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Strain-controlled band engineering and self-doping in ultrathin $LaNiO_3$ films

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We report on a systematic study of the temperature-dependent Hall coefficient and thermoelectric power in ultrathin metallic $LaNiO_3$ films that reveal a strain-induced, self-doping carrier transition that is inaccessible in the bulk. As the film strain varies from compressive to tensile at *fixed* composition and stoichiometry, the evolution of the transport coefficients is strikingly similar to those of bulk hole-doped superconducting cuprates with *varying* doping level. Density functional calculations reveal that the strain-induced changes in transport properties arise from changes in the low-energy electronic band structure that induce self-doping, a transfer of charge between O p and Ni d states. The results suggest that thin-film epitaxy can serve as a means to vary the charge-carrier concentration in other (negative) charge-transfer gap transition-metal oxides without resorting to chemical substitution.

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Introduction. Atomic-level control over the deposition of transition-metal oxide (TMO) films and multilayers has generated considerable interest in harnessing two-dimensional (2D) confinement and misfit strain to tailor the carrier concentration of correlated electron systems for electronic applications.[1] An important research avenue toward this goal is to establish to what extent confinement and strain mimic chemical doping—the principal means for accessing metal-insulator (MI), superconducting, and colossal magnetoresistive transitions in perovskite titanates,[2] cuprates[3], and manganites.[4] Recently, electrostatic hole doping has been demonstrated in vanadate quantum wells[5] and manganite heterostructures[6] using interfacial dipole engineering. Here we demonstrate the controlled variation of charge-carrier concentration in ultrathin films of the metallic oxide $LaNiO_3$ (LNO) at *fixed stoichiometry* through substrate-induced misfit strain alone, without real-space charge transfer (CT) at the heterointerface.

We choose to study the self-doping effect in the correlated perovskite metal LNO because it has a low-energy electronic structure derived from two bands with A_{1g} symmetry (d_{z^2} and $d_{x^2-y^2}$) at quarter filling[7,8] and is classified as a CT oxide.[9] Recent epitaxial film studies demonstrate that biaxial strain-induced lattice distortions and orbital-level energy splitting determine the transport properties,[10,11] orbital polarization,[12,13] and strength of electron-electron correlations,[14,15] indicating that the near-Fermi surface (FS) electronic structure is highly sensitive to misfit strain.

Furthermore, LNO is considered a Cu-free analog to the cuprates,[16,17] as it is also a covalent, strongly correlated material with a partial $d_{x^2-y^2}$ band filling that governs transport behavior. However, LNO differs from cuprates in a few important respects: It is neither 2D nor a doped Mott insulator in bulk. There is no nickelate equivalent to the antiferromagnetic, $S = \frac{1}{2}$ insulating cuprate parent compound.[16] The physics governing the two systems could be fundamentally different. Nonetheless, the systematics of our Hall and thermoelectric power (TEP) data for LNO films over a range of strains reveal a surprising commonality with doped cuprates. The implication is that changes in the electronic structure of the nickelate films via substrate-induced misfit strain are similar to those induced by charge-carrier doping through direct cation substitution in cuprates. Density functional calculations performed within the local spin density approximation plus Hubbard U (LSDA + U) method corroborate the *misfit strain-induced self-doping* picture, indicating that epitaxially strained LNO films are proximal to a self-doped MI transition as are rare-earth substituted nickelates.[18]

Growth and characterization. Epitaxial 10 unit cell ultrathin films of LNO were grown on $YAlO_3$ (YAO), $SrLaAlO_4$ (SLAO), $LaAlO_3$ (LAO), $SrLaGaO_4$ (SLGO), $(LaAlO_3)_{0.3}(Sr_2AlTaO_6)_{0.7}$ (LSAT), $SrTiO_3$ (STO), and $GdScO_3$ (GSO) (001)-oriented substrates by pulsed laser deposition following procedures in Ref. 19. A physical property measurement system was employed to measure the dc Hall coefficient (R_H) and resistivity (ρ) of the films with fields up to $B = 3$ T applied perpendicular to the film plane. The TEP was measured with a steady-state technique using a fine-wire chromel-constantan thermocouple and gold leads. One end of each film was bonded with silver epoxy to a Cu heat sink; a thin Cu "shim" supporting a small heater was glued to the free end of the film to provide uniform heat flow.

Transport. Figure 1(a) shows the temperature-dependent inverse Hall coefficient $R_H^{-1}(T) \equiv n_H e$ for LNO films under a range of strains. As seen, R_H^{-1} is linear in T and positive for all T and systematically decreases in magnitude with increasing tensile (positive) strain. Note, in simple one-band metals, R_H is independent of T. An asymmetric strain dependence of the Hall data is revealed when we plot the slope dR_H^{-1}/dT and power-law (T^α) temperature exponent α of the inverse Hall angle, $\cot\theta_H = \rho/(R_H B)$, against strain [Fig. 1(b)]. As shown, both the effective carrier density and scattering are highly sensitive to compressive strains, while showing negligible variation under tensile strains.

The behavior of the observed T-dependent Hall data bear a striking resemblance to those of cuprates, where R_H^{-1} is also approximately linear in T over a broad temperature range. The $R_H^{-1} \propto T$ and $\cot\theta_H \propto T^2$ dependencies for compressively strained films [Fig. 1(b)] can be reproduced within the

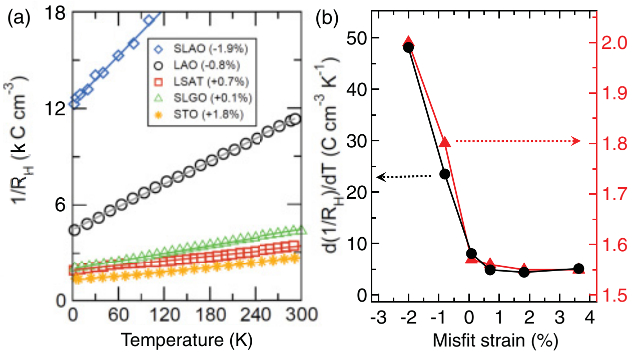

FIG. 1. (Color online) (a) Temperature-dependent inverse Hall coefficient R_H^{-1}, (b) temperature derivative of R_H^{-1} (left ordinate), and $\cot\theta_H$ power-law temperature exponent α (right ordinate) for LNO films vs misfit strain.

single-band Boltzmann theory by a Fermi-liquid-like T^2 scattering rate that varies sharply about the FS, a model developed to describe these behaviors in cuprates.[20–22] Within this picture, these characteristic T dependencies of the Hall data directly reflect such scattering anisotropy, and their weakening in LNO films with increasing tensile strain signals a decrease in the effective scattering anisotropy. In close similarity, a decrease in the power-law exponent α from 2 to 1.65 with increasing hole doping for Bi-based cuprates[23,24] has been attributed to increased structural disorder that tends to smear out scattering anisotropy on the FS.[20,21] Alternatively, a strong T variation of R_H^{-1} is possible when electron and hole contributions (in a two-band model) possess different T-dependent mobilities. However, recent photoemission observations of a substantial mass enhancement for the electron pocket in LNO,[25] but not for the hole pocket, suggest that the respective carrier conductivities obey $\sigma_h \gg \sigma_e$, and hence a single band picture may indeed be appropriate.

Electronic structure. To better understand the unusual strain-dependent Hall data, we carry out first-principles density functional calculations on LNO films using the local spin density plus Hubbard U approximation.[26] Figure 2(a) depicts the electronic band structure of LNO at ∼0% strain using the "fat-bands" method,[27] which allows us to distinguish the different orbital character of the Bloch states near the Fermi level. Consistent with the ionic picture of low-spin Ni^{3+}, the states at E_F are primarily of Ni d_{z^2} and $d_{x^2-y^2}$ symmetry, with partial occupation of majority-spin (blue/dark gray) Ni states. The minority-spin (red/light gray) Ni states are exchange split by ∼0.80 eV to higher energy, making LNO under zero strain a half metal.

In addition to the Ni e_g bands at E_F, there are low-lying oxygen $2p$ bands located less than 0.50 eV below the Fermi level. The fat-band analysis shows that these states at the A point, $k = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, are completely of oxygen character—no hybridization with the Ni d states occurs. Because these states are purely oxygen derived, they could act as a source (sink) for holes (electrons) to the nearby Ni d states if they become partially occupied.[28,29] This electronic configuration, with O $2p$ states close in energy to the occupied Ni d manifold, classifies LNO as a negative CT-gap compound susceptible to self-doping.[18]

Consider the changes in low-energy electronic structure about the high-symmetry Γ and A points with misfit strain [Fig. 2(b)]. On going from compressive to tensile strain, an electronic transition from fully metallic—both spin channels are occupied at E_F—to a half-metallic state occurs. In other words, the metallic state present under compressive strain requires a change in the hole population at the Fermi level in order to keep the chemical potential fixed.[30] Indeed, the O $2p$ states, fully occupied at zero strain, are partially empty at the A point under compressive strain: Electrons are transferred from the minority-spin O $2p$ states to the minority-spin Ni states. Specifically, the d_{z^2} orbital at Γ is partially occupied with electrons [cf. -3.2% and -2.1% strain panels in Fig. 2(b)]. Consistent with this CT to the minority-spin manifold, there is a reduction in the Ni-spin moment under compressive strain ($0.4\mu_B$/Ni) compared to that at zero strain ($0.75\mu_B$/Ni). In other words, biaxial compressive strain induces a self-doping effect on the FS at fixed composition. As a result, the relative volume of the electron (hole) pocket increases (decreases) as the strain goes from compressive to tensile [Fig. 2(b)], qualitatively consistent with the trend in R_H^{-1}. While the precise band occupancies as a function of strain depend on the value of U, the self-doping and evolution of the electronic structure are robust features of the calculations.

Self-doping. The temperature-dependent TEP (S) for strained LNO films further confirms the proposed self-doping picture [Fig. 3(a)]. The TEP for all films at $T \geqslant 120$ K is accurately described by a linear-T form ($A + BT$), with

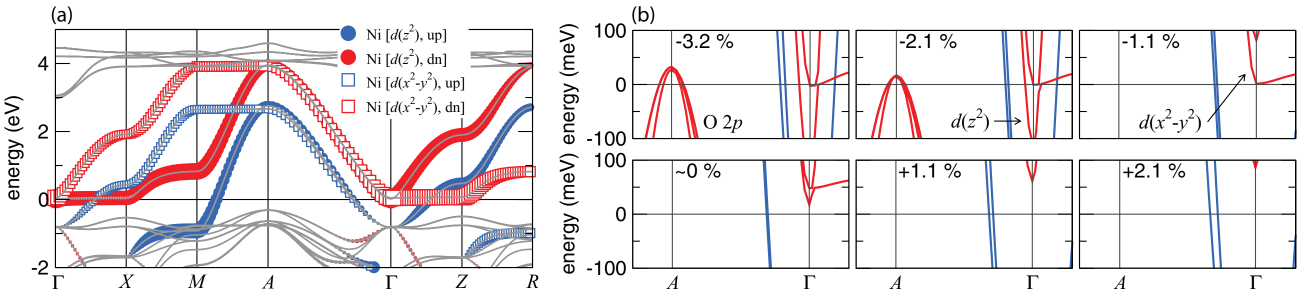

FIG. 2. (Color online) (a) Electronic band structure plot for LNO at ∼0% strain. The majority spin (blue, dark grey) and minority spin (red, light grey) are highlighted for the spin-polarized (up or down) Ni d_{z^2} and $d_{x^2-y^2}$ orbitals. The symbols' sizes correspond to the magnitude of the Bloch states projected onto each atomic orbital. (b) Low-energy electronic structure for tetragonal $P4/mmm$ LNO about the Γ and A points at different biaxial strain states.

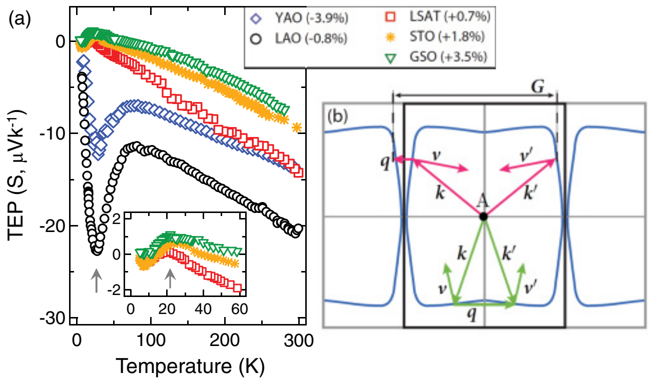

FIG. 3. (Color online) (a) T-dependent TEP for strained LNO films. (b) Scattering geometry on the (011)-projected majority-spin FS sheet centered at the A point for -2.1% strain: Normal (lower, green) and umklapp (upper, pink) processes are shown (the latter involving reciprocal lattice vector $\boldsymbol{G}$).

$B = -0.041 \pm 0.004\ \mu\mathrm{V/K}^2$ approximately independent of strain, and with a constant offset A that increases with tensile strain (the film grown on YAO is an exception[31]). If the linear-T term is interpreted as diffusion TEP, the value of B allows the calculation of the Fermi energy using the Mott expression $S = \pi^2 k_B^2 T/(3eE_F)$ under the assumption of a linear energy dependence of the conductivity at the Fermi level.[32] We find $E_F \approx 0.6$ eV, in good agreement with recent photoemission data on LNO.[25]

These systematics of the TEP are also strikingly similar to those of the normal-state TEP of bulk, superconducting cuprates near optimal doping. For cuprates, the constant term A increases with *decreasing* hole doping of the $\mathrm{CuO_2}$ planes, achieved via cationic substitution.[33,34] This hole-doping behavior matches the trend that we observe in our stoichiometric films with strain: The self-doping decreases (A increases) as the strain state goes from compressive to tensile. The constant term in the TEP of cuprates has been variously attributed to strong electron-phonon coupling,[35] strong correlations,[36] or a weakly T-dependent (positive) phonon drag contribution.[37]

A sharp peak in the TEP[38] near $T = 25$ K (arrowed) also correlates with strain [Fig. 3(a)]. It is large and negative for films under compressive strain and small and positive for those under tension [Fig. 3(a), inset]. The magnetic-field independence (to 9 T) of this feature (data not shown) argues against its magnetic origin.

Low-T TEP peaks in metals are typically attributed to phonon drag. To reproduce the behavior of the LNO films, a negative phonon-drag TEP contribution that becomes positive and weakens in the misfit strain progression from compressive to tensile is needed. Because strain affects the electronic structure near E_F [Fig. 2(b)], the scattering geometry relevant to phonon-drag TEP (S_g) should also be significantly altered. For LNO under -2.1% strain, the majority-spin FS sheet centered at the A point nearly touches the Brillouin zone (BZ) boundary [Fig. 3(b)]. Superimposed on the FS are the normal (lower, green) and umklapp (upper, pink) scattering processes ($\mathbf{k} \to \mathbf{k}'$) involving phonon wave vectors $\mathbf{q}$ that cross unoccupied regions of the BZ. Both yield $S_g \propto -\Delta\mathbf{v}\cdot\mathbf{q} < 0$ ($\mathbf{v}$ is the Fermi velocity). We anticipate the umklapp contributions to be particularly strong given the flatness of the FS near the BZ boundary. As this FS sheet shrinks and moves away from the BZ boundary with increasing tensile strain, the umklapp contribution will be suppressed as the low-T phonon population with increasingly large spanning vector $\mathbf{q}$ is sharply depleted. The disappearance of these umklapp scattering contributions to phonon drag is consistent with the disappearance of the sharp negative peak in the TEP near 25 K that occurs under tensile strain [Fig. 3(a)], further supporting the concept of strain-induced self-doping.

Carrier doping of CT oxides. Our calculations indicate that the ground-state electronic structure and oxygen hole density are directly modulated by biaxial strain: As the strain changes from compressive to tensile, the O $2p$ states shift to lower binding energy. When strain approaches zero, the oxygen levels become fully occupied and self-doping is quenched. This shift in oxygen-band filling mirrors the change in occupation of the minority-spin Ni e_g states at Γ. The orbital-level splitting between the d_{z^2} and $d_{x^2-y^2}$ states decreases as biaxial strain approaches zero; it increases with larger tensile strains, but both minority-spin Ni d states remain unoccupied, producing the half-metallic ground state. Thus strain, which directly alters the crystal field, is responsible for the self-doping.

A small or negative CT gap, occurring when the ligand p levels lie close in energy to or overlap the d levels (upper Hubbard band), is a key ingredient to the strain-controlled self-doping of LNO films. Other TMO compounds, particularly perovskites involving late $3d$ and $4d$ transition metals, likely fall into this category.[28,29,38,39] It is anticipated that the self-doping may be manipulated through strain in some of these compounds in a manner similar to that demonstrated here, i.e., different charge-doping regimes may become accessible at fixed compositions by judicious selection of the misfit strain. Given the significant redistribution of charge evident for LNO from our transport measurements, it is feasible that such self-doping effects could allow access to metal-insulator, superconducting, or magnetic transitions without introducing chemical disorder, and in the absence of interface dipoles.

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