Surface lattice dynamics of layered transition metal oxides: 
$\text{Sr}_2\text{RuO}_4$ and $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$

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Momentum resolved inelastic electron scattering has been used to study the surface lattice dynamics of two layered isostructural perovskite crystals ($\text{Sr}_2\text{RuO}_4$ and $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$), two materials with different physical properties. There were three surface optical phonons observed with the energies at 30.0, 50.0, and 75.0 meV with a shoulder appearing at 67.5 meV for $\text{Sr}_2\text{RuO}_4$ and at 26.0, 56.5, and 78.5 meV for $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$. In the $\text{K}_2\text{NiF}_4$-type structure, these phonons are associated with the La/Sr vibrational (external), Mn-O-Mn (Ru-O-Ru) bending, and MnO$_6$ (RuO$_6$) stretching modes, respectively. The observed surface phonons, especially for breathing and stretching modes, are at significantly higher energies than the corresponding modes in the bulk, which are directly associated with the relative reduction of out-of-plane Mn-O/Ru-O bond lengths at the surfaces. The line shapes of the quasielastic scattering peaks reflects the surface conductivity of $\text{Sr}_2\text{RuO}_4$ and which are directly associated with the relative reduction of out-of-plane Mn-O/Ru-O bond lengths at the surfaces. The line shapes of the quasielastic scattering peaks reflects the surface conductivity of $\text{Sr}_2\text{RuO}_4$ and $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$, the broad character of both the bending and the stretching modes results from surface electronic inhomogeneities. In contrast to the bulk, the absence of phonon restructuring in the observed temperature range suggests that the long-range charge/orbital ordering transition occurring in the bulk may not take place on the surface, probably correlated with stiffening of observed optical phonons at the surface.

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I. INTRODUCTION

Transition metal oxides (TMO’s) have been investigated extensively because this class of materials exhibits an array of fascinating phenomena. The physical complexity in these unconventional phenomena is the result of the strong coupling between charge, lattice, orbital, and spin degrees of freedom. 1,2 Conceptually, creating a surface by truncating a single crystal is a controlled way to disturb a coupled system by breaking the translation symmetry, providing a fresh approach to the study of the charge-lattice-orbital-spin coupling in TMO’s. In reality, many surfaces of TMO’s end up with a polar character, leading to surface reconstruction and relaxation, or the processing of the surface leads to surface segregation, yielding a different chemical stoichiometry from the bulk. 3,4 A possible solution is to use a layered TMO that can be cleaved in the vacuum. Many TMO’s are layered perovskite compounds with the general formula of Ruddlesden-Popper (RP) series of $(R_{1-x}A_x)_nM_{2n+1}O_{3n+1}$. In these compounds, R is usually a trivalent rare earth, A is a divalent alkaline earth, M is a transition metal ion, and O is oxygen, while n represents the number of connected layers of vertex sharing MO$_6$ octahedra. Figure 1 displays three members of RP series $n = 1$, $n = 2$, and $n = \infty$. Except those with $n = \infty$ [so-called three-dimensional (3D) materials], these layered-compounds exhibit quasi-two-dimensional character and are amenable for creating a surface by cleaving without altering the stoichiometry.

In this work, we report a study of the surface lattice dynamics on ultrahigh vacuum (UHV) cleaved $\text{Sr}_2\text{RuO}_4$ and $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$—two single-layered compounds ($n = 1$ in the RP series). Both materials have the same $\text{K}_2\text{NiF}_4$-type bulk structure [see Fig. 1(a)] with the tetragonal $D_{4h}^{17}$ symmetry, but they exhibit quite different physical properties. $\text{Sr}_2\text{RuO}_4$ is a good metal and a $p$-wave superconductor below $\sim 1.5$ K. 5 However, $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ is nonmetallic, undergoes a charge and orbital ordering (CO/OO) transition at $T_{CO} \sim 210$ K, and is antiferromagnetically (AFM) ordered below $T_N \sim 110$ K. 6 Both these materials can be easily cleaved along a plane normal to the c axis without breaking the RuO$_6$/MnO$_6$ octahedra [see dotted lines in Fig. 1(a)], creating Sr (La/Sr)-O surfaces with extremely large and flat terraces. 7,8 However, the surface of $\text{Sr}_2\text{RuO}_4$ exhibits a ($\sqrt{2} \times \sqrt{2}$)R45$^\circ$ surface reconstruction resulting from the freezing of the soft bulk phonon corresponding to the RuO$_6$ octahedron rotation about the c axis. 7 In contrast, the surface of $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ preserves a ($1 \times 1$) truncated lattice structure but exhibits nanometer scale electronic inhomogeneity as revealed by scanning tunneling microscopy. 8 The objective of this investigation is to measure and compare the surface lattice dynamics of these two quite different materials.

Momentum resolved high-resolution electron energy loss spectroscopy (HREELS) has been utilized to measure phonon modes at the surfaces [see Fig. 1(b)]. HREELS is a highly surface-sensitive technique with both energy and momentum resolution capable of probing the electronic and lat-
Specific and well-defined selection rules, depending upon the nature of the low energy excitation of electron-hole pairs across the Fermi energy. These excitations show up as modes presented in Fig. 2 will be observed. In the specular scattering direction where there is almost no momentum transfer parallel to the surface HREELS is sensitive to modes that have dynamic dipole moments perpendicular to the surface. This is usually referred to as dipole-active modes. The inspection of Fig. 2 shows that the dipole-active modes are $A_{1g}(2)$, $A_{2u}(2)$, $A_{2u}(3)$, $A_{2u}(1)$, and $A_{1g}(1)$. Excitation of these modes should appear with strongest intensity in the specular direction and exponentially decay as the electron scattering angle increases. Off normal scattering or scattering with large momentum transfer, called impact scattering, can excite modes that are not dipole active, but they will have small cross sections and are limited to the modes with displacement vector components in the scattering plane. HREELS has a substantial advantage over surface infrared spectroscopy due to its momentum resolution and selection rules.

II. EXPERIMENTAL DETAILS

Single crystals of Sr$_2$RuO$_4$ (Ref. 11) and La$_{0.5}$Sr$_{1.5}$MnO$_4$ (Ref. 12) were grown by the optical floating zone technique. The samples with about $3 \times 3 \text{ mm}^2$ area were cleaved in a UHV chamber at room temperature (RT). For cleaving, a metal post was glued with silver epoxy onto the samples, and the sample itself was glued onto the sample holder plate. The sample was then cleaved by breaking off the post. Detailed sample preparation is explained elsewhere. Sharp low-energy electron diffraction (LEED) patterns were observed for both surfaces ensuring ordered surface lattice structures.

Surface phonons of Sr$_2$RuO$_4$ and La$_{0.5}$Sr$_{1.5}$MnO$_4$ were measured with a high-resolution electron energy loss spectrometer (HIB-1000) with an energy (momentum) resolution of 5 meV ($0.05 \text{ Å}^{-1}$). Energy loss spectra were collected with both specular and off-specular geometries. Off-specular geometry was achieved by varying the scattering angle ($\theta$) along the bulk [100] direction by rotating the monochromator while keeping the sample position fixed. The incident electron energy was 20 eV for Sr$_2$RuO$_4$ and 15 eV for La$_{0.5}$Sr$_{1.5}$MnO$_4$ with the specular scattering direction at 45$^\circ$. The scattering setup is schematically shown in Fig. 1(b).

III. RESULTS AND DISCUSSIONS

A. Surface phonons of Sr$_2$RuO$_4$

A typical sharp LEED pattern observed from the surface of cleaved Sr$_2$RuO$_4$ is presented in Fig. 3(a). The appearance of fractional spots (marked by arrows) indicates a $(\sqrt{2} \times \sqrt{2})R45^\circ$ reconstruction at the surface that has also been confirmed by scanning tunneling microscopy. The reconstructed surface has a $p4gm$ plane group symmetry where the RuO$_6$ octahedra at the surface rotate about the c axis by $\approx 8.5^\circ$ with respect to the bulk. As shown in Fig. 3(a), the LEED spots are quite sharp and exhibit very low background, indicating the surface is well ordered with a long coherence length ($\approx 200 \text{ Å}$). This is confirmed by our HREELS data as shown in Fig. 3(b), where the intensity of the quasielastic scattering peak drops very quickly as the scattering angle ($\theta$) increases away from the specular direc-
A series of HREELS spectra with different momentum transfer \( q_1 \) along the [100] direction of \( \text{Sr}_2\text{RuO}_4 \) at \( T = 80 \) K is displayed in Fig. 4(a). There are three distinct energy loss features observed in the specular direction with the energies of \( \omega_1 \sim 30 \) meV, \( \omega_2 \sim 50 \) meV, and \( \omega_3 \sim 75 \) meV. A distinct feature appears at \( \omega_4 \sim 67.5 \) meV, as a low-energy shoulder of the \( \omega_3 \) peak, indicating at least two phonon modes in the highest energy loss feature. The FWHM’s angular profile of these modes is comparable to that obtained from the normal metal or semiconductor surface.9

The inherent widths of surface optical phonons of \( \omega_1 \), \( \omega_2 \), and \( \omega_3 \) at \( \Gamma(q_1 = 0) \) are found to be \( \Delta \omega_1/\omega_1 = 0.18 \), \( \Delta \omega_2/\omega_2 = 0.05 \), and \( \Delta \omega_3/\omega_3 = 0.07 \), respectively. These widths can be compared to HREELS measurements on conventional metals.15 \( \Delta \omega/\omega \) is 0.09 for Mg, 0.04 for Be, 0.05 for Al, and 0.09 for Cu. Notice that the inherent width of \( \omega_1 \) at the surface of \( \text{Sr}_2\text{RuO}_4 \) is anomalously large. This indicates that there might be multiple phonon modes in the \( \omega_1 \) peak. One possibility is the convolution of the \( A_{1\sigma}(2) \) and \( A_{2\alpha}(3) \) modes at the surface. However, the energy difference of these two modes [24.5 meV for \( A_{1\sigma}(2) \) and 25.0 meV for \( A_{2\alpha}(3) \)] is rather small.11,14 A more plausible explanation is that there are two unresolved modes associated with surface \( (\sqrt{2} \times \sqrt{2})R45^\circ \) reconstruction.7,13 The reconstruction creates two kinds of Sr-atom environments in the surface layers and consequently splits the original external mode in the bulk into two components of Sr vibrations at the surface.
The experimental data indicates that these modes have very little dispersion or temperature dependence. The temperature dependence of HREELS spectra taken in the specular direction at the SBZ center is presented in Fig. 5. The surface phonon modes are the same at low temperature and room temperature, except for a small shift in energy. As the temperature is increased the surface phonons soften, i.e., the peak positions shift to lower energies, by 2 meV for \( \omega_1 \) and 1 meV for \( \omega_2 \) and \( \omega_3 \). The softening rates are \(-0.009\) meV/K for \( \omega_1 \), and \(-0.005\) meV/K for \( \omega_2 \) and \( \omega_3 \), respectively. This behavior is different than the bulk where the energy of the phonons at 60 K is almost the same as that at 290 K, suggesting that the anharmonicity at the surface of Sr\(_2\)RuO\(_4\) is larger than in the bulk. The measured dispersion of surface optical phonons in the [100] direction at both 80 and 300 K is shown in Fig. 5(b). There is no dispersion for these modes in the SBZ region accessible in these experiments.

As has been mentioned in the Introduction, the shape of the quasielastic peak in a HREELS spectrum is influenced by the surface conductivity. The more metallic a system is, the more asymmetric the quasielastic peak will be. The asymmetry of the elastic peak in the specular scattering at \( q_i = 0 \) (dipole sensitive) is influenced by the conductivity/resistivity in the \( c \) axis (perpendicular to the surface); while for off-specular (\( q_i \neq 0 \)) scattering, it is influenced by the conductivity in the \( ab \) plane (parallel to the surface). A sequence of quasielastic peaks on the surface of Sr\(_2\)RuO\(_4\) as a function of momentum transfer at 80 and 300 K is shown in Fig. 6. Unfilled circles and solid lines are experimental data and the fit by Gaussian function, respectively. At \( T = 80 \) K, the asymmetry of the quasielastic peak in the specular direction (\( q_i = 0 \)) is substantially different from that in the off-specular direction. There is a significant increase in the asymmetry for \( q_i > 0.03\) Å\(^{-1}\) [see Fig. 6(a)]. The difference in the asymmetry at \( q_i = 0\) Å\(^{-1}\) and at \( q_i > 0.03\) Å\(^{-1}\) indicates that the surface is more metallic in the \( ab \) plane (parallel to the surface) than in the \( c \) axis (perpendicular to the surface) at LT. This is consistent with the bulk resistivity measurements [\( \rho_{ab} \) is lower than \( \rho_c \) as shown in the inset of Fig. 6(a)], and the optical conductivity measurements. The \( T \) dependence of the quasielastic peak at RT is shown in Fig. 6(b). In contrast to the LT case, the asymmetry of the quasielastic peak in the specular and off-specular directions is...
about the same at RT, indicating $\rho_{s}^{\text{surface}} \approx \rho_{s}^{\text{bulk}}$ at the surface, which is different than that in the bulk.

**B. Surface phonons of La$_{0.5}$Sr$_{1.5}$MnO$_{4}$**

Cleaving La$_{0.5}$Sr$_{1.5}$MnO$_{4}$ results in a sharp (1×1) LEED pattern as shown in Fig. 7(a) indicating an ordered surface. Unlike the surface of Sr$_2$RuO$_4$, there is no sign of surface reconstruction for La$_{0.5}$Sr$_{1.5}$MnO$_{4}$. This (1×1) LEED pattern was observed from 80 to 300 K even though there is a superstructure in the bulk below the charge ordering temperature ($T_{\text{CO}} \sim 210$ K).$^6$ As shown in Fig. 7(b), the FWHM of the angular profile for the intensity of the quasielastic scattering peak for La$_{0.5}$Sr$_{1.5}$MnO$_{4}$ is about 4°, which is larger than that for Sr$_2$RuO$_4$ (FWHM=2.5°) or ordinary metals.$^{15}$ This indicates that the surface of La$_{0.5}$Sr$_{1.5}$MnO$_{4}$ is either structurally or electronically rough. This roughness is presumably dominated by the electronic inhomogeneity observed by STM/STS.$^8$

A series of HREELS spectra of La$_{0.5}$Sr$_{1.5}$MnO$_{4}$ at 80 K with different momentum transfer along the [100] direction is shown in Fig. 8. There are three loss features observed with energies of 26 meV ($\omega_{1}$), 56.5 meV ($\omega_{2}$), and 78.5 meV ($\omega_{3}$).

**TABLE I. Optical phonons of Sr$_2$RuO$_4$ in the bulk and surface (80 K) at the center (Γ') of SBZ.** Δω/ω is the ratio of surface linewidth (Δω) to the surface phonon ω. Δω is the difference of energies between surface and bulk modes.

<table>
<thead>
<tr>
<th>Modes</th>
<th>Bulk (meV)</th>
<th>Surface (meV)</th>
<th>Width (Δω)</th>
<th>Δω/ω</th>
<th>Δω (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Refs. 20, 23)</td>
<td>80 K (300 K)</td>
<td>80 K (300 K)</td>
<td>80 K (300 K)</td>
<td>80 K</td>
</tr>
<tr>
<td>$\omega_{1}$ [A$_{2u}$ (3)]</td>
<td>25.0</td>
<td>30.0 (28.0)</td>
<td>5.0 (5.9)</td>
<td>0.18 (0.21)</td>
<td>+5.0</td>
</tr>
<tr>
<td>[A$_{1g}$ (2)]</td>
<td>24.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\omega_{2}$ [A$_{2u}$ (2)]</td>
<td>45.0</td>
<td>50.0 (49.0)</td>
<td>2.5 (3.4)</td>
<td>0.05 (0.07)</td>
<td>+5.0</td>
</tr>
<tr>
<td>$\omega_{3}$ [A$_{2u}$ (1)]</td>
<td>60.0</td>
<td>67.5 (66.5)</td>
<td>2.7 (4.0)</td>
<td>0.04 (0.06)</td>
<td>+7.5</td>
</tr>
<tr>
<td>$\omega_{3}$ [A$_{1g}$ (1)]</td>
<td>67.0</td>
<td>75.0 (74.0)</td>
<td>4.5 (5.9)</td>
<td>0.06 (0.08)</td>
<td>+8.0</td>
</tr>
</tbody>
</table>

**FIG. 5.** (a) Temperature dependence of HREELS spectra from the Sr$_2$RuO$_4$ surface at the center (Γ′) of the SBZ. (b) The measured dispersion of the Sr$_2$RuO$_4$ surface phonons along the [100] direction. Filled (unfilled) circles are at $T=80$ K (300 K).

**FIG. 6.** The in-plane momentum-transfer ($q_{||}$) dependence of quasielastic scattering peak from the Sr$_2$RuO$_4$ surface along the [100] direction at temperature $T=80$ K (a) and 300 K (b). Unfilled circles are experimental data and solid lines are Gaussian functions. The inset is the in- and out-of-plane resistivity of bulk Sr$_2$RuO$_4$ reproduced from Ref. 5.
meV ($\omega_2$). Compared to those obtained from the surface of Sr$_2$RuO$_4$, the feature $\omega_2$ has a relatively higher intensity, while $\omega_3$ is rather broad without any noticeable shoulder as observed for Sr$_2$RuO$_4$. The angular intensity profile of these phonon features mimics the profile of the quasielastic peak indicating the phonon profile is also a result of surface roughness. There are five dipole active modes [$A_{1g}(2)$, $A_{2u}(2)$, $A_{2u}(3)$, $A_{2u}(1)$, and $A_{1g}(1)$] expected to be observed at the surface (see Fig. 2). However, there are only three phonon modes that are clearly observed. A recent optical spectroscopy study from bulk La$_{0.5}$Sr$_{1.5}$MnO$_4$ showed four optical phonon modes at RT with the energies of 27.5, 46.4, 52.0, and 59.0 meV with $E_{1c}$ axis.$^{17}$ The lowest mode, 27.5 meV was assigned to $A_{2u}(3)$. There is no information available for the $A_{1g}(2)$ mode in the bulk. However, as in the case of Sr$_2$RuO$_4$, the energy of this mode is very close to that of $A_{2u}(3)$. Therefore, the observed surface feature at 26 meV ($\omega_1$) is assigned to either or both the $A_{1g}(2)$ or $A_{2u}(3)$ bulk modes. The second surface feature at 56.5 meV ($\omega_2$) should be the $A_{2u}(2)$, a bending mode which has the energy of 46.4/52.0 meV in the bulk.$^{17}$ The highest surface mode is observed at the energy of 78.0 meV ($\omega_3$). Similar to the case of Sr$_2$RuO$_4$, this mode should be related to either the $A_{1g}(2)$ or $A_{2u}(1)$ mode or even a convolution of both. In the bulk, the energy of the $A_{2u}(1)$ mode is 59.0 meV, while it is unknown for the $A_{1g}(2)$ mode. Presumably the energy of $A_{1g}(2)$ mode is similar to that in Sr$_2$RuO$_4$, i.e., ~67 meV in the bulk. Therefore, it is reasonable to assign the observed surface mode at 78.5 meV to the $A_{1g}(2)$ mode. While the $A_{2u}(1)$ mode at the surface may be a low-energy shoulder of $\omega_3$ mode and unresolved in our experiments.

The surface phonons, particularly these associated with internal vibrations in the octahedra, exhibit noticeable hardening compared to their counterparts in the bulk.

We have examined the line widths of surface phonons for this system. Since the FWHM of the angular profile for the intensity of the quasielastic scattering peak is rather large as compared to the case of Sr$_2$RuO$_4$, we have taken out the linear background (incoherent part) in obtaining the line widths. The linear background was determined from the angular profile of the intensity of the quasielastic scattering peak [see Fig. 7(b)] by subtracting the expected intensity of Gaussian function from the measured intensity. We found that the line width of $\omega_1$, $\omega_2$, and $\omega_3$ at the $\Gamma$ point ($q_i=0$) at 80 K to be $\Delta \omega_1 = 1.8$ meV, $\Delta \omega_2 = 4.5$ meV, and $\Delta \omega_3 = 8.8$ meV, respectively (see Table II). The linewidths of surface phonons for different $q_i$ values are about the same. One can see that the surface phonon features of $\omega_2$ and $\omega_3$ have substantially large inherent line widths, larger than...
those similar modes observed from Sr$_2$RuO$_4$. However, the
linewidth of $\omega_1$ measured at the surface is quite small and
even compatible to that for phonons on metal surfaces such as Mg and Cu in spite of the doping effect and the surface roughness. This is in sharp contrast to the surface external mode of Sr$_2$RuO$_4$ that was split by reconstruction. Normally, one would expect a splitting of the external mode due to the difference between La and Sr (doping effect). If this doping effect changes only the reduced mass but not the force constant of the oscillator associated with the external mode, the splitting between La- and Sr-associated modes is estimated as only $-0.74$ meV by simple approximation. Thus the doping effect or even possible Sr surface segregation should not cause significant broadening for the external mode if there is no change in force constant by doping or reconstruction.

Therefore, the local surface roughness of La$_{0.5}$Sr$_{1.5}$MnO$_4$ observed by STM (Ref. 8) should be the source for the broadening of these optical phonon peaks. Now we need to understand why the surface roughness broadens only the JT-active modes ($\omega_2$ and $\omega_3$) but not the external mode $\omega_1$. The surface roughness observed by STM may include local "physical" lattice or electronic roughness. Since most of the observed surface phonons are rather localized with negligible dispersion, local "physical" lattice roughness will cause only a small shift in the phonon energy. However, local electronic roughness can drastically change phonon energy as well as inherent line width by changing the force constant. Particularly, electronic roughness may affect mostly the JT-active modes but less the external mode, because the JT modes are associated with the $M_O$ octahedron deformations which can be drastically affected by local lattice/electronic distortions (i.e., local polarons). This may explain the contrast linewidths of the observed modes.

One important observation at the surface of La$_{0.5}$Sr$_{1.5}$MnO$_4$ is the lack of a $T$ dependence of the surface phonons, in contrast to that in the bulk. A multiple phonon splitting in both bending and stretching modes (i.e., $\omega_2$ and $\omega_3$) occurs in the bulk below the CO/OO transition temperature $T_{CO}$, reflecting a structural phase transition accompanied by the CO/OO transition. However, no evidence of a new surface phonon structure was observed at the surface both in the specular [Fig. 9(a)] and off-specular directions below $T_{CO}$ or $T_S$. As shown in Fig. 9, very little temperature dependence was observed in the surface phonon energy or width. These clearly indicate that no lattice distortion occurs at the surface in the observed temperature range from RT to 80 K, consistent with the results of the LEED measurements, where no superlattice was observed at $T \sim 80$ K. Therefore, the results from STM, LEED, and HREELS suggest that the CO/OO phase transition occurring in the bulk may not take place in the plane of the surface, at least not down to 80 K. This may be directly correlated with the stiffening of these observed optical phonons at the surface. It should be noted that the current results could not exclude the possibility of CO/OO transition occurring in the direction perpendicular to the surface that cannot be clearly identified with these surface-sensitive techniques.

### Table II. Optical phonons of La$_{0.5}$Sr$_{1.5}$MnO$_4$ in the bulk and surface (80 K) at the center (Γ) of SBZ.

<table>
<thead>
<tr>
<th>Modes</th>
<th>Bulk (meV) (Ref. 9)</th>
<th>Surface (meV) 80 K (300 K)</th>
<th>Width ($\Delta\omega$) 80 K (300 K)</th>
<th>$\Delta\omega/\omega$</th>
<th>$\Delta\omega_1$ (meV) 80 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega_1$</td>
<td>27.5</td>
<td>26.0 (27.0)</td>
<td>1.8 (2.8)</td>
<td>0.07 (0.10)</td>
<td>-1.5</td>
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<tr>
<td>[A$_{2u}$ (3)]</td>
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<td>[A$_{1g}$ (2)]</td>
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<tr>
<td>$\omega_2$</td>
<td>46.4/52.0</td>
<td>56.5 (55.8)</td>
<td>4.5 (5.7)</td>
<td>0.08 (0.10)</td>
<td>+10.1/4.5</td>
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<td>[A$_{2u}$ (2)]</td>
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<tr>
<td>$\omega_3$</td>
<td>59.0</td>
<td></td>
<td>8.8 (9.9)</td>
<td>0.11 (0.13)</td>
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<tr>
<td>$\omega_4$</td>
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<td>[A$_{1u}$ (1)]</td>
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![Fig. 9](image_url) (a) Temperature dependence of HREELS spectra from the La$_{0.5}$Sr$_{1.5}$MnO$_4$ surface at the center (Γ) of SBZ. Both impact energy and incident angle were kept the same for low and room temperature measurements. (b) The measured dispersion of the La$_{0.5}$Sr$_{1.5}$MnO$_4$ surface phonons along the [100] direction. Filled (unfilled) circles are at $T = 80$ K (300 K).
We also measured the dispersion of the surface phonons and examined the asymmetry of the quasielastic scattering peak from La$_{0.5}$Sr$_{1.5}$MnO$_4$. The measured dispersion of surface optical phonons of La$_{0.5}$Sr$_{1.5}$MnO$_4$ in the [100] direction of bulk at both $T = 80$ K and $T = 300$ K is presented in Fig. 9(b). All surface phonon modes are dispersionless, very similar to those from Sr$_2$RuO$_4$. The changes of phonon energies with temperature are also negligible. However, in contrast to the results from Sr$_2$RuO$_4$, we found that there is no significant change in the asymmetry of the quasielastic peak at $q_i = 0$ Å$^{-1}$ and $q_i > 0$ Å$^{-1}$ for both temperatures. Furthermore, the asymmetry is much less for La$_{0.5}$Sr$_{1.5}$MnO$_4$ than that for Sr$_2$RuO$_4$, indicating much weaker Drude-like excitations.

**IV. DISCUSSION AND SUMMARY**

We have studied the surface phonons of both cleaved Sr$_2$RuO$_4$ and La$_{0.5}$Sr$_{1.5}$MnO$_4$ surfaces at $T = 80$ K and RT by using HREELS. Three types of surface optical phonon modes, i.e., external, bending, and stretching, were clearly observed with small dispersion for both systems. At the surface of Sr$_2$RuO$_4$, the large inherent width of the external mode $\omega_i$ gives a signature of the existence of two non-equivalent Sr vibrational sites associated with the observed surface reconstruction with a $p^4 gm$ planar symmetry. The spectral linewidth of the quasielastic scattering peak clearly indicates a T-dependent anisotropy of metallicity in this layered material, consistent with the bulk transport and optical spectroscopy studies. The ratio of the in- and out-of-plane spectral weight due to low-energy Drude-like excitations drastically increases with decreasing temperature. At the surface of La$_{0.5}$Sr$_{1.5}$MnO$_4$, the unusually large inherent width of bending and stretching modes at all the measured temperatures indicates the existence of the electronic phase inhomogeneities at the surface that substantially affect the force constants for JT-active modes in MO$_6$ octahedra. The absence of surface phonon restructuring by lowering the temperature clearly shows that the CO/OO phase transition occurring in the bulk may not take place at the surface; at least there is no static long-range CO/OO ordering.

Our study clearly shows that the optical phonons have different behaviors at the surface. Such differences are intimately related to the structural changes due to lattice relaxation at the surface. The surface phonons have noticeably higher energies than their counterparts in the bulk for both Sr$_2$RuO$_4$ and La$_{0.5}$Sr$_{1.5}$MnO$_4$, especially for JT-active breathing and stretching modes. This behavior is similar to that of another surface of a 3D TMO, a La$_{0.65}$Ca$_{0.35}$MnO$_3$ film. The main reason for this is a relative change of bond lengths between transition-metal ion and oxygen in the MO$_6$ octahedra at the surface observed by LEED $(V)$ structural refinements. In the case of the surface of La$_{0.5}$Sr$_{1.5}$MnO$_4$, the Mn-O bond length in the $c$ axis (i.e., out-of-plane) direction is shorter by 0.022 Å than that in the bulk while the in-plane Mn-O bond length is unchanged. At the surface of Sr$_2$RuO$_4$, the out-of-plane Ru-O bond length is about the same as in the bulk, but the in-plane length is longer by 0.021 Å at the surface than in the bulk. For both cases, this relative change between in- and out-of-plane $M$-$O$ bond lengths somehow triggers a change of the force constants associated with these JT-active modes. Particularly, a relative reduction of the out-of-plane $M$-$O$ bond length increases the force constants and the phonon energies as we observed at the surface of these TMO’s. It can be expected that such changes of lattice dynamics (from bulk to surface) will affect the surface electronic and magnetic properties due to the strong correlation between charge, lattice, orbital, and spin degrees of freedom. The absence of the CO/OO transition at the surface of La$_{0.5}$Sr$_{1.5}$MnO$_4$ in our measured temperature range may be directly related to the surface phonon stiffening. Therefore, instead of doping, creating a surface by breaking symmetry is an alternative way to disturb a highly correlated electron system and create new phenomena, while providing a fresh approach to the study of the spin-charge-lattice coupling in these complex materials.

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