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The observation of a surface resonance state in the valence-band structure of the perovskite $\text{La}_{0.65}\text{Ba}_{0.35}\text{MnO}_3$

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Abstract. The valence-band electronic structure of a crystalline thin film of $\text{La}_{0.65}\text{Ba}_{0.35}\text{MnO}_3$ has been investigated using angle-resolved photoemission. The observed valence-band structure has a substantial surface contribution and is strongly influenced by the surface conditions. Surface contamination and disorder attenuate the emission from a Mn-3d-derived state at a binding energy of 3.3 eV. This state was found to be localized at the surface with dispersion only in the plane of the surface and exhibited a strong intensity dependence on emission angle. On the basis of a simple LMTO-ASA bulk band calculation, it is clear that this state does not fall within a bulk band gap. We have therefore identified this Mn-3d-derived state at 3.3 eV below E_F as a surface resonance.

The $\text{La}_x\text{M}_{1-x}\text{MnO}_3$ perovskites ($M = \text{Ca}, \text{Sr}, \text{Ba}$) have attracted considerable attention, in part because they exhibit giant magnetoresistance (GMR). Extensive experimental [1–8] and theoretical [9–16] efforts have been undertaken to explore the electronic structure of these materials. Although the electronic and magnetic phase transitions of these materials appear to be coupled [2], a fundamental understanding of this relationship does not yet exist. As with the perovskite superconducting materials, photoemission provides insight into the electronic structure of the manganite materials. Nonetheless, it is unclear whether photoemission studies are representative of the bulk electronic structure. Recently Liu and Klemm [17] pointed out that the surface of the high- T_C superconductor materials can have a larger T_C than the bulk and a surface electronic structure that differs from that of the bulk. We believe that a similar situation exists in the manganite perovskite materials, which, in many respects, are similar oxide materials. In this article we will demonstrate that the valence-band structure of $\text{La}_{0.65}\text{Ba}_{0.35}\text{MnO}_3$, as probed with angle-resolved valence-band photoemission, is subject to extensive contributions from the electronic structure that is localized at the surface.

The $\text{La}_{0.65}\text{Ba}_{0.35}\text{MnO}_3$ thin film was grown on a LaAlO_3 (100) substrate at 700 °C by RF sputtering in a 2:1 argon/oxygen atmosphere maintained at 20 mTorr. The ceramic sample was subsequently annealed at 900 °C in an oxygen atmosphere at 2 atm for 10 h to optimize the compositional stoichiometry and homogeneity. On the basis of room temperature x-ray diffraction studies, the crystalline structure was determined to be cubic and single domained. Rhombohedral or orthorhombic distortions were not observed with x-ray diffraction. The film thickness was nominally 2500 Å. A clean and well ordered surface of the $\text{La}_{0.65}\text{Ba}_{0.35}\text{MnO}_3$ film was obtained *in situ* by repeated cycles of annealing at ≈ 450 °C and photo-stimulated desorption of the surface by exposing the sample surface

to white light from the synchrotron. The surface cleanliness and order were monitored by means of low-energy electron diffraction (LEED) and photoemission. For the clean surface, a (1×1) LEED pattern was observed, occasionally with the indication of a superlattice structure.

Our photoemission experiments were carried out in a UHV chamber equipped with a hemispherical electron energy analyser with an angular acceptance of $\pm 1^\circ$. The light was provided by a 3 m toroidal grating monochromator at the Synchrotron Radiation Center in Stoughton, Wisconsin. The combined energy resolution was approximately 150 meV. The chamber base pressure was 6×10^{-11} Torr. All spectra relevant for this paper were acquired with p-polarized light ($\alpha = 65^\circ$) and have been referenced to the Fermi level, as determined from a Ta foil.

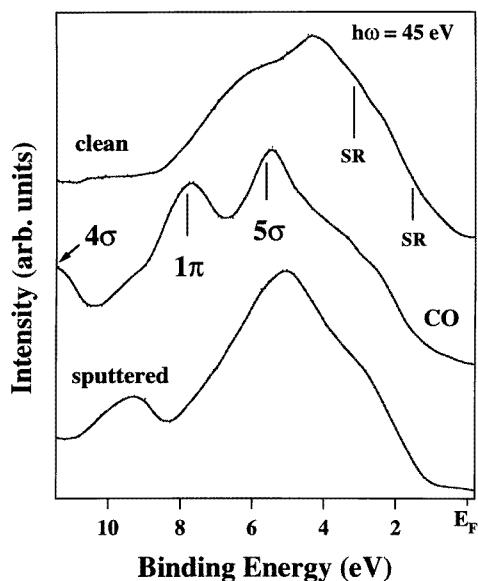


Figure 1. The valence-band spectra of a clean surface, a CO-adsorbed surface and a sputtered surface of a thin film of $\text{La}_{0.65}\text{Ba}_{0.35}\text{MnO}_3$ at 220 K. The three spectra were collected at normal emission with p-polarized light and a photon energy of 45 eV. SR marks the possible surface resonances.

We have tested the surface sensitivity of the valence bands by adsorbing CO onto the surface, as well as introducing surface disorder by Ar^+ -ion sputtering (at 1 kV energy). In figure 1, valence-band spectra are displayed for a clean surface, a surface with molecularly adsorbed carbon monoxide and a sputtered surface. The figure demonstrates clearly that the valence-band electronic structure of $\text{La}_{0.65}\text{Ba}_{0.35}\text{MnO}_3$ is highly dependent on the surface environment. Molecular CO adsorption induces photoemission features at approximately 5.6 eV, 7.8 eV and 11.7 eV binding energy, which are the 5σ , 1π and 4σ molecular orbitals of CO, respectively [18]. In addition, both CO adsorption and the sputtering of the surface result in additional changes in the valence-band structure. These changes include a significant loss in the density of states in the regions between 3–4 eV and at approximately 1.5 eV below E_F , as well as a relative increase at ~ 5.5 eV. The existence of this strong band at 3 to 4 eV is clearly evident at large emission angles, as seen in figure 2. The major changes in the occupied electronic structure with surface modification are indicative of a

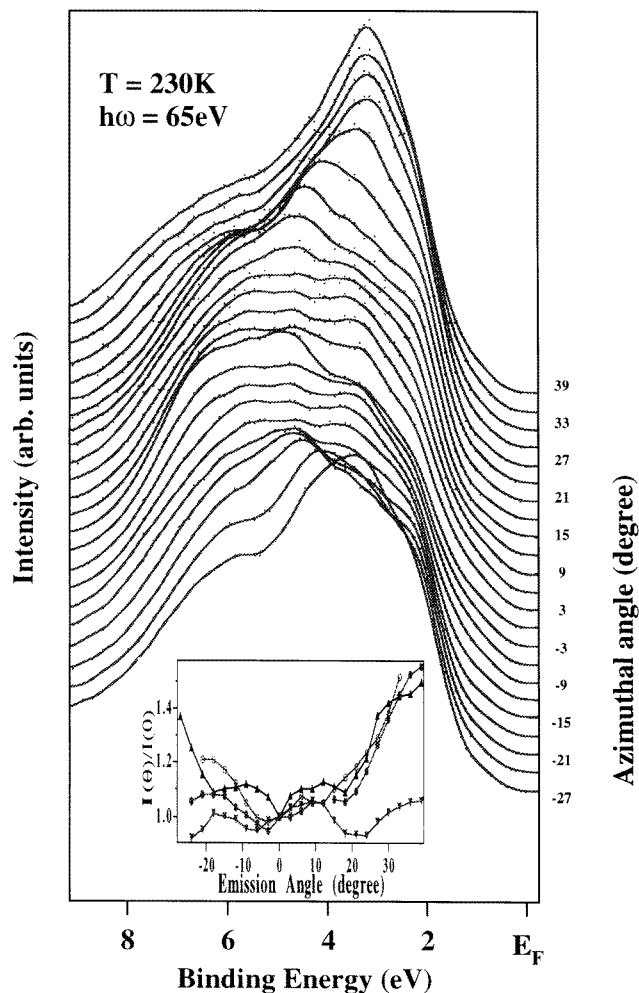


Figure 2. The normalized photoemission spectra of $\text{La}_{0.65}\text{Ba}_{0.35}\text{MnO}_3$ taken at 230 K with 65 eV photons for various photoelectron emission angles. The spectra were acquired with p-polarized light ($\alpha = 65^\circ$). The inset shows the spectral intensity of the 3.3 eV $\text{La}_{0.65}\text{Ba}_{0.35}\text{MnO}_3$ surface resonance feature as a function of the photoelectron emission angle. The emission intensities were extracted from photoemission spectra acquired with photon energies of 65 eV (\bullet and \circ), 55 eV (\blacktriangle), and 45 eV (\blacktriangledown), respectively.

high degree of surface sensitivity. The decrease in emission intensity of both features does provide evidence of the importance of the question of whether there is a distinct surface electronic structure of $\text{La}_{0.65}\text{Ba}_{0.35}\text{MnO}_3$ and other perovskites.

The two-dimensional character of these states can be verified by probing their k_\perp -dependence. This is achieved by changing the photon energy with photoelectron detection at normal emission. A surface state (SS), or surface resonance (SR), is localized at the surface and will not disperse in k_\perp . In figure 3 we show typical room temperature (RT) valence-band spectra of $\text{La}_{0.65}\text{Ba}_{0.35}\text{MnO}_3$ that were acquired for a variety of photon energies ranging from 52 eV to 90 eV. The solid markers in figure 3, as well as the chain line, locate the binding energies of some of the Mn-3d- and O-2p-derived states above the Mn

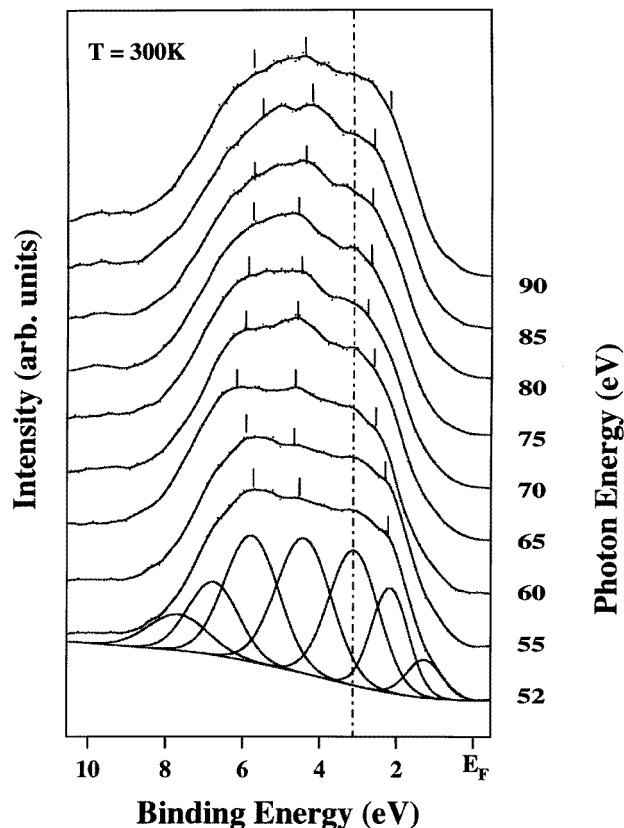


Figure 3. The normalized valence-band spectra of $\text{La}_{0.65}\text{Ba}_{0.35}\text{MnO}_3$ at 300 K for various photon energies. The photoelectrons were collected at normal emission with p-polarized light ($\alpha = 65^\circ$). The solid markers and the chain line locate some Mn-3d- and O-2p-derived features. A convolution of the valence band into seven gaussian components is shown for the valence band acquired with a photon energy of 52 eV.

3p absorption edge. It is evident from figure 3 that the feature at 3.3 eV below E_F is fairly constant in binding energy (the chain line) with changing photon energy, while the other states at 2.3 eV, 4.6 eV and 6.6 eV binding energy disperse with changes in the photon energy. The rigid 3.3 eV binding energy of this state is a signature of its two-dimensional character and is an indication of its localization at the surface. The valence bands of the $\text{La}_{0.65}\text{Ba}_{0.35}\text{MnO}_3$ perovskite are dispersive, in contrast to the related bands of $\text{La}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$ [1], which show little or no dispersion in either k_\perp or k_\parallel [24]. The dispersion of bands is indicative of some degree of electron itineracy.

More evidence for the surface contribution to the valence-band electronic structure of $\text{La}_{0.65}\text{Ba}_{0.35}\text{MnO}_3$ is obtained from the valence-band dispersion and the changes in the photoemission intensities of the valence-band features as a function of emission angle. In figure 2 we show the valence-band spectra of $\text{La}_{0.65}\text{Ba}_{0.35}\text{MnO}_3$ acquired at different points along the $\Gamma\Delta X$ symmetry direction of the surface Brillouin zone (SBZ). Clearly the valence-band exhibits a large increase in spectral weight in the 3.3 eV region at large emission angles. This is quantified in the inset of figure 2, which shows the dependence of the intensity of this feature on photoelectron emission angle for photon energies of 45 eV, 55 eV and 65 eV.

The intensity at large emission angles is much stronger than anticipated from the perturbing Hamiltonian $\mathbf{A} \cdot \mathbf{p} + \mathbf{p} \cdot \mathbf{A}$. This behaviour is characteristic of states which are localized at the surface. This phenomenon has been observed for surface states of Cu(100) [19] and Si(111) [20]. The enhancement of the 3.3 eV feature at large emission angles has not been observed for the disordered (sputtered) surface and supports our assignment of the origin of this state to the surface.

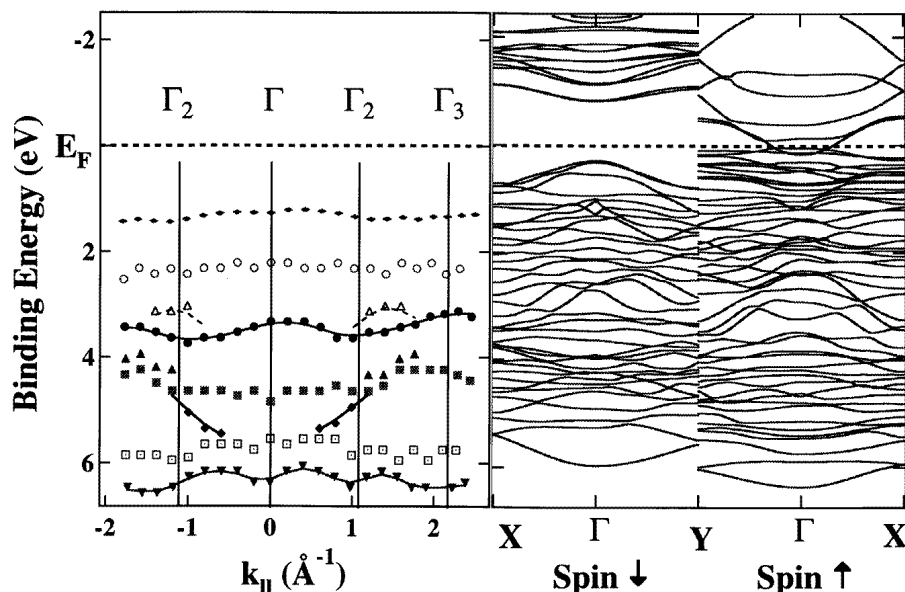


Figure 4. The experimentally determined band dispersion of seven identified bands of $\text{La}_{0.65}\text{Ba}_{0.35}\text{MnO}_3$ (left-hand panel) along the $\Gamma\Delta X$ high-symmetry line, distinguished using different symbols. The vertical lines indicate the Γ points of the Brillouin zone, as determined by the periodicity of the bulk band at the binding energy of 6.6 eV (\blacktriangledown). The surface-sensitive resonance is indicated by \bullet . The right-hand panel shows the theoretical bulk band projection obtained using a linearized muffin-tin orbital method with an atomic sphere approximation (LMTO-ASA). The calculations are based on a simplified orthorhombic ferromagnetic LaMnO_3 structure with a 25% Ba doping concentration. The binding energies of the experimental and calculated bands are referenced to the Fermi level and scaled accordingly.

A line-shape analysis of the valence-band spectra of figure 2 (shown in figure 3) allowed us to extract the dispersion of seven different bands. The results are presented in figure 4. The vertical lines indicate the Brillouin zone centres, as determined from the periodicity of the bulk feature at a binding energy of approximately 6.6 eV. The bulk Brillouin zone size was determined to be 1.15\AA^{-1} , which corresponds to a real-space lattice vector of approximately 5.4\AA . This is in excellent agreement with the results of bulk measurements performed on closely related perovskite structures [21–23]. The surface-sensitive band at 3.3 eV binding energy, however, disperses with a periodicity that is different from that of the bulk feature(s). This implies a surface electronic structure with a surface Brillouin zone that may be different from that of the bulk. Occasional evidence of this sublattice, while not completely compelling, is also found in LEED. The valence states of the sputtered surface were found to be dispersionless. This clearly indicates that the surface was well ordered and that the electronic structure probed by ultra-violet photoemission is dominated by the

surface.

The surface-sensitive features with 1.5 eV and 3.3 eV binding energy appear to be embedded in the bulk bands, which would suggest that they are surface resonances rather than surface states. In order to clarify this issue, we have calculated the bulk band structure using a linearized muffin-tin orbital (LMTO) calculation with an atomic sphere (ASA) approximation. The bulk band-structure calculations were based on a simplified orthorhombic ferromagnetic LaMnO_3 structure with a doping concentration of 25%. The simplification is quite reasonable since La and Ba make minimal contributions to the valence-band electronic structure. The calculated bulk bands are displayed in the right-hand panel of figure 4. The bands are separated into majority-spin (spin up) and minority-spin components (spin down), where the band dispersion has been calculated along the $\overline{Y\Gamma X}$ high-symmetry directions. The binding energies of the calculated bands are referenced to the Fermi level and plotted on the same scale with the experimentally derived band dispersion in the left-hand panel of figure 4. This allows a direct comparison of the experimental band dispersion and the calculated projected bulk band structure. The surface-sensitive band at a binding energy of 3.3 eV at $\overline{\Gamma}$ clearly lies in the region of the bulk continuum. Since this state does not fall within a bulk band gap it should be correctly defined as a surface resonance state (SR) [25]. We believe that the feature at 1.5 eV binding energy may also be a SR state on the basis of its sensitivity to surface conditions (see figure 1). This band, however, is fairly weak in emission intensity. This makes the characterization of this state difficult and the assignment inconclusive.

The calculations also show the half-metallic character of the ferromagnetic orthorhombic manganese perovskite structure, with a band gap in the spin-minority states, but Fermi level crossings of the spin-majority bands. The half-metallic behaviour is believed to play an important role in producing giant magnetoresistance in these perovskite systems [13, 14]. The calculations indicate an anisotropy in band dispersion in the $\overline{\Gamma\Delta X}$ and $\overline{\Gamma\Delta Y}$ directions with an enhanced dispersion along $\overline{\Gamma\Delta X}$ (maximum band width $\Delta E \approx 0.9$ eV), as compared to the $\overline{\Gamma\Delta Y}$ direction ($\Delta E \approx 0.6$ eV). This is in reasonable agreement with experimentally determined band widths of $\Delta E \approx 0.5$ eV for both the 6.6 eV bulk band and the 3.3 eV surface resonance (SR) state. The other states at 1.5, 2.3, 4.8 and 5.7 eV remain within 0.2 eV of their binding energy position at the zone centre ($\overline{\Gamma}$). A reduced bandwidth along the $\overline{\Gamma\Delta Y}$ direction has also been observed.

The experimental valence-band mapping in k_{\parallel} indicates the existence of a feature which is only observed near the centre of the second bulk Brillouin zone. The binding energy of this state at this point in the bulk Brillouin zone is close to the binding energy of the surface resonance. One explanation for this state is the existence of an as-yet unresolved bulk band which is degenerate with the surface resonance except for in some regions in the Brillouin zone where the surface and bulk dispersion amplitudes are out of phase. This is consistent with the apparent difference between the Brillouin zone size of the surface and the bulk. The implication of this observation is that the valence band of $\text{La}_{0.65}\text{Ba}_{0.35}\text{MnO}_3$ is characterized by a mixture of bands that are localized at the surface and the bulk bands.

In order to identify the origin of the surface resonance(s), we have studied the photon dependence of these valence features in the vicinity of the Mn 3p edge (~ 47.2 eV). Figure 5 shows two valence-band spectra that were acquired with photon energies of 47 eV and 52 eV, i.e. just below and slightly above the Mn 3p resonance edge. The enhancement at 52 eV is due to coupling of the direct photoemission with resonant enhancements across the Mn 3p edge. The difference curve at the bottom of figure 5 clearly identifies the regions in the valence band with strong Mn 3d character. The features located at 1.5 eV, 2.3 eV, 3.3 eV, 5.8 eV and 6.6 eV, as indicated by the arrows, are clearly enhanced above the Mn 3p

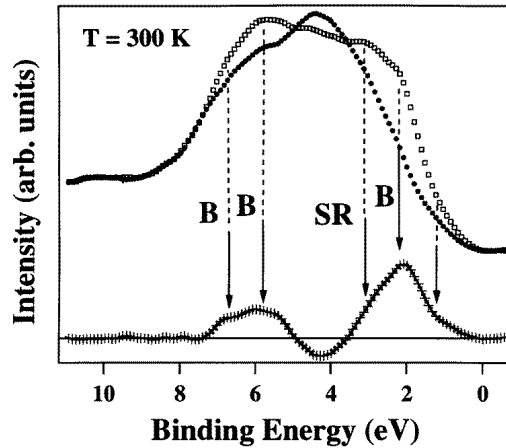


Figure 5. The normalized valence-band spectra of $\text{La}_{0.65}\text{Ba}_{0.35}\text{MnO}_3$ at 300 K for 47 eV (\bullet) and 52 eV (\square), respectively. The photoelectrons were collected at normal emission with p-polarized light ($\alpha = 65^\circ$). The difference curve (\dagger) is shown in the bottom of the figure. The arrows indicate the location of valence-band features with mainly Mn 3d character. The surface-sensitive states are accentuated with bold arrows.

threshold energy and therefore are largely dominated by the emission from Mn-3d-derived states. The state at 4.3 eV which does not exhibit an enhancement across the Mn 3p edge is attributed to a state with a large O 2p contribution. Though the binding energies for the $\text{La}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$ bands are greater, in general, than those for $\text{La}_{0.65}\text{Ba}_{0.35}\text{MnO}_3$, this is consistent with results on $\text{La}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$ [1]. On the basis of these results, we assign the surface resonance state at 3.3 eV as being of largely Mn 3d character. This is also supported by the reduced intensity of this state for off-normal emission at a photon energy of 45 eV, as compared to photon energies above the Mn 3p threshold (see the inset of figure 2). On the basis of Mn-3p-edge photoemission data and work on $\text{La}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$ [1], we postulate that the spectral weight at 3–4 eV is mainly due to a Mn-3d-induced state at 3.3 eV below E_F which is possibly associated with t_{2g} symmetry of the bulk. The feature at ~ 1.5 eV is extremely surface sensitive, although weak in its spectral intensity, and the symmetry of this state is possibly associated with the bulk e_g band.

Unlike the layered Cu–O superconductors, the manganese perovskite oxides appear to have few gaps in the bulk band structure large enough to support a surface state. Nonetheless the possibility of the existence of a surface electronic structure, raised by Liu and Klemm [17], has support in the data here. Unlike the predictions of Liu and Klemm concerning the high-temperature superconductors [17], the observed surface electronic structure of these manganese oxides, while different from that of the bulk, does not result in true surface states. This makes it difficult to identify different magnetic properties, such as enhanced magnetic ordering, at the surface—though the possibility of such unique surface properties is suggested by the work of Liu and Klemm [17].

In summary, our results demonstrate the existence of at least one surface resonance state in the valence band of $\text{La}_{0.65}\text{Ba}_{0.35}\text{MnO}_3$, and consequently prove that the theoretical predictions of the existence of such surface-induced features by Liu and Klemm [17] are valid. The surface is very sensitive and develops its own surface electronic structure which is different from that of the bulk. Our results generally indicate that one needs to be extremely careful with interpretations which correlate the surface-sensitive

electronic structure measurements with the bulk transport properties. The valence-band electronic structure obtained with ultra-violet photoemission spectroscopy (UPS) is not only representative of the bulk electronic structure, but also has contributions from the surface. The surface resonance feature(s) have considerable Mn 3d spectral weight and indicate that the surface is terminated by the Mn–O–Mn plane. Our results are further supported by preliminary EELS experiments which indicate that the surface vibrational modes of $\text{La}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$ are different from that of the bulk [26]. The surface has a strong influence on the observed electronic structure of $\text{La}_{0.65}\text{Ba}_{0.35}\text{MnO}_3$.

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