

# Superconducting Transition at 38 K in Insulating-Overdoped $\text{La}_2\text{CuO}_4\text{-La}_{1.64}\text{Sr}_{0.36}\text{CuO}_4$ Superlattices: Evidence for Interface Electronic Redistribution from Resonant Soft X-Ray Scattering

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(Received 12 June 2008; published 12 March 2009)

We use resonant soft x-ray scattering (RSXS) to quantify the hole distribution in a superlattice of insulating  $\text{La}_2\text{CuO}_4$  (LCO) and overdoped  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  (LSCO). Despite its nonsuperconducting constituents, this structure is superconducting with  $T_c = 38$  K. We found that the conducting holes redistribute electronically from LSCO to the LCO layers. The LCO layers were found to be optimally doped, suggesting they are the main drivers of superconductivity. Our results demonstrate the utility of RSXS for separating electronic from structural effects at oxide interfaces.

DOI: 10.1103/PhysRevLett.102.107004

PACS numbers: 74.78.-w, 73.21.-b, 74.72.-h

The interface between two correlated electron systems can exhibit ground states that are not stable in the bulk of either of its constituents. This tendency could provide a novel route to new devices [1–5]. An interesting realization of this idea is the two-dimensional electron gases (2DEGs) observed at the interfaces between  $\text{LaTiO}_3$  and  $\text{SrTiO}_3$  [6],  $\text{SrTiO}_3$  and  $\text{LaAlO}_3$  [7,8],  $\text{LaMnO}_3$  and  $\text{SrMnO}_3$  [9–11],  $\text{La}_2\text{CuO}_4$  and  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  [12,13], and  $\text{ZnO}$  and  $\text{Mg}_x\text{Zn}_{1-x}\text{O}$  [14], which exhibit phenomena ranging from magnetoresistance to the quantum Hall effect to superconductivity.

One of the outstanding questions in this field is whether the 2DEGs observed in these heterostructures are truly “intrinsic” interface properties that arise from charge accumulation, or if they simply arise from defects like oxygen vacancies or cation interdiffusion. These two effects are virtually impossible to distinguish with transport measurements alone.

In this Letter, we present a quantitative study, using resonant soft x-ray scattering (RSXS), of the charge distribution in a superlattice of insulating  $\text{La}_2\text{CuO}_4$  (LCO) and overdoped  $\text{La}_{1.64}\text{Sr}_{0.36}\text{CuO}_4$  (LSCO). Despite its nonsuperconducting constituents, this heterostructure is superconducting with  $T_c = 38$  K [13]. Using RSXS, a technique that can probe the holes independently of the atomic lattice, we find that the hole density varies more gradually than the distribution of  $\text{Sr}^{2+}$  cations, indicating redistribution of carriers among the layers. Applying a linear response model, we show that this redistribution takes place over a characteristic distance of  $\lambda_0 = 6.1 \pm 2.0$  Å. The LCO layers are found to be highly doped, with filling  $p = 0.18$  holes/Cu, suggesting that superconductivity arises in the “insulating” substructure. Our results show that genuine charge accumulation can be achieved in oxide heterostructures and can be observed with RSXS.

Superlattices with LCO and LSCO sublayers of various thicknesses were grown in a unique atomic layer-by-layer MBE (ALL-MBE) system on  $\text{LaSrAlO}_4$  (LSAO) substrates. Structures were monitored during growth with time-of-flight ion scattering and recoil spectroscopy (TOF-ISARS) and reflection high-energy electron diffraction (RHEED). The samples were annealed to remove any excess, interstitial oxygen. The single-phase overdoped LSCO has in-plane lattice constants almost the same (to within 0.03%) as the LSAO substrate. LCO layers are strained, but even under maximal strain, single-phase LCO remains insulating and not superconducting. The sample selected for RSXS studies consisted of 15 repeats

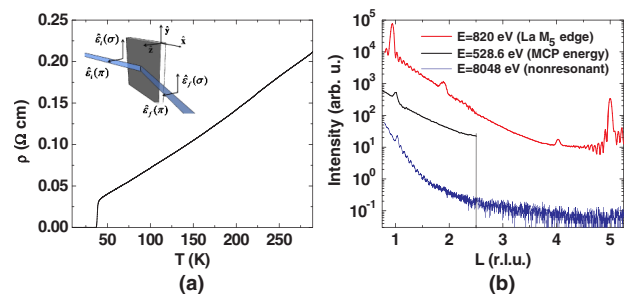


FIG. 1 (color online). (a) Superlattice resistivity showing  $T_c = 38.4$  K. (Inset) Experimental geometry showing the direction of incident and scattered polarizations. (b) Specular x-ray reflectivity measurements as a function of  $L$  (bottom line) off resonance, (top) near the La  $M_5$  edge, and (middle) at the mobile carrier peak (MCP) below the O  $K$  edge. At the La  $M_5$  edge, the peaks are slightly shifted from the integer values because of refraction effects. Thickness oscillations are visible, indicating flat interfaces. The width of the  $L = 1$  peak is determined by the thickness of the superlattice. The  $L = 2$  reflection is visible at the La edge, but not at the MCP, indicating that the holes do not follow the profile of Sr dopants.

of  $2 \times \text{LCO} + 4 \times \text{LSCO}$ , which despite its nonsuperconducting constituents had  $T_c = 38$  K [13], close to the value for optimally doped LSCO crystals. Hard x-ray measurements [Fig. 1(b), bottom line] were done on a reflectometer. X-ray absorption (XAS) measurements [Fig. 2(b), square symbols] showed the sample to be highly doped on average, with a small peak at the upper Hubbard band (UHB) that is seen more clearly in the resonance profile (red circles).

RSXS measurements were done at the undulator beam line X1B at the National Synchrotron Light Source in an ultrahigh vacuum (UHV) diffractometer. Measurements were made in the specular geometry, i.e., in reflectivity mode, with the momentum transfer perpendicular to the plane of the superlattice. Momenta will be written in terms of the third Miller index  $L$ , i.e.,  $Q = 2\pi L/c$ , where  $c = 39.84$  Å is the superlattice period. The X1 undulator produces both horizontally and vertically polarized light in the proportions  $P_\pi = 0.93$  and  $P_\sigma = 0.07$ , defined by the orientation with respect to the scattering plane [Fig. 1(a), inset]. The detector integrated over both scattering channels. XAS measurements were done *in situ* in fluorescence yield mode. The incident energy resolution was set to

$\Delta E = 0.2$  eV, and all measurements were done at  $T = 90$  K which was found to eliminate radiation damage.

Initial RSXS measurements are summarized in Fig. 1(b), which shows the scattered intensity as a function of  $L$  for various photon energies. The data are rather featureless far from resonance (8048 eV). Near the La  $M_5$  edge (820 eV), however, several peaks are visible at integer  $L$ , which are reflections from the superlattice period [15]. The reason these are visible at the La edge is that the contrast between LCO and LSCO layers, which have different La content, is enhanced. The relative intensities of these peaks are determined by the profile of Sr dopants in the superlattice.

The scattering of x-rays from the doped holes, which reflects their distribution, is enhanced if the beam energy is tuned to the mobile carrier peak (MCP) below the O  $K$  edge [16,17] [Fig. 2(b), arrow]. In Figs. 2(a) and 2(b) (red circles), we show scattering near this energy (528.6 eV). A giant resonance is visible near  $L = 1$ , indicating that, as expected, the holes are modulated with the period of the superlattice [18]. In contrast to scattering at the La edge, however, no peak is visible at  $L = 2$  for scattering at the MCP energy [Fig. 1(b)]. This shows that the distribution of holes does not exactly follow that of the Sr atoms. Suppression of a harmonic, in fact, suggests that the hole density varies more gradually than the profile of the  $\text{Sr}^{2+}$  ions, which is evidence for redistribution of holes among the layers.

The hole distribution can be determined quantitatively from this scattering. The integrated intensity of the charge reflection at momentum  $L$  is given by

$$\frac{I_L}{AV} = P_\sigma |\hat{\epsilon}_f^*(\sigma) \cdot \mathbf{S}_L \cdot \hat{\epsilon}_i(\sigma)|^2 + P_\pi |\hat{\epsilon}_f^*(\pi) \cdot \mathbf{S}_L \cdot \hat{\epsilon}_i(\pi)|^2 \quad (1)$$

where  $\mathbf{S}_L$  is the structure factor tensor,  $\hat{\epsilon}_f$  and  $\hat{\epsilon}_i$  are final and initial polarization states [defined as in Fig. 1(a), inset],  $V$  is the scattering volume, and  $A$  contains all proportionality factors, e.g., beam intensity, unit cell volume, etc. The  $\sigma$  term must be included since, although  $P_\sigma$  is small,  $\hat{\epsilon}_{i,f}(\sigma)$  lies in the  $\text{CuO}_2$  plane so this scattering has a large resonant enhancement.

The structure factor comprises two terms  $\mathbf{S}_L = \mathbf{S}_L^0 + \mathbf{S}_L^D$ . The first term

$$(\mathbf{S}_L^0)_{ij} = \delta_{ij} \sum_{l,n} d_l^n f_n(\omega) e^{i2\pi L z_l / c} \quad (2)$$

is the lattice structure factor, which is isotropic and describes scattering from the atomic lattice. Here,  $z_l$  is the position of layer  $l$ ,  $d_l^n$  is the number of atoms of type  $n$  in one  $a \times a$  area of this layer, and  $f_n(\omega)$  is the scattering factor of atom type  $n$  [19]. The matrix  $d_l^n$  defines the structure of the superlattice, including the distribution of defects. For clarity, we will first analyze our data assuming

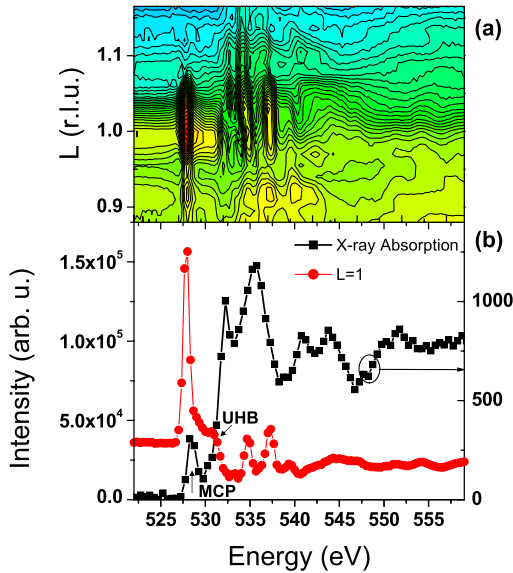


FIG. 2 (color online). Energy dependence of the  $L = 1$  superlattice reflection near the O  $K$  edge. (a) Color plot (logarithmic color scale), showing that the reflection is enhanced at the energy of the mobile carrier prepeak (MCP), which indicates that the holes are modulated with the period of the superlattice. (b) Summary plot comparing the intensity of the  $L = 1$  reflection from (a) (red circles), to the x-ray absorption spectrum (black squares). The slight energy shift between the XAS and resonance maximum occurs because of interference between resonant and off-resonant scattering. This interference allows us to determine quantitatively the amplitude of the hole modulation.

a perfect structure, and correct the result for defects afterward.

The second term

$$(\mathbf{S}_L^D)_{ij} = f_{ij}^D(\omega) \sum_l \frac{p_l^0}{2} e^{i2\pi Lz_l/c} \quad (3)$$

is anisotropic and describes scattering from the doped holes.  $p_l^0$  is the hole count per Cu atom in layer  $l$  in an ideal structure, and  $f_{ij}^D(\omega)$  is the scattering power of a doped hole [16,20]. The factor 1/2 accounts for the fact that there are two planar oxygen atoms for each Cu atom.

We wish to determine  $p_l^0$ , which is the distribution of holes in the superlattice. This task is simplified by realizing that, by symmetry [Fig. 3(b)], our structure has only three inequivalent  $\text{CuO}_2$  planes: the two central LSCO layers, the two outer LSCO layers, and the two LCO layers. We denote the hole occupancies in these layers by  $p_{\text{max}}^0$ ,  $p_{\text{int}}^0$  and  $p_{\text{min}}^0$ , respectively [see labels in Fig. 3(b)]. Further, by charge conservation, it must be that  $p_{\text{max}}^0 + p_{\text{min}}^0 + p_{\text{int}}^0 = 0.72$  holes. Therefore, to completely determine the hole distribution in this superlattice, we need only two more independent measurements of these three values.

The first measurement is the scattering near  $L = 2$ . Written out, the structure factor of this reflection is

$$(\mathbf{S}_2)_{ij} = 0.84x[f_{\text{La}}(\omega) - f_{\text{Sr}}(\omega)]\delta_{ij} + 0.5(p_{\text{min}}^0 + p_{\text{max}}^0 - 2p_{\text{int}}^0)f_{ij}^D(\omega) \quad (4)$$

where  $x = 0.36$  is the doping of the LSCO layers. The origin  $z = 0$  was chosen between two LCO layers. This reflection is not visible off resonance, but becomes visible near the La  $M_5$  edge because the difference  $f_{\text{La}}(\omega) - f_{\text{Sr}}(\omega)$  becomes large. However, near the MCP resonance, where  $f_{ij}^D$  is large (164 electrons at the resonance maximum [16]), the peak is not observed. That it is absent is evidence that it is forbidden by symmetry, i.e.,  $p_{\text{max}}^0 + p_{\text{min}}^0 - 2p_{\text{int}}^0 \approx 0$ . With the constraint of charge conservation, this gives  $p_{\text{int}}^0 \approx 0.24$ . The nominal doping of this layer is 0.36 holes, so this result shows—prior to knowledge of  $p_{\text{max}}^0$  and  $p_{\text{min}}^0$ —that holes have diffused from the interface layer.

The second measurement comes from the scattering near  $L = 1$ . The structure factor of this reflection is

$$(\mathbf{S}_1)_{ij} = 1.66x[f_{\text{Sr}}(\omega) - f_{\text{La}}(\omega)]\delta_{ij} + 0.87(p_{\text{max}}^0 - p_{\text{min}}^0)f_{ij}^D(\omega). \quad (5)$$

Unlike the  $L = 2$  reflection, this peak is visible at both the La  $M_5$  and MCP resonances, indicating that it is allowed by symmetry; i.e., the difference  $p_{\text{max}}^0 - p_{\text{min}}^0$  is nonzero. Knowledge of this difference would completely determine the hole distribution in the superlattice.

To determine  $p_{\text{max}}^0 - p_{\text{min}}^0$  directly from this reflection, however, would require a measurement of  $\mathbf{S}_1$  in absolute units, i.e., the knowledge of the overall constant  $A$  in Eq. (1), whose value derives from many different effects. We can eliminate  $A$ , however, by noting that  $f_{ij}^D$  quickly goes to zero away from the resonance energy [16], and that the remaining terms  $f_{\text{La}}$  and  $f_{\text{Sr}}$  are tabulated [21].  $p_{\text{max}}^0 - p_{\text{min}}^0$  can therefore be determined from the relative increase in intensity of  $L = 1$  scattering at MCP from that a few eV below the edge [22]. A detailed energy dependence of  $L = 1$  scattering is shown in Fig. 2. From the relative increase in integrated intensity at MCP of 560%, and using the method outlined above to eliminate  $A$ , we obtain  $p_{\text{max}}^0 - p_{\text{min}}^0 = 0.18$ . From these constraints, we calculate  $p_{\text{max}}^0 = 0.33 \pm 0.025$  and  $p_{\text{min}}^0 = 0.15 \pm 0.025$ .

This result is significant because it shows that the carriers are not bound to the  $\text{Sr}^{2+}$  ions, but rearrange between layers, presumably to minimize their kinetic energy. For the perfect structure (roughness effects will be considered below), the “undoped” LCO layers have a hole count of at least 0.15 holes/Cu, which is close to optimal doping for the LSCO system. This suggests that superconductivity originates in the nominally insulating LCO layers.

Having determined the hole distribution, it is useful to characterize it with a screening length,  $\lambda_0$ . The simplest way to define  $\lambda_0$  is in linear Thomas-Fermi theory, relating the charge  $\rho^{\text{ind}}$  induced in a medium to the external charge density  $\rho^{\text{ext}}$  by

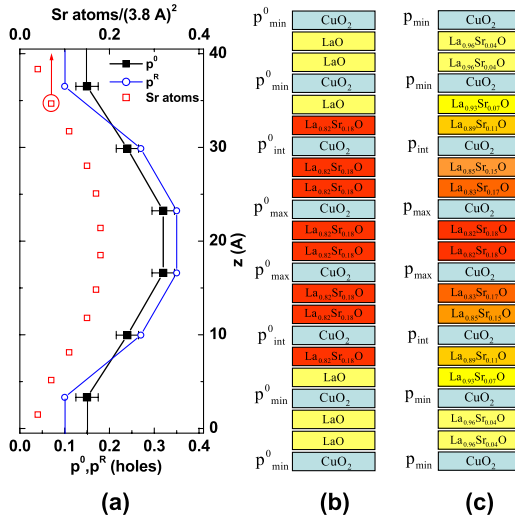


FIG. 3 (color online). (a) Layer-resolved hole count in an ideal structure (solid squares) and the hole count that would obtain from structural roughness only (open circles). These two distributions are convolved to achieve the hole distribution in the real structure (panel c). The error bars represent our uncertainty in determining  $P_\sigma$  and  $P_\pi$  in Eq. (1), as well as statistical errors. Also shown is the nominal distribution of  $\text{Sr}^{2+}$  ions (open squares). (b) Sketch of the superlattice hole distribution in an ideal structure, aligned to panel (a) for comparison. (c) Sketch of the hole distribution in the real structure, accounting for La/Sr interdiffusion.  $p_{\text{min}}^0$  and  $p_{\text{min}}^R$  are the hole counts in the LCO layers contributed by electronic effects and by roughness, respectively.



$$\rho^{\text{ind}}(Q) = -\frac{k_0^2}{k_0^2 + Q^2} \rho^{\text{ext}}(Q), \quad (6)$$

where  $k_0 = 1/\lambda_0$  is the Thomas-Fermi wave vector.

In the present case, the “external” charge is that of the  $\text{Sr}^{2+}$  ions [23], and the induced charge is the hole occupancy  $p_i^0$ , i.e.,  $\rho^{\text{ext}}(Q) = \sum_i d_i^{\text{Sr}} e^{iQz_i}$  and  $\rho^{\text{ind}}(Q) = \sum_i p_i^0 e^{iQz_i}$ , where  $d_i^{\text{Sr}}$  and  $p_i^0$  were defined in Eqs. (2) and (3). For the  $L = 1$  reflection, for which  $Q = 2\pi/c$ ,  $\rho^{\text{ext}} = -1.66x$  and  $\rho^{\text{ind}} = 1.73(p_{\text{max}}^0 - p_{\text{min}}^0)$ , resulting in  $\lambda_0 = 6.1 \pm 2.0 \text{ \AA}$ . This would be the characteristic size of the accumulation region in a device made of these two materials.

We now consider the effect of interfacial roughness on the previous conclusions. The structure is not perfect, but contains step edges from island formation during growth [13], as well as some La-Sr interdiffusion. For specular measurements, such defects can be modeled well by a convolution of the La-Sr profile with a Gaussian roughness function. From convolution theorem, this correction enters as a multiplicative factor in momentum space  $R(Q) = e^{-Q^2\sigma^2/2}$ , where  $\sigma$  is the interface roughness. This factor has the effect of suppressing higher order reflections. From the ratio of the  $L = 1$  and  $L = 2$  reflections at the La edge, we determine  $\sigma = 5.3 \text{ \AA}$ . This roughness causes a smearing of the hole density *in addition* to the electronic redistribution we have already shown. Including roughness, the structure factor at  $L = 1$  is modified as

$$(\mathbf{S}_1)_{ij} = 1.66x[f_{\text{Sr}}(\omega) - f_{\text{La}}(\omega)]\delta_{ij}R(2\pi/c) + 0.87(p_{\text{max}} - p_{\text{min}})f_{ij}^D(\omega), \quad (7)$$

where  $p_{\text{max}}$  and  $p_{\text{min}}$  are the actual hole occupancies in the real, imperfect structure. From Eq. (6), it follows that  $p_{\text{max}} - p_{\text{min}} = (p_{\text{max}}^0 - p_{\text{min}}^0)R(2\pi/c)$ . Thus, in our earlier analysis, in which  $S_1^D$  was determined by normalizing to the value of  $S_1^0$ , the term  $R(2\pi/c)$  divided out. As a result, the method used above to obtain  $\lambda_0$  is independent of roughness effects. Further, the quantities  $p_{\text{max}}^0 = 0.33$ ,  $p_{\text{int}}^0 = 0.24$ , and  $p_{\text{min}}^0 = 0.15$  can be thought of as those that would have obtained if the structure were defect-free. Including the roughness contribution, the true  $p$  values in our structure are  $p_{\text{max}} = 0.30 \pm 0.03$ ,  $p_{\text{int}} = 0.24 \pm 0.03$ , and  $p_{\text{min}} = 0.18 \pm 0.03$ . We note that if we include only the roughness, the values are  $p_{\text{max}}^R = 0.35$ ,  $p_{\text{int}}^R = 0.27$ , and  $p_{\text{min}}^R = 0.10$ .  $p^R$  is defined as the  $\text{CuO}_2$  layer doping due solely to the roughness of the structure. Therefore, the dominant cause of doping of LCO layers is electronic accumulation, not defects.

In conclusion, we have used RSXS to quantify the distribution of holes in a superlattice of insulating LCO and nonsuperconducting LSCO. We find that the distribution of holes differs from that of the  $\text{Sr}^{2+}$  ions, indicating

true charge accumulation. The filling of the LCO layers is found to be close to 0.18 holes/Cu, suggesting that the “insulating” layers are the main drivers of superconductivity. Our study demonstrates that charge accumulation can be achieved at transition metal oxide interfaces with existing synthesis methods. Our study also demonstrates the usefulness of RSXS for distinguishing atomic from electronic reconstruction at transition metal oxide interfaces.

This work was supported by the Office of Basic Energy Sciences, U.S. Department of Energy. RSXS studies were supported by Grant No. DE-FG02-06ER46285, with use of the NSLS supported under Contract No. DE-AC02-98CH10886. Superlattice growth and characterization were supported under Contract No. MA-509-MACA. Work in the FSMRL was supported by Grants No. DE-FG02-07ER46453 and No. DE-FG02-07ER46471.

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