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ABSTRACT

The pseudoperovskite $BiMnO_3$ is a multiferroic candidate, but missing details of materials properties are impeding potential technological applications. $BiMnO_3$ has a centrosymmetric structure that precludes ferroelectricity in bulk stoichiometric samples, while some films have reported ferroelectricity along with a decreased magnetic response. This puzzle motivated a study of one such film, deposited by pulsed laser deposition onto $SrTiO_3$. Probes utilized include microscopy, diffraction, reflectometry, and X-ray absorption. These experiments in the context of the existing literature show an anomalous unit-cell volume and a (magnetic) depth profile. Then, the resulting inhomogeneous deficiency of Bi and Mn metals may stabilize a multiphase system that explains the decreased magnetism. Film nanostructure and strain effects are also considered.

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I. INTRODUCTION

This paper focuses on the structure, stoichiometry, and magnetism of a BiMnO₃ (BMO) film deposited on an SrTiO₃ (STO) (001) oriented crystalline substrate (BMO@STO₀₀₁).¹ Our motivation is the potential coexistence of ferromagnetism and ferroelectricity in this BMO pseudoperovskite that has been the subject of debate.² Looking ahead, this possible multiferroicity would open BMO to many applications, and one example is electric field control of magnetism for exploitation in low-power memory devices.³ Moreover, the ferromagnetic aspect of BMO has shown potential as a tunnel barrier for spintronics.^{4,5} Looking back, the first report of high pressure synthesis stabilizing the pseudoperovskite higher-density, ferromagnetic BMO phase was in 1965.⁶ The details of ionic positions within such a phase were found to be difficult to ascertain. Indeed, the experimental differences between a centrosymmetric, antipolar and noncentrosymmetric, polar phase are subtle to the point that the same pair distribution function data are consistent with both models and have been interpreted

the literature is that stoichiometric, bulk crystals of BiMnO3 are C2/c monoclinic, ferromagnetic, and paraelectric,⁸ although there is a minority report of a stoichiometric Pnma phase that is orthorhombic and antiferromagnetic.9 Some thin films have been reported to follow the centrosymmetric, ferromagnetic bulk behavior,¹⁰ while other thin films showed a hysteresis effect in charging as a function of the applied field and a decreased magnetic response.^{11,12} These confusions regarding BMO behavior seem to have removed BMO from ongoing multiferroic material considerations, as evidenced by the absence of BMO from a recent topical review.3 However, with appropriate clarification of apparent inconsistencies, BMO may be well enough understood to again consider for application. So we ask the question: how are the ferroelectric BMO@STO₀₀₁ different from other films and the bulk? The metastable nature of the pseudoperovskite BMO phase and the sensitivity of the structure, magnetic, and electric response to small changes in synthesis conditions and chemical content are connected to the difficulty in understanding this system. Moreover, the

differently at different times.^{2,7} After deliberation, the consensus in

technologically interesting thin film geometry adds another degree of complexity to the problem, as films preclude some measurement methodologies and may be strained or nanostructured compared to the free polycrystalline phases.

Previous reports show that temperature, pressure, and stoichiometry can induce structural phase transitions within the umbrella of BMO pseudoperovskite phases. The parent phase (I) is monoclinic and stable at room temperature; heating to 210 °C, there is a change to a different monoclinic phase named II; heating to 490 °C, a phase III, IV, or V is observed depending upon the atmosphere; and above 600 °C, BMO decomposes.¹³ Remaining at room temperature but applying hydrostatic pressure, a monoclinic P-phase appears at ~1 GPa, and an orthorhombic O-phase appears at ~6 GPa.¹⁴ Interestingly, changing the stoichiometry induces similar changes, where increasing relative oxygen content stabilizes the phases II, P, and O.¹⁵ For trivalent manganese compounds like BMO, static Jahn-Teller distortions yield short, medium, and long Mn-O distances that may induce long-range orbital ordering. The I phase has a three-dimensional orbital order, here dubbed α -BMO and illustrated in Fig. 1(a). The I, II, and P phases have similar symmetries, with long-range orbital order decreased or destroyed in II and P. The O-phase is different as it has a two-dimensional orbital order, here dubbed β -BMO and illustrated in Fig. 1(b).



FIG. 1. Orbital order and antiferromagnetism in BMO. (a) The *C2/c* monoclinic ground state structure of α -BMO. (b) The *Pnma* orthorhombic β -BMO phase observed at high pressure and off-stoichiometry. (c) The afmG2 magnetic structure in α -BMO. (d) The afmA magnetic structure in β -BMO. Unit cells are shown as black outlines.

This two-dimensional, $\beta\text{-BMO}$ orbital order is similar to that of LaMnO_3 (LMO). 16,17

The decreased magnetic response of films may then be due to stabilization of one of the known pseudoperovskite BMO phases in the previous paragraph, or perhaps yet another phase, having antiferromagnetic interactions. The ferromagnetism of BMO is stabilized by the complicated α -BMO orbital order,¹⁸ and a disturbance of the interstitial cation (e.g., Bi) off-centering by La substitution stabilizes the $\beta\text{-BMO}$ orbital order. 19 Antiferromagnetism may arise in α -BMO or β -BMO. In α -BMO, an antiferromagnetic phase (afmG2) was calculated to be energetically competitive.² Alternatively, for β-BMO, an LMO-like magnetic state (afmA) may be stabilized. In terms of the pseudocubic unit cell containing one formula unit of BMO, the afmG2 is quadrupled along each Cartesian axis and has a $k_{G2} = (1/4, 1/4, 1/4)_{cubic}$ ordering wavevector [Fig. 1(c)], while the afmA is doubled along only one pseudocubic Cartesian axis such that $k_A = (0, 1/2, 0)_{cubic}$ [Fig. 1(d)]. The afmA is A-type antiferromagnetic order, while the afmG2 is similar to the familiar G-type antiferromagnetic order but with two ferromagnetic planes perpendicular to the body diagonal rather than just the usual one. This afmG2 has been referred to as $\uparrow\downarrow\downarrow\uparrow$ previously.^{20,21} For afmG2, a ferroelectric response has been predicted²⁰ that shows a magnetoelectric effect qualitatively similar to that reported experimentally.²² The magnetic structure in that reference²⁰ referred to as $\uparrow\uparrow\downarrow\downarrow$ has a k_G = (1/2, 1/2, 1/2)_{cubic} ordering wave-vector and is G-type antiferromagnetism (afmG).

Here, we focus on the structure, stoichiometry, and magnetism of BMO@STO₀₀₁ that gives a ferroelectric response,¹¹ looking for similarities and differences compared to other BMO@STO₀₀₁ films. This style film of BMO@STO₀₀₁ has also been reported as magnetoelectric, in which an applied magnetic field reduces the ferroelectric response²² and with a strain dependence of the ferroelectric response.²³ Experimental probes were chosen to measure both intrinsic and extrinsic variables, ranging from nanostructure to crystal structure to chemical content, to look for the cause of the decreased magnetization and potential links to the electric properties. Epitaxial relationships are considered, and then we seek to convince the reader that cation vacancies play an important role by presenting various lattice constants and a chemical depth profile, ultimately correlating to the magnetization. Strain and ferroelectricity in this stoichiometry driven picture are touched upon, and then finally conclusions are summarized. Technical details are reported in Appendix A.

II. RESULTS AND DISCUSSION

A. Epitaxy of $\alpha\text{-}\mathsf{BMO}$ and $\beta\text{-}\mathsf{BMO}$ onto STO

For epitaxy, considering the relationship of the crystallographic cells to pseudoperovskite cells provides additional insight. The BMO structures may be represented as a combination of displacive and strain modes applied to a parent STO-like perovskite structure. A basis set that transforms between a parent perovskite lattice and the strained α -BMO lattice is then a' = a - 2b + c, b' = a - c, and c' = a + 2b + c, and for the β -BMO lattice, a transformation is a'' = a - c, b'' = 2b, and c'' = a + c, where a, b, and c are pseudoperov-skite lattice vectors.

table I.	Relating	α-BMO	pseudoperovskite	lattice	parameters	to	crystallographic
parameter	s.						

	STO exp. ²⁴	BMO exp. ¹⁸	α-BMO (DFT)	
a (Å)	3.905	3.932	3.918	
b (Å)	3.905	3.986	3.996	
c (Å)	3.905	3.932	3.918	
α (°)	90	88.59	88.65	
β (°)	90	90.88	90.96	
γ (°)	90	88.59	88.65	
a′ (Å)	9.57	9.532	9.540	
b' (Å)	5.52	5.606	5.591	
c' (Å)	9.57	9.854	9.853	
α′ (°)	90	90	90	
β′ (°)	109.47	110.67	110.98	
γ′ (°)	90	90	90	
V/f.u. (Å ³)	59.55	61.59	61.31	

Experimental data are available for α -BMO, as it is the stoichiometric BiMnO₃ ground state, and these are compared with density functional theory (DFT) + U|J calculations (Table 1). The calculated DFT + U|J ground state is ferromagnetic, with ferrimagnetic states, afmG, and afmG2 states all at ~10 meV per formula unit higher in energy. The pseudoperovskite α -BMO has an elongating tetragonal distortion that has minimal strain when matching the a- and c-axes to STO in-plane and then the b axis would be out-of-plane approximately along STO₀₀₁ [Fig. 2(a)]. For this configuration, there will be twinned structural domains that correspond



FIG. 2. Visualizing pseudoperovskite cells in relation to crystallographic cells. (a) The monoclinic α -BMO structure and (b) the orthorhombic β -BMO structure. The pink box represents the parent perovskite unit cell, the white boxes are crystallographic cells, and thick orange lines highlight the Mn–O long bonds.

	STO exp. ²⁴	β-BMO (DFT)		
a (Å)	3.905	4.007		
b (Å)	3.905	3.761		
c (Å)	3.905	4.008		
α (°)	90	90		
β (°)	90	95.29		
γ (°)	90	90		
a″ (Å)	5.523	5.930		
b″ (Å)	7.810	7.520		
c″ (Å)	5.523	5.406		
α″ (°)	90	90		
β″ (°)	90	89.97		
γ″ (°)	90	90		
V/f.u. (Å ³)	59.55	60.27		

TABLE II. Relating β-BMO pseudoperovskite lattice parameters to crystallographic

to $\approx 90^{\circ}$ rotations of the pseudoperovskite cell about the b axis. Having a larger population of long Mn–O bonds out-of-plane as in this epitaxy is consistent with the X-ray absorption (Appendix D).

The β -BMO phase has only been observed with elevated temperature, applied pressure, or off-stoichiometry so the DFT + U|J structure is considered (Table II). The β -BMO magnetic ground state is afmA, with a ferromagnetic state 1.1 meV per formula unit higher in energy and an afmG state 4.8 meV per formula unit higher in energy. The pseudoperovskite β -BMO has a compressive tetragonal distortion. Here, the epitaxial relationship may be when the pseudoperovskite a and b are in the plane having compressive and tensile strains, respectively, with c out of the plane approximately along STO₀₀₁ [Fig. 2(b)]. This c out-of-plane epitaxy would be consistent with the X-ray absorption Mn–O bonds, while b out-of-plane would not.

B. Lattice constants, stoichiometry, and magnetism

The pseudoperovskite lattice constants of BMO@STO₀₀₁.Jeen were measured with diffraction and microscopy and compared with the reported lattice constants of $BiMnO_{3+\delta}$ while considering the effect of the substrate-induced strain. Using a momentum transfer perpendicular to the film plane, X-ray diffraction (XRD) is sensitive to the [00L]STO family of planes. The strongest peaks are from the STO substrate, but additional peaks are seen due to the BMO film [Fig. 3(a)]. The BMO peaks are at positions consistent with an out-of-plane spacing of 3.944 Å. To investigate the in-plane registry, an additional sample rotation stage was used. This 3-circle X-ray diffraction experiment utilized an attenuator for scans in the vicinity of the STO peak to avoid detector saturation. Using a momentum transfer with a finite in-plane projection, Fig. 3(b), shows registered epitaxy with an in-plane pseudotetragonal lattice constant consistent with the STO substrate and the peak separation gives an out-of-plane lattice spacing of 3.961 Å. A cross-sectional high-resolution transmission electron micrograph (magnification 490 000×) of BMO@STO₀₀₁:Jeen with the $[110]_{STO}$ parallel to the electron beam viewing axis shows the registered-epitaxial nature of



FIG. 3. Epitaxy and crystallographic unit cells of BMO@STO₀₀₁. Jeen from diffraction and microscopy. (a) A locked-coupled 0-20 scan with the momentum transfer along the film normal, with 20 in the [002]_{STO} region. (b) $\omega \gamma \chi$ X-ray diffraction. The solid line is along the [211]_{STO} direction. The horizontal dashed line separates the STO region without any attenuator and the BMO region with an attenuator. (c) The interface of STO to BMO, where STO is at the left and BMO is at the right. The red lines are drawn along the $\approx 60^{\circ}$ intensity modulation. (d) Column-integrated image intensity as a function of distance across the image.

the film and the substrate [Fig. 3(c)]. There are stripes of intensity observed at an angle of $\approx 60^{\circ}$ to the STO interface, which are reminiscent of the monoclinic unit cell oriented with the $[010]_{BMO}$ normal to the plane of the image and the $[10-1]_{BMO}$ axis normal to the interface, and one explanation is cation vacancy ordering. The out-of-plane metal to the metal spacing of STO was measured to be 3.905 Å and the out-of-plane metal to the metal spacing of the BMO was measured to be 3.936 Å, by using the distance

between intensity maxima and minima as per Fig. 3(d). Within the resolution of the micrograph, no difference was found for the in-plane lattice constant of BMO compared to STO. Discrepancies between these BMO@STO₀₀₁:Jeen out-of-plane lattice spacing measurements (3.947 Å \pm 0.013 Å, with the uncertainty being one standard deviation) may be due to unquantified experimental uncertainties or the processing required for microscopy. Within apparent uncertainty, these pseudoperovskite lattice constants are consistent with a previous report of 3.94 Å measured with XRD on a similarly manufactured BMO@STO₀₀₁:Jeen film.²⁵

The measured unit-cell volume of BMO@STO₀₀₁:Jeen is anomalously smaller than the bulk BMO. This BMO@STO₀₀₁:Jeen volume of $V_{\rm film} = 60.19$ Å³ ± 0.19 Å³, 3.905 Å × 3.905 Å × (3.947 Å ± 0.013 Å),²⁶ has $\Delta V/V - 2.3\%$ compared to the bulk BMO volume $V_{\rm BMO} = 61.59$ Å³.¹⁸ Strain in films may affect the volume, with ceramics typically having a Poisson ratio of $v = 0.2 - 0.3,^{27}$ where biaxial strain relates the in-plane lattice constant change ($\Delta a_{\rm in}/a_{\rm in}$) to the out-of-plane lattice constant change ($\Delta b_{\rm out}/b_{\rm out}$) in the linear regime as

$$\Delta b_{\rm out}/b_{\rm out} = -2\nu/(1-\nu) \,\Delta a_{\rm in}/a_{\rm in}. \tag{1}$$

With DFT calculations reporting v = 0.26 for α -BMO and v = 0.32 for β -BMO phases,²⁸ the α -BMO epitaxy onto STO with an unstrained in-plane BMO lattice constant of 3.932 Å has an in-plane strain of $\Delta a_{in}/a_{in} = -0.69\%$ that predicts $\Delta b_{out}/b_{out} = 0.48\%$ or $b_{out} = 4.005$ Å, and $\Delta V/V = -0.84\%$ or $V_{film} = 61.08$ Å³. So, strain alone does not explain the observed BMO@STO₀₀₁:Jeen volume.

The anomalous volume reduction must then arise from off-stoichiometry. Thin film perovskites without valence tautomerism, such as STO, show an increased unit-cell volume for either oxygen rich or oxygen poor off-stoichiometry.²⁹ Conversely, off-stoichiometry in orthomanganites like BMO may show decreased unit-cell volumes when defects oxidize the Mn^{3+} to Mn^{4+} for charge balance as in $La^{3+}Mn^{3+}O_3 V = 61.20 \text{ Å}^3$ (Ref. 16) $(V^{1/3} = 3.941 \text{ Å})$ compared to $Ca^{2+}Mn^{4+}O_3 = 51.67 \text{ Å}^3$ (Ref. 30) $(V^{1/3} = 3.725 \text{ Å})$. The presence of both Mn^{3+} and Mn^{4+} in BMO@STO₀₀₁:Jeen is also supported by the observation of two Mn 2p-3/2 peaks, for an as-grown film, in the X-ray photoelectron spectroscopy (Appendix B).

The orthomanganites have a well-studied defect chemistry for off-stoichiometry. The accepted description of defect chemistry of $LaMnO_{3+\delta}^{31}$ is taken as a model for $BiMnO_{3+\delta}$, where vacancies as a result of off-stoichiometry are incorporated equally on the metal Bi and Mn sites to have the chemical formula more accurately written as $Bi_{3/(3+\delta)}Mn_{3/(3+\delta)}O_3$. Charge balance is then achieved by changing manganese valence, so the formula with oxidation states is

$$Bi_{3/(3+\delta)}Mn^{3+}_{(3-6\delta)/(3+\delta)}Mn^{4+}_{6\delta/(3+\delta)}O_3.$$
 (2)

Moreover, there can be unequal populations of the cation A (e.g., La or Bi) and B (e.g., Mn) site vacancies in LaMnO_{3+δ},³² where La_{0.961}Mn_{0.961}O₃ (δ = 0.12) was refined to La_{0.952}Mn_{0.973}O₃ such that usage of the simpler parameterization is expected to introduce vacancy quantity determination uncertainties at the 1% level.

The crystallographic lattice constants of BMO are sensitive to the stoichiometry. The unit-cell volume of BiMnO_{3+δ} as a function of excess oxygen, δ , was measured for powders,¹⁵ and the $\delta > 0$ data can be fit well to a line with

$$V(\delta) = 61.658 \,\mathring{A}^3 - 14.366 \,\mathring{A}^3 \delta. \tag{3}$$

This straightforward linear relationship masks observed subtleties in the lattice constants. As stoichiometry changes, the aforementioned four distinct crystallographic phases were reported as I, II, P, and O, where I has α -BMO orbital order, O has β -BMO orbital order, and long-range orbital order is apparently lost or decreased for II and P. Mapping these four phases onto a pseudoperovskite lattice to consider BMO@STO₀₀₁ epitaxy, there is a nonmonotonic dependence of the tetragonal distortion on δ such that b/a > 1 for I and P and b/a < 1 for II and O. Epitaxial relationships for I, P, and O have less strain when matching the a (and c) BMO axes in-plane to STO with b out-of-the plane, as opposed to having b in-plane. For II that has the shorter unique b axis closer to matching with STO, b and c are taken in-plane with a out-of-plane. Then, Eq. (1) can be applied with the reported $BiMnO_{3+\delta}$ in-plane lattice constants fixed to STO to predict the out-of-plane lattice constant for the four phases. Taking v = 0.26, a roughly linear dependence emerges with

$$b_{out}(v = 0.26, \delta) = 4.005 \text{ Å} - 0.780 \text{ Å} \delta,$$
 (4)

and for with the approximately volume conserving v = 0.5, this approach yields

$$b_{out}(v = 0.5, \delta) = 4.045 \text{ Å} - 1.070 \text{ Å} \delta.$$

These strained (to STO in-plane) and unstrained pseudoperovskite lattice constants are shown in Fig. 4(a). Casting these values a different way, and approximating the pseudoperovskite cells as orthorhombic, the volume dependence of BMO@STO₀₀₁ with v = 0.26 is

$$V_{\text{film}}(v = 0.26, \delta) = 61.068 \text{ Å}^3 - 11.895 \text{ Å}^3 \delta.$$
 (6)

Then, by inverting either Eq. (3) or Eq. (6), an approximation of δ can be made from the measured volumes, as shown in Fig. 4(b). The changing oxidation states of manganese that are a primary cause of the volume change are shown as a function of δ in Fig. 4(c). The magnetic response is also affected by stoichiometry, Fig. 4(d), and the reported powder data of BiMnO_{3+ δ} at 5 K and 5T can be fit to a quadratic dependence,

$$M(\delta) = 3.92 \,\mu_B / Mn - 8.60 \,\mu_B / Mn \,\delta - 44.54 \,\mu_B / Mn \,\delta^2, \qquad (7)$$

from which lattice constant derived δs may be used to compare with the reported BMO@STO₀₀₁ magnetization values. The effect of stoichiometry reproduces some of the observed changes in



FIG. 4. Influence of stoichiometry on BMO(@STO₀₀₁) lattice constants, oxidation states, and magnetism. (a) The pseudoperovskite lattice constants a, b, and c of BiMnO_{3+δ}, as defined in Fig. 2, and the BMO@STO₀₀₁ lattice constants under biaxial strains, as described in the text. The I, IP, and O are the observed crystallographic phases of BiMnO_{3+δ}, while α-BMO and β-BMO are the orbital orders of stoichiometric BiMnO₃ relevant to those phases. (b) The unit-cell volumes normalized to the number of formula units, Z, for BiMnO_{3+δ} with and without biaxial strain. Linear fits are described in the text. The experimentally determined volumes for BMO@STO₀₀₁.De Luca,³³ BMO@STO₀₀₁:Lee,¹⁰ and BMO@STO₀₀₁. Ohshima,³⁴ and this BMO@STO₀₀₁.Jeen film are plotted using the δ positions from the linear fits. (c) The oxidation states of manganese from Eq. (2). (d) The magnetization data at 5 K, 5 T per formula unit, Z, are shown for BiMnO_{3+δ}, where the quadratic fit parameters are listed as Eq. (7). Throughout this plot, the unstrained BiMnO_{3+δ} data powder data are taken from Ref. 15, and the extra data point at δ = 0 for (a) and (b) is from Ref. 18.

β-ΒΜΟ

ARTICLE

α-BMO

	b _{out} (Å)	V (Å ³)	δ′	δ	$M_{exp} \ (\mu_B/Z)^a$	$M(\delta')~(\mu_B/Z)$	$M(\delta)~(\mu_B/Z)$	"Thickness" (nm)
Jeen <i>et al.</i> ¹¹	3.947	60.19	0.07	0.10	1.1 (1.8) ^b	3.1	2.6	60
De Luca <i>et al.</i> ³³	3.99	60.84	0.02	0.06	2.8	3.7	3.2	60
Lee et al. ¹⁰	3.985	60.89	0.01	0.05	3.6	3.8	3.4	88
Ohshima <i>et al.</i> ³⁴	4.00	60.92	0.01	0.05	2.5	3.8	3.4	250
Ohshima	4.01	61.15	0.00	0.04	0.8	3.9	3.5	20

TABLE III. Estimating stoichiometry of BMO@STO₀₀₁ from measured lattice constants and comparing magnetizations. δ' is from Eq. (6) that considers biaxial strain, δ is from Eq. (3) that uses unstrained bulk BiMO_{3+ δ}, Z is the number of formula units, and M_{exp} is the reported magnetization.

^aThe BMO@STO₀₀₁:Jeen was measured at 10 K and 5 T, BMO@STO₀₀₁:De Luca at 8 K and 2 T, and BMO@STO₀₀₁:Ohshima at 5 K and 1 T. ^bThe value in parentheses was corrected for voids.²⁵

magnetization for BMO@STO₀₀₁ films, Table III, but the imperfect agreement implies the need for additional parameters to describe the films, and "thickness" (in quotes here because a single geometrical parameter to describe a nanostructured film is insufficient) is also correlated to the magnetic response. We looked for afmG2 and afmA magnetic reflections from BMO@STO₀₀₁:Jeen with the CORELLI neutron diffractometer, but we observed no signal above background that is reminiscent of the spin-glass-like behavior reported for BiMnO_{3.14} also showing no magnetic neutron diffraction. So, the unit cells of ferroelectric BMO@STO₀₀₁:Jeen are smaller than and suggest greater cation deficiency than bulk BMO

and other reported BMO@STO $_{001}$ films, which partly explains the decreased magnetic response in BMO@STO $_{001}$:Jeen.

C. Magnetic depth profile and stoichiometry

Depth profiles of electronic density, nuclear scattering density, and magnetic scattering density were measured with reflectometry to extract magnetic and stoichiometric depth profiles. Specular X-ray reflectometry (XRR) is sensitive to the one-dimensional electron scattering length density (SLD) profile along the normal axis of a film. A clear oscillation in the XRR data is observed, Fig. 5(a), with a sharp



FIG. 5. Depth profiling magnetization and stoichiometry. (a) The X-ray reflectivity. (b) The unpolarized neutron reflectivity. (c) The spin asymmetry from polarized neutron reflectivity. For reflectivity plots, the model is a solid black line plotted behind the data; the vertical reflectivity uncertainties are from counting statistics, and the horizontal reflectivity uncertainties are related to the instrumental resolution. (d) The electron scattering length density that reproduces the curve in (a). (e) The nuclear scattering length density that reproduces the curve in (c). The atomic force microscopy (AFM) volume fraction described in Appendix C, and reflectivity determined volume fraction [Ξ of Eq. (8)] determined from fitting the scattering length density and the most extreme deviation corresponds to the 95% confidence interval³⁶ and z = 0 corresponds to the STO[BMO interface. (g) The oxygen excess (cation deficiency), δ , determined from fitting the scattering length densities of (d) and (e). The horizontal dashed line at $\delta = 0.1$ is the approximate value that β -BMO is seen in BiMnO₃₊₆ powders.¹⁵

decay and subtle hump at $\approx 0.1 \text{ Å}^{-1}$ momentum periodicity. Specular neutron reflectometry (NR) is sensitive to the one-dimensional nuclear scattering length density profile along the normal axis of a film, in a similar way to XRR but with a different scattering source and therefore different elemental contrast. Oscillations are also observed in the NR data, Fig. 5(b), although the data are limited by neutron flux and the weaker contrast between the surface and substrate. Polarized neutron reflectometry (PNR) can compare different neutron spin cross sections to extract magnetic and nonmagnetic contributions to scattering length densities, giving a depth profile of magnetization. The so-called up-up (R_{++}) and down-down (R_{--}) reflectivity cross sections were measured that are sensitive to the non-spin-flip, in-plane magnetization (the same direction in which the magnetic field is applied for this geometry). The spin-flip cross sections up-down (R₊₋) and down-up (R₋₊) showed no signal above background, meaning that this experiment did not detect any coherent in-plane moment perpendicular to the applied magnetic field and neutron spin. The onset of magnetic order in BMO@STO₀₀₁:Jeen occurs at nominally 75 K,11 so the sample was cooled in a cryostat down to 5 K. To better visualize these cross sections, the data are plotted as spin asymmetry, $SA = (R_{++} - R_{--})/(R_{++} + R_{--})$. At 5 K with an applied field of 0.8 T in the plane, a finite spin asymmetry is observed, Fig. 5(c), which highlights the magnetic scattering from the sample. The fits shown on these reflectivities correspond to the models described in the next paragraph.

Often, the reflectivity of films may be modeled as monoslabs with an error function and a well-defined thickness, but the complex void structure of these films (as seen in the microscopy of Appendix C) requires a more-highly-parameterized, free-form profile where no analytical function is assumed and scattering length densities are allowed to vary with spline-interpolations between fixed points. The data were considered hierarchically to consistently constrain the parameter space, starting with XRR, then unpolarized NR, and then the PNR. For XRR, the STO scattering length density was taken from the reported crystal structure²⁴ to be $\{39.7 - 1.8i\} \times 10^{-6} \text{ Å}^{-2}$, the thickness of the BMO film was allowed to vary, and the refined model is shown in Fig. 5(d) with $\chi^2 = 14.5$. The largest SLD value is $\{57 - 5i\} \times 10^{-6} \text{ Å}^{-2}$ within the first $\approx 2 \text{ nm}$ of the substrate, drops to $53 - 5i \ 10^{-6} \text{ Å}^{-2}$ for the next $\approx 15 \text{ nm}$, and finally drops slowly to zero at \approx 45 nm from the substrate. For unpolarized NR, the poor contrast of STO (SLD = $3.54 \times 10^{-6} \text{ Å}^{-2}$) to the BMO film made fits to film thickness unstable, so the thickness from XRR was taken as a fixed value to create the profile shown in Fig. 5(e) with $\chi^2 = 1.8$. The peak value of nuclear SLD is observed to be $3.69 \times 10^{-6} \text{ Å}^{-2}$ and drops to $3.45 \times 10^{-6} \text{ Å}^{-2}$ before decaying to zero with a similar shape as the electron SLD. Finally, for the PNR, the nuclear SLD was fixed from the unpolarized data, and only the magnetic SLD was varied to generate the profile in Fig. 5(f) with $\chi^2 = 47.9$. The largest value of the magnetic SLD being $0.4 \times 10^{-6} \text{ Å}^{-2}$ corresponds to $0.8 \,\mu_B/Mn$.

The electron and nuclear scattering length densities from reflectometry can be used as a measure of stoichiometry by using the two-parameter model for the chemical formula per unit cell (volume),

$$\Xi Bi_{3/(3+\delta)} Mn_{3/(3+\delta)} O_3,$$
(8)

where $\Xi = [0,1]$ is the depth dependent physical volume fraction that takes into account the decrease in the film material present toward the BMO air interface due to nanovoids between film islands, as described in Appendix C. Using Eq. (8) and the tabulated values of (neutron or X-ray) scattering lengths, b_i, gives an expression for the $SLD(z) = \Xi(z) \left(\frac{3}{3+\delta(z)} b_{Bi} + \frac{3}{3+\delta(z)} b_{Mn} + 3b_O \right) / V.$ This reflectivity determined physical volume fraction compares well to the volume fraction measured by atomic force microscopy (AFM) (Appendix C) as shown in Fig. 5(f). The excess volume fraction above 50 nm in the AFM data is due to the breakdown of the convexity ansatz in the microscopy analysis due to the presence of surface chunks. The oxygen excess (cation deficiency) strikingly shows a depth dependence [Fig. 5(g)] that anticorrelates to the magnetic depth profile.³ To summarize the depth profile results for BMO@STO₀₀₁:Jeen, the magnetic response (cation deficiency) is greater (less) near the STO BMO interface than the BMO air interface, and there is a nontrivial void structure.

This depth dependence of the physical volume due to nanostructure may then be used to refine the comparison of BMO@STO₀₀₁ magnetizations. The BMO@STO₀₀₁:Ohshima films span "thickness" of 25 nm to 250 nm, with an approximately linear increase in magnetization with thickness up to 60 nm that plateaus for larger thicknesses. This crossover in BMO@STO₀₀₁:Ohshima may then be explained by a transition from island formation to layer-plus-island growth. Indeed, this BMO@STO₀₀₁:Jeen film is very near such a crossover point, as the increased SLD in the first few nanometers may be explained by layer-growth topped by coalescing islands. A semiquantitative model for BMO@STO₀₀₁:Jeen that takes the data for Ξ and δ at 10, 20, 30, and 40 nm and uses the M(5 K, 5 T, δ) of Eq. (8) then gives 1.9 μ _B/Mn, while ignoring the effects of magnetic coherence between different $\boldsymbol{\delta}$ regions and surface effects. The original report on BMO@STO₀₀₁:Jeen assumed a 60 nm "thick" film and $1.0 \mu_B/Mn$ for BMO@STO₀₀₁:Jeen at 10 K, 5 T, but utilizing AFM to more carefully normalize the same magnetization data to film volume yielded $1.8 \,\mu_B/Mn$,²⁵ which is in excellent agreement with the semiquantitative Ξ and δ model.

D. Strain

It has been established that substrate-induced strain may induce ferroelectricity in pseudoperovskite thin films,³⁷ and the difference between the electric response of bulk BMO and the BMO@STO₀₀₁ films may be due to a strain effect. Bolstering the likelihood of this possibility is the observation of strain modulation of the remnant polarization of BMO@STO₀₀₁, where mechanically applied compressive and tensile strain, respectively, decrease and increase the remnant polarization.²³ However, a DFT study of the ferromagnetic ground state of a-BMO showed no induced polarization with strain.³⁸ Additional strain investigations were performed with DFT to test the energetic favorability of other potential BMO crystal structures, but for the STO in-plane lattice constant, no energetically competitive phase was predicted.³⁹ A Pnma phase that we classify here as β-BMO (having LMO-like orbital order) was tested in the aforementioned DFT study, but only for orientations with short and long Mn-O bonds in the plane of the film. Here, we do not need to

explicitly invoke any substrate-induced strain to reproduce the observed magnetic properties of BMO@STO₀₀₁.

E. Ferroelectricity

With parameterization for the structure and magnetism of films that can account for the differences between bulk-stoichiometric-BMO and various BMO@STO₀₀₁ films, it begs the question if the (ferro) electrical properties may be captured by the same parameter set. For a definitive answer, additional experiments are required in which the electrical polarization is measured for different BMO@STO₀₀₁ samples that are grown with specific stoichiometry and nanostructure, as parameterized by high-field magnetization, unit-cell constants, and depth profiles. Here, a few hypotheses are listed. The multiphase nature of the ferroelectric BMO@STO₀₀₁:Jeen may not require ferroelectric regions at all, but instead a mixture of different antiferrodistortive regions that together produce a ferrielectric state.⁴⁰ The controversy of ferroelectricity in BMO centered on stoichiometric samples, but defects such as the cation vacancies of BMO@STO₀₀₁: Jeen may play a primary role in the electrical field induced distortions or even stabilize the afmG2 phase. The effect of nanostructure on the electrical response in BMO is also unclear. The ferroelectric response of BMO@STO₀₀₁ may be a result of changes in STO, as there is a structural transition in STO near to the observed onset of hysteresis in polarization, and this STO transition even manifests itself in a surface rumpling⁴¹ that is observed in the neutron reflectometry (Fig. S2 in the supplementary material).

III. CONCLUSIONS

The decreased magnetism in BMO@STO₀₀₁:Jeen may be explained by a combination of cation deficiency and nanostructure, both of which are depth dependent. This conclusion results mainly from the observed (magnetic) scattering length density profiles and decreased unit-cell volumes and is consistently supported by the additional chemical and nanoscale probes. As such, substrate strain is not found to be a primary factor, but the chemical pressure induced by off-stoichiometry can drive structural changes that stabilize antiferromagnetic interactions. From these considerations, the A-type (afmA) antiferromagnetism and disorder by defects are more relevant to explain the decreased magnetic response than the thought-provoking afmG2 state. There is still more work to be done to understand the remnant electric polarization of BMO@STO₀₀₁:Jeen. The application potential for these BMO films may be considered in an analogous way to bismuth ferrite,³ and while bismuth ferrite has room temperature effects and BMO does not, BMO ferroelectricity persists at temperatures above that of liquid nitrogen and may yet have technological application depending upon the emerging material properties.

SUPPLEMENTARY MATERIAL

See the supplementary material for a photograph of the sample, neutron reflectivity rocking curves, and X-ray diffraction of wider angles.

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APPENDIX A: TECHNICAL DETAILS

The BiMnO₃ film was grown on a 1 mm \times 1 cm² [001]-oriented STO (STO₀₀₁) substrate using pulsed laser deposition (PLD) following the reported protocol.¹¹ Visual inspection shows an evenly deposited film that is smooth, reflective, and nearly translucent (Fig. S1 in the supplementary material).

This work employed three microscopy techniques. An FEI Helios NanoLab 660 Dual Beam microscope was used for Scanning Electron Microscope (SEM), and nanomachining was performed with a Focused Ion Beam (FIB). Atomic force microscope (AFM) images were taken using a Digital Instruments multimode scanning probe microscope at room temperature. An FEI Titan 80-300 Analytical microscope was used to collect Transmission Electron

Microscope (TEM) images. Microscopy images were quantified with the Gwyddion software. $^{\rm 42}$

Three different reflectometry probes were utilized. X-ray reflectometry (XRR) experiments were performed on a Bruker D8 Advance diffractometer using a copper anode and a Sol-X detector. Specular reflectivity data were taken with the detector angle equal to the incident beam angle, and an attenuator was used for positions near and below the critical edge when the reflected intensity was at maximum. Unpolarized neutron reflectometry (NR) was performed on the NG-7 reflectometer ($\lambda = 4.768$ Å) at the NIST Center for Neutron Research (NCNR). Polarized neutron reflectometry (PNR) was performed on the Polarized Beam Reflectometer $(\lambda = 4.75 \text{ Å})$ reflectometer at the NIST Center for Neutron Research.⁴³ The magnetic field of 0.8T is in the plane of the film. Reflectometry data were reduced to a reflectivity profile and corrected for the footprint using reflred in the reflpak suite.44 Profile fitting was performed using the Refl1D software package, with the DREAM and differential evolution algorithms that attempt to avoid local minima in the parameter space.³⁶ The fitting algorithm in Refl1D, by way of a Monte Carlo Markov-Chain based optimization, allows for parameter uncertainty estimation via the standard deviation (σ_{STD}) of the tested cases, and n = 1000 test cases were used in all fits. For reference, $1\sigma_{STD}$ is the 68% confidence interval, $1.96\sigma_{STD}$ is the 96% confidence level, and $2.58\sigma_{\text{STD}}$ is the 99% confidence level. Throughout, the momentum transfer Qz is normal to the plane of the film.

Two diffractometers were used for elastic scattering. Specular X-ray diffraction (XRD) experiments were performed on a Rigaku Ultima III Analytical X-ray diffractometer with a θ -2 θ design using a copper anode ($\lambda_{K\alpha 1} = 1.5406$ Å, $\lambda_{K\alpha 2} = 1.5444$ Å). The off-specular XRD reciprocal space map was measured using an anode with the K_{α} line of Cr ($\lambda \approx 2.29$ Å).

X-ray spectroscopy was also performed. The X-ray photoelectron spectroscopy (XPS) data were collected on a Kratos AXIS Ultra DLD spectrometer equipped with a monochromatic Al source (1486.6 eV) operating at 140 W under a vacuum of 1×10^{-8} Torr. In region scans, the pass energy of the analyzer was set at 20 eV using an energy step size of 0.05 eV, while survey scans used an analyzer pass energy of 160 eV with a step size of 1 eV. The C 1 s peak of the adventitious carbon was set to 284.8 eV as a point of reference. Relative sensitivity factors provided with the instrument were used for elemental analysis. Shirley backgrounds were used, and peaks were fit to pseudo-Voigt functions. The X-ray absorption fine structure (XAFS) data were collected at the National Synchrotron Light Source on beamline X23a2. The double crystal monochromator was operated with a pair of Si 311 crystals. A four-element Si-drift detector was used to detect fluorescence data. Transmission data from reference metal foils, positioned after the sample and recorded simultaneously with each scan, were used for energy calibration. Background correction and normalization of spectra were done using Athena,²⁵ and the FEFF²⁶ interface Artemis²⁵ was used for quantitative fitting. The effective scattering amplitudes, phase shifts, and mean free paths were calculated using FEFF 6L.

The ISODISTORT suite of programs was used to understand the structural distortions from perovskite in the BMO.⁴⁵ The detailed, quantitative descriptions of the strain modes (irreducible representations) may be found by accessing the ISODISTORT website.

Density functional theory (DFT) was used to calculate magnetic and electric properties. The VASP software^{46,47} was used

with the generalized gradient approximation (GGA) functional of Perdew-Burke-Erzenhof as PBEsol.⁴⁸ The projector augmented wave (PAW) method^{49,50} was used for valence electrons with the included pseudopotentials applied via Bi_d (15, 6s25d106p3), Mn_sv (15, 3p4s3d), and O (6, s2p4) where valence electrons and states are in parentheses. For the monoclinic cells, a Γ -centered mesh was generated with (4 × 6 × 4) k-points, and for the orthorhombic cells, a Γ -centered mesh was generated with (5 × 5 × 5) k-points. Plane waves were cut above a kinetic energy of 550 eV. Hubbard and Hund energy parameters are from the DFT exploration of LaMnO₃; U_{Mn} = 8.0 eV and J_{Mn} = 1.9 eV.⁵¹ Polarization was calculated with the Berry phase implementation of VASP.⁵²

APPENDIX B: CHEMICAL COMPOSITION FROM X-RAY PHOTOELECTRON SPECTROSCOPY

X-ray photoelectron spectroscopy (XPS) was performed over a broad range of energies in order to investigate the chemical composition of the film, with Ar⁺ etching to measure as a function of depth. In order to extract stoichiometry, element efficiency calibrations depend upon the chemical matrix, which is a potential source of uncertainty. The surface of the film has carbon, as expected, and this carbon is used to calibrate the energy. A few elemental ratios are plotted as a function of sputtering cycles in Fig. 6(a), where some breakthrough is made to the substrate by the 13th cycle where Ti and Sr are first detected as illustrated by the Sr/Mn ratio. The Bi/Mn and O/Mn ratios are seen to be much greater than 1 at the surface and then decrease, which leads to an assignment of surface chunks in microscopy to Bi₂O₃ that is consistent with the unattenuated X-ray diffractogram in Fig. S3 of the supplementary material. Some variability of Bi/Mn and Ti/Sr is expected to arise from different ejection potentials of those ions. Focusing on etching cycles 1, 2, 9, and 15 gives information on the as-grown surface, partially etched, deep into the BMO region, and after breaking through to the STO, respectively. For the bismuth signal, Fig. 6(b), at the surface, there is a dominant Bi 4f7/2 signal at a binding energy of 158.0 eV that is attributed to the preponderant BMO as well as a side peak at 159.3 eV that is consistent with Bi_2O_3 .⁵³ With etching, there is a chemical shift to higher binding energies of the dominant signal that is typically due to increased oxidation number. Eventually, when the STO layer is reached, a small peak at 156.9 eV appears that is consistent with metallic Bi.⁵² The manganese region shown in Fig. 6(c) shows a splitting of the Mn 2p3/2 at the surface, with peaks at 640.5 eV and 641.2 eV. These two populations may be from multiple phases in the volume of the film or from a separate surface termination state. These Mn 2p3/2 peaks do not shift appreciably with etching, but there is some increased population of the higher binding energy component. After etching, a shakeup peak appears at 646.6 eV that is attributed to Mn^{2+} evolving from the Ar^{+} processing. Strontium is not present in the BMO, but after etching through to the STO, a Sr 3d5/2 peak appears at 133.8 eV, Fig. 6(d), which is close to the 132.8 eV reported for STO.⁵³ Similarly, Ti is seen only after etching through and has 3p3/2 at 459.8 eV, Fig. 6(e). The oxygen 1s XPS shows changes with the sputter cycle, Fig. 6(f). At the surface, there is a dominant peak 528.8 eV attributed to a pseudo-perovskite phase and also physisorbed oxygen (532.0 eV), which is mostly



FIG. 6. Chemical content from X-ray photoelectron spectroscopy. (a) Selected elemental content ratios as a function of Ar⁺ sputtering cycle. At different stages of etching, region scans for (b) Bi 4f, (c) Mn 2p, (d) Sr 3d, (e) Ti 2p, and (f) O 1 s are shown.

removed after the 1st cycle. By the 2nd cycle, the dominant peak has shifted to 529.2 and the broadside peak near 531.4 meV may be chemisorbed oxygen. A chemical shift continues with etching, such that at the 9th cycle and the 15th cycle, there is one asymmetric peak at 529.4 eV and 529.6 eV, respectively.

APPENDIX C: NANOSTRUCTURE

Atomic force microscopy (AFM) shows discrete islands on the surface of the film that have distinct facets, Fig. 7(a). The x and y coordinates denote direction in the plane of the film, with the z coordinate normal to the interface. A two-dimensional slope distribution, ρ_{2d} , shows the faceting of the islands, Fig. 7(b). The diffuse background is due to the surface chunks. There is a clear peak at the origin, which corresponds to "flat" facet//STO₀₀₁ regions of the sample. There are four peaks at nominally $(dz/dx, dz/dy) = (\pm 0.13,$ ±0.13) that correspond to facet//STO_{11L}. A series of facet//STO_{10L} peaks are seen, which are visualized in Fig. 7(c), and may be fit to a series of gaussians at nominally dz/dx = [-0.64, -0.47, -0.11], -0.03] on the better resolved negative side, with areas relative to the central (dz/dx, dz/dy) = (0,0) peak of [0.03, 0.25, 0.90, 0.27] and variance $\sigma = [0.04, 0.20, 0.20, 0.25, 0.01]$. From this identification, an approximate segregation of the facet populations is color coded in Fig. 7(d) and mapped onto the AFM image in 2 (e). This definition gives relative surface areas for the different regions: 25% facets// STO₀₀₁, 24% facets//STO_{11L}, 44% facets//STO_{10L}, and 7% are surface chunks. Height distributions, ρ_{zz} may be extracted for the different facets, Fig. 7(f), and the facet//STO₀₀₁ may be fit to two gaussians: 90% are island tops at a height of $z = 48.2 \text{ nm} \pm 0.3 \text{ nm}$ with variance $\sigma = 7.2 \text{ nm} \pm 0.5 \text{ nm}$ and 10% are interisland valleys at a height of $z = 27.0 \pm 0.3 \text{ nm}$ with variance $\sigma = 3.6 \text{ nm} \pm 1.1 \text{ nm}$. A distribution of the magnitude of the inclination angle, ρ_{0} , is shown in Fig. 7(g). The facet//STO₀₀₁ is slightly bimodal but may be fit by one gaussian with variance $\sigma = 5.84^{\circ} \pm 0.2^{\circ}$. The facet//STO_{10L} has multiple peaks that were already fit in slope-space above. The facet//STO_{11L} may be fit by one gaussian with variance $\sigma = 3.7^{\circ} \pm 0.1^{\circ}$. The uncertainties in this paragraph are those of the fitting variances.

Cross-sectional SEM (CS-SEM) gives another way to look at local nanoscale morphology and extract relevant length scales for the film nanostructure. For CS-SEM, the BMO@STO₀₀₁ was first coated with 100 nm of carbon, then $2\,\mu m$ of platinum. After coating, a $1 \mu m$ strip aligned along the $[100]_{STO}$ was removed for imaging, which effectively integrates through lateral features to create a two-dimensional profile. Two different magnifications show the integrated islands, Figs. 8(a) and 8(b). A binary threshold of the CS-SEM image extracts a representation of the BiMnO₃ film without ghosting or lensing effects, Fig. 8(c). A one-dimensional depth profile of intensity is generated by integrating over the lateral dimension that is horizontal on this page. Alternatively, a depth profile can be generated from the AFM data by assuming the grains are convex and summing pixels up to a rolling height threshold (this assumption fails for the surface chunks). The CS-SEM depth profile is comparable to the AFM derived volume and both show that island heights vary between 20 nm and 60 nm, and can be



FIG. 7. Crystal facets from AFM. (a) A typical AFM image of BMO@STO₀₀₁ where the x and y directions are approximately along the STO₁₀₀ and STO₀₁₀, respectively. (b) The slope distribution, ρ_{2d} , with a logarithmic intensity scale. (c) An integration of ρ_{2d} for dz/dy = [-0.07 to 0.07] with a rotation correction for the slight misalignment between x and y with STO₁₀₀ and STO₀₁₀. Lines are gaussian fits to the data. (d) A binning of ρ_{2d} that color codes four distribution regions. (e) A colorization showing the projected area of the different facet populations. (f) The height distribution (of facets). (g) The inclination angle distribution (of facets).

approximated by a normal distribution (error function) centered at 40 nm with a 10 nm spread, Fig. 8(d). The lateral length scales are quantified with a height-height-correlation-function, $H(r) = 2\sigma^2 \{1 - \exp[-(r/\xi^2)]\}$, where ξ is an autocorrelation length that measures the distance over the surface with the least correlations as a peak to a valley, and σ is the surface roughness. The fit in Fig. 8(e) yields $\xi = 90 \text{ nm} \pm 10 \text{ nm}$ and $\sigma = 7.05 \text{ nm} \pm 0.08 \text{ nm}$, with uncertainties derived from least squares variances.



FIG. 8. Length scales from microscopy. (a) A cross-sectional scanning electron microscopy $8.5\,\mu$ m × 500 nm image taken at 15000× amplification. (b) A 2.15 μ m × 350 nm image taken at 65000× amplification. Both (a) + (b) show, from the top down, Pt coating, C coating, BiMnO₃, and SrTiO₃. (c) A binary threshold representation displays BiMnO₃ only, as black pixels. (d) Depth profiles of the BiMnO₃ film as a function of height normal to the interface, z, along with a fit to the AFM data. (e) The height-height-correlation-function, H, as a function of lateral distance, t.

APPENDIX D: LOCAL STRUCTURE FROM X-RAY ABSORPTION SPECTROSCOPY

X-ray absorption (XAS) is sensitive to atomic distances and was used to investigate the orbital order of manganese. Measurements were performed in the vicinity of the Mn K-edge at ambient temperature with polarization, p, oriented 2° from the surface normal $[001]_{\text{STO}}$ (p₀₀₁) and polarization along the $[010]_{\text{STO}}$ that is the same as the $[100]_{STO}$ (p₁₀₀). Because the absorption $\chi(k)$ is proportional to $|\mathbf{p} \cdot \mathbf{r}|^2$, bonds in the direction of the X-ray polarization vector are preferentially sampled by polarized extended X-ray absorption fine structure (EXAFS). In this manner, the out-of-plane and in-plane scattering path distances may be decoupled and independently modeled. The extended X-ray absorption fine structure (EXAFS) show a difference between p_{001} and p_{100} measurements, Fig. 9(a). These data are shown (and fit) with so-called k-weights of 3, where the signal intensity is multiplied by k³ in order to better visualize the oscillations against the inherent damping. To focus on the scattering from the Mn-O pairs, a Fourier filter is applied from r = 1 Å to r = 2.5 Å, Fig. 9(b), where the main difference between in-plane and out-of-plane is seen in the intensity around 7 Å^{-1} to 10 Å^{-1} where the out-of-plane data increase intensity as a function of k. A single Mn-O distance can only reproduce this type of intensity increase if unphysical negative Debye-Waller factors are used while if more than one Mn-O distance is present in similar quantity then a beating between the two components creates such an intensity modulation. Modeling three or more Mn-O distances was found to be unstable during minimization, so a model having two Mn-O distances was used to semiquantitatively reproduce the data, Fig. 9(c). For the out-of-plane data, two Mn-O distances are found to be 1.918 Å and 2.237 Å,

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FIG. 9. Manganese to oxygen distances from X-ray absorption. (a) Mn K-edge EXAFS spectra. (b) Fourier-filtered first-shell contributions to the EXAFS. (c) Model fits as described in the text.

with relative amplitudes of 1 and 0.3846, respectively. For the in-plane data, two Mn-O are found to be 1.910 Å and 2.125 Å, with relative amplitudes of 1 and 0.1930, respectively.

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