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Madelung potentials and covalency effect in strained $La_{1-x}Sr_xMnO_3$ thin films studied by core-level photoemission spectroscopy

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We have studied the effects of Madelung potentials on the shifts in the core-level photoemission spectra by investigating $La_{0.6}Sr_{0.4}MnO_3$ 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 in the La 4*d* and Sr 3*d* core levels are almost the same as the calculated Madelung potentials, which we attribute to the nearly ionic character of these atoms. On the other hand, the experimental shifts in the O 1*s* and Mn 2*p* core levels are negligibly small. We consider that this is due to the strong covalent character of the Mn-O bonds.

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I. INTRODUCTION

Madelung potential is one of the most fundamental physical concepts in solids, and explains the cohesive mechanism of crystals.[1] The interest in Madelung potential has recently revived when we consider the interface of polar and nonpolar materials because metallicity at the interface of two insulating materials has been discussed in terms of avoiding the divergence of Madelung potentials in polar materials.[2–6]

In spite of such fundamental importance of Madelung potentials in condensed-matter physics, direct experimental observation of Madelung potentials has not been reported so far. One approach is to use core-level photoemission spectroscopy. The binding energy of a core level observed by photoemission spectroscopy is determined by several factors. The shift in the energy ΔE of the core level measured relative to the chemical potential μ, when the band filling is varied and/or the crystal structure is changed, is given by[7]

$$\Delta E = -\Delta\mu + K\Delta Q - \Delta V_M + \Delta E_R, \qquad (1)$$

where $\Delta\mu$ is the change in the chemical potential μ, ΔQ is the change in the number of valence electrons on the atom, K is the constant, ΔV_M is the change in the Madelung potential V_M, and ΔE_R is the change in the extra-atomic relaxation energy of the core-hole state. When the band filling is varied, both μ and V_M should change, but the effect of ΔV_M has not been observed so far in experiments on transition-metal oxides. This has been most clearly demonstrated for $La_{2-x}Sr_xCuO_4$,[8,9] where ΔV_M is on the order of ~ 1 eV in the point-charge model with formal ionic charges, but is not detectable experimentally by photoemission spectroscopy within the accuracy of $\lesssim 100$ meV.

In this study, we have investigated the effect of ΔV_M from the shifts in 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.*[10] 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 μ 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 on the order of ~ 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 in 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.[11] The films were grown on the three substrates, LAO (001) (which causes compressive strain), LSAT (001) (which causes almost no strain), and STO (001) (which causes tensile strain). The thickness of the films was about 40 nm. We confirmed that all the films exhibited the same electrical and magnetic properties as those reported in the previous studies.[10,12] The lattice constants were determined by four-circle x-ray diffraction as summarized in Table I. In this table, the in-plane (a) and out-of-plane (c) lattice constants are shown and the degree of strain effects are given as c/a, where $c/a > 1$ and $c/a < 1$ correspond to compressive and tensile strain, respectively. The photoemission spectra were taken using a Gammadata Scienta SES-100 spectrometer. All the spectra were measured at room temperature. The energy resolution was about 200 meV. The chemical potential was determined by

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

measuring the spectra of gold, which is in electrical contact with the thin films.

The Madelung potentials were calculated by Ewald's method.[1] When we try to obtain Madelung potentials by directly summing over all ions as in the following formula

$$V_M = \sum_l \frac{q_l}{r_l}, \tag{2}$$

it is very slow in convergence. In Ewald's method, it is given in the following formula

$$\psi(i) = \sum_l \frac{q_l}{r_l} F(\eta^{1/2} r_l) + \frac{4\pi}{\Delta} \sum_{\mathbf{G}} S(\mathbf{G}) G^{-2} \exp(-G^2/4\eta) - 2q_i(\eta/\pi)^{1/2}, \tag{3}$$

where

$$F(x) = \frac{2}{\sqrt{\pi}} \int_x^{\infty} \exp(-s^2) ds. \tag{4}$$

$S(\mathbf{G})$ is the structure factor and η is the parameter for rapid convergence. The trick in Ewald's method is that the difficulty in convergence can be overcome by taking summation in both real [the first term in Eq. (3)] and reciprocal [the second term in Eq. (3)] spaces with one correction term [the third term in Eq. (3)]. The limit of $\eta \to 0$ corresponds to direct summation.

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 1*s* peak indicates that the surface was reasonably clean owing to the *in situ* measurements. The midpoints of the lower-binding-energy slopes are indicated by vertical bars in Fig. 1, and they are taken as representing the shifts in the peaks because this part is generally least affected by possible contamination. One notices here that the experimental shifts in the core levels are on the order of ~100 meV.

Figure 2 shows the binding-energy shifts in 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. First we notice that the energy scales of the shifts (~200 meV) are similar to experiment (~100 meV). If we look into more details, however, different behaviors are seen between experiment and calculation. For the O 1*s* 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 1*s* core-level photoemission spectra, but we do not observe such a splitting as shown in Fig. 1(a).

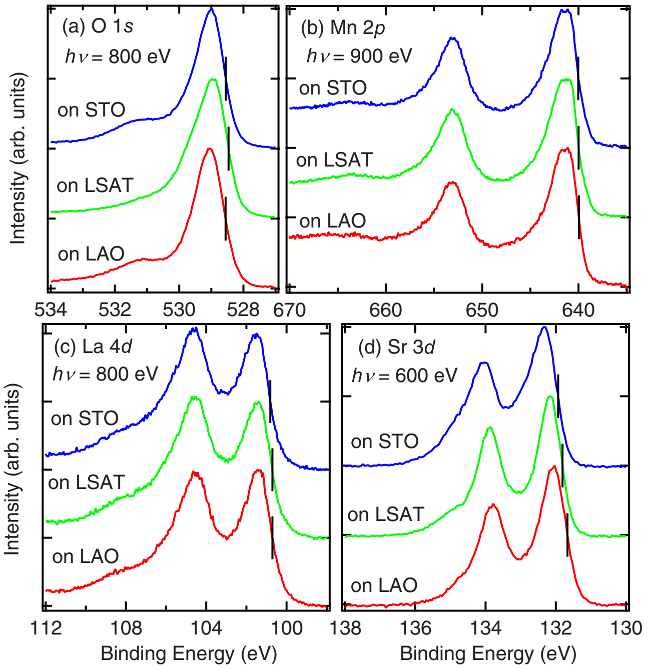

FIG. 1. (Color online) Core-level photoemission spectra of LSMO thin films epitaxially grown on STO, LSAT, and LAO substrates. (a) O 1*s*, (b) Mn 2*p*, (c) La 4*d*, and (d) Sr 3*d*.

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 in La 4*d* and Sr 3*d* 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. Agreement in the case of $c/a = 0.98$ (on STO) is extremely good, but in

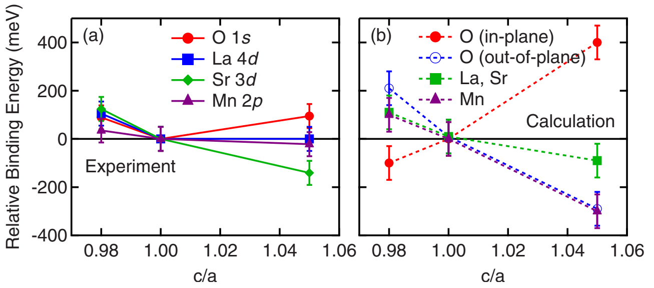

FIG. 2. (Color online) Binding-energy shifts in each core level in LSMO thin films. (a) Experimental values determined by photoemission spectroscopy. (b) Calculated values determined from the effect of ΔV_M calculated using the point-charge model with formal ionic charges.

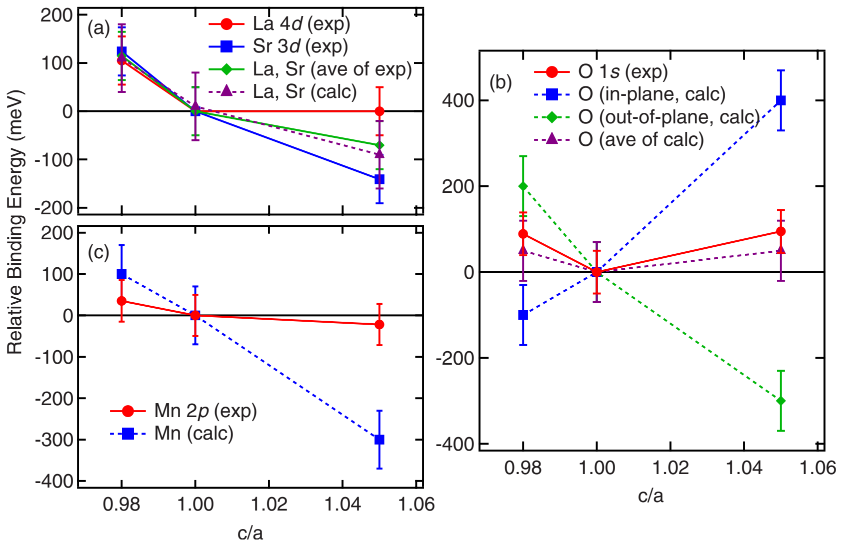

FIG. 3. (Color online) Comparison of the binding-energy shifts in each core level in LSMO thin films between experiment and calculation for the model of $\mathrm{La}_{0.6}^{3+}\mathrm{Sr}_{0.4}^{2+}\mathrm{Mn}^{3.4+}\mathrm{O}_3^{2-}$. (a) La 4*d* and Sr 3*d*, (b) O 1*s*, and (c) Mn 2*p*.

the case of $c/a=1.05$ (on LAO), only the average of the experimental La 4*d* and Sr 3*d* shows good agreement, which may suggest the limitation of our simple assumption of the formal ionic charges of the La and Sr sites as 2.6+ and those of the Mn sites as 3.4+. Figures 3(b) and 3(c), on the other hand, show that the experimental shifts in the O 1*s* and Mn 2*p* 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 assumed to be 0.4+. The calculated results are compared with experiment in Figs. 4 and 5, respectively. As for the La 4*d* and Sr 3*d* 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 1*s* core level does not split and shows good agreement with experiment for the $\mathrm{O}^{1.5-}$ model as shown in Fig. 4(b). As for Mn 2*p*, the agreement becomes better as we decrease the charge on O atoms from −2 to −1, as shown in Figs. 4(c) and 5(c). From the above results, one can see that better agreement between experiment and calculation is obtained when the effects of strong covalency of the Mn-O bonding are taken into account through the reduction in the electric charges on the Mn and O atoms. However, we should also note here that neither the $\mathrm{O}^{1.5-}$ nor O^{1-} model can simultaneously fit both the Mn 2*p* and the O 1*s* experimental data, which suggests that actual effect of covalency cannot be described by simply reducing the effective charges on Mn and O atoms.

The present scenario described above is also consistent with the negligible effects of ΔV_M when the band filling is varied. In the case of filling control, the doped carriers would be relatively uniformly distributed between the Mn and O atoms and ΔV_M is kept almost unchanged in all the core levels.[8,9]

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 would exist. The general increase in the binding energies in the strained samples (on the STO and LAO substrates) relative to the unstrained one

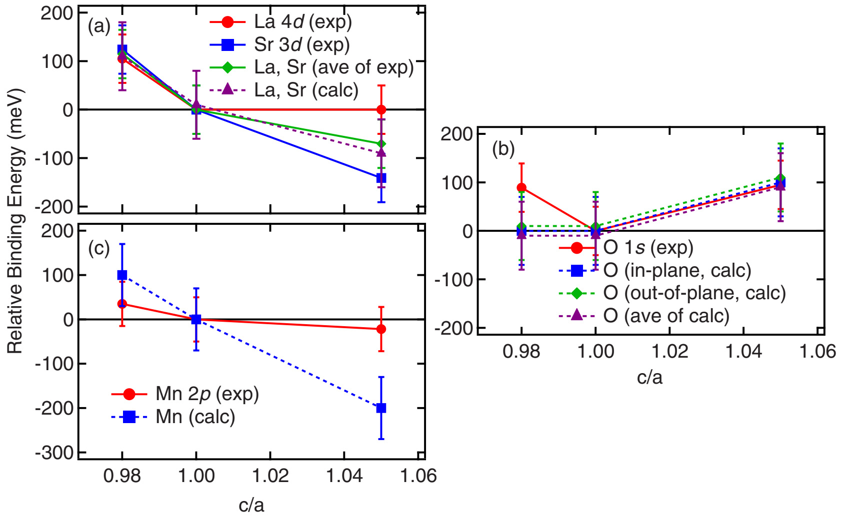

FIG. 4. (Color online) Comparison of the binding-energy shifts in each core level in LSMO thin films between experiment and calculation for the model of $\mathrm{La}_{0.6}^{3+}\mathrm{Sr}_{0.4}^{2+}\mathrm{Mn}^{1.9+}\mathrm{O}_3^{1.5-}$. (a) La 4*d* and Sr 3*d*, (b) O 1*s*, and (c) Mn 2*p*.

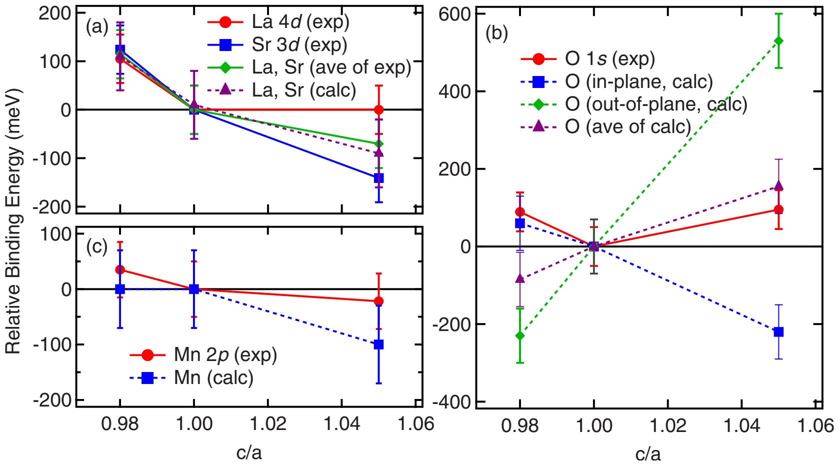

FIG. 5. (Color online) Comparison of the binding-energy shifts in each core level in LSMO thin films between experiment and calculation for the model of $\mathrm{La}^{3+}_{0.6}\mathrm{Sr}^{2+}_{0.4}\mathrm{Mn}^{0.4+}\mathrm{O}^{-}_{3}$. (a) La 4*d* and Sr 3*d*, (b) O 1*s*, and (c) Mn 2*p*.

(on the LSAT substrate) seen in the experiment in Fig. 2(a), suggests upward shifts in the chemical potential for nonzero 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 (~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 in 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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