MnO$_6$ Octahedral Tilt Control of Emergent Phenomena at LaMnO$_3$/SrMnO$_3$ Interfaces

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Emergent phases at the interfaces in strongly correlated oxide heterostructures display novel properties not akin to those of constituting materials. The interfacial ferromagnetism in LaMnO$_3$/SrMnO$_3$ (LMO$_m$/SMO$_n$) superlattices (SLs) is usually considered to be a result of the interfacial charge transfer. We report a decisive role of atomic interface structure in the development of emergent magnetism and phonon transport in (LMO)$_m$/(SMO)$_n$ SLs ($m/n=1, 2$). The observed common octahedral network with MnO$_6$-tilt-free interfaces in $m/n=1$ SLs suppresses interfacial electron transfer and enhances thermal (phonon) conductivity. For $m/n=2$ SLs two distinct LMO and SMO lattices result in an MnO$_6$ tilt mismatch, which enhances the emergent ferromagnetism and suppresses thermal conductivity. Furthermore, the interface thermal conductance increases strongly from 0.29 up to 1.75 GW/m$^2$K in SLs with ($m/n=2$) and without ($m/n=1$) tilt mismatch, respectively. Experimental results, fully supported by first principle calculations, emphasize a fundamental role of electron-spin-lattice interplay at interfaces and open new avenues of lattice engineering of emergent phases.
Correlated oxide heterostructures provide a rich material platform to search for emergent interfacial phenomena\textsuperscript{1-4} not present in the constituting layers. As the interplay of charge, spin, and lattice degrees of freedom\textsuperscript{5} is believed to control phase transitions in bulk correlated materials, their interfacial reconstructions should serve as guiding mechanisms for emergent phenomena. In particular, a charge transfer/leakage at the interface\textsuperscript{6,7} was thought to be intimately coupled to the formation of emergent phases. An important but rather not answered question is whether such charge transfer could be viewed as a purely electronic effect or it is accompanied or even controlled by structural changes in the underlying crystal lattice. The long-term interest in the LMO/SMO SLs is motivated by observations of interfacial ferromagnetism\textsuperscript{8-16} (IFM) with $T_C \sim 180$ K located at chemically sharp LMO(top)/SMO(bottom) interfaces by using polarized neutron scattering\textsuperscript{11}. Very recently, we have observed an IFM with $T_C \sim 360$ K at SMO/LMO interfaces in SLs prepared by metalorganic aerosol deposition (MAD) technique\textsuperscript{17}. Besides magnetism, perovskite heterostructures are very important systems for studies of thermal transport phenomena\textsuperscript{18-23}. Current scientific questions address for instance phonon blocking\textsuperscript{22,23} in novel solar cells and coherent thermal transport\textsuperscript{21,24}. Manganite perovskites add to this playground the complexity and opportunity to explore electronic correlations\textsuperscript{5,25,26}. Note that, a first experimental evidence for a correlation between thermal resistivity of single films and octahedral distortions, measured by neutron scattering, was published by Cohn et al.\textsuperscript{27} already in 1997.

Here we report a detailed study of the oxygen octahedral rotations in the LMO\textsubscript{m}/SMO\textsubscript{n} SLs (m,n=3-10 and m/n=1, 2) and their influence on electronic and phonon properties. The MnO\textsubscript{6} octahedral tilt mismatch between the LMO and SMO was found to drive the interfacial charge transfer, drastically changing the emergent electronic and phonon behavior. Growth and experimental details are described in Supplemental Material (SM, ref. 28).

In Fig. 1a) and b), the high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images of the LMO\textsubscript{m}/SMO\textsubscript{n} SLs (m/n=1,2) demonstrate epitaxially grown layers with atomically sharp and flat interfaces with a roughness $\leq 1$ u.c. X-ray diffraction (XRD) and X-Ray reflectometry (XRR) patterns (see Ref. 28) support the high structural quality of layers and interfaces observed by STEM. From XRR and XRD simulations thicknesses and out-of-plane lattice parameters of SMO and LMO were determined (see Tab. SM-1\textsuperscript{28}). The integrated Differential Phase Contrast (iDPC)\textsuperscript{29,30}-STEM images, shown in Fig. 1c) and d), are used to estimate the Mn-O-Mn bond
angle $\varphi_{OOR}$ in LMO and SMO layers in the SLs. A quantitative analysis of the positions of oxygen and manganese columns has been done in terms of statistics of the bond angle deviation $\Delta\varphi=0.5(180^\circ-\varphi_{OOR})$ shown in Fig. SM-3$^{28}$. It reveals that in all SLs the SMO layers possess $\varphi_{OOR}\approx180^\circ$ characteristic for bulk SMO$^{31}$. In contrast, LMO layers inside the 12/6 SL display $\varphi_{OOR}<180^\circ$ as manifested by periodic zigzag-like features in between the La atoms. The statistics obtained from the LMO layers in 12/6 SL reveals apparently a bimodal distribution and significantly smaller $\varphi_{OOR}=165^\circ\pm3^\circ$ characteristic for bulk rhombohedral LMO$^{32,33}$. The other m/n=2 SLs, i.e. 6/3 and 10/5 (see Fig. SM-4$^{28}$) show the same behavior. The situation changes in m/n=1 SLs, where both LMO and SMO layers possess the same $\varphi_{OOR}\approx180^\circ$. In Fig. 1e) and f) the enlarged images of selected areas in Fig. 1a), b), c) and d), overlaid by a structural model, highlight the presence/absence of octahedral distortion in the LMO layers. SMO layers in the 12/6 SL display $\varphi_{OOR}=180^\circ\pm3^\circ$ similar to bulk
SMO$^{31}$. Thus, a large MnO$_6$ octahedral interfacial tilt mismatch is present in the m/n=2 SLs, whereas interfaces in the m/n=1 SLs are misfit free.

Results of temperature and field dependent SQUID magnetization in m/n=1, 2 SLs with bilayer thicknesses, Λ=m+n, are summarized in Fig. 2; representative M(T) and M(H) curves are shown in Fig. SM-5$^{28}$. Two ferromagnetic (FM) phase transitions, separating FM phases with Curie temperatures $T_{C1}$ and $T_{C2}$, respectively, were observed in agreement with Ref. 17. The $T_{C1}$ decreases with decreasing the interface density, $1/\Lambda=(m+n)^{-1}$ and approaches $T_{C}$ of a single LMO film, indicating the LMO-like FM. In contrast, $T_{C2}$, being independent on $\Lambda^{-1}$ for both SL series, characterizes the onset of the interfacial emergent phase$^1$. Surprisingly, $T_{C2}$ depends on the m/n ratio – $T_{C2} \approx 350$ K (m/n=2) and 300 K (m/n=1), suggesting the charge transfer as a reason of the HTP FM phase$^{17}$ is influenced by the LMO/SMO ratio. In Fig. 2b) saturation magnetization $M_{sat}(5K)$ as a function of the interface density $1/\Lambda$ is shown; the data of LSMO films with x=0.5 (m/n=1) and x=0.33 (m/n=2) are added for comparison. Apparently, SLs with $1/\Lambda \leq 0.1$ possess reduced values $M_{sat}=0.4$–2.6 $\mu_B$/Mn compared to bulk LSMO$^{34}$, indicating the presence of antiferromagnetic (AFM)

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**Fig. 2.** Magnetic properties of LMO/SMO SLs as a function of interface density: a) ferromagnetic transition temperatures $T_{C1}$ (low-$T_{C}$ phase, open symbols) and $T_{C2}$ (high-$T_{C}$ phase, close symbols), respectively. Symbols with blue (red) colour refer to SLs with m/n=1 (m/n=2). The grey shaded area indicates the $T_{C}$ of a single LMO film. All other curves are guides to the eye; and b) saturation magnetization, $M_{sat}$ measured at $T=5$ K. Blue and red symbols refer to SLs with m/n=1 and 2, respectively. All curves are guides to the eye. Horizontal dashed line segments in (a) marked by * and ** indicate the expected $M_{sat}$ values for SLs with m/n=2 and 1, respectively. Open symbols in b) denote data taken from Ref. 17).
phase in all SLs. Particularly, the AFM dominates in m/n=1 SLs, yielding very low $M_{\text{sat}}=0.4$-$1.2 \ \mu_B/Mn$, and enhanced coercive and exchange bias fields\(^{28}\). For an SL with very thick layers ($1/\Lambda \to 0$) and vanishingly small interfacial FM the $M_{\text{sat}}$ should originate from the geometric LMO contribution. With $M_{\text{sat}}(\text{LMO})=3.4$-$3.9 \ \mu_B/Mn$, measured in a single LMO film the extrapolated values in SLs (see Fig. 2b) result in $M_{\text{sat}}(m/n=1) \approx M_{\text{sat}}(\text{LMO}) \times 1/2 \approx 1.8$ and $M_{\text{sat}}(m/n=2) \approx M_{\text{sat}}(\text{LMO}) \times 2/3 \approx 2.4 \ \mu_B/Mn$. A good agreement with measurements prove the validity of this model.

Now we will take a closer look on thermal transport, which is dominated by phonons\(^{27}\) in perovskite oxides. Fig. 3 shows the results of the pump-probe thermal transient reflectivity (TTR)\(^{35}\) measurements of SLs at room temperature (for details see Ref. 28). To assess the thermal conductivity $\kappa$ of SLs as a whole the raw data were fitted by a thermal model\(^{36}\). In Fig. 3a) the inverse thermal conductivity $1/\kappa$ or thermal resistivity is plotted as a function of $1/\Lambda$. Apparently, for a given interface density the m/n=1 SLs possess a significantly lower thermal resistivity than m/n=2 SLs. Furthermore, plotting $1/\kappa$ vs $1/\Lambda$ allows for a linear regression of a thermal SL model\(^{24}\) (see Fig. 3b, c)) containing serial thermal resistances with weighted bulk LMO and SMO contributions:

![Fig. 3: a) thermal resistivity $1/\kappa$ as a function of the interface density determined by TTR. The grey shaded area and grey dotted line represent experimental and literature data for LMO and SMO. Blue and red horizontal dashed lines are compositional averages, continuous lines are linear fits of Eq. (2) to the experimental resistivity data. The brackets indicate an outlier (LMO\(_{10}\)/SMO\(_{10}\)) that we did not consider for the fitting procedure. A sketch of our understanding of the magnetic and thermal properties of (LMO\(_m\)/SMO\(_n\)) SLs with m/n=2 (b) and m/n=1 (c) with depicted atomic lattice and superimposed thermal serial resistance model Eq. (2) as a wiring diagram. The size of the different resistances refers to their magnitude. The magnetic model on the right side of a) and (b) is taken from ref. 17.](image-url)
\[ 1/\kappa_b = (m/\kappa_{LMO} + n/\kappa_{SMO}) \times (m+n)^{-1} \] (1) and contributions from internal interfaces (Kapitsa resistances), quantified by the thermal boundary conductance \( h_{bd} \) (ref. 37). In total: \[ 1/\kappa = 1/\kappa_b + 2/(\Delta h_{bd}) \] (2). Fitting data in Fig. 3 by Eq. (2) reveals that thermal resistivity of m/n=1 SLs for \( 1/\Lambda \rightarrow 0 \) extrapolates to \( 1/\kappa_b = 0.214(4) \) mK/W. This is close to bulk SMO with 0.162 and 0.25 mK/W, respectively. By inserting into Eq. (1) the measured value of a single LMO film \( 1/\kappa_{LMO} \sim 1.4(1) \) mK/W and the averaged literature value for SMO, the estimated resistivity of \( \text{La}_{1/2}\text{Sr}_{1/2}\text{MnO}_3 \) of 0.8 mK/W is four times larger than the \( 1/\kappa_b \). Thus, LMO layers in m/n=1 SLs possess the similar low thermal resistivity as SMO layers. The same analysis of Eq. (2) for SLs with m/n=2 yields an extrapolated value of \( 1/\kappa_b = 0.41(6) \) mK/W, which also differs significantly from the composition average for \( \text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3 \) of \( \sim 1 \) mK/W, determined from Eq. (1). However, in contrast to m/n=1 SLs, the extrapolated bulk thermal resistivity is significantly larger than that for SMO. Considering the LMO layers inside the m/n=2 SL, one can solve Eq. (1) for \( 1/\kappa_{LMO} \sim 0.5 \) mK/W, which being significantly smaller than that of an LMO film (1.4 mK/W) is much larger than the resistivity of SMO (\( \sim 0.2 \) mK/W). Thus, in case of m/n=2 SLs the thermal behaviour of LMO and SMO layers is very different. Finally, thermal interface resistances, calculated from the slopes of linear fits by Eq. 2 in Fig. 5, are equal to \( 1/h_{bd} = 0.57(1) \) and 3.4(3) m²K/GW for m/n=1 and m/n=2 SLs, respectively.

To disclose the origin of structural differences between the LMO and SMO layers in SLs with m/n=1 and m/n=2 we performed first principles simulations of the representative 6/6 and 12/6 SLs, using the \( \sqrt{2}\times\sqrt{2} \) in-plane geometry and constructing the supercells with 120 and 180 atoms, respectively. Then, the accurate structural optimization was performed using the code VASP. All LMO and SMO layers were assumed to have the same in-plane lattice parameter, \( a = 0.3905 \) nm, due to epitaxy on the STO, while the coordinates of each atom were allowed to relax. The results presented in Fig. 4a) and 4b) demonstrate unambiguously the presence and absence of octahedral tilts, \( \Delta \phi \), in LMO within the 12/6 and 6/6 SLs, respectively. Also for 6/3 SL, the simulations (see Fig. SM-11) reveal the MnO\(_6\) octahedral tilts. The relaxed structure of the 6/6 and 12/6 SLs in Fig. 4e and 4f) is tetragonally distorted along [001] as evidenced from the out-of-plane lattice parameters (the La-La, La-Sr and Sr-Sr distances). For both SLs their first interfacial SMO unit cells are always tetragonally compressed, while the scenario for LMO differs. For 12/6 SL the first LMO u.c. from the interface is tetragonally expanded compared to deeper lying layers. It seems that the LMO layers in 6/6 SL are not sufficiently thick to stabilize their “natural” tilted structure. However, for thicker LMO layers in 12/6 SL the tilting of MnO\(_6\) octahedra becomes energetically favorable as shown in Fig. 4d) by the...
Bond angle deviations $\Delta \phi$ plotted for each atomic layer along the [001] axis. Angles $\Delta \phi$ for LMO layers vary robustly around 10° except those strongly suppressed at the interfaces matching SMO boundary condition ($\Delta \phi=0$). Most importantly, the here calculated tilting angles $\Delta \phi$ are in good agreement with TEM data in Fig. 1 and Fig. SM-3$^{28}$. 

Fig. 4 Structure of the LMO$_m$/SMO$_n$ SLs optimized from first principles for $m=6$, 12 and $n=6$. The left panels (a), (c), and (e) show the details of 6/6 SL while the right panels (b), (d), and (f) illustrate the case of 12/6 sample. Atomic structure of $m/n=1$ is tetragonal distorted (a) along [001] axis, whereas in the case $m/n=2$ clearly the tilting of MnO$_6$ octahedra is clearly seen (b). The displacements of the cation/oxygen $z$-coordinates within the same layer, $\delta z=z($cation$)-z($O$)$, as well as the bond angle deviations are plotted as a function of each atomic layer position along [001] in the panels (c) and (d), respectively. In the panel (c) the directions of electric dipole at the interface are marked by arrows. The out-of-plane lattice parameters, calculated as the La-La, La-Sr and Sr-Sr separations along [001], are plotted in the panels (e) and (f).
The observed correlation between the MnO$_6$ octahedral tilt mismatch in LMO/SMO SLs, on one hand, and emerging magnetism and phonon transport, on the other hand is summarized by Fig. 3b), c). Regarding magnetism, the absence (presence) of tilt mismatch in m/n=1 (m/n=2) SLs points towards a suppressed (enhanced) charge transfer across the SMO/LMO interface, resulting in reduced (enhanced) emergent FM phase. Regarding phonon transport, the mismatch-free m/n=1 SLs result in the superior matching of the LMO and SMO phonon spectra, yielding an exceptionally high Kapitsa conductance 1.75 GW/m$^2$K, which is comparable to the highest thermal conductance 4 GW/m$^2$K measured in Al/Cu interfaces$^{41}$. In contrast, the interfacial MnO$_6$ tilt mismatch in m/n=2 SLs strongly modifies the phonon band structure, opening an effective channel for phonon scattering in LMO. Furthermore, the MnO$_6$ tilt mismatch in m/n=2 SLs suppresses the Kapitsa conductance down to 0.29 GW/m$^2$K.

An important issue is the electrostatic mismatch due to interfacing of formally charged (La-O)$^{+1}$(Mn-O$_2$)$^{-1}$ and neutral (Sr-O)$^0$(Mn-O$_2$)$^0$ layers. According to the present study the charge transfer is suppressed at MnO$_6$ tilt-mismatch free LMO/SMO interfaces and, hence, in m/n=1 SLs one can expect charged interfaces with electrons hosted in LMO as Mn$^{3+}$ ions and holes in SMO (Mn$^{4+}$). Indeed, the ab initio calculations of the relaxed 6/6 SL (see Fig. 4c)) reveal large polar displacements of the cation and oxygen z-coordinates, $\delta z$. They indicate formation of emerged electric dipoles, shown by arrows in Fig. 4c) and directed from the LMO into the SMO layers. Within each layer $\delta z$ decreases away from the interfaces, which being oppositely charged compensate each other within LMO and SMO. Thus, the LMO/SMO interfaces in SLs with very thin layers, m=n\leq6 u.c., might be still charged. Notably, the MnO$_6$ tilt mismatch recovers in the LMO$_{10}$/SMO$_{10}$ SL (see Fig. SM-4$^{28}$), leading to an increase of interfacial $T_c$($\sim$314 K (see Fig. 2) and a deviation of thermal resistivity from the linear trend (Fig. 3). A relevant driving force for the formation of tilt-mismatch-free m/n=1 SLs could be large polar displacements (see Fig. 4e), yielding strong tetragonal distortions at the interfaces in thin LMO layers.

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References
28. Supplemental Material at http:
MnO$_6$ Octahedral Tilt Control of Emergent Phenomena at LaMnO$_3$/SrMnO$_3$ Interfaces

(Supplemental Material)

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I. Growth of LMO$_n$/SMO$_n$ SLs on SrTiO$_3$(100) substrates was realized by a metalorganic aerosol deposition (MAD) technique by using La(III)-, Sr(II)- and Mn(II) acetylacetonate (acac) as precursors. The LMO and SMO precursor solutions in dymethilformamide with empirically determined molar ratios La(acac)$_3$/Mn(acac)$_2$=1.3 and Sr(acac)$_2$/Mn(acac)$_2$=1.2 were alternatingly sprayed by using of dry compressed air onto the substrate heated up to 900°C at ambient atmospheric pressure conditions, i.e. pO$_2$=0.2 bar. The volumes of precursor solutions, required for the deposition of one monolayer of LMO and SMO, were determined from the growth of single LMO and SMO films with thicknesses, $d$=5-20 nm. The growth of SLs was monitored in situ by optical ellipsometry analogously to Ref. 1.
II. Global structural characterization was performed by X-ray diffraction (XRD) and X-ray reflection (XRR) using a Bruker D8 diffractometer with CuKα radiation. XRD and XRR patterns were simulated by ReMagX program. Surface morphology of SLs was inspected at room temperature using an atomic force microscope (AFM) from Innova-Bruker. Here we present the structural data, obtained by means of XRR (Fig. SM-1), XRD (Fig. SM-2). In Table SM-1 we summarize structural parameters derived from XRR and XRD.

![Graph with measured data and simulation](image1)

\[ d_{\text{LMO}} = 2.00(4) \text{ nm} \]
\[ d_{\text{SMO}} = 1.78(4) \text{ nm} \]
\[ \sigma_{\text{STO}} = 1.0(3) \text{ nm} \]
\[ \sigma_{\text{Vac}} = 0.3(1) \text{ nm} \]
\[ \sigma_{\text{LMO/SMO}} = 0.1(1) \text{ nm} \]
\[ \sigma_{\text{SMO/LMO}} = 0.3(1) \text{ nm} \]

![Graph with measured data and simulation](image2)

\[ d_{\text{LMO}} = 3.98(5) \text{ nm} \]
\[ d_{\text{SMO}} = 1.93(6) \text{ nm} \]
\[ \sigma_{\text{STO}} = 1.1(3) \text{ nm} \]
\[ \sigma_{\text{Vac}} = 0.4(1) \text{ nm} \]
\[ \sigma_{\text{LMO/SMO}} = 0.3(2) \text{ nm} \]
\[ \sigma_{\text{SMO/LMO}} = 0.5(2) \text{ nm} \]

Fig. SM-1: X-ray reflectivity (red) and simulation (black) of representative \( LMO_m/SMO_n \) SLs with \( m/n=1 \) (5/5, top) and \( m/n=2 \) (10/5, bottom).
Fig. SM-2: X-ray diffraction pattern (red) and simulation (black) of representative LMO<sub>m</sub>/SMO<sub>n</sub> superlattices with m/n=1 (5/5, top) and m/n=2 (10/5, bottom).
### III. TEM analysis

Preliminary TEM characterization was done using a FEI environmental Transmission Electron Microscope (ETEM) Titan 80-300. STEM image simulations were carried using a QSTEM package. Atomic models were built using Vesta software. HR-STEM, iDPC-STEM and EELS experiments were performed at 300 kV using a FEI Titan Themis Z with probe and image aberration correctors, a monochromator and an X-FEG. TEM lamellas were prepared in the [100] and [110] directions using a Thermofischer (former FEI) Helios UC focused ion beam instrument with a beam energy of 30 kV. A final cleaning step was performed at low energy (2 kV). The integrated differential phase contrast (iDPC) STEM technique was used to map simultaneously both light and heavy elements at the atomic scale with accuracy comparable with other TEM methods.
The Mn-O-Mn bond angles were determined quantitatively for 6/6 (Fig. S3a-c) and 12/6 (Fig. SM-3d-f) SLs within the plane of zone axis projection, in terms of statistics of the bond angle deviation $\Delta \phi = 0.5(180^\circ - \phi_{OOR})$, resolved as a function of the atomic layer number, counted along the growth direction. The histograms, obtained from selected atomic layers within SMO and LMO are shown in Fig. SM-3a, 3d) and Fig. SM-3b, 3f), respectively. For a direct comparison, all histograms are plotted together in the colour-coded map depicted in the left panel of Fig. SM-3c, 3f). From Gaussian fits we have determined the average angular deviation $\Delta \phi_{av}$ and the corresponding variance $\sigma$ for each atomic layer. Results for 6/6 and 12/6 SLs are shown in the right panel of Fig. SM-4c, f).

Fig. SM-3. Quantitative analysis of iDPC-STEM images in terms of angular deviation $\Delta \phi$ of Mn-O-Mn rotation angle from 180°. Histogram (a) depicts the relative frequency of $\Delta \phi$ for being within certain frequency intervals within a particular SMO layer as indicated inside SL with $m/n = 6/6$. The black curve is a Gaussian fit. (b) depicts a histogram for the same SL, but refers to a LMO layer. (c) The left panel shows all histograms interpolated along the angular axis as a color-coded logarithmic map. Dashed lines indicate the origin of the data shown in (a) and (b). The right panel shows the average angular deviation $\Delta \phi_{av}$ for each atomic layer, determined by Gaussian fits. The error bar indicates the variance $\sigma$ of the distribution. In (d), (e) and (f) similar plots as in (a), (b), (c) are shown, but here for a SL with $m/n = 12/6$. Note that in this SL a double Gaussian distribution within the LMO layer describes the data well.
Fig. SM-4 HAADF-STEM (left) and iDPC-STEM (right) images of 10/5 (a, b), 6/3 (c, d) and 10/10 (e, f) SLs. The contrast between iDPC images of LMO and SMO layers is caused by the deviations of octahedral oxygen rotation angle $\phi_{\text{OOR}}$ from 180° in LMO.
IV. Magnetization was measured by using a SQUID magnetometer (MPMS XL, Quantum Design) for temperatures, T=5-400 K and applied magnetic fields, B=0-5 T, aligned parallel to the film surface.

Fig. SM-5 Temperature (top) and magnetic field (bottom) dependences of representative SLs with m/n=2 (12/6) and m/n=1 (6/6). The inset in a) shows the TCM(T) function, from which the Curie temperatures of a high-(T_{C1}) and low-(T_{C2}) temperature ferromagnetic phases were determined; the inset in b) is the zoomed view illustrating strong difference between coercive fields of SLs.
FIG. SM-6: a) Coercive fields, $H_C$ and b) exchange bias fields, $H_{EB}$ of LMO/SMO SLs all measured at $T=5$ K. Blue and red symbols refer to SLs with $m/n=1$ and $2$, respectively. All curves are guides to the eye. Data in vertical dashed segments around $1/\Lambda=1$ represent bulk values for LSMO with Sr-doping $x=1/3$ (red circles) and $x=1/2$ (blue squares).
V. Transient Thermoreflectance (TTR)

A. Method and Setup

Thermal characterization was performed using a custom build optical thermal transient reflectivity setup. For the thermal conductivity measurements discussed in this article we employ a custom built optical setup (see Fig. SM-7), featuring a pump laser and a second cw-laser to continuously measure the reflectance of the sample. A pulsed pump laser (Coherent Inc., FLARE NX, wavelength $\lambda=515$ nm, pulse duration 1 ns, repetition rate 2 kHz) is used to rapidly heat the sample surface ($\Delta T_{\text{max}} \approx 100$ K) covered by an absorber film, e.g. Cu with thickness $d \approx 50$ nm. The energy of the pump beam was reduced to 90 mJ using a 0.5 neutral density filter. As a probe laser, we use a diode cw-laser with a wavelength of 643 nm, and an adjustable output power with maximum 150 mW. For the measurements reported in this article the power was set to 50 mW. The temporal evolution of the surface temperature is monitored by a sampling oscilloscope (Agilent Technologies DSO-X 3054A), detecting via a fast, balanced photodiode (FEMTO Messtechnik GmbH, HCA-S) the change in optical reflectivity $\Delta R \propto \Delta T_{\text{surf}}$ of a continuous wave diode laser (TOPTICA Photonics AG, iBEAM-SMART-640-S, wavelength $\lambda=640$ nm) directly in the time domain.

Transient thermoreflectance (TTR) is a contactless optical pump-probe method to measure the thermal conductivity, $\kappa$, interfacial thermal conductance and the specific heat, $C_p$, of thin film samples$^8$-$^{10}$. As the complex refractive index $N=n+i*k$ is typically temperature dependent, the reflectivity, $R=[(n-1)^2+k^2]/[(n+1)^2+k^2]$, of a material depends on temperature. The temperature

![Fig. SM-7 A sketch of our TTR setup](image-url)
dependent change in reflectivity can be expressed in a first order Taylor expansion as $\Delta R/R = C \Delta T$ (ref. 11). We call $C$ the thermoreflection coefficient, which is usually in the range of $10^{-2} \text{K}^{-1}$ to $10^{-5} \text{K}^{-1}$ (ref. 8). Note that, $C$ typically depends on the wavelength of the probing light and on the angle of incidence.

The actual beam paths of the lasers, as well as all optical components are sketched in Figure 5. The probe beam passes a 50:50 cube beam splitter $\text{BS}$, and is thereby separated in a probe and a reference beam. The probe beam is collinearly focused by the lens $\text{L1}$ onto the samples surface. The reflected beam is again collected by $\text{L1}$, and split from the incoming beam by passing the beam splitter $\text{BS}$. After passing the thin-film polarizer $\text{POL1}$, a lens $\text{L3}$ focuses the beam into a balanced photo detector. The reference beam, splitted at $\text{BS}$ is likewise passing a polarizer $\text{POL2}$, and focused with lens $\text{L2}$ on the reference port of the photo detector. The polarizers can be used to manually balance the power in the probe and the reference beams. Two colored glass filters $\text{CGF}$ directly in front of the balanced photo detector filter unwanted pump light from the probe and reference beams.

![Fig. SM-8 A typical TTR curve, obtained from the SL with m/n=5/5 (continuous black line), together with a fit of our thermal model Eq. (6) (red dashed line)](image-url)
The pump beam is directed at the sample at an angle of 45°. The reflection is dumped into a block of anodized aluminium BD. The beam diameter of the unfocused pump beam on the sample surface is 1.9 mm, while the probe spot is focused down to 23 µm. Although already the large difference in beam diameters facilitates finding of a good overlap, an off-axis CCD-camera is used to monitor position and overlap of the beams on the sample, and to check for laser induced damage. The balanced output of the photo detector is displayed on an oscilloscope with 1 GHz band width, which is triggered by a reference photo detector observing the pump-pulses. The laser induced temperature spike, and the following energy dissipation into the sample is measured by observing the change in reflectance. Raw measurement data typically looks like depicted in Fig. SM-8.

While theoretically all materials with a sufficiently high reflectivity can be probed this way, the signal-to-noise ratio can be drastically increased by using a transducer layer with a high thermos-reflectance coefficient C. For probe light with a wave length of 643 nm copper, which has a rather large \( C_{Cu} = 8.5 \times 10^3 \text{K}^{-1} \) (ref. 12) is a reasonable choice. Due to the high thermal conductivity of copper, this metallic material is also ideal as a heat transducer: since the time resolution of the oscilloscope is as short as the pump pulse, and thermal equilibration in the copper layer is even faster, the initial temperature increase can be considered spatially homogeneous inside the copper layer. This eliminates the need for modeling the lasers energy transfer as a function of the absorption depth, and thus significantly reduces the complexity of fitting a model to the measured TTR curves. For these reasons, all SL samples were covered by a 50 nm thick copper film grown by means of electron beam physical vapor deposition in UHV conditions. The film thickness was controlled in-situ by a quartz crystal balance, and cross-checked ex-situ by XRR measurements.

**B. Numerical model**

To extract information about the thermal conductivity of the SL samples, the measured TTR curves are compared to an analytic description of thermal transport, based on a modelling technique introduced by Balageas et al.\textsuperscript{13}. In general, thermal transport in a multilayer film can be described classically by a system of coupled partial differential equations. To simplify the calculations, we assume the direction of the heat transport to be purely normal to the sample surface. The mathematical problem then reduces to a single spatial dimension. The system consists of one Fourier (diffusion) equation (Eq. (1)) for each material layer (namely the Cu-capping layer, the SL-layer and the STO-substrate), plus interface conduction equations between neighboring layers (Eq. (3)), and boundary
conditions at the top and bottom of the sample. As initial condition, we assume that the energy of the pump laser is absorbed at the surface of the Cu-capping layer at $z = 0$ at time $t = 0$ (Eq. (2)).

$$\frac{\partial T_i}{\partial t} = \frac{\kappa_i}{\rho_i c_i} \frac{\partial^2 T_i}{\partial z^2}, \quad i \in \{1, 2, 3\}$$ (1)

$$-\kappa_1 \frac{\partial T_1}{\partial z}(z = 0, t) = \delta(t)$$ (2)

$$-\kappa_i \frac{\partial T_i}{\partial z}(z_i, t) = -\kappa_{i+1} \frac{\partial T_{i+1}}{\partial z}(z_{i+1}, t)$$

$$= h_i [T_i(z_i, t) - T_{i+1}(z_i, t)]$$ (3)

Upon applying a Laplace transform, the equations change from the time domain to the Laplace space. Thereby the time-derivatives vanish and become multiplicative expressions. The remaining normal differential equations can be solved with an appropriate ansatz for each layer:

$$\tilde{T}_i = A_i(s) \sinh \left( (z - z_{i-1}) \sqrt{\frac{\rho_i c_i}{\kappa_i}} s \right)$$

$$+ B_i(s) \cosh \left( (z - z_{i-1}) \sqrt{\frac{\rho_i c_i}{\kappa_i}} s \right).$$ (4)

Here $\tilde{T}_i$ is the Laplace-transformed temperature at the $i$-th layer and $z_i$ the $i$-th boundary position with $i = 0$ being the surface of the sample. The ansatz results in a system of six linear equations, $M \cdot \tilde{a} = (1,0,0,0,0,0)^T$. Here, $\tilde{a}$ contains the unknown constants of the ansatz $(A_i, B_i)$. The system can be solved for the surface temperature in Laplace-space, which corresponds to the second entry $a_2$ of $\tilde{a}$:

$$\tilde{T}_{surf}(s) = b_1(s) = \det(M_{12}^i)/\det(M),$$ (5)

where $M_{12}^i$ is the minor matrix, which is obtained by omitting the first row and second column of $M$. To obtain the time dependent expression, the inverse Laplace transform of $T_{surf}(s)$ is calculated. This requires solving a complex integral by means of the residual theorem:
$$T_{surf}(t) \propto 1 + \sum_{i=1}^{\infty} \left( \frac{\det(M_{12}^i)}{(\partial \det(M)/\partial s)} \right) \cdot \exp(s_i \cdot t) .$$

<table>
<thead>
<tr>
<th></th>
<th>$c_{p,x}$ [J kg$^{-1}$ K$^{-1}$]</th>
<th>$\kappa_x$ [W m$^{-1}$ K$^{-1}$]</th>
<th>$\rho_x$ [kg m$^{-3}$]</th>
<th>$h_{x+y}$ [W m$^{-2}$ K$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu (50 nm)</td>
<td>385 (ref. 8)</td>
<td>400 (ref. 9)</td>
<td>8960</td>
<td></td>
</tr>
<tr>
<td>SL $m/n=1$</td>
<td>532</td>
<td></td>
<td></td>
<td>0.087(1) (Cu $\leftrightarrow$ SL)</td>
</tr>
<tr>
<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>STO (0.5 mm)</td>
<td>544 (ref. 10)</td>
<td>12 (ref. 10)</td>
<td>5110</td>
<td>20(1) (SL $\leftrightarrow$ STO)</td>
</tr>
</tbody>
</table>

Table SM-II: This table shows assumed and fitted values (including error margins) for heat capacities $c_{p,x}$, thermal conductivities $\kappa_x$, mass densities $\rho_x$, and interface conductances $h_{x+y}$.

The arguments $s_i$ of the exponentials are the real, negative roots of $\det(M)$, which give rise to poles of $T_{surf}(s)$, which contribute to the inverse Laplace transform according to the residual theorem. The final solution is an infinite series of weighted decaying exponentials, proportional to the surface temperature, and therefore to the reflectivity measured in TTR. The numerically obtained curves are parametrized by the material properties of the layers, as well as by the interface conductances. Note that we truncate the series after the 2000$^{th}$ term. Larger summands only contribute to very small time scales $< 5$ ns directly after the excitation, where this model does not hold true anyway, because of the assumed delta peak as starting condition. We then use non-linear optimization to best approximate the measured data with our numerical solution, in the form of a least squares-fit. The free parameters are the interface conductivities between the SL and the Cu layer, and between the SL and the substrate, as well as the effective thermal conductivity of the SL. The other necessary parameters for the description of the samples are taken from literature, and are listed in Table II. Because of our assumption that the interface conductivities do not depend on the superlattice period $m + n$, these parameters are optimized simultaneously for all samples with the same $m/n$. The optimization method of choice is the Nelder-Mead method, which is a derivative free algorithm and therefore very stable and fast. It optimizes the parameters by iteration, where in each step the values on the corners of a multidimensional simplex are compared and said simplex modified (e.g. by scaling, mirroring or stretching).
For each sample, the thickness of the SL layer was calculated from the nominal composition $m$ and $n$ and the lattice constant. The effective heat capacities and densities of the SLs were interpolated from material parameters of LSMO$^{14-16}$, according to the actual La and Sr content for a given $m$ and $n$.

**VI. The density functional theory calculations.** The structural optimization and all electronic structure calculations were performed from first principles within the density functional theory using the projector augmented-wave (PAW) method as implemented in the VASP code$^{17}$. The exchange-correlation energy was treated using the generalized gradient approximation. The energy cutoff for

Fig. SI-9 Atomic structure of the LMO/SMO SLs with $m/n=2$ optimized from first principles for 12/6 SL (a) and 6/3 SL (b). The tilting of MnO6 octahedra is clearly to be seen in both structures.

[Diagram showing atomic structures with labels]
the plane-wave expansion was set to 450 eV. For the calculated LMO$_m$/SMO$_n$ SLs, i.e. 6/6, 6/3 and 12/6, we used the $\sqrt{2}\times\sqrt{2}$ in-plane geometry. The structural optimizations were obtained with a conjugate-gradient algorithm and a force tolerance criterion for convergence of 0.015 eV/Å. The Brillouin zone integration was performed using 4×4×1 Monkhorst–Pack k-mesh.

Fig. SI-10: From incoherent particle-like, to coherent wave-like thermal transport. (a) Sketch of coherent transport in tilt-mismatch-free superlattices with $m/n=1$, where for ultrathin SLs the coherence length $\ell > \Lambda$. (b) Thermal conductivity as a function of the superlattice period. For $m/n=1$ and $\Lambda \geq 6$, the serial resistance model discussed in the main article applies, and fails below. The occurrence of the peculiar minimum is due to band folding. Below $\Lambda = 6$, phonons propagate coherently across several interfaces. (c) Sketch of incoherent transport in MnO$_6$ tilt-mismatched superlattices with $m/n=2$, where the coherence length $\ell < \Lambda$.

**VII. Coherent thermal transport in superlattice with $m/n=1$ approaching the atomic limit**

Down to $\Lambda=6$, the thermal conductivity can be modelled using a simple series of thermal resistance. Such a picture should indeed be suitable, as long as the phonons can be considered as randomly diffusing particles. The coherence length $\ell$ of such phonons is then in the range of the SL period $\Lambda$ or even smaller ($\ell \leq \Lambda$) (see Figure SI-10(c)). Such a normal kind of thermal transport, where the wave nature of the phonons is not important, is also called incoherent transport. Phonons then only see a small part of the surrounding material - within our SLs either LMO or SMO. From a spectral point-of-view, such a SL can be described as a periodic stacking of two different phonon band structures. The larger the thermal conductivity, the more coherent is the transport. From the usual assumption that, $\kappa \sim \ell$, one can estimate that, in SLs with $m/n=1$, the coherence length is a factor of 2 to 4 larger than in SLs with $m/n=2$. As we have explained in the main article, this is a consequence of the absence of octahedral distortions.

The significant increase of the thermal conductivity in LMO/SMO SLs with $m/n=1$ opens up the exciting perspective to enter into a coherent transport regime for truly atomic scale when $\ell > \Lambda$ (see Figure SI-10(a)). Thus, phonons experience multiple self-interference. In such a situation, instead of imagining a stack of individual phonon band structures, one has to consider a single, collective band structure. Due to the periodicity of the SLs, the Brillouin zone in the out-of-plane direction is artificially reduced from $\frac{2\pi}{a}$ to $\frac{2\pi}{\Lambda}$, including new gaps opening at its boundaries. Such gaps effectively slow down the propagation of the phonons, and thus decrease the thermal conductivity. From simple theoretical modelling [18] one knows
that, in the idealized case of $\ell \to \infty$, this effect should increase with increasing $\Lambda$. At finite $\ell$, a minimum in the thermal conductivity should show up as a function of $\Lambda$. So far, a clear experimental fingerprint has only been reported once in literature [19], obtained from a series of non-magnetic perovskite oxide SLs (SrTiO$_3$/CaTiO$_3$). In our SLs with $m/n=1$, one can see a much more pronounced minimum of $\kappa=0.3$ W/m*K at $\Lambda=4$ (see Figure SI-10(b)), signaling a transition from incoherent particle-like ($\Lambda>4$) to coherent wave-like ($\Lambda<4$) phonon transport. Interestingly, the saturation magnetic moment at 5 K also shows a minimum at $\Lambda=4$ (see Fig. 2 b)), indicating a possible correlation between spin and phonon degrees of freedom in our SLs.

3. C.T. Koch "Determination of core structure periodicity and point defect density along dislocations" ProQuest Dissertations and Theses, Thesis (PhD) - Arizona State University (2002).