PHYSICAL REVIEW B **71**, 220408(R) (2005)

Real-space imaging of coexisting charge-ordered and monoclinic phases in $La_{1-x}Ca_xMnO_3$ ($x=0.67$ and 0.71)

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(Received 26 April 2005; published 23 June 2005)

Using transmission electron microscopy, we have observed the coexistence of two nonferromagnetic phases in $La_{1-x}Ca_xMnO_3$ ($x=0.67$ and 0.71) at 90 K: a modulated "charge-ordered" phase and a modulation-free region composed of monoclinic needle twins. Micron-sized regions containing these needle twins formed below 170 K over 30 s in $La_{0.33}Ca_{0.67}MnO_3$ when cooled at a rate of $\sim$0.2 K/min. A tweed microstructure was observed in the interface region between these two phases. We estimate that the needle twins occupied less than 10% of the volume of the manganites investigated here.

DOI: 10.1103/PhysRevB.71.220408 PACS number(s): 71.45.Lr, 61.50.Ks, 64.70.Kb, 71.27.+a

Manganites are noted for displaying a rich variety of coexisting phases at low temperatures. In this investigation, we consider the coexistence of "charge-ordered" and monoclinic phases near $x=0.7$ in $La_{1-x}Ca_xMnO_3$. In 1955, a neutron-diffraction study by Wollan and Koehler[1] reported that a *C*-type antiferromagnetic structure (composed of chains of parallel spins aligned antiferromagnetically) coexisted with the more complicated *CE*-type antiferromagnetic structure (defined in Ref. 1) at low temperatures near $x=0.7$ in $La_{1-x}Ca_xMnO_3$. Subsequently, Ling *et al.*[2] have used neutron diffraction to show that the *C*-type antiferromagnet is associated with a monoclinic distortion of the orthorhombic parent lattice and Radaelli *et al.*[3] have associated the *CE*-type antiferromagnet with the charge-ordered phase.

It should be noted that we use the historical term "charge ordered" to refer to the well-known structural modulation that occurs in the manganites. We have previously shown that the nature of the modulation is inconsistent with an ordering of Mn^{3+} and Mn^{4+} (Ref. 4) ions and interpret it instead as a charge-density wave with a uniform periodicity.[5] Despite the name, a charge-density wave is a modulation of the positions of the atoms within the crystal and the density of the valence electrons is modulated in order to *screen* the new charge distribution that arises from the movement of the atomic cores. This keeps the whole structure as electronically neutral as possible.

Here we use transmission electron microscopy to examine the coexistence of the charge-ordered and monoclinic phases in real space. We demonstrate that the monoclinic phase forms as needle twins near the Néel temperature and these twins grow along their long axes. There is no sharp interface between regions where needle twins are present and regions that show the charge-ordered modulation. Instead, one phase appears to blend into the other through an intermediate region which shows a "tweed" structure.[6] Hervieu *et al.*[7] observed similar twins in $Sm_{1-x}Ca_xMnO_3$ for $0.75<x<0.85$ using transmission electron microscopy, but here we show images of these two structural distortions occurring in the same manganite.

Polycrystalline samples with a grain size of 2 μm were synthesized by a standard solid-state reaction and prepared for transmission electron microscopy by conventional mechanical polishing and argon-ion milling as described in Ref. 8. Microscopy was performed using Philips CM30 and CM300 transmission electron microscopes operating at 300 kV, equipped with Gatan liquid-nitrogen-cooled specimen stages.

Superlattice reflections characteristic of the charge-ordering modulation were observed in diffraction patterns from $La_{0.33}Ca_{0.67}MnO_3$ and $La_{0.29}Ca_{0.71}MnO_3$ at 90 K. However, there were also micron-sized regions of these specimens where superlattice reflections were not observed: in-

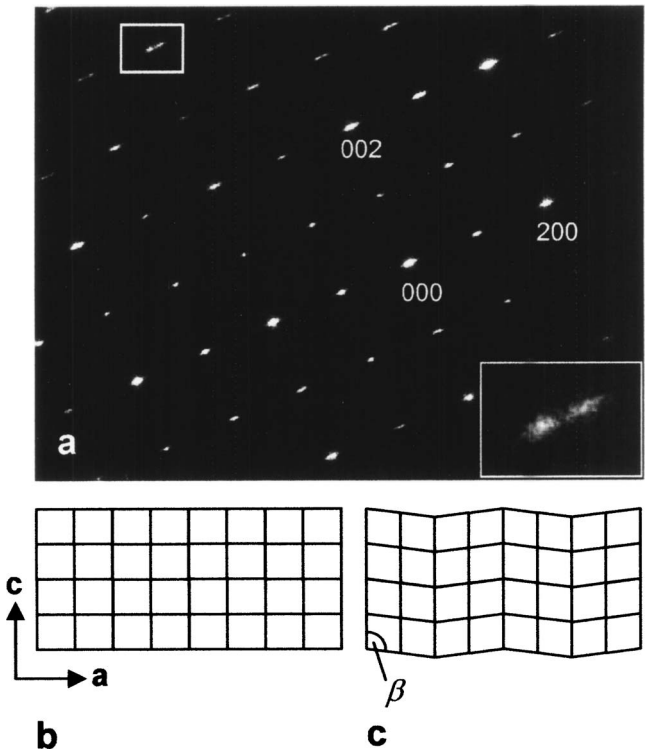

FIG. 1. (a) Diffraction pattern from a region containing needle twins. No superlattice reflections are present but the parent lattice reflections are split as shown in the inset, which is an enlargement of reflections in the white box. (b) Diagram of the parent orthorhombic lattice. The needle twins are formed from a monoclinic distortion of this lattice as shown in (c).

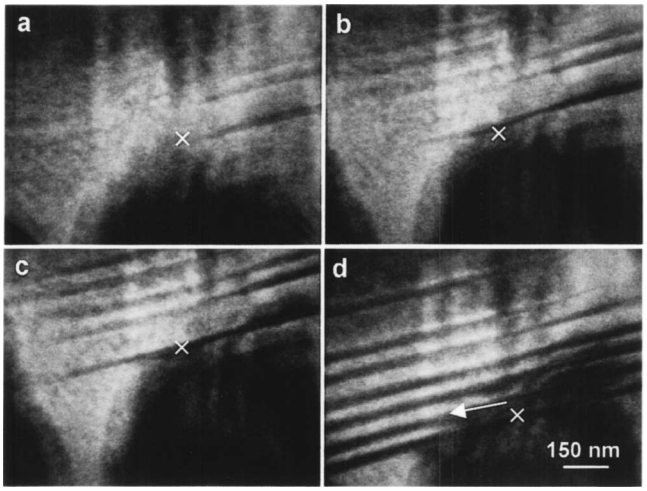

FIG. 2. Bright-field images from a video sequence showing the growth of needle twins in $La_{0.33}Ca_{0.67}MnO_3$ as the sample was cooled at ~0.2 K/min. (a) 0, (b) 9, (c) 17, and (d) 25 s. Needle twins can be seen growing from right to left in the image. The specimen moved during the video acquisition due to thermal drift and the white cross indicates the same place on the specimen in all four frames. The twin in (d) indicated by a white arrow appeared after the other twins had formed and grew explosively fast (<1/15 s). The transformation took place on cooling at a temperature of 170 K as registered on the thermocouple on the cooling stage. (Note that electron-beam heating could cause the specimen temperature to be a few degrees higher in the illuminated region.)

stead, parent reflections were split into two spots and the splitting increased the further the reflection was from the origin of the diffraction pattern as shown in Fig. 1(a). This splitting was caused by a monoclinic distortion of the parent orthorhombic lattice (indexed in the *Pnma* setting) resulting in "needle" twins as shown schematically in Figs. 1(b) and 1(c). The monoclinic angle (β) was $90.9 \pm 0.2^{\circ}$ in this region. This is similar to the monoclinic angles of 90.8° and 91.3° measured by Ling *et al.*[2] for $x=0.78$ and $x=0.80$, respectively.

The formation of these needle twins was observed at 170 K (as recorded on the thermocouple of the liquid-nitrogen cooling stage) in $La_{0.33}Ca_{0.67}MnO_3$, and Fig. 2 shows stills (bright-field images) from a video sequence of the growth of these needle twins as the specimen was cooled at ~0.2 K/min. The twins grew along the direction of the twin boundaries over a period of 30 s although one of the twins (marked with an arrow) grew explosively fast (faster than the frame rate of the video: 1/15 s).

Figure 3(a) shows needle twins coexisting with the charge-ordering modulation in $La_{0.29}Ca_{0.71}MnO_3$ at 90 K and this is displayed schematically in Fig. 3(b). It can be seen that in reality, there is no sharp boundary between modulated regions and the needle twins, and that one phase blends into the other. Charge ordering was identified from fine scale fringes that can be seen in the image. The fringe spacing in box 1 was 2.3 nm (corresponding to a modulation wave vector of $q=0.23a^*$) and 1.9 nm ($q=0.28a^*$) for box 2, and these correspond to the period of the charge-order modulation (1.9 nm) expected for the composition. (From other measurements, we have found that the wavelength of the modulation can vary considerably from one region to another.[8]) In the region where no twins are seen, a tweedlike structure was observed. Tweed is a lattice modulation with no long-range order often regarded as a precursor to twinning.[6] This tweed structure was also reported by Hervieu *et al.*[7] in $Sm_{1-x}Ca_xMnO_3$. The high-resolution image in Fig. 4(a) appears to show that regions with the charge-ordering modulation can also exhibit tweed contrast, although we cannot distinguish between this and the possibility that the tweed structure and the charge modulation are two separate phases lying on top of one another with respect to the electron-beam direction. Other parts of the charge-ordered region, further from the needle twins, did not exhibit tweed as shown in Fig. 4(b).

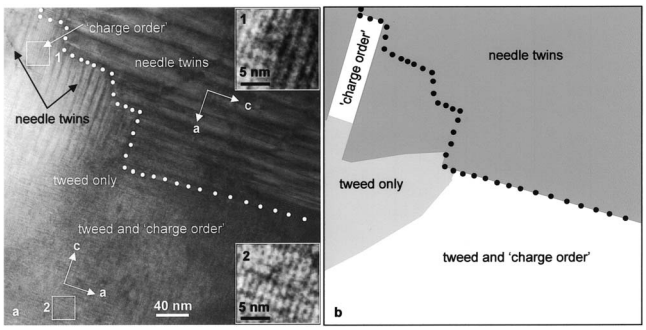

FIG. 3. (a) Bright-field image taken at 90 K showing coexistence of needle twins and the charge-ordering modulation. The dots indicate a 90° twin boundary. Two charge-ordered regions shown in boxes 1 and 2 are enlarged in the insets and the modulation can clearly be seen. The region containing needle twins blends into the charge-ordered region via a region which shows only tweed. The schematic in (b) shows the location of each phase.

We now speculate on a mechanism that could cause either needle twins or the charge-ordering modulation at low temperatures in the manganites. It is known that the charge-ordering modulation starts with relatively long wavelengths which become shorter as the specimen is cooled.[9] Furthermore, the greater the Ca doping, the longer the initial and

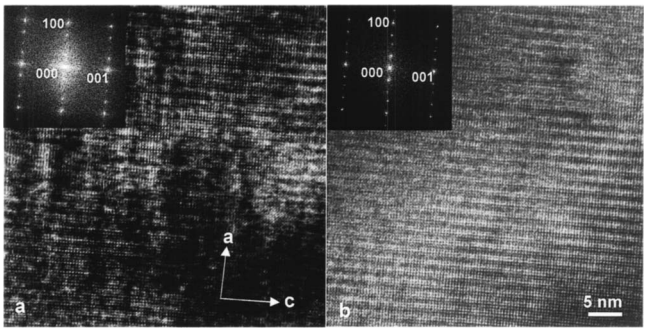

FIG. 4. Charge ordering with and without tweed. (a) High-resolution image in which the charge-ordering modulation (seen as stripes running in the **c** direction) has a tweed structure superimposed. (b) The modulation in a region free of tweed. Power spectra from each image are shown as insets. Streaking characteristic of the tweed structure can be observed in the power spectrum of (a) but not (b).

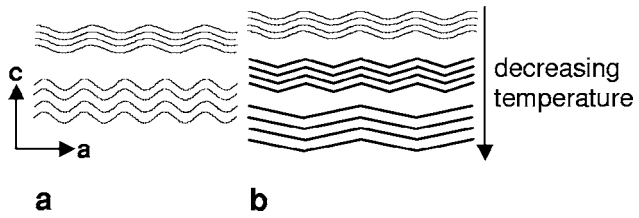

FIG. 5. Possible mechanism from which the charge-ordering modulation and needle twins could arise. (a) Long-wavelength modulation in the structure becoming shorter in wavelength and greater in amplitude to become the charge-ordering modulation. (b) The same initial modulation which coarsens to become needle twins.

final wavelengths. The initial distortion is likely to be a long-wavelength modulation and one can speculate that it can either coarsen to become needle twins or the wavelength can fall and the amplitude increase to give the charge-ordered modulation as shown in Fig. 5. We consider the tweed structure to be a metastable intermediate between these two possibilities and so it occurs in the interface region between the two phases.

The temperature at which the twins form in $La_{0.33}Ca_{0.67}MnO_3$ (170 K) is considerably below the charge-ordering temperature of 260 K but close to the temperature at which antiferromagnetic peaks are first observed by neutron diffraction (160 K) (Ref. 3). Although we estimate that the monoclinic needle twins occupy less than 10% of the volume of the specimens investigated here, Ling *et al.* have shown that as x is increased, the monoclinic phase becomes the dominant phase and by $x=0.82$, occupies about 92% of the sample volume at 20 K. As x is further increased, they show that a G-type antiferromagnet (composed of spins aligned antiferromagnetically with repect to their nearest neighbors) coexists with the C-type antiferromagnet and by $x=0.95$ the sample is entirely G type.

Needle twins form in such diverse systems as leucite ($KAlSi_2O_6$) when cooled through its cubic to tetragonal phase transition at 938 K (Ref. 6) and the orthorhombic phase of the high-temperature superconductor $YBa_2Cu_3O_{7-\delta}$ (Ref. 10), and there can be considerable size differences between the different generations of twin that arise as they grow and coarsen.[6] Podzorov *et al.*[11] have used polarized light microscopy to observe the occurrence and growth of needle twins that are microns wide and several hundred microns long in single-crystal $Bi_{0.2}Ca_{0.8}MnO_3$ below 175 K. If these are the same type of twins as observed in this investigation, their size can range from tens of nanometers to hundreds of microns.

Note added in proof. Since the submission of this paper, Ref. 12 has been published which confirms the findings presented here.

We wish to thank A. J. Williams for synthesizing the samples used in this investigation and N. D. Mathur for helpful discussions. This work was funded by EPSRC, U. K. and Homerton College, University of Cambridge.

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