Unraveling the effect of uniaxial strain on thermoelectric properties of Mg_2Si: A density functional theory study*

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In this work, the effect of uniaxial strain on electronic and thermoelectric properties of magnesium silicide using density functional theory (DFT) and Boltzmann transport equations has been studied. We have found that the value of band gap increases with tensile strain and decreases with compressive strain. The variations of electrical conductivity, Seebeck coefficient, electronic thermal conductivity, and power factor with temperatures have been calculated. The Seebeck coefficient and power factor are observed to be modified strongly with strain. The value of power factor is found to be higher in comparison with the unstrained structure at 2% tensile strain. We have also calculated phonon dispersion, phonon density of states, specific heat at constant volume, and lattice thermal conductivity of material under uniaxial strain. The phonon properties and lattice thermal conductivity of Mg_2Si under uniaxial strain have been explored first time in this report.

Keywords: semiconductors, thermoelectric and thermo magnetic effects, electric and thermal conductivity, density functional theory

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1. Introduction

The materials which can directly convert heat into electricity and *vice versa* are called as thermoelectric materials. These materials have great interest in science community because of environmental issues and energy crisis. One important parameter, a dimensionless figure of merit[1] gauges the performance of thermoelectric materials, which is defined as

$$ZT = \frac{S^2 \sigma T}{k}, \tag{1}$$

where S is Seebeck coefficient (in unit V/K), σ is electrical conductivity (in unit S/m), k is total thermal conductivity (in unit W/mK), and T is temperature (in unit K) respectively. Good thermoelectric materials have high thermo power and low thermal conductivity.

Owing to their non toxic nature, thermal stability, low density, relative abundance, and low cost of production, magnesium silicide and related alloys have become promising material for thermoelectric applications. Mg_2Si material has been considered as a high performance thermoelectric material in the temperature range of 500 K–800 K.[2,3] We have already discussed the importance and applications of Mg_2Si in our previous work.[4] In our earlier studies,[4] we have reported that the value of figure of merit is 1.83×10^{-3} at 1000 K for pure Mg_2Si. This value is very low as compared to other thermoelectric materials. So to enhance the figure of merit, there are various methods proposed. To improve the thermoelectric efficiency, the electronic band engineering via electronic doping, introduction of resonant levels in the electronic density of state is widely explored.[5–7] Mechanical stress applied to the materials induces a modification in the electronic band structure which may improve the thermoelectric properties.[8,9] Under the effect of mechanical stress (pressure and strain), the bands of material are shifted, splitted, and the effective mass changes. These changes affect the thermoelectric properties. Balout *et al.*[10,11] have studied the electronic and thermoelectric properties of Mg_2Si under isotropic strain. They found that under the effect of isotropic strain the Seebeck coefficient and power factor values increase by 40% and 100% respectively as compared to the unstrained Mg_2Si. Balout and his coworkers[12] found the thermoelectric properties of Mg_2Si under uniaxial [100] strains versus (100) oriented thin films. The electronic and electronic transport properties of this material under uniaxial strain with different concentration have been already discussed in previous literature.[12] But the variation of electronic thermoelectric properties with temperature and lattice thermal conductivity, specific heat, phonon dispersion curves, and phonon density of states of Mg_2Si material with temperature and strain have not been studied yet as per our knowledge. The purpose of present study is to give a comprehensive description of the electronic and thermoelectric properties of Mg_2Si under uniaxial strain. In this work the following points have been systematically explored:

(i) The effect of uniaxial strain on the electronic and thermoelectric properties of Mg_2Si.

(ii) Evaluation of the lattice thermal conductivity, specific heat, phonon dispersion relation, and phonon density of states of strained Mg_2Si material.

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This paper is organized as: In the following section, computational approach is discussed. Thereafter, calculations for electronic and thermoelectric properties are given in Section 3. Finally we summarize the results and conclude in the last section.

2. Theoretical and computational approach

In our calculations, the electronic structure calculations were carried out using density functional theory (DFT) based on plane wave pseudo-potential method as implemented in the Quantum Espresso package.[13] The generalized gradient approximation (GGA)[14] of Perdew–Burke–Ernzerhof (PBE) was used for exchange–correlation functional. The cutoff for the kinetic energy was set to 40 Ry (1 Ry = 13.6056923 eV) for the plane-wave expansion of the electronic wave functions. The charge–density cutoff was kept at 400 Ry and the Marzari-vanderbilt cold smearing size was fixed at 0.003 Ry. The Brillouin zone integration was performed using Monkhorst–Pack scheme[15] with $4 \times 8 \times 8$ meshes. For the density of state (DOS) calculation, we used tetrahedron method with $16 \times 16 \times 16$ denser k-point mesh.

BoltzTraP code[16] was used to calculate the thermoelectric properties. The detail description of methodology is given in our previous work.[4,17,18] To calculate lattice thermal conductivity (k_l), ShengBTE code[19] based on phonon Boltzmann transport equation (pBTE) has been used. The phonon properties have been calculated using density functional perturbation theory (DFPT).[20] The dynamical matrices have been calculated for $4 \times 4 \times 4$ q-points grid generated according to Monkhorst and pack.[15] Quasi harmonic approximation (QHA)[21] implemented in Quantum espresso Code[13] has been used to calculate the specific heat of the lattice.

3. Results and discussion

3.1. Electronic properties under uniaxial strain

Pristine Mg_2Si is a face centered cubic structure with space group $Fm3m$. The calculated lattice constant of Mg_2Si is 6.364 Å.[4] We have applied uniaxial strain on Mg_2Si. In uniaxial strain, tensile and compressive strains correspond to $\Delta a_0/a_0 > 0$ and $\Delta a_0/a_0 < 0$, where a_0 is the lattice parameter of unstrained structure. Figure 1 shows the variation of band gap of the system under tensile and compressive strains. The band gap increases with tensile strain and decreases with the compressive strain. The electronic band structures of Mg_2Si under compressive and tensile strains were calculated for percentage -3% to $+3\%$. Figures 2 and 3 show the band structures under tensile strain and compressive strain respectively. To have a clear understanding of the contribution of different atomic orbitals, density of states (DOS) and projected density of states (PDOS) have been calculated and plotted in Figs. 4 and 5.

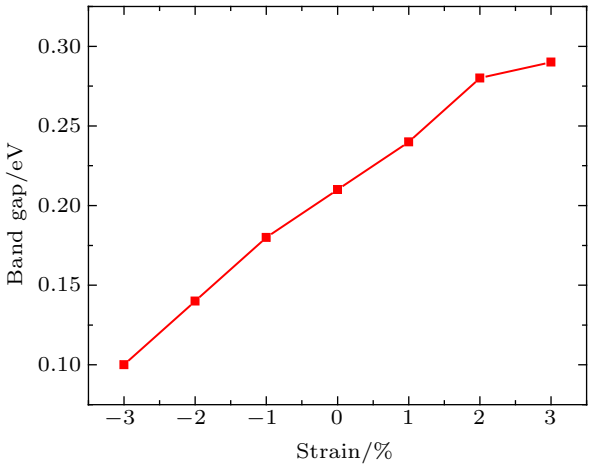


Fig. 1. (color online) Evolution of band gaps under uniaxial strains.

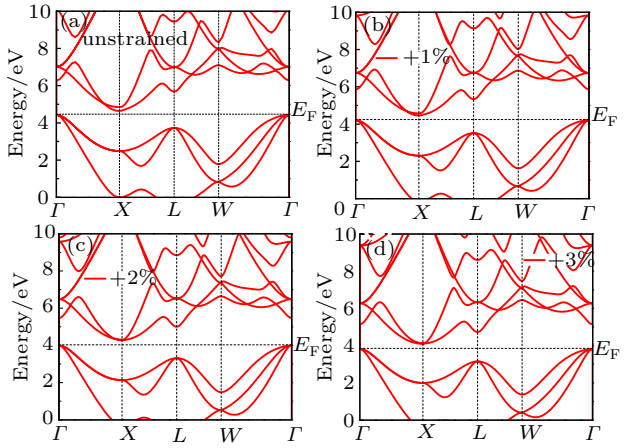


Fig. 2. (color online) Electronic band structure of uniaxial tensile strain: (a) unstrained, (b) 1%, (c) 2%, (d) 3%.

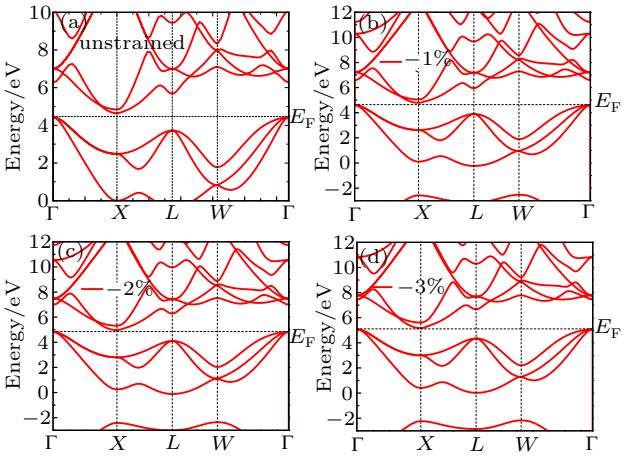


Fig. 3. (color online) Electronic band structure of Mg_2Si under uniaxial compressive strain: (a) unstrained, (b) −1%, (c) −2%, (d) −3%.

In case of tensile strain (Fig. 2), the conduction band first minima and conduction band second minima at X point come close to each other. At 2%, these two minima merge into each other. Similarly when Mg_2Si is subjected to the compressive strain [Figs. 3(a)–3(d)] the conduction band minima at X k-point move apart from each other. A similar trend

has been found when Mg_2Si is mixed with Mg_2Sn to form $Mg_2Si_{1-x}Sn_x$ at $x = 0.4$.[22,23] This is caused by the downward movement of upper conduction band and an upward movement of the lower conduction band until the two fold degeneracy of these bands occurs around 2% of tensile strain where the density of states attains its maximum value. Analogous features have been seen by Balout[10] when they applied isotropic strain on Mg_2Si.

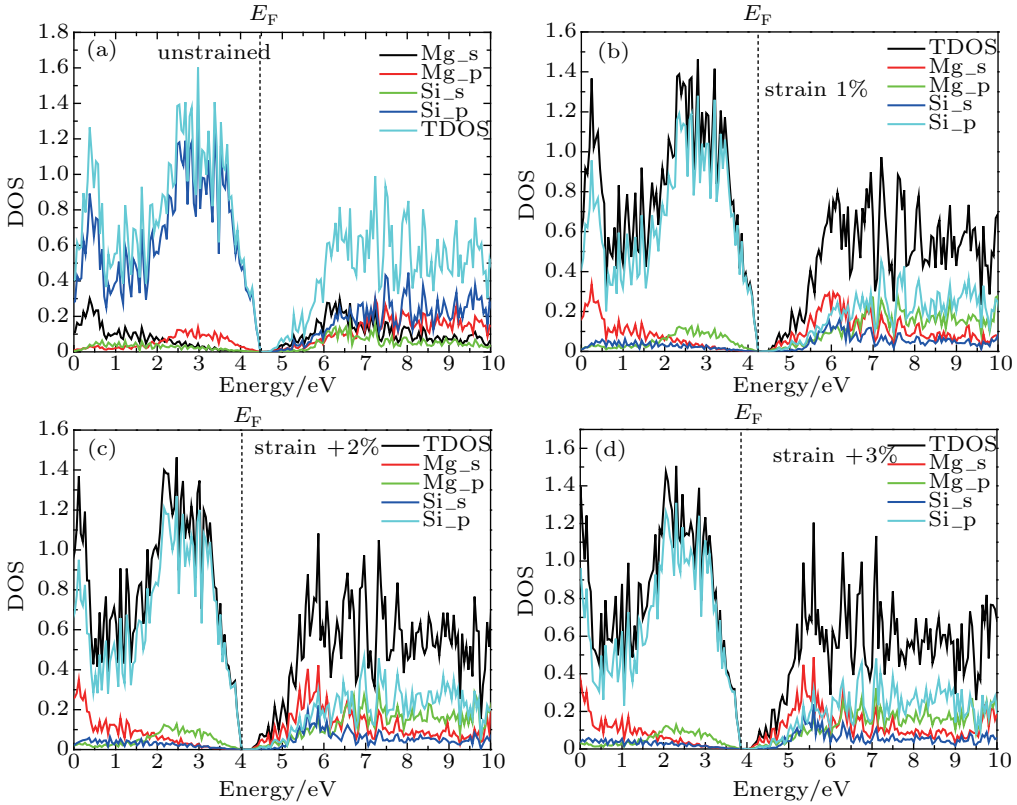


Fig. 4. (color online) Density of states and PDOS of Mg_2Si under uniaxial tensile strain: (a) unstrained, (b) −1%, (c) −2%, (d) −3%.

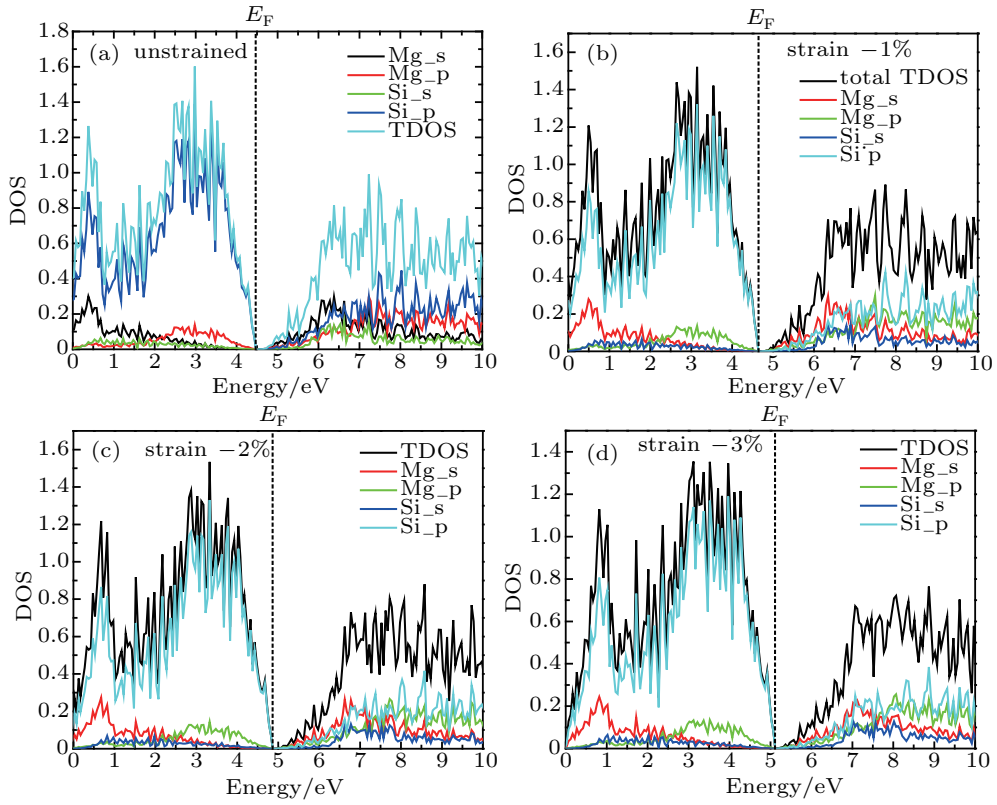


Fig. 5. (color online) Density of states and PDOS of Mg_2Si under uniaxial compressive strain: (a) unstrained, (b) −1%, (c) −2%, (d) −3%.

3.2. Thermoelectric properties under uniaxial strain

Under the effect of uniaxial strain, the shape of conduction band plays main role to enhance the thermoelectric performance of Mg_2Si. In this study, we have noticed that the size of conduction band is affected by the compressive and tensile strains at high symmetry point X. Figure 6 represents the variation of the Seebeck coefficient, electrical conductivity, electronic thermal conductivity, and power factor with temperature.

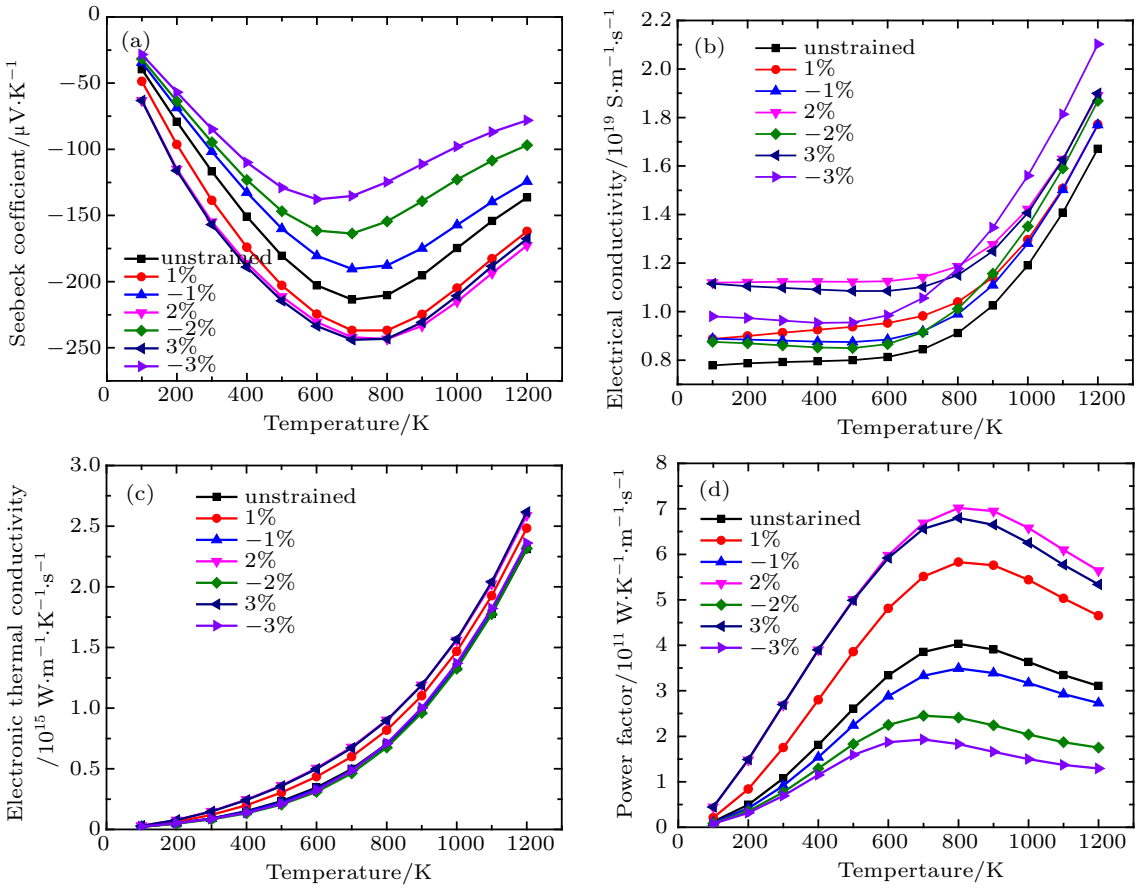


Fig. 6. (color online) (a) Seebeck coefficient (S), (b) the electrical conductivity (σ/τ), (c) the electronic thermal conductivity (k_e/τ), and (d) power factor ($S^2\sigma/\tau$) versus temperature under strains.

In Fig. 6(a), the Seebeck coefficient decreases in the case of compressive strain and remains lower than the unstrained material with respect to temperature. According to the Mott equation,[24] the Seebeck coefficient (S) also depends upon the density of state (DOS) at Fermi level.

$$S = \frac{\pi^2 k_b^2 T}{3e}\left\{\frac{\mathrm{d}\ln\sigma(E)}{\mathrm{d}E}\right\}_{E=E_F}, \tag{2}$$

$$S \propto \left[\frac{1}{\mathrm{DOS}(E_F)}\frac{\mathrm{dDOS}(E)}{\mathrm{d}E}\right]_{E=E_F}. \tag{3}$$

These equations show that S, directly depends upon the derivative of DOS and is inversely proportional to the DOS at Fermi level.[24,25] In general, as the density of carriers and the doping level increases, the electrical conductivity increases but the value of Seebeck coefficient decreases. Equation (2) gives the relation of the Seebeck coefficient and the energy dependence of electrical conductivity $\sigma(E)$ of degenerately doped solid.[26,27]

Under tensile strain, the Seebeck coefficient increases. It is apparent that a tensile strain tends to enhance the absolute value of the Seebeck coefficient. There is significant enhancement in the Seebeck coefficient as compared to strain free material. This is due to the fact that the Seebeck coefficient is proportional to the energy logarithmic derivative of the density of states at the Fermi level (as explained above). The variation of the Seebeck coefficient is related to the modification of density of states near the Fermi level.

When electronic bands become steeper, the density of states decreases and the Seebeck coefficient also decreases. In the compressive strain, the electronic bands become steeper which cause to decrease in the Seebeck coefficient. At high temperature, at 2% strain the value of the Seebeck coefficient is large as compared to other values.

The variation of the electrical conductivity with temperature and strains is depicted in Fig. 6(b). The electrical conductivity increases with temperature irrespective of strain which is a characteristic of semiconductors. The parameter σ/τ increases with strain and temperature. Both compressive and tensile strains enhance the electrical conductivity as compared to the unstrained structure. Here, 2% tensile strain gives the

best results in temperature up to 800 K, above this temperature the electrical conductivity is similar to that for 3% tensile strain and −2% compressive strain. At high temperature, −3% compressive strain enhances the electrical conductivity. The evolution of the electrical conductivity can be explored on the basis of trend observed for energy gap during compression and tensile strains. The gap decreases upon compression, the electrons are easily transferred to the conduction band. Therefore the electrical conductivity increases. In contrast, the band gap increases under the effect of the tensile strain so that the electrical conductivity decreases as compared to compressive strains. In conclusion we can say that the electrical conductivity increases when either tensile or compressive strains are applied.

Figure 6(c) shows the electronic thermal conductivity for strained material. The electronic thermal conductivity increases with temperature. But there is no effect of strain on the electronic thermal conductivity. Under all strains, it always remains same. The behavior of PF (power factor) is depicted in Fig. 6(d). The power factor increases with temperature and at 800 K it decreases under strain. The maximum value of the power factor occurs at 2% tensile strain. The power factor degrades under the compressive strain. The tensile strain improves the power factor as compared to the unstrained material. Here the Seebeck coefficient plays the main role to enhance the PF. Similar trends have been found by Balout[10,12] when they applied strain to Mg_2Si.

Figure 7 shows the variation of specific heat of strained material with temperature. Figure 8 shows the phonon dispersion and the phonon density of states of Mg_2Si compound under compressive and tensile strains. Mg_2Si under strain is stable because there is no existence of negative frequency. This calculated total phonon density of states was used to evaluate the temperature-dependent specific heat (C_v) of systems in a quasi-harmonic approximation. The constant volume specific heat (C_v) is written as

$$C_v(T) = k_B \int_0^\infty \frac{\left(\frac{\hbar\omega}{k_B T}\right)^2 \exp\left(\frac{\hbar\omega}{k_B}\right)}{\left(\exp\left(\frac{\hbar\omega}{k_B}\right) - 1\right)^2} F(\omega)\, d\omega, \qquad (4)$$

where k_B is Boltzmann's constant, $\hbar$ is Planck's constant, $F(\omega)$ is the phonon density of states, and T is temperature. Our calculated value of the specific heat of unstrained material is in good agreement with the previous reported experimental value of specific heat.[28] In present calculations, at 300 K, the value of the specific heat of unstrained Mg_2Si is 68.02 J/mol·K. The experimental value specific heat of Mg_2Si is 67.2 J/mol·K[29] and previously reported value is 67.6 J/mol·K.[30] From Fig. 8, in low frequency range (0 THz–2.3 THz), the phonon density of states in the case of compressive strained Mg_2Si increases with the increase in the compressive strain and decreases with the increase in the tensile strain. The specific heat directly depends upon the phonon density of states. That is why the system under the compressive strain has maximum value of the specific heat as compared to tensile strained material at low temperature range.

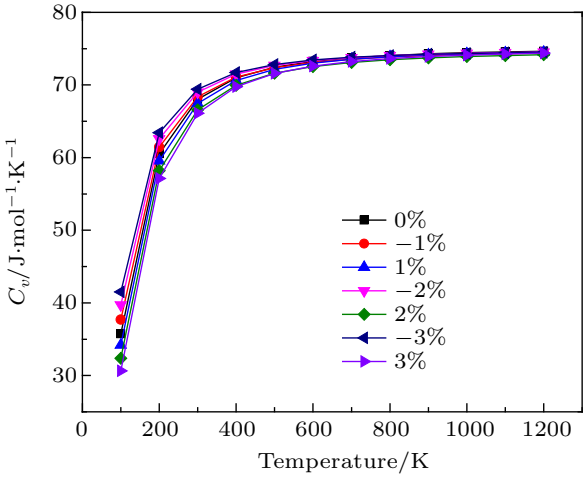


Fig. 7. (color online) Constant volume specific heat of Mg_2Si under strains.

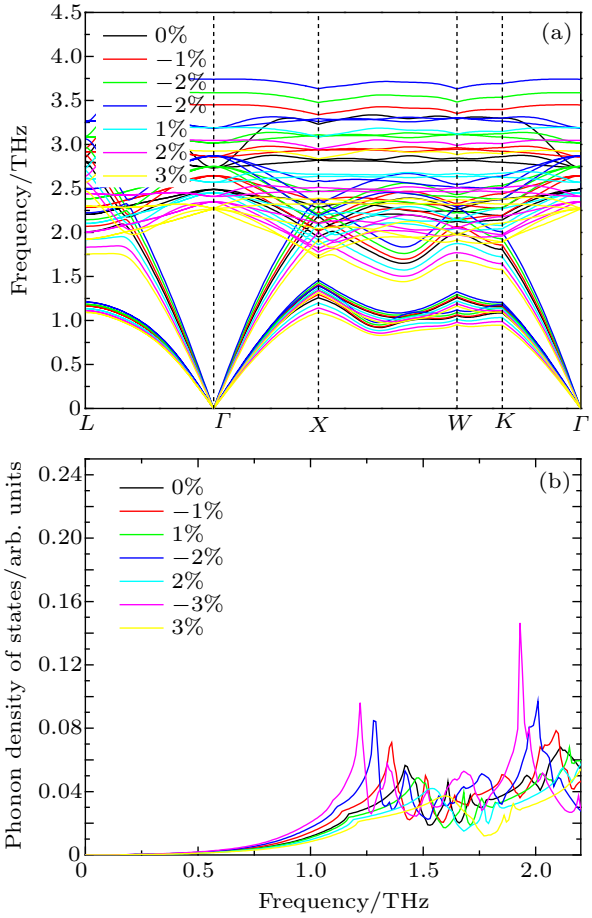


Fig. 8. (color online) Phonon dispersion and phonon density of state of Mg_2Si under strains.

Figure 9 shows the variation of lattice thermal conductivity of Mg_2Si under the compressive and tensile strains with temperature. Under the compressive strain, the lattice thermal conductivity increases with the increase in the strain. But

in the tensile strain, the lattice thermal conductivity decreases with the strain. Under compressive strains, the phonon group velocity of acoustic phonons ($v_g = \partial\omega/\partial k$) is large because of the upward shift of phonon dispersion as shown in Fig. 8. This type of shift in phonon dispersion curve will increase the specific heat of the material. In the tensile strain, this shift goes in opposite direction and results in both decrease in phonon group velocity and specific heat. These two effects decrease the thermal conductivity from compressive strain to tensile strain.

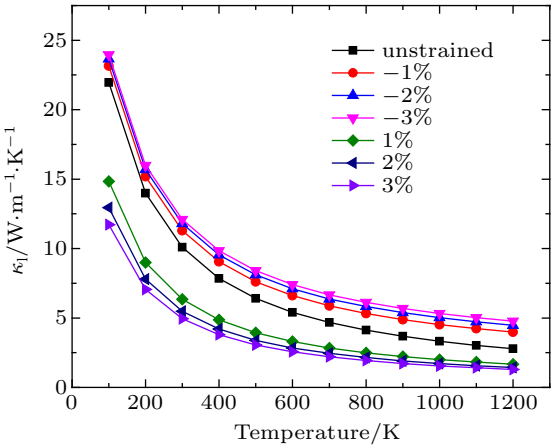


Fig. 9. (color online) Lattice thermal conductivity of Mg_2Si under strains.

4. Conclusions

In this work, an attempt is made to employ first-principle calculations in order to predict the effect of uniaxial strain on Mg_2Si. Up to 3% strain, the material remains semiconductor. The band gap increases or decreases under tensile strain or compressive strain. The most remarkable result is that a substantial improvement is observed for the Seebeck coefficient when the tensile strain is applied to material. The power factor is almost doubled compared to unstrained material. Under compressive and tensile strain, the electrical conductivity increases. This result could be attractive for the tensile strain that leads to the improvement in the power factor of material. The specific heat of Mg_2Si increases with the increase in the compressive strain and decreases with the increase in the tensile strain. The lattice thermal conductivity decreases continuously when the applied strain is changed from compressive strain to tensile strain due to the shift of phonon dispersion curves under the strain. Tuning of electronic and thermal conductivities of bulk materials under strains has lot of applications in energy conversion and thermal management. This work may serve as an increase for researchers in future.

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