Recalculate Structural, Elastic, Electronic, and Thermal Properties in LaAlO$_3$ Rhombohedral Perovskite

Abdelkader Boudali, Fatiha Saadaoui, Mostefa Zemouli, Mohamed Driss Khodja, Kadda Amara
Laboratory of Physico-chemical Studies, University of Saida, Saida, Algeria
Email: boudaliabdel@yahoo.fr, *Abdelkader1954@live.fr
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ABSTRACT

We study the structural, elastic and electronic properties of perovskite insulator LaAlO$_3$ using two different methods: the full-potential linearized augmented plane wave method and the pseudo-potential plane wave scheme in the frame of generalized gradient approximation and local density approximation GGA + mBJ. We have evaluated the ground state quantities. Also, we have presented the results of the band structure and densities of states. These results are in favour of agreement with previous theoretical works and the existing experimental data. To complete the fundamental characteristics of this compound, we have analyzed the thermodynamic properties.

Keywords: Ab-Initio Calculations; Elastic Properties; Electronic Structure; Thermodynamic

1. Introduction

Lanthanum aluminate (LaAlO$_3$) is a promising alternative gate dielectric for the replacement of SiO$_2$ in silicon MOSFETs due to its high-$k$ value (~25) [1], wide energy band gap (~5 - 6 eV) [2,3], large optical band gap 6.2 eV [2-4] and good thermal stability in contact with Si [5,6]. Being a perovskite (ABO$_3$), LaAlO$_3$ is also structurally compatible with many functional compounds, like manganites, superconductors and ferroelectrics. There have been many studies of the electronic and structural properties of LaAlO$_3$, both of experimental [7-16] and theoretical aspects of bulk [17-22] as well as surface [23-26]. The structure of LaAlO$_3$ is rhombohedral at room temperature and usually defined as hexagonal with space group R-3c (No.167). The lattice parameters are $a = 0.536$ nm and $c = 1.311$ nm [27] Figure 1.

To the best of our knowledge, there are no theoretical reports on the thermal behaviour of LaAlO$_3$ in the literature. Consequently, the primary purpose of this work is to provide some additional information to the existing data on the physical properties of LaAlO$_3$ with state-of the-art first-principles calculations. After introducing the problem, the remaining paper is organized as follows: in Section 2, we describe the calculation procedure. Results are presented in Section 3. Section 4 contains the conclusion.

2. Theoretical Method

The zero-temperature energy calculations are performed using both the all-electron full-potential linear augmented-plane-wave method (FP-LAPW) [28] and the plane-wave pseudopotential (PPs-PW) [29] method. In both cases exchange-correlation effects were described using the Perdew et al. (GGA96) form [30] and local density approximation Tr-Blaha LDA + mBJ [31]. The FP-LAPW calculations have been carried out using the WIEN2k code [28]. The sphere radii used in the calculations are 2.32, 1.74 and 1.60 a.u. for La, Al and O, respectively. Within these spheres, the charge density and potential are expanded in terms of crystal harmonics up to angular momenta $L = 10$, and a plane wave expansion has been used in the interstitial region. The Brillouin zone integrations for the total energy have been carried out using 35 special $k$-points in the irreducible Brillouin zone. Brillouin zone integrations for the total energy have been carried out using 35 special $k$-points in the irreducible Brillouin zone. Well converged solutions were found for $R_{\text{cut}}K_{\text{max}} = 8$, where $K_{\text{max}}$ is the plane wave cut-off and $R_{\text{cut}}$ is the atomic sphere radii. Both the muffin-tin radius and the number of $k$-points are varied to ensure convergence. Core states are treated fully relativistic but for valence states relativistic effects have been included in a scalar relativistic treatment.

The PP-PW calculations were performed using the CASTEP computer code [29,32] and the thermodynamic properties of LaAlO$_3$, we apply the quasi-harmonic Debye model [33-41], in which the non-equilibrium Gibbs
function $G^*(V; P, T)$ details can be found in my article Cubic LaAlO$_3$ [33].

3. Results and Discussions

3.1. Structure and Elastic Constants

We firstly calculate the structural and elastic properties using FP-LAPW and PPs-PW methods. Figure 2 shows the variation of the total energy as a function of volume and fitted to a Murnaghan equation of state [42] to obtain the equilibrium lattice constant, bulk modulus, and its pressure derivative. The results are summarized in Table 1, together with some theoretical results and the available experimental data. Obviously, the obtained results by FP-LAPW method are in better agreement with the

<table>
<thead>
<tr>
<th>Present work (FP-LAPW)</th>
<th>Experiment (PW-PP )</th>
<th>[50]</th>
<th>[51]</th>
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<tbody>
<tr>
<td>$a$ (Å)</td>
<td>5.46</td>
<td>5.43</td>
<td>5.37</td>
</tr>
<tr>
<td>$C$ (Å)</td>
<td>13.13</td>
<td>13.30</td>
<td>13.110</td>
</tr>
<tr>
<td>$B$ (GPa)</td>
<td>189.30</td>
<td>184.26</td>
<td>195.76</td>
</tr>
<tr>
<td>$B'$</td>
<td>4.06</td>
<td></td>
<td></td>
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<tr>
<td>$C_{11}$ (GPa)</td>
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<td>337</td>
<td>381.56</td>
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<td>$C_{33}$ (GPa)</td>
<td>410.89</td>
<td>411</td>
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<td>$C_{14}$</td>
<td>43.12</td>
<td>46</td>
<td>29.66</td>
</tr>
</tbody>
</table>
experiment compared to those calculated by PP-PW. The elastic constants are summarized in Table 1, which are in good agreement with the theoretical results and the available experimental data. It is clearly seen that the results we have calculated by FP-LAPW are in better agreement with experiment compared to those calculated by PP-PW. Our data will be beneficial to future investigation. We have performed elastic constants, calculations with the PW-PP method using the CASTEP code. The obtained values are presented in Table 1. Unfortunately, to our knowledge, no other results are available in literature for comparison. In Table 2, we report CASTEP calculations of the atomic positions after relaxation.

3.2. Electronic Properties

Density of states and electronic band structure often provide sufficient information for a thorough characterization of the electronic properties of a material. The energy band structure, total and partial density of states of LaAlO$_3$ were calculated by FP-LAPW method scheme in the frame of local density approximation Tr-Blaha + mBJ. From Figures 3 and 4, it appears that the main effect of TB-mBJ potential, with respect to GGA [43], is to shift up the unoccupied La $d$ states. This is due to the kinetic-energy density term which increases the energy of unoccupied states and changes the corresponding band structure and density of states [44]. In PBE calculation [43], the states at the bottom of the conduction band derive from La $d$ states hybridized with the states of the La $f$ band which occur just above the conduction band edge. In our TB-mBJ calculations, the La $d$ unoccupied states are shifted to higher energies. This gives rise to pure and narrower band of La $f$ localized states at the bottom of the conduction band. Similar observations had been made by D. J. Singh for La$_2$O$_3$ [45]. Our calculations show that the valence band maximum is located at $\Gamma$ and the conduction band is minimum at $\Gamma$ point.

Figure 3. Band structure for high-symmetry directions in the Brillouin zone. The zero of energy corresponds to the fermi level.

Figure 4. Calculated partial density of states and total density of states of LaAlO$_3$.
Table 2. Positions of the atoms obtained by relaxation.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Number</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
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<td>1</td>
<td>0.224639</td>
<td>0.275361</td>
<td>0.750000</td>
</tr>
<tr>
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<td>0.750000</td>
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<td>0.275361</td>
</tr>
<tr>
<td>O</td>
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<td>0.275361</td>
<td>0.750000</td>
<td>0.224639</td>
</tr>
<tr>
<td>O</td>
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<td>-0.275361</td>
<td>-0.750000</td>
</tr>
<tr>
<td>O</td>
<td>5</td>
<td>-0.750000</td>
<td>-0.224639</td>
<td>-0.275361</td>
</tr>
<tr>
<td>O</td>
<td>6</td>
<td>-0.275361</td>
<td>-0.750000</td>
<td>-0.224639</td>
</tr>
<tr>
<td>Al</td>
<td>1</td>
<td>0.000000</td>
<td>0.000000</td>
<td>0.000000</td>
</tr>
<tr>
<td>Al</td>
<td>1</td>
<td>0.500000</td>
<td>0.500000</td>
<td>0.500000</td>
</tr>
<tr>
<td>La</td>
<td>1</td>
<td>0.250000</td>
<td>0.250000</td>
<td>0.250000</td>
</tr>
<tr>
<td>La</td>
<td>1</td>
<td>-0.250000</td>
<td>-0.250000</td>
<td>-0.250000</td>
</tr>
</tbody>
</table>

From Figure 4, we can find that the DOS can be mainly divided into four parts. The first part extending from −13.89 to −12.34 eV is of the combination of Al s, Al p, O s and La p states, and it is mainly due to the contribution of O s states; the second part from −6.73 to 0 eV is mainly made from La p states, with slight contributions of O s; the third part from −7.3 to 0 eV is mainly the contribution of O 2p states; the forth part extending from 5.40 to 10 eV is mainly composed of La d and Al s, p states.

Our calculation show that the valence band maximum is located at Γ and the conduction band minimum is at Γ resulting in an direct gap of 5.4 eV in FP-LAPW, and 3.4 eV in PPs-PW, compared to 5.6 eV experimentally [2,3]. We have to remember that GGA is known to underestimate band gaps in semiconductors. Robertson et al. [22]. Who used a screen exchange (SX) GGA [23] found that LaAlO3 was a semiconductor with an indirect gap of 4.4 eV. Our calculation with LDA + mBJ shows that LaAlO3 is an insulator. This modification of the electronic properties implies automatically changes in the optical properties.

3.3. Thermodynamic Properties

The thermal properties are determined in the temperature range from 0 to 600 K, where the quasi-harmonic model remains fully valid. The pressure effect is studied in the 0 - 30 GPa range. The temperature effects on the lattice parameters are shown in Figure 5. The Volume parameter increases with increasing temperature but the rate of increase is very moderate. On the other hand, it is noted from Figure 6 that the relationships between bulk modulus and pressure are all nearly linear at various temperatures of 0, 100, 200, 300, 400, 500 and 600 K, respectively. The bulk modulus increases with pressure at a given temperature and decreases with temperature at given pressure. These results are due to the fact that the effect of increasing pressure on the material is the same as decreasing temperature of the material.

The investigation on the heat capacity of crystals is an old topic of condensed matter physics with which illustrious names are associated [46-48]. Knowledge of the heat capacity of a substance not only provides essential insight into its vibrational properties but is also mandatory for many applications. Two famous limiting cases are correctly predicted by the standard elastic continuum theory [48]. At high temperatures, the constant volume heat capacity Cv tends to the Petit and Dulong limit [49]. At sufficiently low temperatures, Cv is proportional to T[48]. At intermediate temperatures, however, the temperature dependence of Cv is governed by the details of vibrations of the atoms and for a long time could only be determined from experiments. Figures 7 and 8 represent the variation of the heat capacity, Cv (T), and volume expansion coefficient, α(T) as function of the temperature, respectively. These two quantities indicate a sharp increase up to ~400 K which is due to the anharmonic approximation of the Debye model used here. However, at higher temperature, the anharmonic effect on Cv is suppressed, and Cv is very close to the Dulong-Pettit
The ground-state parameters, such as lattice parameter, bulk modulus and its pressure derivative and the elastic constants are in good agreement with some theoretical results and the available experimental data. The partial contribution of each atom to the total density of states was calculated. From the band structure, we find that LaAlO$_3$ is a direct $\Gamma \rightarrow \Gamma$ gap close about 98% to the experimental value indicating that the material is an insulator. With this change of electronic properties, the optical properties must be recalculated. To complete the basic characteristics of this compound, we analyzed their thermodynamic properties using the quasiharmonic model of Debye. We see that the predicted heat capacity $C_v$ is close to the Dulong-Petit limit, which is common to all solids at high temperatures.

**REFERENCES**


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