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FIRST-PRINCIPLES CALCULATIONS OF THE ELECTRONIC SPECTRUM AND THE DENSITY OF STATES OF THE $LaMnO_3$ CRYSTAL

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Abstract. The results of calculations from first principles within the framework of the density functional theory of the electronic spectrum of the $LMnO_3$ crystal are presented. The crystal and electronic structures of this compound have been theoretically studied. It was determined that the crystal structure of the lanthanum manganite compound corresponds to the orthorhombic symmetry with Pbnm space group. The lattice parameters of this compound are: a = 5.5345 Å, b = 5.7481 Å, c = 7.6932 Å. The origin of the bands from *s*-, *p*-, *d*- electronic states of atoms La, Mn, O was investigated. It was found that this crystal is a semiconductor crystal with a band gap of 2 eV.

Keywords: *Debye temperature, atomic radius, atomic volume, temperature coefficient, atomization energy, sublimation energy.*

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1. Introduction

Perovskite manganese is a widely used material in modern electronics and spintronics. Their magnetic properties increase their application in various fields. Because perovskites have a simple crystalline structure, they are also used as model objects to explain many physical processes that take place in complex oxides: magnetic and structural phase transitions and so on (Hashimov *et al.*, 2019; Hashimov *et al.*, 2020; Jabarov, 2019).

Investigation of the magnetic properties of manganese have shown that these compounds show antiferromagnetic properties mainly in the low temperature region (Matsumoto, 1970; Hashimov *et al.*, 2018). However, there is also manganese that can exhibit magnetic properties at room temperature (Dang *et al.*, 2018). This indicates that manganese can exhibit different functional properties. Therefore, their crystal and magnetic structures have been studied for a long time.

The study of the thermal properties of $Ba_{1-x}La_xMnO_3$ compounds showed that the thermodynamic parameters of these compounds change depending on the cation-cation substitutions: enthalpy, heat capacity, free energy (Hashimov *et al.*, 2019; Hashimov *et al.*, 2020). It is known that when the thermodynamic parameters change, the physical properties of the system change. Therefore, the study of the effect of changes in crystal structure on physical properties is considered an important issue. The obtained results play a key role in the synthesis of new materials.

It is important to study the electronic structures and band gap of compounds that can be used in electronics and spintronics. The electronic structure of $BaMnO_3$, which has a similar chemical form to $LaMnO_3$, has been studied (Hashimov *et al.*, 2018). It

was determined that the width of the forbidden band of this compound is *Eg* = 0eV. Therefore, this compound is considered a metal. Although many physical properties of $LaMnO_3$ compound have been studied, its electronic structure has not been studied yet. In this study, the crystal structure and electronic structure of lanthanum manganese were studied by theoretical calculations.

2. Method of calculation

Self-consistent electronic band structure calculations were performed using a full potential linearized augmented plane wave method implemented in the Wien2k code (Blaha *et al.*, 2008). The cut-off energy for separation of the core and valence states was set to −8.5 Ry. Self-consistency was achieved with an energy convergence of 10−5 eV. The results obtained make it possible to establish the nature of the localization of d-electrons in this crystal and their role in the formation of chemical bonds. The La, Mn, O atoms are located in the standard positions 4 (c), 4 (a), and the O atoms are in 8 (d) 4 (c), respectively. The number of electrons considered as valence electrons was 3 for La $5d^{16}s^2$, 7 for Mn $3d^{54}s^2$, 6 for O $2s^{22}p^4$.

3. The discussion of the results

The crystal structure of the lanthanum manganese compound has been studied at *T*=0K temperature. It was found that the crystal structure of this compound corresponds to the orthorhombic symmetry with Pbnm space group. The parameters of the lattice parameters correspond to the: *a* = 5.5345 Å, *b* = 5.7481 Å, *c* = 7.6932 Å.

In Fig. 1 is illustrated the calculated band structure of $LaMnO_3$. It can be seen from the figure that the crystal is a semiconductor compound with a band gap of 2 eV. The bottom of the conduction band is located at the symmetric point of the Brillouin zone Γ, and the top of the valence band is located between the symmetric points Γ and Y. This fact shows that fundamental absorption region of the crystal are formed by indirect transitions.

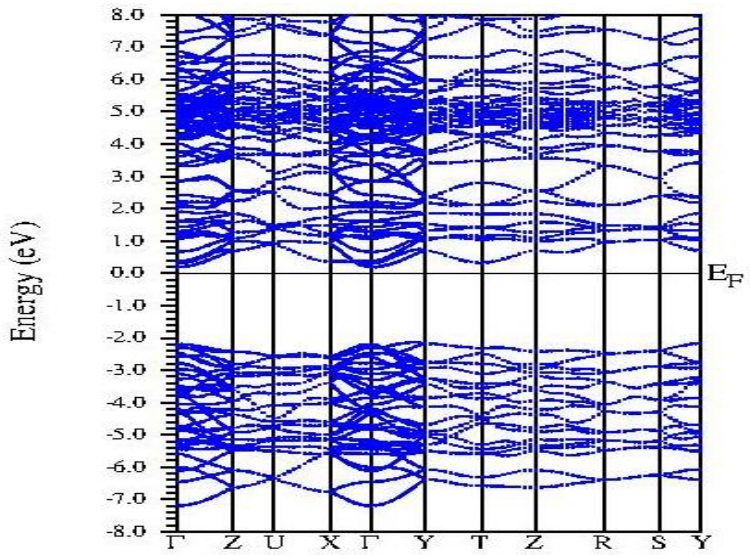

Fig.1. Electronic structure of$LaMnO_3$

Calculated density of states is shown in Fig. 2. From the total and partial densities of states (Fig. 2) it follows that the upper valence band in the region (-2 – -4) eV mainly contains 2p-states of oxygen. The –6p states of lanthanum atoms are partially involved in the formation of these bands.

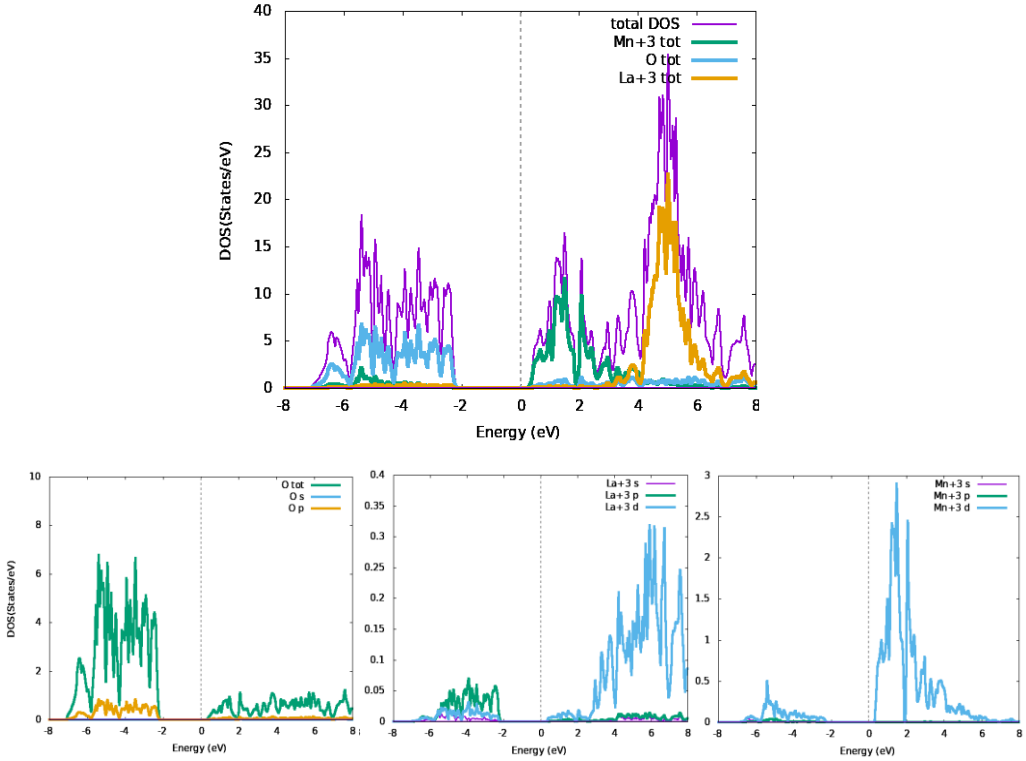

Fig. 2. Calculated total and partial densities of states

It is also seen that the 3d states of manganese make the largest contribution to the bottom of the conduction band in the region (0 - 2) eV. Conduction bands are formed from the 5d states of lanthanum in the range of (3 - 6) eV, these states also partially participate in the formation of valence bands in the range (-3 - -5) eV. The valence band in the range (- 3 - - 6) eV partially takes its origin from the –6s states of lanthanum atoms. It can be seen from the above analyzes that the fundamental absorption edge is formed mainly from the 3d state of manganese and from the 2p state of oxygen.

Calculations have shown that $LaMnO_3$ has semiconductor properties. It is known that many compounds with perovskite structure ($BaTiO_3$, etc.) are semiconductors. However, manganese contains compounds with metallic properties ($BaMnO_3$, etc.). As can be seen, lanthanum manganese is closer to classical perovskites in this respect.

4. Conclusion

The crystal structure of lanthanum manganese has been studied theoretically. It was found that the crystal structure of this compound corresponds to the orthorhombic symmetry with Pbnm space group. The calculated lattice parameters are in good

agreement with previous result. The electronic structure of the $LaMnO_3$ compound has also been studied.

It was found that $LaMnO_3$ compounds have semiconductor properties with a band gap of 2 eV. The top of the valence band is located between the symmetric points Γ and Y, the bottom of the conduction band is located at the symmetric point of the Brillouin zone Γ. The main contribution in the formation near of forbidden gap from – 3d states of manganese atoms and –2p states of oxygen atoms.

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