Large thermoelectric power factor of high-mobility transition-metal dichalcogenides with 1T'' phase

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A great number of studies about monolayer transition metal dichalcogenides in recent years have revealed that this kind of compound has many metastable phases with unique physical properties, not just a 1*H* phase. Here, we focus on the 1*T*" phase, already existing in the experiments, and systematically investigate the electronic structures and transport properties of MX_2 (M = Mo, W; X = S, Se, Te) using first-principles calculations with Boltzmann transport theory. It is found that only three molybdenum compounds have a small direct band gap at the *K* point, which derives from the distortion of octahedral coordination [MoX₆]. Among these three cases, the hole carrier mobility of MoSe₂ is estimated to be as high as 690 cm²/V s at room temperature, far higher than that in the other two MoX₂. For this reason, the combination of the modest carrier effective mass and weak electron-phonon coupling leads to the outstanding transport performance of MoSe₂. The Seebeck coefficient of MoSe₂ is also evaluated to be as high as ~300 μ V/K at room temperature. Due to the temperature-dependent mobility of $T^{-1.9}$ and higher Seebeck coefficient at low temperature, the highest thermoelectric power factor of MoSe₂ is 10.2×10^{-3} W/mK² at 200 K. More importantly, MoSe₂ has a large thermoelectric power factor with a value of ~6.0 × 10^{-3} W/mK² in the temperature range from 100 to 500 K. The present results suggest that 1T'' MoSe₂ has high-performance carrier transport and is an excellent candidate for thermoelectric material.

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I. INTRODUCTION

Since the discovery of two-dimensional (2D) materials, transition metal dichalcogenides (TMDCs) with structural formula MX_2 [1–5] have become particularly interesting due to their semiconducting characteristics with strong stability and large flexibility. Their unique structural, mechanical, optical, electrical, and thermal properties [6,7] indicate potential applications in photovoltaics, transistors, optoelectronics, photodetectors, and molecular sensing [8–16]. The usual crystallographic form of monolayer TMDCs is the hexagonal 1Hphase, whose exciton energy and strong spin-valley coupling provide a novel platform for intriguing nanoelectronic devices [17–21]. Meanwhile, experimental researches have explored other metastable trigonal polymorphic forms with different degrees of structural distortion (1T', 1T'', and 1T''') [22–32] on the basis of the primary 1T phase. In the octahedral crystal field of the 1T phase, 4d orbitals of M atoms are split into e_g orbitals $(d_{x^2-y^2}, d_{z^2})$ over t_{2g} orbitals (d_{xy}, d_{xz}, d_{yz}) , and the partially filled t_{2g} orbitals induce metallic conductivity [4]. In addition, due to the Peierls instability, the distortion

batteries, and supercapacitors [39–41]. Many novel physical properties have also been discovered in the distorted structures. Strong spin-orbital coupling (SOC) makes 1T'TMDCs large-gap quantum spin hall insulators [42–44]. The nontrivial geometry with the trimerization of M atoms in the 1T''' phase leads to ferroelectricity with high carrier mobility simultaneously [23]. In addition, due to the proportional relation between the Seebeck coefficient and the energy derivative of the electronic density of states (DOS) around the Fermi level in the Mott formula [45], low-dimensional materials made of TMDCs have natural advantages in thermoelectric (TE) applications, an important and meaningful crossing point in the fields

of octahedral $[MX_6]$ results in other metastable polymorphs with lower symmetry [33,34], where *M*-*M* associations take

place, such as dimerization (1T') [35] and trimerization (1T'')

and 1T''' [36–38]. The spontaneous symmetry breaking of

structural distortion lifts the degeneracy of electronic states to

lower the energy. In the four metastable structures, the high

electrical conductivity of the metallic 1T phase makes it an

excellent electrocatalyst for hydrogen evolution, rechargeable

of physics, materials, and energy [46–49]. Therefore, more recently people have paid attention to TMDCs in the prospect of thermoelectricity [50–59]. The efficiency of TE materials depends on the dimensionless figure of merit ZT defined as $ZT = \sigma S^2 T/\kappa$. S is the Seebeck coefficient, σ is the electrical conductivity, and T is the absolute temperature. κ is the sum of electronic and lattice thermal conductivities and characterizes the heat leakage. Reaching high ZT has

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remained demanding because of the complicated relationship between these individual parameters, especially the electrical conductivity and Seebeck coefficient. In general, the competition appears between σ and S: a small carrier effective mass favors high σ , but opposes a large S. Hence, the TE power factor (σS^2) is often used to represent the electron energy conversion capability in TE materials. Recently, by using the electric double-layer technique (EDLT) with gate dielectrics of ionic liquids, researchers obtained a TE power factor of $\sim 4 \times 10^{-3}$ W/mK² in ultrathin *H*-phase WSe₂ [55]. Another experiment reports a TE power factor of H-phase MoS₂ as high as 8.5×10^{-3} W/mK² at room temperature [58]. While TE power factor in other experiments of TMDCs is much lower than the above values by two orders of magnitude, which is mainly limited by the low electrical conductivity and leads to poor prospects for TE applications.

As is well known, prevalent TE materials are heavily doped small-band-gap semiconductors [60-62], which can hold the balance between the high Seebeck coefficient of semiconductors and high electrical conductivity of metals. Therefore, in the present work, we focus on the 1T'' phase of transition-metal dichalcogenides with small band gap, such as 0.1 eV in 1T'' MoS₂, caused by the structure distortion. Since carrier doping at a high concentration of EDLT has been successfully used to improve the performance of TMDCs, this work also systematically explores the doping dependence of electronic transport by considering the electron-phonon scattering without chemical impurities. The low hole carrier effective mass and the weak electron-phonon scattering make 1T'' MoSe₂ have high mobility of 690 cm²/Vs at room temperature. Moreover, due to the advantages of small band gap and suitable carrier effective mass on the enhancement of the Seebeck coefficient (300 μ V/K), it is obtained that MoSe₂ has a high TE power factor around $6 \times 10^{-3} \text{ W/mK}^2$ in a larger temperature range (100–500 K).

II. METHODS

In the diffusive transport regime, the phonon-limited electronic transport can be calculated based on the Boltzmann transport equation (BTE). In the consideration of electron-phonon scattering in and out of the state $|n\mathbf{k}\rangle$ ($\varepsilon_{n\mathbf{k}}$), via emission or absorption of phonons ($\omega_{\mathbf{q}\nu}$), the relaxation time $\tau_{n\mathbf{k}}^{0}$ is associated with the imaginary part of the Fan-Migdal electron self-energy [63], defined by [64]

$$\frac{1}{\tau_{n\mathbf{k}}^{0}} = \frac{2\pi}{\hbar} \sum_{m\nu} \int \frac{d\mathbf{q}}{\Omega_{\mathrm{BZ}}} |g_{mn\nu}(\mathbf{k},\mathbf{q})|^{2} \\
\times \left[\left(1 - f_{m\mathbf{k}+\mathbf{q}}^{0} + n_{\mathbf{q}\nu}\right) \delta(\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}+\mathbf{q}} - \hbar\omega_{\mathbf{q}\nu}). \\
+ \left(f_{m\mathbf{k}+\mathbf{q}}^{0} + n_{\mathbf{q}\nu}\right) \delta(\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}+\mathbf{q}} + \hbar\omega_{\mathbf{q}\nu}) \right], \quad (1)$$

where Ω_{BZ} is the volume of the first Brillouin zone and f and n are the Fermi-Dirac and Bose-Einstein distribution functions, respectively. In Eq. (1), The electron-phonon coupling (EPC) matrix elements $g_{mn\nu}(\mathbf{k}, \mathbf{q})$ are the probability amplitudes for scattering from an initial electronic state $|n\mathbf{k}\rangle$ into a final state $|m\mathbf{k} + \mathbf{q}\rangle$ via a phonon $|\mathbf{q}\nu\rangle$, as obtained from density-functional perturbation theory (DFPT) [63–65].

In the self-energy relaxation time approximation (SERTA) [64], the electron carrier mobility takes the form

$$\mu_e = \frac{-e}{n_e \Omega} \sum_{n \in CB} \int \frac{d\mathbf{k}}{\Omega_{BZ}} \frac{\partial f_{n\mathbf{k}}^0}{\partial \varepsilon_{n\mathbf{k}}} v_{n\mathbf{k}} v_{n\mathbf{k}} \tau_{n\mathbf{k}}^0, \qquad (2)$$

where $v_{n\mathbf{k}}$ is the group velocity of electronic state $|n\mathbf{k}\rangle$ and Ω is the volume of the crystalline unit cell. Based on the relaxation time $\tau_{n\mathbf{k}}^{0}$, the TE transport parameters (σ and S) as functions of the chemical potential μ and of the temperature T are the following expressions [66,67]:

$$\sigma = e^2 \int \Xi(\varepsilon) \left(-\frac{\partial f^0}{\partial \varepsilon} \right) d\varepsilon, \tag{3}$$

$$S = \frac{e}{\sigma} \int \Xi(\varepsilon) \left(-\frac{\partial f^0}{\partial \varepsilon} \right) \frac{\varepsilon - \mu}{T} d\varepsilon, \tag{4}$$

where $\Xi(\varepsilon)$ is the transport distribution function, defined as $\Xi(\varepsilon) = \sum_{n,\mathbf{k}} v_{n\mathbf{k}} v_{n\mathbf{k}} \tau_{n\mathbf{k}}^0 \delta(\varepsilon - \varepsilon_{n\mathbf{k}}) / \Omega.$

The above quantitative values of the electronic transport with electron-phonon scattering can be evaluated with selfconsistent first-principles calculations. The technical details of the calculations are as follows. All calculations in this work were carried out in the framework of density-functional theory (DFT) as implemented in the QUANTUM ESPRESSO package [68]. The exchange and correlation energy was in the Perdew-Burke-Ernzerhof (PBE) form [69]. Due to the existence of heavy transition metal elements, the fully relativistic SOC was included in all calculations. By requiring a convergence of results, a kinetic-energy cutoff of 40 Ry and a Monkhorst-Pack k mesh of $16 \times 16 \times 1$ were used in the calculations dealing with the electronic ground-state properties. The phonon spectra were calculated on a $4 \times 4 \times 1$ q grid in DFPT. To obtain a stable structure, the atomic positions were relaxed fully with the energy convergence criterion of 10^{-5} Ry and the force convergence criterion of 10^{-4} Ry/a.u. In the monolayer structure, a vacuum layer with 15 Å was set to avoid interactions between adjacent atomic layers. Moreover, in order to define the volume for 2D materials in the study of transport properties, the nominal layer thicknesses h =6.60, 6.78, and 7.30 Å were used for MoS_2 , $MoSe_2$, and MoTe₂, respectively, corresponding to the half thickness of van der Waals bulk structures. Within the EPW code [70] of QUANTUM ESPRESSO in conjunction with WANNIER90 [71,72], EPC was calculated on a $40 \times 40 \times 1$ q grid and dense k points of $160 \times 160 \times 1$ by the Wannier-Fourier interpolation technique of maximally localized Wannier functions [73,74]. Due to the nonzero Born effective charge tensors in polar MX_2 , polar longitudinal optical (LO) phonons could couple to electrons by the Fröhlich interaction [75–79]. The EPC in the present work also included the Fröhlich correction [80-84]. The above method has been applied to many semiconductors, such as cubic III-V compounds, halide perovskites, and twodimensional materials [80–87].

III. RESULTS

According to the previous experimental results [22-32], there are mainly three distorted phases from the 1*T* phase (space group *P*-3*m*1). The symmetric structures lower than 1*T* can be classified into two cases: dimeric structure 1*T*'



FIG. 1. (a) Total energy of different monolayer structures relative to the 1*H* phase. Crystal structure diagrams of 1*T* (b), 1*T'* (c), 1*T''* (d), and 1*T'''* (e). The black box shows the periodically repeated unit in this work and the red arrows mark the displacement vectors of distorted phases relative to the 1*T* phase. The distorted 1*T'*, 1*T''*, and 1*T'''* phases correspond to dimerization, trimerization, and trimerization of Mo atoms, respectively. In the 1*T''* phase, the equilibrium lattice constant a_0 is 6.44 Å. The Mo atoms are divided into two categories: three trimeric Mo atoms, Mo₃ (green circles), and another single Mo atom, Mo₁ (blue circle).

(space group $P2_1/m$) and trimeric structures 1T'' (space group P3) and 1T''' (space group $P3_1m$), as shown in Fig. 1. The Peierls distortions of the prototypical 1T phase in one direction and two directions along lattice vectors lead to the dimerization (1T') and trimerization (1T'') of nearest-neighboring transition-metal atoms [25], respectively. The K_3 distortion [37], a small rotary polymerization of three nearest-neighboring Mo atoms, leads to a lower symmetry cell tripled 1T'''' structure. In a case study of MoS₂, the total energy difference relative to the 1H phase shows that 1T and 1T' phases have the highest and lowest total energy in the metastable phases, respectively, when two trimeric structures have similar total energy. The equilibrium lattice constant ($a_0 = 6.44$ Å) of 1T'' MoS₂ agrees well with the previous studies [25,29]. In the

TABLE I. Equilibrium lattice constant (a_0) , band gap (E_{gap}) , and carrier effective mass (m^*) of MoS₂, MoSe₂, and MoTe₂.

	MoS_2	MoSe ₂	MoTe ₂
$\overline{a_0}$ (Å)	6.44	6.68	7.11
$E_{\rm gap}$ (eV)	0.10	0.12	0.16
$m_{h}^{*}(m_{0})$	0.227	0.535	0.707
$m_e^*(m_0)$	0.303	0.937	0.872
	WS_2	WSe ₂	WTe ₂
$\overline{a_0}$ (Å)	6.50	6.71	7.13
$E_{\rm gap}~({\rm eV})$	metal	metal	0.03
$m_{h}^{*}(m_{0})$			0.566
$m_e^*(m_0)$			0.437

1T'' phase, it is found that the interatomic distance (2.77 Å) of three Mo atoms is much shorter than that in the 1T phase (3.22 Å), labeled Mo₃ for simplicity [Fig. 1(d)]. Another one-Mo atom (labeled Mo₁) has little deviation relative to the corresponding Mo atom in the 1T phase. Moreover, the heavy chalcogens elongate a_0 significantly, accompanied by a slight bigger space between the *X* atomic layer and the Mo atomic layer, because of the increasing ionic radius. While the ionic radius of Mo is almost identical to that of W, the change of a_0 induced by W is much smaller than the effect of heavy chalcogens (see Table I).

Because the small band gap [26] of MoS_2 in the 1T'' phase is advantageous for thermoelectricity, here we mainly study 1T'' phase MX_2 (M = Mo, W; X = S, Se, Te). All MX_2 in the following text, in the absence of special mention, are 1T'' phase. As shown in Fig. S1 of the Supplemental Material [88], The band structures indicate that the three MoX_2 all have direct band gaps at the K point, while only WTe₂ among the three WX_2 is a semiconductor, with a very small indirect band gap of 0.03 eV (see Table I). In the valence band, there is a second energy maximum (Γ_v) at the Γ point for all MX_2 , closing to a valence band maximum (VBM) with small energy difference. The second energy minimum of the conduction band at the Γ point (Γ_c) exists only in MoS₂ and WS₂. The stronger SOC of heavy transition-metal atoms also generates a larger spin splitting at both conduction band minimum (CBM) and VBM.

Now we analyze the source for the bandgap in 1T'' phase according to the projected band structure of MoS_2 (see Fig. 2). CBM and VBM are mainly composed of Mo atomic orbitals, while there are only S atomic orbitals at Γ_c [Fig. 2(a)]. The short interatomic distance of trimeric Mo3 results in a short Mo₃-S bonding length as well as the large energy difference between the bonding states and antibonding states of Mo_3-4d orbitals. The distribution of Mo_3 -4d orbitals is far away from CBM and VBM, which are actually the contribution from the Mo₁-4d orbitals, as shown in Fig. 2(b). According to a comparison between the distorted octahedral [Mo₁S₆] in the 1T'' phase and O_h -[MoS₆] in the 1T phase [Fig. 2(d)], it is found that the angles between paraposition Mo₁-S bonds θ is 175° of the 1T'' phase, different from 180° of the 1T phase, and the six Mo₁-S bond lengths of the 1T'' phase do not have the same value. These small distortions break the double degeneration of e_g orbitals $(d_{x^2-y^2}, d_{z^2})$ in the metallic 1T



FIG. 2. (a) Projected band structure of Mo and S atoms in 1T'' MoS₂. (b) Projected band structure of Mo₁ and Mo₃ atoms. (c) Projected band structure of different orbitals of the Mo₁ atom. (d) The building of [Mo₁S₆] in 1*T* and 1*T''* MoS₂. The angles between paraposition Mo₁-S bonds (θ) are 180° and 175° in 1*T* and 1*T''* phases, respectively.

phase and produce the small band gap [Fig. 2(c)]. For the case of heavy chalcogens, X atoms move backward the Mo atoms slightly, which strengthens the interaction between the X-pand Mo₁- d_{z^2} orbitals and weakens the interaction between the X-p and Mo₁- $d_{x^2-y^2}$ orbitals. This leads to the higher bonding state of $d_{x^2-y^2}$ (CBM), the lower bonding state of d_{z^2} (VBM), and the rise of Γ_c . Hence, a bigger band gap exists in the cases of heavier chalcogens (see Table I). In addition, the space between the W atomic layer and the X atomic layer is smaller than that in MoX₂, so the effect of the W atom is contrary to that of the heavy chalcogens and makes WX₂ have very small band gap, even being metal.

To ensure the dynamic stability of the 1T'' phase, the phonon spectra of MX_2 are calculated, as shown in Fig. S1 of the Supplemental Material [88], and the imaginary frequency only presents in WSe₂. The quadratic energymomentum relation is also found in the ZA mode around Γ point, similarly to many 2D materials [89]. Because the Γ point in the 1T" phase has symmetry of the C_{3v} (3m) point group, 33 optical phonon modes can be decomposed by three irreducible representations: A_1 (8 modes), A_2 (3 modes), and E (11 double degenerate modes). With the increase of atomic mass, the highest phonon frequency decreases clearly, to 448.6 cm⁻¹ for MoS_2 and 235.8 cm⁻¹ of WTe₂. The greater proportion of chalcogens in MX_2 also gives rise to the more obvious changes in phonon frequency with the different chalcogens. Besides, when the mass ratio between M and X atoms becomes small, the frequency gap between acoustic phonons and optic phonons is closed gradually, as shown in Fig. S1 of the Supplemental Material [88]. Moreover, in order to show

the effect of doping on stability in the present work, we also recalculate the phonon spectra of different doping concentrations, which is realized by increasing the valence charge and at the same time introducing the same amount of uniform background charge. In this condition, the phonon spectra with the increasing doping concentration have little change, as shown in Fig. S3 of the Supplemental Material [88]. So the invariable phonon spectra in the following calculation of EPC with the EPW code are reasonable.

For the stable semiconductor MX_2 with a suitable band gap, the carrier doping and temperature dependences of the mobility in MoX₂ (X = S, Se, Te) are investigated with the consideration of electron-phonon scattering. It is first found that m_h^* is lighter than m_e^* of MoX₂ (see Table I) and m_h^* increases with the atomic number of chalcogens. By contrast, WTe₂ has a heavier m_h^* than m_e^* , because the VBM locates at the Γ point, rather than the K point as in MoX₂. The effective mass indicates that the next study could be focused on the hole carrier transport properties of MoX_2 . To facilitate analysis of the relative contribution of phonons with different frequencies to EPC, the transport spectral function $\alpha_{tr}^2 F(\omega)$ [90,91] is obtained by the phonon self-energy in the doped semiconductor. Figure 3(a) plots $\alpha_{tr}^2 F(\omega)$ of MoX₂ with $n_{2D}^h = 2 \times 10^{12}$ cm⁻² and shows that the peak intensities of $\alpha_{tr}^2 F(\omega)$ in MoS₂ are higher than those in the other two cases, and MoSe₂ has the lowest value in the whole spectrum space. Of particular note are the low-frequency region around 40 cm^{-1} and intermediate-frequency region around 200 cm^{-1} . In the former, MoS₂ and MoTe₂ have strong EPC, which is almost absent from MoSe₂. In the latter, the peak value of MoS_2 is much higher than that in $MoSe_2$ and $MoTe_2$. From the above, the weakest EPC of MoSe₂ means few electron-phonon scattering processes, which is to the benefit of high-performance carrier transport. As shown in Fig. 3(b), the room-temperature hole carrier mobilities of MoS₂, MoSe₂, and MoTe₂ are 42, 690, and 176 cm^2/V s, respectively, at the low carrier concentration. The low electron carrier mobilities are also plotted in the inset as a contrast. It is important that the hole carrier mobility of MoSe₂ is much higher than that of 1H TMDCs in experiments and predicted calculations with the electron-phonon scattering [15,16,86,92–97]. The data can be rationalized simply by the elementary Drude model [98]. The relation of carrier mobility (μ) , effective mass (m^*) and relaxation time (τ) is expressed as $\mu = e\tau/m^*$.

First, the influence of effective mass on the carrier mobility is mainly reflected in the lower electron carrier mobilities with heavier electron carrier effective mass than that of hole carrier in the three materials [Fig. 3(b)].

Second, the reciprocal of carrier relaxation time $(1/\tau)$ is approximately proportional to the EPC strength and to the DOS. The increasing DOS of the Fermi level appears at the high carrier concentrations and enhances EPC slightly, as shown by the phonon linewidths in Figs. 4(a) and 4(b). Consequently, the carrier mobilities for all cases have a downward trend versus the carrier concentration. The EPC of electron doping is only slightly stronger than EPC of hole doping, while the main region of large phonon linewidths has little change (Fig. 4 and Fig. S2 of the Supplemental Material [88]) because of the similar band-edge structures around VBM and CBM.



FIG. 3. (a) Transport spectral function $\alpha_{tr}F(\omega)$ of MoS₂, MoSe₂, and MoTe₂ with hole carrier concentration $n_{2D}^{h} = 2 \times 10^{12}$ cm⁻². (b) The hole carrier mobilities of MoS₂, MoSe₂, and MoTe₂ vary with the carrier concentration at room temperature. Inset: The electron carrier mobilities of MoS₂, MoSe₂, and MoTe₂. (c) The hole and electron carrier mobilities of MoSe₂ vary with the temperature at the carrier concentration $n_{2D} = 2 \times 10^{12}$ cm⁻².

Third, the highest hole carrier mobility of MoSe₂ in all cases should comprehensively suggest the important roles of carrier relaxation time and effective mass. The order of EPC from weakest to strongest is MoSe₂ < MoTe₂ < MoS₂, as shown by $\alpha_{tr}F(\omega)$ in Fig. 3 and phonon linewidths in Fig. 4. Thereby medium carrier effective mass and the weak EPC result in the much higher hole carrier mobility of MoSe₂ than the other cases. Furthermore, phonon concentration has a positive correlation relationship with temperature, thus the high temperature causes increased EPC, as the mobility of $MoSe_2$ declines with the increase of temperature [Fig. 3(c)]. The temperature-dependent hole carrier mobilities of MoX_2 (X = S, Se, Te) are fitted to be proportional to $T^{-2.0}, T^{-1.9}$, and $T^{-1.9}$, respectively. Deeper analysis of phonon linewidths reveals that acoustical phonons of the three materials have in common large phonon linewidths around the K point. K momentum phonons can assist the intervalley electronic transition process from K to K valleys in the first Brillouin zone,



FIG. 4. (a) Phonon spectra and phonon linewidths of $MoSe_2$ at $n_{2D}^h = 1.0 \times 10^{12} \text{ cm}^{-2}$, (b) $MoSe_2$ at $n_{2D}^h = 4.0 \times 10^{12} \text{ cm}^{-2}$, (c) MoS_2 at $n_{2D}^h = 1.0 \times 10^{12} \text{ cm}^{-2}$, and (d) $MoTe_2$ at $n_{2D}^h = 1.0 \times 10^{12} \text{ cm}^{-2}$. The magnitude of the phonon linewidth is indicated by the size of the red error bar. The blue arrows mark the polar LO phonon modes in the three materials separately.

similar to the intervalley scattering in $1H \text{ MoS}_2$ [86,92–95]. In addition, it is found that the phonon linewidths of MoS₂ are much larger than those of MoSe₂ and MoTe₂, in coordination with the above analysis of $\alpha_{tr}F(\omega)$. The coupling between polar LO phonon modes (blue arrows in Fig. 4) and electrons in MoS₂ is also much stronger than in the other two materials. As a consequence, Fröhlich correction of MoS₂ is the most conspicuous and makes the hole carrier mobility of $n_{2D}^h =$ 2.0×10^{12} cm⁻² at 300 K drop from 55 to 42 cm²/V s, while the variation range of hole carrier mobilities in MoSe₂ and MoTe₂ is about 10% with the Fröhlich correction, similar to the small Fröhlich correction on carrier scattering in the previous works about TMDCs [92,94]. In order to distinguish the contributions of different phonon modes to the carrier scattering, we also show the scattering rates near the VBM of MoSe₂ in Fig. 5. Thirty-six modes are split into three groups: the 12 lowest-frequency modes (denoted by Group-1 for simplicity), 12 medium-frequency modes (Group-2), and the 12 highest-frequency modes (Group-3). Obviously, the phonons of Group-1 contribute to the main scattering rates. Through the comparison of the scattering rates from different



FIG. 5. The total electron scattering rates below the VBM at 300 K. The energy of the VBM is set to be zero. The scattering rates of the three groups of phonons are also shown.

phonon modes in Group-1 (Fig. S5 of the Supplemental Material [88]), it is found that the ZA mode contributes the highest scattering rates, and is also present in MoS₂ (Fig. S8 of the Supplemental Material [88]) and many 2D materials without horizontal mirror symmetry [99]. The LA mode and the optical modes around 132 cm⁻¹ (denoted by O_7 and O_8 for simplicity) also have high scattering rates near the VBM, being consistent with the large linewidths around the *K* point (Fig. 4), while the scattering rates of O_7 and O_8 are also high in MoS₂ (Fig. S8 of the Supplemental Material [88]). In addition, the scattering rates from LO modes in MoSe₂ are much smaller than those in MoS₂ (Figs. S6 and S8 of the Supplemental Material [88]).

According to Eqs.(3) and (4), the electrical conductivity σ and Seebeck coefficient S of MoSe₂ are calculated with the relaxation time of electron-phonon scattering. The proportionality between σ and $n_{2D}*\mu$ (* indicates multiplication) derives from the ascending curve of σ with carrier concentration and low σ at high temperature [Fig. 6(a)]. The hole-doping Seebeck coefficients as functions of carrier concentration at different temperatures are also plotted in Fig. 6(b). The results show that MoSe₂ has a large Seebeck coefficient, and the maximum values of S, 422 μ V/K at 100 K to 205 μ V/K at 500 K, shift to high doping concentration and decrease with increasing temperature, similar to the previous results of *H*-phase TMDCs [100,101]. At room temperature, *S* of 300 μ V/K with $n_{2D}^h = 1 \times 10^{12}$ cm⁻² catches up to and even surpasses the experimental values of many 2D materials [55,58,102-108]. In the Mott formula [45], hole doping S of a semiconductor is inversely proportional to doping concentration (in direct proportion to the chemical potential). However, the small band gap easily causes a bipolar effect at low doping concentration [102], which makes S proportional to doping concentration and causes the sign reversal of S with increasing negative contribution of thermally excited electrons at low doping concentration. Then it is obtained that the TE power factor σS^2 has a large value in the temperature range from 100 to 500 K [Fig. 6(c)]. The highest value of 10.2×10^{-3} W/mK² with $n_{2D}^{h} = 2 \times 10^{12}$ cm⁻² appears at 200 K.



FIG. 6. (a) Electrical conductivity σ , (b) Seebeck coefficient *S*, and (c) TE power factor σS^2 vary with the hole carrier concentration at different temperatures. σ is proportional to n_{2D} and inversely proportional to *T*. The peak value of *S* is inversely proportional to *T* and shifts to high n_{2D} with the increase of *T*.

More importantly, the maximal TE power factors in a large range of temperature can stay around $\sim 6.0 \times 10^{-3}$ W/mK², well above the experimental measurements of intrinsic TE power factor in the vast majority of TMDCs and some classic TE materials, such as SnSe ($\sim 4 \times 10^{-3}$ W/mK² at 300 K), Bi₂Te₃ ($\sim 3.5 \times 10^{-3}$ W/mK² at 300 K), and PbTe ($\sim 2.5 \times 10^{-3}$ W/mK² at 500 K) [107–110]. This indicates 1*T*″-phase MoSe₂ as a high-performance candidate TE material.

Inspired by the similar effects of heavy chalcogens and compressive strain, which both lead to the increase of



FIG. 7. Band structure of MoSe₂ under compressive strain of $\epsilon = -2.0\%$. The band gap slightly increases from 0.12 eV of $\epsilon = 0.0\%$ to 0.19 eV of $\epsilon = -2.0\%$, and the energy difference between VBM and Γ_v almost disappears.

monolayer thickness and impact the interaction between Mo-4d and Se-p orbitals [111], we also expect and study the effect of small compressive strain, $\epsilon = (a - a_0)/a_0 \times 100\% \leq$ -2.0%, on the TE transport property of MoSe₂, in order to enhance the band gap as well as the temperature range of thermoelectric application. In the band structure with $\epsilon =$ -2.0% (see Fig. 7), the band gap increases to 0.19 eV due to the enhanced layer thickness under compressive strain. In addition, the hole carrier effective mass m_h^* is light, 0.488 m_0 . But it is worth noting that the energy difference between Γ_v and VBM almost disappears, which may produce the intervalley scattering processes between Γ and K valleys. Consequently, the introduction of small compressive strain makes the hole carrier mobility drop [Fig. 8(a)]. As shown in Figs. 8(b) and 8(c), the bigger band gap under small compressive strain pushes the highest value of the TE power factor to higher temperature, but it also happens that the overall decrease of TE power factor $(1-3 \times 10^{-3} \text{ W/mK}^2)$ and the peak values occur at the high doping concentrations ($\geq 2 \times 10^{12} \text{ cm}^{-2}$).

IV. CONCLUSION

In summary, by using the first-principles calculations with Boltzmann transport theory, we have studied systematically the physical properties of the metastable monolayer 1T'' phase of MX_2 , including electronic structure, EPC, carrier mobility, and TE power factor. The small direct band gap at the *K* point of three molybdenum compounds is attributed to the distorted octahedral coordination of [MoX₆]. The lighter hole carrier effective mass indicates higher carrier mobility than electron



FIG. 8. (a) The hole carrier mobilities of MoSe₂ vary with the carrier concentration under four compressive strains (-0.5%, -1.0%, -1.5%, and -2%). TE power factor σS^2 varies with the hole carrier concentration under compressive strains of (b) $\epsilon = -0.5\%$ and (c) $\epsilon = -2.0\%$.

carrier mobility when a small difference of EPC presents between two types of doping in the three MoX_2 . The results about EPC show that MoS_2 and $MoSe_2$ have the strongest and weakest EPC, respectively. Also, the intervalley scattering between K and K valleys, assisted by K-momentum phonons, has a great contribution to the electron-phonon scattering in all three MoX_2 , while the Fröhlich correction in MoS_2 has a much higher effect than the others. Therefore, the medium carrier effective mass and the extremely weak EPC of MoSe₂ give rise to its high hole carrier mobility of $690 \text{ cm}^2/\text{V}$ s at 300 K, which is far higher than that in the 1H TMDCs. Combining the Seebeck coefficient around 300 μ V/K, it is obtained that the TE power factor of $MoSe_2$ remains around $6.0 \times$ 10^{-3} W/mK² in a large range of temperature (100–500 K). In addition, the bigger band gap under the small compressive strain can enhance the temperature range of thermoelectric application, although the TE power factor is slightly below the strainless case. The present results illustrate the highperformance carrier transport and the outstanding potential of 1T'' MoSe₂ in TE materials.

For a thermoelectric material, the low thermal conductivity is essential. In the equation of ZT, κ is total thermal conductivity including electronic (κ_e) and lattice (κ_{latt}) contributions, while the very small electronic thermal conductivity κ_e is neglected in semiconductors generally. Here, the lattice thermal conductivity κ_{latt} of 1T'' MoSe₂ is calculated in the simple Slack equation [112–114], which assumes that only the acoustic phonon modes participate in the heat conduction process. Two key parameters, Debye temperature and Grüneisen parameter, are directly proportional to and inversely proportional to κ_{latt} (see Supplemental Material). As shown in Fig. S4 of the Supplemental Material [88], the small Grüneisen parameter γ of ~0.56 at room temperature is simulated with the PHONOPY code [115,116] and illustrates the weak anharmonic interaction. But the low frequencies of acoustical phonons (Fig. S1 of the Supplemental Material [88]) make 1T'' MoSe₂

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have low Debye temperature. The obtained lattice thermal conductivity at room temperature is 10.7 Wm⁻¹K⁻¹ (Fig. S4 of the Supplemental Material [88]). Also, the dimensionless figure of merit ZT of 1T'' MoSe₂ is estimated as ~0.2, which indicates its TE application potential.

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