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# A first-principles investigation of the structural, electronic, elastic and thermal properties of NiZrSn under pressure

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**Abstract:** We used first-principles calculations based on the density functional theory (DFT) to investigate the structural, electronic, thermal and elastic properties of the half-Heusler alloy, NiZrSn. For this purpose, two electronic codes were used: full-potential local orbital minimum-basis (FPLO) code and WIEN2k softwarepackage. The calculated lattice constant and energy gap were in agreement with the available experimental and theoretical data. Using the FPLO code, the bulk modulus and its first pressure derivative of the NiZrSn compound were calculated to be 141.014 GPa and 4.2, respectively. Using the WIEN2k code, they were calculated to be 118 GPa and 5.1, respectively. The elastic parameters, including elastic constants ( $C_{11}$ ,  $C_{12}$  and  $C_{44}$ ), shear modulus (G), anisotropy factor (A), Young's modulus (Y) and Poisson's ratio, were calculated under higher pressures. The effect of pressure on the density of states, band structure, energy gap and elastic constants were then investigated. Using Cauchy pressure and Pugh's ratio, we demonstrated the brittle nature of NiZrSn under ambient conditions and pressure. There is currently no theoretical or experimental data that displays the effects of pressure on these properties for comparison. We found that the specific heat of NiZrSn is saturated at 98 J/mol K, which is above the Debye temperature.

Keywords: Bulk modulus, Half-Heusler, Pressure effects, Elastic constants, NiZrSn.

# **1** Introduction

There has been a great interest of researchers on the different properties of the Heusler alloys [1,2,3] for spintronics applications, e.g., magnetic, elastic, and structural properties. In this research, we predict the structural, electronic, thermal and elastic properties of the half-Heusler alloy NiZrSn. This compound crystallizes in the cubic structure C1b with the space group F43m of the half-Heusler alloys XYZ. Heusler and Half-Heusler alloys have been widely investigated [4,5] due to their spintronic and thermoelectric applications. Their characteristics, such as structure and electronic properties, are diverse and have attracted the interest of many groups in recent years [6,7,8]. This research paper uses two different electronic codes: full-potential local-orbital minimum-basis code (FPLO) [9,10] and full-potential linearized augmented plane waves plus the local-orbital (FP-LAPW + lo) method as implemented in the WIEN2k code [11,12].

First-principles calculations play an important role in providing a theoretical basis for discovering new experimental properties. Fiedler et al. [13] studied two compounds of this type: NiZrSn and CoZrBi. Using the Quantum Espresso package [14], this research explained why NiZrSn is often reported as an intrinsic n-type and why p-type conductivity is difficult to be occupied with group III elements with different concentrations. The calculated lattice constants and density of states ( DOS )of the NiZrSn compound supported our results. Özisik et al. [15] studied the Heusler alloy NiYSn (y = Zr and Hf) using ab initio calculations based on DFT. They calculated the lattice constant of NiZrSn to be 6.15 Å. The bulk modulus and its first pressure derivative were calculated to be 119.4 GPa and 4.35, respectively. Kawaharada et al. [16] prepared NiZrSn<sub>1-x</sub>Sb<sub>x</sub> with different concentrations (0 < x < 0.28). They calculated the thermoelectric properties of these compounds and found that all studied properties of these compound showed a strong dependence on the concentration of antimony (Sb). According to their calculations, the NiZrSn compound exhibited semiconductor-like behavior, while NiZrSn<sub>0.67</sub>Sb<sub>0.33</sub> exhibited behavior more characteristic of a metallic.

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A further study conducted by Andrea, Hug and Chaput was also based on first-principles calculations and focused on the phonon properties of NiZrSn [17]. Many studies on the optical properties of NiZrSn have been carried out [18,9]. The mechanical, optoelectric and thermoelectric properties of NiZrSn (Y=Zr and Hf) alloys were investigated by Hamioud and Mubarak [20]. Recently, Fang et al. [21] reviewed the different properties of the half-Heusler family, including NiZrSn. The transport properties of this interesting compound were also investigated by Katre et al. [22]. They reported that the vacancy anti-site in the Ni atom affected the thermal transport properties in NiZrSn. This research paper found different properties for the half-Heusler NiZrSn compound in its stable rock salt structure. These included the lattice constant, energy gap and bulk modulus. The density of states and band structure were calculated. In addition, the elastic parameters and different moduli of NiZrSn were calculated under different hydrostatic pressure using generalized gradient approximation (GGA). We used GGA to predict the pressure effect on the Debye temperature, hardness, melting temperature, Kleinman parameter, the longitudinal elastic and transverse elastic wave velocities.

This research paper studies the effects of pressure on different characteristics, including the density of states, the energy gap and elastic properties. In addition, the pressure effect on Debye temperature and melting temperature is predicted for first time in this research.

## 2 Theory and computation

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Our calculations are a first-principles study of the elastic, electronic and structural properties of the NiZrSn compound within a framework of density functional theory (DFT) [23,24]. The theoretical values of the equilibrium lattice constant, magnetic moment, bulk modulus and its pressure derivative were calculated using two electronic structure codes: FPLO [9, 10] and WIEN2k [11, 12] using GGA [25,26]. This compound crystallizes in the cubic C1b crystal structure. The Wyckoff positions in this structure were (0, 0, 0), (0.25, 0.25, 0.25) and (0.75, 0.75, 0.75) for atoms Ni, Zr and Sn, respectively (fig. 1). The space group of this structure was  $F_{m3m}$  (216) and the number of plane waves were restricted by  $K_{max}RMT = 8.0$  a.u. However, the spherical harmonics waves were extended in the muffin-tin spheres, RMT, up to  $I_{max} = 6$  and the energy separation between the valence states and the core states was -6.0 Ry. The charge density was computed using Fourier expansion up to  $G_{max} = 12(Ry)^{1/2}$ . The calculations are assumed to converge when the charge and energy are less than  $0.1 \times 10^3$  e and  $0.1 \times 10^{-3}$  Ry/atom, respectively. For the k-space integration under pressure range, 0-100GPa in the irreducible Brillouin Zone (IBZ) and 35 k-points in a grid of  $12 \times 12 \times 12$  meshes (which is equivalent to 1728 k-points in the entire Brillouin zone), were used to obtain self-consistency. For GGA, the Vxc-version of Perdew Burke Ernzerhof 96 was used.

#### **3** Results and discussion

#### 3.1 Structural Properties

The NiZrSn Half-Heusler alloy crystallize in the cubic structure CIb with four sublattices, as shown in fig. 1. The variation of total energy as a function of unit cell volume was calculated for the optimized structure using the GGA, as shown in fig. 2. The minimum energy of this compound was calculated at –22575.226957 and –22598.481877 Ry using FPLO and WIEN2k, respectively, which indicates good agreement between the two codes. The lattice constants of this compound were 6.05 Å and 6.15 Å using the FPLO and WIEN2k, respectively. There was a good agreement between the lattice constants obtained using the theoretical method put forward by Fiedler et al. [13] and the experimental results obtained by Villars et al. [27], as presented in table 1.

The ground state of the lattice constant  $a_0$  and bulk modulus B at 0 k and 0 GPa were computed by fitting the total energy of the unit as a function of volume using the Murnaghan equation of state (EOS), which is given in eq. (1) [28,29]:

$$E(V) = E_0 + \frac{9BV_0}{16} \left[ B' \left\{ \left( \frac{V_0}{V} \right)^{\frac{3}{2}} - 1 \right\}^3 + \left\{ \left( \frac{V_0}{V} \right)^{\frac{3}{2}} - 1 \right\}^2 \left\{ 6 - 4 \left( \frac{V_0}{V} \right)^{\frac{3}{2}} \right\} \right]$$
(1)

The computed lattice constant  $a_0$ , bulk modulus B, its pressure derivative B', and the equilibrium energy  $E_0$  for NiZrSn Heusler alloys at T = 0 K and 0 GPa are shown in table 1.

Using the WIEN2k code, the calculated lattice constant and bulk modulus value using EOS were 5.1 and 118.3 GPa, respectively, which are similar to those calculated in previous theoretical studies [13, 15]





Fig. 1: Crystal structure of NiZrSn compound.



Fig. 2: The minimization energy curve of NiZrSn compound using WIEN2k code.

The variation of lattice constants under volume compression due to induced pressure (P) in the range 0-100 GPa can be computed using Murnaghan's equation of state:

$$P(V) = \frac{B}{B'} \left[ \left( \frac{V_0}{V} \right)^{-B'} - 1 \right]$$
(2)



Fig. 3: The DOS of NiZrSn using GGA approximation at ambient pressure.

**Table 1:** The lattice constant, energy gap, bulk modulus and its first pressure derivative for NiZrSn compound using FPLO and Wien2k electronic codes using GGA approximation.

	a(Å)	E <sub>0</sub> (Ry)	$E_g$ (eV)	B(GPa)	<b>B</b> ′
FPLO	6.05	-22575.226957	0.632	141.014	4.2
WIEN2k	6.153525	-22598.479205	0.514	118.0191	5.1003
Ref.	6.15 (PBE)[13]	-	0.46 (PBE)[13]	9.4[15]	4.35[15]
	6.10 (HSE06)[13]		0.60(HSE06)[13]	119[13]	
	6.11 (exp.)[32]			129[34]	
	6.151 [ <b>15</b> ]				
	5.99 [17]				

where P is pressure and V is the deformed volume B, B', and  $V_0$  are optimized ground state bulk modulus, the derivative of the bulk modulus with respect to pressure and the volume of the unit cell in the ground state, respectively. The obtained lattice constant values, along with the various external pressure, are listed in table 2. The lattice constants were found to be inversely proportional to the external pressure due to the compression of the unit cell volume. The present alloy was expected to be brittle when the external pressure was increased due to the decrease in volume. The stability of the alloy was investigated by computing the formation energies using the formula:

$$E_{form} = E_{tot} - (E_{Ni} - E_{Zr} - E_{Sn}) \tag{3}$$

where  $E_{tot}$  is the total energy of the half-Heusler alloy NiZrSn per formula unit.  $E_{Ni}$ ,  $E_{Zr}$  and  $E_{Sn}$  are the total energies per atom for each element in the alloy in its bulk form. Table 2 shows that the formation energies of all alloys at ambient pressure and in the presence of pressure are negative. This confirms that this alloy is thermodynamically stable.

# 3.2 Electronic properties

We used ab initio calculations to predict the electronic properties of a NiZrSn compound using FPLO and WIEN2k with GGA. Using FPLO and WIEN2k, the energy gaps were calculated at 0.632 and 0.514 eV, respectively. When using FPLO, the energy gap was higher by nearly 0.1 eV than when using WIEN2k. We used GGA to calculate the total density of states for NiZrSn, as shown in fig. 3. The DOS demonstrated the presence of an energy gap in both spin directions. This was nearly 0.63 eV when using the FPLO code and located very close to the Fermi level. The symmetry presented in both density of state channels (up and down) confirmed the non-magnetic behaviour of this half-Heusler compound. The

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Fig. 4: The DOS of NiZrSn under hydrostatic pressures (0, 20, 40,60,80 and 100 GPa) using the GGA approximation.

effect of pressure on the density of states at different values from 0 to 100 GPa is shown in fig. 4. The effect of pressure on the density of states was very weak for this compound. The band structures at different pressure values are displayed in fig. 5. At ambient pressure, it is clear that the energy gap is touching  $E_f$  at one-point  $\Gamma$ . The 3d states of the Ni atom hybridized efficiently with the 4d states of the Zr atom and both states contributed equally to the conduction band. As a result of this strong hybridization, the conduction band was dispersive, to a small energy gap. By increasing the pressure, the hybridization between the 3d states of the Ni atom and the 4d states of the Zr atom increased. In turn, this caused an increase in the energy gap value. The effect of high pressure on the energy gap value for the NiZrSn compound is shown in fig. 9. By increasing the pressure, the energy gap dependence on the lattice constant is shown in fig. 10. By increasing the lattice constant in the NiZrSn compound, the value width of the energy gap decreased. However, it retained semiconductor behaviors.

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Fig. 5: The band structures of NiZrSn compound under hydrostatic pressures (0, 20, 40,60,80and 100 GPa) using the GGA approximation.

# 3.3 Mechanical properties

Elastic constants can allow a better understanding of the stability and stiffness of various materials. NiZrSn crystallized in the cubic crystal (C1b) structure, which has three crystal elastic parameters:  $C_{11}$ ,  $C_{12}$  and  $C_{44}$ . The elastic constants,  $C_{11}$ ,  $C_{12}$  and  $C_{44}$ , were calculated using the elastic 1.1 code with the exchange-correlation potential of GGA-PBE at 0

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Fig. 6: The calculated elastic constants of NiZrSn under pressure.



**Fig. 8:** Pressure vs  $V/V_o$  of NiZrSn compound.

Fig. 9: The pressure effect on the energy gap.

**Table 2:** The elastic parameters and different moduli of NiZrSn compound using the GGA approximation under pressure up to 100GPa.

P(GPa)	0 GPa	20 GPa	40 GPa	60 GPa	80 GPa	100 GPa
$a(A^0)$	6.153525	5.91566	5.779476	5.684389	5.61156	5.552669
E <sub>form</sub> (eV)	-3.2	-2.95	-2.32	-2.56	-1.01	-0.434
C <sub>11</sub> (GPa)	212.4	356.3	520.6	537.4	610.8	775.5
C <sub>12</sub> (GPa)	87.1	115.5	116.5	198.2	226.1	167.1
C <sub>44</sub> (GPa)	120.3	175.2	199.4	249.8	284.3	295.5
B(GPa)	128.867	195.767	251.2	311.267	354.333	369.9
G(GPa)	92.5868	150.748	200.456	213.893	243.092	298.95
Y(GPa)	224.093	359.872	475.015	522.091	593.542	706.516
B/G	1 20195	1 20864	1 25214	1 45525	1 45761	1 22722
Pough's Ratio	1.39183	1.29604	1.23314	1.45525	1.43701	1.23/33
G/B	0.71947	0.770030	0.707002	0.687160	0.686055	0.808101
Frantesvich Ratio	Frantesvich Ratio 0.71847		0.797993	0.08/109	0.080033	0.000191
Poisson's ratio	0.210175	0.193622	0.184836	0.220448	0.220817	0.181663
Anisotropy Factor	1.92019	1.45515	0.986884	1.47288	1.47803	0.9714



Fig. 7: The calculated Bulk modulus values versus pressure.



Fig. 10: The lattice constant vs energy gap.



Fig. 11: The longitudinal elastic wave velocity  $(v_l)$ , the transverse elastic wave velocity  $(v_l)$ , and the average wave velocity  $(V_m)$  for NiZrSn compound under pressure up to 100GPa.

k and various pressures up to 100 GPa. These elastic constants indicate the mechanical stability, hardness and stiffness of materials and are used to determine the mechanical properties for NiZrSn alloys. We calculated the elastic parameters of this compound, including the bulk modulus (B), shear modulus (G), anisotropy factor (A), Young's modulus (Y) and Poisson's ratio (v) using Voigt-Reuss-Hill approximations [30,31,32].

$$B = \frac{(C_{11} + 2C_{12})}{3} \tag{4}$$

$$G_V = \frac{(C_{11} - C_{12} + 3C_{44})}{5} \tag{5}$$

$$G_R = \frac{5C_{44}(C_{11} - C_{12})}{4C_{44} + 3(C_{11} - C_{12})} \tag{6}$$

$$G = \frac{G_V + G_R}{2} \tag{7}$$

$$E = \frac{9BG}{3B+G} \tag{8}$$

$$v = \frac{3B - 2G}{2(3B + g)}\tag{9}$$

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$$A = \frac{2C_{44}}{C_{11} - C_{12}} \tag{10}$$

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The calculated elastic parameters ( $C_{11}$ ,  $C_{12}$ ,  $C_{44}$ ) included the bulk modulus (B) and shear modulus (G), Young's modulus (Y), anisotropy factor (A) and Poisson's ratio (v) at 0 k and at various pressures are displayed in table 2. To study the mechanical stability of NiZrSn, we used Born's stability conditions [33] for cubic systems:

$$C_{11} > 0, (C_{11} - C_{12}) > 0, C_{44} > 0, (C_{11} + 2C_{12}) > 0 \text{ and } C_{12} < B$$
 (11)

By applying these conditions to the half-Heusler NiZrSn compound at zero pressure, we concluded that this compound is mechanically stable. We also used modified stability criteria to check the stability of the compound under pressure [34]:

$$\frac{C_{11} + 2C_{12}}{3} + \frac{P}{3} > 0, C_{44} - P > 0, \frac{C_{11} + C_{12}}{2} - P > 0$$
(12)

We found that NiZrSn maintained a stable cubic phase under compression up to 100 GPa. Figure 6 shows the pressure dependence of elastic constants  $C_{ij}$ . It is noted that  $C_{11}$ ,  $C_{12}$  and  $C_{44}$  increase with applied pressure. The pressure effect on the bulk modulus of NiZrSn is shown in fig. 7. When increasing the pressure, the bulk modulus increased from nearly 128.9 GPa at zero pressure to nearly 370 GPa at a pressure of 100 GPa. It should be noted that the value of bulk modulus calculated from the elastic constants had nearly the same value as that obtained from fitting the total energy versus volume according to Murnaghan's equation of state. Using different electronic codes, the calculated bulk modulus showed a good agreement with the available theoretical and experimental results [15,33]. The bulk modulus of this compound in its stable rock salt structure demonstrates that the compound is a hard material. By increasing the pressure, the ratio V/V<sub>0</sub> decreased from 1 at 0 GPa to 0.73 at 100 GPa (fig. 8).

The bulk modulus (B) measures the resistance to volume change in solids and, therefore, gives an estimate of the elastic response of material to hydrostatic pressure. Alternatively, Young's modulus (Y) and shear modulus (G) can be used to measure the stiffness and resistance to the plastic deformation of materials respectively.

Three parameters were used to decide the ductility of the alloy. The results indicate that the alloy is ductile (brittle) as Pugh's index (B/G) was greater (lower) than the critical value of 1.75. A positive (negative) result for Cauch's pressure  $(C_{12}-C_{44})$  indicates that the alloy has a ductile or brittle nature. According to the Frantsevich rule, the alloy is ductile (brittle) if Poisson's ratio (v) is greater (smaller) than the critical value of 0.26 [20]. The results displayed in table 2 show that NiZrSn exhibits a brittle nature under applied pressure (0-100 GPa).

Cauch's pressure,  $(C_{12}-C_{44})$ , was also used to analyze the origin of the angular attributes of atomic bonding present in the unit cell. If the value is negative, then the alloy's bonds exhibit covalent bonding. However, if the resultant value is positive, this indicates that ionic bonding has been retained in most bonds. In this study, NiZrSn mostly exhibited covalent bonds that were retained under pressure.

The anisotropy factor (A) was calculated from the elastic constants. This factor is used to deduce the degree of anisotropy. For isotropic materials, A = 1, while for anisotropic materials, A  $\neq$  1. In this study, we assumed that NiZrSn was an anisotropic alloy since A  $\neq$  1 under applied pressure (0–100 GPa).

Additionally, we evaluated the hardness of NiZrSn using the Vickers hardness test,  $H_V = 0.92(G/B)^{(1.137)} G^{(0.708)}$ . This was primarily to check NiZrSn's resistance to be dented. We found that increasing the pressure on NiZrSn increased its resistance to being dented.

#### 3.4 Thermal properties and Debye temperature

In solids, the Debye temperature can be used to characterize the strength of covalent bonds. This temperature also relates to many properties of solids including the melting point and specific heat capacity. The effect of pressure on the Debye temperature indicates the stability of the lattice structure under high pressure. The Debye temperature can be estimated from the average sound velocity  $v_m$ :

$$\theta_D = \frac{h}{k_B} \left(\frac{3n}{4\pi v_a}\right)^{-\frac{1}{3}} v_m \tag{13}$$

where *h* Plank's constant,  $k_B$  is Boltzmann's constant and  $V_a$  is the atomic volume. The average sound velocity in polycrystalline materials is given using:

$$\mathbf{v}_m = \left[\frac{1}{3}\left(\frac{2}{v_l^3} + \frac{1}{v_l^3}\right)\right]^{-\frac{1}{3}} \tag{14}$$



P(GPa)	0 GPa	20 GPa	40 GPa	60 GPa	80 GPa	100 GPa
$H_V(GPa)$	510.697	954.147	1367.19	1084.95	1229.38	2095.45
T <sub>m</sub> ±300 (K)	1808.28	2658.73	3629.75	3729.03	4162.83	5136.21
ξ	0.547381	0.469818	0.374652	0.510557	0.511781	0.366547
$v_l [100] (\text{Kms}^{-1})$	5.26702	6.43004	7.50561	7.43834	7.77815	8.6267
$v_l$ [110] (Kms <sup>-1</sup> )	3.96388	4.508.93	4.64512	5.07135	5.30659	5.32516
$v_l[111] ({\rm Km s^{-1}})$	5.93895	6.90685	7.48648	7.97408	8.34309	8.57818
$v_t [100] (\text{Km}^{s-1})$	4.04542	5.28609	6.61269	5.90956	6.17288	7.64097
$v_t [110] (\text{Kms}^{-1})$	6.1463	7.05863	7.4801	8.14483	8.52309	8.56194
$v_t[111] ({\rm Km s}^{-1})$	3.26995	4.01136	4.66565	4.49598	4.6998	5.37717
$\wedge_{min}(WK^{-1}m^{-1})$	0.470115	0.607036	0.705446	0.747331	0.802018	0.877716
$\wedge_{min} [100] (WK^{-1}m^{-1})$	0.488601	0.618962	0.705059	0.762917	0.818929	0.876672
$\wedge_{min} [110] (WK^{-1}m^{-1})$	0.519521	0.700344	0.869447	0.858913	0.921234	1.0851
$\wedge_{min} [111] (WK^{-1}m^{-1})$	0.469781	0.604275	0.705712	0.74364	0.798062	0.878457

where  $v_l$  and  $v_l$  are the longitudinal and transverse sound velocities, respectively. They were obtained using the shear modulus G and the bulk modulus B using Navier's equation [35]:

$$v_l = \left(\frac{3B+G}{3\rho}\right)^{\frac{1}{2}} \tag{15}$$

$$v_t = \left(\frac{G}{\rho}\right)^{\frac{1}{2}} \tag{16}$$

From fig. 10, it is clear that the sound velocities  $v_m$ ,  $v_l$ ,  $v_t$  increase when pressure is increased up to 100 GPa, and the longitudinal mode of oscillation has a large value compared to the transverse mode. In addition, by increasing pressure, the Debye temperature  $\theta(D)$  increases as shown in fig. 11. Pressure has a significant effect on the properties of NiZrSn. As pressure increases, the convergence between levels of different atoms increases as well as ionization.

We also obtained longitudinal and transverse modes of sound velocity along different crystallographic directions. For longitudinal and transverse modes of oscillation along [100], [110] and [111], we used the following equations:

$$V_L([100]) = \sqrt{\frac{C_{11}}{\rho}}, V_L([110]) = \sqrt{\frac{C_{11} + C_{12} + 2C_{44}}{2\rho}} \text{and} V_L([111]) = \sqrt{\frac{C_{11} + 2C_{12} + 4C_{44}}{3\rho}}$$
$$V_T([100]) = \sqrt{\frac{C_{44}}{\rho}}, V_T([110]) = \sqrt{\frac{C_{11} - C_{12}}{\rho}} \text{and} V_T([111]) = \sqrt{\frac{C_{11} - 2C_{12} + 4C_{44}}{3\rho}}$$

We found that the maximum sound velocity in longitudinal mode of oscillation occurred along [111] direction whereas the maximum sound velocity in transverse mode of oscillation occurred along [110]. Using the Cahill criteria [37], the minimum thermal conductivity  $\wedge_{min}$  of NiZrSn was calculated using  $\wedge_{min} = ((k))/2.48([n_b]^{(2/3)}(v_L + v_T))$ , where  $n_b$ , k,  $v_L$  and  $v_T$  are the numbers of atoms per unit volume, the Boltzmann constant and the longitudinal and transverse sound velocities, respectively. We found that the active direction of thermal conductivity for NiZrSn occurred along [110] under pressure of up to 100 GPa. The estimated melting temperature,  $T_m$  of NiZrSn, under pressure can be calculated using  $T_m$ = 553 + (5.91 ×  $C_{11}$ )/GPa. All values are listed in table 3.

For  $\theta < T < T_m$ , a high-frequency mode of phonon oscillation may occur. For  $T < \theta$ , we expected phonon oscillations to be frozen. The increase in Debye and melting temperatures alongside increases in pressure showed high modes of oscillation in NiZrSn.

The Kleinman parameter  $\xi$  that is, the ease of minimizing bond bending and bond stretching, is directly related to piezoelectric effects. This parameter can be calculated using  $\xi = \frac{(C_{11}+8C_{12})}{(7C_{11}+2C_{12})}$ . For  $\xi \to 0$ , in bond bending minimization, the piezoelectric effect decreases where for  $\xi \to 1$ , in a bond-stretching situation, the piezoelectric effect increases. In this study,  $\xi$  decreased when the pressure increased. This indicates that the piezoelectric effect may decrease when pressure increases.



Fig. 12: The influence of pressure on Debye temperature for NiZrSn compound.



Fig. 13: (a) Thermal heat capacity for NiZrSn at Debye temperature (b) Thermal entropy for NiZrSn at Debye temperature.

The quasi-harmonic Debye model [31] was used to predict the thermal heat capacity (CV) and thermal entropy (S) as shown here [36]:

$$C_V = 3nk \left[ 4D(\frac{\theta}{T}) - \frac{\frac{3\theta}{T}}{e^{(\frac{\theta}{T})} - 1} \right]$$
(17)

$$S = nk \left[ 4D(\frac{\theta}{T}) - 3ln(1 - e^{(\frac{-\theta}{T})}) \right]$$
(18)

Where *n* is the number of atoms per formula unit,  $D(\frac{\theta}{T})$  represents the Debye integral,  $\theta$  is the Debye temperature and k is Boltzmann constant. We calculated the lattice specific heat and entropy for NiZrSn at a Debye temperature of 382 K. We found that the specific heat was saturated at 98 J/mol K, which is above the Debye temperature. Entropy reached approximately 230 J/mol K at a temperature of 1000 *K* as shown in fig. 13. Özisik et al. [15] found that the specific heat capacity of NiZrSn reached saturation at nearly 75 J/mol.K and that entropy reached 190 J/mol.K at a temperature of 1000 K.

# **4** Conclusion

We studied the half-Heusler NiZrSn using two electronic codes: FPLO and WIEN2k. This compound crystallize in the C1b cubic structure. The lattice constant, energy gap and bulk modulus were calculated using a GGA approximation. The energy gap values calculated using FPLO and WIEN2k were 0.632eV and 0.514 eV, respectively. The total density of states and partial DOS of the NiZrSn compound were calculated. They demonstrated the semiconductor behavior of





NizrSn. This research investigated the influence of pressure on the energy gap and bulk modulus of this compound. By increasing pressure nearly 60 GPa, the energy gap increased from 0.514 eV to 0.668 eV. The specific heat of NiZrSn saturated at 98 J/mol K, which is above the Debye temperature. The entropy reached approximately 230 J/mol K at a temperature of 1000 K. To the best of our knowledge, there is no current experimental or theoretical data on the effect of pressure on the density of states, bulk modulus and energy gap of the NiZrSn compound for comparison.

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