AB-INITIO FIRST PRINCIPLES CALCULATIONS ON HALF-HEUSLER NiYSn (Y=Zr, Hf) COMPOUNDS
PART 1: STRUCTURAL, LATTICE DYNAMICAL, AND THERMO DYNAMICAL PROPERTIES

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The structural and lattice dynamical properties of the half-Heusler NiYSn (Y=Zr, Hf) compounds, we have been investigated using the ab-initio density-functional theory within the generalized gradient approximations. In particularly, some basic physical parameters such as lattice constant, bulk modulus and its first derivatives, elastic constants, shear modulus, Young’s modulus, and Poison’s ratio are calculated in the ground state configuration. The calculated elastic constants and the related sound velocities and Debye temperatures are also presented. The computed phonon dispersion curves based on the linear response method are predicted. Some thermo dynamical properties such as free energy, entropy, and heat capacity at constant volume are also estimated and interpreted for the first time.

I. INTRODUCTION

At recent years, scientists take an interest half-heusler structures for their electronic and optical properties. Like NiZrSn and NiHfSn, some half-heusler compounds with 18 valance electrons have narrow band gap and sharp slope of density of states (DOS) around the Fermi level [1]. This properties supply large thermoelectric power to semiconductors.

Half-Heusler compounds crystallize in the C1b MgAgAs-type structure, in the space group F\(\bar{3}m\) (No:216). Atoms are positioned at X (½, ½, ½), Y (¼, ¼, ¼) and Z (0, 0, 0) [3].

Although there exist many structural and electronic studies for this compounds, mechanical and thermal properties has not been studied yet. Therefore, we have focused on these properties.

II. METHOD OF CALCULATION

All calculations have been carried out using the Vienna ab-initio simulation package (VASP) [4-5] based on the density functional theory (DFT) within the generalized gradient approximations (GGA). The electron-ion interaction was considered in the form of the projector-augmented-wave (PAW) method [6, 7] with plane wave up to energy of 337 eV. For the exchange and correlation terms in the electron-electron interaction, Perdew-Burke-Ernzerhof (PBE) type functional [8] was used within the GGA. We have used 11x11x11 Monkhorst and Pack mesh for k-space summation.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(a_0) (Å)</th>
<th>(B_0) (GPa)</th>
<th>(B'_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiZrSn</td>
<td>6.151</td>
<td>119.4</td>
<td>4.350</td>
</tr>
</tbody>
</table>

Table 1. Calculated elastic constants \(a_0\), Bulk modulus \(B_0\) (GPa) and it’s pressure derivatives \(B'_0\), for NiYSn (Y=Zr, Hf) in C1b structure.

RESULTS AND DISCUSSION

Structural properties

Firstly (Determination of the electronic structure), the equilibrium lattice parameters have been computed by minimizing the crystal total energy calculated for different values of lattice constants by means of Murnaghan’s eos [9] for XYZ, YXZ and ZXY compounds (X=Ni, Y=Zr and Hf, Z=Sn) to determination of ground state electronic structure (Fig. 1). From Fig. 1 we found that XYZ structure is found to be energetically favored. The bulk modulus, and its pressure derivative have also been calculated based on the same Murnaghan’s eos and the results are listed in Table 1 for ground state structure. The present values of lattice parameters \(a_0\) in C1b phase are found to be 6.151 and 6.108 Å for NiZrSn and NiHfSn, respectively. It is seen that the present lattice constants are in well agreement with experimental and other theoretical ones [See Table 1]. As a fundamental
physical property, the bulk modulus of solids provide valuable information including in average bond strengths of atoms for the given crystals [10], and its correctly calculation is one of the first-steps of the total energy calculations.

The present values of the bulk modulus for all considered compounds are given in Table 1. In the present case, the calculated bulk moduli are 119.4 and 125.3 GPa for NiZrSn and NiHfSn, respectively. So, we can say NiZrSn more compressibility than NiHfSn. The values of the bulk moduli indicate that, these compounds hard material in the ground state phase. Our calculated values are in close agreement with theoretical literature (See Table 1).

**Elastic properties**

The elastic constants of solids provide a link between the mechanical and dynamical behaviors of crystals, and give important information concerning the nature of the forces operating in solids. In particular, they provide information on the stability and stiffness of materials, and their ab initio calculation requires precise methods [15]. Since the forces and the elastic constants are functions of the first-order and second-order derivatives of the potentials, their calculation will provide information on the stability and stiffness of crystals, and give important information concerning the nature of the forces operating in solids. In particular, they provide information on the stability and stiffness of materials, and their ab initio calculation requires precise methods [15]. Since the forces and the elastic constants are functions of the first-order and second-order derivatives of the potentials, their calculation will provide a further check on the accuracy of the calculation of forces in solids. The elastic constants are computed by using the “stress–strain” method [16] implemented in VASP 5.2.2, and are listed in Table 2 for both compounds at the ground state C1b structure. For the stability of lattice, the Born’s stability criteria’s should be satisfied. Elastic moduli and mechanical stability criteria with Voigt-Reuss-Hill relations for the cubic structures are given as follows [15, 17-19]:

\[ B_V = B_R = \frac{(C_{11} + 2C_{12})}{3}, \]
\[ G_V = \frac{(C_{11} + C_{12} + 3C_{44})}{2}, \]
\[ GR = 5(C_{11} - C_{12})K_{44}(4C_{44} + 3(C_{11} - C_{12})). \]

The mechanical stability criteria are given by

\[ C_{11} > 0, \quad C_{44} > 0, \quad C_{11} > |C_{12}|, \quad (C_{11} + 2C_{12}) > 0. \]

From Hill average [19],

\[ B = (1/2)(B_R + B_V) \quad \text{and} \quad G = (1/2)(G_R + G_V) \]

Young’s modulus \( E \) and Poisson’s ratio \( \nu \) are given as

\[ E = 9BG/(3B + G), \quad \nu = (3B - 2G)/(2(3B + G)). \]

The present case elastic constants for NiZrSn and NiHfSn are given in Table 2. Our results show that NiZrSn and NiHfSn are mechanically stable at ambient conditions in C1b phase. Young’s modulus is defined as the ratio of stress and strain, and used to provide a measure of the stiffness of the solid. The material is stiffer if the value of Young’s modulus is high. The calculated value of Young’s modulus 185.0 and 199.4 GPa for NiZrSn and NiHfSn, respectively. The values of the Young’s modulus indicate that, NiHfSn is stiffer than NiZrSn compound in C1b phase. These values are very close to value of (200 GPa) steel. Some experimental values (\( E, G, \nu, v_m, \) and \( \Theta_D \)) of the Sb doped quaternary compound NiZrSn0.9Sb0.1 in ref. [20] are in reasonable agreement with the present results, except for Young modulus (\( E \)).

<table>
<thead>
<tr>
<th>Unit</th>
<th>NiZrSn</th>
<th>NiZrSn0.9Sb0.1</th>
<th>NiHfSn</th>
<th>NiHfSn0.9Sb0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{11}</td>
<td>230.4</td>
<td>140.1</td>
<td>C_{11}</td>
<td>230.4</td>
</tr>
<tr>
<td>C_{12}</td>
<td>69.4</td>
<td>72.2</td>
<td>C_{12}</td>
<td>69.4</td>
</tr>
<tr>
<td>C_{44}</td>
<td>70.1</td>
<td>78.2</td>
<td>C_{44}</td>
<td>70.1</td>
</tr>
<tr>
<td>B_R</td>
<td>123.0</td>
<td>128.1</td>
<td>B_R</td>
<td>123.0</td>
</tr>
<tr>
<td>E</td>
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<td>111</td>
<td>E</td>
<td>185.0</td>
</tr>
<tr>
<td>G</td>
<td>74.0</td>
<td>70.2</td>
<td>G</td>
<td>74.0</td>
</tr>
<tr>
<td>v</td>
<td>0.249</td>
<td>0.240</td>
<td>v</td>
<td>0.249</td>
</tr>
<tr>
<td>v_l</td>
<td>3107</td>
<td>2461</td>
<td>v_l</td>
<td>3107</td>
</tr>
<tr>
<td>v_t</td>
<td>5377</td>
<td>4195</td>
<td>v_t</td>
<td>5377</td>
</tr>
<tr>
<td>v_m</td>
<td>3449</td>
<td>3039</td>
<td>v_m</td>
<td>3449</td>
</tr>
<tr>
<td>\Theta_D</td>
<td>382</td>
<td>304</td>
<td>\Theta_D</td>
<td>382</td>
</tr>
</tbody>
</table>

The typical value of Poisson’s ratio is about 0.1 for covalent materials and 0.25 for ionic materials [21]. In the present case the value of Poisson’s ratio is 0.249 and 0.240 for NiZrSn and NiHfSn, respectively. Thus, the ionic contributions to the atomic bonding are dominant for considered compounds in C1b phase.

Finally, the typical relations between B and G are given by [17]:

\[ G = 1.1B \quad \text{and} \quad G = 0.6B \]

for covalent and ionic materials, respectively. The values of the Young’s modulus indicate that, NiHfSn is stiffer than NiZrSn compound in C1b phase. These values are very close to value of (200 GPa) steel. Some experimental values (\( E, G, \nu, v_m, \) and \( \Theta_D \)) of the Sb doped quaternary compound NiZrSn0.9Sb0.1 in ref. [20] are in reasonable agreement with the present results, except for Young modulus (\( E \)).

**Debye temperature**

As an important fundamental parameter, the Debye temperature (\( \Theta_D \)) is closely related to many physical properties of solids such as the specific heat and melting temperature. One of the standard methods for calculating the Debye temperature is to use elastic constant data since\( \Theta_D \) = \( \frac{h}{k} \left( \frac{3n}{4\pi\Omega} \right)^{1/3} \)

where \( h \) is Planck’s constant, \( k \) is Boltzmann’s constant, \( \Omega \) is the volume of unit cell and \( n \) is the number of atoms in unit cell. The average sound velocity \( v_m \) is given by

\[ v_m = \left( \frac{1}{3} \left( \frac{2}{v_l} + \frac{1}{v_t} \right) \right)^{1/2} \]

\( v_l \) and \( v_t \) are the longitudinal and transverse elastic wave velocities, respectively, which are obtained from Navier’s equations as follows [24]:
where \( \rho \) is the density, \( B \) is the bulk modulus and \( G \) is the shear modulus. The calculated Debye temperature is found to be 382 and 344 K for NiZrSn and NiHfSn, respectively. We also presented the longitudinal \( (v_l) \), transverse \( (v_t) \), and their average \( (v_m) \) elastic wave velocities in Table 2.

### The lattice dynamical properties

The present phonon frequencies of NiYSn (Y=Zr, Hf) compounds in C1b phase are calculated by the PHONOPY program [25] using the interatomic force constants obtained from the VASP 5.2 [4, 5] which is use linear response method within the density functional perturbation theory (DFPT) [26-28]. The Phonopy program which is based on real space supercell calculates phonon frequencies from force constants.

The present phonon dispersion curves have been calculated in high symmetry directions using a 2x2x2 supercell approach. The obtained phonon dispersion curves with the LO-TO splitting along the high symmetry directions are illustrated in Fig. 2 and Fig 3 for NiZrSn an NiHfSn, respectively. These splitting at Gamma point strongly support their ionic character. Fig. 4 and Fig. 5 shows the partial phonon density of states (DOS) for NiZrSn and NiHfSn, respectively. In both plots, the contribution from Nickel atom is clearly dominant.

We also calculated thermo dynamical properties such as free energy, entropy, and heat capacity (See Fig. 6 and Fig. 7). For both compounds the heat capacity almost remains constant at about 250 K. The free energy and entropy curves exhibit the expected behavior at considered temperature range. Unfortunately, there is no experimental or other theoretical data on the lattice dynamical and thermo-elastic data for these compounds for the sake of comparison.

Fig. 2. Phonon dispersion curves with LO-TO along first Brillion zone for NiZrSn compound.

Fig. 3. Phonon dispersion curves with LO-TO along first Brillion zone for NiHfSn compound.

Fig. 4. Partial phonon density of states for NiZrSn compound.

Fig. 5. Partial phonon density of states for NiHfSn compound.

Fig. 6. Temperature dependence of free energy, entropy and heat capacity for NiZrSn in C1b phase.
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III. CONCLUSION

In this work, we have presented the results of ground-state structural, mechanical, vibrational, and thermo dynamical properties of NiZrSn and NiHfSn compounds in the C1b structure, using first-principles calculations based on the generalized gradient approximation (GGA) implemented in VASP. To the best of our knowledge, our calculations are the first theoretical prediction on the elastic and lattice dynamical properties of the studied compounds. The present data on the thermo dynamical properties such as free energy, entropy, and heat capacity provide valuable information about the intrinsic character of solids which are the other original aspects of the present calculations.

ACKNOWLEDGEMENT

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