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Electronic Band Structure of $La_{2/3}Pb_{1/3}Mn_{2/3}Fe_{1/3}O_3$

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We present theoretical studies of electric and magnetic properties in manganese perovskite $La_{2/3}Pb_{1/3}Mn_{2/3}Fe_{1/3}O_3$. The calculations were carried out by means of the first-principles density functional theory (DFT) with general gradient approximation GGA+U using Wien2K package. The P–3c1 crystal structure was chosen from the detailed X-ray diffraction data for the perovskite. For Mn and Fe d electrons exact exchange energy was utilized. Different orientation of magnetic moments on Mn and Fe atoms was considered. The computed density of states display band gap for both spin orientations in accord with our previous work, indicating that this compound should show an insulating ground state

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1. Introduction

A large variety of electric and magnetic properties of manganites with general formula $REAMnO_3$, where RE are trivalent rare earth ions and A — divalent alkaline earth ions, take place as a result of complex interplay between charge and orbital degree of freedom of the mixed-valance Mn cations [1] and the double-exchange (DE) interaction via oxygen Mn^{3+}–O^{2-}–Mn^{4+} modified by Jan Teller distortion interaction and tilting of Mn–0_6 octahedrals [2–5]. As a result, the conduction band has a large spin splitting with majority and minority sub-bands separated by the on-site Hund's interaction [6] with ferromagnetic ordering. Spin splitting has been shown in theoretical calculation by N. Hamada et al. [7] for $La_{0.5}Ba_{0.5}MnO_3$ where half metallic ground-state has been revealed using the linear augmented plane wave method. Similar conclusion was made in the paper [8] for $La_{1-x}Ca_xMnO_3$ system exploiting the local spin-density approximation with the general potential linearized augmented plane-wave [9]. Also in the paper [10] the theoretical density of states (DOS) for the $La_{0.75}Pb_{0.25}MnO_3$ was presented. In the previous papers [11, 12] we studied the magnetisation, magnetoresistance and ultraviolet photoemission spectra (UPS) for samples $La_{2/3}Pb_{1/3}Mn_{1-x}Fe_xO_3$ with x from 0 to 0.1 in order to examine the effect of substitution Mn by Fe ions. The theoretical DOS was computed for undoped case [13]. In this paper we focus our attention on calculation for $x = 1/3$ which is the simplest case close to measured $x = 0.1$.

2. Computational details

The calculations were done in the WIEN 2K code [14] based on the Density Functional Theory (DFT) [15, 16] and the Generalized Gradient Approximation (GGA) [17]. For the 3d Mn and Fe electrons the Hartree–Fock–like exchange energy was included in hybrid functional with $\alpha = 0.25$ fraction [18, 19]. The optimal k point number was examined by calculating total energy as the function of the number of k-points. As a result 104 k points in irreducible Brillouin zone was chosen to perform calculation. The self consistent calculations were continued until a charge convergence was better than 0.001 e.

As a starting point the rhombohedral crystal structure R–3c was chosen (i.e. No. of space group 167 according to International Tables for Crystallography (ITC) [20]). This structure was elongated two times in z direction and one third of La and Mn ion positions were substituted by Pb and Fe, respectively. Next, several structure optimizations were calculated. In the first step an optimal cell volume was achieved as a total energy minimum. In the second step c/a ratio was adjusted whilst keeping optimal volume constant. The final crystal structure optimization was to move the atomic positions in order to minimize the calculated forces at the nuclei [21] to less than 5 mRy/a.u. As a consequence the lattice constants: $a = 10.295$ au, $c = 24.893$ au and atomic positions as follows: of La (2/3, 1/3, 0.9167), of Pb (0, 0, 1/4), of Mn (1/3, 1/3, 2/3) and of O (0.5406, 0, 1/4) (0.874, 2/3, 0.9167) were obtained. The results presented in the next paragraph were calculated based on these crystal settings.

3. Results and their analysis

The measured dependence of metal–insulator transition temperature T_{M-I} as a function of Fe concentration presented on Fig. 1 shows that the compounds with x greater than 0.2 should be insulating [11]. Additionally, the dependence of magnetic moment per formula units versus x speaks in favour of magnetic moment around 2 μ_B/f.u. [11]. So, the theoretical calculation for $La_{2/3}Pb_{1/3}Mn_{2/3}Fe_{1/3}O_3$ should give us similar results

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that are: an insulating gap in DOS and a proper value of magnetic moment. Because total magnetic moment obtained in the Wien2K calculations strongly depends on assumed orientation of magnetic moments at ions, we have considered two different configurations with the parallel and anti-parallel spins on Mn and Fe ions.

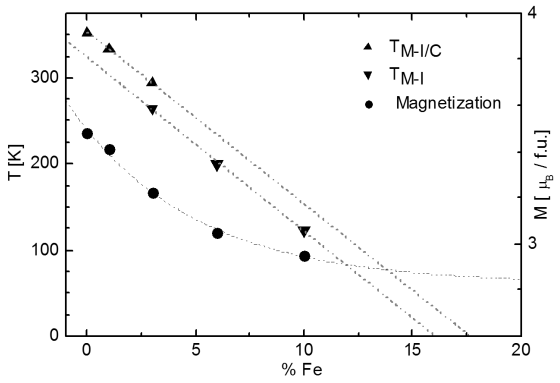

Fig. 1. The resistive metal–insulator transition temperature (▼), the magnetic metal — insulator transition temperature (▲) and the magnetic moment (●) as a function of iron content for $La_{2/3}Pb_{1/3}Mn_{1-x}Fe_xO_3$ [11].

Parallel spin setting at Mn and Fe results in the total DOS presented on Fig. 2. The band exhibits metallic character with the 0.95 eV and 1.53 eV gap below E_F for spin-up and spin-down subbands, respectively. The conducting band (Fig. 3) is composed mostly with d manganese and p oxygen electrons. Iron contributes to this band mainly with the d spin-down electrons. On the contrary, the donation of Fe electrons to valance band is mainly with the d spin up. Also Mn gives the major spin up electrons to this band. The strong hybridization among the Mn, Fe and O electronic states in both bands is visible.

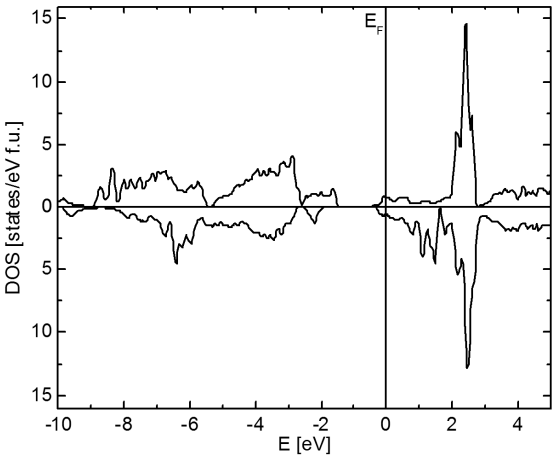

Fig. 2. The calculated total DOS with parallel spin setting on Mn and Fe.

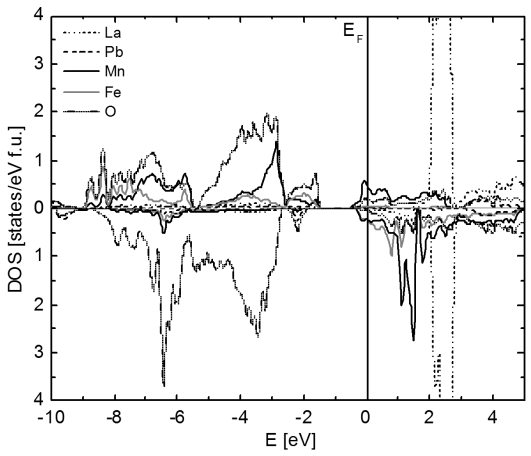

Fig. 3. The calculated partial DOS with parallel spin setting on Mn and Fe.

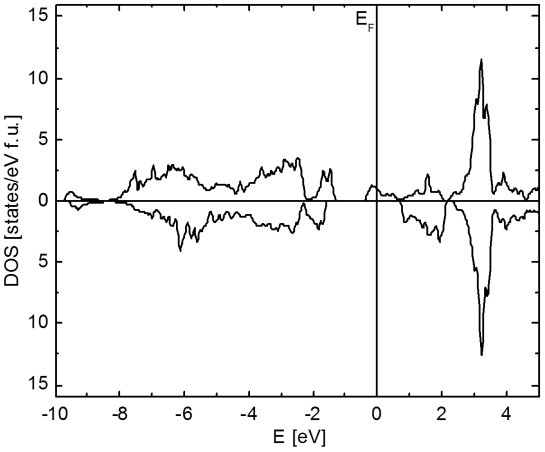

Fig. 4. The calculated total DOS with anti-parallel spin setting on Mn and Fe.

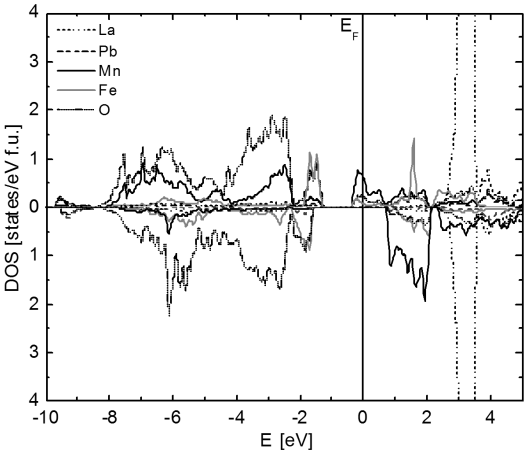

Fig. 5. The calculated partial DOS with anti-parallel spin setting on Mn and Fe.

The DOS for anti-parallel spin setting on Mn and Fe shown on Fig. 4 reveals half metallic character. We can notice the 2.2 eV insulating gap for spin-down sub-band and the 0.9 eV band gap between the valance and conducting spin-up subbands. The conducting band (Fig. 5) as in previous case is mostly composed by d Mn and p oxygen electrons. Iron contributes to this band mainly with spin-up d electrons. Some hybridization is also present like in previous case.

So, the anti-parallel setting of spins on Mn and Fe ions leads to the insulating character of the compound in agreement with the experimental predictions presented on Fig. 1 because for that composition with $x = 1/3$ the extrapolated metal–insulator transition temperature T_{M-I} should be zero. The same conclusion arises from calculation of the total magnetic moment per formula unit.

The magnetic moment was calculated for both cases according to the procedure implemented in the Wien2k package. For the parallel spin setting on Mn and Fe ions we have got about $3.69\mu_B$/f.u. whilst for the anti-parallel case $2\mu_B$/f.u., which is in better agreement with the decreasing magnetic moment versus iron content (Fig. 1).

4. Conclusions

We have computed the electronic band structure of $La_{2/3}Pb_{1/3}Mn_{2/3}Fe_{1/3}O_3$ compound for energy optimized P–$3c1$ crystal structure. We have noticed that the assumed magnetic moments configuration on the Mn and Fe atoms has had a great influence on the calculated DOS with the Wien2k package. Starting with initial parallel magnetic moment at the Mn and Fe atoms has given us DOS with metallic character and band gap in both sub-bands below E_F. The initial anti-parallel magnetic moment set-up at the Mn and Fe has resulted with half-metallic DOS and band-gap (0.9 eV width) below E_F for spin up and insulating gap (2.2 eV width) for spin down configuration. In the all considered cases we do not observe insulating gap for both spin up and down sub-band. The calculated total magnetic moments for parallel and anti-parallel spin setting on Mn and Fe have been $3.69\mu_B$/f.u. and $2\mu_B$/f.u., respectively. The latter value and half metallic DOS character for anti-parallel spin setting on Mn and Fe indicate that anti-parallel spin setting at Mn and Fe better suits to experimental data.

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