Two-dimensional limit of crystalline order in perovskite membrane films

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Long-range order and phase transitions in two-dimensional (2D) systems—such as magnetism, superconductivity, and crystallinity—have been important research topics for decades. The issue of 2D crystalline order has reemerged recently, with the development of exfoliated atomic crystals. Understanding the dimensional limit of crystalline phases, with different types of bonding and synthetic techniques, is at the foundation of low-dimensional materials design. We study ultrathin membranes of SrTiO₃, an archetypal perovskite oxide with isotropic (3D) bonding. Atomically controlled membranes are released after synthesis by dissolving an underlying epitaxial layer. Although all unreleased films are initially single-crystalline, the SrTiO₃ membrane lattice collapses below a critical thickness (5 unit cells). This crossover from algebraic to exponential decay of the crystalline coherence length is analogous to the 2D topological Berezinskii-Kosterlitz-Thouless (BKT) transition. The transition is likely driven by chemical bond breaking at the 2D layer-3D bulk interface, defining an effective dimensional phase boundary for coherent crystalline lattices.

INTRODUCTION
Arguments based on statistical mechanics (1) rigorously excluded the spontaneous breaking of continuous symmetries in two-dimensional (2D) systems, indicating the absence of long-range order (Mermin-Wagner theorem). However, it was later suggested that 2D systems can maintain a quasi-ordered phase at low temperature if they can host pairs of topological defects—such as vortex or dislocation pairs—which maintain continuous symmetry with finite energy (2–9). The unpairing of these topological defect pairs can collapse quasi-long-range order and introduce an unusual phase transition known as the Berezinskii-Kosterlitz-Thouless (BKT) transition, which was experimentally shown in a few systems (10–13). 2D crystalline order is one of the 2D systems initially predicted to undergo the BKT transition by having edge dislocation pairs as the topological defects (3, 5, 6, 9). However, the experimental study of the BKT transition in crystalline lattices has been rare, because the thermal fluctuation energy is typically hundreds of times smaller than chemical bonding energies in crystalline materials, limiting experimental studies to artificial 2D crystalline systems, such as colloidal spheres (14). Within this historical context, the discovery of graphene and its high-crystalline quality are extraordinary (15). It is now understood that graphene forms intrinsic ripples to stabilize the lattice without violating the Mermin-Wagner theorem (16–18). Although graphene and other atomic crystals represent examples of 2D crystalline phases without apparent phase transitions on accessible sample length scales, it is an open question to determine the general phase diagram for 2D lattices, with different chemical properties and bonding nature.

RESULTS
Structural characterization of ultrathin SrTiO₃ membranes
SrTiO₃ is a perovskite oxide compound with ionic bonding and has a cubic structure at room temperature. SrTiO₃ is known for its wide physical and chemical stability windows; for example, the SrTiO₃ (001) surface does not undergo reconstructions for moderate temperatures (19). The TiO₂-terminated surface is stable in most common solvents; thus, SrTiO₃ is a popular substrate for oxide thin film growth (20). The stability and the simple crystal structure suggest that SrTiO₃ is an ideal crystalline lattice for studying 2D lattice physics without dominant contributions from chemical reactions and thermal decomposition. Here, we study the structural evolution of SrTiO₃ in the 2D limit, taking advantage of recently developed methods for fabricating freestanding thin films (21, 22). SrTiO₃ crystalline membranes of different thicknesses were synthesized by pulsed laser deposition (PLD), as previously reported for synthesis of large-area freestanding oxide layers (21). A water-soluble sacrificial layer (Sr₆Al₄O₁₃) and the oxide film of interest (SrTiO₃) were grown epitaxially on a SrTiO₃ (001) substrate (Fig. 1A), and the sacrificial layer was selectively dissolved at room temperature in deionized water to release the top SrTiO₃ layer. Both in situ and ex situ characterization confirmed that the oxide layers grown on the substrate were macroscopically single-crystalline, for which thicknesses were controlled with single u.c. (0.39 nm) accuracy (see Materials and Methods).

We examined the crystalline structure of freestanding SrTiO₃ membranes (Fig. 1B) using TEM. Figure 1C shows HR-TEM images of SrTiO₃ membranes of three different thicknesses (d). In the cases of relatively thicker membranes (8 u.c.), we found that the membrane is effectively single-crystalline with characteristic cubic lattice fringes. However, below a certain thickness, the film evolved to a mixture of crystalline and amorphous domains (4 and 3 u.c.) and further to an almost completely amorphous layer (2 u.c.). To quantify the observed crystalline phase transition, we used selected-area electron diffraction (SAED) patterns and dark-field TEM (DF-TEM) (23). SAED patterns of the entire suspended membrane (Fig. 2A) shows that the orientation of crystalline domains was mostly aligned within the 2-μm-wide area, even for the thinnest (2 u.c.) sample. DF-TEM, a diffraction-filtered imaging tool
using the SAED pattern, was used for spatially mapping the crystalline domains in the membranes of different thicknesses (Fig. 2B).

There are two primary observations from the DF-TEM images. First, the membrane changed from approximately single-crystalline (white) to amorphous (black) as it got thinner, for which domain sizes were well matched to the HR-TEM images. Second, even for single-crystalline membranes, there was a thickness-dependent population of dislocations (local black areas). The density of dislocations observed in the membranes was much larger (~100 times) than the dislocation density originating from the substrate and thin film growth (21, 24, 25). We calculated spatial autocorrelation functions (26) for each thickness and estimated the crystalline coherence length \( L \) to quantify the crystalline order based on DF-TEM images (see Materials and Methods). Figure 2C shows the observed continuous reduction of the crystalline coherence length, with a qualitative change in trend near 5-u.c. thickness.

The observed crystalline to amorphous transition in the 2D limit is surprising, because all SrTiO\(_3\) layers were single-crystalline before re-coherence length, with a qualitative change in trend near 5-u.c. thickness. Figure 2C shows the observed continuous reduction of the crystalline coherence length, with a qualitative change in trend near 5-u.c. thickness. (Fig. 2B).

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The observed crystalline to amorphous transition in the 2D limit is surprising, because all SrTiO\(_3\) layers were single-crystalline before release from the bulk substrates (Fig. 3). Several possible extrinsic factors to induce this transition—such as electron beam damage, surface chemical reactions, mechanical strain, and thermal effects (27)—were considered and examined in control experiments (see the Supplementary Materials). They show that SrTiO\(_3\) layers of a few u.c. thickness remain single-crystalline in all circumstances as long as the layer is epitaxially connected to a heterostructure on a bulk substrate, excluding dominant chemical reactions on the SrTiO\(_3\) surface. Instead, the crystalline phase transition occurs only during lift-off when the SrTiO\(_3\) membranes were detached, as confirmed by the surface crystalline structure observed by reflection high-energy electron diffraction (RHEED) in Fig. 3. The lift-off process involves bond breaking at the bottom interface via dissolution of the sacrificial layer (Sr\(_3\)Al\(_2\)O\(_6\)), which releases a large amount of free energy before the broken bonds are passivated (28). This free energy, as large as a few electron volts for ionic bonds, appears to be the main factor driving the structural transition. By contrast, other fluctuation sources—such as relevant mechanical and thermal energies—are orders of magnitude smaller and thus negligible, consistent with the control experiments showing no effect of temperature up to 1150 K and several percent strains (figs. S4 and S5).

**BKT transition in the perovskite oxide membranes**

Here, the structural transition shares much phenomenological similarity with the BKT transition expected for 2D lattices provided that the thickness can be understood to vary the effective “temperature” of the membrane. The BKT transition describes two phases separated by a critical temperature \( T_{\text{BKT}} \) (3, 6, 7): a quasi-long-range-ordered topological phase and a disordered phase. At low temperature \( T < T_{\text{BKT}} \), an effectively 2D crystalline lattice is stabilized with paired edge dislocations, the density of which increases algebraically with increasing temperature. At \( T_{\text{BKT}} \), where thermal fluctuations reach a fraction of the 2D dislocation energy \( E_{\text{2D}} \), dislocations unbind and freely proliferate, resulting in the exponential decay of the crystalline coherence length. Both of these phases were observed in the SrTiO\(_3\) membranes of different thicknesses (Fig. 2B). Although the thermal fluctuation scale

![Fig. 1. Freestanding SrTiO\(_3\) membranes of a few unit cell thicknesses. (A) A schematic SrTiO\(_3\)/Sr\(_3\)Al\(_2\)O\(_6\) film heterostructure grown on a SrTiO\(_3\) (001) substrate. The Sr\(_3\)Al\(_2\)O\(_6\) layer is dissolved in room temperature water to release the top SrTiO\(_3\) layer. (B) Optical image of a suspended SrTiO\(_3\) membrane [6 unit cells (u.c.) in thickness] on a silicon nitride transmission electron microscopy (TEM) grid with 2-μm diameter holes. Scale bar, 50 μm. (C) High-resolution TEM (HR-TEM) images of SrTiO\(_3\) membranes of different thicknesses. Scale bars, 10 nm.](http://advances.sciencemag.org/)

![Fig. 2. Crystalline domain imaging using DF-TEM. (A) Diffraction patterns from suspended SrTiO\(_3\) membranes (signals from the entire suspended area of 2-μm diameter), from 6- (left), 4- (center), and 2-u.c. thick (right) membranes. The exposure time varies from 1 (6 u.c.) to 10 s (2 u.c.). The red circle indicates the size of the aperture for DF-TEM to selectively collect signals from crystalline domains. (B) DF-TEM images from membranes of different thicknesses, for which crystalline domains are of white color. Scale bars, 10 nm. (C) Thickness-dependent (d) crystalline coherence length (L) calculated from the spatial correlation function (G) deduced from DF-TEM images. Inset: The raw data of the correlation function from a 6-u.c. thick membrane.](http://advances.sciencemag.org/)
from locally constrained dislocations (6 u.c.) to larger amorphous domains to disordered phase in a random manner. The abrupt size change but increased drastically in 5- and 4-u.c. membranes (Fig. 4B). The size configuration, as expected for paired dislocations (Fig. 4B, inset). The RHEED intensity of the 4-u.c. membrane diminished drastically and showed little signature of the crystalline phase. By contrast, the 8-u.c. membrane showed a similar RHEED pattern as the original film. No RHEED pattern was detected from the transferred 2-u.c. membrane.

\((k_B T \sim 25 \text{ meV})\) is far below \(E_{2D}\) even for the thinnest \(\text{SrTiO}_3\) membrane, electron volt–level fluctuation energy from bond breaking/passivation processes can be as large as \(E_{2D}\) in membranes of a few u.c. thickness, driving a BKT-like transition (Fig. 4A). For a given fluctuation energy and Young’s modulus, thickness becomes the effective tuning parameter instead of temperature here, with the phase boundary defined by the critical thickness \(d_{\text{BKT}}\).

On the basis of continuum elastic theory and the BKT transition model, we calculated the critical thickness \(d_{\text{BKT}}\) for \(\text{SrTiO}_3\) membranes. A simplified atomic potential model was used to estimate \(E_{2D}\) (deduced from the in-plane bonding potential \(E_i\)) and the chemical fluctuation energy (out-of-plane bonding potential \(E_x\)) equivalent to \(k_B T_{\text{BKT}}\). For an ionic atomic potential (Born-Landé model), \(d_{\text{BKT}}\) can be expressed as

\[
d_{\text{BKT}} = \frac{16\pi E_i}{\alpha E_x a}
\]

where \(\alpha\) is the Born exponent of the lattice and \(a\) is the lattice constant (details are presented in the Supplementary Materials). In \(\text{SrTiO}_3\), where \(\alpha \approx 8\) (29), for \(E_i = E_x\) (isotropic bonding), \(d_{\text{BKT}}\) is 6.3 u.c.

The snapshots of the evolution of crystalline coherence taken by DF-TEM (Fig. 2) enable quantitative analysis and provide compelling evidence for the transition based on BKT physics. We first examine the dislocation size in \(\text{SrTiO}_3\) membranes starting from the thick regime. Here, we found that nearly all dislocations are of zero Burgers vector configuration, as expected for paired dislocations (Fig. 4B, inset). The size was almost constant for 6-u.c. membranes and thicker membranes but increased drastically in 5- and 4-u.c. membranes (Fig. 4B). The size plot does not follow the percolation scaling law (30), which excludes the clustering of dislocations in a random manner. The abrupt size change from locally constrained dislocations (6 u.c.) to larger amorphous domains (5 u.c.) strongly suggests that there exists a critical thickness for a dislocation depairing transition between 5 and 6 u.c., close to the estimate from the atomic potential model \(d_{\text{BKT}} = 6.3\) u.c. for isotropic bonding—note that the weak bonding anisotropy expected between \(\text{SrTiO}_3\) and \(\text{Sr}_3\text{Al}_2\text{O}_6\) would reduce this value). Another important indication of the BKT transition is the exponential scaling observed in the disordered phase. Figure 4C plots the crystalline coherence length \(\xi\) as a function of the reduced thickness term \((d_{\text{BKT}}/d - 1)^{-\nu}\) for the membrane thicknesses below \(d_{\text{BKT}}\) (2 to 5 u.c.). The gray line represents the least-square fitting of four data points assuming an exponential relation. Inset: critical exponent fitting from the crystalline coherence length, resulting in \(\nu \approx -0.39\).

**Fig. 4. 2D crystalline phase transition in \(\text{SrTiO}_3\) membranes.** (A) Phase diagram of crystalline order in 2D membranes. The phase boundary is set by the BKT transition energy \(\left(1/2 E_{2D}\right)\) proportional to the 2D modulus, thus the membrane thickness (see the Supplementary Materials) (5, 6). Thermal fluctuations at room temperature \((k_B T)\) are far below the BKT transition scale. However, fluctuation energy from interface bond breaking exceeds \(k_B T_{\text{BKT}}\) in the thin limit, collapsing the crystalline quasi-order for membranes thinner than the critical thickness \(d_{\text{BKT}}\) during release from the bulk substrate. (B) Thickness-dependent dislocation area radius \(r_d = (\text{area})^{1/2}\) from DF-TEM images. Inset: An HR-TEM image of a dislocation for an 8-u.c. membrane. The green line encompassing the dislocation is closed, implying zero Burgers vector dislocation configuration. (C) A logarithmic plot of crystalline coherence length \(\xi\) versus \((d_{\text{BKT}}/d - 1)^{-\nu}\) for the membrane thicknesses below \(d_{\text{BKT}}\) (2 to 5 u.c.). The gray line represents the least-square fitting of four data points assuming an exponential relation. Inset: critical exponent fitting from the crystalline coherence length, resulting in \(\nu \approx -0.39\).

**General phase diagram of 2D crystalline lattices**

The simple 2D phase transition model introduced here can be expanded to arbitrary crystalline lattices. Figure 5 describes the phase diagram of crystalline order for different thicknesses and bonding anisotropies.
new opportunities for 2D materials of arbitrary crystalline structures, with controlled crystallinity.

**MATERIALS AND METHODS**

**Sample preparation**

SrTiO$_3$/Sr$_3$Al$_2$O$_6$ films were grown by PLD. On TiO$_2$-terminated SrTiO$_3$ (001) substrates, a 20-nm-thick Sr$_3$Al$_2$O$_6$ film was grown in an Ar partial pressure of $5 \times 10^{-6}$ torr with a laser fluence of 1.3 J/cm$^2$, followed by SrTiO$_3$ film growth at an O$_2$ partial pressure of $5 \times 10^{-6}$ torr with a laser fluence of 0.6 J/cm$^2$. The substrate was preannealed at 950°C with an oxygen partial pressure of $5 \times 10^{-6}$ torr for 30 min, and the growth temperature was maintained at 720°C for both Sr$_3$Al$_2$O$_6$ and SrTiO$_3$ layers. The entire film was grown in a layer-by-layer growth mode, for which the thickness was monitored by RHEED oscillations and later confirmed by atomic force microscopy (AFM) (fig. S1).

SrTiO$_3$ membranes were transferred to TEM grids by the polymer-transfer method similar to the study of Huang et al. (fig. S2) (23). A thin layer (200 nm) of polymethyl methacrylate was spun onto the film and baked at 90°C, followed by additional application of polypropylene carbonate (>100 μm) as a mechanical support to prevent bending of membranes. The entire sample was immersed in deionized water at room temperature until the sacrificial layer of Sr$_3$Al$_2$O$_6$ was completely dissolved, and the polymeer-SrTiO$_3$ layer was detached from the bulk substrate. The polymer-SrTiO$_3$ layer was scooped by a silicon nitride TEM grid. The polymer support was removed by either thermal decomposition in a tube furnace heated at 250°C in flowing O$_2$ or acetone wet etching followed by a critical point drying step. Both thermal decomposition and wet etching gave identical results for SrTiO$_3$ membranes of the same thickness.

**TEM image acquisition and image analysis**

HR-TEM and DF-TEM experiments were conducted using FEI Tecnai G2 F20 X-TWIN TEM and FEI Titan 80-300 TEM, operated at either 80 or 300 kV. Acquisition times for DF-TEM images were 3 to 10 s. The spatial resolution of DF-TEM imaging is 1 nm. A Gatan 628-0500 in situ heating holder system was used to increase the sample temperature up to 900°C. All DF-TEM images were taken at the field of view where no image change was observed for more than 1-min exposure, preventing any change by the beam exposure during the measurement.

The angle-averaged spatial autocorrelation function (G(r)) of the DF-TEM images is the statistical correlation of two points separated by distance r and was calculated following the method of Giraldo-Gallo et al. (26). The characteristic length scale L from G(r) represents \( \xi \) in the disordered phase, although it approximately corresponds to the inverse square root of the paired dislocation density in the quasi-ordered crystalline phase. Each data point in Figs. 2 and 4 was calculated from the correlation functions of multiple (>10) images acquired from the membranes of the same thickness.

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/3/11/eaao5173/DC1


fig. S2. Transfer of SrTiO$_3$ membranes.


fig. S4. Strain test using AFM force spectroscopy.

fig. S5. In situ heating experiment in TEM.

Control experiments
REFERENCES AND NOTES


Acknowledgments: We acknowledge L. Radzihovsky for valuable discussions and P. Giraldo-Gallo for technical support of data analysis. Funding: This work was supported by the Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, under contract no. DE-AC02-76SF00515 (membrane synthesis and testing) and the Gordon and Betty Moore Foundation’s Emergent Phenomena in Quantum Systems Initiative through grant no. GBMF4415 (characterization of crystalline order). Part of this work was performed at the Stanford Nano Shared Facilities, supported by the NSF under award no. ECCS-1542152. Author contributions: S.H.S. and H.Y.H. designed the experiment. S.H.S. and D.L. synthesized and characterized the materials. J.H.Y., S.S.H., and A.F.M. carried out TEM measurements, supported by Y.C. and H.Y.H. S.S.H., Y.H., and H.Y.H. wrote the paper with input from all coauthors. Competing interests: The authors declare that they have no competing interests. Data and materials availability: All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

Submitted 28 July 2017
Accepted 19 October 2017
Published 17 November 2017
10.1126/sciadv.aao5173

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Sci Adv 3 (11), eaao5173.
DOI: 10.1126/sciadv.aao5173