Electronic structures and magnetic properties of a ferromagnetic insulator: La 2 MnNiO 6

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Citation: Journal of Applied Physics **105**, 07E515 (2009); doi: 10.1063/1.3073661
View online: http://dx.doi.org/10.1063/1.3073661
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/105/7?ver=pdfcov
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Electronic structures and magnetic properties of a ferromagnetic insulator: La_2MnNiO_6

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(Presented 12 November 2008; received 17 September 2008; accepted 1 December 2008; published online 13 April 2009)

We have investigated the electronic structures and magnetic properties of La_2MnNiO_6 that is a typical ferromagnetic insulator with the double perovskite structure. We have examined the valence states of Mn and Ni ions using the full-potential linearized augmented plane wave band method. The density of states as well as the charge density plot are in good agreement with the reported experimental and theoretical results. We have examined the ferromagnetic mechanism in terms of the superexchange interaction. We have calculated the x-ray absorption spectrum based on the band structure results and compared it with the experiment. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3073661]

I. INTRODUCTION

Double perovskite La_2MnNiO_6 has drawn much attention due to its stable ferromagnetic insulating phase with high Curie temperature (T_C=270–280 K).[1] At room temperature, La_2MnNiO_6 exists in different two structures depending on the synthesizing condition: orthorhombic *Pbnm* and rhombohedral $R\bar{2}c$. At T_C, upon cooling, the orthorhombic structure transforms to the monoclinic $P2_1/n$ structure, while the rhombohedral structure to the rhombohedral $R\bar{3}m$ or $R\bar{3}$.[1]

There are two main issues for La_2MnNiO_6: (i) the valence states of the Ni and Mn ions, and (ii) the mechanism of ferromagnetic exchange interaction between Ni and Mn magnetic moments. As for the valence states, there are two possibilities, Ni^{3+}–Mn^{3+} and Ni^{2+}–Mn^{4+}. As for the exchange interaction, it is actually connected to the valence states because the sign of the superexchange interaction, which is the plausible magnetic mechanism in this system,[2] is determined by the valence states of Ni and Mn ions through the Goodenough–Kanamori–Anderson (GKA) rules.[3,4] In the octahedral symmetry, Ni^{2+}–Mn^{4+} valence states form the electron configuration of $d^8(t_{2g}^6e_g^2)$-$d^3(t_{2g}^3)$, while Ni^{3+}–Mn^{3+} valence states form the electron configuration of $d^7(t_{2g}^6e_g^1)$-$d^4(t_{2g}^4)$ or $d^7(t_{2g}^6e_g^1)$-$d^4(t_{2g}^3e_g^1)$. The electrons in each t_{2g} and e_g determine the relative size of ferromagnetic and antiferromagnetic interactions, which would give rise to the magnetic order of the whole system. The valence state problem was studied by analyzing neutron diffraction data[5] and also by the *ab initio* band calculation.[6]

In this study, we have investigated the electronic structures and magnetic properties of La_2MnNiO_6 to examine the valence states of Ni and Mn ions. Based on the *ab initio* band results, we have calculated the x-ray absorption spectrum and analyzed the superexchange interaction.

II. RESULTS AND DISCUSSIONS

We have employed the full-potential linearized augmented plane wave band method[7] implemented in the WIEN2K package.[8] For the exchange-correlation energy, we used the generalized gradient approximation (GGA).[9] We have considered the ground state monoclinic $P2_1/n$ structure for La_2MnNiO_6. The optimized equilibrium volume is found to be about 2% larger than the experimental volume. The small overestimation of the volume is known as the general character of the GGA functional.

Figure 1 provides the total and site-projected density of states (DOS) for ferromagnetic La_2MnNiO_6 at the optimized volume. Total DOS shows clearly the insulating nature with a gap size of about 0.5 eV. Mn and Ni ions determine the electronic structure and La *f*-states in Fig. 1(b) seem to be responsible for the peak above the Fermi energy E_F in the total DOS. The t_{2g} and e_g levels of both Mn and Ni ions can be clearly identified. The occupations are t_{2g}^3 for Mn [Fig. 1(c)] and $t_{2g}^6e_g^2$ for Ni [Fig. 1(d)], indicating valence states of Mn^{4+} and Ni^{2+}. The energy splittings between t_{2g} and e_g states, $10Dq$, are about 3 eV for Mn, and about 1–2 eV for Ni. $10Dq$'s for both Mn and Ni are close to the exchange splitting energy, and so their spin states are not the high-spin (HS) states, but the intermediate-spin or the low-spin (LS) states. The oxygen DOS [Fig. 1(e)] is included to show the profound mixing effect between *d*-states of transition metals and *p*-states of oxygen from −7 eV to E_F.

The magnetic moment data also show strong evidence for the Mn^{4+} and Ni^{2+}. For the Mn^{4+} and Ni^{2+} pair, the expected magnetic moments should be $3\mu_B$ and $2\mu_B$, while for the Mn^{3+} and Ni^{3+} pair, the magnetic moments should be $2\mu_B$ and $1\mu_B$ for LS Mn or $4\mu_B$ and $1\mu_B$ for HS Mn. The calculated magnetic moments of Mn and Ni are $2.8\mu_B$ and

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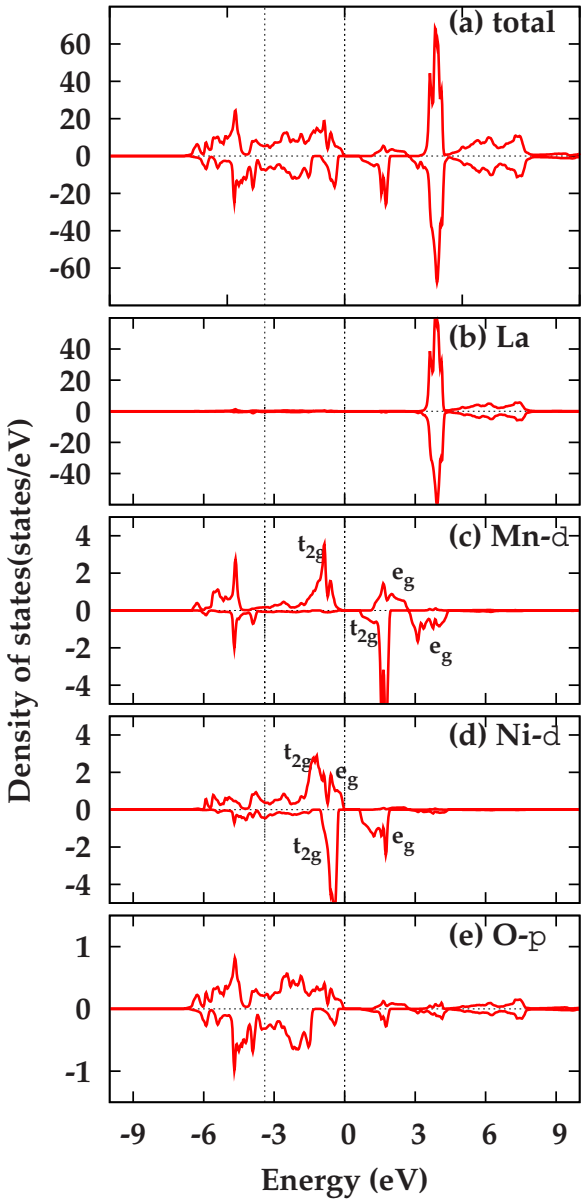

FIG. 1. (Color online) DOS for La_2MnNiO_6. (a) Total DOS, (b) projected DOS of La, (c) partial DOS of Mn *d*, (d) partial DOS of Ni *d*, and (e) partial DOS of O *p* states.

$1.5\mu_B$, respectively, which are somewhat smaller than the experimental values of $3.0\mu_B$ and $1.9\mu_B$.[5] This difference is due to additional magnetic moments distributed at the oxygen sites and the interstitial region. The total magnetic moment in the unit cell is $5\mu_B$, which is in good agreement with the experimental result as well as the previous band calculation results.[5,6,10]

Figure 2 shows the charge density plot in the Mn–O–Ni plane: (a) spin up and (b) spin down. To exclude the mixing effects with oxygen, the energy window is cut from −3.4 eV to E_F as indicated with dotted lines in Fig. 1. In Fig. 2(a), the t_{2g} character of the Mn ion can be seen clearly since there is no electrons in e_g states, whereas Ni ion shows nearly circular shaped charge density indicating the fully occupied spin-up electrons. Small portions of occupied electron are identified at the oxygen sites, which can be expected from the mixed feature shown in the DOS of oxygen [Fig. 1(e)]. In

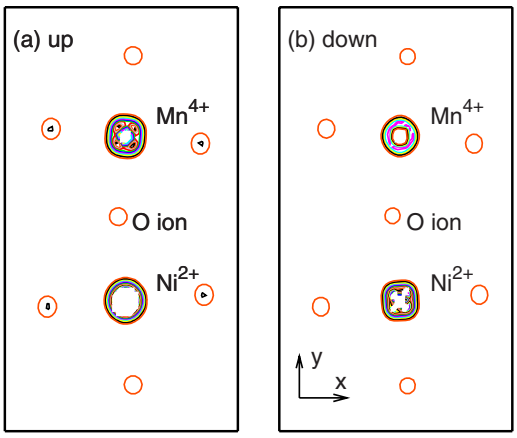

FIG. 2. (Color online) Charge density plot for La_2MnNiO_6 in the energy window in between the dotted lines (-3.4 eV$\sim E_F$) in Fig. 1. (a) Spin-up charge density. At the Mn site, the t_{2g} character can be identified, while at the Ni site, the symmetrical circular shape can be seen due to fully occupied t_{2g} and e_g states. (b) Spin-down charge density. The density at the Mn site has been reduced and the t_{2g} character is seen at the Ni site.

Fig. 2(b), the spin-down charge density at the Mn sites is reduced as compared to the spin-up charge density, and also t_{2g} character disappeared. At the Ni site, t_{2g} character is shown indicating no electrons in the e_g states. All the features from the charge density plot are consistent with the results in Fig. 1, confirming Mn^{4+}–Ni^{2+} valence states with $t_{2g}^{\ 3}$–$t_{2g}^{\ 6}e_g^{\ 2}$.

X-ray absorption spectroscopy (XAS) is a useful experimental tool to examine the valence states of given elements. The XAS intensity I for a specific atom A in the dipole approximation is expressed as follows:

$$I \propto \nu^3 |\langle \Phi_{\text{val}}|r|\Phi_{\text{core}}\rangle|^2 N_l^A(h\nu - \epsilon_{\text{core}}). \quad (1)$$

Here ν is the photon frequency, and $N_l^A(\epsilon)$ is the unoccupied *l*-like partial DOS of the atom *A*. For Mn 2*p* XAS, *l* corresponds to the Mn 3*d* states. The calculated Mn 2*p* XAS based on the band structure results for La_2MnNiO_6 is given in Fig. 3, which is compared with the observed Mn 2*p* XAS.[11] The average peak positions and the spin-orbit split-

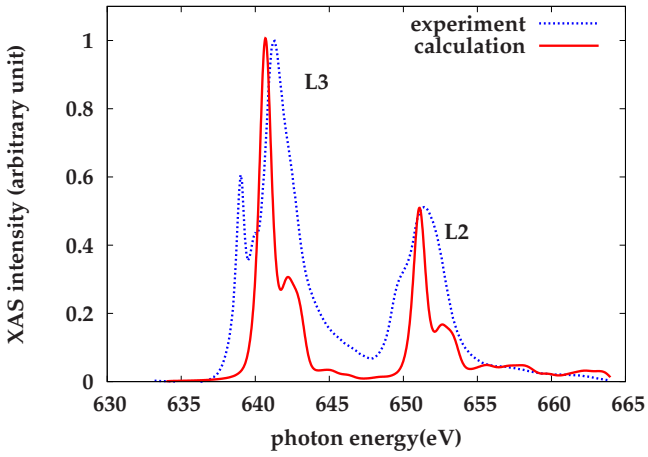

FIG. 3. (Color online) Calculated XAS near the Mn 2*p* edge for La_2MnNiO_6 is compared with the observed XAS. The left and right peaks correspond to *L*3 and *L*2 edges, respectively, which are split by the spin-orbit interaction of Mn 2*p* states.

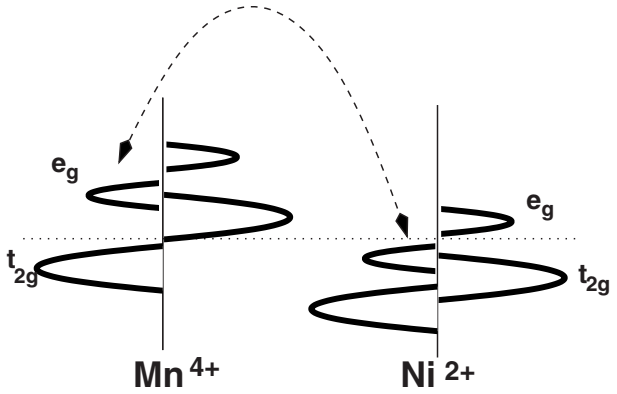

FIG. 4. The superexchange interaction between e_g-e_g gives rise to a ferromagnetic order according to the GKA rules.

ting are more or less similar between the calculation and the experiment. But the detailed shape does not agree between the two. More detailed calculation, which fits with the experiments, is in progress.

According to the GKA rules,[3,4] the interaction between Mn^{4+} and Ni^{2+} is ferromagnetic. Assuming the interaction between two t_{2g} orbitals is smaller than the interaction between e_g orbitals, the superexchange interaction between occupied ${e_g}^2$ and unoccupied e_g gives rise to a ferromagnetic ordering, which is schematically illustrated in Fig. 4. To investigate the interactions more accurately, the interactions coming from t_{2g} orbitals must be considered in cooperation with the angle dependence of the Mn–O–Ni bond. The strength of both ferromagnetic and antiferromagnetic interactions can be considered as parameters as well as the on-site and exchange energies. In this system, the angles of the Mn–O–Ni bond are 159°, 160°, and 162°, at which the microscopic superexchange interaction calculation also produces the ferromagnetic ground state.[12]

In conclusion, we have investigated the electronic and magnetic properties of La_2MnNiO_6 by performing the *ab initio* band calculation. The valence states of Mn and Ni are found to be 4+ and 2+, respectively. We have discussed the insulating ferromagnetic property by examining the superexchange interaction between Mn and Ni magnetic moments.

ACKNOWLEDGMENTS

This work was supported by the SRC program of KOSEF (Grant No. R11–2000–071), by the basic research program of KOSEF (Grant No. R01–2006–000–10369–0), and by the POSTECH Research Fund.

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