

«*ab initio* » study of the structural, electronic, magnetic and thermodynamic properties of perovskite oxide MoScO_3

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ABSTRACT

Perovskite compounds have gained great fame in the field of scientific research due to their well-known properties, which make it suitable for thermoelectric and optoelectronic applications. Allowing these compounds, which are made of alkaline earth metals, it was noted that they have a small energy gap, which classified them as semiconductors, and due to the small energy gap, people of these compounds have been adopted in thermoelectric and optoelectronic applications. In this article, we will attempt to shed light on the compound MoScO_3 by studying its structural, electronic, magnetic and thermodynamic properties, using the Linear Augmented Plane Wave (FP-LAPW) method based on density functional theory (DFT) implemented in the wien2k code. The results obtained showed that the studied compound MoScO_3 is stable in the ferromagnetic phase (polarized spin). For the electronic properties, our results indicated that the studied compound MoScO_3 has a semi-metallic character also the results show that the compound can be used in spintronic and optoelectronic devices due to the nature of gap found. We completed this work by studying the thermodynamic properties through the heat capacity, the Debye temperature and the Gibbs energy as a function of temperature at different pressures using the Debye quasi-harmonic model

I. Introduction

The combustion of greenhouse gases and the remains of expired batteries represented a great danger for the environment, not to mention the increase in the proportion of carbon dioxide in the atmosphere resulting from the combustion of petroleum derivatives. All these risks have led to increased awareness and the need to protect and preserve the environment [1] in order to purify the air of these pollutants; several researches have been published on materials with particular properties that allow them to do. Among the promising materials that have provided many diverse applications, we mention perovskite oxides, where several studies and research have been carried out on one of these oxides, LaFeO_3 , which has recently shown the possibility of having a very good property detection of toxic and combustible gases [2]. Scientists have also been able to engineer perovskite crystals to achieve a variety of physical, optical and electrical properties. Today, they are used in ultrasound machines and memory chips. Recently, they have revolutionized solar energy technology. Among the perovskite, oxides that will be studied in this article MoScO_3 by studying the crystalline, electronic, magnetic and thermodynamic properties through calculations carried out by the wien2k code within the framework of density function theory.

The paper was organized as follows: Calculation method, in which we briefly summarize the calculation method in density functional theory, which is included in the wien2k calculation code.

Then, we briefly presented the obtained results related to the structural, electronic, magnetic and thermodynamic properties using the wien2k code and the generalized gradient approximation GGA. We end this article with a general conclusion of the different results obtained.

II. Calculation Method

This work was carried out by applying the linear augmented plane wave (FP-LAPW) method based on density functional theory (DFT) [3-4] implemented in the wien2k code. In order to evaluate the structural, electronic, magnetic and thermodynamic properties of the compound, the generalized gradient approximation GGA was used. In addition to the previous approximation, we use the approximation developed by Becke and Johnson (mBJ) modified by Tran and Blaha (TB-mBJ) because this approximation provides a better estimate of the energy gap. The Linear Augmented Plane Wave (FP-LAPW) method, space is divided into two regions, the first region in which the atoms are like spheres of RMT radii, the wave function inside these spheres is described by spherical harmonic functions. The second region, which is the interstitial region, represents the remaining space of the first region. The wave function in this region is described as plane waves with cutoff radius $RMT \cdot K_{max} = 7$ (where RMT is the smallest radius of a Muffin-Tin (MT) sphere), K_{max} is the norm of the largest wave vector used for the plane wave expansion of Eigen functions). The number of K points used to sample the first Brillouin zone in the reciprocal space is taken equal to 1000 sufficient value to converge the total energy. Note that the criterion and condition for convergence of the total energy in all calculations carried out for the perovskite oxide $MoScO_3$ is equal to 10^{-4} Ry.

III. Results and Discussions

III.1. Structural Properties

Perovskite oxides have a crystal structure with chemical formula ABX_3 , The studied perovskite oxide $MoScO_3$ crystallizes in a simple cubic structure and belongs to the space group $pm\bar{3}m$ (N0 221), in the case of a cubic structure, the A atoms are located at the vertices of the cube. The B atoms in the middle of the cube and the O oxygen atoms in the center of the faces of the cube. Figure -1- shows the primary cell of the studied perovskite oxide $MoScO_3$, Mo is originally in the position (0, 0,0), Sc is in the center of the cube (1/2,1/2,1/2) and the oxygen's O are in the middle of each face in the position (0.1/2,1/2)

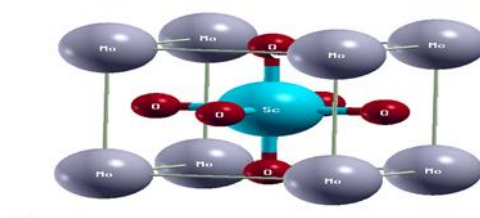


Figure 1. Structure of the perovskite oxide $MoScO_3$.

In order to determine the following equilibrium parameters: equilibrium network parameter a , the compressibility modulus B and their derivative B' , let us draw the curve of the energy variations as a function of volume and adjust it by the equation d state of Murnaghan [5] given by:

$$E(V) = E_0 + \frac{B}{B'(B'+1)} \left[V \left(\frac{V_0}{V} \right)^{B'} - V_0 \right] + \frac{B}{B'} (V - V_0) \quad (1)$$

Where B and B' the compressibility modulus at equilibrium and its derivative with respect to the pressure respectively, v_0 being the volume of the unit cell at equilibrium. The crystal lattice constant a_0 is calculated from the determination of cell volume, which corresponds, to the minimum energy that is to say from the minimum of the E_{tot} curve. In order to study the stability of the phases of the compound studied, we carried out two types of calculation without and with polarized (magnetic) spin in their structure. The most stable state for perovskite oxide studied is the ferromagnetic (spin polarized) state. The variations of total energy as a function of volume for the

studied perovskite oxide MoScO_3 are shown in Figure-2-

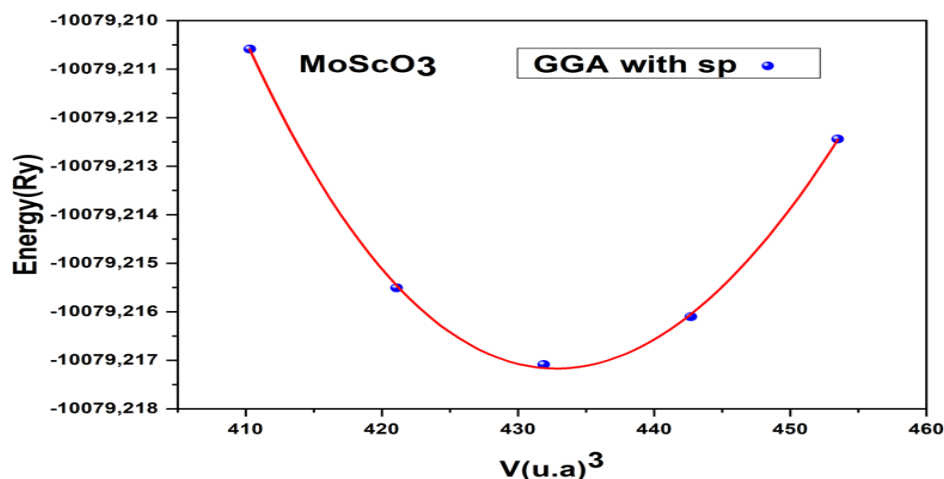


Figure 2. Energy variations as a function of volume of MoScO_3 with polarized spin.

All the equilibrium quantities such as the lattice constant, the compressibility modulus, its derivative and the minimum energy we have collected in Table I

Table 1. Structural parameters of the perovskite oxide MoScO_3

Variable	Lattice constant ($\text{\AA}^0$)	Bulk modulus(GPa)	Derivative of bulk modulus	Energy(Ry)
MoScO_3	4.0035	144.82	3.79207	-10079.21703

There is no theoretical or experimental work of other research in order to compare and judge the results we obtained. The material is considered resistant to deformation when subjected to external pressure if it has a large compressibility modulus, therefore the studied perovskite oxide MoScO_3 can be considered more resistant to pressure, which is a good indicator of the high stability of the compound.

III.2 Electronic Properties

III.2.1 Density of States

The density of total spin up and spin dn states is shown in Figure 3, and it relates to all the atoms of the compound contributing together. The density of spin dn states, the energy band gap is clearly shown in the range (1.53 eV and 2 eV). The contribution of the O oxygen atom in the valence band is evident and in the range (-5.20 eV and -1.50 eV). For the conduction band, it shows the contribution of the Mo atom with a small contribution from the O oxygen atom between approximately 2 eV and 3.31 eV. The rest of the conduction band and between approximately 5.20 eV and 7 eV shows the contribution of the Sc atom. The density of total spin up states clearly shows the metallic behavior of the perovskite oxide MoScO_3 . In the valence band, we notice the contribution of the oxygen atom O and the Molybdenum atom Mo in the energy range between -1 eV and 1 eV. In the conduction band, the contribution of the atom of Scandium Sc appears in the energy range between approximately 5 eV and 7 eV.

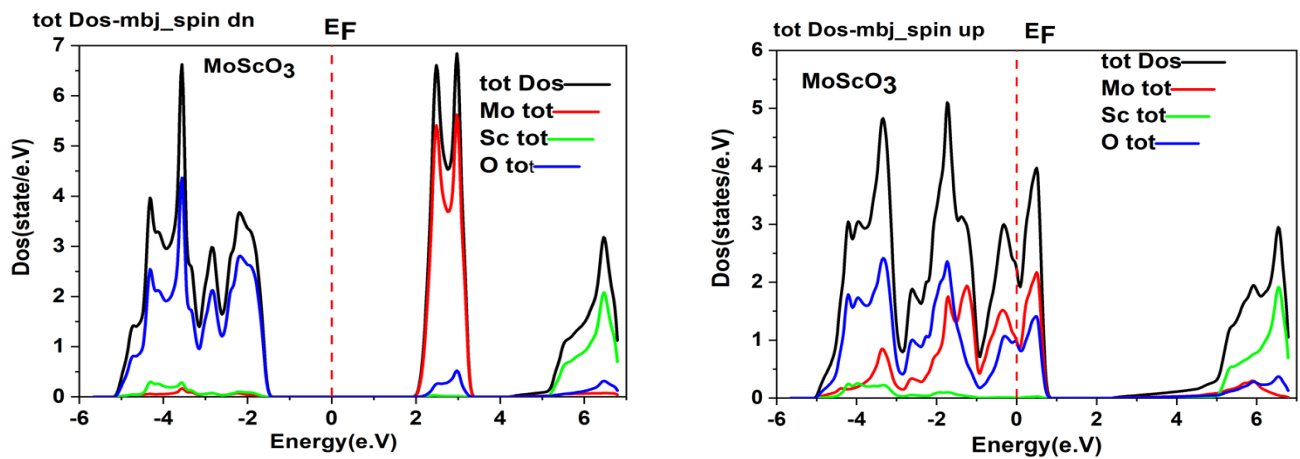


Figure 3. The density of states of MoScO_3 calculated by GGA, (a) the density of total spin up states, (b) the density of total spin states dn

III.2.2. Band structure

In this part we will discuss the energy bands that we obtained using the linearly augmented plane waves with total potential (FP-LAPW) method according to the generalized gradient approximation GGA and along the high symmetry lines in the first Brillouin region. Figure-4- represents the structure of the energy bands of the studied perovskite oxide MoScO_3 .

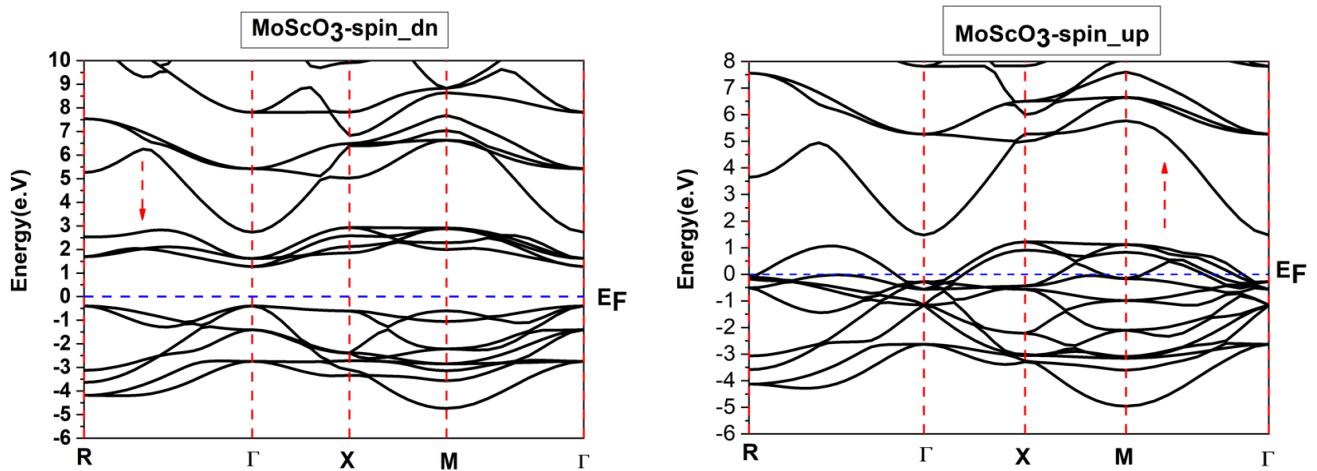


Figure 4. Energy band structure dn and up of MoScO_3 obtained by GGA

What emerges from the graphic representation of the energy band structure is metallic behavior for the case of electrons which have a spin up and semiconductor behavior for the case of electrons which have a spin dn. From this figure, we notice that the maximum of the valence band at point R and at point Γ the minimum of the conduction band we can conclude that the perovskite oxide studied has a semi-metallic appearance. We mentioned previously that perovskite oxide has an indirect gap semiconductor behavior for electrons that have spin Dn. In order to obtain a better value of the gap we calculate it by the MBJ method. The curve given in figure-5- shows the structure of the energy bands for the electrons which have a spin Dn and the electrons have a spin up. We always see a semiconductor behavior of the indirect gap for the spin dn electrons and a metallic behavior for the spin up electrons.

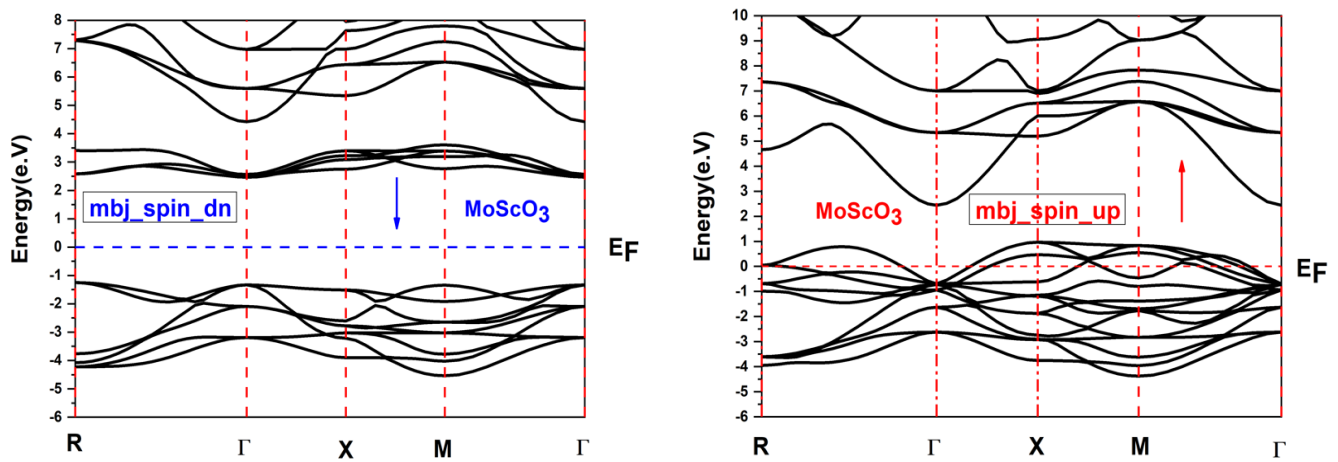


Figure 5. The dn and up energy band structure of MoScO₃ calculated by the mbj method

We can also notice that there is a difference concerning the value of the gap energy since the second value can be considered as a correction by the mbj method.

The values of the gap energies calculated in the GGA approximation and by the mbj method are represented in table 2.

Table 2. The values of the gap energies for MoScO ₃ obtained by GGA and by mbj		
Variable	Energy of the gap (eV)	
	Spin dn	Spin up
GGA	1.61	No gap
GGA+mBJ	3.51	No gap

It should be noted that band gap values, whether direct or indirect, are of great importance in certain applications of perovskite-type systems such as photovoltaic, light-emitting diodes (LEDs) and optoelectronics.

III.3. Magnetic Properties

In this part of this article, we study the magnetic properties of MoScO₃ where the total, partial and interstitial magnetic moments have been calculated using the GGA approximation. The results obtained are listed in Table III

Table 3. Total, partial and interstitial magnetic moments of MoScO₃ perovskite

Variable	Interstitial	μ_{tot}	μ_{Mo}	μ_{Sc}	μ_{O}
MoScO ₃	0.47155	3.00002	2.88119	0.01071	-0.12114

From the table we notice that the magnetic moment value of the Mo atom clearly contributes to the total moment, while the remaining atoms that make up the perovskite can be considered non-magnetic.

III.4. Thermodynamic Properties

The study of thermodynamic properties is based on Debye's quasi-harmonic model [6] and the Gibbs function, which can be written as follows:

$$G^*(V, P, T) = E(V) + PV + A_{vib}[\theta(V), T] \quad (2)$$

Where $\mathbf{E}(\mathbf{V})$ the total energy per unit cell, $\mathbf{PV}$ represents the hydrostatic pressure constant, $\theta(\mathbf{V})$ the Debye temperature and $\mathbf{A}_{\text{vib}}$ represents the vibration term which is expressed using the Debye phonon density model

$$A_{\text{vib}}(\theta, T) = nkT \left[\frac{9\theta}{8T} + 3\ln(1 - e^{-\frac{\theta}{T}}) - D(\theta/T) \right] \quad (3)$$

Figure 6 shows the variation of heat capacity C_v as a function of temperature at different pressures. The curve shows two different behaviors in the temperature range, at low temperature it increases rapidly with temperature, its variation is proportional to T^3 . at high temperature it increases slowly until approaching a limit value [7] ($C_v = 123.57 \text{ J.mol}^{-1}\text{K}^{-1}$) i.e. tends towards the Dulong and Petit limit like other solid compounds

We have shown in Figure 7 the Debye temperature variations θ_D as a function of temperature at different pressures. We see that at a temperature $T < 100\text{K}$, the Debye temperature is almost constant then decreases linearly with the increase in temperature.

At constant temperature, we see that the Debye temperature increases with pressure. Our θ_D calculated at zero pressure and temperature ($P=0, T=0$) is 594.89 K . at ambient temperature ($T=300\text{K}$) and zero pressure the value of θ_D is 594.69 K .

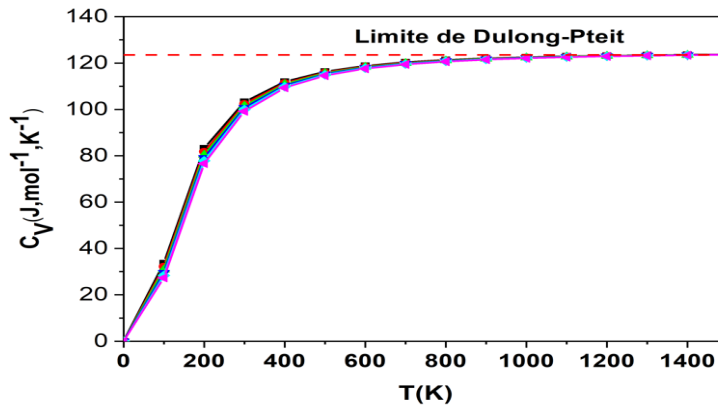


Figure 6. The variation of heat capacity as a function of temperature at different pressures for MoScO_3 .

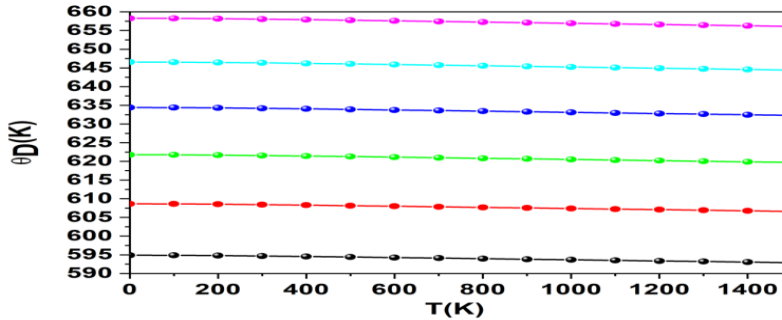


Figure 7. Temperature variation of Debye θ_D as a function of temperature at different pressures for MoScO_3

IV. Conclusion

Our work contributes to the study of the structural, electronic, magnetic, and thermodynamic properties of the perovskite oxide MoScO_3 by the linear augmented plane wave (FP-LAPW) method. The study was carried out within the framework of the density functional theory DFT implemented in the wien2k code. The results obtained indicating that the compound studied is a semi-metal with semiconductor behavior for spin down electrons and metal behavior with spin up electrons, its wide band gap and its large magnetic moment qualify this material and make it very suitable for electronic applications. We completed this work by studying the thermodynamic properties through variations in the heat capacity, the Debye temperature. It is noted that we do not currently have experimental results on the structural, elastic, electronic, optical and thermal constants of the cubic structure of MoScO_3 . We hope that this preliminary work could serve as a reference for subsequent experimental studies to improve the optoelectronic and spintronic applications of MoScO_3 .

References

- [1] Lanz, A., Heffel, J., Messer, C. Hydrogen fuel cell engines and related Technologies: in 2001 College of the Desert, Energy Technology Training Center
- [2] Ponce, S., Peña, M. A., Fierro, J.L.G., Catal, B. Vol.24, 193, 2000.
- [3] Slater, J.C. Damped electron waves in crystals, Phys. Rev. 51, 840, 1937
- [4] Sjöstedt, E., Nordström, L., Singh, D.J. An alternative way of linearizing the augmented plane wave method, Solid State Commun. 114, pp 15–20, 2000
- [5] Murnaghan, F.D. The compressibility of media under extreme pressures, Proc. Natl. Acad. Sci. U. S. A. 30 244, 1944.
- [6] Blanco, M.A., Francisco, E., Luaña, V. Comput. Phys. Commun. 158(7) 2004.
- [7] Petit, A.T., Dulong, P.L., Ann. Chim. Phys. 10, 395, 1819.