Electronic Band Structures of La$_{2/3}$Pb$_{1/3}$Mn$_{2/3}$(Fe,Co,Ni)$_{1/3}$O$_3$

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We present calculations of the electronic band structures of La$_{2/3}$Pb$_{1/3}$Mn$_{2/3}$(Fe,Co,Ni)$_{1/3}$O$_3$ colossal magnetoresistance manganites. The calculations are based on first-principles density functional theory with general gradient approximation GGA+U using WIEN2k package. The calculations show that electronic structures of these compounds consist mainly of Mn 3d, O 2p, and (Fe,Co,Ni) 3d states, which are hybridized over whole valence bands. Substitution Mn ion by Fe, Co, or Ni ions reduces the Mn and O contributions to the valence bands and weakens the double exchange interaction. The results are in good agreement with available experimental data.


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1. Introduction

Manganites with general formula REAMnO$_3$, where RE are trivalent rare earth ions (La, Pr, Nd, Sm) and A are divalent alkaline earth ions (Ca, Sr, Ba, Pb), exhibit a large variety of electric and magnetic properties due to complex interplay between charge and orbital degree of freedom of the mixed-valence Mn cations and the double-exchange (DE) interaction modified by Jahn-Teller distortion and tilting of Mn-O octahedrals [1]. Ferromagnetic (FM) ordering in REAMnO$_3$ has been attributed to the DE interaction between the valence electron state of Mn$^{3+}$-$O^{2-}$-Mn$^{4+}$ [2-5]. The FM state with a large spin splitting of the conduction band into majority and minority sub-bands separated by the on-site Hund interaction is a consequence of DE interaction and lattice distortion [6].

The transport and magnetic properties of REAMnO$_3$ manganites, where TM is a transition metal, are known to be strongly dependent upon changes in the strength of the DE interaction, which can be altered by the substitution of the trivalent RE ions by divalent A ions and also Mn ions by the other TM ions e.g. Fe, Co, Ni [7-10]. The composition La$_{0.7}$Pb$_{0.3}$Mn$_{0.7}$O$_3$ corresponding to a Mn$^{3+}$/Mn$^{4+}$ ratio that maximizes the DE interaction, shows ferromagnetism and raises magnetic ordering temperature $T_C$ [9, 10]. From experimental studies at low temperatures it is known that Fe, Co and Ni ions enter into the La$_{0.7}$Pb$_{0.3}$Mn$_{0.7}$TM$_{0.3}$O$_3$ as high-spin Fe$^{3+}$, as diamagnetic low-spin Co$^{3+}$ and as low spin Ni$^{3+}$, respectively. Fe ions couple antiferromagnetically with Mn ions, on the contrary to Ni ions, which are coupled ferromagnetically [9, 10].

All considered TM substitutions weaken DE interaction and lead to decrease in both magnetic ordering temperatures $T_C$ and low-temperature magnetic moments.

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These changes occur with increasing TM content. Substitution level up to only 30% generates low distortion in the crystal structure of these compounds [7-10].

In this work we present results of theoretical ab initio band structure calculations for the La$_{2/3}$Pb$_{1/3}$Mn$_{2/3}$(Co,Fe,Ni)$_{1/3}$O$_3$ manganites in P31 crystal structure.

2. Computational details

The calculations were done in the WIEN2k code (version 11.1) [11] based on the density functional theory (DFT) [12, 13] and the generalized gradient approximation (GGA) [14, 15]. For the 3d Mn, Fe, Co and Ni electrons the Hartree-Fock-like exchange energy was included in hybrid functional with $\alpha = 0.25$ fraction [16, 17]. The spin-orbit interaction is planned to be included into calculation. The optimal k point number was examined by calculating total energy as the function of the number of k-points. As a result 202 k points in irreducible Brillouin zone was chosen. The self-consistent calculations were continued until a charge convergence was better than 0.0001 e. The density of states (DOS) was calculated using the modified tetrahedron method [18].

The X-ray powder analysis of compounds with similar substitution showed rhombohedral crystal structure R3c, i.e. no. 167 according to the International Tables for Crystallography (ITC) [7-10, 19]. In our calculations the P31c (i.e. no. 165 according to ITC) crystal structure was chosen (Fig. 1) in order to achieve proper substitution of La ions by Pb ions and Mn ions by Fe, Co or Ni ions. The detailed description of crystal structure determination and its structure optimization, which is required to fair electronic band structure computation, can be found in our previous papers [20, 21]. Computed lattice constants are $a = 10.1685 \ a_0$, $c = 25.6286 \ a_0$, $a = 10.2988 \ a_0$, $c = 24.8973 \ a_0$, and $a = 10.3009 \ a_0$, $c = 24.8921 \ a_0$ for the Fe, Co, and Ni substituted compounds, respectively, and $a_0$ is the Bohr radius. Atomic positions of Pb and TM ions are (0, 0, 0) and (0, 0, 0), respectively. They do not vary with TM ion. Other atomic
3. Results and their analysis

To investigate the changes of the DE interaction triggered off by the substitution of manganese ions by other TM ions, the \textit{ab initio} electronic band structure calculations for the La$_{2/3}$Pb$_{1/3}$Mn$_{2/3}$[(Fe,Co,Ni)$_{1/3}$]O$_3$ manganite in $P\overline{3}c1$ crystal structure were undertaken.

The calculated total densities of states (DOS) and the local contributions from the particular atoms are presented in Fig. 2. The main contributions to the valence band (VB) come from Mn 3$d$ and O 2$p$ electronic states. Contributions from TM 3$d$ states and La, Pb states are minor and irrelevant. In contrary to oxygen ion the contribution of Mn ion to the VB and conduction band is mostly by majority subband. In case of Fe and Ni ions the corresponding contributions are mostly by minority and majority subbands, respectively. For the diamagnetic Co the contributions from majority and minority subbands are similar.

In comparison to unsubstituted La$_{2/3}$Pb$_{1/3}$MnO$_3$ [20] the Mn and O contributions to the VB are smaller, which results in weaker DE interaction in La$_{2/3}$Pb$_{1/3}$Mn$_{2/3}$[(Fe,Co,Ni)$_{1/3}$]O$_3$ family of compounds. This result agrees well with magnetic experimental and transport data [7–10].

The calculated DOS for the Fe and Co substituted compounds have half-metallic character and insulating character for Ni substitution. In the last case the DOS is dominated by oxygen states revealing the charge transfer like insulating character. The Fermi level lies close to a gap in the majority band. This gap is shifted below $E_F$ for Fe and Co substitution, whilst above $E_F$ for Ni. Contrary to Fe ion, the Co and Ni ions introduce to the VB one and two electrons, respectively. This results in shifting $E_F$ to the lower binding energy. The small electron pocket is present for majority band for Fe and Co substitutions.
The calculated magnetic moments for Fe, Co, and Ni substitutions are 2.00 $\mu_B$/f.u., 2.33 $\mu_B$/f.u. and 2.67 $\mu_B$/f.u., respectively, close to the experimental ones [7–10].

The examples of calculated valence band ultraviolet photoemission Ni- and Co-substituted spectra are shown in Fig. 3. The calculated spectrum for the case of Fe is quite similar to that of Co. The theoretical spectrum was calculated taking into account the partial electronic densities of states weighted with atomic photoemission cross-section [22] for the He(I) photon energy 21.2 eV and the experimental energy resolution was taken as the energy-dependent Lorentzian function with a half-width of about 0.3 eV.

Fig. 3. Calculated UPS spectra of La$_{2/3}$Pb$_{1/3}$Mn$_{2/3}$TM$_{1/3}$O$_3$.

4. Conclusions

We have computed the electronic band structures of La$_{2/3}$Pb$_{1/3}$Mn$_{2/3}$(Fe,Co,Ni)$_{1/3}$O$_3$ compounds for energy optimized P3c1 crystal structure. Initial magnetic moments configurations at 3d ions, based on experimental data, give half-metallic DOS for Fe- and Co-substitutions and insulating DOS for Ni substitution. These DOS consist mainly of Mn, Fe, Co, Ni 3d and O 2p states, which are hybridized over the whole valence bands.

The substitution of Mn ions by TM ions reduces the Mn and O contributions to the VB which weaken the DE interactions in La$_{2/3}$Pb$_{1/3}$Mn$_{2/3}$(Fe,Co,Ni)$_{1/3}$O$_3$ manganites.

Substitution of Mn ions by Co or Ni ions increases the number of 3d electrons in VB and shifts the Fermi level toward lower binding energy. According to the electronic band structure calculations a shifting of $E_F$ should be seen in photoemission spectroscopy measurements.

The calculated total magnetic moments for Fe, Co and Ni substitutions are 2.00 $\mu_B$/f.u., 2.33 $\mu_B$/f.u. and 2.67 $\mu_B$/f.u., respectively. These results are in good agreement with experimental data.

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