The surfaces of oxide materials, both in their bulk form and as (ultra)thin films, are rarely bulk-terminated. Instead they form a multitude of diverse and complex structural configurations as a function of their oxygen content [1–6], their cation composition (for multielement materials) [7, 8], and, in case of metal-supported ultrathin films, the support itself [3, 5]. This manifold of phases is determined by a delicate interplay between polarity compensation [9], variability of the oxidation state of the metal atoms as a function of the oxygen chemical potential (1/2µO2) [10, 11], henceforth µO for simplicity), strain and defect-formation energies [12], and, depending on the preparation conditions, kinetic effects [5].

The surface structure of metal oxides dictates their surface properties through the coordination, arrangement, and electronic structure of the topmost atoms [13–20]. Hence, it is important to map out the parameter space of the equilibrium surface phases of these materials, including their evolution with µO. Such a characterization has come a long way for binary oxides, but is still in its infancy for perovskite oxides (ABO3), despite the undisputed role of their surfaces in many emerging and established technologies [21–24].

One prominent example is lanthanum–strontium manganite (LSMO). Owing to its many and diverse physical properties (among others, half-metallicity, colossal magnetoresistance, metal–insulator transition, anti/ferromagnetic to paramagnetic transitions, high electronic conductivity at elevated temperatures), LSMO is used in a wide range of applications, e.g., spintronics [25–27], catalysis [28, 29], energy production [30, 31], and various thin-film technologies [32–34]. Because many relevant processes and interactions take place at the LSMO surfaces and interfaces, gaining a comprehensive understanding of the equilibrium surface phases of LSMO at the local (i.e., atomic) level is of paramount importance. Such investigations must be performed as a function of both, the cation, and the oxygen concentrations (the latter depends on the value of µO at which the surface is treated): Both these parameters define a rich phase diagram including the physical properties named above [35], the performance of LSMO-based devices [36–39], and emergent phenomena in LSMO thin films [40]. To date, however, there exists no comprehensive investigation that simultaneously maps out the equilibrium surface phases of LSMO (nor of any other multielement oxide) as a function of the cation composition and µO. The few studies available have unveiled that perovskite oxide surfaces typically consist of B-site-rich structures made of one or two atomic layers of differently linked polyhedra [41, 42], and have focused on their relation to the A:B cation ratio at the surface. In some cases, quantitative compositional relations between the different structures have been established [7, 8, 43, 44].

This work pushes the experimental characterization of perovskite oxide surfaces, by investigating the effect of the cation composition and µO on the local surface properties of (110)-oriented LSMO. Single-crystalline films of La0.8Sr0.2MnO3 were grown on Nb-doped SrTiO3(110) substrates by pulsed laser deposition (PLD) (≈ 100 nm, 700°C, 1 Hz, 2.2 J/cm², 4 × 10⁻² mbar O₂) [8]. Their surfaces were investigated in an ultra-high vacuum (UHV) surface science setup attached to the PLD chamber, equipped with scanning tunneling microscopy (STM), low-energy electron diffraction (LEED), x-ray photoelectron spectroscopy (XPS), and low-energy He⁺-ions scattering (LEIS) (for details about the experimental methods, see Refs. 8 and 45, and Section S1). Previous studies have shown that these films exhibit composition-related surface reconstructions at 700°C and 0.2 mbar O₂, and have established the differences in cation coverages between them [8]. These structures, here referred to as “high-pressure” (HP), are shown for reference at the left-hand side of Fig. 1, and are described in detail in Section S2. The current work is based on the behavior of the HP reconstructions over a wide range of µO values (between ≈ −2.1 eV and ≈ −1.4 eV, corresponding to annealing between UHV and 0.2 mbar O₂ at 700°C): When decreasing µO (i.e., at more reducing conditions), new surface structures are formed, and a rich phase diagram emerges. These new structures, referred to as “low-pressure” (LP), are collected at the right-hand
side of Fig. 1, and are described in detail in Section S3. Their relative compositions, as derived in this work, are reported in the bottom axis in terms of monolayers (ML) of Mn.

After exploring in detail the behavior of the HP structures with decreasing $\mu_O$ and the process of phase separation, this work will propose a novel, STM-based approach to organize the equilibrium surface phases of LSMO(110) (both HP and LP) in a quantitative diagram as a function of the cation composition and $\mu_O$.

The first HP structure whose behavior with $\mu_O$ is considered is the A-site-rich (1 \times 1)$_{\text{HP}}$ of Fig. 1(a): This structure stays unaltered upon annealing at 700°C and $2 \times 10^{-3}$ mbar $\leq \rho_{\text{O}_2} \leq 0.2$ mbar, but transforms into the (1 \times 1)$_{\text{LP}}$ of Fig. 1(d) at lower pressures (down to UHV). The (1 \times 1)$_{\text{LP}}$ is characterized by the same periodicity as its HP counterpart, and the same cation composition [see LEIS data in Fig. S1(b)]. However, it displays a glide plane that is not present in the (1 \times 1)$_{\text{HP}}$, and possesses a smaller oxygen content [Fig. S1(b)].

The other HP phases of LSMO(110) behave differently than the (1 \times 1)$_{\text{HP}}$ with decreasing $\mu_O$, as shown below. These structures are significantly Mn-rich and belong to a different family with respect to the (1 \times 1)$_{\text{HP}}$, and are henceforth referred to as HP, ‘Mn-rich’ phases. Notably, they continuously evolve into one other as a function of the Mn content, such that various surface structures exist between the fishbone and the (2 \times 1) of Fig. 1(b, c) [8]. The qualitative behavior of these HP, Mn-rich phases with decreasing $\mu_O$ is exemplified by Fig. 2, which shows the evolution of the fishbone phase of Fig. 1(b), initially prepared at 0.2 mbar and 700°C. When decreasing the $\text{O}_2$ pressure to $2 \times 10^{-3}$ mbar at 700°C, small (1 \times 1)$_{\text{HP}}$ areas appear (orange in Fig. 2). These patches become larger as $\mu_O$ decreases, and change their atomic structure to (1 \times 1)$_{\text{LP}}$. Meanwhile, the remaining fishbone-reconstructed surface undergoes a minor structural change: The small features highlighted by the short yellow lines in Fig. 2(a$_2$)$_{\text{b}_2}$ orient closer to the [1\overline{1}0] direction, an indication of a slight Mn enrichment [8]. Between $1 \times 10^{-4}$ and $5 \times 10^{-6}$ mbar [Fig. 2(c)], larger (1 \times 1)$_{\text{LP}}$ patches form, while the remaining surface exposes the oblique structure of Fig. 1(e). Below $5 \times 10^{-6}$ mbar and down to UHV [Fig. 2(d)], even larger (1 \times 1)$_{\text{LP}}$ patches are observed, while the remaining areas exhibit the stripes of Fig. 1(f). Importantly, the process is reversible: STM confirms that the initial surface is regained when annealing back at high $\rho_{\text{O}_2}$. A semi-ordered phase assigned to a transition state between the fishbone and the oblique structures appears around $10^{-4}$ mbar (not shown).

Quantifying the (1 \times 1)$_{\text{HP/LP}}$ areal coverages at each step of the phase separation with STM [Fig. 3(a)] allows to determine the composition of the LP Mn-rich structures, as shown below. Note that because the following discussion focuses on relative cation compositions, which is the same on the two (1 \times 1)$_{\text{HP}}$ and (1 \times 1)$_{\text{LP}}$ phases, these will be henceforth referred to simply as (1 \times 1), disregarding the change in atomic structure and oxygen content occurring below $2 \times 10^{-3}$ mbar $\text{O}_2$ at 700°C. In Fig. 3(a), full, black symbols represent the experiment of Fig. 2: As discussed, decreasing $\mu_O$ produces increasingly larger (1 \times 1) coverages. The same trend is observed for starting Mn-richer surface compositions (gray), albeit with a smaller slope: Mn-richer surfaces form less of the Mn-poorer (1 \times 1) areas. Importantly, the same phases

![FIG. 1. Equilibrium surface structures of LSMO(110). Top: 12 \times 12 \text{ nm}^2 \text{ STM images; bottom: LEED. } \text{O}_2 \text{ pressure ranges (millibar) where each reconstruction is stable at 700°C are reported at the top. (a–c) High-pressure (HP) structures, obtained by depositing Mn or La in PLD plus O}_2 \text{ annealing [8]. (d–f) Low-pressure (LP) structures, formed by annealing the HP structures at low pressure. The (1 \times 1)$_{\text{HP/LP}}$ surfaces have the same cation composition. Each structure is identified at the top by its superstructure periodicity and/or by a descriptive, short-hand label used in the text. Relative compositions are given in the bottom axes [1 ML is the number of Mn atoms in an (AMnO)$_2$ plane of LSMO(110), 4.64 \times 10^{14} \text{ cm}^{-2}].}](image-url)
FIG. 2. Evolution of the fishbone surface upon annealing at increasingly reducing conditions. (a1–d1, a2–d2) STM images (100 × 70 nm², and 26 × 26 nm², respectively). (a) Monophase fishbone surface. After annealing at 2 × 10⁻³ mbar (b), small (1 × 1)HP patches appear, and small structural changes occur in the fishbone. Annealing at 2 × 10⁻⁵ mbar (c) produces (1 × 1)LP areas, and transforms the remaining surface into the oblique structure of Fig. 1(e). UHV annealing (d) enlarges the (1 × 1)LP areas, and transforms the remaining surface into the stripes of Fig. 1(f). The process is reversible.

with the same quantitative coverages are observed under the same value of μO, obtained from different combinations of temperature and pO₂ [dashed oval in Fig. 3(a)]: This indicates that the observed surface structures are equilibrium phases, and that the phase separation is not kinetically limited. Recall that no phase separation occurs when starting from a (1 × 1) surface (orange): The (1 × 1) remains always monophase, hence the plot with μO shows a constant area fraction of 100%.

What drives the phase separation? One can rule out evaporation of cations (due to the reversibility), as well as cation diffusion to or from the bulk (at the employed conditions, cations can travel in bulk LSMO at most one atomic layer [46]): The phase separation thus occurs by mass transport across the surface. This is consistent with the fact that the average surface cation composition is conserved, as indicated by the reversibility of the process, and from the XPS data of Fig. 3(b): These show that the intensity ratios of selected core level peaks have no trend with μO. Given the sensitivity of XPS to the cation composition of monophase LSMO(110) structures [8], the absence of a trend indicates that the average surface composition is conserved. The proposed mechanism, sketched in Fig. 3(c), is that Mn travels across the surface and exposes the very stable, Mn-poor (1 × 1) phase, while enriching the remaining areas. The LEIS data of Fig. 3(d), showing that the monophase oblique phase is Mn-richer than the monophase fishbone, further support this scenario. Moreover, the stabilization mechanism of the Mn-rich phases at reducing conditions via the increase in their Mn content is consistent with the lower Mn oxidation state displayed by Mn-richer HP structures [8].

Because of the current lack of knowledge on the surfaces of perovskite oxides, one cannot determine whether the μO-dependent phase separation witnessed for LSMO(110) can be generalized to this material class. The only other perovskite oxide whose surfaces have been investigated in significant depth, SrTiO₃, shows a phase separation among stable surface structures with different A:B ratio [47], but not as a function of μO. This is presumably because SrTiO₃ does not possess the same flexibility in the oxidation state of the B cation as LSMO [48–50], and because of its much smaller tendency to form oxygen vacancies. Materials with easily reducible cations are expected to behave similarly to LSMO(110): After all, structurally complex B-site-rich reconstructions that depend on the cation- and anion-composition seem to be a general trait of perovskite oxides [41, 42, 51]. Moreover, an AO termination was preferentially exposed at reducing conditions also in another manganite [52], and a similar effect was predicted for LSMO(001) [53].

The remarkable diversity of the surface phases of perovskite oxides calls for methods capable of accessing and controlling their local surface properties as a function of different cation and anion compositions. Here, such a
with $\mu_0$ is a vertical line. The solid black circles represent the evolution of the initial fishbone surface, which phase-separates into $(1 \times 1)$ areas and regions characterized by LP, Mn-rich structures (oblique or stripes, see Fig. 2). The other curves represent surfaces that have been prepared initially to exhibit a slightly Mn-rich structure [between the fishbone and the $(2 \times 1)$ of Fig. 2(b, c)].

To derive the compositions of the LP phases formed during the phase separation, the number of cations on the whole surface was taken as constant at each annealing step, as supported by the reasonings above. This condition can be expressed as $S = \sum \theta_i s_i = \text{const}$, where $S$ is the density of Mn cations for a surface with multiple structures exposed, whose density of Mn cations and areal fractions are $s_i$ and $\theta_i$, respectively [54]. Initially (at high pressure) the surface exposes only a Mn-rich, HP surface, and $S = s_{\text{HP}}$. Referring this quantity to the density of Mn cations of the $(1 \times 1)$, $s_{(1 \times 1)}$, one has $\Delta s = \Delta s_{\text{HP}} = s_{\text{HP}} - s_{(1 \times 1)}$, which is known from Fig. 1: for the fishbone, $\Delta s_{\text{HP}} = 1.88(5)$ ML. By annealing at low pressure, the surface phase-separates into $(1 \times 1)$ areas and new LP Mn-rich areas. Now, $\Delta s = \Delta s_{\text{LP}} \theta_{\text{LP}}$, where $\Delta s_{\text{LP}}$ is the (unknown) density of Mn cations on the new LP phase [referred to $s_{(1 \times 1)}$], and $\theta_{\text{LP}}$ is the corresponding areal coverage (measured by STM). Since $\Delta s = \text{const}$ by assumption, one obtains that $\Delta s_{\text{LP}} \theta_{\text{LP}} = \Delta s_{\text{HP}}$. The only unknown, $\Delta s_{\text{LP}}$, can be derived and plotted in the phase diagram of Fig. 4(a).

Note that most of the investigated structures belong to a common family in which a minor change of the cation composition induces a slight modification of the surface structure [consider the reconstructions between the fishbone and the $(2 \times 1)$ [8], or the stripes discussed in Section S3]. As a result, they appear as ‘coexistence’ regions in the phase diagram, not as lines [grey and blue in Fig. 4(b), respectively].

In conclusion, this study demonstrates that the surfaces of perovskite oxides like LSMO(110) are very sen-

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**FIG. 4.** Experimental 2D surface phase diagram of LSMO(110). (a) Each curve describes the evolution of a given high-pressure surface of LSMO(110) with decreasing $\mu_0$. (b) Corresponding sketch.

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**FIG. 3.** Evaluation of surface compositions. (a) STM quantification of $(1 \times 1)$ coverages during the phase separation of LSMO(110) surfaces, starting from different high-pressure phases. Each point averages over 10–12 images acquired on $300 \times 300$ nm$^2$ on different sample spots. Orange: starting $(1 \times 1)_{\text{HP}}$. Full circles: starting fishbone (Fig. 2). Other symbols: starting surfaces between fishbone and $(2 \times 1)$. Dashed oval: different ($T$, $p_{O_2}$) combinations, equivalent to the same $\mu_0$. The table indicates the annealing parameters for each data point. Lines are a guide for the eye. (b) XPS intensity ratios show no trend with $\mu_0$ within the error bars (the data correspond to the experiment of Fig. 2, and are representative of all experiments). (c) Proposed mechanism: Mn travels across the surface to expose $(1 \times 1)$ and form new Mn-rich structures, preserving the overall cation composition. (d) LEIS spectra of different monophase surfaces (see also Section S2).

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Method is showcased for LSMO(110). As detailed below, it yields the quantitative cation compositions of Mn-rich, LP phases relative to $(1 \times 1)_{\text{LP}}$, based on the measured coverages of the phase-separated structures [Fig. 3(a)], and on the known differences in Mn content of the HP phases [8]. The outcome is shown in Figs. 4(a) and 4(b), displaying the experimental 2D surface phase diagram of LSMO(110) as a function of $\mu_0$ and the cation composition, and the corresponding sketch, respectively. In Fig. 4(a), each curve describes the evolution of a surface with given composition (horizontal axis) prepared at high $p_{O_2}$, and then annealed at decreasing $\mu_0$ (vertical axis). For instance, the left-most curve represents the evolution of the initially monophase $(1 \times 1)$ surface: Its cation composition never changes, hence its evolution
sitive to the cation composition and $\mu_O$. Depending on the treatment conditions, the local structural properties and compositions may be affected drastically: Even if a monophase surface is obtained at some oxygen chemical potential, different annealing conditions might cause a phase separation and the emergence of new structures. This rich behavior agrees with Gibbs’ phase rule, showcased here for the first time for the surface of a multielement oxide. The surfaces of other multielement oxides with easily reducible cations are expected to behave similarly, and to thus affect the performance of oxide-based-devices at different operating conditions. This work advances the needed knowledge and control of the surfaces of multielement oxides: It demonstrates how one can establish an experimental surface phase diagram over a wide range of cation and anion compositions, and how to quantify surface cation concentrations using phase separations.

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