Electronic and Piezoelectric properties of half-Heusler compounds: A first principles study

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Electronic and Piezoelectric properties of half-Heusler compounds: A first principles study

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Abstract. We have investigated the semiconducting and piezoelectric properties of bulk MNiSn (M=Ti, Zr, Hf) type a half-Heusler compound with cubic F-43m symmetry by means of density functional theory (DFT). For electron exchange correlation a generalized gradient approximation (GGA) was used. Special attention was paid to establish a most favourble ground state configuration on magnetic as well as non-magnetic ordering. With fully optimized structure the electronic and ferroelectric calculation was performed. The formation of band gap was discussed on the basis of d-d orbital hybridization. Further we have calculated the spontaneous polarization by means of structural deformation.

1. Introduction

The rapid environmental hazards due to the over consumption of fossil fuels and depletion of natural energy resources is a great threat to the modern world. In order to tackle problems of energy crisis, there arises a critical need of innovative and eco-friendly technologies based on multi-functional materials. Nevertheless, the current researches are devoted in the exploitation of material's properties for technological application or designing of such kind of materials that act smartly in response to external parameters like temperature, field and stresses. The materials are to be design in such a way to obtain high speed, high accuracy, low power consumption, improved communications and yield high energy conversion/storage. Until now different variety of materials are studied from experiment and theoretical approach (first principles calculation) and diverse functional properties were reported. Such as Chalcopyrites for solar cells [1], Heusler compounds for spintronic [2-5], Skutterudite for thermoelectric [6], Perovskite for solar cell, ferroelectric[7,8], etc. Among all other Heusler compounds a half-Heusler compounds are of great interest as they crystallizes in $C1_b$ cubic structure with space group F-43m and possess high curie temperature [9]. Also the half-Heusler compounds with 18 total valence electrons are non-magnetic semiconductors with band gap at the Fermi level. The formation of band gap is due to the hybridization between M-d and Ni-d orbitals [10]. Possessing semiconductor characteristic with no inversion center in MNiSn makes as it a potential candidate for ferroelectric/piezoelectric materials. Therefore, we employed a first-principles calculation to explore the microscopic origins of the functional properties of interest, and to obtain the information regarding the ferroelectric/piezoelectric properties by deforming the crystal structures.

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2. Computational Detail

The crystal structure of MNiSn is shown in Fig. 1. In this work, we have employed the FP-LAPW method within the framework of the density functional theory (DFT) [11] as implemented in the WIEN2k code [12]. We have also used another code called BerryPI an interface with WIEN2k to calculate the piezoelectric properties. Experimental lattice constants 6.11 A^o and 5.94 A^o [13] were used for volume optimization to obtain optimized lattice constants 6.23 A^o and 6.06 A^o for ZrNiSn and TiNiSn, respectively.

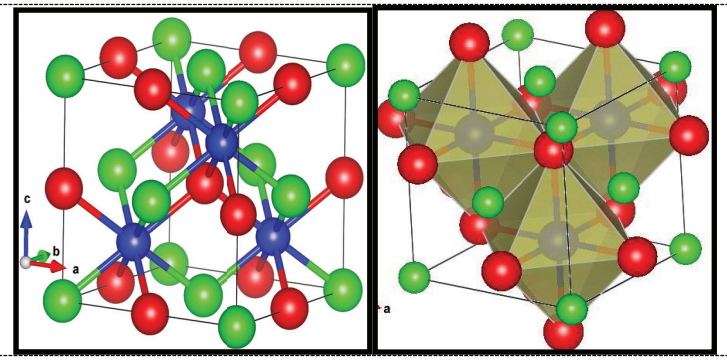

Figure 1. Crystal structure of MNiSn hal-Heusler compounds with F-43m cubic symmetry (M-Green, Ni-Red & Sn-Blue).

3. Results and Discussion

In this section we have discussed the electronic and piezoelectric properties of MNiSn, a half-Heusler compounds. The calculated electronic structures of MNiSn is presented in the form of density of states, as shown in Fig. 3(a-d). Figure 3(a) shows the result of total DOS, as we have seen the energy gap is located exactly at the Fermi level, which is a signature of semiconducting characteristic. The formation of band gap in MNiSn compounds with 18 valence electrons are described by Galanakis *et al.* [10] on the basis of d-d hybridization, as shown in Fig. 2. Fig. 3(a-d) displayed the DOS of MNiSn with majority contribution from Ni-d states in the valence region and M-d states contributes maximum in the conduction region. The hybridization of d-d orbitals take place near the Fermi energy. The bondings are formed between the M (d-t_{2g}) and Ni (d-t_{2g}) also between M(d-e_g) and Ni(d-e_g) as a result the energy level shifts down in the valence region. Corresponding anti-bondings are formed between M(d-e_g/d-t_{2g}) and Ni(d-e_g/d-t_{2g}) which gives an unstable state, and shifts the energy level high above the Fermi energy in the conduction region. Thus, the measure of energy difference between the highest occupied band and the lowest unoccupied gives the value of energy gap. Our calculated band gaps are in good agreement with the previous results [4, 14, 15, 16].

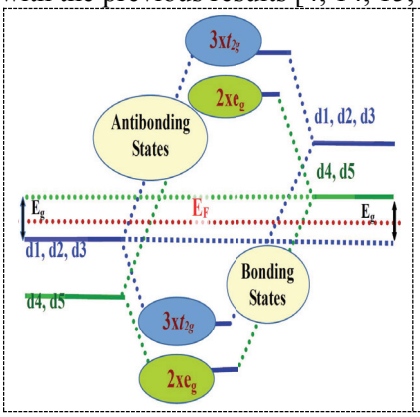

Figure 2. A schematic diagram shows the hybridization of d-d orbitals with the opening of the band gap. As we know d-orbitals are degenerated into 5 states 3 d-t_{2g} and 2 d-e_g states.

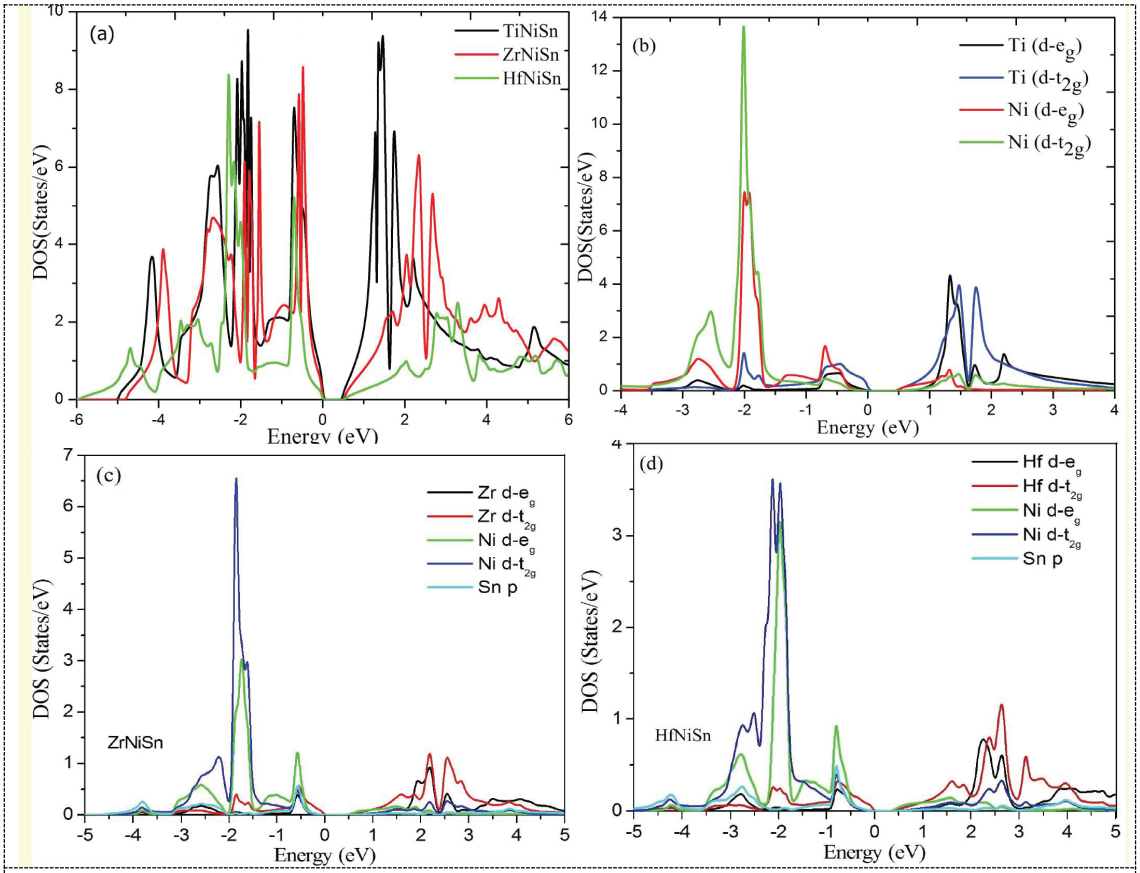

Figure 3. (a) Total DOS, partial DOS of (b) TiNiSn, (c) ZrNiSn and (d) HfNiSn

The presence of band gap in MNiSn predicts the semiconducting behaviour along with no inversion center. As we know these type of compounds are very interesting and may give some functional properties like ferroelectricity/piezoelectricity. The calculation of ionic contribution is based on the position of atomic nuclei and corresponding ionic charges. Hence, the piezoelectric properties are calculated by deforming the structures along the z-axis with shreaing stress C_{44}. The piezoelectric coefficient '*P*' is calculated by $P = P_{ion} + P_{el}$, here P_{ion} is the polarization due to ionic displacement and P_{el} is the electronic polarization. The complete equation of total polarization is given as [17]

$$P = \frac{e}{\Omega}\sum_{s}^{atoms} Z_s^{ion} r_s - \frac{2ei}{(2\pi)^3}\int_{BZ} dk < u_{nk} \left| \tilde{N}_k \right| u_{nk} > \qquad (1)$$

where Ω is the simulation cell volume, 'e' is the elementary charge, Z_s^{ion} is the ionic charge represented by the number of valence electrons in the atom 's' and r_s is its position vector. The factor of 2 in the numerator of second term corresponds to the band occupancy. The integration of second term in Eq.(1) is performed over the Brillouin zone (BZ) and the integrand is closely related to the geometrical phase change [18]. The piezoelectric constant is calculated as $d = P/C_{44}$. The calculated values of piezoelectric parameters are presented in Table 1.

Table 1. *a* is lattice constant, E_g is band gap, *P* is piezoelectric coefficient, *d* is piezoelectric constant, C_{44} is shearing stress and ε_o is static dielectric constant. (*Ref. [11])

MNiSn	*a (A°)*	*E_g (eV)*	*P(C/m^2)*	*C_{44} (GPa)*	*d (pC/N)*	*ε_o*
TiNiSn	5.94*/6.06	0.44*	0.59/0.81*	67.78/62.0*	8.78/12.9*	27.94/30*
ZrNiSn	6.11*/6.23	0.52*	0.16/0.19*	77.21/70.0*	2.0/2.8*	24.57/26*
HfNiSn	6.08*/6.13	0.41*	0.19/0.28*	80.77/80.0*	2.4/3.4*	21.74/24*

4. **Conclusion.**

We have calculated the electronic structure and piezoelectric properties of MNiSn (M=Ti, Zr, Hf) within FP-LAPW method. Our calculated results of electronic band gaps are in good agreement with the experimental one. We have discussed the presence of 18 valence electrons and its importance in the formation of band gap with d-d orbital hybridization. The presence of band gap at the Fermi level predict our compounds MNiSn is a semiconductor. The compounds with semiconducting behaviour possess diverse functional properties, one of them is piezoelectricity. We have also calculated the piezoelectric parameters which are in good agreement with the previous data.

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