Length scales of interfacial coupling between metal and insulator phases in oxides

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Controlling phase transitions in transition metal oxides remains a central feature of both technological and fundamental scientific relevance. A well-known example is the metal–insulator transition, which has been shown to be highly controllable. However, the length scale over which these phases can be established is not yet well understood. To gain insight into this issue, we atomically engineered an artificially phase-separated system through fabricating epitaxial superlattices that consist of SmNiO3 and NdNiO3, two materials that undergo a metal-to-insulator transition at different temperatures. We demonstrate that the length scale of the interfacial coupling between metal and insulator phases is determined by balancing the energy cost of the boundary between a metal and an insulator and the bulk phase energies. Notably, we show that the length scale of this effect exceeds that of the physical coupling of structural motifs, which introduces a new framework for interface-engineering properties at temperatures against the bulk energetics.

Phase transitions characterized by a strong coupling of charge, spin, orbital and lattice degrees of freedom are ubiquitous in transition metal oxide materials1. A well-known example is the metal–insulator transition, which is typically first order and exhibits regions of phase coexistence. Many studies have focused on manipulating the metal-to-insulator transition (MIT) through intrinsic and extrinsic effects2–5. Moreover, experimental techniques, such as photoemission electron microscopy and near-field scanning optical microscopy, have been used to observe the phase coexistence at the MIT6. However, remarkably little is known about the characteristic lengths of the two possible phases. Important open issues include the minimum length scale over which a metallic or an insulating state can be established and the physics that sets this length scale. Is this length scale controlled by the propagation of lattice distortions or by more subtle interfacial effects? To answer these questions is important both to understand the fundamental physics of the metal–insulator transition and to obtain the control that is essential for applications in new generations of electronic devices.

In this Article, we present experimental and theoretical analyses of a series of specially designed structures of two oxide materials that undergo MITs at different temperatures while sharing the same order parameter. We created atomic-precision epitaxial superlattices that consisted of alternating layers of the two materials and we studied the temperature dependence of their conductivity as a function of layer thickness. For thicker layers, two separate transitions were observed, such that the engineered bicomponent system mirrors the independent properties of the individual compounds. For thinner layers, the system behaved as one material, with a single metal–insulator transition, which implies that we engineered properties unique to this superlattice system. The characteristic length scale above which two separate transitions were observed implies a critical minimum thickness of around 3 nm. This is remarkably large given the first-order nature of the metal–insulator transition, which is not associated with diverging length scales. By combining our data with theoretical modelling, we demonstrate that the length scale of interfacial coupling between the metal and insulator phases in the superlattices is set neither by the length scale of the propagation of structural motifs nor by that of the electronic-order parameter from one material to the other. Rather, the length scale is set by the competition between the interface and bulk energetics—the interplay between the two was recently brought to light, for instance, in the context of VO2, (ref. 7).

As a model system for this study, we used NdNiO3, and SmNiO3, two members of the rare earth nickelate family RNiO3, where R is a rare earth cation. The rare earth nickelates are well-known for the sharp MIT, observed when the temperature decreases below a characteristic temperature, TM, which depends on the rare earth size8–11. The TM for bulk SmNiO3 is ~400 K, and for bulk NdNiO3, it is ~200 K. The rare earth nickelates crystallize in slightly distorted versions of the perovskite structure, visualized as a network of corner-sharing NiO6 octahedra. The distortions involve rotations and tilts of the octahedra, which modify the Ni–O–Ni bond angle (ϕ) and so determine the bandwidth of the system and TMI (ϕSmNiO3 ≈ 157° and ϕNdNiO3 ≈ 153° at room temperature in bulk)8–11. The MIT further involves a two-sublattice modulation of electron density15 accompanied by a bond disproportionation (BD) of alternating larger and smaller NiO6 octahedra.

To understand the length scale over which an MIT can develop we grew epitaxial superlattices that consisted of L repetitions of the basic (SmNiO3)m/(NdNiO3)n unit (m in pseudocubic (pc) unit cells (u.c.) on top of the [001]m-oriented LaAlO3 substrates. The total thickness of all the samples was kept at ~30 nm. Therefore, to match...
this thickness, the number of repetitions, \( L \), was adjusted for each \((\text{SmNiO}_3)_{m}/(\text{NdNiO}_3)_{m}\) unit or superlattice wavelength \( \Lambda \) equal to 2\( m \); Fig. 1a. The superlattices were characterized ex situ by X-ray diffraction, atomic force microscopy and aberration-corrected scanning transmission electron microscopy in combination with electron energy-loss spectroscopy (STEM-EELS). As shown in Fig. 1b, finite thickness oscillations and satellite peaks that correspond to the superlattice periodicity were observed, which indicates high-quality samples and good agreement with the designed layering. The atomically flat surface reveals that the superlattices preserve the step-like topography of the substrate (corresponding inset in Fig. 1b). The structural properties and the chemical composition of the designed \((m,m)\) superlattices were evaluated in detail by means of STEM-EELS. Figure 1c shows a high-angle annular dark-field (HAADF) Z-contrast image of a \((5,5)_{10}\) superlattice viewed along the \([100]_{pc}\) zone axis of the LaAlO\(_3\) substrate. The HAADF image confirms that the superlattice is fully epitaxial with the substrate (see the reciprocal space map in Supplementary Fig. 1) and that no obvious defects, such as dislocations or Ruddlesden–Popper faults, were generated, either within the crystal or at the interfaces. EELS compositional maps obtained from the area indicated on the HAADF image (Fig. 1c) are displayed in Fig. 1d. All the imaged interfaces were atomically sharp and no obvious cationic intermixing between the NdNiO\(_3\) and SmNiO\(_3\) layers was identified. We also note that the oxygen content was constant over the structure, as shown in Supplementary Fig. 5. The same crystal and interface quality were observed in a \((12,12)_{10}\) superlattice viewed along the \([100]_{pc}\) zone axis of the LaAlO\(_3\) substrate. Scale bar, 500 nm. Inset: typical atomic force microscope topography of a \((7,7)_{8}\) superlattice. Scale bar, 500 nm.

**Fig. 1** | Detailed characterization of the \((\text{SmNiO}_3)_{m}/(\text{NdNiO}_3)_{m}\) superlattices. **a**, Schematic representation of the superlattice heterostructures. \( \Lambda \) indicates the superlattice period. **b**, X-ray diffractograms for \((7,7)_{8}\), \((10,10)_{5}\) and \((15,15)_{4}\) superlattices. The satellite peaks indicate the periodicity of the superlattices. Inset: typical atomic force microscope topography of a \((7,7)_{8}\) superlattice. Scale bar, 500 nm. **c**, Cross-sectional HAADF image of a \((5,5)_{10}\) superlattice viewed along the \([100]_{pc}\) zone axis direction of the LaAlO\(_3\) substrate. Scale bar, 2 nm. **d**, EELS compositional maps obtained from the area indicated in **c**. The La, Nd and Sm signals are displayed together in the superlattice map. a.u., arbitrary units.

Figure 2 displays the resistivity as a function of temperature for three \(\text{SmNiO}_3/\text{NdNiO}_3\) superlattices with different periods \( \Lambda \). The dashed lines indicate the \( T_{\text{MI}} \) of 10-nm-thick NdNiO\(_3\) and SmNiO\(_3\) films grown on \([001]_{pc}\)-oriented LaAlO\(_3\). As can be seen in Fig. 2, superlattices with a large \( \Lambda \), that is, thick SmNiO\(_3\) and NdNiO\(_3\) layers \((10,10)_{5}\) and \((15,15)_{4}\), display two distinct MITs. The lower MIT seen at 100 K < \( T \_{\text{MI}} < 200 \) K is accompanied by a hysteresis loop and resembles the MIT behaviour observed in NdNiO\(_3\) (ref. 16). The second MIT manifests at higher temperatures, 300 K < \( T \_{\text{MI}} < 400 \) K, and resembles the MIT of SmNiO\(_3\). In contrast, superlattices with a short \( \Lambda \) (for instance, \((7,7)_{8}\)) go from a fully metallic to a fully insulating state through a single MIT. By analysing the entire data set (Supplementary Fig. 2), we see that the conductive behaviour of the higher-period SmNiO\(_3\)/NdNiO\(_3\) superlattices tends towards the independent SmNiO\(_3\) and NdNiO\(_3\) single film behaviours. With decreasing \( \Lambda \), the two MITs come closer together in temperature until a joint MIT is measured at \( T_f \approx 155 \) K. This behaviour with a unique MIT is observed below a critical wavelength, \( \Lambda_{pc} \), of 16 u.c. We return to these results shortly. Additional transport data, including the Hall effect, are shown in the Supplementary information.

The resistivity trends clearly demonstrate that a remarkably long length scale of 8 u.c. (~3 nm) \((\Lambda/2)\) is required to decouple the two materials and to establish independent phases determined by the bulk energetics. We now consider possible explanations for this long length scale. As a first step, we address the issue of cationic intermixing. We observed that a solid-solution film of Sm\(_{0.5}\)Nd\(_{0.5}\)NiO\(_3\) exhibits a single MIT at approximately the same temperature as that of the short-wavelength superlattices (Supplementary Fig. 2). However, as can be seen from Fig. 1d, STEM-EELS analyses performed on a \((5,5)_{10}\) superlattice show that intermixing is extremely limited in these structures and does not extend further than 1 u.c. from the interfaces, and therefore the long coupling length scale is not chemical in origin.
A second possibility is interfacial structural coupling, as previous studies have found that rotations and tilts of the oxygen octahedral cages, determining the B–O–B bond angle in ABO₃ perovskites, can be modulated across interfaces. We also consider for this specific nickelate system that the BD could propagate from one material to the other. To investigate the interfacial structural coupling, we determined the crystal structure of SmNiO₃/NdNiO₃ superlattices from density functional theory (DFT) + U calculations and corroborated our findings using STEM analyses that allowed the oxygen positions to be resolved. In the calculations, we considered the low-temperature phases of SmNiO₃ and NdNiO₃, which have P2₃/n symmetry (with Glazer notation a b̅ a c̅). Further details are reported in Methods and the Supplementary Information.

From the DFT and the STEM investigations, we conclude that neither the bond angle nor the BD structural motifs propagate beyond 1 u.c. from the interface. This indicates that the effect of a purely structural propagation across interfaces cannot account for the persistence of the joint MIT behaviour up to a superlattice period of as long as 16 u.c. Importantly, this suggests that the transition temperature in these heterostructures is not directly set by the local octahedral rotation, as in the case of the bulk.

We show now that the observed behaviour is, instead, due to the energy cost of establishing a phase boundary—linked to the short-range mismatch across the interface of the coupled electronic and structural order parameters that correspond to the metal–insulator transition. As the structural and electronic order parameters are strongly coupled, we can focus on just one. We set the theory in terms of N, the electronic disproportionation that characterizes the nickelate insulating state. N is defined as the difference between the occupation of the long bond and short bond Ni sites (N = Nₗₐₚ − Nₗₛₚ) within a low-energy extended antibonding ξ orbital picture. Previous theoretical calculations have found that N = 0 in the metallic state (ξ⁺ − ξ⁻) and in the insulating state it is around 1.2–1.5, depending on the material.

Based on this electronic disproportionation order parameter we developed a Landau theory, which is described in detail in the Supplementary Information. In the simplest scenario, the key ingredients in the model are the relative free energies of the metallic and insulating phases of the two components of the superlattice, and the energy cost of the phase boundary that separates them. Without loss of generality, we set the free energy of the metallic phase to zero, $E_M(T) = 0$, and refer to the free energy (per unit cell volume (J m⁻³)) of the insulating phase as $E_I(T)$, noting that only the difference between the two is of physical relevance. We take the phase-boundary energy between two metallic or two insulating phases to be zero. In reality, an interfacial energy cost associated with the difference between the two materials is expected, but its magnitude should be minimal compared with the energy of the phase boundary that separates the metallic and insulating states, which we denote $E_{pp}$, an energy per surface area (J m⁻²).

We assume that near the transition temperature the $E_I$ for SmNiO₃ ($E^{I}_{I}$) and NdNiO₃ ($E^{I}_{II}$) have a linear temperature dependence:

$$E^{I}_{I}(T) = K_{I,S} \left( \frac{T - T^{I}_{S}}{T^{I}_{N,S}} \right)$$

Here K is a material-dependent constant that describes the stabilization energy (per unit cell) of the insulating phase relative to the high-temperature metallic phase in SmNiO₃ ($K_S$) and NdNiO₃ ($K_S$). $T^{I}_{S}$ and $T^{I}_{N}$ are the experimental $T^{I}_{N}$ values of individual films of NdNiO₃ and SmNiO₃, respectively.

We express the energy of the three possible states for our (SmNiO₃)₉/(NdNiO₃)₉ superlattices:

$$E_{MM} = mE^{I}_{M} + mE^{I}_{M} = 0$$

where $E_{MM}$ is the energy of the mixed state and $m$ is the thickness of the metal or insulator layer.
(2) NdNiO$_3$ is metallic and SmNiO$_3$ is insulating:

$$E_{MI} = E_{MI}^M + 2E_{PB} + mE_T(T) = 2E_{PB} + mE_T(T)$$

(3) And both materials are insulating:

$$E_{II} = E_{II}^S(T) + mE_T(T)$$

At the bifurcation point, the energies with both materials insulating, with both metallic and with NdNiO$_3$ metallic and SmNiO$_3$ insulating (metallic–insulating phase coexistence with a phase boundary in between cost energy) are equal:

$$mE_T^S(T) + mE_T^S(T) = mE_T^S(T) + mE_T^S(T)$$

where $\Lambda_s (\Lambda_s = 2m_s$) and $T_s$ are the experimental critical wavelength of the bifurcation and temperature of the joint $T_{MI}$, respectively.

We may now write an equation for the higher temperature metal–insulator transition ($T_{HI}$), at which $E_{MI}$ becomes equal to $E_{II}$:

$$mE_T^S(T_{HI}) + mE_T^S(T_{HI}) = mE_T^S(T_{HI}) + mE_T^S(T_{HI}) + 2E_{PB}$$

and for the lower transition temperature ($T_L$) at which $E_{II}$ becomes equal to $E_{MI}$:

$$mE_T^S(T_L) + mE_T^S(T_L) = mE_T^S(T_L) + mE_T^S(T_L) + 2E_{PB}$$

Solving this system of equations, we obtain:

$$T_L(m) = T_N \left(1 + \frac{2E_{PB}}{mK_N}\right)$$

$$T_H(m) = T_S \left(1 - \frac{2E_{PB}}{mK_S}\right)$$

For large $m$ (large $\Lambda$), the two transitions tend towards the $T_{MI}$ values for individual layers of NdNiO$_3$ and SmNiO$_3$ ($T_N$ and $T_S$). When $T_L = T_{MI}$, we obtain the critical wavelength $\Lambda_z$:

$$\Lambda_z = m_z = 2E_{PB} \frac{T_SK_N + T_NK_S}{K_N(T_S - T_N)}$$

and $T_I$ (assuming $K_N = K_S$):

$$T_I = \frac{2T_N T_S}{T_N + T_S}$$
this version of the model. Using the experimental values for SmNiO$_3$ and NdNiO$_3$ individual layers ($T_S = 352$ K and $T_N = 100$ K), the joint transition temperature ($T_J$) is estimated as 156 K, in remarkable agreement with experiment.

For the higher temperature branch, however, the fit can be quantitatively improved by refining the model through introducing a saturation temperature ($T_{sat}$), by releasing the assumption $K_N = K_S$ and by using the measured $T_J$ as an input parameter. $T_{sat}$ restricts the linear temperature dependence of the energy of the SmNiO$_3$ insulating state to a temperature range close to $T_S$ (for $T > T_{sat}$, $E_P^I(T) = K_S (T - T_S)$, whereas for $T < T_{sat}$, $E_P^I = K_S (T - T_{sat})$). This better reflects the physical nature of phase transitions. From this input and an estimated value of $T_{sat}$ (280 K), we obtain:

$$K_N = \frac{T_N}{T_S} \frac{T_S - T_{sat}}{T_S - T_N}$$

The equations for $T_{sat}$ and $T_J$ remain the same; however, their values are now computed from the newly determined ratios, $K_S/K_N = 0.4$ and $E_{PB}/K_N = 4.8$. The excellent fit (dashed line) obtained can be seen in Fig. 4a, which summarizes the experimental data and the output of the Landau theory.

Figure 4b,c displays the calculated energies of the three possible phases (insulating–insulating, insulating–metallic and metallic–metallic) versus temperature. This is shown for two superlattice wavelengths, $\Lambda = 10$ u.c., for which, experimentally, the system transitions from a fully metallic state to a fully insulating state, and $\Lambda = 20$ u.c., for which a coexistence of a metallic and an insulating phase was found at intermediate temperatures. As can be seen in Fig. 4b, in the case of $\Lambda = 10$ u.c., the lowest energy is the metallic–metallic phase at a high temperature with a transition to an insulating–insulating phase at 160 K. Examining the calculations for $\Lambda = 20$ u.c. (Fig. 4c), two transitions are seen to occur: from a high-temperature metallic–metallic phase to a mixed (metallic–insulating) phase and, at a lower temperature, from the mixed phase to the insulating–insulating one, which neatly reproduces what was observed experimentally, as shown in Fig. 4a.

Figure 4d,e shows the evolution of the order parameter, $N$, across the interface of two different wavelength superlattices, $\Lambda = 10$ and 20 u.c., for the various possible phases. As shown in Fig. 4e, at an interface between an insulating region and a metallic one, the order parameter has to go from a value of 1.2 to 0 and the energy cost of bending the order parameter goes as ($V_N$)$. It is only in Fig. 4c, for $\Lambda = 20$ u.c., that the phase coexistence is stable. However, with a reduced superlattice wavelength of 10 u.c. (Fig. 4d), the higher density of phase boundaries makes the cost of bending the order parameter between the two distinct electronic phases higher than the energy gained by the individual component materials being in their optimal states. Thus, for $\Lambda = 10$ u.c., phase coexistence cannot be stable and, over some temperature range, the phase-boundary energy forces either SmNiO$_3$ to be metallic or NdNiO$_3$ to be insulating against the energetics of the bulk phases.

The critical wavelength of 16 u.c. is now readily understood despite being rather long given the short-range extension of the structural motifs and of the order parameter itself. The ratio between the phase-boundary energy and the free-energy cost of the thin films to be in the unfavoured state is the main parameter that determines the physics of the system. The phase-boundary energy is determined by two factors: the local elastic cost of the structural mismatch between the phases, and the energy cost of interpolating the order parameter between the two values. This latter cost depends crucially on the energy landscape: in a first-order
situation, the order parameter goes from one minimum to the other by passing over a local maximum, the height of which is an important component of the interface energy. The energy cost of the phase boundary can be estimated to be tens of millielectronvolts per pseudocubic unit cell area, as described in the Supplementary Information.

Through engineering specifically designed superlattices, we were able to clearly isolate the role of the different physical phenomena in setting the length scale of the MIT in the nickelates. We found that the length scale of coupling between the metal and insulator phases is controlled by an interfacial phase-boundary energy. Notably, it is not determined by long-range propagation of the BD nor by the direct long-range physical coupling of bond angles, which until now has been the standard approach to understanding interfacially coupled behaviour. This result highlights a framework to engineer functional properties in heterostructures and can be applied to other combinations of materials, such as vanadium and manganese oxides, as well as to the naturally occurring phase coexistence at a first-order phase transition. Further, we have shown that heterostructures can be used to engineer temperature-dependent properties to go against the bulk energetics, and as a model system to provide new insights into the fundamental physical energy scales of the bulk materials themselves.

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Methods

Sample preparation. We used radiofrequency off-axis magnetron sputtering at a temperature of 460 °C and a pressure of 0.18 Torr (Ar:O₂ mix of ratio 3:1) to grow epitaxial superlattices that consisted of L repetitions of the basic (SmNiO₃)ₓ/(NdNiO₃)ₙ system, with n on top of [011], oriented LaAlO₃ substrates. Prior to deposition, the LaAlO₃ substrates were thermally treated to ensure atomically flat terraces and a step-like topography. Bulk SmNiO₃ and NdNiO₃ have pc lattice constants, a₀ = 3.799 and 3.808 Å, respectively, whereas a₀ = 3.787 Å for LaAlO₃. Hence, the corresponding lattice mismatch (Δa/a₀) = Δa₀/a₀ = 0.6% for SmNiO₃ and NdNiO₃ layers, respectively.

Transport measurements. Transport measurements were carried out in a four-point configuration, after being patterned with ultraviolet lithography in a standard Hall bar geometry with Pt contacts in the temperature range 4 K < T < 400 K. Below 300 K, the samples were slowly dipped into a liquid helium bath, whereas measurements made above room temperature were achieved using two Peltier elements. The T₀ of the superlattices was determined from the maximum of −d(lnR)/dT on heating.

Aberration-corrected STEM measurements. STEM specimens were prepared by mechanical tripod polishing, followed by argon ion beam milling to electron transparency with a Gatan PIPS II. Several simultaneous series of HAADF and ABF STEM images were acquired using a double-aberration-corrected FEI Titan Themis 60–300 microscope located at the Interdisciplinary Centre for Electron Microscopy (École Polytechnique Fédérale de Lausanne). The instrument was operated at a 300 kV, using a ∼20 nm convergence semi-angle for the electron probe. From each image series, Smart Align software was used to produce an averaged image with a reduced statistical image noise and the correction of linear and non-linear scan distortions. The central position associated with each atomic column was localized by using a two-dimensional Gaussian fitting procedure. From the obtained set of coordinates, one per atomic sublattice, we estimated the depth evolution of the structural parameters. Each data point shown in Fig. 3c,f corresponds to the mean over around 25 u.c. and the error bars derive from the standard deviation.

STEM-EELS spectrum image datasets were acquired with a Gatan GIF Quantum ERS spectrometer, using the following conditions: a collection semi-angle of 2 eV Å⁻¹, respectively. For simplicity, all points derive from the standard deviation. The authors acknowledge access to the electron microscopy facilities at the Interdisciplinary Centre for Electron Microscopy, École Polytechnique Fédérale de Lausanne. The Flatiron Institute is a division of the Simons Foundation, P.G., Y.Z. and A.M. acknowledge support from the Office of Naval Research. The authors thank H. Strand and M. Zingl for fruitful discussions and acknowledge M. Lopes for fruitful discussions. The authors acknowledge access to the electron microscopy facilities at the Interdisciplinary Centre for Electron Microscopy, École Polytechnique Fédérale de Lausanne. The Flatiron Institute is a division of the Simons Foundation, P.G., Y.Z. and A.M. acknowledge support from the Office of Naval Research. The authors thank H. Strand and M. Zingl for fruitful discussions and acknowledge M. Lopes for fruitful discussions.

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Author contributions

M.G. and J.-M.T. conceived the project. C.D. fabricated the superlattices and carried out the transport measurements with A.W. The Landau model was developed by A.B.G., A.M. and J.-M.T. Transmission electron microscopy was performed and analysed by B.M. and D.T.L.A. The first-principles calculations were carried out by Y.Z., A.M. and P.G. C.D. and J.F. wrote the manuscript with input from all the authors. All the authors contributed to the analysis and interpretation of the experimental results.

Competing interests

The authors declare no competing interests.

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Author contributions

M.G. and J.-M.T. conceived the project. C.D. fabricated the superlattices and carried out the transport measurements with A.W. The Landau model was developed by A.B.G., A.G. and A.M. Transmission electron microscopy was performed and analysed by B.M. and D.T.L.A. The first-principles calculations were carried out by Y.Z., A.M. and P.G. C.D. and J.F. wrote the manuscript with input from all the authors. All the authors contributed to the analysis and interpretation of the experimental results.

Additional information

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