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 magneto-resistance 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.

1. Introduction

Manganites with general formula REAMnO₃, 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 interaction and tilting of Mn-O₆ octahedrals [1]. Ferromagnetic (FM) ordering in REAMnO₃ 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 REAMnTMO₃ 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 La₀.₇Pb₀.₃MnO₃ 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 La₀.₇Pb₀.₃Mn₀.₇TM₀.₃O₃ 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.

These changes soar 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 $P\bar{3}c1$ 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 0.001 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 $R\bar{3}c$, i.e. no. 167 according to the International Tables for Crystallography (ITC) [7–10, 19]. In our calculations the $P\bar{3}c1$ (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 $a = 10.1685\ a_o$, $c = 25.6286\ a_o$, $a = 10.2988\ a_o$, $c = 24.8973\ a_o$, and $a = 10.3009\ a_o$, $c = 24.8921\ a_o$ for the Fe, Co, and Ni substituted compounds, respectively, and a_o is the Bohr radius. Atomic positions of Pb and TM ions are $(0, 0, 1/4)$ and $(0, 0, 0)$, respectively. They do not vary with TM ion. Other atomic

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positions for Fe substituted manganite are La (1/3, 2/3, 0.9165), Mn (1/3, 2/3, 0.6662), O(1) (0.5293, 0, 1/4) and O(2) (0.8763, 0.6595, 0.9200). Other atomic positions for Co substituted manganite are La (1/3, 2/3, 0.9158), Mn (1/3, 2/3, 0.6651), O(1) (0.5318, 0, 1/4) and O(2) (0.8736, 0.6579, 0.9205). Other atomic positions for Ni substituted manganite are La (1/3, 2/3, 0.9167), Mn (1/3, 2/3, 0.6653), O(1) (0.5353, 0, 1/4) and O(2) (0.8705, 0.6476, 0.9178). The results presented in the next paragraph were calculated based on these crystal settings.
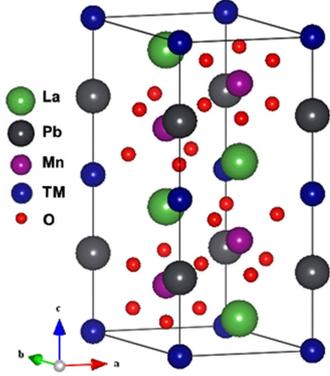

Fig. 1. Unit cell of $La_{2/3}Pb_{1/3}Mn_{2/3}(Fe,Co,Ni)_{1/3}O_3$.

Considering the results of magnetic measurements of $La_{0.7}Pb_{0.3}Mn_{0.7}(Fe,Co,Ni)_{0.3}O_3$ manganites [7–10] and strong dependence of electronic band structure calculation in WIEN2k code [21] on the configuration of magnetic moments at ions, the initial moment at Co ions was set to zero in $La_{2/3}Pb_{1/3}Mn_{2/3}Co_{1/3}O_3$, parallel configuration of magnetic moments on Mn and Ni ions and antiparallel configuration on Mn and Fe ions were set for the Ni- and Fe-substitutions, respectively.

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 *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 $P\bar{3}c1$ 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 $3d$ and O $2p$ electronic states. Contributions from TM $3d$ 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.

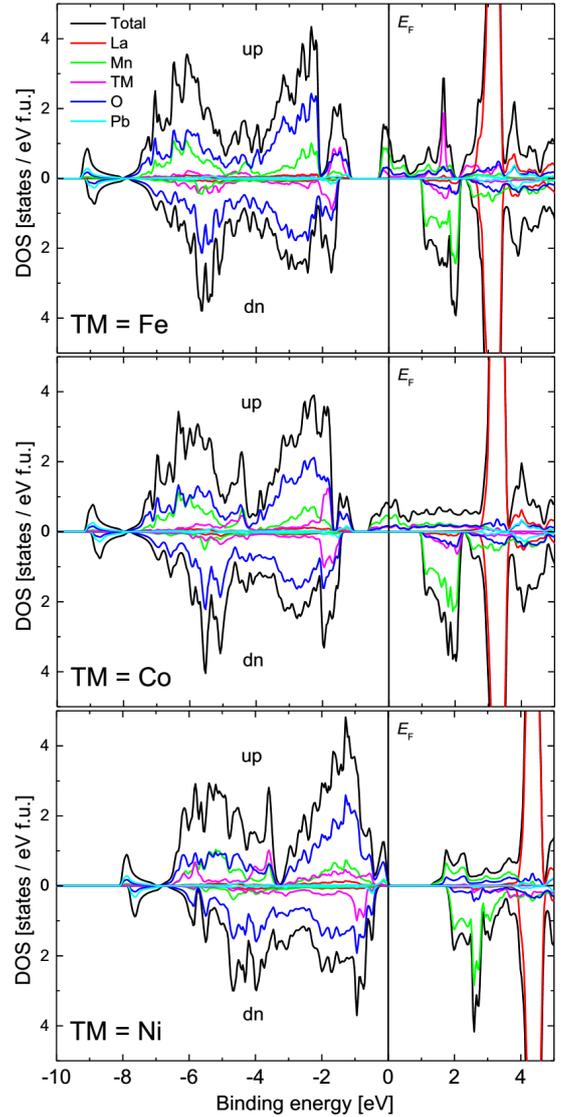In comparison to unsubstituted $La_{2/3}Pb_{1/3}MnO_3$ [20] the Mn and O contributions to the VB are

Fig. 2. Total calculated partial DOS for $La_{2/3}Pb_{1/3}Mn_{2/3}TM_{1/3}O_3$.

smaller, which results in weaker DE interaction in $La_{2/3}Pb_{1/3}Mn_{2/3}(Co,Fe,Ni)_{1/3}O_3$ 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 μ_B/f.u., 2.33 μ_B/f.u. and 2.67 μ_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.
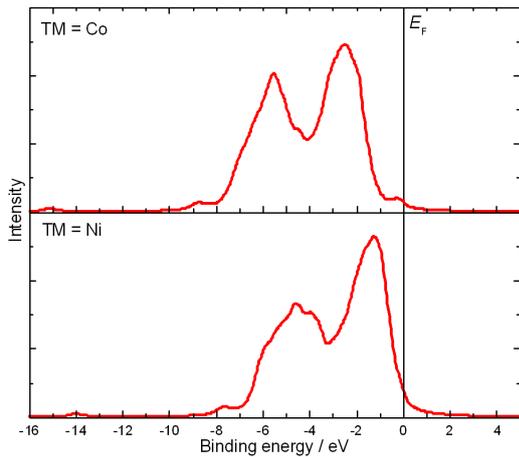

Fig. 3. Calculated UPS spectra of $La_{2/3}Pb_{1/3}Mn_{2/3}TM_{1/3}O_3$.

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 $P\bar{3}c1$ 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 spectrometry measurements.

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

References

[1] E. Dagotto, *Nanoscale Phase Separation and Colossal Magnetoresistance*, Springer, Berlin 2002.

[2] C. Zener, *Phys. Rev.* **82**, 403 (1951).

[3] P.W. Anderson, H. Hasegawa, *Phys. Rev.* **100**, 675 (1955).

[4] J. Goodenough, *Phys. Rev.* **100**, 564 (1955).

[5] P.G. de Gennes, *Phys. Rev.* **118**, 141 (1960).

[6] P.G. de Gennes, J. Friedel, *J. Phys. Chem. Solids* **41**, 71 (1958).

[7] J. Gutiérrez, A. Peña, J.M. Barandiarán, J.L. Pizarro, T. Hernández, L. Lezama, M. Insausti, T. Rojo, *Phys. Rev. B* **61**, 9028 (2000).

[8] J. Gutiérrez, A. Peña, J.M. Barandiarán, J.L. Pizarro, L. Lezama, M. Insausti, T. Rojo, *J. Phys. Condens. Matter* **12**, 10523 (2000).

[9] A. Peña, J. Gutiérrez, I.G. de Muro, J. Campo, J.M. Barandiarán, T. Rojo, *Eur. J. Inorg. Chem.* **2006**, 3227 (2006).

[10] A. Peña, J. Gutiérrez, J. Campo, J.M. Barandiarán, L. Lezama, I.G. de Muro, T. Rojo, *Eur. J. Inorg. Chem.* **2008**, 2569 (2008).

[11] P. Blaha, K. Schwarz, G.K.H. Madsen, D. Kvasnicka, J. Luitz, *WIEN2K: An Augmented Plane Wave and Local Orbitals Program for Calculating Crystal Properties*, Vienna University of Technology, Vienna 2001.

[12] P. Hohenberg, W. Kohn, *Phys. Rev. B* **136**, 864 (1964).

[13] W. Kohn, L.J. Sham, *Phys. Rev.* **140**, 1133 (1965).

[14] J.P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).

[15] J.P. Perdew, A. Ruzsinszky, G.I. Csonka, O.A. Vydrov, G.E. Scuseria, L.A. Constantin, X. Zhou, K. Burke, *Phys. Rev. Lett.* **100**, 136406 (2008).

[16] S. Kümmel, L. Kronik, *Rev. Mod. Phys.* **80**, 3 (2008).

[17] F. Tran, P. Blaha, K. Schwarz, P. Novák, *Phys. Rev. B* **74**, 155108 (2006).

[18] P.E. Blöchl, O. Jepsen, O.K. Andersen, *Phys. Rev. B* **49**, 16223 (1994).

[19] G. Gritzner, M. Koppe, K. Kellner, J. Przewoźnik, J. Chmist, A. Kołodziejczyk, K. Krop, *Appl. Phys. A* **81**, 1491 (2005).

[20] W. Tokarz, M. Kowalik, R. Zalecki, A. Kołodziejczyk, *Acta Phys. Pol. A* **121**, 1151 (2012).

[21] W. Tokarz, M. Kowalik, A. Kołodziejczyk, *Acta Phys. Pol. A* **121**, 876 (2012).

[22] J.J. Yeh, I. Lindau, *At. Data Nucl. Data Tables* **32**, 1 (1985).