Spectroscopic Evidence of a Dimensionality-Induced Metal-to-Insulator Transition in the Ruddlesden–Popper La\textit{n+1}Ni\textit{n}O\textit{3n+1} Series

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ABSTRACT: Perovskite-based heterostructures have recently gained remarkable interest, thanks to atomic-scale precision engineering. These systems are very susceptible to small variations of control parameters, such as two-dimensionality, strain, lattice polarizability, and doping. Focusing on the rare-earth nickelate diagram, LaNiO\textit{3} (LNO) catches the eye, being the only nickelate that does not undergo a metal-to-insulator transition (MIT). Therefore, the ground state of LNO has been studied in several theoretical and experimental papers. Here, we show by means of infrared spectroscopy that an MIT can be driven by dimensionality control in ultrathin LNO films when the number of unit cells drops to 2. Such a dimensionality tuning can eventually be tailored when a physically implemented monolayer in the ultrathin films is replaced by a digital single layer embedded in the Ruddlesden–Popper La\textit{n+1}Ni\textit{n}O\textit{3n+1} series. We provide spectroscopic evidence that the dimensionality-induced MIT in Ruddlesden–Popper nickelates strongly resembles that of ultrathin LNO films. Our results can pave the way to the employment of Ruddlesden–Popper La\textit{n+1}Ni\textit{n}O\textit{3n+1} to tune the electronic properties of LNO through dimensional transition without the need of physically changing the number of unit cells in thin films.

KEYWORDS: nickelates, Ruddlesden–Popper, metal-to-insulator transition, infrared spectroscopy, X-ray absorption spectroscopy, thin films, perovskite oxides

INTRODUCTION

Rare-earth nickelate ReNiO\textit{3} and its heterostructures have represented in the past decade a very flourishing field of research. Nickelates are prototype compounds for strong correlations in which the change of the rare earth (Re) modifies the Ni–O–Ni bond angle, thus allowing tuning of the Mott metal-to-insulator (MIT) temperature from 600 K (as in LuNiO\textit{3}) to about 100 K in PrNiO\textit{3}. By further increasing the angle, as in LaNiO\textit{3}, the MIT disappears, leaving the field to a paramagnetic metal ground state. Being on the verge of a Mott transition makes it possible to achieve control of the nickelate’s ground state through the application of a small perturbation, thereby allowing for many appealing technological applications. For instance, great interest has also been sparked by the proposal from Chaloupka and Khaliullin that LaNiO\textit{3} could be combined in some superlattice structure so as to possibly mimic the CuO\textit{2} planes of high-temperature superconductors. This was motivated by the presence of strong correlations in a layered structure with a low (3\textit{d}f\textit{2}) spin configuration. Unfortunately, this promise remains unfulfilled so far but the research efforts in the direction of controlling fully strained ultrathin LaNiO\textit{3} films lead to new intriguing discoveries. In this respect, a remarkable finding has been the discovery of a dimensionality-induced MIT in LaNiO\textit{3}. Angle-resolved photoemission spectroscopy (ARPES) shows indeed that the electronic structure of LaNiO\textit{3} (LNO) is unchanged for thicknesses ranging from 50 to 3 unit cells (u.c.). However, for 2 u.c., the coherent quasiparticle peak at the Fermi level disappears, while for 1 u.c., the incoherent spectral weight close to Fermi ($E < E_F < 1$ eV) also vanishes. The quasiparticle residue $Z$ turns out to be flat between 50 and 3 u.c. and drops to zero below 2 u.c.

Such an abrupt transition strongly suggests that the transition is not due to charge redistribution at the interface between a LNO film and substrate rather than due to the confining effect on the electron’s wave function taking place below 3 u.c. thickness. Indeed, at variance with the case of LNO/LaMnO\textit{3} (LMO) and LMO/SrMnO\textit{3} (SMO) superlattices, in which interfacial doping is identified as the origin of...
the occurrence of an MIT, in the case of thin LNO films, the intrinsic dimensionality can rather be the explanation of the transition.4,7

The question then naturally arises whether the same confinement effects take place in films where the dimensionality is induced by a peculiar crystal structure as in the La\(_{n+1}\)Ni\(_{2n+1}\)O\(_{3n+2}\), Ruddlesden–Popper (R–P) series. The R–P series can be indeed visualized as a slab of \(n\) LaNiO\(_3\) layers, which are separated by two LaO blocking layers, and can therefore be seen as an alternative way for dimensionality tuning.6

The Ruddlesden–Popper films, despite the difference in the electronic configuration of Ni ions with respect to ultrathin LNO films, exhibit a similar behavior of the optical conductivity when the number of rock-salt blocks changes. We will provide first spectroscopic evidence of the interchangeable behavior of ultrathin LNO films and R–P films by dimensionality tuning. As we will see in the following sections, our measurements suggest that the dimensional transition is the driving mechanism underlying the metal-to-insulator transition (MIT) in both families. Moreover, the anomaly of electronic properties of R–P series, arisen from XAS measurements (reported in Section 3), with respect to the ionic model also mirrors an unconventional origin of their MIT. We will also show how such a transition occurs when the thickness of the correlated metal LNO drops across 2 u.c., exactly the same value found by ARPES in ref 4 in ultrathin films.

GROWTH AND STRUCTURAL CHARACTERIZATION

Figure 1 shows the crystal structure of the R–P member of lanthanum nickelate with \(n = 1, 2,\) and 3. Each unit cell of this series is made up of a sequence of LaO, and NiO\(_2\) layers stack in the \(c\) direction. For \(n = 2\) compound, there is an extra LaO layer between each of the two perovskite layers of lanthanum nickelate, consisting of LaO and NiO\(_2\) layers. Therefore, one u.c. of La\(_2\)NiO\(_3\) has two perovskite layers plus a rock-salt LaO layer. For the \(n = 3\) compound, the number of perovskite layers separated by the extra LaO layer is three.

Epitaxial films of LaNiO\(_3\) (LNO), La\(_2\)NiO\(_4\) (RP-214), La\(_3\)NiO\(_5\) (RP-327), and La\(_4\)NiO\(_6\) (RP-4310) were grown on a (001) pseudocubic LaAlO\(_3\) (LAO) substrate by a laser molecular-beam epitaxy (laser-MBE) system equipped with reflection high-energy electron diffraction (RHEED) in an oxygen background pressure of 7 Pa.5,9 Before the growth, the substrates were etched with HCl and annealed in oxygen pressure to achieve an Al\(_2\)O\(_3\)-terminated surface.10 Ceramic targets were ablated using a KrF excimer laser with a 1 Hz pulse rate and 1 J/cm\(^2\) energy density. Substrates were kept at 600 °C during the growth. We used La\(_2\)O\(_3\) and NiO as separate oxide targets. Targets were alternatively ablated by a UV laser beam for each atomic layer. We used the intensity of the RHEED diffraction spot to monitor the growth and ensure the completion of each atomic layer. Starting from ablation of the La\(_2\)O\(_3\) target, one atomic layer of rock-salt LaO was grown. RHEED diffraction spot intensity decreased from its maximum. We continued ablation of the La\(_2\)O\(_3\) target to grow the LaO layer of perovskite LaNiO\(_3\). After the completion of this layer, the RHEED diffraction spot reached its minimum intensity. The target was switched to the NiO target for the growth of one complete NiO\(_2\) atomic layer, which gave a local maximum to the RHEED intensity. The growth of another perovskite layer by ablation of La\(_2\)O\(_3\) and NiO targets completes one unit cell of La\(_2\)NiO\(_3\). It has been shown that layer by layer growth of R–P series requires that both the cation stoichiometry and full monolayer dose are within 1% precision. To calibrate the number of pulses for each atomic layer, perovskite LaNiO\(_3\) was grown prior to the growth of R–P phases. In laser-MBE, the intensity of the diffraction spot changes with both surface chemistry and roughness, therefore a combination of in situ control of the growth using RHEED and ex situ characterization of the crystal structure and thickness of the LaNiO\(_3\) films enable us to calibrate the number of pulses needed for each atomic layer of LaO and NiO\(_2\). Detailed structural characterization of LNO thin films was previously reported.7 Symmetrical \(\theta–2\theta\) measurements of the R–P members are shown in Figure 2 (XRD spectrum of a thick LNO sample is also reported as reference). The XRD \(\theta–2\theta\) scans show all of the expected diffraction peaks for the \(n = 1, 2,\) and 3 R–P phases without any impurity peaks or peak splitting. Details of the synthesis of LNO R–P members as well as nanostructural characterization by cross-sectional scanning transmission electron microscopy (STEM) high-angle annular dark-field (HAADF) of selected samples are reported elsewhere.7,10

SOFT X-RAY ABSORPTION SPECTROSCOPY

To probe the electronic valence state of Ni ions in both thin films as well as in the R–P series, X-ray absorption spectroscopy (XAS) experiments were performed at APE-IOM beamline at Elettra.11 The XAS signal was acquired in the total electron yield (TEY) mode and the drain current from a highly transparent mesh, upstream the sample, was used to normalize the signal with the incident photon flux. Due to the significant overlap between Ni L\(_1\) and La M\(_4\) absorption edges, we have focused our attention on the Ni L\(_1\) edge (Figure 3), where significant differences are expected depending on the Ni valence state. In particular, a double-peak structure has been measured for Ni in a +2 state, while a single-peak structure should appear for Ni\(^{3+}\). Such a prediction was experimentally confirmed by results obtained on NiO and LNO. As a matter of fact, in accordance with the ionic model, the charge-neutrality requirement within the structure would require \(V_{Ni}

on the thickness of the LNO films, L₂-edge absorption spectra always showed the Ni³⁺ characteristic feature down to 1.5 unit cell (panel b in Figure 2). However, the insulating LNO single-unit-cell film did show an XAS spectrum resembling the ones measured in the NiO films (LNO single-unit-cell was probed by growing LaNiO₃/LaAlO₃ 1 × 1 superlattices consisting of LNO single layers piled up in a LAO matrix, with 22 repetitions, corresponding to the sample labeled LNO-1). Such an abrupt change in the XAS spectra cannot be trivially interpreted since both intrinsic (i.e., metal-to-insulator Mott transition observed in ARPES spectra⁴) as well as extrinsic mechanisms (e.g., cation interdiffusion at the film/substrate interface, local oxygen deficiency) can be at play. Yet, it is crucial to underline that all of the LNO metallic samples do show similar XAS absorption spectra, thus inferring a similar electronic valence state for Ni ions.

On the contrary, Laₓ₋₁NiₓO₃₊₁ RP-members are expected to show a mixed Ni³⁺/Ni²⁺ population within the series. In more detail, according to the ionic model, the charge-neutrality requirement would here correspond to

\[(n + 1) \cdot (3) + n \cdot V_{Ni} + (3n + 1) \cdot (-2) = 0\]  

(1)

By simple math, the \(V_{Ni}\) valence state for a single Ni ion can be therefore calculated as a function of \(n\) and is reported in Table 1

\[V_{Ni} = -\frac{(n + 1) \cdot (3) + (3n + 1) \cdot (-2)}{n}\]  

(2)

 unsuspected, regardless of the predicted mixed Ni³⁺/Ni²⁺ population, XAS spectra of all conductive RP-series members (i.e., RP-4310 and RP-327) always resemble the one belonging to Ni³⁺ ions. To quantitatively evaluate the Ni valence state, the XAS spectra of RP-3410 and RP-327 were overlapped to the one measured in an LNO 5 u.c. thick film, perfectly matching it within an experimental fitting indetermination of about 2%. As a matter of fact, the possible presence of a partial Ni²⁺ contribution should be clearly visible in the pre-edge region as well as in the form of a double-peak structure at its maximum, as clearly visible in the XAS spectrum of the insulating RP-214 sample. Only the insulating RP-214 sample showed the strong splitting of the absorption peaks expected for Ni³⁺. In other words, the electronic configuration of Ni ions does not appear to substantially change for all of the metallic members of the Laₓ₋₁NiₓO₃₊₁ RP-series, and a mixed valence is observed only for the insulating RP-214 sample, therefore questioning the validity of the ionic model in describing the electronic properties of Ni ions in these compounds.

It is worth underlining that XAS measurements of thin and ultrathin films (e.g., 5 and 1.5 u.c. correspond to about 2.0 and 0.8 nm, respectively) clearly probes the whole film thickness.
In the case of 1 u.c. LNO layer as well as the RP-members, ultrathin LaNiO$_3$ layers are both embedded in a superlattice structure (i.e., $1 \times 1 \ LaNiO_3/LaAlO_3$ for SL and $n \times 1 \ LaNiO_3/LaO$, with $1 \sim 2 \sim 3$ u.c. LaNiO$_3$ perovskite blocks for RP-members, respectively). In this case, XAS features are determined by a 1–2-nm-thick region of materials close to the surface and then duplicated within the superlattices, therefore again making the measured XAS features representative of the bulk of the structure and, therefore, comparable with those investigated by the infrared spectroscopy reported in the following paragraph.$^{12,13}$

### INFRARED SPECTROSCOPY

Reflectivity measurements were performed at room temperature on five representative samples of LNO thin films on a LAO substrate, with 1 (×22 repetitions in a superlattice), 3, 5, 10, and 50 unit cells (u.c.), and three samples of the R–P series with $n = 1$, 2, and 3. The list of samples and their labels as used in the whole text is reported in Table 2. We were able
to cover the whole infrared (IR) range by means of a Bruker 70v interferometer, available at the SISSI-Material Science beamline at Elettra,\textsuperscript{14} using a gold mirror as a reference and various beam splitters, detectors, and thermal sources. In particular, in the lowest-frequency region, we took advantage of the high brilliance of the infrared synchrotron light delivered by Elettra. In the far-IR, we used a He-cooled bolometer as a detector, while for the mid-IR and visible measurements, we used conventional sources and MCT and Si-diode detectors.

In Figure 4, all reflectivity data are reported. In the far-IR region, the phonon peaks of the LAO substrate are clearly recognizable. The overall reflectivity level is higher when the number of unit cells and rock-salt layers increases both for ultrathin LNO and R–P films, respectively. The LAO phonons also become less pronounced for higher u.c. (n) when a better-defined Drude term screens them more.

To extract the optical conductivity from our data, we have performed Kramers–Kronig consistent Drude–Lorentz (DL) fits to the reflectivity data by taking into account the contributions from both the film and the substrate, using standard formulas for thin films.\textsuperscript{15} Best DL fits need either one or two components: a free carrier (Drude) term and a mid-infrared (MIR) band.

In Figure 4, the comparison of data and fits are shown for LNO films (a) and R–P samples (b), respectively. Such a comparison is crucial to identify the set of samples, which can be ascribable to the same optical response independent of their thickness. Indeed, reflectivities of LNO films with 5, 10, and 50 u.c. in Figure 4(a) were fitted using the same DL parameters, hence providing the same optical conductivity (blue curve in Figure 5(b)). On the other hand, employing the same DL parameters for the sample with 1 u.c. does not give a reasonable fit (as indicated by the brown curve in the right panel in Figure 4(a)). Only this ultrathin LNO film requires, indeed, new DL parameters (i.e., one single MIR band), which corresponds to the best fit (pink curve). These different parameters provide the optical conductivity, as shown in Figure 5(b) (pink curve). The sample with 3 u.c. is an intermediate case. Indeed, its fit is still reasonable with the same parameters of the 50 u.c. sample, even though the best fit gives a different optical conductivity (light blue curve in Figure 5). It is worth noting that such an optical conductivity is already metallic-like, as in the case of 50–5 u.c. samples.

The same analysis has been used to process the reflectivity data of R–P samples. As shown in Figure 4(b), each sample needs two different sets of DL parameters to best fit the data. The corresponding optical conductivities are reported in panel (c) of Figure 5.

For sake of comparison, all of the conductivities are collected in panel (a) of the same Figure 5. A transition from an insulating to a metallic behavior occurs at a critical number of 2 u.c. in thin LNO films in perfect agreement to what is found in ref 4. Interestingly, the R–P films behave in a very similar way when the number of rock-salt layers increases above 2. This observation suggests that the number of rock-salt layers plays the same role of the unit cells in LNO thin films, even though the former results from a crystal growth procedure, without the need of physically implementing a single-layer sample.

To better quantify these results, in Figure 6 it is shown the DC conductivity values (as calculated from resistivity data reported in Table 2) of each sample and the effective number of carriers calculated from the optical spectral weight (SW) is given by

\[
SW(\Omega, T) = \int_0^\Omega \sigma_\text{eff}(\omega, T) d\omega
\]

where \(\sigma_\text{eff}(\omega, T)\) is the optical conductivity.

SW(\Omega, T), hence, represents the area underneath \(\sigma_\text{eff}(\omega, T)\) to a frequency cutoff \(\Omega\) and at a particular temperature \(T\) (\(\Omega = 7000 \text{ cm}^{-1}\) and \(T = 300 \text{ K}\), respectively, in this case). We choose the cutoff frequency corresponding to a minimum in the optical conductivity. This value counts only the contribution of the carriers due to intraband transitions.

The effective number of electrons contributing to electromagnetic absorption at frequencies below \(\Omega\) can then be calculated by

\[
N_\text{eff}(\Omega, T) = \frac{2m_e}{e^2}SW(\Omega, T)
\]

where \(e\) and \(m_e\) are the electronic charge and mass, respectively.\textsuperscript{16}

The comparison between \(N_\text{eff}\) and DC conductivity shown in Figure 6 clearly highlights the same abrupt drop with respect to the number of layers for both thin films (red dots) and R–P samples (green dots). This behavior suggests that the whole...
electron contribution derived from a spectroscopic approach well resembles that of the transport measurement for both families. As mentioned before while discussing the DL fit, the electronic contribution can be further decomposed in a coherent (Drude) contribution and in an incoherent (MIR) term.\textsuperscript{17,18}

It is well known that the ratio between the SW of Drude and MIR components (SW\textsubscript{Drude}/SW\textsubscript{MIR}) by giving the value of the quasiparticle residue Z represents a measure of the suppression of the incoherent part in favor of the coherent one.\textsuperscript{12,19–21} In other words, it represents a measure of the “dressing” of the fermionic quasiparticle and of the consequent renormalization of its dynamic properties.

In Figure 7, we report the values of SW\textsubscript{Drude}/SW\textsubscript{MIR} for each sample (left scale) compared with the estimate of Z by ARPES\textsuperscript{4} for ultrathin films. The qualitative trend resembles the one of Z\textsuperscript{ARPES}, i.e., the sigmoidal shape of our data is also centered between data with the number of layers equal to 2 and 3. A further analysis, which follows the extended Drude model has been performed. The trend of the resulting quasiparticle residue is in good agreement with what is reported in Figure 7 (left scale), confirming the equivalence between the two methods of extracting Z from optical data.\textsuperscript{16,22}

Figure 7 also suggests that R-P samples behave very much similar to the ultrathin films, thereby further supporting the hypothesis that a common physics is at play for the two families.

■ CONCLUSIONS

By combining synchrotron-based infrared spectroscopy and X-ray absorption spectroscopy measurements, the metal-to-insulator transition in ultrathin LaNiO\textsubscript{3} films grown on LaAlO\textsubscript{3} and in the corresponding La\textsubscript{x+1}Ni\textsubscript{x}O\textsubscript{3+1} R-P series demonstrated to be essentially equivalent from an electro-dynamics point of view and can be understood within a dimensionality-induced transition.

This scenario is supported by an optical estimate of both the number of carriers and the quasiparticle residue, which have been compared with transport and ARPES measurements, respectively. This shows that the MITs observed in the two families are substantially equivalent within the point of view of both collective and single-particle behaviors. Our result provides a novel perspective to address the nickelate phase diagram beyond the ionic model. Tailored as-grown LNO-based systems may thus represent a new strategy to explore the physics of the perovskite ground-state properties, opening the way for innovative and tunable materials.

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Notes
The authors declare no competing financial interest.

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