Strain-induced enhancement of thermoelectric performance in a ZrS$_2$ monolayer

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The increase of a thermoelectric material’s figure of merit ($ZT$ value) is limited by the interplay of the transport coefficients. Here we report the greatly enhanced thermoelectric performance of a ZrS$_2$ monolayer by the biaxial tensile strain, due to the simultaneous increase of the Seebeck coefficient and decrease of the thermal conductivity. Based on the first-principles calculations combined with the Boltzmann transport theory, we predict that the band gap of the ZrS$_2$ monolayer can be effectively engineered by the strain and the Seebeck coefficient is significantly increased. The thermal conductivity is reduced by the applied tensile strain due to the phonon softening. At the strain of 6%, the maximal $ZT$ value of 2.4 is obtained for the $p$-type doped ZrS$_2$ monolayer at 300 K, which is 4.3 times larger than that of the unstrained system.

Thermoelectric (TE) devices can directly convert the heat energy to electricity and vice versa, and thus have promising applications in solid-state cooling and power generation. The efficiency of a TE device is determined by the TE material’s dimensionless figure of merit $ZT = S^2\sigma T/(\kappa_e + \kappa_p)$, where $S$, $\sigma$, $T$, $\kappa_e$ and $\kappa_p$ are the Seebeck coefficient, electrical conductivity, absolute temperature, electronic and lattice thermal conductivities, respectively. Because the transport coefficients ($S$, $\sigma$, $\kappa_e$ and $\kappa_p$) are strongly coupled to each other, none of them can be independently tuned to largely enhance the TE performance.

It was theoretically proposed that one- (1D) or two-dimensional (2D) materials could have much larger $ZT$ values than their bulk counterparts. In recent years, with the rapid pace of progress in nanotechnologies, a large variety of low-dimensional materials beyond graphene have been successfully prepared. Among them, single layers of transition metal dichalcogenides (TMDCs) have received a lot of attention because some of them, such as MoS$_2$, are semiconductors with sizable direct band gaps, making them promising candidates for applications in field effect transistors and optoelectronic devices. In addition, MX$_2$ ($M=Mo, W; X=S, Se$) monolayers were reported to have much improved TE performance, opening up a new opportunity of TMDCs monolayers in the TE field.

A ZrS$_2$ monolayer is another typical 2D TMDC and has been successfully synthesized experimentally. The thermal conductivity of the ZrS$_2$ monolayer is much lower than those of MX$_2$ ($M=Mo, W; X=S, Se$) monolayers, which is desirable for the TE application. However, the TE performance of the ZrS$_2$ monolayer has not been explored. Recently, it was reported that the electronic structure of the ZrS$_2$ monolayer can be tuned by external strains. In previous reports, strain has proven to be a flexible and effective method to tune the electronic phonon and thus the TE properties of 2D systems. For example, the Seebeck coefficient of phosphorene can be greatly enhanced due to strain-induced band convergence. The thermal conductivity can either be increased or reduced by the applied strains, depending on the particular materials. It is thus interesting to investigate how the TE performance of the ZrS$_2$ monolayer will be influenced by the external strain. In this work, by using the first-principles calculations combined with the Boltzmann transport theory, we predict that the TE performance of the ZrS$_2$ monolayer can be largely enhanced by the biaxial tensile strain, due to the simultaneous increase of the Seebeck coefficient and decrease of the thermal conductivity.

The structural and electronic properties of the ZrS$_2$ monolayer were calculated within the framework of the density functional theory (DFT) as implemented in the ABINIT code. The projector augmented-wave (PAW) pseudopotential approach were used. The exchange-correlation potential was in form of the Perdew-Burke-Ernzerhof (PBE) expression of the generalized-gradient approximation (GGA). The spin-orbital coupling was included in the calculations of electronic prop-
FIG. 2: Calculated band gap of ZrS$_2$ monolayer as a function of the applied biaxial strain.

FIG. 3: (a) Absolute values of the Seebeck coefficient, (b) electrical conductivity and (c) power factor of ZrS$_2$ monolayer as a function of the carrier concentration under different biaxial strains.
a function of the carrier concentration under different strains. The results for the zigzag and armchair directions are the same (due to the high structural symmetry of the ZrS$_2$ monolayer), so the transporting directions are not distinguished here. From Fig. 3(a), we can see that the compressive strains have little impact on the Seebeck coefficient of the $p$-type doped system while reduce the Seebeck coefficient of the $n$-type doped one. For the tensile strain, the maximal absolute values of the Seebeck coefficient of both the $p$- and $n$-type doped systems first increase as increasing the strain, reach the maximum at the strain of 6% and then decrease when the strain is further increased. If we notice the strain-dependence of the band gap (see Fig. 2), we can see that such a trend of the Seebeck coefficient coincides with that of the band gap. Therefore, the Seebeck coefficient is efficiently tuned by the strain via the band-gap engineering. The greatly increased Seebeck coefficient of the ZrS$_2$ monolayer is very favorable for the TE application.

Figure 3(b) shows the electrical conductivity $\sigma/\tau$ as a function of the carrier concentration. When the doping is not very high ($n < 10^{14}$ cm$^{-2}$), $\sigma/\tau$ generally decreases as increasing the band gap, which is in contrast with the tendency of the Seebeck coefficient. The decrease of the electrical conductivity is detrimental to the TE performance. Whether the applied strain will benefit the electronic transport properties or not will be determined by the competition of the two factors. In Fig. 3(c), we plot the power factors of the ZrS$_2$ monolayer under different strains. For the tensile strain, the maximal power factor generally increases as increasing the band gap, indicating that the increase of the Seebeck coefficient compensates the negative effect from the electrical conductivity. For the $p$-type doped ZrS$_2$ monolayer, the power factor is significantly increased by the applied tensile strain. Compared with the unstrained system, in which the power factor of the $n$-type doping is much larger than that of the $p$-type one, the tensile strain makes the power factors of the $p$- and $n$-type doped systems more balanced.

As mentioned above, within our method, the electrical conductivity $\sigma$ can only be calculated with the relaxation time $\tau$ inserted. The relaxation time is determined by

$$\mu = e\tau/m^*$,$$

where $\mu$ is the carrier mobility and $m^*$ is the effective mass. The carrier mobility $\mu$ of the ZrS$_2$ monolayer can be calculated using the deformation potential (DP) theory based on the effective mass approximation [32,34]

$$\mu = \frac{e\hbar^2 C}{k_B T m^* m_d E_1^2},$$

where $m_d$ is the average effective mass defined by $m_d = \sqrt{m_e^2 m_h^2}$, $C$ is the elastic modulus and can be determined by $C = (\partial^2 E/\partial \delta^2)/S_0$, where $E$, $\delta$, $V_0$, and $S_0$ are, respectively, the total energy, the applied strain, the volume, and the area of the investigated system. The DP constant $E_1$ is obtained by $E_1 = dE_{\text{edge}}/d\delta$, where $\delta$ is the applied strain by a step of 0.5% and $E_{\text{edge}}$ is the energy of the band edges (VBM for the holes and CBM for the electrons). Since the ZrS$_2$ monolayer has the largest power factor at the strain of 6%, we will only consider this strain condition. The calculated $m^*$, $m_d$, $C$, $E_1$, and room-temperature $\mu$ and relaxation time $\tau$ of the unstrained and 6% strained ZrS$_2$ monolayers are summarized in Table I. For the unstrained case, the effective mass of the electron along the armchair direction is much larger than that along the zigzag direction, since the conduction band dispersion around the M point is highly anisotropic (see Fig. 1(c)), that is, the conduction band is much flatter along the $\Gamma$-M direction (armchair direction in real space) than that along the $M$-$K$ direction (zigzag direction in the real space). However, the valence band dispersion around the $\Gamma$ point is nearly isotropic, which results in the almost same effective masses of the hole along the zigzag and armchair directions. The case for the strained ZrS$_2$ monolayer is similar, except that the corresponding effective masses are enhanced by the strain. The elastic modulus $C$ and DP constant $E_1$ for both the electron and hole have little difference along the two directions. Accordingly, the anisotropy of the carrier mobilities is dominated by the corresponding anisotropy of the carrier effective masses. For the electron, the mobility along the zigzag direction is much larger than that.

### Table I: Effective mass ($m^*$), average effective mass ($m_d$), elastic modulus $C$, DP constant $E_1$, carrier mobility ($\mu$), relaxation time ($\tau$) at 300 K in the zigzag and armchair directions of the unstrained and 6% strained ZrS$_2$ monolayers.

| Strain       | Direction | Carrier  | $m^*$ (m_e) | $m_d$ (m_e) | $C$ (eV/Å$^2$) | $E_1$ (eV) | $\mu$ (cm$^2$V$^{-1}$s$^{-1}$) | $\tau$ (10$^{-13}$ s) |
|--------------|-----------|----------|-------------|-------------|----------------|-----------|-------------------------------|------------------------|
| Unstrained   | Zigzag    | Electron | 0.28        | 0.74        | 6.36           | -3.17     | 1045.3                        | 1.66                   |
|              |           | Hole     | -0.27       | 0.26        | 6.36           | -6.67     | 695.8                         | 1.07                   |
|              | Armchair  | Electron | 1.97        | 0.74        | 6.34           | -3.99     | 93.3                          | 1.04                   |
|              |           | Hole     | -0.26       | 0.26        | 6.34           | -6.46     | 769.2                         | 1.14                   |
| Strained     | Zigzag    | Electron | 0.43        | 1.13        | 6.36           | -4.02     | 276.7                         | 0.68                   |
|              |           | Hole     | -0.72       | 0.80        | 6.36           | -3.61     | 289.3                         | 1.18                   |
|              | Armchair  | Electron | 2.97        | 1.13        | 6.34           | -3.73     | 46.5                          | 0.79                   |
|              |           | Hole     | -0.90       | 0.80        | 6.34           | -3.64     | 225.3                         | 1.15                   |
The electron mobility along the zigzag direction of the unstrained system is 1045.3 cm²V⁻¹s⁻¹, comparing favorably with that of the MoS₂ monolayer. The applied strain reduces both the electron and hole mobilities, mainly due to the increased effective masses. Based on Eqs. (1) and (2), the relaxation time will depend on the average effective mass \( m_d \) but not \( m^* \), so the anisotropy of \( m^* \) will not be reflected in \( \tau \). As a result, there is little difference in the relaxation time \( \tau \) along different directions. In the following, we will use the averaged \( \tau \) of the two directions to estimate the TE performance.

Next, we will investigate the strain effect on the thermal transport properties of the ZrS₂ monolayer. The lattice thermal conductivities \( \kappa_p \) of the unstrained and 6% strained ZrS₂ monolayers are shown in Fig. 4(a). For both cases, the \( \kappa_p \) decreases as increasing the temperature, following a \( T^{-1} \) dependence, as indicated by the fitting lines in the figure. This implies the dominant scattering mechanism is the Umklapp process. Moreover, in the temperature range investigated, the thermal conductivities of the 6% strained ZrS₂ monolayer are much smaller than those of the unstrained system. In particular, at 300 K, the \( \kappa_p \) decreases from 3.29 to 1.99 W/(mK), reduced by 40% when the strain of 6% is applied. To investigate the origin of the reduction in the thermal conductivity, in Fig. 4(b), we plot the corresponding phonon dispersions. At the strain of 6%, the phonon dispersions of transverse and longitudinal acoustic (TA and LA) modes become softened, while the out-of-plane acoustic (ZA) mode is slightly stiffened. The contribution of each phonon mode to the total thermal conductivity can be expressed as

\[
\kappa_i(q) = C_i(q)v_i^2(q)\tau_i(q),
\]

where \( C_i \), \( v_i \), and \( \tau_i \) are the specific heat, group velocity and phonon relaxation time, respectively; \( q \) is the wave vector. The group velocity is calculated based on \( v_i(q) = \frac{\partial \omega}{\partial q} \). Our results show that the three acoustic phonon branches contribute mostly to the thermal conductivity. The phonon softening leads to the reduced phonon branches contribute mostly to the thermal conductivity. The phonon softening leads to the reduced phonon-phonon scattering, resulting in the reduced phonon relaxation time and thus the phonon relaxation rate decreases.

Combining the electronic and thermal transport properties, we now evaluate the TE performance of the ZrS₂ monolayer. The room-temperature \( ZT \) values of the unstrained and 6% strained systems are shown in Fig. 5. For the unstrained ZrS₂ monolayer, the maximal \( ZT \) value of the \( n \)-type doped system is much larger than that of the \( p \)-type doped one. When the strain of 6% is applied, the maximal \( ZT \) value of 2.40 is obtained for the \( p \)-type doping, which is 4.3 times larger than that of the unstrained system. For the \( n \)-type doping, the enhancement of the maximal \( ZT \) value is relatively smaller, from 1.65 for the unstrained system to 1.76 for the 6% strained one. The increase of the Seebeck coefficient as well as the decrease of the lattice thermal conductivity contribute to the enhanced TE performance.

In summary, we have investigated the strain effect on the electronic, phonon, and TE properties of the ZrS₂ monolayer. The band gap first increases and then decreases as increasing the biaxial strain, reaching the maximum at the strain of 6%. The Seebeck coefficient of the ZrS₂ monolayer is found to be effectively tuned by the strain via the band-gap engineering. The increase of the Seebeck coefficient compensates the decrease of the electrical conductivity and thus the maximal power factor of the ZrS₂ monolayer increases as increasing the strain.
ZT values at 300 K as a function of the carrier concentration of the unstrained and 6% strained ZrS$_2$ monolayers.

This work was supported by the National Natural Science Foundation of China under Contracts No. 11274311, 11404340, and No. U1232139, the Anhui Provincial Natural Science Foundation under Contract No. 1408085MA11, the China Postdoctoral Science Foundations (Grant Nos. 2014M550352 and 2015T80670). The calculation was partially performed at the Center for Computational Science, CASHIPS.

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1 L. D. Hicks and M. S. Dresselhaus, Phys. Rev. B 47, 12727 (1993).
2 L. D. Hicks and M. S. Dresselhaus, Phys. Rev. B 47, 16631(R) (1993).
3 J. N. Coleman, M. Lotya, A. O’Neill, S. D. Bergin, P. J. King, U. Khan, K. Young, A. Gaucher, S. De, R. J. Smith, I. V. Shvets, S. K. Arora, G. Stanton, H.-Y. Kim, K. Lee, G. T. Kim, G. S. Duesberg, T. Hallam, J. J. Boland, J. J. Wang, J. F. Donegan, J. C. Grunlan, G. Moriarty, A. Shmeliov, R. J. Nicholls, J. M. Perkins, E. M. Grieveson, K. Theuwissen, D. W. McComb, P. D. Nellist, and V. Nicolosi, Science 331, 568 (2011).
4 S. Jeong, D. Yoo, M. Ahn, P. Miró, T. Heine, and J. Cheon, Nat. Commun. 6, 5763 (2015).
5 M. Buscema, M. Barkelid, V. Zwiller, H. S. J. van der Zant, G. A. Steele, and A. Castellanos-Gomez, Nano Lett. 13, 358 (2013).
6 W. Huang, H. Da, and G. Liang, J. Appl. Phys. 113, 104304 (2013).
7 D. Wickramaratne, F. Zahid, and R. K. Lake, J. Chem. Phys. 140, 124710 (2014).
8 H. Babaei, J. M. Khodadadi, and S. Sinha, Appl. Phys. Lett. 105, 193901 (2014).
9 Z. Zeng, Z. Yin, X. Huang, H. Li, Q. He, G. Lu, F. Boey, and H. Zhang, Angew. Chem. Int. Ed. 50, 11093 (2011).
10 X. Gu and R. Yang, Appl. Phys. Lett. 105, 131903 (2014).
11 Y. Li, J. Kang, and J. Li, RSC Adv. 4, 7396 (2014).
12 Z. H. Ni, T. Yu, Y. H. Lu, Y. Y. Wang, Y. P. Feng, and Z. X. Shen, ACS Nano 2, 2301 (2008).
13 K. He, C. Poole, K. F. Mak, and J. Shan, Nano Lett. 13, 2931 (2013).
14 R. Fei and L. Yang, Nano Lett. 14, 2884 (2014).
15 H. Y. Lv, W. J. Lu, D. F. Shao, and Y. P. Sun, Phys. Rev. B 90, 085433 (2014).
16 M. Hu, X. Zhang, and D. Poulilakos, Phys. Rev. B 87, 195417 (2013).
17 L. Zhu, T. Zhang, Z. Sun, J. Li, G. Chen, and S. A. Yang, Nanotechnology 26, 465707 (2015).
18 P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).
19 X. Gonze, J.-M. Beuken, R. Caracas, F. Detraux, M. Fuchs, G.-M. Rignaneese, L. Sindic, M. Verstraete, G. Zerah, F. Jollet, M. Torrent, A. Roy, M. Mikami, Ph. Ghosez, J.-Y. Raty, and D. C. Allan, Comput. Mater. Sci. 25, 478 (2002).
20 X. Gonze, G.-M. Rignaneese, M. Verstraete, J.-M. Beuken, Y. Pouillon, R. Caracas, F. Jollet, M. Torrent, G. Zerah, M. Mikami, Ph. Ghosez, M. Veithen, J.-Y. Raty, V. Olevano, F. Bruneval, L. Reining, R. Godby, G. Onida, D. R. Hamman, and D. C. Allan, Z. Kristallogr. 220, 558 (2005).
21 X. Gonze et al., Comput. Phys. Commun. 180, 2582 (2009).
22 J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
23 G. K. H. Madsen and D. J. Singh, Comput. Phys. Commun. 175, 67 (2006).
24 E. A. Stern, Phys. Rev. 157, 544 (1967).
25 R. Venkatasubramanian, E. Sivola, T. Colpitts, and B. O’Quinn, Nature (London) 413, 597 (2001).
26 G. Kresse and J. Hafner, Phys. Rev. B 47, 558 (1993).
27 G. Kresse and J. Hafner, Phys. Rev. B 49, 14251 (1994).
28 G. Kresse and J. Furthmüller, Comput. Mater. Sci. 6, 15 (1996).
29 A. Togo and I. Tanaka, Scr. Mater. 108, 1 (2015).
30 W. Li, J. Carrete, N. A. Katcho, and N. Mingo, Comput. Phys. Commun. 185, 1747 (2014).
31 D. L. Greenaway and R. Nitsche, J. Phys. Chem. Solids 26, 1445 (1965).
32 S.-i. Takagi, A. Toriumi, M. Iwase, and H. Tango, IEEE Trans. Electr. Dev. 41, 2357 (1994).
33 S. Bruzone and G. Fiori, Appl. Phys. Lett. 99, 22108 (2011).
34 J. Qiao, X. Kong, Z.-X. Hu, F. Yang, and W. Ji, Nat. Commun. 5, 4475 (2014).
35 B. Radisavljevic and A. Kis, Nat. Mater. 12, 815 (2013).