

Anomalous enhancement of the superconducting transition temperature of electron-doped $\text{La}_{2-x}\text{Ce}_x\text{CuO}_4$ and $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4$ cuprate heterostructures

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The superconducting transition temperature T_c of multilayers of electron-doped cuprates, composed of underdoped (or undoped) and overdoped $\text{La}_{2-x}\text{Ce}_x\text{CuO}_4$ (LCCO) and $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4$ (PCCO) thin films, is found to increase significantly with respect to the T_c of the corresponding single-phase films. By investigating the critical current density of superlattices with different doping levels and layer thicknesses, we find that the T_c enhancement is caused by a redistribution of charge over an anomalously large distance.

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One of the striking properties of the high- T_c cuprates is the strong dependence on the number of charge carriers put into the CuO_2 planes of many of their electronic properties. For example, for low carrier concentration (underdoped regime) the material is insulating; it is metallic for high carrier concentration (overdoped regime) and superconducting in between, with a maximal T_c for the optimum doping. The charge carriers can be either holes or electrons.¹

Recently, it has been shown that heterostructure bilayers (BL's) and superlattices (SL's), composed of metallic and insulating hole-doped cuprates, can be superconducting.^{2,3} Also, a BL of superconducting $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (LSCO) and metallic, nonsuperconducting $\text{La}_{1.65}\text{Sr}_{0.35}\text{CuO}_4$ has a critical temperature (T_c) greater than the superconducting single-phase LSCO itself, with a maximal enhancement for $x = 0.125$.^{4,5} In this case, the superconducting layer was shown to be confined to the interface. The T_c enhancement in Refs. 4 and 5 has been interpreted in terms of an interplay between the large pairing amplitude in the underdoped (UD) cuprate and the phase stiffness originating from the metallic overdoped (OD) layer.⁶ In this model, T_c in UD cuprates is not the temperature where the pairs are formed and condensed as in the BCS theory, but a temperature at which phase order is destroyed by fluctuations despite the persistence of pairing amplitude.⁷ Other possible explanations for the T_c enhancement are oxygen diffusion or uptake, strain induced by the substrate,⁸ and cationic diffusion between the layers. The latter was shown to be negligible for LSCO.²

In hole-doped cuprates, a large phase fluctuation region above T_c has been observed by different techniques, such as the Nernst effect and torque magnetization,^{9,10} and scanning tunneling microscopy measurements.^{11,12} In contrast, in the electron-doped cuprates, the pairing amplitude seems to follow T_c even for the UD side,¹³ and phase fluctuations appear to be small as indicated by the narrow region of vortex Nernst effect observed above T_c .¹⁴ The normal state tunneling gap was interpreted as preformed superconductivity; however, this gap vanished at rather low temperatures, not very far away from the T_c for UD samples.¹⁵ If the interplay between the pairing amplitude in the UD layer and the phase stiffness in the OD layer is the origin of the T_c enhancement in cuprate SL's one would expect a smaller enhancement for electron-doped heterostructures.

Here we report a large T_c enhancement in electron-doped cuprate heterostructures of both $\text{La}_{2-x}\text{Ce}_x\text{CuO}_4$ (LCCO) and $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4$ (PCCO) SL's. This large T_c enhancement argues against an increased phase stiffness in the UD layer as proposed in Ref. 6. However, we find that the critical current of the SL's scales with the total layer thickness and not with the number of interfaces. This suggests that the observed T_c enhancement is not confined to the interfaces but is caused by a global redistribution of charge carriers. In addition, we find that the T_c of the SL's scales with the c -axis lattice parameter as found in single-phase PCCO films.¹⁶ From these results we conclude that the T_c enhancement in electron-doped SL's is caused by an anomalous charge redistribution over a very large length scale of at least 20 nm. Our results suggest that the T_c enhancement found in hole-doped cuprates may have the same origin.

Epitaxial films were grown on SrTiO_3 (STO) substrates by the pulsed laser deposition (PLD) method.^{17,18} We took extra care optimizing the annealing conditions for each geometry and composition to obtain the maximal T_c . LCCO is chemically stable for $x \geq 0.06$, whereas it has a contaminative T phase for lower Ce concentrations.^{19,20} PCCO can be deposited with $x < 0.20$. SL's of LCCO were prepared with successive layers of $x = 0.06$ (UD) and OD layer with $x = 0.17, 0.19$, and 0.21 . For PCCO SL's we used consecutive layers of $x = 0.19$ (OD) and PCCO with $x = 0.00, 0.11$, and 0.12 . BL's of PCCO are composed of $x = 0.12$ and $x = 0.19$. For all the SL's in this study the total thickness is kept ~ 140 nm, and each layer has the same thickness. We use the notation $(x/0.06)_n$ for n interfaces between alternate OD LCCO ($x = 0.17, 0.19$, and 0.21) and UD $x = 0.06$.

Figure 1(a) presents x-ray θ - 2θ diffraction (XRD) spectra of LCCO sample $(0.19/0.06)_{n=10}$, which has 11 layers with each layer ~ 13 nm (~ 10 u.c.). Well-defined multiple satellite peaks originated from the modulated structure can be observed along with the main peaks of single-phase films. This confirms the periodic layered structure. The modulation period can be calculated from $\Lambda = \lambda/2(\sin \theta_i - \sin \theta_{i+1})$, where i and $i + 1$ represent the two nearest satellite peaks.²¹ From our data we obtain $\Lambda \sim 26$ nm, consistent with the expected 20-u.c. periodicity from the deposition rate. Resonant soft x-ray scattering³ for $(0.19/0.06)_{n=10}$ sample show a SL modulation at the Ce edges. As seen in Fig. 1(b), several satellite peaks that

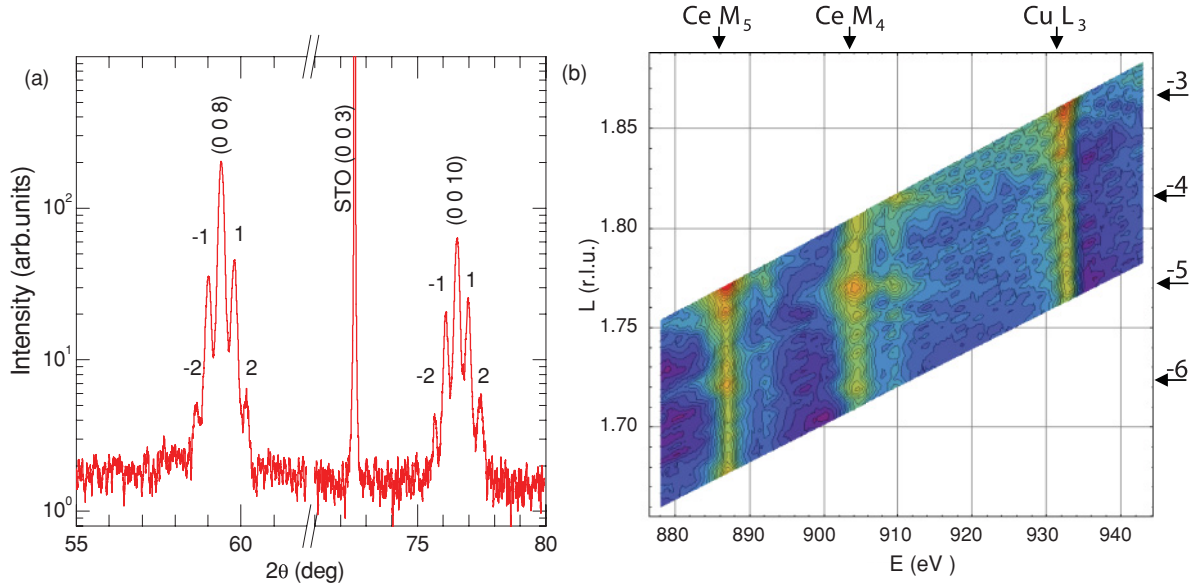


FIG. 1. (Color online) (a) XRD θ - 2θ spectra of $(0.19/0.06)_{n=10}$. The main Bragg peaks of (0 0 8) and (0 0 10) and the superlattice satellite peaks are marked. (b) Energy dependence of SL reflections near Ce and Cu edges measured with resonant soft x-ray scattering for sample $(0.19/0.06)_{n=10}$. Horizontal arrows (with -3 , -4 , -5 , -6) point to positions of superlattice peaks predicted from XRD measurements. Peaks are clearly visible at Ce M_4 and M_5 edges around 910 and 890 eV, respectively, but not at the Cu L_3 edge. Shorter period oscillations in the figure are fringes due to finite sample thickness. The soft x-ray energy limits the scattering momentum at high L .

coincide with the positions predicted from the above equation with $i = -3, -4, -5, -6$ are clearly visible at ~ 910 eV (Ce M_4 edge) and 890 eV (Ce M_5 edge), respectively. This observation indicates that the SL reflections really arise from a selective modulation in the Ce density, whereas the Cu atoms reside in their usual, lattice positions. We also did an electron energy-loss spectroscopy (EELS) measurement on a similar SL film and found a clear Ce modulation.

Figure 2(a) shows one example of T_c enhancement in a LCCO SL, $(0.19/0.06)_{n=10}$. The $x = 0.06$ single-phase films have a broad transition with onset transition temperature $T_c^{\text{onset}} < 12$ K; the OD $x = 0.19$ is metallic and nonsuperconducting. After constructing the SL, the T_c^{onset} of $(0.19/0.06)_{n=10}$ reaches 24 K, comparable to the value of optimal doping $x = 0.11$ with $T_c^{\text{onset}} \sim 26$ K. The real part of the ac susceptibility for $(0.19/0.06)_{n=10}$ and single-phase $x = 0.11$ are shown in the inset of Fig. 2(a). In Fig. 2(b) and 2(c), the transition temperatures T_{c0} (zero resistance of superconducting transition) and T_c^{onset} are plotted against the doping for LCCO and PCCO, respectively. All the SL's show an obvious T_c enhancement with respect to the single-phase films themselves—almost constant for either LCCO with varying OD layer or PCCO with varying UD layer—and are higher than that of BL's. Since for the SL the T_c enhancement is not small, the question naturally arises as to what mechanism is responsible for this enhancement.

One possible explanation is a substrate strain effect, which is expected to be important in very thin films.^{8,22} In our experiment the thickness of the bottom layer changed from 5 to 20 nm while T_c remained approximately constant. It is therefore unlikely that the enhancement is caused by strain.

Next, we check if the T_c enhancement in the SL is confined to the interface. Assuming well-defined superconducting interfaces and a nonsuperconducting bulk film, the super-

current should flow along the interfaces and “short-circuit” the entire film. In this scenario, one expects the critical current (I_c) to scale with n , the number of the interfaces.²³ In Fig. 3(a), typical current (I) and voltage (V) characteristics are shown

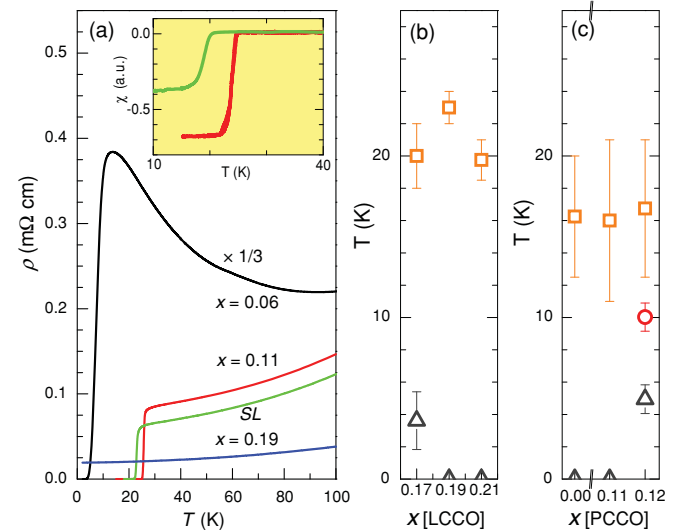


FIG. 2. (Color online) (a) The resistivity, $\rho(T)$, of single-phase LCCO with $x = 0.06, 0.11$, and 0.19 , and also the $(0.19/0.06)_{n=10}$ SL. Note that $\rho(T)$ of $x = 0.06$ is divided by a factor of 3. (Inset) The real part of ac susceptibility vs. temperature for single-phase LCCO with $x = 0.11$ (red) and $(0.19/0.06)_{n=10}$ (green). (b) T_c of single-phase LCCO (Δ), $(x/0.06)_{n=10}$ SL's (\square). (c) T_c of single-phase PCCO (Δ), SL's with fixed OD $x = 0.19$ (\square) and BL's (\circ). The BL data are obtained from the structure of 240 nm $x = 0.12$ and 60 nm $x = 0.19$. T_c of single-phase PCCO with $x = 0.19$ is ~ 7.3 K. The top and bottom of the error bars correspond to T_c^{onset} and T_{c0} , respectively.

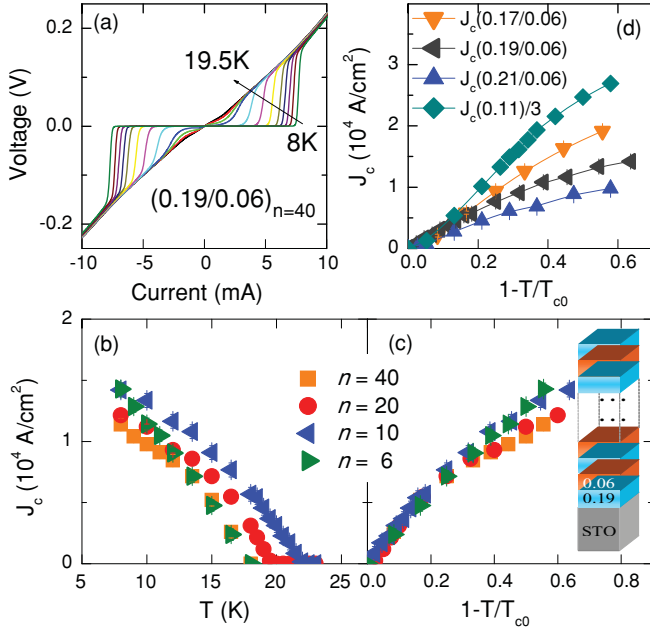


FIG. 3. (Color online) (a) I - V of LCCO SL (0.19/0.06) _{$n=40$} from 8 to 19.5 K. Critical currents were determined using a 1×10^{-6} V criteria. [(b) and (c)] The critical current density J_c versus T and $(1 - T/T_{c0})$ of LCCO SL's (0.19/0.06) _{n} with $n = 40, 20, 10, 6$, respectively. (Inset) The structure configurations for (0.19/0.06) _{n} . (d) J_c versus $(1 - T/T_{c0})$ of LCCO single-phase $x = 0.11$ (divided by a factor of 3) and SL's $(x/0.06)_{n=10}$ with $x = 0.17, 0.19$, and 0.21.

for LCCO (0.19/0.06) _{$n=40$} at various temperatures. The value for $J_c(T)$ is calculated from $I_c/(w \times t)$ with w the width of the current bridge and t the total thickness of the film. Since both the w and t are kept the same for different SL's, then $J_c(T)$ should be proportional to n in the interface-effect scenario. We repeat these measurements for various n 's. In particular we measured LCCO (0.19/0.06) _{n} with $n = 40, 20, 10, 6$. These SL's have approximately the same T_c . Surprisingly, at all temperatures J_c is approximately independent of n as seen in Fig. 3(b). In Fig. 3(c) we plot J_c for various n 's against the reduced temperature $(1 - T/T_{c0})$. It can be clearly seen that J_c is not proportional to n but approximately the same, so the T_c enhancement is not confined to the interface. This can also rule out that the T_c enhancement is caused by slight Ce doping, i.e., several unit cells at the interface. Note that our x-ray data [Fig. 1(b)] and EELS data (not shown) have excluded the case of heavy Ce diffusion since Ce modulation is clearly observed.

It has been reported that in La_2CuO_4 (LCO)/LSCO SL the conducting holes do not follow the distribution of the Sr atoms, and the LCO layers become highly doped. This suggests a redistribution of the charge carriers among the layers.³ A similar effect must take place in our films, where the charge carriers redistribute between the OD and UD layers. In the charge-redistribution scenario, the total effective thickness of the T_c -enhanced region is determined by the Ce difference in the adjacent layers, irrespective of n . Exactly how the charge redistributes is not known but our data in Fig. 3(c) suggest that this charge is spread over at least 20 nm since the J_c of (0.19/0.06) _{n} is approximately the same for all n 's (for $n = 6$, the layer thickness is 20 nm). Figure 3(d) shows the J_c data

for SL's $(x/0.06)_{n=10}$ with $x = 0.17, 0.19$, and 0.21, and also the single-phase $x = 0.11$ film. We note that as x increases the J_c of $(x/0.06)_{n=10}$ decreases. This is understandable in the charge-redistribution scenario since the T_c -enhanced region with optimal charge count should be smaller as the Ce range becomes larger for the same total film thickness. Future T_c and J_c experiments will be needed on thicker layers to determine a more definitive number for the anomalous length scale. We have attempted to make superlattices with $n = 4$ and 2 but so far without success.

Figure 4 presents the T_c versus c axis lattice parameter (c_0) for LCCO films deposited in various techniques and SL's with different annealing times. T_c decreases on the overdoped side as c_0 decreases, both for SL's and single-phase films. Similar results were shown for single-phase PCCO films with various Ce concentrations.¹⁶ Since Ce^{4+} ion is smaller than Pr^{3+} , this can explain the decrease of c_0 with increasing Ce doping as observed by Maier *et al.*¹⁶ In our case we observe a systematic change of c_0 with T_c . This can be explained by charge redistribution in the SL's causing an effect similar to that of Ce substitution in the single-phase films. Since XRD is a bulk measurement the systematic variation of c_0 gives further indication that the charge redistribution occurs in the entire film thickness.

Oxygen diffusion is one plausible explanation for this charge redistribution over a very large distance. Unfortunately, the oxygen content in a single-phase thin film or in various parts of a SL or BL cannot be precisely measured. Oxygen diffusion from UD to OD layers would increase T_c since this would add carriers (electrons) to the UD layer. Higgins *et al.*²⁵ demonstrated that such a process increased the carrier concentration in the UD layers and decreased it in the OD ones. In that case, the T_c enhancement will take place only in

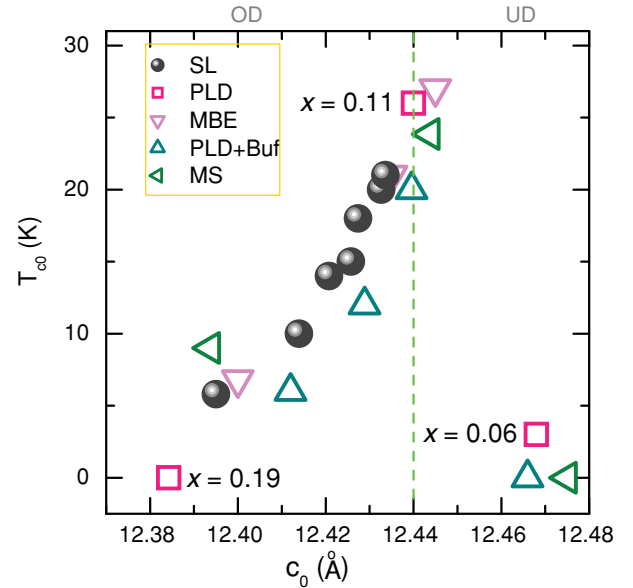


FIG. 4. (Color online) The c -axis lattice parameter dependence of T_{c0} for LCCO single-phase films prepared by PLD (\square), molecular beam epitaxy (∇),¹⁹ PLD with buffer layer BaTiO_3 (\triangle),²⁰ and magnetron sputtering (\blacktriangleleft),²⁶ and also for (0.19/0.06) _{n} SL's with different T_c (\circ). The dashed line marks the optimal doping. UD and OD represent underdoped and overdoped single-phase LCCO, respectively.

the UD layers, because for the overdoped layers the effect of carrier reduction is overwhelmed by the disorder introduced by the apical oxygen (the site of the added oxygen) resulting in a total decrease of T_c .²⁵ So oxygen diffusion from UD to OD layers appears to be a plausible explanation for the global charge redistribution. However, the oxygen-diffusion length is of the order of the film thickness for the annealing temperature and time used in our deposition. Thus, it is difficult to explain, using an oxygen-diffusion scenario, the difference between the BL, where the T_c enhancement is relatively small, and the SL T_c enhancement. Therefore, it is possible that the charge redistribution may have a different origin.

We tried to estimate the charge redistribution length scale (d) in a SL using a naive calculation. If we allow charge to move from the OD layer to the UD one, the electrostatic energy increases. However, the free energy can still decrease due to the enhanced superconductivity. Minimizing the free energy yields a length scale of the order of $d \approx \frac{H_c}{16\pi\rho} \sim 0.2 \text{ \AA}$, using the thermodynamic critical field $H_c = 0.5 \text{ T}$ and the charge density $\rho \approx 0.04$ electrons per Cu (or holes per Cu). This means that the electrostatic energy is too high to explain the large length scale over which the charge redistributes in our experiment.

Another possibility is that charge redistribution occurs on a length scale determined by the screening length (λ_{TF}). Using the Thomas-Fermi approximation we obtain a length scale of $\sim 10 \text{ \AA}$, which is two orders of magnitude smaller than what we

observe. Certainly, this approximation is oversimplified for the cuprates. Yet, in the hole-doped LCO/LSCO SL an analysis of RSXS data yielded a screening length of $\sim 6 \text{ \AA}$,³ which does not differ very much from our electron-doped results. So both the naively calculated λ_{TF} and d length scales are small and cannot explain the anomalously large charge redistribution length that is inferred by our experiments.

In conclusion, we fabricated electron-doped superlattice and bilayer films composed of underdoped (or undoped)/overdoped $\text{La}_{2-x}\text{Ce}_x\text{CuO}_4$ (LCCO) and $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4$ (PCCO), and find an enhanced T_c which is comparable to optimally doped single-phase films for both LCCO and PCCO. Our results suggest that a charge carrier redistribution occurs on an anomalously large length scale of $\gtrsim 20 \text{ nm}$. This charge redistribution is the cause for the T_c enhancement. The exact mechanism of the charge redistribution is not known, although oxygen diffusion is the most plausible explanation. Further theoretical and experimental studies will be needed to understand these remarkable results.

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