Electronic and elastic properties of Ba$_2$HgSn and Ca$_2$HgSn
Rattling Heusler

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Abstract. Semiconductor electronic components are the active elements of integrated circuits, and they are at the origin of all advances in electronics. A new semiconductor class consists in Rattling Heusler. The purpose of this work is to study the structural, electronic and elastic properties of X$_2$HgSn (X=Ba, Ca) Heusler alloys by using the first-principle projector augmented wave potential within the generalized gradient approximation. Our calculations show that these compounds are all semiconductor and are ductile manner.

1. Introduction
Currently, the new technology seeks its raw material in the elements periodic table, based on the fact that the combination of two different materials does not present a combination of their properties but rather gives rise to new specific features to the formed alloy. This motivation was a driving force of the development of materials science and engineering as an important branch like chemistry, physics and metallurgy. Materials science aims to determining the relationships between structures and material properties, while materials engineering is focused on the development and the design of materials with known structures and properties. Heusler X$_2$YZ alloys are among the materials that are attracting growing interest since the pioneer discovery, made by the German chemist Friedrich Heusler in 1903, of ferromagnetism in Cu-Mn-Al alloys in which the constituent elements are not ferromagnetic [1]. Indeed, compounds of Heusler form present a remarkable class of materials due to their various physical properties and potential applications. Whereas, the properties of these X$_2$YZ compounds, with alkaline earth elements (Ba, Sr, Ca) in the X sublattice, whereas Y are noble metals (Au, Hg) and Z are main group elements (Sn, Pb, As, Sb, Bi) [2], have not yet been reported in literature. In this paper, we present a detailed study on the site preference, electronic and elastic properties of Heusler alloys X$_2$HgSn (X=Ba, Ca) using first-principles calculations.

2. Computational Method
The first-principles calculations are performed using the Full-Potential Linearized Augmented Plane Wave (FP-LAPW) method as implemented in WIEN2K code [3]. The exchange-correlation potential

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is calculated within the Generalized Gradient Approximation (GGA) by Perdew Burke Ernzerhof (PBE) [4] is also applied in calculations. In this method, no shape approximation on either potential or the electronic charge density is made. Using this method, valence and core states origin energy have been separate, and –6 Ryd energy bound separated between valence electrons and core states was chosen. In the calculations reported here, we use an RMT $K_{max}$=8 parameter, which determines matrix size (convergence), where $K_{max}$ is the plane wave cut-off and RMT is the smallest atomic sphere radius. The density of states is calculated by the histogram method and the position of the Fermi level is found by integrating consistent calculations. The energy convergence criterion for the self-consistent field calculations was set to $10^{-4}$ Ryd, whereas the charge convergence was set to $10^{-4}$. The Fermi level energy was adjusted to zero, and we used $13 \times 13 \times 13$ meshes which represent 84 k points in the first Brillouin zone integrations in reciprocal space. The density of states is calculated by the histogram method and the position of the Fermi level is found by integrating consistent calculations. The energy convergence criterion for the self-consistent field calculations was set to $10^{-4}$ Ryd, whereas the charge convergence was set to $10^{-4}$. The Fermi level energy was adjusted to zero, and we used $13 \times 13 \times 13$ meshes which represent 84 k points in the first Brillouin zone integrations in reciprocal space. The density of states is calculated by the histogram method and the position of the Fermi level is found by integrating consistent calculations. The energy convergence criterion for the self-consistent field calculations was set to $10^{-4}$ Ryd, whereas the charge convergence was set to $10^{-4}$. The Fermi level energy was adjusted to zero, and we used $13 \times 13 \times 13$ meshes which represent 84 k points in the first Brillouin zone integrations in reciprocal space. The density of states is calculated by the histogram method and the position of the Fermi level is found by integrating consistent calculations. The energy convergence criterion for the self-consistent field calculations was set to $10^{-4}$ Ryd, whereas the charge convergence was set to $10^{-4}$. The Fermi level energy was adjusted to zero, and we used $13 \times 13 \times 13$ meshes which represent 84 k points in the first Brillouin zone integrations in reciprocal space.

3. Results and discussion

3.1. Structural stability

Heusler alloys $X_2YZ$ (Cu$_2$MnAl-type) crystallize in the Fm3m (N 225) regular cubic space group [5, 6], where the X atoms occupy the 8c Wyckoff position (1/4, 1/4, 1/4) and the Y and Z atoms are respectively at the 4a (0, 0, 0) and 4b (1/2, 1/2, 1/2) positions (see figure 1(a)). The crystal can be crystallized in F43m (N 216) inverse cubic structure (Hg$_2$CuTi-type) [7], the X atoms are placed on the positions 4a (0, 0, 0) and 3d (3/4, 3/4, 3/4) while the atoms Y and Z are respectively located at 4b (1/2, 1/2, 1/2) and 4c (1/4, 1/4, 1/4) as shown in figure 1(b).

![Figure 1](image.png)

Figure 1. Different types of Heusler structures: (a) regular-Heusler, (b) inverse-Heusler.

We have calculated the total energy as a function of lattice constant of $X_2$HgSn ($X$=Ca, Ba) compounds, in the regular cubic and the inverse cubic structures, for the ferromagnetic (Ferro) and nonmagnetic (NM) states. The plot of calculated total energies versus reduced volume for compounds Ca$_2$HgSn and Ba$_2$HgSn are given in figure 2 and figure 3 respectively. The total energies versus changed volumes have been fitted to Murnaghan's equation of state [8] in order to determine the ground state properties, such as equilibrium lattice constant $a$, bulk modulus $B$ and its pressure derivative $B'$. The calculated structural parameters of these compounds are reported in table 1. The results obtained with the GGA-PBE method shows that the most stable structure for all compounds is Cu$_2$MnAl-type in the nonmagnetic phase.
Table 1. Calculated lattice constants a, bulk modulus B, first derivatives B’ and equilibrium energies E for Ba$_2$HgSn and Ca$_2$HgSn compounds.

| Alloy   | Type      | Phase | a (Å) | B (GPa) | B’   | E (eV)       |
|---------|-----------|-------|-------|---------|------|--------------|
| Ba$_2$HgSn | Cu$_2$MnAl | FM    | 8.48  | 25.36   | 4.29 | -84239.640248 |
|         |           | NM    | 8.48  | 25.35   | 4.27 | -84239.640250 |
|         | Hg$_2$CuTi | FM    | 8.31  | 23.20   | 4.46 | -84239.537754 |
|         |           | NM    | 8.31  | 23.29   | 4.51 | -84239.537761 |
| Ca$_2$HgSn | Cu$_2$MnAl | FM    | 7.68  | 36.07   | 4.14 | -54403.727262 |
|         |           | NM    | 7.68  | 36.11   | 4.50 | -54403.727271 |
|         | Hg$_2$CuTi | FM    | 7.75  | 30.56   | 3.88 | -54403.609839 |
|         |           | NM    | 7.75  | 30.40   | 4.21 | -54403.609802 |

Figure 2. Calculated total energies as functions of volume for Ba$_2$HgSn Heusler alloys.
3.2. Electronic properties

The calculated band structures of Heusler alloys $X_2\text{HgSn}$ ($X=\text{Ba, Ca}$) at equilibrium lattice constant along the high symmetry lines of the BZ are presented in figure 4. This figure shows clearly the semiconducting behaviour of $\text{Ba}_2\text{HgSn}$ and $\text{Ca}_2\text{HgSn}$ which are drawn along the symmetry directions in the first Brillouin zone. Calculations predict the valence band maximum at between $L-\Lambda$ and the conduction band minimum at $\Delta$ point resulting in an indirect band gap for the $\text{Ba}_2\text{HgSn}$ alloy. In contrast, the $\text{Ca}_2\text{HgSn}$ compound exhibits direct band gap ($L-L$).

![Graph showing energy levels for Ca$_2$HgSn and Ba$_2$HgSn Heusler alloys.]

**Figure 3.** Calculated total energies as functions of volume for Ca$_2$HgSn Heusler alloys.

**Figure 4.** Band structures of Ca$_2$HgSn (left graph) and Ba$_2$HgSn (right graph) Heusler alloys.
3.3. Elastic properties
The elasticity of a solid body is its response in the form of slight deformation when subjected to external mechanical stresses. The stresses are described by tensors which determine the direction of forces and the plane on which they are applied.

The numerical calculation of the elastic constants for the studied alloys can be performed by the method of Thomas Charpin implemented in the code WIEN2k. In cubic crystal, there are only three independent elastic constants, namely, \( C_{11}, C_{12} \) and \( C_{44} \). By calculating the total energy as a function of strain, these elastic constants can be determined [9]. The conditions of elastic stability in cubic crystal are \( C_{11} - C_{12} > 0, C_{11} > 0, C_{44} > 0, C_{11} + 2C_{12} > 0, C_{12} < B < C_{11} \) [10]. Besides, other elastic parameters can be calculated such as the Shear modulus \( G \), Young’s modulus \( E \), Poisson’s ratio \( \nu \) and Anisotropy factor \( A \) of \( X_2\text{HgSn} \) (X= Ba, Ca) using the Voigt–Reuss–Hill approximations [11]:

\[
G = \frac{1}{2} \left( \frac{C_{11} - C_{12} - 3C_{44}}{5} + \frac{5C_{44}(C_{11} - C_{12})}{4C_{44} + 3(C_{11} - C_{12})} \right)
\]

\[
E = \frac{9BG}{G + 3B}
\]

\[
\nu = \frac{3B - 2G}{2(3B + G)}
\]

\[
A = \frac{3C_{44}}{C_{11} - C_{12}}
\]

Our results are presented in table 2. One should note that no experimental values or theoretical calculations for the elastic constants of \( \text{Ba}_2\text{HgSn} \) and \( \text{Ca}_2\text{HgSn} \) have been reported before. According to the stability criteria, the studied compounds with GGA are mechanically stable because the value \( (C_{11} - C_{12}) \) is positive for all the compounds. Our calculated values using GGA of B/G are 1.74, 1.67 for \( \text{Ba}_2\text{HgSn} \) and \( \text{Ca}_2\text{HgSn} \) respectively and \( \nu > 1/3 \) for all compounds. We can conclude the studied components are ductile manner according to [12,13].

Table 2. Calculated elastic constants: Anisotropy factor \( A \), Shear modulus \( G \), Young’s modulus \( E \) and the Poisson’s ratio \( \nu \) of \( \text{Ba}_2\text{HgSn} \) and \( \text{Ca}_2\text{HgSn} \).

| Alloy     | \( C_{11} \) | \( C_{12} \) | \( C_{44} \) | \( G \) | \( E \) | \( \nu \) | B/G | A  |
|-----------|---------------|---------------|--------------|-------|------|--------|-----|----|
| \( \text{Ba}_2\text{HgSn} \) | 43.0          | 16.579        | 15.6         | 14.6  | 36.8 | 0.26   | 1.74| 1.18|
| \( \text{Ca}_2\text{HgSn} \) | 59.5          | 24.5          | 25.1         | 21.7  | 54.8 | 0.25   | 1.67| 1.43|

4. Conclusion
In summary, we have performed first principles calculations based on the FP-LAPW method within the GGA. We have studied structural, electronic and elastic properties of \( \text{Ba}_2\text{HgSn} \) and \( \text{Ca}_2\text{HgSn} \) full Heusler alloy. The study shows that the most stable structure for all compounds is \( \text{Cu}_{2}\text{MnAl} \)-type in the nonmagnetic phase. The characterization of electronic properties shows that the compounds \( \text{Ba}_2\text{HgSn} \) and \( \text{Ca}_2\text{HgSn} \) are semiconductor materials. The elastic constants \( C_{11}, C_{12} \) and \( C_{44} \) of these alloys were calculated for the first time, and the obtained results could provide a basic reference for other similar work.
References

[1] Heusler Verh F. 1903 *Deutsch. Phys. Ges.* 5 219

[2] He J 2016 arXiv:1604.03827v2

[3] Blaha P, Schwarz K, Madsen G K H, Kvasnicka D and Luitz J, 2008 WIEN2K, Augmented Plane Wave Plus Local Orbital’s Program for Calculating Crystal Properties, University of Technology, ISBN 3-9501031-1-2 Vienna, Austria

[4] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* 77 3865

[5] Heusler O 1934 *Ann. Phys.* 155 411

[6] De Groot R A, Mueller F M, van Engen P G and Buschow K H J 1983 *Phys. Rev. Lett.* 50 2024

[7] Puselj M and Ban Z 1969 *Croat. Chem. Acta.* 41 79

[8] Murnaghan F D 1944 *Proc. Natl. Acad. Sci. USA* 30 244

[9] Mehl M J, Osburn J E, Papaconstantopoulos D A and Klein B M 1990 *Phys. Rev.* B 41 103112

[10] Sin’ko G V and Smirnov N A 2002 *J. Phys. Condens. Matter* 14 6989

[11] Hill R 1952 *Proc. Phys. Soc. Lond.* A 65 349

[12] Pugh S F 1954 *Philos. Mag.* 45 823

[13] Frantsevich I N, Voronov F F and Bokuta S A 1983 Elastic Constants and Elastic Moduli of Metals and Insulators Handbook, ed. I. N. Frantsevich, Kiev