Density Functional Theory Study of the Electronic Structure and the Thermoelectric Properties of Strained Mn$_4$Si$_7$

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The effect of strain on the electronic structure and the thermoelectric properties of higher manganese silicide (HMS) Mn$_4$Si$_7$ was studied by using density functional theory (DFT) and by solving Boltzmann transport equation (BTE). We found that tensile strain reduced the band gap while compressive strain did not affect the band gap much. The electrical conductivity shows highly anisotropic with the in-plane direction being more dominant while the Seebeck coefficient does not change much, which leads to the the power factor along the in-plane direction being higher compared with that along the out-of-plane direction. The anisotropy of the electrical conductivity was due to a change of the band dispersion in the valence-band maximum (VBM). It was suggested that compressive strain can improve the power factor of Mn$_4$Si$_7$.

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I. INTRODUCTION

The search for a new source of energy has recently increased rapidly because of the high demand due to high price and possible exhaustion of traditional energy sources such as fossil fuel. However, current systems are not so effective, with more than 60% of the energy being wasted as heat [1]. In the search for new sources of energy, thermoelectric materials have received much attention owing to their capability to convert thermal energy into electrical energy. Thermoelectric materials have many advantages: there are no moving parts so they have high durability, and they are environmentally friendly. However, the current state of art of thermoelectrics is limited in wide-scale applications because of their low conversion efficiencies and the high costs of materials. The efficiency of thermoelectric materials is strongly related to the dimensionless figure of merit, which is defined as $ZT = \frac{\sigma S^2}{\kappa T}$, where $\sigma$, $S$, $\kappa$, and $T$ are the electrical conductivity, the Seebeck coefficient, the thermal conductivity, and the absolute temperature, respectively [2]. Some materials having high ZT, such as Bi$_2$Te$_3$, PbTe, and Zn$_4$Sb$_3$, however, contain toxic elements or have high-cost elements (Te, Sb) [3]. Higher manganese silicides (HMSs), MnSi$_4$, have been considered as alternative promising thermoelectric materials because they exhibit relatively high values of $ZT$, and contain two abundant and non-toxic elements. Furthermore, they possess mechanical stability to corrosion and oxidation [4,5]. Depending on the $\delta$ value, several closely-related phases, such as Mn$_4$Si$_7$, Mn$_{11}$Si$_{19}$, and Mn$_{15}$Si$_{26}$, have been identified in this class of material [6,7].

A number of studies have been done on the thermoelectric properties of HMSs. Due to the rather low thermal conductivity, high Seebeck coefficient, and electrical conductivity, the values of $ZT$ for HMSs are relatively high, ranging from 0.4 to 0.75 [3,8,9]. The improved values of the $ZT$ in the HMSs seem fascinating. In this study, the effect of strain on the electronic structure and the thermoelectric properties of HMSs has been investigated by using first-principles calculations and the Boltzmann transport equation (BTE).

II. METHODOLOGY

First-principles density functional calculations are performed by using Vienna Ab Initio Simulation Package (VASP) [10]. For the exchange-correlation potential, the generalized gradient approximation (GGA) is employed with Perdew, Burke, and Ernzerhof (PBE) parametrizatio-
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Fig. 1. Dependences of the (a) volume and the (b) band gap on the strain for different values of the strain from −3% to +3% and electronic band structure of Mn$_4$Si$_7$ for (c) −3% compressive strain and (d) +3% tensile strain.

III. RESULTS AND DISCUSSION

Mn$_4$Si$_7$ is well-known to be a degenerate $p$-type semiconductor with a hole carrier concentration on the order of 10$^{21}$ cm$^{-3}$. Its crystal structure belongs to the well-known Nowotny Chimney-Ladder compounds, consisting of two sublattices: a manganese “chimney” sublattice and a silicon “ladder” sublattice [15]. Calculated lattice constants are $a = 5.508$ Å and $c/a = 3.158$. The electronic band structure of Mn$_4$Si$_7$ shows a semiconducting behavior with an indirect band gap of 0.82 eV between the Γ-point in the valence band maximum (VBM) and the Z-point in the conduction band minimum (CBM). Both lattice parameters and electronic band structure agree very well with the results of experiments and other previous calculations [15–18]. To study the strain effect, we applied different strain from −3% (compressive strain) to +3% (tensile strain) along the $x$-axis and the $y$-axis with respect to the unstrained lattice. The lattice constant along the $z$-axis is optimized for each set of lattice constants along the $x$- and the $y$-axis. As a result, the change in the lattice constant along $z$-axis is from 5.1% to −4.4% compared with the unstrained lattice. This change of lattice constants leads to an increase in volume from −4.2% to +4.4%, as shown in Fig. 1(a).

The change in band gap is more dramatic, as shown in Fig. 1(b). The band gap is not changed much under compressive strain, but does change under tensile strain. The band gap is reduced from 0.82 eV (0 strain) to 0.77 eV at +3% tensile strain. This trend in band gap change is totally different from that of other materials such as SnSe, where the band gap was found to increase due to increasing lattice separation along $z$ direction [19].
Fig. 2. (Color online) Effect of strain on the thermoelectric properties of Mn₄Si₇: (a) Seebeck coefficient, (b) electrical conductivity $\sigma/\tau$ and (c) power factor along the in-plane direction and (d) Seebeck coefficient, (e) electrical conductivity $\sigma/\tau$ and (f) power factor along the out-of-plane direction.

In Figs. 1(c) and (d), we show comparisons of the band structures for compressive (−3%) and tensile strain (+3%). Other strains are not shown here, but the general trends are similar. The band structure topology is almost the same under strain, except for the band gap. This behavior is predictable due to the fact that the properties of the HMS Mn₄Si₇ are stable under ambient conditions, as reported in previous studies [4, 5]. The band dispersion on the VBM along the $\Gamma - Z$ direction is quite flat compared with that along the $\Gamma - X$ direction. However, under compressive strain, the band along the $\Gamma - Z$ direction on the VBM is slightly more dispersive while it is less dispersive along the $\Gamma - X$ direction. This change in band dispersion will affect the electrical conductivity, which will be discussed later.

The Seebeck coefficient, electrical conductivity $\sigma/\tau$, and power factor $PF/\tau = \sigma/\tau . S^2$ were calculated and the results are showed in Fig. 2 for various temperatures, where $\tau$ is the relaxation time. In all calculations, the hole carrier concentration was fixed at the experimental value $10^{21}$ cm$^{-3}$ [8]. The Seebeck coefficient in unstrained Mn₄Si₇ increases with increasing temperature, which shows very good agreement with experimental data [8]. However, the electrical conductivity $\sigma/\tau$ is highly anisotropic, where $\sigma/\tau$ along the in-plane direction is almost three times bigger compared with that along the out-of-plane direction. The large difference between the in-plane and the out-of-plane electrical conductivity comes from the difference in band dispersion on the VBM, which we discussed above, because the electrical conductivity is proportional to the electron velocity, which is defined as the derivative of the energy band versus k-vector data [14]. As a result, the $PF/\tau$ along the in-plane lattice is much higher compared with that along the out-of-plane lattice.

Under strain, the Seebeck coefficient does not change very much in either the in-plane or the out-of-plane direction. However, the behavior of the electrical conductivity is quite different and exhibits some anisotropy. Due to the change in the band dispersion in the VBM, $\sigma/\tau$ shows different behaviors: $\sigma/\tau$ along the in-plane direction decreases under increasing tensile strain, and to increase under the compressive strain while $\sigma/\tau$ along the out-of-plane direction is reduced under compressive strain and is increased under tensile strain. As a results, the power factor (PF) shows the same trend as the electrical conductivity. Noticeable is that even with a reduction in the out-of-plane lattice, the PF along the in-plane lattice is dominant. Therefore, the increase in the PF along this direction leads to an increase in the overall PF and ZT.

IV. CONCLUSION

The effect of strain on the electronic structure and the thermoelectric properties of Mn₄Si₇ has been studied by using density functional theory calculations and by solving the Boltzmann transport equation. The Seebeck coefficient was found to increase with increasing temperature. In addition, both the electrical conductiv-
ity and the PF increases along the in-plane direction and decreased along the out-of-plane direction as a result of a band dispersion change at the VBM. Based on the results, we suggest that compressive strain can improve the PF and the ZT of Mn$_4$Si$_7$.

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