PHYSICAL REVIEW B **77**, 201403(R) (2008)

Direct evidence for the suppression of charge stripes in epitaxial $La_{1.67}Sr_{0.33}NiO_4$ films

C. K. Xie, J. I. Budnick, W. A. Hines, and B. O. Wells
Department of Physics, University of Connecticut, Storrs, Connecticut 06269, USA

Feizhou He
Canadian Light Source, University of Saskatchewan, Saskatoon, SK, Canada S7N 0X4

A. R. Moodenbaugh
Condensed Matter Physics and Materials Science Department, Brookhaven National Laboratory, Upton, New York 11973-5000, USA

(Received 10 April 2008; revised manuscript received 24 April 2008; published 20 May 2008)

We have successfully grown epitaxial $La_{1.67}Sr_{0.33}NiO_4$ films with a small crystalline mosaic using pulsed laser deposition. With synchrotron radiation, the x-ray-diffraction peaks associated with charge stripes have been successfully observed for relatively thick films. Anomalies due to the charge-ordering transition have been examined using four-point probe resistivity measurements. X-ray scattering provides direct evidence for suppression of the stripe phase in thinner samples; the phase disappears for film thicknesses $\leqslant$2600 Å. The suppression appears to be a result of shrinking the stripe phase domains. This may reflect the stripe phase progressing from nematic to isotropic.

DOI: 10.1103/PhysRevB.77.201403 PACS number(s): 71.27.+a, 61.30.−v, 75.40.−s, 75.70.−i

The real space ordering of charges, spins, and electronic orbitals in correlated electron materials has been a major topic in condensed-matter physics in recent years. Such behavior has been found in a variety of transition-metal oxides that exhibit a range of physical properties. A typical situation occurs when antiferromagnetic insulators of these oxides are electronically doped: the charge carriers tend to localize and order.[1,2] One of the most important types of order is generally known as stripes. This is best known in doped compounds of the La_2CuO_4 family of high-temperature superconductors. At a particular density of doped holes, $n_h=\frac{1}{8}$, there is a static, ordered arrangement of spins and charges forming stripes along the Cu-O bond direction.[3] The isostructural system $La_{2-x}Sr_xNiO_{4+y}$ shows a similar stripe structure but with an orientation rotated by 45° with respect to the Ni-O bond direction in the planes. However, it does not exhibit superconductivity and even remains insulating for a wide doping range.[4] Furthermore, a variety of manganese oxide materials appears to show various types of charge, spin, and orbital ordering, some of which are stripelike.[5,6] More recently, a short-range charge ordering in Ho-doped $SrCoO_{3-x}$ cobaltite with charge-ordered clusters size down to 50 Å was observed for a broad compositional range.[7] As more examples of charge inhomogeneity arediscovered, one might think that the spin-charge ordering may be a ubiquitous property of transition-metal oxides. However, there are certainly many examples of charge-doped transition-metal oxides for which no such charge inhomogeneity has been reported. It is thus important to understand the nature of charge-ordering correlations, their effect on physical properties, and under what situations they will occur. To further such a goal, it would be very helpful to find a single materials system in which the charge orders through an external tuning parameter that does not affect the charge concentration itself.

There have been several efforts to investigate the correlation between the stripe phase and lattice distortion by applying mechanical strain in cuprate materials. The static stripe phase in $La_{1.875}Ba_{0.125}CuO_4$ and $(LaNd)_{1.875}Sr_{0.125}CuO_4$ is accompanied by a structural phase transition from a low-temperature orthorhombic (LTO) to a low-temperature tetragonal (LTT) phase and an anomalous suppression of superconductivity.[8,9] It appears that the application of hydrostatic pressure to materials with the $\frac{1}{8}$-doped stripe phase causes the LTO to LTT structural phase transition to be suppressed and superconductivity to be partially recovered, with a transition temperature (T_C) of 15 K.[10–13] Studies of similar cuprate films with an in-plane compressive strain have shown a similar effect.[14,15] However, since none of these studies provide direct information about the behavior of stripe phase, their interpretation may be questioned. Typically, it has been assumed that the static charge stripe phase requires the presence of the LTT structural phase. However, it is possible that the stripe phase can form without the structural phase transition, and indeed some recent studies have found just such a case.[16] Therefore, direct evidence is important to understand the nature of the stripe phase under these conditions.

In this Rapid Communication, we report studies of the behavior of the stripe phase in $La_{1.67}Sr_{0.33}NiO_4$ (LSNO) films as a function of film thickness. The nickelate films were chosen for study because the appropriate stoichiometry is relatively stable and the stripe ordering is pronounced, with relatively strong diffraction peaks and a high stripe ordering temperature of 240 K. Using direct evidence from x-ray diffraction (XRD) and resistivity measurements, we demonstrate that the stripe phase in LSNO films is suppressed as the films become thin. By examining the scattering profiles and the full temperature-dependent resistivity, we can understand how the stripes disappear and what short-range order remains.

Epitaxial LSNO films were deposited on (100) $SrTiO_3$ (STO) substrates using a pulsed laser deposition technique. The substrate temperature was kept at 780 °C in 100 mTorr oxygen during the deposition. After the deposition, the samples were slowly cooled down to room temperature in 200 Torr oxygen. Various thicknesses of LSNO films ranging from 480 to 8000 Å were grown with *c*-axis orientation

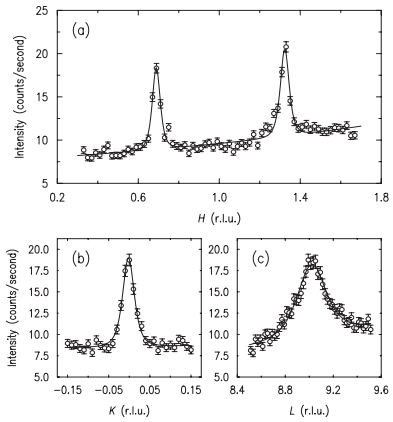

FIG. 1. The charge stripe peak of an 8000 Å LSNO film on a STO substrate at 15 K. (a) H scan along (h, 0, 9), showing two peaks at $h=0.67$ and 1.33; (b) K scan along (0.67, k, 9); (c) L scan along (0.67, 0, l).

perpendicular to the sample surface. X-ray diffraction showed excellent epitaxy with mosaics ranging from 0.27° to 0.36° and no detectable disoriented regions. XRD measurements were carried out at beamline X22A and X22C at the National Synchrotron Light Source, Brookhaven National Laboratory. A graphite (002) single bounce analyzer was used for suppressing the background counts by constraining the angular resolution to reveal the charge stripe peaks. Finite thickness oscillations were observed in reflectometry measurements, indicating a smooth surface and also giving a measurement of the film thickness. The samples were cooled in a closed-cycle refrigerator between $15 \leqslant T \leqslant 300$ K with a temperature control better than 0.5 K. A standard four-probe technique was utilized to obtain the electrical transport properties of the films as a function of temperature ranging from 140 to 340 K in a Quantum Design MPMS system.

The stripe phase in $La_{2-x}Sr_xNiO_4$ can be studied through the examination of magnetic and nuclear superlattice peaks observed in diffraction experiments.[17] With synchrotron XRD, we are able to directly study the charge stripe phase in films by the inspection of incommensurate superlattice peaks associated with the charge stripe order. We indexed all the reflections in the orthorhombic notation with lattice units $a=b=5.4145$ Å and $c=12.715$ Å. Incommensurate reflections due to charge ordering appear with the characteristic wave vectors $(h \pm 2\varepsilon, 0, l)$, where $\varepsilon \sim x$, h=even and l =odd. We have successfully observed the charge-ordering peaks in relatively thick LSNO films. Figure 1 presents linear scans over the stripe peaks (0.67, 0, 9) and (1.33, 0, 9) of an 8000 Å LSNO film on a STO substrate along the H, K, and L directions in reciprocal space, respectively. The observed peaks are well developed at a low measurement temperature of about 15 K. The solid lines represent the best fit with a Lorentzian function, from which the intensity and peak width can be derived. The widths of the charge stripe peaks in the H and K directions are approximately equal, with the full width at half-maximum (FWHM) of 0.049 and 0.033 reciprocal-lattice units (r.l.u.), respectively. However, the peak is much broader along the L direction, with a FWHM of 0.28 r.l.u. The inverse correlation length ξ^{-1} is

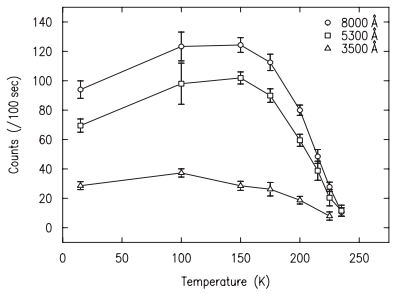

FIG. 2. Intensity of the stripe peak (0.67, 0, 9) versus temperature for LSNO films with various thicknesses.

defined as $\xi_d^{-1}=\frac{2\pi}{d}w$, where w is the half-width at half-maximum (HWHM) of the reflection and d is the lattice constant. According to this, the charge order has a correlation length of approximately 7 and 10 unit cells in the H and K directions, respectively. The correlation length is only 1 unit cell in the L direction. This suggests that the charge ordering is primarily two-dimensional in nature. Our result is in agreement with that from a bulk LSNO crystal sample, though the correlation lengths are smaller in our films.[18]

The intensity of the charge stripe peak (0.67, 0, 9) as a function of temperature is shown in Fig. 2, for a series of LSNO films on STO substrates with different thicknesses. The stripe ordering temperature is about 240 K for all films, in agreement with experiments on bulk materials.[19] It appears that the ordering temperature does not change with the film thickness. Upon cooling, the peak intensity increases steadily and reaches a maximum at about 140 K and then decreases slightly for lower temperatures. The loss of intensity at low temperatures appears to be universal for all our LSNO films. This phenomenon is also seen in bulk crystals when investigated using x-ray diffraction.[20]

Figure 3 shows the thickness dependence of the integrated intensity of stripe peaks (0.67, 0, 9) and their width, for scans along the H direction at 100 K. Note that the photon energy we used for measurements is 10.2624 keV. For most materials, the penetration depth of the x-ray is approximately around 10 μm, which is far larger than the thickness of all of our samples in the present study. Thus, the integrated intensity decreases in a roughly linearly manner, as we would expect from a simple scattering volume argument for pro-

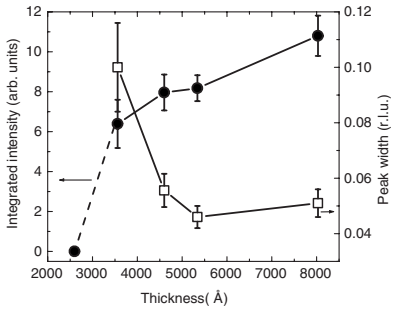

FIG. 3. Integrated intensity and peak width of the stripe phase (0.67, 0, 9) along the H direction versus film thickness. The dashed line shows a sudden drop of the peak intensity, which indicates the suppression of the stripe phase. All LSNO films are measured at 100 K.

gressively thinner films. However, the peak height itself decreases much faster than linearly; the difference is accounted for by the increasing peak width. Thus the disappearance of the stripe peak is primarily through the broadening of the peaks. For samples where the stripe peaks can be detected, the peak intensity per scattering volume remains roughly constant and there is very little change in the stripe ordering temperature. The broadening of the stripe peak width suggests that the domain size of the stripe phase shrinks as the film thickness decreases. An examination of the (2, 0, 8) Bragg peak for the same films suggests that the main structural peaks are much narrower, about 0.01 r.l.u., and more importantly do not broaden as the films become thin. Thus, the crystallinity of the films themselves is similar for the different thicknesses and we can attribute the increased width of the charge-order peak directly to domain size. Compared with the 8000-Å-thick film, the stripe peak from the thin film, 3500 Å, has broadened such that the correlation length of the stripe phase has decreased by about 50% to nearly 3 unit cells. For thinner films, we could not observe any stripe peak, suggesting further reduction of the correlation length. Thus the charge stripes disappear as their domain size is reduced to levels below which stripes cannot be measured and stripe order may no longer be meaningful.

The films in Fig. 3 have very small in-plane tensile strain, about 0.1% for each. Although the lattice mismatch between LSNO and STO is about 2% in tetragonal notation, all these films are thick enough so that strain is fully relaxed. Thus the suppression of stripe order is not a direct effect of lattice mismatch strain. However, once grown, the films are epitaxially constrained to remain in registry with the substrate, known as the clamping effect. This effect will tend to suppress any phase transition with a structural component. It has been shown to alter structural phase transitions in various ways.[23] Clamping is an interface effect and thus the energy cost varies with the area of the interface. The energy associated with suppressing the bulk transition varies with the entire film volume. Thus we expect the clamping effect to be more important for thinner films but is still long range. Our result demonstrates that the stripe phase can be switched off through the influence of a structural control parameter, suggestive of the sensitivity of the stripes to the lattice distortion.[8]

We also studied the temperature dependence of the resistivity of LSNO films. The first derivatives of resistivity versus temperature measurements for a thick film (4600 Å) and a thin film (480 Å) on STO(100) substrate are displayed in Figs. 4(a) and 4(b), respectively. The thick sample was measured to have stripes as shown in Fig. 3; the thinner sample did not. The insets of Fig. 4 show the resistivity as a function of temperature. Insulating behavior is demonstrated in both films. For the thick sample, there is a perceptible kink in the slope [Fig. 4(a)]. This becomes clearer in the derivative curve, with a minimum near 220 K. This kink appears to be associated with the charge-ordering transition, and has been identified as such in transport measurements conducted on bulk samples.[21] The anomaly in transport properties is thus indicative of the formation of charge stripes in the film. As shown in Fig. 4(b), the development of the resistivity as a function of temperature for thin films with no stripe ordering

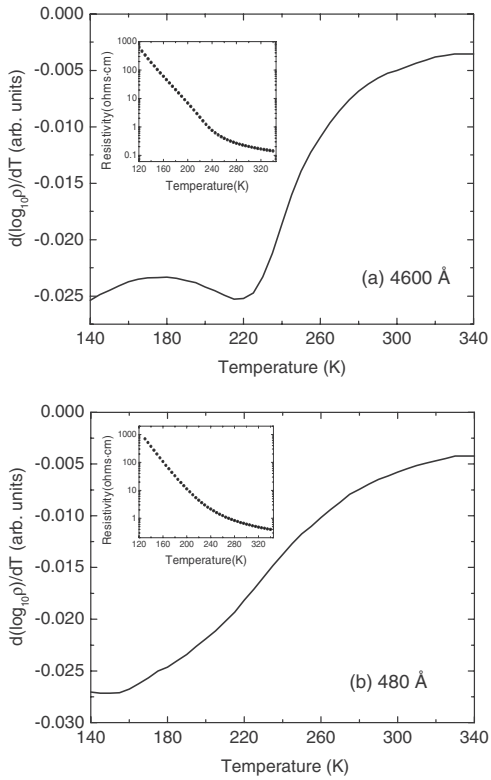

FIG. 4. Resistivity versus temperature for LSNO films. (a) Film thickness 4600 Å, (b) film thickness 480 Å. The 480 Å film does not show the resistivity anomaly.

is smooth, without a dip in the derivative curve. Unlike $\frac{1}{8}$-doped cuprates, there is no structural phase transition for LSNO that is related to the formation of the stripe phase.[22] Thus this anomaly in resistivity is not related to any change in atomic structure, such as the transition from LTO to LTT in cuprates, but must be due to the ordering of doped charges themselves. The absence of the anomaly in the resistivity confirms that the stripe phase itself is truly suppressed in thin films. The transport measurements are consistent with the stripe phase disappearing through a collapse of the correlation length or domain size. Away from the transition, the actual resistivity values for the thick and thin films are similar. We would expect little change in parameters such as the hopping energy of the doped holes if in fact the local order is unaffected and only longer-range ordering is suppressed. Therefore, at low temperatures the stripelike order of the doped holes is not simply gone. The stripe phase is suppressed as the size of the stripe domains collapses. However, the local hopping environment for the holes remains essentially unchanged.

A popular model to describe the stripelike charge ordering has been that of an electronic liquid crystal.[24,25] Within this model, there is a direct analogy between the various stripelike features found in the layered transition-metal oxides and the crystalline, smectic, nematic, and isotropic phases of classical liquid crystals. According to Kivelson *et al.*,[24] it appears that the stripes we measure are most likely in a nematic or a disrupted smectic phase. The diffraction profile for the thicker films is much like that found in $(LaNd)_{2-x}Sr_xCuO_4$ but with considerably broader peaks in

the in-plane directions. Such a profile may arise from a disrupted smectic phase with significant disorder as one might expect in a film. However, the peaks broaden further as the film thickness decreases while the main Bragg peaks of the film remain sharp. The broadening of the charge-order peaks as a function of decreasing film thickness is qualitatively similar to the broadening seen as a function of temperature in classical liquid crystals.[26] When the scattering peaks disappear for very thin films, the stripes may be entering an isotropic or may still be nematic with peaks too broad to measure here. The fact that the low-temperature resistivity has not changed substantially would indicate that the stripes maintain their local integrity in the samples measured. Note that neutron diffraction has revealed that the magnetic peak associated with stripelike ordering grows in intensity with an applied magnetic field on bulk samples of the cuprates.[27] That was explained as a nematic-to-smectic transition by Zaanen *et al.*[25] While the transition studied here moves in the opposite direction, nematic to isotropic, both data sets are characterized by a transition temperature that does not change while the intensity is altered by the tuning parameter.

Finally, we note an apparent similarity between the topography of stripes we infer and that was measured in recent scanning tunneling microscopy (STM) studies.[29] Diffraction has been the main tool for identifying charge-ordered phases, striped phases for layered perovskite oxides. However, only a limited number of materials have shown appropriate diffraction peaks. The clearest cases are $La_{2-x}Sr_xNiO_4$ (Ref. 22) and the $\frac{1}{8}$-doped cuprates.[8,9] Another possible candidate for stripe phases identified through diffraction is superoxygenated and phase-separated $La_{2-x}Sr_xCuO_{4+y}$.[16] Some other cuprates have shown magnetic diffraction consistent with striped phases but without the charge-order peaks.[27,28] Our work shows that even when diffraction does not detect an ordered striped phase, and where resistivity does not detect a transition, the layered nickelates may still support at least an incipient form of electronic stripes. This might be similar to the phenomenon seen in underdoped cuprates,[29] where STM images revealed features of stripe phase but with short-range-order correlation length $\sim 4a_0 \times 4a_0$, where the a_0 is the lattice constant of the sample. Those samples are not known to show diffraction peaks associated with stripes, but are in a similar doping region to samples that do show stripes. Taken together, this is evidence that at least an incipient form of electronic stripes might be more prevalent in layered transition-metal oxides than previously believed. While measurement of nonordered phases is difficult, it would be valuable to investigate a wider range of layered, transition-metal oxides for possible short-ranged stripe order.

This work is supported through NSF Grant No. DMR-0239667 and the U.S. DOE, Contract No. DE-FG02-00ER45801. Work at Brookhaven National Laboratory is supported by the U.S. DOE under Contract No. DE-AC02-98CH1-886, at CMPMSD by the Division of Materials Sciences, and at NSLS by the Division of Chemical Sciences. B.O.W. acknowledges support from the Cottrell Scholar program of the Research Corporation.

[1] C. H. Chen, S-W. Cheong, and A. S. Cooper, Phys. Rev. Lett. **71**, 2461 (1993).
[2] J. M. Tranquada, B. J. Sternlieb, J. D. Axe, Y. Nakamura, and S. Uchida, Nature (London) **375**, 561 (1995).
[3] J. M. Tranquada, J. D. Axe, N. Ichikawa, A. R. Moodenbaugh, Y. Nakamura, and S. Uchida, Phys. Rev. Lett. **78**, 338 (1997).
[4] J. M. Tranquada, D. J. Buttrey, V. Sachan, and J. E. Lorenzo, Phys. Rev. Lett. **73**, 1003 (1994).
[5] S. Mori, C. H. Chen, and S.-W. Cheong, Nature (London) **392**, 473 (1998).
[6] P. Dai, J. A. Fernandez-Baca, N. Wakabayashi, E. W. Plummer, Y. Tomioka, and Y. Tokura, Phys. Rev. Lett. **85**, 2553 (2000).
[7] S. Streule, M. Medarde, A. Podlesnyak, E. Pomjakushina, K. Conder, S. Kazakov, J. Karpinski, and J. Mesot, Phys. Rev. B **73**, 024423 (2006).
[8] A. R. Moodenbaugh, Y. Xu, M. Suenaga, T. J. Folkerts, and R. N. Shelton, Phys. Rev. B **38**, 4596 (1988).
[9] B. Nachumi, *et al.*, Phys. Rev. B **58**, 8760 (1998).
[10] S. Katano, S. Funahashi, N. Mori, Y. Ueda, and J. A. Fernandez-Baca, Phys. Rev. B **48**, 6569 (1993).
[11] M. K. Crawford, *et al.*, Phys. Rev. B **71**, 104513 (2005).
[12] S. Arumugam, N. Mori, N. Takeshita, H. Takashima, T. Noda, H. Eisaki, and S. Uchida, Phys. Rev. Lett. **88**, 247001 (2002).
[13] W. J. Liverman, J. G. Huber, A. R. Moodenbaugh, and Youwen Xu, Phys. Rev. B **45**, 4897 (1992).
[14] Y. Liu, J. F. Qu, M. Zhu, S. D. Zhang, S. J. Feng, and X. G. Li, Phys. Rev. B **70**, 224512 (2004).
[15] H. Sato, A. Tsukada, M. Naito, and A. Matsuda, Phys. Rev. B **62**, R799 (2000).
[16] H. E. Mohottala, *et al.*, Nat. Mater. **5**, 377 (2006).
[17] J. M. Tranquada, D. J. Buttrey, and V. Sachan, Phys. Rev. B **54**, 12 318 (1996).
[18] C-H. Du, M. E. Ghazi, Y. Su, I. Pape, P. D. Hatton, S. D. Brown, W. G. Stirling, M. J. Cooper, and S-W. Cheong, Phys. Rev. Lett. **84**, 3911 (2000).
[19] P. D. Hatton *et al.*, Physica B **318**, 289 (2002).
[20] M. E. Ghazi, P. D. Spencer, S. B. Wilkins, P. D. Hatton, D. Mannix, D. Prabhakaran, A. T. Boothroyd, and S. W. Cheong, Phys. Rev. B **70**, 144507 (2004).
[21] S.-W. Cheong, H. Y. Hwang, C. H. Chen, B. Batlogg, L. W. Rupp, and S. A. Carter, Phys. Rev. B **49**, 7088 (1994).
[22] M. Hücker, K. Chung, M. Chand, T. Vogt, J. M. Tranquada, and D. J. Buttrey, Phys. Rev. B **70**, 064105 (2004).
[23] F. He, B. O. Wells, Z. G. Ban, S. P. Alpay, S. Grenier, S. M. Shapiro, W. Si, A. Clark, and X. X. Xi, Phys. Rev. B **70**, 235405 (2004).
[24] S. A. Kivelson, E. Fradkin, and V. J. Emery, Nature **393**, 550 (1998).
[25] J. Zaanen and Z. Nussinov, Phys. Status Solidi B **236**, 332 (2003).
[26] P. M. Chaiin and T. C. Lubensky, *Principles of Condensed Matter Physics* (Cambridge University Press, Cambridge, New York, NY, 1995).
[27] B. Lake, *et al.*, Nature, **415**, 299 (2002).
[28] S. Katano, M. Sato, K. Yamada, T. Suzuki, and T. Fukase, Phys. Rev. B, **62**, R14677 (2000).
[29] Y. Kohsaka, *et al.*, Science **315**, 1380 (2007).