**La\textsubscript{7/8}Sr\textsubscript{1/8}MnO\textsubscript{3}: long period orbital order with hole stripes**

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The electronic structure of \textit{La}\textsubscript{7/8}Sr\textsubscript{1/8}MnO\textsubscript{3} was studied by using the rotation-invariant LSDA (Local Spin Density Approximation)+U formalism. We found the specific kind of charge and orbital order for ferromagnetic insulating solution in 2\texttimes 2\times 4c supercell, where \(a\), \(b\), and \(c\) denote cubic perovskite axes. The holes are distributed over 3-line stripes in every second \(ac\) plane along \(a\) axis. The stabilization mechanism of the hole stripe is attributed to the strong \(p-d\) hybridization.

Much attention has been focused on doped perovskite manganite systems \(\text{La}_{1-x}\text{Sr}_x\text{MnO}_3\), because of its metal-insulator transition, colossal magnetoresistance, spin structures and properties, and charge and orbital order. The lightly doped \(\text{La}_{7/8}\text{Sr}_{1/8}\text{MnO}_3\) shows the reentrant structural transition of orthorhombic structure \(O^+\rightarrow O'\rightarrow O^+\), where the transition temperatures are 160 K and 260 K, respectively \[1\]. Further, the sample shows the ferromagnetic transition at \(T_c=200\) K \[1\]. The ferromagnetic order suppresses drastically the static Jahn-Teller distortion. The resistivity in the \(O'\) phase below \(T_c\) is affected by the metallic temperature dependence and, therefore, the boundary of the low temperature \(O^+\) and \(O'\) phases coincides with the insulator-metal phase boundary. The paramagnetic state is insulating. Yamada et al. \[2\] reported the observation of satellite spots in the low temperature \(O^+\) phase, corresponding to \(2a\times 2b\times 4c\) supercell structure \[3\], and proposed the polaron order in this phase. Endoh et al. \[4\] confirmed the super-lattice structure in the low temperature \(O^+\) phase of \(\text{La}_{0.88}\text{Sr}_{0.12}\text{MnO}_3\) but reported no signal for charge order in the \(x\)-ray study. They also reported the G-type orbital order in the low temperature \(O^+\) phase, deduced from the resonant \(x\)-ray scattering. Mizokawa et al. \[5\] found several stable spin, orbital and charge ordered states, using the model Hartree-Fock Hamiltonian. They introduced small Jahn-Teller distortion for opening the band gap. The most striking feature of \(\text{La}_{7/8}\text{Sr}_{1/8}\text{MnO}_3\) may be the observation of orbital order and insulating property in a ferromagnetic system without any (or very small) Jahn-Teller distortion.

In this Letter, we present the results of \textit{ab-initio} self-consistent calculations of the electronic structure of \(\text{La}_{7/8}\text{Sr}_{1/8}\text{MnO}_3\), obtained by using the LSDA+U formalism \[6\] in the framework of linear muffin-tin orbital method in the atomic sphere approximation (LMTO-ASA) \[7\]. and the experimentally determined crystalline data of low temperature \(O^+\) phase \[6\]. The Coulomb and the exchange parameters are set to be \(U=8.0\) eV and \(J=0.88\) eV for Mn \(d\)- and \(U=6.0\) eV for O \(p\)-shell, respectively \[6\]. The inclusion of LSDA+U potential correction for O \(p\)-shell was found to be crucial in the present calculations, since it controls the value of charge transfer energy between Mn \(d\)- and O \(p\)-valence orbitals \[6\].

In order to understand the nature of the doped material, we have calculated the electronic structure of the model ferromagnetic undoped \(\text{LaMnO}_3\) compound with the crystal structure parameters corresponding to the doped case. It was found that one \(e_g\) majority spin electron per Mn site occupies alternatively \(\frac{1}{\sqrt{2}}(\phi_{3z^2-r^2}+\phi_{x^2-y^2})\) and \(\frac{1}{\sqrt{2}}(\phi_{3z^2-r^2}-\phi_{x^2-y^2})\) orbitals \[6\] (Fig. 1 (i)). The band gap of 0.68 eV is opened in the energy spectrum between majority spin states (Fig. 2), since there is already an extended gap of 4.42 eV in the minority spin subband in the vicinity of the Fermi energy. One can suppose that unusual ferromagnetic insulating state of model undoped \(\text{LaMnO}_3\) compound is stabilized due to fine balance between double-and super-exchange interactions. Without orbital order the double-exchange mechanism would bring the ferromagnetic metal ground state. The insulating state appears due to the orbital polarization in the twofold degenerated \(e_g\) majority spin band occupied by one electron. The super-exchange interaction in orbitally ordered state is ferromagnetic due to specific overlapping of \(\frac{1}{\sqrt{2}}(\phi_{3z^2-r^2}+\phi_{x^2-y^2})\) and \(\frac{1}{\sqrt{2}}(\phi_{3z^2-r^2}-\phi_{x^2-y^2})\) orbitals on neighboring Mn ions on \(ac\) plane. That is an example of an \textit{antiorbital} but ferromagnetic order (for review of mutual correspondence between orbital order and preferable magnetic interactions in insulators containing orbitally degenerate transition metal ions see, e.g. \[8\]). The alignment of the same \(e_g\) orbitals along \(b\) direction (see Fig. 1 (i)) gives rise to the larger band width and resultant further stability than the case of the alignment of the alternative \(e_g\) orbitals.

To investigate the influence of the Sr doping, we have calculated the energy spectrum of \(\text{La}_{7/8}\text{Sr}_{1/8}\text{MnO}_3\) for the minimal possible unit cell containing eight Mn atoms and one hole. It was found to be a ferromagnetic half-metal with low density of states at the Fermi level equal.
FIG. 1. Angular distributions of $e_g$ electron spin density (ADESD) of Mn atoms and corresponding spatial orbital order in the $2a \times 2b \times 4c$ unit cell of La$_{7/8}$Sr$_{1/8}$MnO$_3$ compound for undoped (i), doped metallic (ii), and doped insulating (iii) solutions. For case (iii) there are translated atoms from the top to the bottom plane along $c$ axis, and there are no translated atoms along $a$ and $b$ axes. The unit cells for (i) and (ii) cases are increased up to the same size as for (iii) case to make the comparison more convenient. The ADESD is defined as $\rho(\theta, \phi) = \sum_{m,m'} Q_{m,m'} Y_m(\theta, \phi) Y_{m'}(\theta, \phi)$, where $Q_{m,m'} = n_{m,m'}^+ - n_{m,m'}^-$ is $2 \times 2$ $e_g$-orbital occupation matrix obtained in our self-consistent calculation and $Y_m(\theta, \phi)$ are corresponding spherical harmonics.

to 0.10 states/(eV·atom Mn). One would expect the uniform distribution of hole state over all eight Mn atoms for the metallic solution. However it is not the case. The Mn1 atom (for denotations see Fig. 1 (ii)) shows the maximum loss of its $d$-electron density (0.06 e) and reduces its $d$-magnetic moment by 0.10 $\mu_B$ in comparison with undoped state [14]. This deficiency of $d$-electron density looks as the decrease of the $e_g$ orbital size in Fig. 1 (ii). Thus all these facts indicate the preferable occupation of Mn1 site by the hole states.

The influence of Mn1 hole on the nearest sites Mn2 and Mn3 (Fig. 1 (ii)) is so strong that the changes of Mn2 and Mn3 atoms in $d$-occupancy (0.04 e), $d$-magnetic moment (0.07 $\mu_B$) and $e_g$ orbital density angular redistribution allow to consider these sites as those containing the hole together with Mn1. At the same time the change of $e_g$ states of Mn1’ atom is mainly in shape. There are no essential changes of $d$-occupancy and $d$-magnetic moment in comparison with model undoped case in the electronic states of second plane Mn atoms (backplanes in Fig. 1 (i) and (ii) look similar). Thus we conclude that one hole per eight Mn sites is distributed in such a way that only three Mn atoms out of eight change significantly their $e_g$ electronic shell.

All these three hole-doped Mn atoms are in the same $ac$ plane (frontplane in Fig. 1 (ii)). In frontplane the $e_g$ orbitals of the hole-doped Mn atoms overlap strongly leading to the formation of a wide band. On this stage – for small unit cell restricted by eight Mn atoms – double exchange would win super-exchange and the spectrum is metallic. It is interesting to note that partial densities of states have vanishing values at the Fermi level for Mn atoms on the backplane. Thus, the backplane remains insulating even for doped metallic solution.

However, the real La$_{7/8}$Sr$_{1/8}$MnO$_3$ compound demonstrates the insulating properties. We observed the appearance of the small (0.03 eV) band gap in the energy spectrum of La$_{7/8}$Sr$_{1/8}$MnO$_3$ (Fig. 2) when the unit cell was increased up to $2a \times 2b \times 4c$ size, where $a$, $b$, and $c$ denote cubic perovskite axes. In this ferromagnetic insulating case there are two holes per sixteen Mn atoms. One can see two “impurity” peaks in the density of states in the energy region of former band gap for model undoped case (Fig. 2). The low-energy peak has capacity precisely equal to 1 and is well separated from the rest band. It is mostly originated from Mn3 and Mn4 states with the admixture of Mn2 states. The second peak is not split enough from the band to be single but its capacity reaches 1 in the deep. States of Mn1 and Mn2 contribute mostly to this peak. In these two “impurity” peaks, 79 % of hole states are localized on six Mn1-Mn4 atoms forming a 3-line stripe (Figs. 1 (iii), 3) and their...
nearest oxygen neighbors. The distribution of hole states between these Mn and O atoms belonging to the stripe is 44 % and 35 %, correspondingly.

The same conclusion – hole states localization on stripe follows from the values of Mn d-occupancy and d-magnetic moment values. The deficiency of d-occupancy is 0.07, 0.05, 0.04, 0.04 e and that of d-magnetic moment is 0.11, 0.09, 0.07, 0.07 µB for Mn1, Mn2 Mn3, and Mn4 atoms, correspondingly; for the rest of Mn atoms these decreases are essentially less.

The comparison of the mutual orientation of e_g orbitals between undoped and doped solutions also support this conclusion. One can see from Table 1 for frontplane Mn atoms that Mn5 and Mn6 atoms contain no holes in their majority spin (↑) e_g shell. Wave function of e_g^1 electron of Mn6 atom is the closest to that of undoped case (close to equal contributions of φ_3z^2−r^2 and φ_5x^2−y^2), whereas e_g^1 electron of Mn5 atom occupies the orbital close to φ_3y^2−r^2 wave function. Other Mn atoms presented in Table 1 contain the hole because of their reduced e_g^1 occupancy. The contributions of φ_3z^2−r^2 and φ_2z^2−y^2 wave functions provide the angular distribution presented in Fig. 1 (iii). And as for the model doped metallic case, the backplane of Mn atoms is free of holes. The holes are localized on Mn atoms in the 3-line stripes along a axis in every second ac plane (Fig. 2) [15].

In LSDA+U formalism, the less occupied is a localized orbital the higher is its energy position[16]. The difference in e_g orbital occupancy of the most empty Mn1 and e.g. Mn2,3 atoms (see Table 1) explains the appearance of two hole peaks. There is no contribution to the first low-energy hole peak from Mn1 e_g states. They are the most empty and contribute only to the second hole peak.

One would expect that two holes per unit cell move apart from each other as far as possible to minimize the Coulomb repulsive energy. However the situation is more complicated due to the strong p-d hybridization. With the help of model hamiltonian describing in the simplest way the interaction t between oxygen p level with d levels of two neighboring manganese ions

$${H} = \begin{pmatrix} d_1 & 0 & t \\ 0 & d_2 & t \\ t & t & p \end{pmatrix}$$

it is easy to simulate the process of hole distribution among the Mn sites. Suppose that one hole is on the first Mn site. Then the presence of the hole leads to the increasing of the d_1 energy due to its smaller occupancy and hence to the increasing of the d_2 level energy due to hybridization via p oxygen. Then the second hole will occupy the d_2 level because it has higher energy. If one hole locates on one specific site (let it be Mn1 in Fig. 1 (iii)), that leads to decreased electron content on the neighboring sites in a (Mn2) and c (two Mn3) directions as it was demonstrated for the doped metallic solution. The second hole occupies Mn2 site with higher energy level and in its turn makes more empty its nearest neighbors along c direction (two Mn4). The hole-rich sites Mn1 and Mn2 are not the same due to essentially different orientation of e_g orbitals of neighboring Mn atoms along c axis. Such system consisting of six hole-doped Mn atoms (Mn1, Mn2, two Mn3, and two Mn4) per 2a×2b×4c supercell is closed and produces small influence on the atoms of next ab-slab (Mn5 and Mn6) and on the Mn atoms in the back ac-plane. The break of long-range e_g orbital

![FIG. 2. Total density of states in the vicinity of Fermi energy (E_F = 0) for doped insulating La_7/8Sr_1/8MnO_3 (solid line; right ordinate) and model undoped LaMnO_3 (dashed line; left ordinate) compounds.](image)

![FIG. 3. The pattern of hole order for La_7/8Sr_1/8MnO_3 obtained in our calculations. Gray circles represent Mn sites containing the hole states, white circles – Mn^{3+} ions.](image)

| atom    | φ_3z^2−r^2 | φ_2z^2−y^2 | occupancy |
|---------|------------|------------|-----------|
| Mn1     | .044       | +.999      | .852      |
| Mn3     | .257       | −.966      | .941      |
| Mn5     | .537       | +.844      | 1.00      |
| Mn2     | .117       | −.993      | .941      |
| Mn4     | .348       | +.938      | .952      |
| Mn6     | .657       | −.754      | 1.00      |
overlapping along $c$ axis leads to the appearance of the insulating state.

The calculated energy gap of 0.03 eV in the doped insulator is very small and can be smeared out with elevating temperature. This temperature may correspond to $T_{OO}$ or the $O^* \rightarrow O'$ transition temperature.

Present orbital order for one undoped plane looks similar to that previously proposed in [10] and thus can be used for the explanation of their experimental dependence of polarization on azimuthal scan. The fact that holes accumulate on one doped $ac$ plane but there are no holes on the other plane is consistent with the observed superlattice satellite spots [2] in neutron diffraction. The charge difference between hole sites and other sites is actually small. Since two holes are localized on six Mn atoms, the hole charge is 1/3 in average. It was demonstrated earlier that hole charge is also spread over oxygen atoms neighboring the stripe, causing the further reduction of charge difference between doped and undoped sites. This may be the reason why several experiments could not detect the present pattern of charge order.

It was demonstrated theoretically for a wide range of magnetic compounds containing Jahn-Teller ions [13] that the exchange mechanism (caused by interplay between on-site Coulomb interaction $U$ and intersite hopping $t$) by itself, without taking Jahn-Teller distortions into consideration, is able to give a correct picture of the orbital order. This conclusion was supported by band structure calculations [10] of undistorted model PrMnO$_3$ compound. The system La$_7$Sr$_1$MnO$_3$ is unique real compound which has an orbital order without Jahn-Teller distortion. And the super-exchange mechanism overcomes the double exchange mechanism and provides the insulating state with orbital order.

In conclusions, we have investigated the electronic structure of ferromagnetic insulating La$_7$Sr$_1$MnO$_3$ using the LSDA+U formalism. We obtained alternative sequence of undoped and doped $ac$ planes with alignment of holes in 3-line stripe along $a$ axis. The long period orbital order and holes in stripe are consistent with experimentally observed properties of this compound.

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