Electronic structure of the layered manganite $LaSr_2Mn_2O_7$

P. K. de Boer and R. A. de Groot
Electronic Structure of Materials, Research Institute for Materials, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands
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Ab initio electronic structure calculations, based on density-functional theory within the generalized gradient approximation, on $LaSr_2Mn_2O_7$ are reported. The bulk electronic structure shows a gap in the minority-spin channel, while the Fermi energy lies at the bottom of the minority conduction band. At the surface of $LaSr_2Mn_2O_7$, the magnetic moment per formula unit and the spin polarization at the Fermi energy are lowered with respect to the bulk values. [S0163-1829(99)08139-4]

I. INTRODUCTION

Manganese-based perovskites have received considerable attention in recent years due to their wide variety of fascinating physical properties. Those properties include, for instance, colossal magnetoresistance,[1,2] magnetostructural transition,[3] magnetic polarons,[4] current switching of resistive states,[5] light-induced metal-insulator transition,[6–8] and charge ordering.[9]

The layered variants of the perovskite structure have the general formula $A_{n+1}Mn_nO_{3n+1}$, with A being an admixture of trivalent and divalent cations. From an experimental point of view, the layered manganites are more easily prepared and characterized. Especially the $(n=2)$ compounds[10] have attracted intensive interest. The layered crystal structure affects many properties. For instance, magnetoresistances are larger,[11–13] Curie temperatures T_c are lower, pressure dependences are different,[14] and magnetic polarons are larger.[15]

One of the interesting properties of the manganites is the electronic structure. Several *ab initio* electronic structure calculations on the $(n=\infty)$ perovskite compounds have been reported.[16–18] They showed that the ferromagnetic manganites are half-metallic, which has recently been verified experimentally.[19,20] There could be a relationship between half-metallic magnetism and the occurrence of magnetoresistance. Half-metallic materials are of importance as the source of spin-polarized electrons in, e.g., spin electronics. Since layered manganites cleave more easily and form well-defined electrically neutral surfaces, a study of the amount of spin polarization is timely.

Ab initio calculations on layered manganites have not been reported, with the exception of a bulk LSDA+U calculation,[21] which shows only a very limited amount of data and no details of the calculation. We have calculated the electronic structure of the layered manganite $LaSr_2Mn_2O_7$. The choice for this compound is based on the following considerations. Most reports on the layered manganites have focused on the compounds $La_{2-2x}Sr_{1+2x}Mn_2O_7$. The ferromagnetic regime, where the highest values of the magnetoresistance occur, is roughly between the doping levels $x=0.2$ and $x=0.5$. For efficiency reasons the unit cell should be taken as small as possible in the calculations. Therefore, we have focused on the $x=0.5$ compound.

Hence, we have calculated the electronic structure of $LaSr_2Mn_2O_7$. Furthermore, in order to reveal the influence of the presence of a surface on the electronic structure, we also performed a slab calculation.

II. CALCULATIONS AND STRUCTURE

The crystal structure of $LaSr_2Mn_2O_7$ can be viewed as a stacking of sheets of double layers of MnO_6 octahedra. The space group of the crystal structure is $I4/mmm$ (No. 139). Unit-cell parameters are taken from Ref. 22. The La and Sr atoms occupy the $2b$ and $4e$ $(z=0.318)$ sites. The La and Sr atoms are, to some extent, randomly distributed among those sites, although the $4e$ site is preferred by the Sr atoms.[22] In our calculations the Sr atoms were placed at the $4e$ sites and the La atoms at the $2b$ sites.

The calculation of the surface electronic structure of $LaSr_2Mn_2O_7$ was performed with a slab, built by a stacking of three double Mn layers and a vacuum region with a length of 6 Å in the stacking direction. This resulted in a unit cell with a c axis of 35.9946 Å. The surface layer consisted of a SrO layer, which is the most probable geometry both from considerations on the crystal structure and from considerations on the charges of the ions. The SrO layer, consisting of Sr^{2+} and O^{2-} ions, is electrically neutral in the sense that it bears no net electrical charge. The slab and bulk unit cells are shown in Fig. 1.

The calculations were performed with the full potential linearized augmented plane wave (LAPW) method,[23] which is based on the density-functional theory (DFT). Exchange and correlation were treated within the generalized gradient approximation.[24] The standard basis set of plane waves was extended with local orbitals. In the calculation of the electronic structure of bulk $LaSr_2Mn_2O_7$ approximately 1000 plane waves were used. In the slab calculation planes waves up to the same maximum plane-wave length K_{max} as in the bulk calculation were used, resulting in a basis set with approximately 3600 plane waves. The radius of the La and Sr spheres was 2.5 a.u., while the radius of the Mn and O spheres was 1.8 a.u. The Brillouin-zone integration was performed with the modified tetrahedron method on a special mesh of 56 k points for the bulk calculation. This was more than enough in order to reach numerical convergence. The slab calculation was performed with 15 k points, which was enough for calculating integrated properties, such as charges and magnetic moments, reliably.

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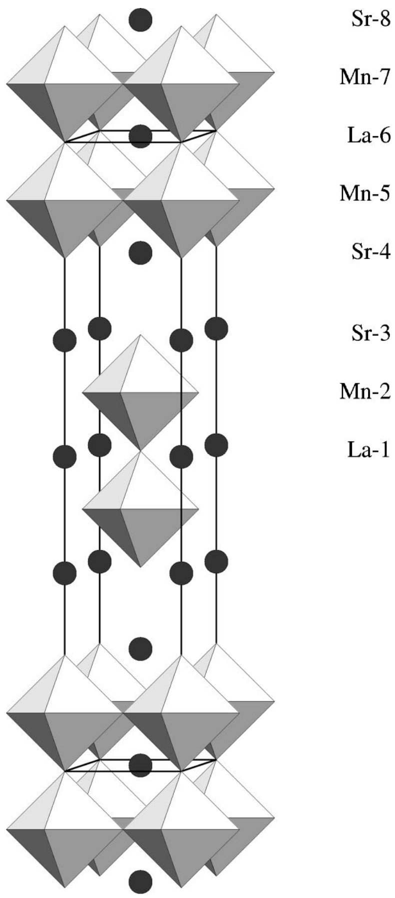

FIG. 1. The crystal structure of $LaSr_2Mn_2O_7$. Oxygen atoms are placed at the corners of the octahedra, Mn atoms at the center of the octahedra. The octahedra in the figure are undistorted. They are in fact distorted both experimentally and in the calculations. The black spheres denote La/Sr atoms. The solid line encloses the conventional unit cell of bulk $LaSr_2Mn_2O_7$. Shown are three double Mn layers. The unit cell of the slab calculations is built by these three double layers plus an extra vacuum region of 6 Å. Each layer of atoms is labeled by a number and the metal atom in the layer.

III. RESULTS

The band structure of bulk $LaSr_2Mn_2O_7$ is shown in Figs. 2 and 3 (majority- and minority-spin channel, respectively). The total and sphere projected density of states, as well as the density of states in the interstitial space, is shown in Fig. 4.

The bands between 17 and 20 eV below the Fermi energy are the O 2s bands. The La 5p states and the Sr 4p states lie at 15–16 eV below E_F. The bands between 1.5 and 7.5 eV below the Fermi energy are primarily derived from O 2p states. Considering the majority-spin direction, the bands between 1.5 eV below the Fermi energy and 2.5 eV above the Fermi energy are mainly formed by Mn 3d states. The wide-bands crossing the Fermi level have mainly e_g character, while the more narrow t_{2g} states lie near 1 eV below E_F. Due to the exchange splitting, the Mn 3d states of the minority-spin channel lie approximately 2 eV higher than the corresponding states of the majority-spin direction. As a consequence, the minority channel shows a gap of 1.7 eV in the electronic structure near the Fermi energy. The Fermi energy lies just at the bottom of the minority conduction band. The narrow bands at 2.5 eV above E_F are formed by unoccupied La 4f states.

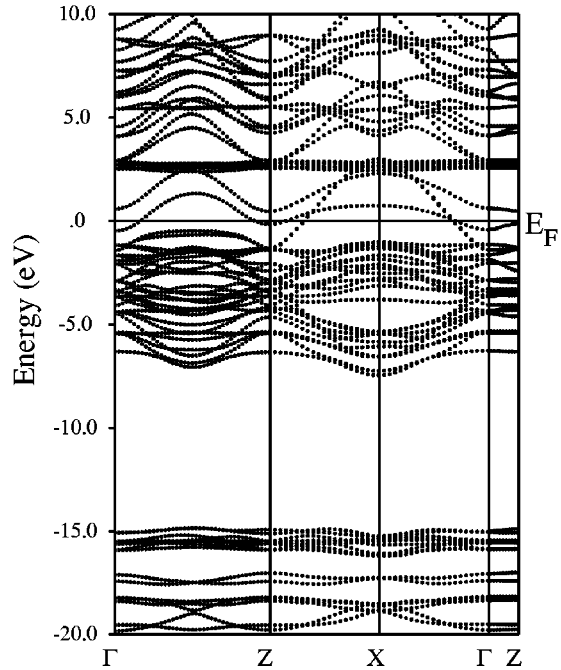

FIG. 2. Band structure of the majority-spin channel of $LaSr_2Mn_2O_7$.

The O 2p and Mn 3d states, especially those of the majority-spin direction, are strongly hybridized. This is reflected, for instance, in the broader width of the majority O 2p bands. Further, the density of states at the Fermi energy, which is mainly formed by Mn e_g states, has a substantial O character, as can be seen in Fig. 4.

If $LaSr_2Mn_2O_7$ would be really half-metallic, the spin polarization at the Fermi energy would be 100%, and the mag-

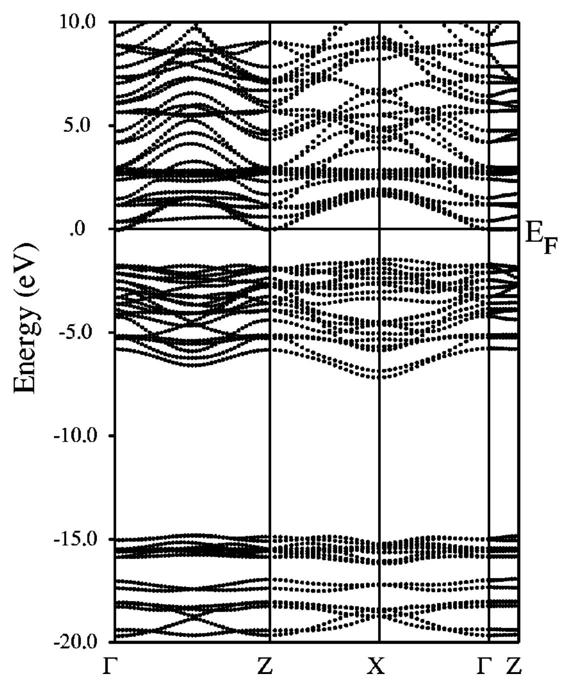

FIG. 3. Band structure of the minority-spin channel of $LaSr_2Mn_2O_7$.

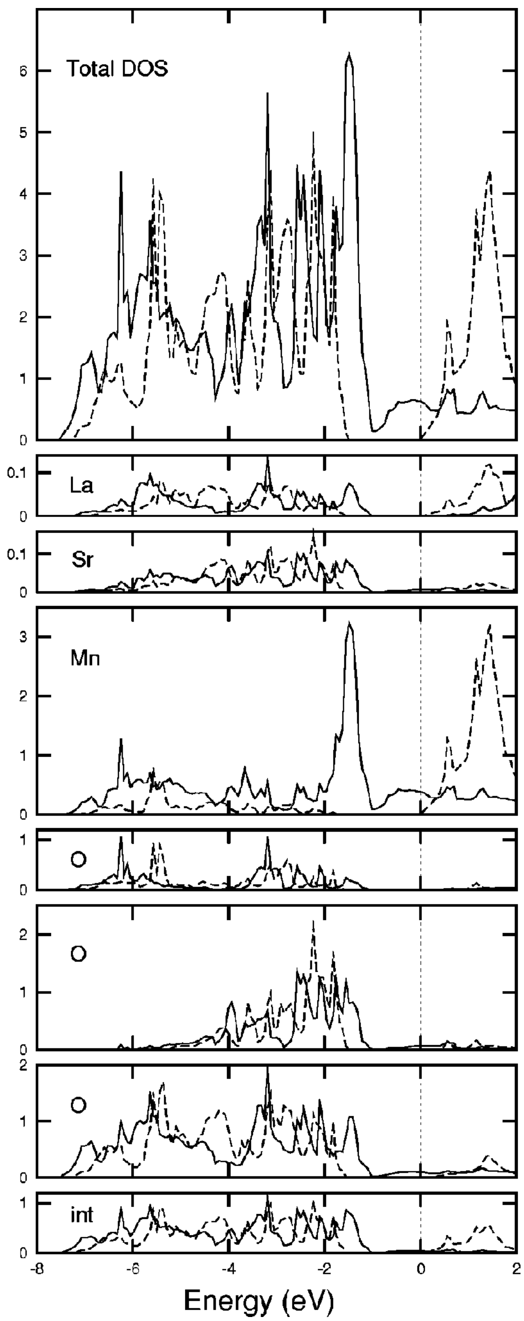

FIG. 4. Total density of states, density of states per atom, and density of states in the interstitial space (in states/eV). The solid (dashed) line denotes the density of states of the majority- (minority-) spin channel. The three different O atoms successively lie in the same layer as the La, Sr, and Mn atoms.

netic moment would be an integer number, in this case 7 μ_B. Since the bottom of the minority conduction band lies just below the Fermi energy, the electronic structure is not half-metallic, but the characteristic values are close to the half-metallic ones. The minority density of states at the Fermi energy is very low, resulting in a spin polarization of 90% at E_F. The primitive unit cell bears a magnetic moment of 6.995 μ_B.

The strong anisotropy, due to the layered crystal structure, is well reflected in the band structure. In the directions perpendicular to the stacking direction, i.e., the lines $\Gamma ZX\Gamma$, the bands show an appreciable dispersion. Along the line ΓZ parallel to the stacking direction, almost no dispersion is present.

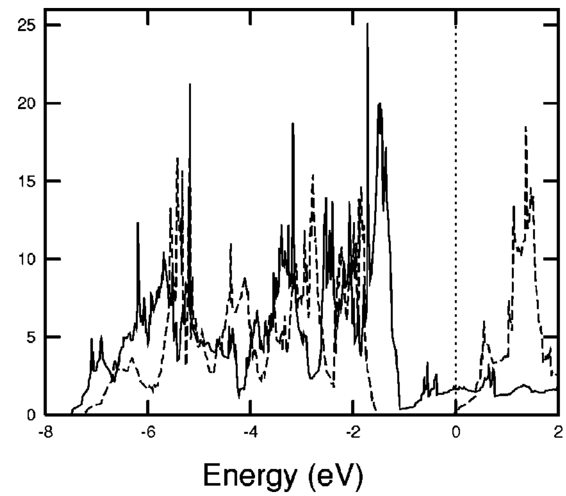

FIG. 5. Total density of states (in states/eV), resulting from the slab calculation.

The electronic structure, resulting from the slab calculation, shows many similarities to the bulk electronic structure of $LaSr_2Mn_2O_7$. The band structure is strongly anisotropic, a gap is present near the Fermi energy in the minority channel, and the widths of the bands are the same within 0.1 eV. Figure 5 shows the total density of states of the slab unit cell. The density of states has basically the same energy dependence as the bulk density of states, besides a factor of 3 due to the larger unit cell. The main difference is the size of the gap for the minority-spin direction, which is now 1.5 eV. The densities of states per atom (not shown) are very similar to the bulk, even for the Sr and O atoms at the surface.

The charges and magnetic moments within each sphere are listed in Table I. Those numbers are dependent on the choice of the sphere radii, of course. However, this does not affect a comparison between the bulk and the slab calculations, which were performed with the same set of radii. The differences between the bulk and slab calculations are very small for most atoms, especially for the central layers (La-1, Sr-3). This shows that the central layers are already quite well converged to the bulk electronic structure.

We will now discuss the differences that are larger than 0.005 electrons and/or 0.005 μ_B. The Mn spheres in layer Mn-5 contain 0.016 majority electrons less than in the bulk, and 0.007 less minority electrons, resulting in a magnetic moment which is 0.009 μ_B smaller. The charges in the Mn sphere in layer Mn-7 are larger than the bulk values, 0.002 (majority) and 0.014 (minority) electrons, respectively. The magnetic moment in this sphere is 0.012 μ_B smaller. The Sr and O atoms in the surface layer both have lower charges for both spin directions. The Sr atom contains 0.025 (0.027) less electrons for the majority (minority) spin direction, while these numbers are 0.024 and 0.027, respectively, for the O atom.

The charge differences show that there is some oscillation present in the direction perpendicular to the surface. The magnetic moments in the layers near the surface are lowered with respect to the bulk. As a consequence, the magnetic moment of the slab unit cell is 20.915 μ_B. Assuming that the central layers (La-1, Mn-2, Sr-3, including the interstitial

TABLE I. Total number of electrons and magnetic moments within each atomic sphere.

Layer	Atom	No. electrons majority	No. electrons minority	Magnetic moment (μ_B)
		Slab		
La-1	La	26.907	26.883	0.024
	O	3.897	3.849	0.048
Mn-2	Mn	12.618	9.698	2.920
	O	3.916	3.846	0.070
Sr-3	Sr	17.951	17.947	0.004
	O	3.845	3.805	0.040
Sr-4	Sr	17.951	17.947	0.004
	O	3.844	3.806	0.038
Mn-5	Mn	12.597	9.687	2.910
	O	3.913	3.846	0.067
La-6	La	26.907	26.883	0.024
	O	3.896	3.849	0.047
Mn-7	Mn	12.615	9.708	2.907
	O	3.914	3.848	0.066
Sr-8	Sr	17.926	17.920	0.006
	O	3.818	3.777	0.041
		Bulk		
La-1	La	26.907	26.883	0.024
	O	3.894	3.848	0.046
Mn-2	Mn	12.613	9.694	2.919
	O	3.914	3.844	0.070
Sr-3	Sr	17.951	17.947	0.004
	O	3.842	3.804	0.038

space in that region) carry a bulklike magnetic moment ($6.995\,\mu_B$), the magnetic moment per formula unit at the surface is only $6.960\,\mu_B$.

The spin polarization of electrons at the Fermi energy is shown in Table II. The spin polarization is a quantity that is more sensitive to the number of k points used in the integration scheme than integrated properties such as charges and moments. This could be an explanation why the polarization at the central layers is lower than the polarization resulting from the bulk calculations, while other properties of the central layers are almost the same as the bulk properties. It is, however, still possible to compare the polarizations of the different layers in the slab calculation. The global trend is a decrease in polarization towards the surface, although the polarization in the Mn layers shows again an oscillation effect. The decreasing polarization is in agreement with the lowering of magnetic moments near the surface, indicating the reliability of the polarization calculation.

IV. DISCUSSION

Results of calculations, performed within the scope of DFT, should be considered with caution, especially in the case of transition-metal oxides. Localized states, such as the Mn d states, are usually predicted to have an energy that is too high in calculations that make use of approximations like the local-density approximation (LDA) or the general gradient approximation. The calculations show an electronic

TABLE II. Spin polarization at the Fermi energy in the whole unit cell, in the interstitial space, and in each layer of atoms. The spin polarization P is defined as $P=[N_\uparrow(E_F)-N_\downarrow(E_F)]/[N_\uparrow(E_F)+N_\downarrow(E_F)]$. Only contributions from the density of states within the atomic spheres are taken into account in the calculated polarizations per layer.

Region	Polarization
Slab	
Total	76%
Int.	54%
La-1	79%
Mn-2	78%
Sr-3	98%
Sr-4	99%
Mn-5	97%
La-6	73%
Mn-7	58%
Sr-8	96%
Bulk	
Total	90%
Int.	75%
La-1	91%
Mn-2	90%
Sr-3	99%

structure that is very close to being half-metallic. The ($n=\infty$) perovskite manganites show a calculated electronic structure that is very resemblant to the electronic structure of $LaSr_2Mn_2O_7$: a gap in the minority-spin direction, the Fermi level being positioned at—or just below—the bottom of the minority conduction band. Recent experiments showed that perovskite manganites are indeed half-metallic.[19,20] It is expected that corrections to the approximation applied in this paper (like self-interaction correction or an LDA+U scheme) will tend to shift the occupied states to lower energies with respect to the unoccupied states. If this will be the case, a truly half-metallic electronic structure could be the result for the layered manganites as well. This would favor the layered manganites over the ($n=\infty$) perovskite manganites in experimental research, since the layered manganites are more easily prepared and characterized.

A priori, it is expected that the possible half-metallic character is even enhanced at the surface, due to band narrowing. However, band narrowing, a common feature at the surface even in layered transition-metal dichalcogenides,[25] does not occur here. Further, near the surface the bands are not shifted in energy, showing that the Madelung potential at the surface is similar to that in the bulk. This is related to the electrical neutrality of the surface layer. Hence, the bulk and the surface electronic structure of $LaSr_2Mn_2O_7$ are in fact remarkably similar. The main differences are the slightly lower magnetic moment per formula unit and spin polarization of electrons at the Fermi energy at the surface as compared with the bulk. Due to the small differences between bulk and surface, experimental techniques that are surface sensitive are still valuable tools for determining bulk properties here.

The occurrence of magnetoresistance is related to the asymmetry between the electronic structure of the two spin directions. Layered manganites generally exhibit larger magnetoresistances than the original perovskite manganites. Since the electronic structure of $LaSr_2Mn_2O_7$ is less asymmetric than the electronic structure of the perovskite manganites, the higher magnetoresistances cannot be explained from electronic structure calculations alone.

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