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Ab initio Hartree-Fock calculations of LaMnO_3 (110) surfaces

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Abstract

We present the results of ab initio Hartree-Fock calculations of the LaMnO_3 (110) surface. Using seven-plane slabs, periodic in 2D and containing three formula units, we compare the properties of a stoichiometric surface with oxygen vacancies, and non-stoichiometric, defect-free surfaces, analyze the dispersion of the effective charges near the surface, and calculate the surface energy before and after relaxation, for both ferromagnetic and antiferromagnetic spin orderings in a slab.

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1. Introduction

Sr-doped LaMnO_3 (LMO) attracts great attention as cathode material for solid oxide fuel cells [1] as well as with respect to its bulk magnetic properties [2–5]. Surprisingly, LMO surface properties have practically not been studied. To our knowledge, there exist only two surface structure LSDA calculations for manganese perovskites; they refer to CaMnO_3 and $\text{La}_{1/2}\text{Ca}_{1/2}\text{MnO}_3$ (100) surfaces in their non-cubic modifications, with a main focus on magnetic properties [6]. However, in fuel cell applications, the operational temperature is so high ($T > 800$ K) that the LMO unit cell is cubic [4,5], and thus Jahn–Teller (JT) lattice deformation around Mn ions and related magnetic and orbital orderings no longer take place.

Of primary interest for fuel cell applications are the LMO surface properties, e.g. the optimal positions for oxygen adsorption, its surface transport properties, as well

as the charge transfer behavior. Typical surface energies for ABO_3 perovskites are several eV [7], much larger than the JT energy in LMO (< 0.4 eV per Mn [5]), or the magnetic exchange energy (10^{-2} eV). In this paper, we present the results of the first ab initio Hartree-Fock (HF) calculations for the LMO surfaces. We start with the bulk properties in Section 2, and show that these are in good agreement with previous ab initio studies and experiments. Then in Section 3 we analyze the results obtained for a polar (110) surface with oxygen vacancies and without them (stoichiometric and non-stoichiometric slabs, respectively). We demonstrate that the surface oxygen vacancies greatly stabilize the polar surface.

2. Bulk LaMnO_3 calculations

Ab initio calculations of the bulk LMO electronic structure were performed earlier in the HF LCAO approximation [2,3] and using the relativistic full-potential-GGA LAPW [4]. In these calculations, several different crystalline structures were considered. The ideal perovskite

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(cubic) structure with five atoms (one formula unit) per a primitive unit cell, is stable above 750 K, with the experimental lattice constant $a_0 = 3.947 \text{ \AA}$. The UHF LCAO calculations [3] give the optimized lattice constant 3.953 \AA , which is very close to the experimental value (3.95 \AA).

In the HF calculations [2] the tetragonal structure, consisting of $\sqrt{2} \times \sqrt{2} \times 2 = 4$ primitive unit cells of the undistorted perovskite structure, was assumed. For such a structure, it was found, in both HF and LSDA approximations, that the ground state of LMO is ferromagnetic (FM, spins of all four Mn atoms in a supercell are parallel).

The low-temperature LMO structure is orthorhombic (comprising four formula units, space group *Pbnm*). The experimental values of the lattice parameters $a = 5.532 \text{ \AA}$, $b = 5.742 \text{ \AA}$, $c = 7.668 \text{ \AA}$, can be compared with $a = b = 5.582 \text{ \AA}$, $c = 7.894 \text{ \AA}$ for the above mentioned tetragonal structure containing four formula unit cells, and the experimental value of the cubic lattice constant $a_0 = 3.947 \text{ \AA}$. The difference in these two sets of structure parameters arises due to strong JT distortions of the MnO-octahedra and their rotations. For the orthorhombic structure, HF, LSDA calculations [2,3], as well as LAPW [4] predict the LMO ground state to be an antiferromagnetic (AFM) insulator, in agreement with the experiment (Mn spins are parallel on a basal plane containing a and b translation vectors, and antiparallel for nearest planes). The calculated energy of the AFM state is lower than for the FM state, by 1.055 eV per Mn in the HF calculation and 0.156 eV per Mn in the LSDA calculation [2]. This demonstrates a strong dependence of the FM–AFM energy difference on the calculation scheme. The orthorhombic lattice parameters optimized in HF calculations [3] are $a = 5.620 \text{ \AA}$, $b = 5.740 \text{ \AA}$, $c = 7.754 \text{ \AA}$. Corresponding to these parameters the ‘virtual’ cubic structure has the lattice constant $a_0 = (1/6)(a\sqrt{2} + c + b\sqrt{2}) = 3.97 \text{ \AA}$. (The latter value is obtained by averaging over the orthorhombic lattice parameters.)

Being interested in a surface modelling for the *high* temperature situation, we performed here LMO bulk calculations for the tetragonal structure neglecting the JT effect and placing the atoms into positions which correspond to the cubic structure. The use of such a supercell allows us to compare the ground state energy for different types of magnetic ordering of Mn atoms. We performed UHF LCAO calculations using the CRYSTAL 95 code [8]. The basis set consists of Gaussian type atomic orbitals and included:

- (a) on La-atom—5s, 5p semicore states, 6s, 5d valence states and outer 6p, 7s, 7p orbitals; the orbital exponents were taken from calculations for La_2CuO_4 [9].
- (b) on Mn-atom the basis was taken from CRYSTAL web-site [10] and includes 3s, 3p-semicore states, 3d, 4s-valence states and outer 4p, 5s, 5p, 4d orbitals.

The Hay-Wadt small core (HWSC) effective pseudopotentials have been adopted for both La and Mn atoms. The all-electron oxygen atom basis set was taken from the HF MnO calculations [11]. In the surface calculations the same basis set was used as for the bulk. However, the reduced point symmetry of a slab and a slow convergence make the surface calculations very time consuming. The electronic configuration of the Mn^{3+} ion was assumed to be $t_{2g}^3 e_g^1$ (all four electrons have the same spin projection, i.e. high spin state). It gives the total spin projection $S_z = 16 \cdot 1/2$ for the FM configuration.

The relative smallness of the various total energy differences (FM–AFM, or bulk-slab) requires a high numerical accuracy in the lattice summations. The direct lattice summation of Coulomb and exchange series is controlled in the CRYSTAL program by five TOLINTEG parameters. The number of sampling points in the Brillouin zone summation over special points of Monkhorst–Pack sets [12] is controlled by a shrinking factor IS. The parameter TOLSCF controls the accuracy of self-consistency in the HF calculations. Our results correspond to the calculations with TOLINTEG = (7 7 7 7 14), IS = 8, TOLSCF = 5, i.e. in these calculations the accuracy in the total energy per unit cell is at least 10^{-5} a.u.

The lattice constant of $a_0 = 3.98 \text{ \AA}$, optimized in our bulk UHF calculations, is close to both the experimental value of 3.95 \AA for the high-temperature cubic perovskite structure, and to the value of $a_0 = 3.97 \text{ \AA}$, found by averaging the orthorhombic lattice parameters optimized in the HF calculations [2]. The ground state energy in our tetragonal structure calculations corresponds to the FM ordering of Mn spins in the unit cell. The calculated energy difference between FM and AFM configurations (0.244 eV per Mn) is larger than 0.0004 eV per Mn obtained in the HF calculations [2] but closer to 0.11 eV per Mn obtained in the LAPW calculations [13].

The calculated LMO valence band (VB) structure is composed of several regions. The lowest-energy region contains semicore Mn 3s (-3.8 a.u.) and Mn 3p (-2.6 a.u.) states. Above this lie the La 5s narrow band (-1.6 a.u.) and the O 2s band. The latter ranges between -1.09 and -1.03 a.u. The next La 5p band (between -0.86 and -0.81 a.u.) is well separated from the bands in the vicinity of the Fermi level. The highest-energy region contains hybridized O 2p and Mn 3d bands, indicating the covalent interaction between the Mn and O atoms. The negligible contribution of La electrons in the VB region indicates that the interaction between La and the MnO_6 octahedra is mostly of Coulombic nature. The whole pattern of VB found in our bulk calculations is in agreement with that obtained in the LAPW [4] as well as with the experimental photoemission data discussed in Ref. [5].

The atomic charges calculated using Mulliken’s population analysis, are $Q(\text{La}) = 2.56e$, $Q(\text{Mn}) = 2.09e$ and $Q(\text{O}) = -1.55e$, which are close to the atomic charges [2] for the orthorhombic LMO structure ($Q(\text{La}) = 2.58e$,

$Q(\text{Mn}) = 2.14e$, $Q(\text{O}) = -1.55e$, and $-1.59e$; in the orthorhombic structure there are two non-equivalent oxygens per unit cell). The calculated charges and the bond populations indicate a covalency of chemical bonding not only for Mn–O atoms, well known in perovskites, but also for La–O atoms. The latter covalency seems to be overestimated since the La atom has relatively diffuse 7s, 7p, 5d atomic orbitals (orbital exponents 0.2237, 0.2239, 0.1602 a.u., respectively).

In Section 3 we discuss the choice of a slab modelling the LMO (110) surface.

3. LaMnO₃ (110) surface calculations

Periodic ab initio calculations of the crystalline surfaces are usually performed considering the crystal as a stack of planes perpendicular to the surface, and cutting out a 2D slab of the finite thickness but periodic in x, y plane. Use of the PW basis requires the introduction of an artificial periodicity in the z direction which makes the results dependent on the vacuum gap between repeated slabs. In contrast, the use of the LCAO basis allows us to consider a *single* slab, as was done in our calculations.

Depending on the crystalline structure and a particular surface, three types of planes may appear in a stack [14]: neutral planes (so-called *type 1* surface), charged planes arranged symmetrically so that there is no dipole moment perpendicular to the unit cell (*type 2*) and lastly, charged planes arranged non-symmetrically (there is a perpendicular dipole moment on *type 3* surfaces). The type 1 (non-polar) planes exist only for the (001) surface of Ba, Sr and Pb titanates with the perovskite structure. In contrast, the LMO has only polar planes of types 2 and 3: for the (001) surface there is a plane sequence LaO–MnO₂–LaO–MnO₂···; for the (110) surface O₂–LaMnO–O₂–LaMnO···; and for the (111) surface Mn–LaO₃–Mn–LaO₃···. The magnitudes of dipole moments depend on the choice of plane sequence and the chemical composition of a perovskite. In present LMO (110) surface calculations we studied type 2 O-terminated slab consisting of seven planes, i.e. four O₂

planes and three LaMnO planes, shown in Fig. 1. The 2D periodic unit translation vectors are shown there on the topmost and lowest planes.

However, such a symmetrical slab is non-stoichiometric. To restore the stoichiometry of the seven-plane slab, we removed one oxygen atom from both O₂-planes terminating the slab, i.e. used the slab of three bulk primitive unit cells with periodically repeated surface *oxygen vacancies*. Such approach is justified since it is well known that the polar surfaces are stabilized by surface defects and surface atom relaxation. The surface energy (*per surface unit cell*) equals $E_s = 0.5(E_o - 3E_{\text{bulk}})$ where E_o and E_{bulk} are the total energies for the O-terminated slab and bulk unit cells.

On the other hand, the defectless surfaces could be modelled only using non-stoichiometric slabs: O₂-terminated or LaMnO terminated. In this case the surface energy E_s could be calculated as

$$E_s = \frac{1}{4}(E_{\text{O}_2} + E_{\text{LMO}} - 7E_{\text{bulk}}), \quad (1)$$

where E_{O_2} and E_{LMO} are the total energies of the slabs with O₂ and LaMnO terminations, respectively.

The comparison of energies for the stoichiometric and non-stoichiometric slabs permits to draw the conclusion on the role of surface oxygen vacancies in a surface stabilization. The O-terminated slab in our calculations consists of three Mn-containing planes. We performed the UHF calculations for both the FM (the number of α – β electrons is $3 \cdot 4 = 12$) and the AFM (α – $\beta = 4$ electrons) states. Since the SCF calculations of these slabs are extremely slow and time-consuming, we used, to a first approximation, the relaxed surface geometry (Table 1) optimized by means of the classical Shell Model [15] based on atom–atom potentials. Since we remove one of the two surface O atoms per unit cell, the remaining atoms reveal displacements not only perpendicularly to the surface, but also in-plane [15]. We take into account only ionic displacements in the first two top planes, which are considerably larger than those in deeper planes.

Similar to the bulk calculations, the FM stoichiometric slab turns out to be energetically more favorable than AFM, by 0.9 eV per Mn. The calculated surface energy is 3.5 eV for the unrelaxed slab and 0.7 eV for the relaxed one, i.e. the

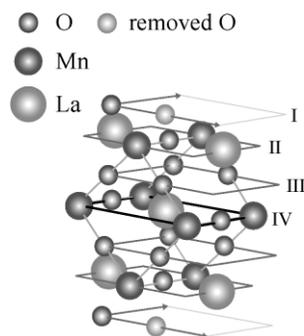


Fig. 1. Seven-plane slab of the stoichiometric O-terminated LaMnO₃ (110) surface with numbered four top planes.

Table 1

Surface relaxation for the two top planes as obtained in the Shell Model calculations [15]. Atomic displacements (in Å) from crystalline sites occur both in-plane (y) and perpendicularly to the surface, along the z axis. Positive z means the displacement outwards the surface

Plane	Atom	y	z
I	O	–0.44	–0.34
II	La	–0.05	0.03
	Mn	–0.24	–0.06
	O	0.22	0.18

relaxation energy (per surface unit cell) is 2.8 eV. Table 2 shows the effective atomic charges Q of slab ions and the deviation of the plane charges ΔQ (per unit cell) from those calculated with the bulk atomic charges. For example, in the plane II for the O-terminated stoichiometric surface the effective charge of the La deviates from that in the bulk by $2.45e - 2.56e = -0.11e$. The effective charges of Mn and O deviate from those in the bulk by $0.1e$ and $-0.05e$, respectively. That is, the LaMnO plane's charge deviates from that in the bulk by $-0.06e$. This value characterizes the charge redistribution in near-surface planes compared to the bulk. For stoichiometric surfaces the sum of ΔQ over all planes is zero.

First of all, the effective charge of surface O atom is considerably reduced with respect to that in the bulk. The charges of both metal atoms in the second plane are slightly more positive, which is almost compensated by the charge of a more negative O atom. Charges of the two O atoms in the third plane are close to those in the bulk. Surprisingly, in the central, fourth plane, the Mn charge turns out to be considerably (by $0.22e$) less positive than in the bulk. This is enhanced by the same trend for the O atoms, which results in a considerable ($-0.35e$) effective charge of the central plane with respect to the bulk.

The calculation for the surface energy of the non-stoichiometric slabs, obtained using Eq. (1), gives $E_s = 6.8$ eV, i.e. about factor of 2 larger than the surface energy of the stoichiometric slab. This demonstrates that oxygen vacancies strongly stabilize the polar (110) surface. The charge distribution for the non-stoichiometric O₂- and LaMnO-terminated surfaces is summarized in Table 2. As one can see, the effective charge of Mn in the central plane of the O₂-terminated surface with respect to the bulk value is $-0.22e$, i.e. the same in absolute value but with the sign opposite to that on the O-terminated surface. The two

surface O atoms share nearly the same charge as a single O atom possesses on the stoichiometric surface. Other planes are only slightly perturbed. Since the O₂- and LaMnO-terminated surfaces complement each other, their total charges (with respect to those in the bulk) are expected to be equal in magnitude but of the opposite signs, which indeed takes place.

4. Conclusions

In this Communication, we presented and discussed the ab initio slab calculations of the electronic structure of the polar LnMnO₃ (110) surface. This reveals a considerable surface relaxation (2.8 eV) and a strong (3.3 eV) surface stabilization by the oxygen vacancies. It should be stressed that these oxygen vacancies are energetically required and hence are essential elements of the polar surface structure. We have also demonstrated a considerable near-surface charge redistribution as compared to the bulk material. The HF calculations of a similar slab for the SrTiO₃ (110) O-terminated stoichiometric surface [16] give the surface energy of 1.4 eV, larger than calculated for the LMO in this paper. We are well aware of the fact that at high temperatures (e.g. under fuel cell conditions) local entropy contributions can significantly affect the structure of the surface. To check this, classical and quantum molecular dynamics simulations would be of great interest.

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Table 2

The effective atomic charges Q (e) in four unrelaxed top layers of the LMO (110) surface, both stoichiometric O-terminated, and non-stoichiometric (O₂- and LaMnO-terminated), as well as the relevant deviations of plane charges, ΔQ (e) from those in the bulk ($Q(\text{La}) = 2.56e$, $Q(\text{Mn}) = 2.09e$, $Q(\text{O}) = -1.55e$)

Plane	Atom	Stoichiometric O-terminated, Q, e	$\Delta Q, e$	O ₂ -terminated, Q, e	$\Delta Q, e$	LaMnO-terminated, Q, e	$\Delta Q, e$
I	O	-1.16	0.39	-0.77	1.56	-1.86(O)	-1.40
						1.73(La)	
						1.83(Mn)	
II	La	2.45	-0.06	2.52	-0.06	-1.67(O)	-0.24
	Mn	2.19		2.10			
	O	-1.60		-1.58			
III	O	-1.66	-0.16	-1.58	-0.06	-1.69(O)	0.17
	O	-1.60		-1.58		2.56(La)	
IV	La	2.54	-0.35	2.55	0.18	-1.63(O)	-0.16
	Mn	1.87		2.31			
	O	-1.66		-1.58			

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