Theoretical study on the electronic and magnetic properties of double perovskite La$_{2-x}$Sr$_x$MnCoO$_6$ ($x = 0, 1, 2$)

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Abstract. In this paper, the electronic and magnetic properties of double perovskite La$_{2-x}$Sr$_x$MnCoO$_6$ ($x = 0, 1, 2$) have been studied using the local-spin-density approximation + $U$ method. For the three compositions investigated, the low symmetry $P2_1/n$ structure yields consistently lower energy than that of the high symmetry $Fm3m$ structure. The strong electronic correlation and the orbital polarization of Co-$d$ electrons play crucial roles. In agreement with experiments, we find that La$_2$MnCoO$_6$ is a ferromagnetic insulator with both Mn and Co ions in their high-spin states. The tilting of oxygen octahedrons is most significant in this case and is responsible for its insulating behavior; for LaSrMnCoO$_6$, the ground state remains a ferromagnetic insulator with Mn and Co ions in their high-spin states. The optimized $P2_1/n$ and $Fm3m$ crystal structures are nearly the same, and the $P2_1/n$ structure is stabilized by the spontaneous layer-wise antiferro-orbital ordering of Co-$d$ electrons. We also predict that Sr$_2$MnCoO$_6$ is a ferromagnetic metal, and its electronic structure can be viewed as a rigid band shifting from that of LaSrMnCoO$_6$. Due to the strong covalency between transition metal and oxygen ions, the valences of Mn and Co ions differ considerably from those derived from purely ionic model. Also, doping induced holes mainly go to oxygen sites though the density of states near the Fermi energy has strong mixed character. This feature, together with the orbital ordering phenomenon, should be observable via the X-ray near-edge absorption spectroscopy and the polarized X-ray diffraction spectra.

1 Introduction

The interests in perovskite oxides have been revitalized in the past 15 years largely due to their importance in fundamental physics and in application potential in information technology industry. The attention was initially focused on Re$_{1-x}$D$_x$MnO$_3$ [1–3] (Re is rare-earth ion and D is divalent ion such as alkaline earth) because of the discovery of colossal magnetoresistance (CMR). Since then, comprehensive studies have been carried out both experimentally and theoretically to unveil the physical properties of Re$_{1-x}$D$_x$MnO$_3$. It is well known now that LaMnO$_3$ is an A-type antiferromagnetic (A-AFM) insulator and belongs to an orthorhombic $Phmm$ space group [4]. Due to strong electronic correlation and Jahn-Teller distortion, the magnetically ordered state takes an intra-plane ferromagnetic (FM) and inter-plane antiferromagnetic (AFM) configuration. To conform to such spin ordered state, Mn-$e_g$ electrons take an intra-plane antiferro-orbital (AFO) and an inter-plane ferro-orbital (FO) configuration. The A-AFM structure is made possible because of a combination of the double exchange interaction among neighboring $e_g$-electrons and superexchange interaction among neighboring $t_{2g}$-electrons [5,6]. Substituting La by divalent elements such as Ca or Sr introduces mixed valence on Mn ions, and further initiates the conventional double-exchange mechanism [7,8]. However, the full understanding on CMR effect in manganese based oxides can only be achieved by combining the double-exchange mechanism with the Jahn-Teller effect [9,10].

In addition to the manganese based oxides, a sizeable CMR effect was also observed in cobalt based perovskite Re$_{1-x}$D$_x$CoO$_3$ [11,12]. However, the physical phenomena are more complex due to the varying spin state of Co ions, for which the subtle competition between the Hund’s coupling and the crystal-field splitting is responsible. For undoped LaCoO$_3$ compound [13–16], the insulator with a low-spin state is favored at low temperature. As temperature increases, a spin-state transition takes place at $T \approx 90$ K from a nonmagnetic state to a paramagnetically ordered state, and the high temperature phase is proposed to be either a high-spin state [15,14] or an intermediate-spin state [15,16]. Substituting La by Sr further enriches the electronic and magnetic phase diagram. Besides an
insulator-metal transition [17], there exists a phase transition from a nonmagnetic state to a FM state [18]. This suggests that the double-exchange mechanism also plays an important role after doping.

Recently, a new type of transition metal based perovskite with simultaneous magnetic and ferroelectric orderings (multiferroic) has attracted much attention [19–25]. The interest in such magnetodielectric materials arises from the possibility of making devices where the dielectric properties can be controlled with an external magnetic field and vice versa. The magnetodielectric effect usually takes place in semiconductors and insulators which exhibit ferromagnetism. However, previous experiments [26–28] showed that the magnetodielectric effect is significant only at low temperature, therefore imposes severe restrictions on its application. Such difficulty was partly overcome in B-site doped double perovskite. In the newly prepared La$_2$MnBO$_6$ (B = Ni, Co) compounds, excellent high temperature magnetodielectric effects were observed [24,25]. To address the physical mechanism of multiferroic materials, information on crystal structure, valence states, and exchange interaction among various transition metal ions is often helpful. For La$_2$MnCoO$_6$ compound, earlier polycrystalline samples are not well stoichiometric because of the uncertainty in oxygen content [19,20]. The magnetic measurement indicated that there exist two ferromagnetic phases under different preparation conditions, the so-called high-$T_C$ phase ($T_C \approx 230$ K) and low-$T_C$ phase ($T_C \approx 150$ K). The measured core-level Mn and Co $2p$ X-ray photoelectron spectroscopies suggest that high-$T_C$ phase corresponds to Mn$^{3+}$-O-Co$^{3+}$ exchange interaction while low-$T_C$ phase corresponds to Mn$^{4+}$-O-Co$^{2+}$ exchange interaction [19,20].

Dass and Goodenough [21] have successfully synthesized the well stoichiometric double perovskite compound La$_2$MnCoO$_6$. The refined X-ray diffraction pattern identified the crystal structure of La$_2$MnCoO$_6$ as monoclinic $P2_1/n$ space group which was further confirmed by the neutron scattering experiment [22]. The magnetic properties suggest that both Mn and Co ions are in their high-spin states and the compound is an insulator. A ferromagnetic to paramagnetic phase transition takes place at $T_C \approx 226$ K, and the saturation magnetization, at 5 K and 50 kOe, is 5.78$\mu_B/f.u.$ By analyzing polycrystalline samples with varying degree of oxygen vacancy, they concluded that oxygen vacancies are responsible for the low-$T_C$ phase observed in the previous experiments. For the stoichiometric high-$T_C$ phase, they deduced the valence states of transition metal ions to be Mn$^{4+}$ and Co$^{2+}$. The estimation is made after taking the saturation magnetic moment and ferromagnetic exchange interaction into consideration. Note that the valence states derived here differ from those given in references [19,20] where Mn$^{3+}$ and Co$^{3+}$ ions are predicted. The valence states of transition metal ions are difficult to deduce because double perovskite compound La$_2$MnCoO$_6$ has strong covalence bonds and ionic model is hardly applicable. The crystal field splitting and spin state of Co ions also complicate the satellite structure of the near-edge X-ray absorption spectra. From recent X-ray absorption spectra on La$_2$MnCoO$_6$, Co$^{2+}$ is deduced if Co-$L_2$ line is compared to CoO, and Co$^{3+}$ is deduced if Co-$L_2$ line is compared to LaCoO$_3$. Therefore, the valence state of transition metal ions is still an unresolved issue.

Apart from the parent La$_2$MnCoO$_6$ compound, Sr doped double perovskite LaSrCoMnO$_6$ was also synthesized and investigated. The crystal structure of LaSrCoMnO$_6$ was tentatively identified as $Fm\bar{3}m$ space group. The compound undergoes a ferromagnetic to paramagnetic phase transition at $T_C \approx 250$ K [30], below which the compound is a ferromagnetic semiconductor and the effective magnetization is 5.641$\mu_B/f.u.$.

Although considerable experimental efforts have been made on double perovskite compounds, theoretical study is still rare up to now. The early tight-binding linear-muffin-tin-orbital calculation reported a half-metal band structure of La$_2$MnCoO$_6$ [31]. This study was based on the old incorrect orthorhombic structure, and half-metal property is also in contradiction with the measured ferromagnetic insulator. In addition, the double exchange interaction, though, may work in the insulating phase if a certain type of orbital ordering exists. Such case occurred before only in two dimensional $ab$ plane of A-type antiferromagnetic state of LaMnO$_3$, it is not clear whether similar mechanism still works in three dimensional ferromagnetic insulators. In fact, the double-exchange mechanism in this case is seriously questioned because of the high resistance measured [21,24]. Though qualitative discussion can be made within the Goodenough-Kanamori’s (GK) rules [5,6] on the magnetic exchange interaction between the $d$-electrons of neighboring transition metal ions, the microscopic origin of the ferromagnetic insulator for double perovskite is still an open question.

Clearly, more theoretical studies are still needed in order to understand the nature of the ferromagnetic insulator of double perovskite compounds. Towards this goal, the band structures of various possible magnetically ordered states of varying Co spin are calculated for La$_2$MnCoO$_6$, LaSrMnCoO$_6$, and Sr$_2$MnCoO$_6$ under the $P2_1/n$ and the $Fm\bar{3}m$ structures. The local-spin-density approximation + $U$ (LSDA + $U$) calculations are performed within the linear augmented plane wave plus local orbital method [32]. The most probable ground state is obtained by comparing the energy both across different crystal structures and across different magnetically ordered spin states. In agreement with experiments, our ground state of La$_2$MnCoO$_6$ belongs to the $P2_1/n$ space group. It is a ferromagnetic insulator with both Mn and Co ions in high-spin states. The tilting of oxygen octahedrons is most significant in this case, and the antiferro-orbital ordering of Co $d$-electrons is responsible for the ferromagnetic insulator state; for LaSrMnCoO$_6$, the tilting of oxygen octahedrons is so small in the $P2_1/n$ structure that the $P2_1/n$ and the $Fm\bar{3}m$ structures are hardly distinguishable. The low symmetry $P2_1/n$ structure prevails due to the spontaneous antiferro-orbital ordering at Co ions. We believe that such spontaneous antiferro-orbital

\[1\] See Figure 1. [29].