surface. In Fig. 6B we display $c_{A}$, $c_2$, and $c_1$ for the average over all $M$ samples. Notice that there is no change in $c_1$ and, in contrast to the situation in $M + I$ films, $c_{A}$ is systematically smaller than $c_2$.

In single-phase $S$ films $c_{A}$ likewise remains almost constant within the experimental error (slightly larger than the bulk value). Thus, we can compare $c_{A}$ averaged over all the measured single-phase $M$ and $S$ films versus the $M + I$ bilayer samples in Fig. 7.
It shows a compelling picture: The copper-apical-oxygen distance \( c_A \) in the bottom metallic UCs of \( M+I \) bilayers is equal (within the experimental error) to those in single-phase \( M \) and \( S \) films, while the apical-oxygen displacement occurs only in the \( I \) layers of bilayer samples. This result suggests that the anomalous behavior is associated with the \( M-I \) interface. It has been argued already (10 and 17) that, in particular in insulating cuprates, the Coulomb interaction along the \( c \)-axis direction is strong, poorly screened, and long ranged; the origin of anomalous expansion of the copper-apical-oxygen bond in \( M-I \) bilayers must likewise be in the long-range Madelung energy contributions.

According to (15), \( c_A = 2.7 \) Å should correspond to a \( T_c \) of \( \sim 80 \) K at optimum doping. However, from (31) we know that hole density drops sharply on the \( I \) side of the interface and the screening length is equal to \( 6 \pm 2 \) Å. This consideration implies that on the \( I \) side and next to the \( M-I \) interface only one or two \( \text{CuO}_2 \) layers are doped via carrier accumulation while the others remain insulating. Thus, unfortunately, we have a mismatch: In the \( \text{La}_2\text{CuO}_4 \) layer optimally doped by charge transfer, \( c_A \) is close to its standard (bulk) value, while it is greatly elongated only in insulating layers. It is tempting to speculate that one could synthesize \( M-I \) bilayers with \( T_c \) much higher than 36 K, perhaps as high as 80–90 K, if only one could achieve the maximal \( c_A \) elongation and optimal doping in the same \( \text{La}_2\text{CuO}_4 \) layer. An obvious avenue for further research is to try making \( I \) layers even thinner, thus bringing the interface superconductivity closer to the film surface. Another is to try engineering more sophisticated hetero-structures and superlattices combining \( \text{La}_2\text{CuO}_4 \) with other metallic oxides (nickelates, zincates, etc.).

**Conclusions**

In summary, we have used a unique atomic layer-by-layer molecular beam epitaxy system to synthesize precise ultrathin bilayers using metallic but nonsuperconducting \( \text{La}_{1.35}\text{Sr}_{0.65}\text{CuO}_4 \) and insulating \( \text{La}_2\text{CuO}_4 \) blocks, and observed interface superconductivity with \( T_c = 34–36 \) K. We have used synchrotron x-ray diffraction and the combined COBRA/Difference-Map phase-retrieval method to determine accurately the atomic structure and found the UC size to be constant despite dramatic atomic displacements within the cell. In particular, the Cu-apical-O distance, known to strongly affect \( T_c \), increases by as much as 0.45 Å from the metal-insulator interface of the bilayer towards the surface. In contrast, within our experimental accuracy this distance remains constant in single-phase metallic and superconducting films. We conclude that in cuprates the crystal structure can be modified in near-surface layers, and in such a way that superconductivity properties can be dramatically altered; subtle lattice contributions apparently can play an important role. This finding underlines the importance of detailed surface-structure determination in conjunction with surface-sensitive probes of electronic states such as scanning tunneling microscopy or angle-resolved photoemission spectroscopy.
Methods
The error bars of the parameters of interest, such as the copper to apical-oxygen distance in this work, have been estimated for each individual sample using the following method, referred as Noise Analysis. This method resembles the widely used Bootstrap resampling approach for uncertainty estimation in statistical analysis. The number of data values is much larger than the number of points where the ED is to be determined. So if the measured and COBRA-calculated diffraction intensities are equal, the electron density is most likely unique and correct. The fact that there is a difference between the measured and COBRA-calculated diffraction intensities along the Bragg rods $\Delta I(h, k, l)$ is a result of experimental and theoretical errors, both systematic and stochastic. To estimate the error bars of the parameters of interest we add to the experimental data a random artificial noise $\Delta I(h, k, l)$ such that the envelopes of $\Delta I$ and its Fourier transform into real space are equal to those of $\Delta I$. We then reanalyze the new data and recalculate the parameters of interest. This process is repeated a number of times and the scatter in the values of the parameters of interest determines their error bars, which converge to a consistent value after approximately eight resamples. The error bars for each individual sample (typically $\pm 3\%$) were found to be somewhat smaller than the scatter due to sample-to-sample variations. The sample-to-sample variations include most of the individual sample uncertainties; therefore, the standard deviations from various samples are shown with the average of the parameters of interest in Figs. 4, 6, and 7.

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