Electronic and crystal structure of fully strained $LaNiO_3$ films

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First-principles band structure calculations have been used to investigate epitaxially strained $LaNiO_3$ films. Experimentally, tensile biaxial strain has been realized in pseudomorphic $LaNiO_3$ films grown on $SrTiO_3$ (001) substrates using ozone-assisted molecular beam epitaxy. Measured and calculated out-of-plane lattice parameters are in excellent agreement. This demonstrates the viability of the computational method as well as the high quality of the films.

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Among the diverse family of perovskite oxides, $LaNiO_3$ is a rare example exhibiting paramagnetic metallic behavior. To date, technological interest in this compound has been limited to the development of highly conductive electrodes for ferroelectric thin-film devices, including nonvolatile memories.[1] Excellent heteroepitaxy with doped lanthanum manganites[2] implies that $LaNiO_3$ thin films can also be used as electrodes in magnetoelectronic devices based on these highly spin-polarized compounds.[3,4]

Thin films, which are required in many applications, may possess physical properties altered from those of the bulk due to epitaxial strain. It is well established that strain significantly affects the properties of high-T_c superconductors[5] and colossal magnetoresistive compounds.[6] While the rapid development of thin-film growth techniques has facilitated experimental investigation of this problem, progress in the methods of computational materials science now allows first-principles investigation of the coupling between structure and electronic properties.

In this paper, we investigate biaxially strained $LaNiO_3$ thin films using an *ab initio* plane-wave pseudopotential approach. To test the theoretical predictions, pseudomorphic atomically smooth $LaNiO_3$ films were fabricated on $SrTiO_3$ (001) substrates by ozone-assisted molecular beam epitaxy (MBE).

Below we present some results of the structural characterization of a pseudomorphic $LaNiO_3$ film grown under optimized conditions. Film deposition was carried out employing ozone-assisted MBE, a scheme similar to that used for the growth of oxide superconductors and colossal magnetoresistors, which is described elsewhere.[7] The high reactivity of ozone allows for complete oxygenation under high-vacuum conditions without a post-deposition anneal. Persistent intensity oscillations of the reflection high-energy electron diffraction pattern were observed during block-by-block[8] growth. Streaked patterns seen after the completion of each unit cell indicated flat epitaxial growth and the absence of second-phase inclusions. Ion channeling results (3-MeV He^+ ions) for the film discussed here showed a minimum channeling yield of only 4%, demonstrating a high degree of both in- and out-of-plane epitaxy. A four-circle x-ray diffractometer with Cu $K\alpha_1$ radiation was used to characterize the crystal structure. Figure 1 shows a θ-2θ scan in the vicinity of the (002) Bragg peak of the film. The well-defined interference pattern (sample size oscillations) suggests a thickness unifor-

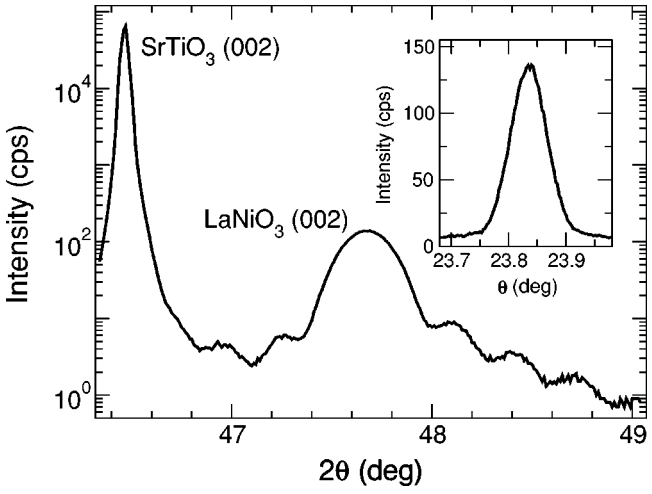

FIG. 1. θ-2θ symmetric x-ray diffraction scan in the vicinity of the (002) Bragg peak of a 360-Å-thick $LaNiO_3$ film. Well-defined sample size oscillations are superimposed on the Bragg peak. Inset: rocking curve of the (002) film peak.

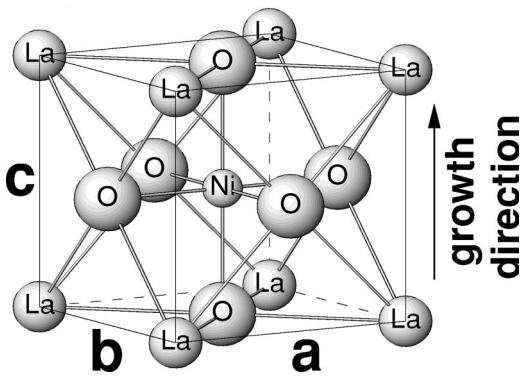

FIG. 2. Crystal structure of the films used in calculations. In-plane lattice parameters $a=b$ are determined by the substrate, while the out-of-plane lattice parameter c is determined from the x-ray data and optimized in the calculations.

TABLE I. Reference configurations and cutoff radii (in a.u.) of *s*, *p*, and *d* orbitals.

Element	Ref. conf.	$r_c(s)$	$r_c(p)$	$r_c(d)$
La	$5s^2 5p^6 5d^3$	1.6	1.6	2.2
Ni	$4s^2 4p^0 3d^8$	2.2	2.3	2.2
O	$2s^2 2p^4$	1.45	1.45	-

mity on the order of a unit cell. The full width at half maximum of a rocking curve of the Bragg peaks of the film was measured to be 0.07° (see the inset of Fig. 1); the very low value indicates a crystalline structure of high quality. The out-of-plane lattice constant $c=3.811$ Å was determined from the symmetric x-ray scan of Fig. 1. The in-plane lattice parameters of the film obtained from reciprocal area scans of the (033) peaks of $SrTiO_3$ and $LaNiO_3$ were equal to those of the substrate ($a=b=3.905$ Å); i.e., this 360-Å-thick film was pseudomorphic with the substrate.

Films were metallic with a low-temperature resistivity $\rho(4.2\ \mathrm{K})\approx 30\ \mu\Omega\,\mathrm{cm}$ and a resistivity ratio $\rho(300\ \mathrm{K})/\rho(4.2\ \mathrm{K})\approx 3$, both of which are comparable to bulk values.[9] To the best of our knowledge, these films were superior in structural quality to any previously reported, including laser MBE grown films.[10]

In our calculations we assume that the films have tetragonally distorted perovskite structure (see Fig. 2). Because the films are fully strained, their in-plane lattice constants $a=b$ are equal to those of the substrate, while their out-of-plane constant c is determined in the calculation by energy minimization. The calculations are based on the local-density approximation (LDA) of the density-functional theory, with the exchange-correlation potential of Ceperley and Alder as parametrized by Perdew and Zunger.[11] The smooth norm-conserving Troullier-Martins[12] pseudopotentials with a partial core correction[13] were generated using reference configurations and cutoff radii listed in Table I. A plane-wave basis set with an energy cutoff of 90 Ry was used. Brillouin-zone summations were performed over 230 k points in the irreducible wedge.

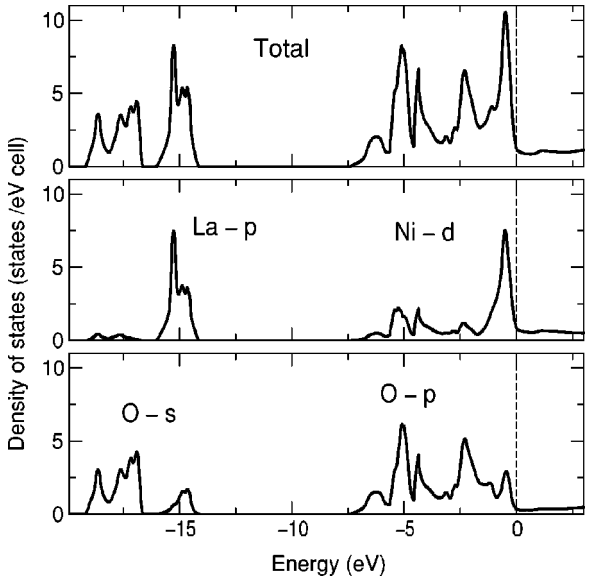

FIG. 3. Calculated total DOS and atom-resolved partial DOS for unstrained $LaNiO_3$. The Fermi level is set at zero energy and is shown as a vertical dashed line.

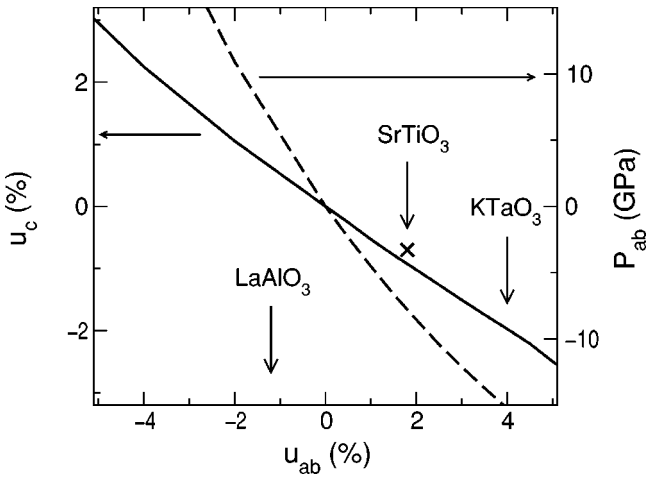

FIG. 4. Solid line: calculated out-of-plane strain u_c vs in-plane strain u_{ab} for $LaNiO_3$ films. ×: experimental value for a fully strained film grown on $SrTiO_3$ (001) substrate. Dashed line: calculated in-plane stress P_{ab} vs in-plane strain u_{ab}. Vertical arrows designate in-plane strains that can be achieved on commercially available substrates.

The nonstrained equilibrium lattice constant, optimized in our calculation, is $a=b=c\equiv a_0=3.815$ Å. This value is only 0.6% smaller than the corresponding ''pseudocubic'' constant which can be extracted from the experimental data.[14,15] The underestimation of the equilibrium lattice constant is typical of a LDA calculation.[16] We also optimized the structure using the generalized gradient approximation (GGA).[17] The GGA lattice constant is 1.5% larger than the experimental value, which follows the expected trend.

The total density of states (DOS) for the nonstrained film calculated using the linear tetrahedron method,[18] as well as

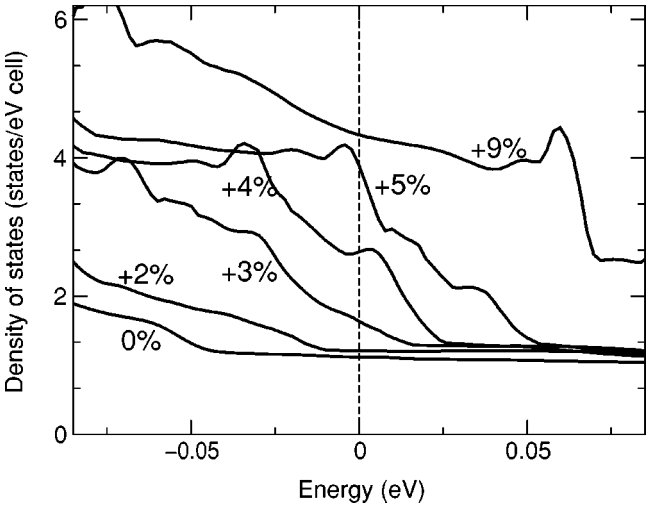

FIG. 5. Calculated total DOS (in the vicinity of the Fermi level) for several values of the tensile in-plane strain u_{ab}.

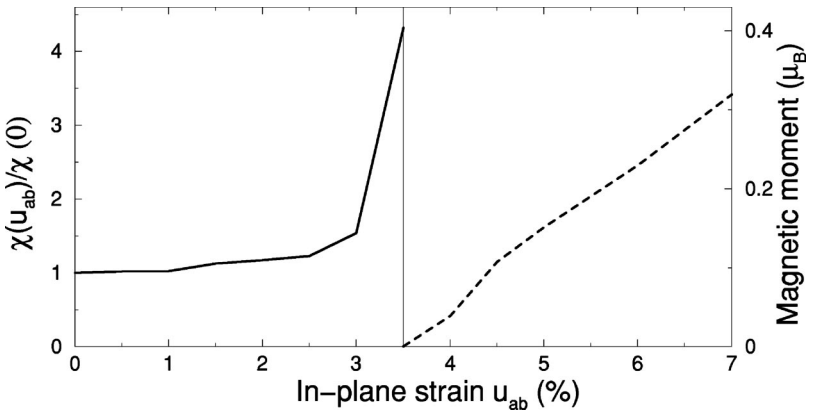

FIG. 6. *Solid line* (*left-hand vertical axis*): magnetic susceptibility enhancement (relative to the bulk value). *Dashed line* (*right-hand vertical axis*): spontaneous magnetic moment (in Bohr magnetons per formula unit) as a function of tensile in-plane strain u_{ab}.

atom- and angular-momentum-decomposed DOS is shown in Fig. 3. The conduction band is formed by strongly hybridized O $2p$ and Ni $3d$ orbitals. This indicates that there is a substantial covalent contribution to the Ni-O chemical bond. The Ni t_{2g} triplet is completely filled with electrons, while the e_g doublet gives rise to a one-quarter-filled metallic band. The lower valence bands are formed by semicore O $2s$ and La $5p$ orbitals, which are also noticeably hybridized, resulting in a weak covalency of predominantly ionic La-O bond.[19] Remarkably, the chemical bonding in $LaNiO_3$ is not purely ionic, but exhibits substantial covalent (Ni-O and La-O) and metallic (Ni-O-Ni) parts. Directional covalent chemical bonds in this metallic oxide facilitate its formation by epitaxial growth techniques.

In the case of a pseudomorphic film the in-plane lattice parameters are determined by the substrate. Figure 4 shows the variation of the optimized out-of-plane strain $u_c = c/a_{calc} - 1$ as a function of the in-plane strain $u_{ab} = a/a_{calc} - 1$, where a_{calc} is the calculated equilibrium pseudocubic lattice constant. For comparison we present the experimentally determined strains of a pseudomorphic $LaNiO_3$ film grown on a $SrTiO_3$ (001) substrate. For this film lattice constants were obtained from x-ray diffraction measurements and strains were evaluated with respect to the experimental pseudocubic lattice constant $a_{exp} = 3.837$ Å (from Ref. 14). While the in-plane lattice parameters are increased by 1.8% over the unstrained values, the out-of-plane parameter is found to decrease only by 0.7% in the experiment as compared to 0.9% in the calculation. We regard this agreement as a further demonstration of the film quality as well as the viability of our calculations.

High values of computed in-plane stress (see the right-hand graph in Fig. 4) imply that epitaxial strains can be used to fabricate compounds which require high pressure for bulk synthesis. The properties of epitaxially stabilized films are altered in a manner similar to the effect of high pressure on bulk material.[20]

The evolution of the total DOS with in-plane strain is presented in Fig. 5. Deformations smaller then 2% do not noticeably alter the electronic structure. Large tensile strains, however, lead to a giant increase of the DOS. Since electron-electron interactions are strong in bulk $LaNiO_3$,[21] it is expected that this large increase of the DOS may trigger a ferromagnetic instability in a pseudomorphic film. Note that all the above calculations were nonmagnetic; i.e., the electron spin density in the calculation was restricted to zero. Our spin-polarized calculations show that the electron-electron interaction leads to a significant Stoner-type susceptibility enhancement. The variation of the magnetic susceptibility with biaxial tensile strain is presented in Fig. 6. The susceptibility increases drastically with tensile strain until the paramagnetic state becomes unstable towards the formation of an itinerant ferromagnetic state, which is characterized by a nonzero spontaneous magnetic moment. The ferromagnetic state becomes energetically favorable for large strains $(a/a_0 \gtrsim 3.5\%)$. Our films are less strained and no magnetic signal was detected. The experimental realization of larger strains would provide a rigorous test of the theory.[22]

In conclusion, we have combined first-principles calculations with atomically controlled synthesis and characterization techniques to study the electronic and crystal structure of $LaNiO_3$ pseudomorphic films. This approach may be used for a less empirical tailoring of thin-film properties.

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