Moiré supercells through SrTiO₃ nanolayer relaxation

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ABSTRACT. The interface of complex oxide heterostructures sets the stage for various electronic and magnetic phenomena. Many of these collective effects originate from the precise structural arrangement at the interface that in turn governs local spin- and charge interactions. Currently, interfacial straining, so the naturally evolving compressive or tensile strain by mismatch of the neighboring lattices, is the most common route towards engineering collective material properties – yet, significant progress might require exploration of entirely new approaches towards interface correlations. In this work, we turn the page by looking at the interface of a perfectly relaxed, unstrained heterostructure, where we identify a highly ordered Moiré lattice at an inherently disordered SrTiO₃ (STO) - LSAT interface. Using high-resolution reciprocal space mapping via synchrotron based X-Ray diffraction, we find long-ranged ordered supercells of
106/107 unit cells of STO/LSAT, caused by lattice relaxation through high-temperature annealing. Model calculations confirm the experimentally observed scattering phenomena, showing that cross-interfacial bonding is locally different at the Moiré-overlap points. Notably, the presence of such super-ordered structures in the family of 2D electron gas systems sets the ideal conditions for Moiré-motif tuned plasmonic responses and ferroelectric super-crystallinity and opens up the possibility to novel interface functionalities in these simple perovskites.

Complex-oxide heterostructures with their unique set of physical and chemical properties are of looming interest for magneto-electronic devices\(^1\)–\(^8\). Here, intrinsic material properties, such as (i) rich spin-interactions\(^9\), (ii) strong multiferroic character\(^10\) and (iii) high thermal and operational stability\(^11\), are extended by electronic interactions at the hetero interface\(^8,12\)–\(^14\). Indeed, accurate interface engineering has led to a new functional repertoire\(^15\), including observations of quasi-2D electron gas (q-2DEG)\(^14,16,17\), charge writing\(^18\), resistance switching\(^19\), occurrence of electronic\(^20\) and magnetic order\(^21\), giant thermoelectric effect\(^22\) and colossal ionic conductivity\(^23\). The origins of these collective phenomena lie in site-specific spin and charge interactions\(^24\)–\(^26\) that are in turn governed by the local atomic arrangement\(^27\). Indeed, simple misalignment of two equal lattices induces a long-range ordered superstructure termed “Moiré-motif” that manifests itself in new collective properties, such as e.g. plasmonic minibands\(^28\) or Moiré-excitons\(^29\). Precise knowledge of the atomic structure at the interface, even between seemingly equal lattices, is hence key in understanding and enhancing the collective material-system behavior.

Prominent candidates for such oxide-based heterostructures are perovskite titanates, including SrTiO\(_3\) (STO). The strong interest in STO stems from (i) its involvement in the first report of an
interfacial q-2DEG\textsuperscript{14} that is strongly linked to (ii) its high and tunable dielectric constant\textsuperscript{30,31}. Quantum fluctuations of the cell-centered Ti-atom (see Fig.1a) suppress the paraelectric to ferroelectric transition\textsuperscript{32}, whereas these fluctuations are driven by the STO soft phonon-mode\textsuperscript{33}. As a result, the phononic landscape determines the dielectric anisotropy and magnitude of the material. Lattice straining effects that drastically alter the respective phonon modes therefore play a crucial role in heterostructure growth of STO, leading either to (i) a polar structure\textsuperscript{34,35} or to (ii) suppression of lattice polarizability and strong reduction in dielectric character\textsuperscript{31,36}. Obtaining ideal bulk-material properties in STO films hence requires perfect relaxation of the crystalline lattice by structural decoupling from the substrate – a non-trivial task particularly for strain-susceptible nanolayered systems.

Here, we look at the interface between a nanolayer of STO grown on a (La,Sr)(Al,Ta)-oxide (LSAT) substrate - a material combination with minimal potential strain: both compounds have a cubic lattice \(a_{\text{STO}} = 3.904 \text{ Å}\textsuperscript{37}; a_{\text{LSAT}} = 3.869 \text{ Å}\textsuperscript{38}\) and a mismatch of only +0.93\% (see Fig 1a). Despite this small lattice mismatch, straining from lattice matching of the grown STO layer is sufficient to initially suppress the soft phonon-mode\textsuperscript{32,39}. As previously shown one can recover the bulk-like phononic landscape by high temperature annealing in ambient atmosphere\textsuperscript{32,39}, suggesting structural relaxation of the STO nanolayer. We follow this approach and use a 54 ± 2 nm thick film of STO on LSAT [001] (see Fig. 1b for X-Ray rocking-curve scan) grown by pulsed laser deposition, followed by 12 h of annealing at 1200°C at ambient conditions\textsuperscript{39}. We find that this heat-treatment leads to complete relaxation of the STO nanolayer, resulting in a Moiré pattern at the STO/LSAT interface. Comparison with theoretical calculations shows that this Moiré interference only occurs if the atomic bond-length at the interface varies at the overlap points. Our explanation not only help to understand recent reports of 3D supercrystalline vortex structures\textsuperscript{40},
but also implies a long-range ordered modulation of the plasmonic nature of the interfacial electron gas\textsuperscript{41}, opening new applicative perspectives for plasmon tuneable complex oxide devices.

As structural motifs of the hetero-interface are often projected onto the sample surface\textsuperscript{42}, we characterize the STO nanolayer morphology by atomic force microscopy (AFM). As seen in Fig. 1c, AFM shows disordered islands with 5-8 nm thickness and 146 nm mean lateral correlation length (see Supporting Figure S1 for Fourier-analysis of the AFM image). Such island-growth has been linked to segregation effects during annealing and is usually found to seed at lattice-defects, such as dislocations and/or steps\textsuperscript{42-45}. The absence of a long-range ordered island arrangement (here evidenced by disorder) hence points towards an isotropic STO nanolayer morphology decoupled from the crystallographic lattice.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{(a) Illustration and dimension of the cubic unit cells of STO and LSAT. (b) X-Ray rocking curve (black dots) along the [001] direction at the (201) reflection together with the fringe-}
\end{figure}
pattern fit (blue dashed line), yielding a film thickness of 54 ± 2 nm. (c) AFM image of the surface after annealing, showing a common lateral disordered arrangement of islands.

To obtain information on the atomic lattice strain state, we collect reciprocal space slices (scattering images) by synchrotron X-Ray diffraction, which we map and assemble into a 3D reciprocal space volume (RSV) – see Methods section for detailed description. The final RSV is transferred into the STO-HKL space [named indices relate to STO and not to the LSAT substrate where capital indices (e.g. H, K or L) denote reference positions in reciprocal space while lower-case indices (e.g. h, k or l) denote scanning variables]. First, we select the low-symmetry (2, 0, L) family with L = 2, 3 and 4, providing information on the out-of-plane strain state of the STO film. As shown in Fig. 2, we observe rod-like scattering features extending along the l-axis, typical of an out-of-plane nanolayer. For L=2 and 4, oscillations at k=0 along l can be observed, corresponding to layer-thickness dependent fringes (in fact the rocking-curve in Fig. 1b is extracted from the 3D volume in Fig. 3: L=2). More evidently, the RSV presents two significant scattering contributions along the l-direction, from: (i) the layer (at lower l) and (ii) the substrate (at higher l). From the distance between the two scattering centers, we calculate the difference in out-of-plane d-spacing of STO and LSAT, corresponding to a mismatch of +1.07 ± 0.10 %. This value is only slightly above the theoretical prediction for a perfectly relaxed lattice (+0.93%).
Figure 2. Out-of-plane projection of the reciprocal space volume (RSV) obtained by X-Ray scattering at the (2, 0, L) family peaks. The reciprocal-space distance between substrate and surface-layer peak increases linearly with L-diffraction order, yielding an out-of-plane lattice mismatch of $1.07 \pm 0.10 \%$. Color and transparency are log-scaled with scattering intensity according to the color bar.

Interestingly, the scattering-rods seen as streaks along the out-of-plane l-direction (see Fig. 2) present coherent repetitions along the in-plane k-direction. Note, that the small distance between these rods in reciprocal space must relate to a large origin in real space. Indeed, such scattering features are characteristic of a large-scale and long-range order as found in superstructures$^{20,46–48}$, here relating to an in-plane d-spacing of 41.1 nm (corresponding to the reciprocal-space distance of $\Delta k = 0.0095$ between the modulations – see Supporting Figures S2 and S3 for peak-fits).
Figure 3. (a) Out-of-plane and (b) in-plane projection of the reciprocal space volume (RSV) obtained by X-Ray scattering on the (2, K, 4) family peaks, showing a commensurate relation between atomic lattice reflections and the superstructure scattering-rods. Black lines mark the center of the Bragg-reflection in the STO reference frame; grey lines are guides to the eye. Color and transparency are log-scaled with scattering intensity according to the color bar. (c) The 2D Fourier-transform of a theoretical 106/107 Moiré lattice reproduces the same scattering behavior.

To understand if there exists a relation between the scattering rods and the underlying atomic lattices, we vary the in-plane index within the same (2, K, 4) family, as shown in Fig. 3a. Remarkably, with varying k between -2 to 2, the substrate peak (at l = 4.045) and the STO peak
(at l = 4.00) always fall on superstructure scattering-rod{s. E.g., at the (2, -2, 4) reflection, the
substrate peak lies on the 2<sup>nd</sup> scattering rod from STO, whereas increasing k to -1 translates the
substrate peak to the neighboring rod. This effect becomes even clearer when looking at orthogonal
projections that show the full in-plane relation (see Fig. 3b). At all reflections, the superstructure-
rods form an in-plane 2D lattice with square symmetry (see Supporting Figure S2 comparison of
cuts along h and k trajectories). Along h, substrate and layer peak are always spaced two scattering-
rods apart (note, that H=2 for this reflection), while the substrate peak varies along k on the 2D
scattering–rod-grid with increasing diffraction order. This commensurate relation between (i)
atomic reflections and (ii) scattering-rod{s therefore strongly suggests a structural relation between
(i) the atomic crystalline lattices and (ii) the formed superstructure.

In regard of the origin of the observed scattering rods, it is important to realize that the
superstructure scattering pattern is seen on both the atomic substrate (LSAT) and layer (STO)
peak, implying that the underlying structural feature originates from the LSAT/STO interface. [We
can rule out surface topology as origin of the observed scattering rods, as we find a coherent
domain size of >300 nm (see Supporting Figure S3 for corresponding peak fits), which is
significantly larger than the surface features with approximately 150 nm identified by AFM (see
Supporting Figure S1).] Further, the ratio between the STO lattice constant (3.904 Å) and the
observed superstructure d-spacing (42.5 nm) corresponds to 0.92%, ideally matching the
theoretical STO/LSAT lattice-mismatch of 0.93%. The observed scattering behavior hence stems
from scattering interference of LSAT and the perfectly in-plane relaxed STO layer, classified as a
Moiré-like motif<sup>28,49,50</sup>.

In short, such Moiré motifs appear through superposition of two (in this case square) base-
lattices with different periodicity \(a_{small}\) and \(a_{large}\), such that spatial interference gives rise to a
new pattern with the same symmetry but a lattice constant of $a_{moire} = a_{small}^2/(a_{large} - a_{small})$. Here, these two base-lattices relate to STO and LSAT, where it takes 106 unit cells of STO and 107 unit cells of LSAT to compensate the lattice mismatch of 0.93%, yielding a Moiré lattice constant of 42.7 nm. Indeed, and as shown in Fig. 3c, a 2D Fourier transform of such an idealized 106/107 Moiré lattice shows the same scattering motif as observed experimentally: the two strong reflections correspond to the original 106- and 107-base-lattices whereas the weak and smaller-spaced reflections correspond to the Moiré interference terms [see Supporting Information – section Model calculations for a discussion on the origin of such superlattice reflections].

![Diagram of STO/LSAT interface](image)

**Figure 4.** Structural illustration of the STO/LSAT interface due to perfect lattice relaxation, shown along the STO (100) direction. Starting from perfect overlap of the corresponding unit cells (uc) [see black dashed area at $u_{c_{STO}}=0$], the local mismatch of the interfacial oxygen atoms increases towards an incoherent and likely disordered arrangement [see red dashed area at $u_{c_{STO}}=53$]. Eventually, the LSAT and STO unit cells overlap again [see black dashed area at $u_{c_{STO}}=106$], effectively forming a 2D 106/107 Moiré pattern.

The observation of this Moiré pattern allows us to draw conclusions about the LSAT/STO interface. First, it is evidence of a perfectly in-plane relaxed STO layer without remanent substrate-
induced strain. Second, just few of the STO TiO$_3$-octahedra (see Fig. 1) within a 106 x 106 square fall directly on-top of LSAT (Ta;Al)O$_3$-octahedra (see Fig. 4). Only within the vicinity of this overlap, shared bonding of the STO/LSAT interface oxygen atoms is feasible (see black-dashed area in Fig. 4). Indeed, when calculating the diffraction intensity of such a Moiré pattern, superstructure-reflections only become visible if the scattering amplitude of the overlapping unit cell is phase-shifted compared to the non-overlapping majority [see Supporting Information – section Model Calculations for details]. In the sample, this phase shift is a consequence of different out-of-plane bond-length that usually occurs in Moiré lattices, where the related atomic-displacement creates a unique chemical surrounding at this overlap point$^{54}$. Third, the remaining vast majority of interfacial oxygen atoms (see red-dashed area in Fig. 4) likely do not coordinate in a long-range order, as we do not find any other higher-order scattering terms in the RSVs. In quantitative terms (and assuming a critical local strain of ±3%), less than 0.5% of oxide-octahedra at the interface bond coherently. This strongly suggests (i) an overall disordered interface layer that is (ii) prone to local structural defects at the interface.

The concept of Moiré-motifs also helps to understand more complex structural arrangements, spanning over three dimensions. In a recent work, V.A.Stoica, et.al.$^{40}$ presented astonishing evidence of a 3D supercrystal in a heterostructured system of STO and PbTiO$_3$ (PTO) grown at 700°C [$a_{\text{STO}} = 3.936$ Å$^{55,56}$; $a_{\text{PTO}} = 4.007$ Å$^{55}$]. Here, a single laser pump induces a metastable phase in which ferroelectric domains form a long-range ordered pattern spanning over all three crystalline dimensions. On the basis of our findings, we can now explain the very interesting but so far not understood appearance of this 3D supercrystal. Looking at the structural differences in the STO/PTO layer system yields a Moiré-lattice constant of 21.7 nm, which ideally matches the observed in-plane double ferroelectric domain-repetition along STO/PTO (100) of 22 nm.$^{40}$ Along
the orthogonal sample direction, corresponding to the crystallographic STO/PTO (110) direction, the Moiré-lattice yields 15.4 nm. Considering the proposed model where ferroelectric polarization occurs along the STO/PTO (100) direction, two orthogonal (positive and negative aligned) domains would hence require 30.8 nm, which again ideally matches the observed 30 nm supercrystalline repetition distance.\(^{40}\) The lattice mismatch therefore explains the laser-annealed formation of this three dimensionally ordered ferroelectric supercrystal and offers a route to predict and tune the superlattice dimensions, without considering complex approaches for equilibration of electrostatic interactions.

In summary, we observe near-perfect relaxation of a thin STO film grown on a low lattice-mismatch LSAT substrate, leading to a 2D-square Moiré-pattern. The resulting Moiré domains with approximately 40 nm relate to a commensurate 106/107 supercell relation – an unprecedented and extraordinary observation, as the here found periodicity is 3-4 times larger compared to reported (few-layer) systems\(^{49,50,53,54,57}\). This perfect lattice relaxation implies a long-range (but not short-range) ordered bonding structure at the hetero-interface, as oxygen-sharing between LSAT and STO is only feasible when the corresponding unit cells overlap. Such a locally disordered interface constitutes the ideal environment for gas- and glass-like phases such as 2D electron gas systems\(^{1,12,23}\): the possibility to detect and characterize the atomic order at the interface, particularly over macroscopic length-scales, will be of significant interest for design and optimization of such promising hetero-structured material systems. Regarding the recent and exciting observation of polar supercrystals\(^{40}\), our explanation now allows prediction of expected polar domain sizes simply based on the atomic lattice, which will greatly facilitate the design of new two and three dimensional ferroelectric vortex geometries. Furthermore, Moiré superlattices are known to induce
collective phenomena (such as e.g. new plasmon modes\textsuperscript{49}) in the electronic landscape, which might open a range of unforeseen potential applications of the LSAT/STO material system.

METHODS

**Surface analysis:** Atomic Force Microscopy (AFM) images were acquired on a Bruker Dimension Icon Scanning Station in tapping mode. Images were analyzed using the Gwyddion package\textsuperscript{58}. To correct for sample non-planarity, a sloped background (fitted polynomial) was subtracted. For correlation-analysis, the AFM image was Fourier transformed using a Hanning window function for spatial filtering. Radial averaging to obtain the mean correlation length was performed by averaging 20 radial cuts through the reciprocal space images.

**Reciprocal Space Volumes:** X-Ray diffraction (XRD) experiments were performed at the surface X-Ray diffraction (SXRD) endstation of the MS beamline\textsuperscript{59,60} at the Swiss Light Source. The X-Ray beam (12.65 keV) was focused and cut to a beamsize at the sample of 500 x 500 \(\mu\text{m}\) (H x V). The sample was mounted on a (2+3)-type surface diffractometer (vertical geometry)\textsuperscript{61} with an angular resolution of 0.002\(^\circ\). Images were collected with a Pilatus 100K detector after a 1300 mm helium fly-tube to reduce air-absorption of weak scattering features. During scans, the primary intensity of the incident beam is automatically adjusted (by a variable transmission-filter array) to optimize the effective dynamic range of each scan. The UB “orientation-matrix” describing sample alignment in the beamline coordinate system was defined by manual alignment of 3 non-orthogonal and 2 orthogonal reflections, resulting in a UB accuracy of \(h,k,l \pm 0.0005\) r.l.u.. Reciprocal space scans (200 images, 1 s each) over each reflection were made along the (001) and (112) directions to check for possible distortion/misalignment effects. Angular to reciprocal space conversion of each detector pixels was done according to
Schlepütz, et al. For each scan, an array of all 3D reciprocal space coordinates with the corresponding scattering intensities were interpolated onto an orthogonal, equidistant (voxel size $h,k,l = 0.0005$ r.l.u) 3D matrix, constituting the reciprocal space volume (RSV). The convolution product of (i) experimental accuracy and (ii) the RSV voxel size yields the effective resolution of the RSV, which in this case is $h,k,l \pm 0.0007$ r.l.u..

**Model Calculations:** Model calculations were carried out by self-written Python procedures using the CuPy package for GPU accelerated computations. A detailed description can be found in the Supporting Information – section Model Calculations.

**ASSOCIATED CONTENT**

**Supporting Information.**

The following files are available free of charge.

Extended Experimental Data: Scattering intensity along $h$, $k$ trajectories of the RSVs; Fourier analysis of AFM images; Details for model calculations.
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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

M.R. and M.C.H. are responsible for sample growth and annealing, respectively. M.B., B.F.P., N.O.H, and H.U., performed XRD experiments, M.B. extended the code for XRD data consolidation into RSVs. AFM measurements were carried out by C.A.F.V.. M.B. consolidated and evaluated all experimental data and performed model calculations. This work was envisioned and initiated by U.S.

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Notes

The authors declare no competing financial interest.

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