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ABSTRACT

Collective rotations and tilts of oxygen polyhedra play a crucial role in the physical properties of complex oxides such as magnetism and conductivity. Such rotations can be tuned by preparing thin films in which dimensionality, strain, and interface effects come into play. However, little is known of the tilt and rotational distortions in films a few unit cells thick including the question of if coherent tilt patterns survive at all in this ultrathin limit. Here, a series of films of perovskite LaNiO₃ is studied and it is shown that the phonon mode related to oxygen octahedral tilts can be followed by Raman spectroscopy down to a film thickness of three pseudocubic perovskite unit cells (~1.2 nm). To push the limits of resolution to the ultrathin regime, a statistical analysis method is introduced to separate the Raman signals of the film and substrate. Most interestingly, these analyses reveal a pronounced hardening of the tilt vibrational mode in the thinnest films. A comparison between the experimental results, first principles simulations of the atomic structure, and the standing wave model, which accounts for size effects on the phononic properties, reveals that in the ultrathin regime, the Raman spectra are a hybrid entity of both the bulk and surface phononic behavior. These results showcase Raman spectroscopy as a powerful tool to probe the behavior of perovskite films down to the ultrathin limit.

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INTRODUCTION

Physical properties of complex oxides are remarkably sensitive to minute details of their crystal structure.^{1,2} In particular, rotations or tilts of the oxygen polyhedra govern the orbital overlap between cations and oxygen-anions and can determine magnetism, electronic conductivity, metal-insulator transitions, or ferroelectricity, as a few examples.^{3,4} In rare-earth nickelates, structural tuning by heterostructuring has been shown to cause remarkable shifts in transition temperatures through the modulation of the orbital overlaps.^{5,6} While biaxial strain tends to extend over

tens of nanometers, octahedral tilts in perovskite oxide heterostructures can vary over single unit cell layers.^{7–13} At an interface, particularly, strong variations can occur, opening up the possibility to design functional heterostructures. For instance, it was previously demonstrated that LaNiO₃ films on the (001)_{pc}-oriented LaAlO₃ substrate display a conductivity modulated by film thickness,¹¹ eventually becoming insulating under 3 pseudocubic unit cells (pc u.c.).^{14–16} This behavior was explained, through analyzing transmission electron microscopy images and first principles calculations, by a depth-differentiated film structure due to the heterointerface and a strong surface influence on the properties toward the atomic limit.

Even though the internal structure of these films may be strongly thickness-dependent, detailed modeling of x-ray diffraction signals has shown that the film-averaged octahedral tilts and rotations of LaNiO_3 on LaAlO_3 are robust and remain unchanged in magnitude down to 5 pc u.c.¹⁷

A further experimental technique that has been successfully applied to investigate the structure of thin films and heterostructures is Raman spectroscopy.^{18–21} Raman spectroscopy has major advantages over the techniques mentioned already: It is non-destructive and does not require large facilities. Furthermore, Raman spectroscopy allows the structural order to be traced via the so-called soft mode.²² This soft-mode spectroscopy approach was previously employed in, for instance, bulk LaAlO_3 ^{23–25} and SrTiO_3 ²⁶ to follow tilt distortions. In contrast to polar soft modes correlated with ferroelectricity,²⁰ there is, to the best of the authors' knowledge, no experimental data on how soft tilt modes behave for ultrathin films. The aim of this work is an in-depth understanding of tilt distortions in the ultrathin limit and how the corresponding Raman spectrum relates to these structural details, as the thickness is decreased from a usually well-known bulk spectrum to a two-dimensional system.

Here, LaNiO_3 films of different thicknesses on the LaAlO_3 substrate in $(001)_{\text{pc}}$ pseudocubic orientation [Fig. 1(a)] are investigated by Raman spectroscopy. Both the bulk LaNiO_3 and the LaAlO_3 substrate are ABO_3 perovskites with the same rhombohedral space group, $R\bar{3}c$, and tilt system, written as $a^-a^-a^-$ in Glazer notation. Both compounds have antiphase octahedral tilts of equal magnitude (5.6° in LaAlO_3 and 5.2° in LaNiO_3 ^{27,28}) about the three pseudocubic directions that can be compounded into one antiphase rotation magnitude around the $[111]_{\text{pc}}$ vector.²⁹ Figure 1(b) displays the thick film Raman spectrum for LaNiO_3 and the bulk Raman spectrum for the substrate LaAlO_3 . In LaNiO_3 , the octahedral rotation distortion, the order parameter of the system, is related to the only fully symmetric A_{1g} phonon mode^{19,30–32} sketched in Fig. 1(c). The A_{1g} mode is, therefore, described as a “soft mode.” The softening of this mode with increasing temperature was evidenced in Ref. 31, in relation to a transition to the cubic phase that is not observed in practice but would occur at about 1780 K.

EXTRACTING RAMAN SPECTRA OF ULTRATHIN FILMS

A major challenge for Raman spectroscopy on very thin films is the predominant signal of the substrate. Here, this issue is overcome by employing a specific strategy, combining confocal micro-Raman spectroscopy and principal component analysis (PCA) to extract the weak phonon signal from the films by demixing the depth-resolved spectra. The basic setup is schematized in Fig. 2(a). The signal of the film and the signal of the substrate have different depth dependencies. The film signal is the strongest for a laser focus in the vicinity of the surface, whereas the substrate signal remains strong for a laser focus deep into the sample, as sketched on the right of Fig. 2(a). These distinct evolutions with the laser focus allow the separation of film and substrate signals by multivariate analysis methods.³³ Here, principal component analysis (PCA) was used to treat the data. This analysis generates three important parameters—(a) The principal components: A set of individual spectra that describe the features of the measured stack of data. (b) The eigenvalues of the principal components: The larger the value, the more important the corresponding component for the dataset. (c) The score of the components: The score shows an evolution of the weight of a principal component throughout the dataset. The image in Fig. 2(b) shows an application of the method for a 7 pc u.c. (2.7 nm) LaNiO_3 sample, where the laser focal point z is varied within $\pm 10 \mu\text{m}$ of the sample surface in $0.2 \mu\text{m}$ steps. The eigenvalues obtained from the PCA are shown in Fig. 2(c). As can be seen, only the first two components have a significant weight and are relevant for the analysis (indicated by the blue and red squares). All other components have a very small variance and can be treated as negligible. The scores of these two components are shown in Fig. 2(d) and have a distinct behavior as a function of z , being step-like and peak-shaped, respectively. The corresponding components are displayed in Fig. 2(e) and compared with the raw spectrum. As anticipated, the first component can be associated with the substrate spectrum and shows the peaks known from LaAlO_3 [see Fig. 1(b)], while the second component is associated with the film spectrum, where the characteristic peaks are clearly distinguished. Especially remarkable is the demixing of

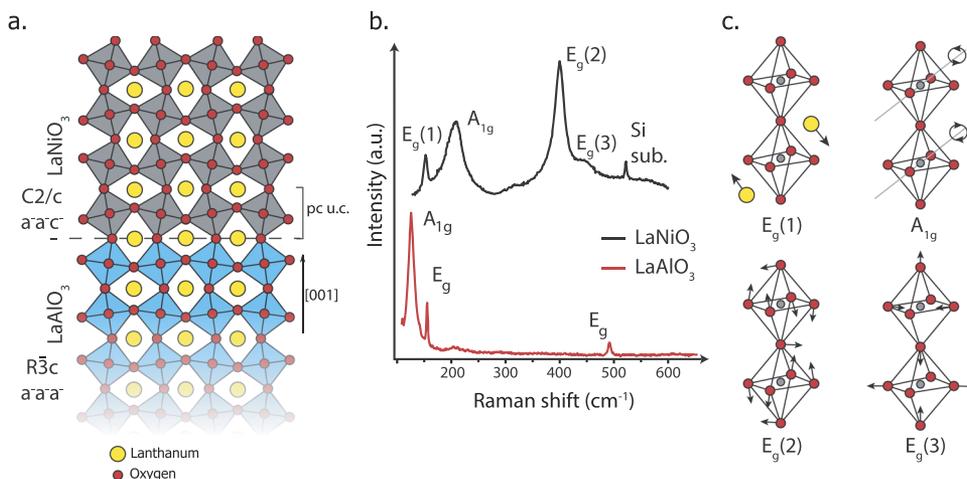


FIG. 1. (a) Sketch of the LaNiO_3 layers on $[001]$ -oriented LaAlO_3 with the pseudocubic unit cell (pc u.c.) indicated. (b) Raman spectra of a thick polycrystalline LaNiO_3 film and a LaAlO_3 substrate. (c) Atomic displacement patterns of the LaNiO_3 Raman modes shown in (b), where the single A_{1g} soft mode is described as a composite octahedral rotation around the $[111]_{\text{pc}}$ vector.

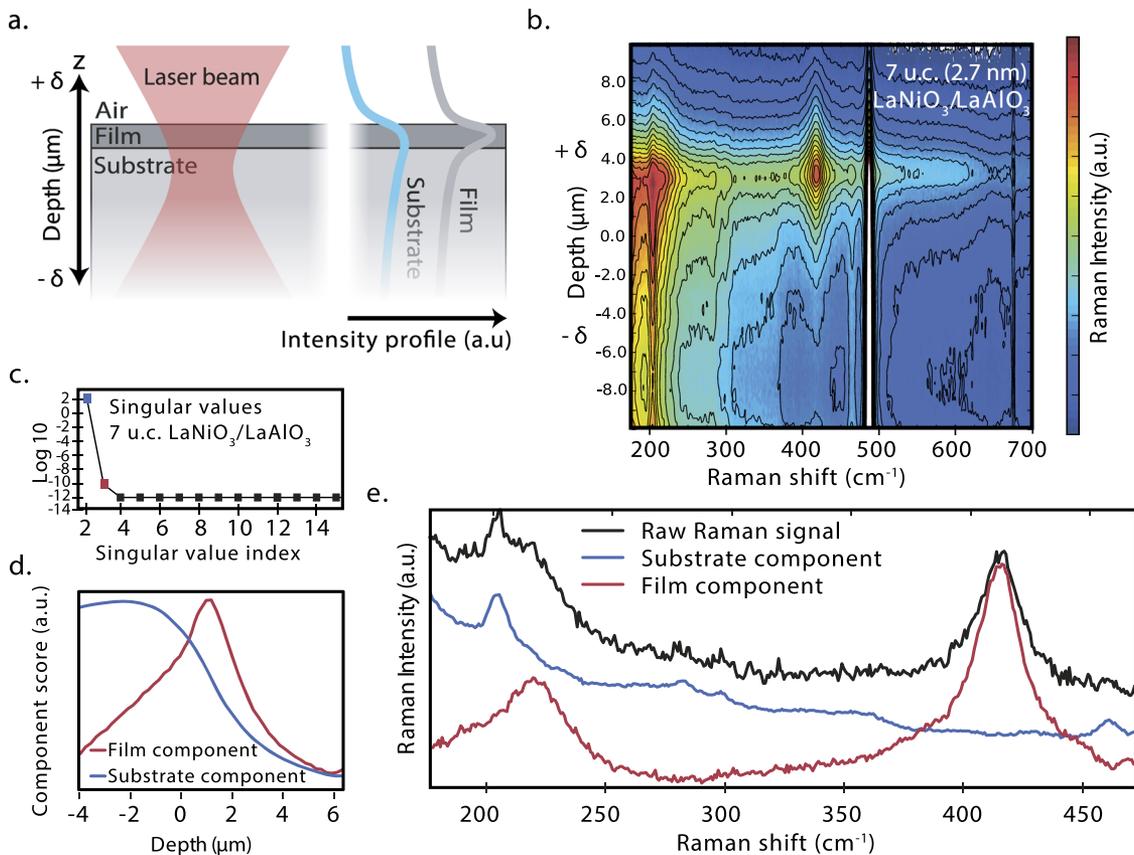


FIG. 2. (a) Simplified sketch of the experimental conditions and the probed volume during the micro-Raman experiment alongside the expected depth dependence of the film and substrate components (not to scale). (b) Full depth measurement dataset for 7 pc.u.c. of LaNiO_3 on LaAlO_3 . (c) Singular value decomposition of the data shown in (b), indicating two major components indicated by the blue and red squares. (d) Principal component analysis (PCA) scores obtained on the same data for the first two components. (e) Final PCA components obtained from the depth-dependent dataset shown in (b) with the raw Raman spectrum recorded at the depth of highest film intensity (black).

the substrate and film peaks at $210\text{--}230\text{ cm}^{-1}$. As can be seen, this method allows the separation of the film and substrate spectra and extraction of detailed film information undisturbed by the substrate signal.

Earlier studies using depth-dependent confocal Raman spectroscopy on oxide thin films rely on the subtraction of the substrate signal.^{21,34} Such a subtraction is based on the assumption that the spectral signature of the substrate is uniform. However, substrate responses are often modified at interfaces and between domains. Thus, a subtraction risks the introduction of artifacts. The statistical treatment of the present work compensates for varying substrate responses and allows for a clean separation of the substrate and film signal.

As displayed in Fig. 2, two Raman modes of the LaNiO_3 films are accessible in this frequency range: the A_{1g} mode and one E_g mode, corresponding to tilts and bending of the BO_6 octahedra [Fig. 1(c)]. The soft mode of interest is the only fully symmetric mode with A_{1g} symmetry. The mode notations relate here to the bulk rhombohedral symmetry, even though it is known that epitaxial strain stabilizes a monoclinic structure $C2/c$ ($a^-a^-c^-$), as revealed by

density functional theory (DFT) and Raman spectroscopy on films down to 14 nm.¹⁹ The symmetry lowering leads to the splitting of E_g Raman peaks as well as the emergence of new peaks, but for simplicity, the labeling with respect to the bulk will be retained in this discussion.

THICKNESS DEPENDENCE OF THE RAMAN MODES

We now apply the same measurement and analysis method to the full series of nine LaNiO_3 films with thicknesses ranging from 3 pc.u.c. to 15 pc.u.c., as verified by x-ray diffraction and scanning transmission electron microscopy. Three representative spectra for 11 pc.u.c., 7 pc.u.c., and 3 pc.u.c. are showcased in Fig. 3(a). Three fits associated with the film component of the data shown in Fig. 3(a) are shown in panel (b). The fits require two Lorentzian distributions for each of the Raman bands, as a consequence of the symmetry lowering from rhombohedral to monoclinic. However, only the main peak remains dominant and can be followed reliably for varying film thickness throughout the series. The weaker

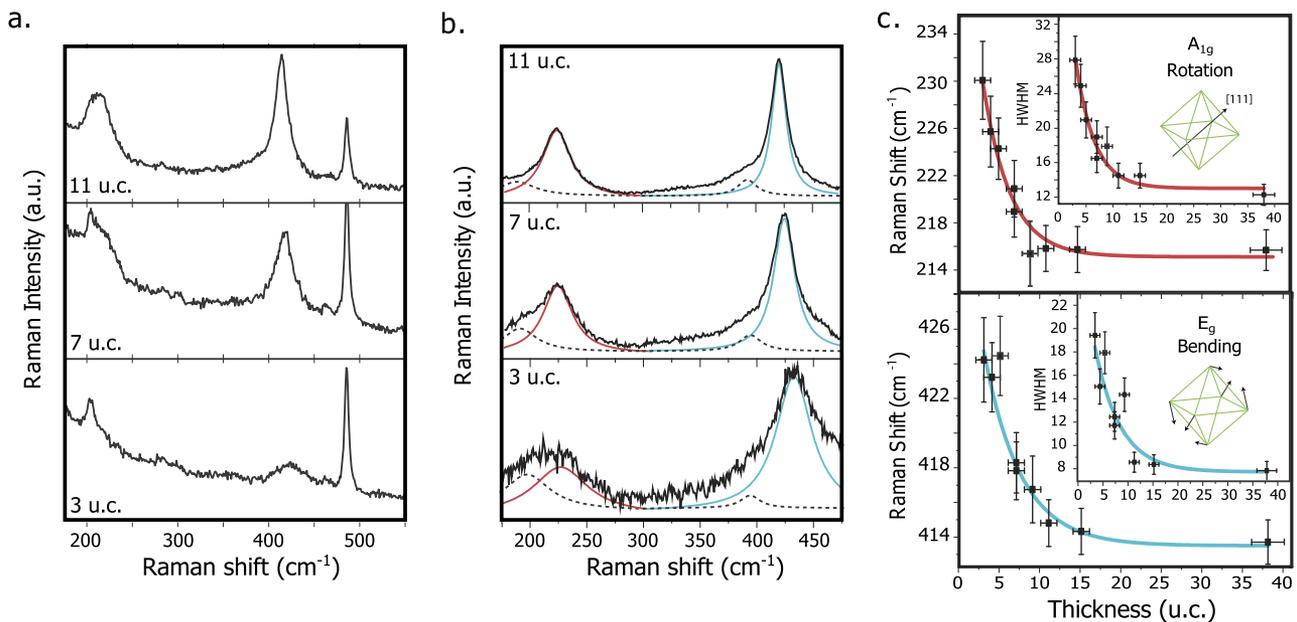


FIG. 3. (a) Raw Raman spectra of LaNiO₃ on LaAlO₃ for 3 pc u.c., 7 pc u.c., and 11 pc u.c. The spectra were chosen from the depth where the film signal is maximal. (b) Film components extracted from the PCA with the A_{1g} and E_g peaks sketched in red and blue, respectively. The additional peaks resulting from the symmetry-lowering are sketched as dashed lines. (c) Position and half width at half maximum (HWHM) of the LaNiO₃ E_g and A_{1g} modes resulting from the fits for the entire series of samples. Solid lines show an exponential decay fit to the data.

shoulders, shown as dotted lines in Fig. 3(b), will not be discussed further.

Figure 3(c) shows the resulting peak positions as well as the half width at half maximum (HWHM) for the A_{1g} mode (top) and E_g mode (bottom) described above for the entire series of LaNiO₃ films with varying thickness. Both modes show a qualitatively similar behavior with two different regimes. For films thicker than 15 u.c., both the positions and widths are constant and coincide with the values reported in previous studies.¹⁹ As thickness decreases, the mode frequency and width enter a second regime and both exhibit a pronounced increase. Figure 3(c) shows a fit of this behavior with an exponential evolution. The critical thicknesses are 8–10 u.c. (3–4 nm), and notably, the mode frequency increases for lower thicknesses, i.e., moves away from the corresponding soft mode of LaAlO₃, which is at lower frequency, as shown in Fig. 1(b), in accordance with reports on the E_g mode by Hepting and co-workers.³⁴

ESTIMATE OF THE RAMAN FREQUENCIES BY FIRST-PRINCIPLES

In order to provide a more thorough understanding of the Raman signature and its relation with the structure of the film, a theoretical model was constructed. Within this model, an estimate of the soft-mode frequency can be obtained directly by starting from the relaxed film structures reported previously.¹¹ These structures were obtained by running first-principles simulations in which finite LaNiO₃ films of different thicknesses and the LaAlO₃

substrate were treated explicitly. Then, the equilibrium solutions are distorted by moving the oxygen atoms within the LaNiO₃ film so as to mimic antiphase rotations of the O₆ octahedra about the $[111]_{pc}$ axis. From this, the harmonic energy variation is computed. The energy curvature κ_{soft} is thus obtained, and the mode frequency can be approximated as $\omega_{soft} = \sqrt{\kappa_{soft}/m_O}$, where m_O is the mass of the oxygen ion. It is assumed that the eigenvector of the soft tilting mode of the $a^-a^-c^-$ -type monoclinic films can be approximated by the well-known symmetry-determined A_{1g} eigenmode of the bulk crystal.

The results of the first-principles approach are shown in Fig. 4(a). Compared to the Raman spectra, here, a similar soft mode hardening on the order of 20 cm⁻¹ is observed. The critical thickness where the mode hardening sets in is slightly reduced in the theory compared to the experiment (5 u.c. compared to 10 u.c.). These first principles calculations based on the microscopic structure, therefore, provide a reasonable description of the mode hardening in ultrathin films.

STANDING WAVE APPROXIMATION

As an alternative, but complementary, approach, the “standing wave” approximation is considered to explain the mode hardening. This approach has proven fruitful in past studies of vibrational properties of ultrathin binary oxides films.^{35–40} A slight adaptation is needed, however, to take into account the different symmetries of the phonon modes: these past works only report studies of polar modes, while the Raman active modes in rhombohedral LaNiO₃ are

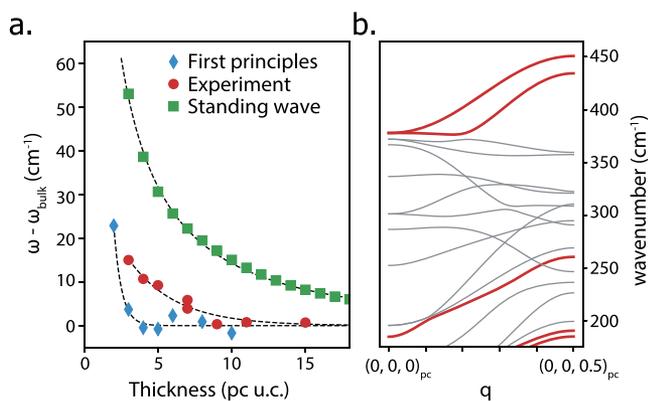


FIG. 4. (a) Comparison of the experimental value for the A_{1g} soft mode frequency (red circles), together with the same parameter derived from direct first principles calculation (blue diamonds) and the standing wave approach (green squares). The dashed lines are guides for the eye. (b) Phonon dispersion of bulk LaNiO_3 along the [001] direction in the wavelength range of interest.

non-polar. As a result, the electrostatic boundary conditions and the dielectric properties of the media are not relevant here. Following the ideas developed in Ref. 36, we assume that non-polar modes will behave like transverse optical modes propagating perpendicular to the films, that is, without any polar component along the direction of the wavevector. The frequency of the phonon in the film is then approximated as the frequency calculated in the bulk on this phonon branch at a wavevector π/d , where d is the number of pseudocubic unit cells in the film. With changing film thickness, the wavevector and the frequency change according to the dispersion relation.⁴⁰ The boundary conditions for the approximation are represented by a wave amplitude vanishing at the interfaces. In other words, the phonon cannot propagate across the interface due to a large mismatch between the phonon frequencies of the two media.⁴¹

In practice, the phonon dispersion for bulk LaNiO_3 , shown in Fig. 4(b), was calculated from first principles and the soft branch followed across the Brillouin zone. Given the complexity of the phonon dispersion relation, care was taken to follow the correct phonon branch originating from the A_{1g} tilt mode by checking the branch symmetry and the phonon eigenvector. As a result of the positive slope of the phonon branch, the soft mode frequency in the films increases as the size effect becomes more significant toward the ultrathin regime, reproducing the trend from experiment. As compared to the mode hardening seen in the Raman spectra, both the critical thickness for the hardening and the overall increase in frequency are greater. Part of this discrepancy may be due to the interface between the LaNiO_3 film and the LaAlO_3 substrate not establishing a sharp boundary condition—as both materials are similar in crystal structure, structural instabilities, and phonon spectrum—and, thus, reducing the effective size effect in practice.

DISCUSSION

These Raman spectroscopy investigations into the ultrathin regime of LaNiO_3 on the LaAlO_3 substrate have brought to light a number of intriguing behaviors. Importantly, owing to the advanced

technical and analytical approaches employed here, both the soft phonon mode associated with the tilts and the octahedral bending mode remained measurable by Raman spectroscopy down to 3 pc u.c. (1.2 nm)—a thickness around which the distorted unit cell itself is almost undefined. Both the A_{1g} and the E_g modes show a very similar hardening beginning below 10 pc u.c.

This picture differs from a number of conventional interpretations of Raman spectra of thin films. In particular, the possibility that the shifts of Raman modes are due to a relaxation of epitaxial strain was put forward in a previous study on the E_g bending mode of LaNiO_3 films³⁴ but can be ruled out here as all the films studied were epitaxially strained to the substrate. Moreover, as the global LaNiO_3 octahedral rotations and tilts were found, by x-ray diffraction, not to vary with thickness down to 5 pc u.c.,¹⁷ it appears that, in contrast with bulk systems, the A_{1g} mode frequency no longer scales linearly with the tilt angle. However, the bulk linear scaling follows a slope on the order of $20\text{--}30 \text{ cm}^{-1}/^\circ$ in the similarly structured chromates and ferrites.^{42,43} This suggests that the tilt could increase by as little as one degree toward the ultrathin limit, which would be within the experimental error of the x-ray diffraction signal fitting reported previously.

On the other hand, it is remarkable that the two observed modes—both bending and tilting—of LaNiO_3 exhibit very similar hardenings, with the same critical thickness, and shifts of nearly equal amplitudes. The standing wave approach employed here partially explains this behavior as both modes have an increase in frequency when moving away from the zone center. Therefore, the observation that both our Raman modes undergo a similar hardening is likely to be material-dependent. Recent reports on ultrathin BaTiO_3 films⁴⁰ show a contrasting behavior for different modes. This underlines that the vibrational frequencies in the ultrathin limit indeed depend on the mode details and dispersion. The frequency increase in LaNiO_3 that is predicted by the standing wave approach is, however, greater in magnitude than that observed in practice, but as discussed, this could stem from vibrational continuity into the substrate.

A comparison with the first-principles results shows that a purely microscopic simulation of the soft mode frequency can go a reasonable way to reproducing the same hardening behavior. As found previously by first-principles calculations and corroborated by experiment,¹¹ the LaNiO_3 surface tends to dominate the overall properties toward the ultrathin limit. Ultimately, for the thinnest films, the energy variation—and, therefore, the Raman frequency—is determined by a region of the film that is relatively stiff against the NiO_6 tilting mode. The complete thickness-dependence is not fully described in this picture, however, with the onset of the mode hardening taking place at 10 pc u.c. in the experiment.

The experimental mode hardening follows a trend that is part way between that predicted by the direct first-principles estimate and that predicted by the standing wave approximation. This leads toward the natural conclusion that, in this ultrathin regime, the thin film cannot be considered as simply a slice of the bulk crystal but rather as a hybrid entity. Therefore, discussion of both the phononic behavior of a crystalline solid and the vibrational properties of a surface is required.

These results showcase Raman spectroscopy coupled with principal component analysis as an efficient tool to investigate vibrational properties in severely reduced sample dimensions. This

method is entirely general and can potentially be implemented in more complex systems—in terms of symmetry and number of modes—than LaNiO_3 on the LaAlO_3 substrate. Interestingly, the change in metallicity due to the altered film thicknesses¹¹ does not impact the quality of the PCA. This further underlines the universality of our approach. Modes corresponding to the oxygen octahedral tilting and bending could still be identified in films as thin as 3 pseudocubic unit cells or 1.2 nm—a testament both to the power of the analysis technique and to the high quality of the thin films. Both of these modes are found to harden significantly toward the atomic limit. The onset of the hardening cannot be fully accounted for by microscopic considerations alone. Incorporating a standing wave approach, commonly employed in the study of surface vibrations, sheds light on the possibility of an unexpected phononic behavior in this pseudo-2D regime that should be general to ultrathin films as a whole.

METHODS

Sample preparation

The samples were grown by radio frequency off-axis magnetron sputtering at a temperature of 510 °C and a pressure of 0.18 mTorr (Ar:O₂ 7:2 mix). The series ranges from 3 to 15 unit cells. The films were characterized by x-ray diffraction, atomic force microscopy, and scanning transmission electron microscopy and were found to be coherently strained, with an atomically flat surface and high crystalline quality.¹¹

Raman spectroscopy

The experiments were performed, at room temperature, with a Renishaw inVia micro-Raman spectrometer. The excitation wavelength was 633 nm, with laser power lower than 1 mW. The exciting light is focused via a $\times 100$ microscope objective with numerical aperture 0.9, resulting in nominal spot size and depths of the field of 0.86 μm and 1.38 μm , respectively. The scattered light was analyzed with a holographic grating with 2400 g/mm and collected on a CCD detector. All data treatments (principal component analysis and fitting with standard Lorentzian line shapes) were performed with a python-based software developed in house.

Ab initio calculation details

We used density functional theory (DFT) as within the local density approximation (LDA), as implemented in the Vienna *ab initio* simulation package (VASP).^{44,45} We treated the ionic cores within the so-called projector-augmented wave (PAW) approach,⁴⁶ solving explicitly for the following electrons: La 5*p*, 5*d*, and 6*s*; Ni 3*p*, 3*d*, and 4*s*; Al 3*s* and 3*p*; and O 2*s* and 2*p*. The 3*d* electrons of Ni were treated at the bare LDA level, which has been shown to be the most realistic way to treat metallic LaNiO_3 .⁴⁷ Details about the structures combining the LaNiO_3 film and LaAlO_3 substrate are described in some detail in Ref. 11. For our phonon calculations for bulk LaNiO_3 , we used the usual 10-atom primitive cell of this compound. Electronic wave functions were represented in a plane-wave basis truncated at 400 eV and 500 eV, respectively, for our $\text{LaNiO}_3/\text{LaAlO}_3(001)$ and bulk LaNiO_3 simulations. Reciprocal space integrals were computed using a $5 \times 5 \times 1$ *k*-point mesh in

our $\text{LaNiO}_3/\text{LaAlO}_3(001)$ calculations, while a mesh of $8 \times 8 \times 8$ *k*-points was used to treat bulk LaNiO_3 in its 10-atom primitive cell. We used phonopy⁴⁸ for the calculation of phonon bands, using a $2 \times 2 \times 2$ multiple of the 10-atom primitive cell (and, correspondingly, a $4 \times 4 \times 4$ *k*-point grid).

AUTHORS' CONTRIBUTIONS

J.F. fabricated and characterized the samples. A.S. performed the Raman experiments and developed the tools for their analysis with input from M. Guennou. M.C.W. initiated the use of a multivariate analysis method to study ultrathin films. H.Z. and J.I. performed and analyzed the DFT calculations. J.-M.T. and J.K. directed the research. All authors contributed to the analysis of the results and the preparation of this manuscript.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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