Vibrational properties of LaNiO$_3$ films in the ultrathin regime

Alexander Schober, Jennifer Fowlie, Mael Guennou, Mads C. Weber, Hongjian Zhao, Jorge Íñiguez, Marta Gibert, Jean-Marc Triscone, and Jens Kreisel
Vibrational properties of LaNiO$_3$ films in the ultrathin regime

Cite as: APL Mater. 8, 061102 (2020); doi: 10.1063/5.0010233
Submitted: 9 April 2020 • Accepted: 14 May 2020 • Published Online: 2 June 2020

Alexander Schober,$^{1,2}$ Jennifer Fowlie,$^3$ Mael Guennou,$^{1,2}$ Mads C. Weber,$^4$ Hongjian Zhao,$^{1,5}$ Jorge Íñiguez,$^{1,2}$ Marta Gibert,$^6$ Jean-Marc Triscone,$^3$ and Jens Kreisel$^{1,2}$

AFFILIATIONS
$^1$Materials Research and Technology Department, Luxembourg Institute of Science and Technology, 41 rue du Brill, L-4422 Belvaux, Luxembourg
$^2$Department of Physics and Materials Science, University of Luxembourg, 41 rue du Brill, L-4422 Belvaux, Luxembourg
$^3$DQMP – University of Geneva, École de Physique, 24, Quai Ernest-Ansermet, CH-1211 Geneva, Switzerland
$^4$Department of Materials, ETH Zurich, Vladimir-Prelog-Weg 4, 8093 Zurich, Switzerland
$^5$Physics Department and Institute for Nanoscience and Engineering University of Arkansas, Fayetteville, Arkansas 72701, USA
$^6$Physik-Institut, University of Zurich, Winterthurerstrasse 190, 8057 Zurich, Switzerland

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 LaNiO$_3$ 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 ($\sim 1.2$ 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.

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.$^{10}$ While biaxial strain tends to extend over tens of nanometers, octahedral tilts in perovskite oxide heterostructures can vary over single unit cell layers.$^{11,12}$ At an interface, particularly, strong variations can occur, opening up the possibility to design functional heterostructures. For instance, it was previously demonstrated that LaNiO$_3$ films on the (001)$_{pc}$-oriented LaAlO$_3$ substrate display a conductivity modulated by film thickness,$^{11}$ eventually becoming insulating under 3 pseudocubic unit cells (pc u.c.).$^{13,14}$ 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.

A further experimental technique that has been successfully applied to investigate the structure of thin films and heterostructures is Raman spectroscopy. 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. This soft-mode spectroscopy approach was previously employed in, for instance, bulk LaAlO$_3$ and SrTiO$_3$ to follow tilt distortions. In contrast to polar soft modes correlated with ferroelectricity, 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]$_p$ 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, R3c, and tilt system, written as $a’$ $a$ $a’$ in Glazer notation. Both compounds have antiphase octahedral tilts of equal magnitude ($5.6^\circ$ in LaAlO$_3$ and $5.2^\circ$ in LaNiO$_3$) about the three pseudocubic directions that can be compounded into one antiphase rotation tilt system. 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 dependences. 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. 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 $\pm 10$ $\mu$m of the sample surface in 0.2 $\mu$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]$_p$ vector.
the substrate and film peaks at 210–230 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
estimates the Raman frequencies by first-principles (APL Mater. 8, 061102 (2020); doi: 10.1063/5.0010233) © Author(s) 2020
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 $\pi/d$, 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. 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.

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$_3$ films 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., 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 $20–30$ cm$^{-1}$/Å in the similarly structured chro-
mates and ferrites. 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$_3$ films 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, 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 strain was put forward in a previous study on the $E_g$ bending mode of LaNiO$_3$ films—such as the surface. This 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 $20–30$ cm$^{-1}$/Å in the similarly structured chro-
mates and ferrites. 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$_3$ films 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, 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 strain was put forward in a previous study on the $E_g$ bending mode of LaNiO$_3$ films—such as the surface. This 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 $20–30$ cm$^{-1}$/Å in the similarly structured chro-
mates and ferrites. 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.
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 thicknesses$^{11}$ 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:O$_2$ 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 ×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).$^{46,47}$ We treated the ionic cores within the so-called projector-augmented wave (PAW) approach,$^{39}$ 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 LaNiO$_3$/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 LaNiO$_3$/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 phonopy$^{10}$ 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.

**ACKNOWLEDGMENTS**

A.S., M. Guennou, H.Z., J.I., and J.K. acknowledge support from the Luxembourg National Research Fund under Project No. CO-FERMA T FNR/P12/4853155/Kreisel and the AFR, Grant No. 7749159. M.C.W. acknowledges support from SNSF (Grant No. 200021_178825). M. Gibert acknowledges financial support through the SNSF, Grant No. PP00P2_170564. This work was supported by the Swiss National Science Foundation through Division II. The research leading to these results has received funding from the European Research Council under the European Union’s Seventh Framework Program (No. FP7/2007-2013)/ERC Grant Agreement No. 319286 (Q-MAC). M. Guennou also gratefully acknowledges discussion and input from W. Widdra (MPI of Microstructure Physics, Halle, Germany).

**DATA AVAILABILITY**

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

**REFERENCES**

1. R. H. Mitchell, *Perovskites: Modern and Ancient* (Almaz Press, Ontario, Canada, 2002).
2. J. B. Goodenough, “Electronic and ionic transport properties and other physical aspects of perovskites,” *Rep. Prog. Phys.* 67, 1915 (2004).
3. J. M. Rondinelli, S. J. May, and J. W. Freeland, “Control of octahedral connectivity in perovskite oxide heterostructures: An emerging route to multifunctional materials discovery,” *MRS Bull.* 37, 261–270 (2012).
4. J. Nordlander, M. Campanini, M. D. Rossell, R. Erni, Q. N. Meier, A. Cano, N. A. Spaldin, M. Fiebig, and M. Trassin, “The ultrathin limit of improper ferroelectricity,” *Nat. Commun.* 10, 5591 (2019).
5. S. Catalano, M. Gibert, J. Fowlie, J. Íñiguez, J.-M. Triscone, and J. Kreisel, “Rare-earth nickelate RNiO$_3$: Thin films and heterostructures,” *Rep. Prog. Phys.* 81, 046501 (2018).
6. S. Middey, J. Chakhalian, P. Mahadevan, J. W. Freeland, A. J. Mills, and D. D. Sarma, “Physics of ultrathin films and heterostructures of rare-earth nickelates,” *Annu. Rev. Mater. Res.* 46, 305–334 (2016).
7. R. Aso, D. Kan, Y. Shimakawa, and H. Kurata, “Atomic level observation of octahedral distortions at the perovskite oxide heterointerface,” *Sci. Rep.* 3, 2214 (2013).
G. Koster, “Symmetry and lattice mismatch induced strain accommodation near 105 and S. J. Pennycook, “Suppression of octahedral tilts and associated changes in electric properties at epitaxial oxide heterostructure interfaces,” Phys. Rev. Lett. 105, 087204 (2010).

A. Vailionis, H. Boschker, Z. Liao, J. R. A. Smit, G. Rijnders, M. Huijben, and G. Koster, “Symmetry and lattice mismatch induced strain accommodation near and away from correlated perovskite interfaces,” Appl. Phys. Lett. 105, 131906 (2014).

R. Schervitzl, S. Gariglio, M. Gabay, P. Zubko, M. Gibert, and J.-M. Triscone, “Metal-insulator transition in ultrathin LaNiO3 films,” Phys. Rev. Lett. 106, 246403 (2010).

S. Son, P. Moetakef, J. M. LeBeau, D. Ouellette, L. Balents, S. J. Allen, and S. Stember, “Low-dimensional Mott material: Transport in ultrathin epitaxial LaNiO3 films,” Appl. Phys. Lett. 96, 062114 (2010).

D. P. Kumah, A. S. Disa, J. H. Ngai, H. Chen, A. Malashevich, S. Ismail-Beigi, F. J. Walker, and C. H. Ahn, “Tuning the structure of nickelates to achieve two-dimensional electron conduction,” Adv. Mater. 33, 196–198 (2020).

S. Gariglio, A. Schober, M. Guennou, J. Kreisel, O. Stéphan, and J.-M. Triscone, “Conductivity and local structure of LaNiO3 thin films,” Adv. Mater. 29, 1605197 (2017).

A. K. Morsh, H. J. Chang, M. Huijben, M. P. Oxley, S. Okamoto, M. K. Niranjan, J. D. Burton, E. Y. Tsymbal, Y. H. Chu, P. Yu, R. Ramesh, S. V. Kalinin, and S. J. Pennycook, “Suppression of octahedral tilts and associated changes in electronic properties at epitaxial oxide heterostructure interfaces,” Phys. Rev. Lett. 105, 087204 (2010).

G. Koster, “Symmetry and lattice mismatch induced strain accommodation near and away from correlated perovskite interfaces,” Appl. Phys. Lett. 105, 131906 (2014).

R. Schervitzl, S. Gariglio, M. Gabay, P. Zubko, M. Gibert, and J.-M. Triscone, “Metal-insulator transition in ultrathin LaNiO3 films,” Phys. Rev. Lett. 106, 246403 (2010).

S. Son, P. Moetakef, J. M. LeBeau, D. Ouellette, L. Balents, S. J. Allen, and S. Stember, “Low-dimensional Mott material: Transport in ultrathin epitaxial LaNiO3 films,” Appl. Phys. Lett. 96, 062114 (2010).

D. P. Kumah, A. S. Disa, J. H. Ngai, H. Chen, A. Malashevich, S. Ismail-Beigi, F. J. Walker, and C. H. Ahn, “Tuning the structure of nickelates to achieve two-dimensional electron conduction,” Adv. Mater. 26, 1935–1940 (2014).

F. W. Close, C. Lichtensteiger, M. Gibert, H. Meley, P. Willmott, and J.-M. Triscone, “Thickness-dependent perovskite octahedral distortions at heterointerfaces,” Nano Lett. 19, 4188–4194 (2019).

K. Kreisel, M. C. Weber, N. Dix, F. Sánchez, P. A. Thomas, and J. Fontcuberta, “Probing individual layers in functional oxide multilayers by wavelength-dependent Raman scattering,” Adv. Funct. Mater. 22, 5044–5049 (2012).

M. C. Weber, M. Guennou, N. Dix, D. Pesquera, F. Sánchez, G. Herranz, J. Fontcuberta, L. López-Conesa, S. Estradé, F. Peiró, J. Íñiguez, and J. Kreisel, “Multiple strain-induced phase transitions in LaNiO3 thin films,” Phys. Rev. B 94, 041118 (2016).

A. D. Tennen, A. Bruchhaus, N. D. Lanzlötti-Kimura, A. Fainstein, R. S. Katiyar, A. Cantarero, A. Sokoussian, V. Vamithanathan, J. H. Haeni, W. Tian, D. G. Schlom, K. J. Choi, D. M. Kim, C. R. Eom, H. P. Sun, X. Q. Pan, Y. L. Li, Q. Chen, Q. X. Jia, S. M. Nakhamkin, K. M. Bade, and X. X. Xi, “Probing nanoscale ferroelectricity by ultraviolet Raman spectroscopy,” Science 313, 1614 (2006).

M. H. Hepting, M. Minola, G. Cristiani, G. Logvenov, E. Schierle, M. Wu, M. Bluschke, E. Weschke, H.-U. Habermeier, E. Benckiser, M. Le Tacon, and B. Keimer, “Tunable charge and spin order in PrNiO3 thin films and superlattices,” Phys. Rev. Lett. 113, 227206 (2014).

J. F. Scott, “Soft-mode spectroscopy: Experimental studies of structural phase transitions,” Rev. Mod. Phys. 46, 83 (1974).

J. F. Scott, “Raman study of trigonal-cubic phase transitions in rare-earth aluminates,” Phys. Rev. 183, 823 (1969).

S. A. Hayward, F. D. Morrison, S. A. T. Redfern, E. K. H. Salje, J. F. Scott, K. S. Knight, S. Tarantino, A. M. Glazer, V. Shuvaeva, P. Daniel, M. Zhang, and M. A. Carpenter, “Transformation processes in LaAlO3: Neutron diffraction, dielectric, thermal, and optical studies,” Phys. Rev. B 72, 054110 (2005).

P. Bouvier and J. Kreisel, “Pressure-induced phase transition in LaAlO3,” J. Phys.: Condens. Matter 14, 3981 (2002).

A. A. Smirnova, J. F. Scott, and J. M. Worlock, “Soft phonon modes and the 110 K phase transition in SrTiO3,” Phys. Rev. Lett. 21, 16–19 (1968).

K. A. Müller, W. Berlinger, and F. Waldner, “Characteristic structural phase transition in perovskite-type compounds,” Phys. Rev. Lett. 21, 814 (1968).

J. L. García-Muñoz, J. Rodríguez-Carvajal, P. Lacroce, and J. B. Torrance, “Neutron-diffraction study of RNiO3 (R = La, Pr, Nd, Sm): Electronically induced structural changes across the metal-insulator transition,” Phys. Rev. B 46, 4414 (1992).

A. M. Glazer, “Simple ways of determining perovskite structures,” Acta Crystallogr. Sect. A 31, 756 (1975).

M. V. Abrašev, A. P. Lávinchuk, M. N. Iliev, L. R. Meng, V. N. Popov, V. G. Ivanov, R. A. Chakalov, and C. Thomsen, “Comparative study of optical phonons in the rhombohedrally distorted perovskites LaAlO3 and LaMnO3,” Phys. Rev. B 59, 4146–4153 (1999).

N. Chaban, M. Weber, S. Pignard, and J. Kreisel, “Phonon Raman scattering of perovskite LaNiO3 thin films,” Appl. Phys. Lett. 97, 031915 (2010).

G. Gou, I. Grinberg, A. M. Rappe, and J. M. Rondinelli, “Lattice normal modes and electronic properties of the correlated metal LaNiO3,” Phys. Rev. B 84, 144101 (2011).

J. F. Scott, “Soft-mode spectroscopy: Experimental studies of structural phase transitions,” Rev. Mod. Phys. 46, 83 (1974).

J. F. Scott, “Raman study of trigonal-cubic phase transitions in rare-earth aluminates,” Phys. Rev. 183, 823 (1969).

S. A. Hayward, F. D. Morrison, S. A. T. Redfern, E. K. H. Salje, J. F. Scott, K. S. Knight, S. Tarantino, A. M. Glazer, V. Shuvaeva, P. Daniel, M. Zhang, and M. A. Carpenter, “Transformation processes in LaAlO3: Neutron diffraction, dielectric, thermal, and optical studies,” Phys. Rev. B 72, 054110 (2005).

A. Togo and I. Tanaka, “First principles phonon calculations in materials spaces,” J. Phys.: Condens. Matter 30, 095001 (2018).

S. V. Tzana, L. Savio, and M. Rocca, “Phonons in thin oxide films,” in Oxide Materials at the Two-Dimensional Limit (Springer, 2016), pp. 169–199.

J. A. Brum, F. O. Schumann, and W. Widdra, “Growth and lattice dynamics of ultrathin BaO films on Pt(001),” Scr. Mater. 48, 405–409 (2003).

G. Benedek and J. P. Toennis, “Helium atom scattering spectroscopy of surface phonons: Genesis and achievements,” Surf. Sci. 299, 587–611 (1994).

J. F. Scott, “Soft-mode spectroscopy: Experimental studies of structural phase transitions,” Rev. Mod. Phys. 46, 83 (1974).

J. F. Scott, “Raman study of trigonal-cubic phase transitions in rare-earth aluminates,” Phys. Rev. 183, 823 (1969).

S. A. Hayward, F. D. Morrison, S. A. T. Redfern, E. K. H. Salje, J. F. Scott, K. S. Knight, S. Tarantino, A. M. Glazer, V. Shuvaeva, P. Daniel, M. Zhang, and M. A. Carpenter, “Transformation processes in LaAlO3: Neutron diffraction, dielectric, thermal, and optical studies,” Phys. Rev. B 72, 054110 (2005).