Madelung potentials and covalency effect in strained La$_{1-x}$Sr$_x$MnO$_3$ thin films studied by core-level photoemission spectroscopy

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We have investigated the shifts of the core-level photoemission spectra of La$_{0.8}$Sr$_{0.4}$MnO$_3$ thin films grown on three kinds of substrates, SrTiO$_3$, (LaAlO$_3$)$_{0.3}$-(SrAl$_{0.5}$Ta$_{0.5}$O$_3$)$_{0.7}$, and LaAlO$_3$. The experimental shifts of the La 4$d$ and Sr 3$d$ core levels are almost the same as the calculation, whereas those of the O 1$s$ and Mn 2$p$ core levels are negligibly small, in disagreement with the calculation. We consider that this is due to the strong covalent character of the Mn-O bonds.

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I. INTRODUCTION

The binding energy of a core level observed by photoemission spectroscopy is determined by many factors. The shift $\Delta E$ of the energy of the core level measured relative to the chemical potential $\mu$, when the band filling is varied and/or the crystal structure is changed, is given by

$$\Delta E = -\Delta \mu + K \Delta Q - \Delta V_M + \Delta E_R,$$

where $\Delta \mu$ is the change in the chemical potential $\mu$, $\Delta Q$ is the change in the number of valence electrons on the atom, $K$ is a constant, $\Delta V_M$ is the change in the Madelung potential $V_M$ and $\Delta E_R$ is the change in the extra-atomic relaxation energy of the core-hole state. When the band filling is varied, both $\mu$ and $V_M$ should change, but the effect of $\Delta V_M$ has not been observed so far in experiments on transition-metal oxides. This has been most clearly demonstrated for La$_{2-2x}$Sr$_x$CuO$_4$ (Ref. 2), where $\Delta V_M$ is of order $\sim$ 1 eV in the point-charge model with formal ionic charges, but is not detectable experimentally by photoemission spectroscopy within the accuracy of $\leq$ 100 meV.

In this study, we have investigated the effect of $\Delta V_M$ from the shifts of the core-level photoemission spectra of La$_{0.6}$Sr$_{0.4}$MnO$_3$ (LSMO) thin films under various epitaxial strain from three kinds of substrates, SrTiO$_3$ (STO), (LaAlO$_3$)$_{0.3}$-(SrAl$_{0.5}$Ta$_{0.5}$O$_3$)$_{0.7}$ (LSAT), and LaAlO$_3$ (LAO). Konishi et al. (Ref. 3) have reported that the electronic structures of LSMO thin films are affected by strains from the substrates. It becomes a ferromagnetic metal on STO and LSAT and a C-type antiferromagnetic insulator on LAO. Among these three samples, one expects that $V_M$ (and $\mu$ to a lesser extent) changes but that the other terms in Eq. (1) are kept unchanged because the band filling remains unchanged. We found that the amount of the shifts was of order $\sim$ 100 meV and is similar to that predicted by the Madelung potential, indicating that changes in $V_M$ are experimentally observed. In particular, the experimental shifts of the La 4$d$ and Sr 3$d$ core levels are almost the same as the calculation, whereas those of the O 1$s$ and Mn 2$p$ core levels are negligible, in disagreement with the calculation. We interpret these results in terms of the strong covalent character of the Mn-O bonding.

II. EXPERIMENT AND CALCULATION

The LSMO thin films were fabricated in a laser MBE chamber and transferred in vacuum to a photoemission chamber at BL-2C of the Photon Factory (Ref. 5). The films were grown on the three substrates, LAO (001) (which causes compressive strain), LSAT (001) (almost no strain), and STO (001) (tensile strain). The thickness of the films were about 40 nm. We confirmed that all the films exhibited the same electrical and magnetic properties as those reported in the previous studies (Ref. 2, 3). The lattice constants were determined by four-circle x-ray diffraction as summarized in Table I. The photoemission spectra were taken using a Gammatdata Scienta SES-100 spectrometer. All the spectra were measured at room temperature. The total energy resolution was
Madelung-potential calculation \[panel (b)\]. To calculate the Madelung potentials, we assumed formal ionic charges for all the atoms, that is, 3+ for La, 2+ for Sr, 2− for O and 3.4+ for Mn. The energy scales of the shifts (∼ 200 meV) are similar to experiment (∼ 100 meV), which means that changes in \( V_M \) are experimentally observed. If we look into more details, however, different behaviors are seen between experiment and calculation. For the O 1s core level, the calculated Madelung potentials felt by the in-plane and out-of-plane O atoms are quite different and should cause a splitting of the O 1s core-level photoemission spectra, but we do not observe such a splitting as shown in Fig. 1(a).

To compare the experiment and calculation for each core level, we show such comparison in Fig. 3. Interestingly, as shown in Fig. 3(a), the experimental shifts of La 4d and Sr 3d are almost the same as the calculation. We consider that the effects of the changes in the Madelung potential on these core-levels are directly reflected on their binding energy shifts probably because the La and Sr ions do not formally have valence electrons that can suppress changes in the Madelung potential through covalency effect. Figure 3(b) and (c), on the other hand, shows that the experimental shifts of the O 1s and Mn 2p core levels are negligibly small compared with the calculation. This may be attributed to the strong covalency of the Mn-O bonding.

To simulate the effects of covalency between the Mn and O atoms, which may reduce the Madelung potential changes, we also calculated the Madelung potentials in two other models in which the charges on the O atoms are reduced from the ionic value of 2− and the charges on La and Sr atoms retain the ionic values. In the first model, O is assumed to be 1.5− and Mn is 1.9+, and in the second model O is assumed to be 1− and Mn is 0.4+. The calculated results are compared with experiment in Figs. 4 and 5 respectively. As for the La 4d and Sr 3d core levels, agreement between experiment and calculation remains good, which means that this agreement does not depend on the Mn-O covalency. The calculated O 1s core level does not split and shows good agreement

### III. RESULTS AND DISCUSSION

Figure 1 shows the core-level photoemission spectra of the LSMO thin films. The weakness of contamination signals on the higher-binding energy side of the O 1s peak indicates that the surface was reasonably clean owing to the in-situ measurements. One notices here that the experimental shifts of the core levels are on the order of ∼ 100 meV.

Figure 2 shows the binding-energy shifts of each core level of the LSMO thin films obtained from experiment (photoemission spectroscopy) [panel (a)] and Madelung-potential calculation [panel (b)]. To calculate the Madelung potentials, we assumed formal ionic charges for all the atoms, that is, 3+ for La, 2+ for Sr, 2− for O and 3.4+ for Mn. The energy scales of the shifts (∼ 200 meV) are similar to experiment (∼ 100 meV), which means that changes in \( V_M \) are experimentally observed. If we look into more details, however, different behaviors are seen between experiment and calculation. For the O 1s core level, the calculated Madelung potentials felt by the in-plane and out-of-plane O atoms are quite different and should cause a splitting of the O 1s core-level photoemission spectra, but we do not observe such a splitting as shown in Fig. 1(a).

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### TABLE I: In-plane (\(a\)-axis) and out-of plane (\(c\)-axis) lattice constants of LSMO thin films grown on LAO, LSAT and STO substrates.

| Substrate | \(a\) (Å) | \(c\) (Å) | \(c/a\) | \(V\) (Å\(^3\)) |
|-----------|-----------|-----------|---------|----------|
| LAO       | 3.79      | 3.98      | 1.05    | 57.2     |
| LSAT      | 3.87      | 3.87      | 1.00    | 58.0     |
| STO       | 3.91      | 3.83      | 0.98    | 58.6     |

### FIG. 1: (Color online) Core-level photoemission spectra of LSMO thin films epitaxially grown on STO, LSAT, and LAO substrates. (a) O 1s, (b) Mn 2p, (c) La 4d, and (d) Sr 3d.

### FIG. 2: (Color online) Binding-energy shifts of each core level in LSMO thin films. (a) Experimental values determined by photoemission spectroscopy. (b) Calculated values determined from the effect of \( \Delta V_M \) calculated using the point-charge model with formal ionic charges.
In the present analysis, we have ignored changes in the chemical potential $\Delta \mu$ under the epitaxial strain, which would be small but in principle exists. The general increase of the binding energies in the strained samples (on the STO and LAO substrates) relative to the unstrained one (on the LSAT substrate) seen in experiment in Fig. 2 (a) suggests upward shifts of the chemical potential for non-zero strain $q \equiv c/a - 1$. In fact, the lowest order shift with respect to $q$ is $\Delta \mu \propto q^2$ in cubic systems. More systematic studies on transition-metal-oxide thin films on various substrates will further clarify this effect.

IV. SUMMARY

We have investigated the effect of Madelung potentials in the core-level photoemission spectra of LSMO thin films epitaxially grown on various substrates. The amount of binding-energy shifts ($\sim 100 - 200$ meV) is similar in both experiment and calculation, indicating that changes in Madelung potentials are experimentally observed. As for the La 4$d$ and Sr 3$d$ core levels, the experimentally observed shifts were almost the same as the calculation. The experimental shifts of the O 1$s$ and Mn 2$p$ core levels were negligibly small, in disagreement with the calculation. These behaviors can be explained by the strong covalent character of the Mn-O bonding.

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