Full potential study of electronic and thermoelectric properties of GdNiSb compound

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Abstract. In the present work we have investigated electronic and thermoelectric properties of GdNiSb compound. The calculations have been performed using local spin density approximation (LSDA) with Hubbard parameter (U) included for exchange correlation effect. The calculated results of a cubic half-Heusler phase of GdNiSb compound shows semiconducting behaviour due to a narrow band gap (0.279 eV) is opened. Thermoelectric properties such as electrical conductivity ($\sigma/\tau$), Seebeck coefficient (S) and figure of merit (ZT) was calculated. Values of thermoelectric parameters show that GdNiSb compound could be used as potential material for thermoelectric applications.

1. Introduction

The Heusler alloys are new and unique class of intermetallic compounds. These compounds attracted attention due to having many different physical properties, such as magnetism, half-metallicity, spintronic and thermoelectric properties. They also have wide range of applications in electronic devices, such as magnetic sensor, random access memory (RAM), thermoelectric module and spintronic [1]. Recently in last decade ternary rare-earth based Heusler compound have been attracted interest [2-7], due to presence of strongly ordered and localized 4f unpaired electron in RE-element. In this context GdNiSb is ternary REME-type (where RE is rare-earth element, M is d-block transition metal, E is p-block element) half-Heusler compound is considered for investigation. The presence of f-electron in Gd-element, d-electron in Ni-element and p-electron in Sb-element of the compound are the decisive electronic states for the different physical properties [8, 9]. In this paper electronic and thermoelectric properties of GdNiSb were calculated using LSDA with exchange correlation effect implemented in full potential local orbital method in Wien2k package [10, 11]. The structure of GdNiSb is face centered cubic (fcc) MgAgAs-type having space group F43m (216). The Wyckoff positions in unit cell of Gd, Ni and Sb atoms are 4 (a) (0, 0, 0), 4(b) ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$) and 4 (d) ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$), respectively. We have used the experimental lattice parameter $a_{\text{exp.}} = 6.338$ Å [12] to performed full potential study of electronic and thermoelectric properties of GdNiSb compound.

2. Computational method

In order to study the electronic and thermoelectric properties of GdNiSb compound, we performed first principle calculations using density functional theory (DFT). Coulomb corrected local spin density approximation (LSDA+U) [13, 14] has been used for exchange correlation potential as implemented in wien2k. Self consistent calculations were performed within 18\times 18 \times 18 k-mesh point. The cutoff energy was taken as -7.0 Ry with charge and energy converged at 0.0001 e and 0.0001 Ry respectively.
Due to presence of localized $f$-electron in Gd element we used the method of effective Hubbard parameter $U_{\text{eff}}=U-J$ (where $U$ is Hubbard potential and $J$ is exchange) for more accurate calculations [15]. The value of $U_{\text{eff}}$ vary with different atoms due to correlation effect induced by the coulomb interaction of localized $f$-electron [16] and we used the value $U_{\text{eff}} = 6.0\text{eV}$ (where $U= 6.7\text{eV}$ and $J=0.7\text{eV}$) for Gd atom. These values have been calculated by Harman et al. [17] using by the super cell approach.

3. Results and Discussions

3.1 Electronic properties

In order to study electronic properties of GdNiSb compound the total and partially density of states (DOS) were calculated and shown in Fig. 1.

![Figure 1. Total and partial DOS for both spin-up and spin-down states of GdNiSb by using LSDA+U approximation.](image)

One can notice that almost zero DOS near Fermi level ($E_F$) is appeared in both spin (up and down) channel and small narrow energy gap (0.279 eV) is opened which reflect the semiconductor nature of GdNiSb compound. We found that Gd-$d,f$ and Ni-$d$ states mainly contribute in total DOS. While, the contribution of Sb-$p$ states are negligible. In the energy range -7eV to 7eV Ni-$d$ and Gd -$f$ states are mainly dominated in total DOS. In the partial DOS distribution we see spin up Gd-$f$ states lie around -7 eV and can be identified as the large peak in the graph. Spin down Gd-$f$ states lie around 4 eV above $E_F$ and contribute in the conduction band. Both spin up and down Ni-$d$ states lie around 2 eV below $E_F$ and contribute to the valence band. Thus Ni-$d$ states and Gd-$f$ states mainly contribute to electronic transitions from valence band to conduction band. The Gd-$5d$ states hybridize with Ni-$3d$ states at
~ 4 eV above the $E_F$ and contribute to the CB. Contribution of Gd - 5d states to the total DOS is small (<2 state/eV/primitive cell) this is mainly because they are quite empty in nature and are partly involved in metallic bonding.

3.2 Thermoelectric properties
Our DOS calculations show the semiconducting nature of GdNiSb compound. We have computed the thermoelectric parameters such as electrical conductivity ($\sigma$), Seebeck coefficient (S) and figure of merit (ZT) (performance indicator of material) of GdNiSb compound by using the Boltzmann transport equation (BTE) within a simple rigid-body approximation and relaxation time approximation (RTA).

3.2.1 Electrical conductivity ($\sigma/\tau$)
The electrical conductivity ($\sigma/\tau$) is an important component of transport properties. The value of $\sigma/\tau$ must be high for desired thermoelectric materials. The electrical conductivity ($\sigma/\tau$) of GdNiSb compound has been investigated with respect to temperature for both spin configurations and is shown in the Figure 2.

![Figure 2](image)

Figure 2. Variation of electrical conductivity ($\sigma/\tau$) verses temperature (T) for spin-up and spin-down.

The value of $\sigma/\tau$ for spin-down channel increases with temperature which shows it semiconductor behaviour. While, in the case of spin-up channel a small variation is observed with temperature. The observed value of electrical conductivity at room temperature is $14.6 \times 10^{19} (\Omega \text{ m s})^{-1}$ which decreases slightly and reaches to $13.8 \times 10^{19} (\Omega \text{ m s})^{-1}$ at 800 K in the spin-up configuration. On the other hand, for spin down configuration, its value increases from $5.88 \times 10^{19} (\Omega \text{ m s})^{-1}$ at room temperature to $6.68 \times 10^{19} (\Omega \text{ m s})^{-1}$ at 800 K.
The electrical conductivity of spin-up configuration is high, i.e. almost double as compared to spin-down configuration for all temperature range.

### 3.2.2 Seebeck coefficient (S)

The Seebeck coefficient (S) is an important parameter of thermoelectric materials which is expressed by equation

\[ S = \frac{B n \beta_k}{3e h^* m^* T^{1/3}} \]

where \( \beta_k \), e, \( m^* \), \( n \) and \( T \) are Boltzmann constant, electric charge, effective mass, carrier concentration and absolute temperature respectively. From the equation, it is known that S depends directly on effective mass and absolute temperature and inversely proportional to carrier concentration. Figure 3 shows the calculated values of Seebeck coefficient with different values of temperature for both spin-up/down configurations.

![Figure 3](image.png)

**Figure 3.** Seebeck coefficient (S) variation with respect to temperature (T) for both spins configurations.

The graph shows that the values of S increase non-linearly with temperature and it attain a maximum value of 110 (\( \mu V/K \)) for spin-down channel and 65 (\( \mu V/K \)) for spin-up channel at 800 K temperature. The value of S remains positive for both the channels for whole temperature range, which indicates that holes are the majority charge carriers in both spin configurations.

Total Seebeck coefficient is calculated by two current modal and expressed by

\[ S = \frac{\sigma' (1) S(1) + \sigma (1) S(1)}{\sigma (1) + \sigma (1)} \]

where \( \sigma' = \frac{\sigma}{r} \). Figure 4 shows the variation of total Seebeck coefficient with temperature. It shows positive values in entire temperature ranges indicate the leading role of p-type charge carriers. The total value of S increases with temperature and reaches highest 80 (\( \mu V/K \)) at 800 K. The calculated value of total S at 380 K is 60 (\( \mu V/K \)). It is in good agreement with experimentally reported value 58 (\( \mu V/K \)) [12] at same temperature.
3.2.3 Figure of merit (ZT)

The Figure of merit is an important factor and performance indicator of any thermoelectric materials. The value of high ZT means materials that are more efficient for thermo electric phenomenon. The dimensionless ZT value calculated and by the equation \( ZT = \frac{S^2\sigma T}{K} \) where \( S \), \( \sigma \), \( K \) and \( T \) are Seebeck coefficient, electrical conductivity, thermal conductivity and absolute temperature respectively. Figure 5 shows the variation of \( ZT \) with temperature of GdNiSb compound in both spin-up and spin-down configurations. The value of \( ZT \) remains high in spin down configuration in whole temperature range as compared to the spin up configuration. It reaches maximum of \(~0.475\) in spin-down channel at 800 K on the other hand in spin-up configuration its value is \(~0.225\) at same temperature.
4. Conclusions
In this work we have investigated the electronic and thermoelectric properties of rare-earth based GdNiSb compound using LSDA+U approximation. The calculated values of total and partially density of states (DOS) show the semiconductor behaviour of GdNiSb compound with narrow band gap (0.279 eV). The valence band which spans from -5 eV to the E_F is dominated by spin up/down Ni-3d. On the other hand, conduction band is mainly dominated by spin down Gd-4f bands and lie about 3.5 eV above the E_F. Also Thermoelectric parameters such as electrical conductivity, Seebeck coefficient and figure of merit were investigated. Values of all the calculated thermoelectric parameters indicate that GdNiSb compound could be a good and efficient candidate of thermoelectric material.

References
[1] Felser C, Fecher G H and Balke B 2007 Angew. Chem. Int. Ed. 46 668
[2] Daniel P, Javorský P, Prchal J, Šantavá E and Daniš S 2008 Acta Phys. Pol. A 113 331
[3] Gondek L, Szytula A and Prokhnenko O 2008 Acta Phys. Pol. A 113 1179
[4] Hermanowicz M, Jezierski A, Kaczkowski J and Kaczorowski D 2009 Acta Phys. Pol. A 115 226
[5] Casper F, Felser C, Seshadri R, Sebastian C and Peter Pöttgen R 2008 J. Phys. D, Appl. Phys. 41 035002
[6] Casper F, Kandpal H C, Fecher G H and Felser C 2007 J. Phys. D, Appl. Phys. 40 3024
[7] Jirsa M, Rameš M and Muralidhar M 2008 Acta Phys. Pol. A 113 223
[8] Liu X B and Altoian Z 2010 J. Appl. Phys. 107 173104
[9] Goremychkin E A, Natkaniec I, Muhle E and Chistyakov O D 1989 J. Mag. Magnet. Mat. 81 63
[10] Hohenberg P and Khon W 1964 Phys. Rev. B 136 864
[11] Blaha P, Schwarz K, Madsen G H K, Kuasnicka D and Luitz J 2001 WIEN2KAn augmented plane wave+ local orbital program for calculating crystal properties, Technical Universitat, Wien, Austria.
[12] Skolozdra R V, Guzik A, Goryne A M and Pierrec J 1996 Acta Physica Polonica A 92 343.

Figure 5. Figure of merit (ZT) verses temperature (T) for both spin configurations.
[13] Schwarz K and Blaha P 2003 Comput. Mater. Sci. 28 259.
[14] Schwarz K 2003 J. Solid State Chem. 176 319.
[15] Anisimov V I, Soovyev I V, Korotin M A, Czyzyk M T and Sawatzky G A 1993 Phys. Rev. B 48 16929.
[16] Hubbard J 1963 Proc. R. Soc. (London) A 276 238.
[17] Harman B N, Antropov V P, Liechtenstein A I and Anisimov V I 1995 J. Phys. Chem. Sol. 56 1521