Direct imaging of lattice-strain-induced stripe phases in an optimally doped manganite film

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In a Lao$_{0.90}$Ca$_{0.05}$MnO$_3$/MgO film without quenched disorder, we show insulating and metallic stripes above and below the Curie temperature ($T_C$), respectively, by a high-resolution scanning tunneling microscopy (STM) and/or spectroscopy measurement. Formation of these stripes involves competing charge, orbital, and lattice orders and is an outcome of an overlapping of electron wave functions mediated by the lattice strain. The presence of the quadrupolar contribution in the second-harmonic generation experiments supports the strain mediated charge-orbital stripes observed by STM.

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Stripes in manganites, like in nickelites, were known to comprise of ordered polarons. As the coupling of the electron to the lattice was shown to be weak, recent experiments suggest a charge-density-wave-type modulation in manganites, instead. In colossal magnetoresistive (CMR) manganites, of the form La$_{1-x}$Ca$_x$MnO$_3$ ($0.2 \leq x \leq 0.33$), the localizing effect of the charge due to the Coulomb repulsion and the Jahn-Teller (JT) effect at the Mn site results in polarons. Accommodation of the JT distortions through a relaxation of strain in the presence or absence of a disorder at the A site is known to influence the transport properties including metal-insulator transition (MIT) temperature and CMR. Consequently, the phase coexistence and the percolative mechanism of the MIT and CMR (Ref. 9) are also associated with the structural distortions.

The nature of the charge modulation and its relationship to the structure and other order parameters is a topic of continuous debate. Recently, it was shown that the JT distortions can periodically modulate resulting in a charge-orbital density wave. In hole-doped manganites, it is well known from x-ray scattering experiments that the number of such quasiparticles detectable, in general, is very small. This further augments the difficulties in obtaining atomic resolution by tunneling experiments on manganites. Apart from point defects and a strong JT-induced charge localization, strain effects have great influence on order parameters and are illustrated to yield exotic new phases in manganites. Atomic scale theory considering lattice deformations, indeed, postulates coupled electronic and elastic textures. In doped manganites, the structural distortions (JT type) are accommodated, and the JT-induced strain is annealed out by cooperative tilting and rotations of octahedra. However, a lack of such cooperativity, locally, perhaps around defects, reduces the screening of the charge within nanometer regions, enhancing the possibility of atomic resolution.

Polarization of the charge leading to stripes in manganites...
FIG. 1. (Color) Scanning tunneling micrographs of La-Ca ordered \( \text{La}_{0.25}\text{Ca}_{0.75}\text{MnO}_3 \) film. (a) \( 49.5 \times 49.5 \) Å\(^2\) and (b) \( 50 \times 50 \) Å\(^2\) stripe images obtained at 115 K; the peak-to-peak (black arrows) distance was \(~6.5-8.5\) Å. (c) and (d) Room-temperature (294 K) STM images of 45X45 and 45X20 Å\(^2\), respectively. (e) Line profiles corresponding to (c) and (d). There are two distinct features as indicated by black and orange arrows. The peak-to-peak distance is \(~5.8\) Å. The two in-plane crystallographic orientations are denoted by arrows at the top left corner in all micrographs.

FIG. 2. (Color) (a) Schematic representation of the unit-cell deformations in the LCMO film. The Mn displacements are deduced from the cross-sectional (a-b plane) HRTEM (Ref. 12). The unit-cell lattice deforms are classified as long \((e_1\) and \(e_2\)) and short range \((e_x\) and \(e_y\)\) (Ref. 8). Strain-free superstructure in the a-b plane is shown by the orange square. (b) Schematic representation of bond stripes. Mn ion in the b-c plane is represented by \(d\) orbitals. The lighter colored orbital represents larger distortion than the darker colored. The green lines represent the direction of the charge-orbital stripe and the nonlinear lines denote local density-of-states (LDOS) modulation across the stripe feature. (c) Probable schematic representation of diagonal stripes within a few nanometer length scale. Two different LDOS features predominantly observed within diagonal stripes are represented by light and dark colored orbitals. "Dimers" of light colored orbitals symbolize clustering (black ovals) of structural distortion that is observed as large and bright features in Figs. 1(c) and 1(d).

\[ \text{magnification of the charge and the lattice, agree well with the alternating La, La/Ca cation ordering in the } \text{b-c plane [Figs. 2(a) and 2(b)]. Taking into account the orientation of the Mn lattice, from the HRTEM measurements, } \text{the lattice-strain-mediated theory discussed above provides rationale for the charge-orbital density-wave features observed along the bond direction [Fig. 2(b)]. The appearance of charge stripes at room temperature with two different corrugations (big and small) and without any apparent lattice, as shown in Figs. 1(c) and 1(d), could also be related to the weak charge-lattice coupling. Accounting incommensurate periodicity of \(~5.8\) Å is nontrivial, and an explanation necessitates structural distortions involving two Mn octahedra—a Peierls-type distortion—as shown in Fig. 2(c).10,11,21,22 Such Peierls-type distortions plausibly explain the larger and brighter features within the diagonal stripes.\]

Given that these stripes in the LCMO film result from a quasiorganization of structural distortions directed by long-range cation ordering, STS offers a better understanding of...
the intricacy of competing charge and orbital orders within the nanoscale stripes. The difference in the screening of the charge carrier reflects in the tunnelling conductance of the stripe phase. The tunneling current-voltage characteristic (Fig. 3) on the bond stripes reveals a metallic behavior (red curve) distinct from the diagonal stripes, which appear insulatorlike (green curve). Therefore, the room-temperature $dI/dV$ spectrum of diagonal stripes averaged over four $I$-$V$ curves obtained on the stripe area of $45 \times 45 \, \text{Å}^2$ (top-left corner).

The fact that the observed stripes are a consequence of quantum interference device (SQUID) measurements. However, it should be noted that the discrepancy between the fit and the actual SHG data near $T_c$ is due to the changes in the optical constants of the substrate and not related to the sample. Thus, the quadratic dependence of the $E_{SHG}(T)$ and almost no magnetic-field dependence, $E_{SHG}(M)$, in the $p$-$p$ geometry (inset Fig. 4) evidence the dominance of the quadrupole contribution. The observation of a strong quadrupolar effect by SHG experiments strengthens the argument proposed for stripe features. Thus, the combined STM and SHG experiments imply a possible orbital ordering within the ferromagnetic phase likely due to the cation order. As regard to stripes, it can be understood to arise from the local strain, which modulates the structural distortions and thereby the orbital. The electron itinerancy in the limit of weak charge-lattice coupling could be due to reduced dimensionality of charge-orbital stripe structure. The charge-density modulation below $T_c$ can be labeled as ferroquadrupolar (orbital) stripes. Further, the nature of the structural distortion, with it the orbital ordering, might be undergoing a change above $T_c$ due to the change associated with the strain component. Therefore, these strain-induced stripes provide rationale for the complex structure-property relationship brought out by the propensity of managements toward new phases such as a polaron liquidlike correlation and metallicity.

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