Phonon transport properties of NbCoSb compound

To cite this article: Havva Bogaz Ozisik et al 2020 Mater. Res. Express 7 025004

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Keywords: half-heusler, anharmonicity, phonon life time, Grüneisen parameter, lattice thermal conductivity

Abstract
We present a first-principles study of the phonon transport properties of the Half-Heusler NbCoSb compound. The single crystal elastic constants have been calculated using the stress-strain method. The mechanical properties such as bulk modulus, shear modulus, Young’s modulus, Poisson’s ratio, and anisotropy factor are estimated using the Voigt–Reuss–Hill approximation. The Grüneisen parameters, phonon life time, and lattice thermal conductivity have been studied in detail. The elastic and phonon properties reveal that this compound is mechanically and dynamically stable. An analysis of the harmonic and anharmonic phonon dispersion and vibrational density of states reveal that, NbCoSb has a very low lattice thermal conductivity, hence, it is a candidate thermoelectric material.

1. Introduction

The interest in renewable energy research is increasing with the increase of world population. Due to limited fossil fuels and environmental problems, thermoelectric events are expected to play an important role in energy production [1, 2]. For instance, they are important for power generation devices that are now designed to convert heat, solar energy, geothermal energy, and other thermal energies directly into electrical energy [3]. Beside these, solid-state cooling based on thermoelectric effects is also important [4]. The efficiency of thermoelectric materials depends on the dimensionless figure of merit (ZT = (S^2σ/k)T); where S is the Seebeck coefficient, σ is the electrical conductivity, k is the thermal conductivity, and T is temperature [5]. For the efficiency of thermoelectric devices, the material must have low thermal conductivity with high electrical conductivity and Seebeck coefficient [5].

The production, cost and thermodynamic stability of thermoelectric materials at high temperatures can be a challenge for these applications [6]. Half Heusler materials show good performance for the thermoelectric applications at medium and high temperatures range [5]. Another noteworthy point is that, Half Heusler materials are located in a crystal structure similar to the zinc blend structure adopted by many semiconductors [7].

To the best of our knowledge, there is no detailed study of the NbCoSb compound. The new thermoelectric NbCoSb is recently synthesized using arc melting followed by ball milling and hot pressing by Huang et al [8, 9]. Also, they have studied the effect of hot pressing temperature on the thermoelectric properties [8]. In order to use this and similar compounds in a healthy way in the technology, physical properties should be examined in detail. In this study, structural, mechanical and vibrational properties of NbCoSb compound are calculated and interpreted in detail using ab initio method. In particular, the detailed understanding of phonons for thermoelectric applications need. Therefore, the anharmonic phonon calculations are made, and the Grüneisen parameter, phonon life-time and lattice thermal conductivity are also examined.

2. Methods and details

The physical properties of NbCoSb are performed with ab initio calculations using the VASP package [10–13]. The projector augmented wave (PAW) method [12, 14] for electron-ion interaction and the generalized gradient approximation of Perdew–Burke–Ernzerhof (GGA-PBE) [15] for exchange-correlation are preferred.
The gamma centered grid of k-points [16] and energy cut off value is taken 13x13x13 and 400eV, respectively. The total energy and all force components for the full geometric optimization are converged to $10^{-9}$ eV and $10^{-7}$ eV/Å, respectively.

We are calculated harmonic and anharmonic phonon dispersion curve with LO-TO splitting along high symmetry points in IBZ and the corresponding phonon DOS using PHONOPY and PHONO3PY code, respectively [17, 18]. The second- and third-order interatomic force constants (IFC) are obtained with the finite difference methods (supercell approach) using $3 \times 3 \times 3$ supercell (81 atoms) and $6 \times 6 \times 6$ k-grid detailed in Ref. [18]. The displacement amplitude is taken as 0.01 Å and 0.03 Å for harmonic and anharmonic calculations, respectively. To minimize systematic errors, all the displacements in positive and negative directions are taken into consideration. The nearest fifth neighborhood is identified as the pair-cutoff distance for the anharmonic calculation. Finally, to compute the Grüneisen parameter, phonon life time, accumulated and lattice thermal conductivities, the reciprocal spaces of the primitive cells are sampled using the $39 \times 39 \times 39$ meshes.

3. Results and discussions

3.1. The dynamical properties and lattice thermal conductivity

NbCoSb compound have MgAgAs structure with space group F $4 \bar{3}$m (see figure 1). Nb, Co and Sb atoms locate in (0,0,0), ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$) and ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) positions, respectively. ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{3}{4}$) position is also empty. In a result of the geometric optimization, the lattice parameter is found to be 5.9790 Å. The calculated lattice parameter is approximately %1.4 higher than the experimental value (5.897 Å), as expected from PBE [8].

Phonons play an important role in understanding of the physical properties of materials such as lattice thermal conductivity, heat capacity, entropy etc. In the present study, the calculated harmonic phonon curves along the high symmetry directions and phonon DOS of NbCoSb are given in figure 2. Unfortunately, no experimental or theoretical data are available. For this reason, analysis of the vibration modes of NbCoSb will provide useful information. The phonon dispersion curves have 9 branches (3 acoustic modes and 6 optic modes). NbCoSb is dynamically stable because of absence negative frequency in the BZ.

We have the LO—TO splitting observed in our phonon dispersion curves of NbCoSb like other Half-Heusler materials were studied in [19, 20]. The LO-TO splitting is 0.222 THz for the upper frequency optical branch at $\Gamma$ point. This value is smaller than the other Half-Heusler compounds in the references mentioned above. The contribution to thermal conductivity can be neglected since LO-TO splitting does not lead to large changes in group velocity near $\Gamma$ point [21].

The acoustic and optic branches are not separated by a gap. The low frequency optic phonon mode interacts with acoustic phonon mode. This interaction increases the likelihood of scattering of the acoustic modes by the optical modes. So, the lattice thermal conductivity could also suppress [22, 23]. Also, some optical modes are nearly flat, and these optical modes contribute little toward heat transport [24, 25]. Both the interaction of acoustic with optic modes and also the low energy scale increase the phonon-phonon scattering [26]. The obtained energy scale of NbCoSb is lower than NbFeSb [27] and ZrCoSb [19].

The calculated $\Gamma$ point frequencies have triply degenerate except the high optical modes due to LO-TO splitting. The $\Gamma$ point frequencies are found to be 5.506 (5.672) and 6.545 (6.642) THz for the harmonic
(anharmonic) calculations. As can be seen from figure 3(a), the dispersion curve of the anharmonic phonon according to the harmonic phonon, all modes, especially the acoustic modes, shift to higher frequency values. The LO-TO splitting is 0.245 THz for the anharmonic phonon and is slightly higher than calculated for harmonic phonon (0.222 THz).

As it can be seen in figure 2, the phonon DOS can be divided into three regions: Acoustic modes, lower optical modes and upper optical modes. The Acoustic branch is contributed by all three atoms. For the lower optical modes, the main contribution comes from Nb with less contributions of other atoms. On the other hand, the upper optical modes have main contributions from Co and Sb with a small one coming from Nb.

The Grüneisen parameter gives information about anharmonic interactions [28]. The Grüneisen parameters along the high symmetry directions are given figures 3(b)–(d) and found to be positive value for all the modes. This positive value indicates a positive thermal expansion coefficient [28]. The Grüneisen parameter values for acoustic modes larger than for optic modes indicating that the lattice anharmonicity for acoustic modes are higher than for optic phonons. In the Γ-K direction, the acoustic mode Grüneisen parameter is the largest. The larger Grüneisen parameter shows high anharmonicity and thus low lattice thermal conductivity [29].

Phonon lifetime is an important physical property to understand the mechanism of the lattice thermal conductivity [18]. The phonon lifetime along phonon frequency at 300, 600 and 900K are given in figures 4(a)–(c), respectively. As seen from the figures 4(a)–(c), the phonon lifetime significantly reduces as the temperature increases. The shorter phonon lifetime shows larger phonon scattering [18] and the larger scattering reduces lattice thermal conductivity. The phonon lifetime reduces between 3 and 5 THz in our calculations. This may be due to the interaction of low-frequency optical modes with acoustic modes (see figure 3).

The accumulated thermal conductivity with respect to frequency at 300, 600 and 900K is given in figure 5. The accumulated thermal conductivity sums all the contributions from the phonons to the thermal conductivity. Also, the contribution to thermal conductivity of phonons is also shown by the dashed lines. As temperature increases, the accumulated lattice thermal conductivity decreases. The main contribution to thermal conductivity comes from the acoustic modes below 2.7 THz. The contribution to lattice thermal conductivity drops abruptly in about 2.7 THz. This result indicates the strong scattering [30]. The contribution of the optical modes to the lattice thermal conductivity is very small. The basic contribution to lattice thermal conductivity of optical modes is in between about 4.6 and 4.9 THz.

The lattice thermal conductivity depending on the temperature is shown in figure 6. Due to the lack of computational resources, the lattice thermal conductivity is calculated within relaxation time approximation. As expected, the lattice thermal conductivity decreases with increasing temperature. The lattice thermal conductivities are 0.680, 0.341, and 0.227 W mK$^{-1}$ at 300, 600 and 900 K, respectively. Our results are very small

**Figure 2.** The calculated harmonic phonon and Phonon DOS of NbCoSb.
compared to the value (about from 2.5 to 4 W mK$^{-1}$ in 700 C) measured by Huang et al[8, 9]. The RTA calculations may also be partially responsible for disagreement between measured and calculated lattice thermal conductivity. This may be due to the very weak diffraction peaks of Nb$_3$Sb are also identified by Huang et al[9].

The lattice thermal conductivity obtained by Huang et al[8] also different for all samples with hot press temperatures.

3.2. Mechanical properties

The elastic constants give important information about mechanical and dynamic properties. The elastic constants were calculated using the stress-strain method[31] and the second order elastic constants were found as $C_{11} = 259.8$, $C_{12} = 106.3$ and $C_{44} = 49.3$ GPa. The NbCoSb compound is mechanically stable due to the calculated elastic constants satisfy the well-known Born stability criterion for cubic structure. The calculated $C_{11}$ value is greater than $C_{44}$ value. This infers that it may show weaker resistance to pure shear deformation compared to unidirectional compression resistance[32].

Figure 3. (a) The phonon dispersion curves calculated from anharmonic IFC (the dashed lines represent the harmonic result) and the Grüneisen parameters along the high symmetry directions (b), (c), and (d) for acoustic, low optic and high optic modes, respectively.
The bulk modulus ($B$) and the shear modulus ($G$) refer to the resistance to volume and shape change in a material, respectively [33]. The Young's modulus is an indication of stiffness of the material [33]. When the value of $E$ is large, the material is stiff. The calculated Bulk, Shear and Young moduli are 157.4, 58.8 and 156.8 GPa, respectively. Furthermore, a material is brittle if the $B/G < 1.75$, otherwise ($B/G > 1.75$) it is ductile [34].

Figure 4. The phonon lifetime along phonon frequency at (a) 300 K, (b) 600 K and (c) 900 K (Colorbar indicates the phonon density).
Thus, $B/G = 2.676$ and NbCoSb, similar to Half-Heusler XMnSb compounds \[35\], is classified as ductile. Also, when Cauchy pressure ($C_{12} - C_{44}$) is positive, the material is ductile otherwise material is brittle \[36\]. It is suggested that NbCoSb shows ductile manner and consistent with $B/G$ value. In addition, the Cauchy pressure can be used to determine the angular character of the atomic bond \[36\]. The Cauchy pressure is positive for metallic bonding, whereas the Cauchy pressure is negative for directional bonding. So, NbCoSb exhibits metallic bonding.

The Poisson’s ratio ($\nu$) provides information about the bonding character of the material. The typical value of Poisson’s ratio is about 0.1, 0.25 and 0.33 for ionic, covalent and metallic materials, respectively \[37\]. The
calculated Poisson’s ratio is 0.33 for NbCoSb compound. So, this result reveals metallic behavior of the material. The value between 0.25 and 0.5 points out the central force in the solid [33]. The interatomic forces are central character for this compound.

The Debye temperature (\(\Theta_D\)) is closely related to many physical properties of solids such as the specific heat, melting temperature and stability of lattices. Above this temperature, all long-range acoustic modes would become active. But below it, only part of them could be evoke [37]. The calculated Debye temperature of NbCoSb is 336.8 K.

The hardness, is related to the elastic and plastic properties of a material, is estimated by
\[H_{\text{Chen}} = 2(k^2G)^{0.585} \times 3 \text{ formula [38].}\]
Where \(k = G/B\) is Pugh’s modulus ratio and the G is the shear modulus. The Vickers hardness values of NbCoSb is 3.9 GPa. Our compound is a soft material because of possessing a low hardness value.

Anisotropy (A), an important parameter for engineering, affects the physical properties of the crystal [39]. If A is 1, the material is isotropic. Since this value is different from 1, the NbCoSb compound is anisotropic.

4. Conclusion

The phonon and mechanical properties of NbCoSb compound have been studied for the first time within the frame work of DFT. The calculated equilibrium lattice constant is found to agree well with the experimental value. The elastic constant values and phonon calculations indicate that, NbCoSb is both mechanically and dynamical stable. It is also ductile, soft and anisotropic manner. In addition to this, NbCoSb compound exhibits low lattice thermal conductivity. We believe that our theoretical results may provide a good reference data to experimentalists to design new half-Heusler compounds exhibiting low thermal conductivity for thermoelectric applications.

Acknowledgments

The numerical calculations reported in this paper were partially performed at TUBITAK ULAKBIM, High Performance and Grid Computing Center (TRUBA resources). This study was supported by Aksaray University Scientific Research Fund, grant number 2016-014.

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