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# Simultaneous enhancement of power factor and suppression of thermal conductivity in bulk $\text{TlFe}_{1.6}\text{Se}_2$ via embedded atomically thin FeSe layers

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FeSe in the monolayer limit exhibits extremely large thermoelectric power factors (PFs). Extending the high-PF concept from two-dimensional FeSe to bulk materials, together with the suppression of lattice thermal conductivity, enables higher-performance thermoelectrics. Here, layered  $\text{TlFe}_{1.6}\text{Se}_2$  is identified as a model system consisting of atomically thin two-dimensional FeSe layers separated by Tl atoms; *i.e.*, FeSe monolayers are naturally confined within a bulk crystal. This compound uniquely exhibits a transition from Fe-vacancy ( $V_{\text{Fe}}$ )-ordered to-disordered states at around 200 °C. Although the  $V_{\text{Fe}}$ -disordered phase exhibits high electrical conductivity, carrier compensation suppresses the Seebeck coefficient and limits PF. In contrast, the  $V_{\text{Fe}}$ -ordered phase shows an enhanced Seebeck coefficient associated with Mott gap formation, resulting in improved PF which is much higher than that of bulk FeSe. The lattice thermal conductivity of the  $V_{\text{Fe}}$ -ordered phase is lower than that of representative thermoelectric chalcogenides and that of the  $V_{\text{Fe}}$ -disordered phase further decreases to  $\sim 0.2 \text{ W (m}^{-1} \text{ K}^{-1})$  at 500 °C due to the  $V_{\text{Fe}}$ -induced bond heterogeneity. Consequently, the dimensionless figure of merit ( $ZT$ ) of  $\text{TlFe}_{1.6}\text{Se}_2$  reaches  $\sim 0.2$  at 50 °C in the  $V_{\text{Fe}}$ -ordered phase, which is two orders of magnitude higher than that of bulk FeSe. These results demonstrate that confining FeSe monolayers within a bulk crystal, alongside vacancy order-disorder control, is an effective design strategy for next-generation thermoelectrics.

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## 1 Introduction

Thermoelectric energy conversion is considered a promising renewable technology for converting waste heat into electricity *via* the Seebeck effect.<sup>1–3</sup> The energy-conversion efficiency of thermoelectric materials is governed by the dimensionless figure of merit ( $ZT$ ), defined as  $ZT = S^2\sigma T/\kappa$ , where  $S$  is the Seebeck coefficient,  $\sigma$  is the electrical conductivity,  $T$  is the absolute temperature, and  $\kappa$  is the thermal conductivity. The electrical output power is given by  $S^2\sigma$ , known as the power factor (PF), and  $\kappa$  includes the electronic thermal conductivity ( $\kappa_{\text{ele}}$ ) and lattice thermal conductivity ( $\kappa_{\text{lat}}$ ). Achieving a high  $ZT$  requires simultaneously attaining a large  $S$  and high  $\sigma$  while minimizing  $\kappa$ . However, this requirement is fundamentally

constrained by well-known trade-offs among these parameters. For example,  $\sigma$  and  $S$  exhibit an inverse dependence on the carrier concentration ( $n$ ): increasing  $n$  enhances  $\sigma$  but reduces  $S$ , resulting in a maximum PF at an optimal  $n$ . Moreover, increasing  $\sigma$  typically raises  $\kappa_{\text{ele}}$  according to the Wiedemann–Franz law ( $\kappa_{\text{ele}} = L\sigma T$ , where  $L$  is the Lorenz number). Owing to this intricate interdependence of transport properties, realizing thermoelectric materials with high  $ZT$  remains a major challenge.<sup>4</sup> In contrast,  $\kappa_{\text{lat}}$  is largely independent of these electronic transport parameters, and materials with intrinsically low  $\kappa_{\text{lat}}$  are therefore well suited for achieving high  $ZT$ .

Recently, a giant PF has been reported in ultra-thin films of layered FeSe,<sup>5</sup> one of the high-critical-temperature ( $T_c$ ) Fe-based superconductors.<sup>6</sup> Ultra-thin FeSe film grown on the  $\text{SrTiO}_3$  substrate has attracted considerable research attention because it exhibits superconductivity with  $T_c$  up to 100 K,<sup>7</sup> dramatically higher than the bulk  $T_c$  of  $\sim 9$  K. When the film thickness is reduced to  $\sim 1$  nm,  $\sigma$  increases due to interface-induced carrier doping from the  $\text{SrTiO}_3$  substrate, while  $S$  also increases due to the enhanced two-dimensionality and electron correlation effects. As a result, the PF reaches  $260 \mu\text{W (cm}^{-1} \text{ K}^{-2})$ , a value much higher than that of practical  $\text{Bi}_2\text{Te}_3$  at room temperature (RT).<sup>5</sup> Furthermore, the PF of ultra-thin FeSe increases to  $13\,000 \mu\text{W (cm}^{-1} \text{ K}^{-2})$  at a reduced temperature of 50 K. Assuming  $\kappa \approx$

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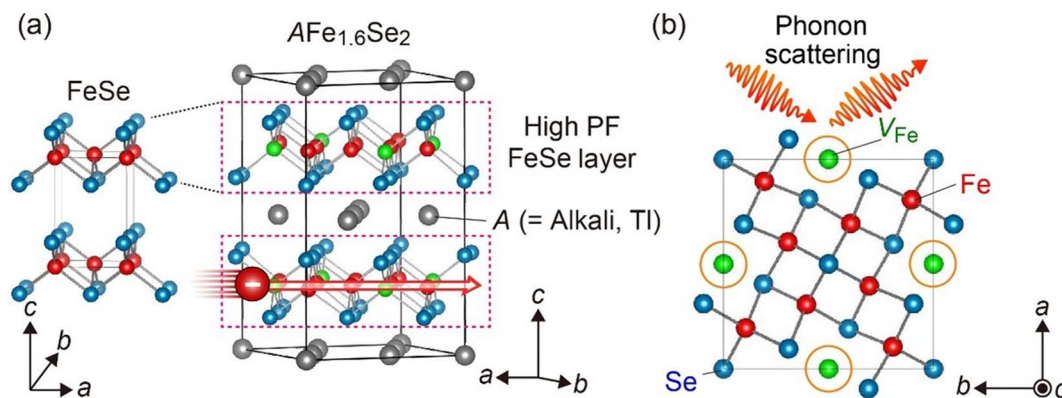


Fig. 1 Crystal structure of the layered  $A\text{Fe}_{1.6}\text{Se}_2$  ( $A$  = alkali metals and Tl) with an Fe-vacancy ( $V_{\text{Fe}}$ ) ordered structure, viewed along the (a) [120] and (b) [001] directions. The spheres represent the Tl (gray), Fe (red), Se (blue) atoms, and  $V_{\text{Fe}}$  sites (green). The structure consists of FeSe layers, crystallographically equivalent to the high-power-factor (PF) FeSe monolayers, sandwiched by the A-ion layers. The Fe sites intrinsically host  $V_{\text{Fe}}$ , which undergo an order–disorder transition upon heating to  $\sim 500$  K, which is expected to enhance phonon scattering. The coexistence of FeSe layers with intrinsic  $V_{\text{Fe}}$  defects is expected to enable a high PF, together with low lattice thermal conductivity.

$5 \text{ W (m}^{-1} \text{ K}^{-1})$ , similar to bulk Fe-based superconductors,<sup>8,9</sup> the  $ZT$  of the ultra-thin FeSe is estimated to be  $\sim 1.5$  at 280 K. However, the excellent PF and  $ZT$  values appear only in the ultra-thin limit, which makes these films unsuitable for thermoelectric power generation. It would therefore be more interesting to achieve such a high PF throughout the bulk phase of FeSe. In addition, FeSe has been reported to exhibit a relatively high  $\kappa_{\text{lat}} \approx 4.5 \text{ W (m}^{-1} \text{ K}^{-1})$  at RT in polycrystalline samples,<sup>10</sup> which is nearly three times higher than that of  $\text{Bi}_2\text{Te}_3$ .<sup>11</sup> Therefore, reducing the  $\kappa_{\text{lat}}$  in FeSe is also crucial for realizing its potential as a high-performance thermoelectric material.

To overcome the limitations of ultra-thin FeSe, we herein focus on a layered  $A_{1-x}\text{Fe}_{2-y}\text{Se}_2$  ( $A$  = alkali metals and Tl), which can be regarded as a natural bulk analogue of FeSe monolayers. This compound crystallizes in a tetragonal  $\text{ThCr}_2\text{Si}_2$ -type structure composed of alternately stacked FeSe layers and A-ion layers along the  $c$ -axis (Fig. 1a).<sup>12</sup> This crystal structure intrinsically contains atomically thin FeSe monolayers within a bulk crystal. The FeSe layers in  $A_{1-x}\text{Fe}_{2-y}\text{Se}_2$  possess an identical crystal lattice to that of FeSe, in which Fe atoms form a square lattice and Se atoms occupy apical positions of the edge-shared  $\text{FeSe}_4$  tetrahedra. The thickness of the FeSe layer in  $\text{TlFe}_{1.6}\text{Se}_2$  is  $\sim 3.0 \text{ \AA}$ , corresponding to a single FeSe slab, which is significantly thinner than the  $\sim 1 \text{ nm}$  minimum thickness reported for ultrathin FeSe films.<sup>5</sup> Notably, the Fe sites intrinsically contain vacancies ( $V_{\text{Fe}}$ ), forming a  $\sqrt{5} \times \sqrt{5} \times 1$  supercell of the  $\text{ThCr}_2\text{Si}_2$ -type structure (Fig. 1b). Upon heating, the arrangement of  $V_{\text{Fe}}$  undergoes a transition between the ordered and disordered states at  $\sim 500$  K. Theoretical calculations have suggested that the  $V_{\text{Fe}}$ -ordered  $A_{1-x}\text{Fe}_{2-y}\text{Se}_2$  is a Mott insulator with a Mott gap of  $\sim 100 \text{ meV}$ ,<sup>13,14</sup> and the gap has been experimentally confirmed to be  $\sim 430 \text{ meV}$ .<sup>15</sup> The  $V_{\text{Fe}}$ -ordered Mott insulator phase also exhibits long-range antiferromagnetic (AFM) order with a Néel temperature as high as 470–560 K.<sup>12</sup> In contrast, by tuning deficiencies at the A site and the Fe site,  $A_{1-x}\text{Fe}_{2-y}\text{Se}_2$  can

exhibit superconductivity with  $T_c = 30 \text{ K}$ .<sup>16,17</sup> Note that the electronic transport in  $A_{1-x}\text{Fe}_{2-y}\text{Se}_2$  is mainly governed by FeSe layers, where the electronic states near the Fermi level are dominated by Fe 3d orbitals.<sup>14</sup> As a result, the contribution of A-site ions to the electron transport is relatively limited. Based on these characteristics,  $A_{1-x}\text{Fe}_{2-y}\text{Se}_2$  is expected to exhibit a high PF owing to its two-dimensional FeSe layers naturally embedded within the bulk crystal. In particular, strong electron correlation may lead to an enhanced  $S$ , while the presence of the ordered and disordered  $V_{\text{Fe}}$  defects is expected to promote phonon scattering and thereby reduce  $\kappa_{\text{lat}}$ .

In this study, we investigate the electronic and phonon transport properties of bulk polycrystalline layered  $\text{TlFe}_{1.6}\text{Se}_2$  as a model system to clarify the effectiveness of embedded two-dimensional FeSe layers in enhancing thermoelectric performance. This compound is much more stable in air than the other  $A_{1-x}\text{Fe}_{2-y}\text{Se}_2$  phases ( $A = \text{K, Rb, and Cs}$ ),<sup>18</sup> and a fully  $V_{\text{Fe}}$ -ordered phase with high chemical homogeneity can be obtained due to the lower vapor pressure of Tl compared with those of alkali metals.<sup>19</sup> We demonstrate that the PF of  $\text{TlFe}_{1.6}\text{Se}_2$  is significantly higher than bulk FeSe; furthermore,  $\text{TlFe}_{1.6}\text{Se}_2$  exhibits an exceptionally low  $\kappa_{\text{lat}}$ , with both the electronic and phonon transport properties strongly modulated by the  $V_{\text{Fe}}$  ordering and disordering, resulting in an enhanced  $ZT$ .

## 2 Synthesis and characterization

### 2.1 Synthesis

FeSe was synthesized by a solid-state reaction using Fe powder (purity: 99.999%, Kojundo Chemical Lab.) and Se powder (purity: 99.999%, Kojundo Chemical Lab.), mixed at the molar ratio of Fe : Se = 1 : 1. The mixed powders were sealed in an evacuated silica-glass ampule and annealed at 400 °C for 5 h, followed by annealing at 800 °C for 10 h.  $\text{TlFe}_{1.6}\text{Se}_2$  was prepared by a solid-state reaction of fine pieces of the Tl metal (purity: 99.9%, Aldrich) and powders of FeSe and Se. The



precursors were mixed in a stoichiometric atomic ratio of Tl : FeSe : Se = 1 : 1.6 : 0.4 and sealed in an Ar-filled stainless-steel tube. The mixture was reacted at 400 °C for 5 h and subsequently at 650 °C for 10 h.<sup>20</sup> The resulting FeSe and TlFe<sub>1.6</sub>Se<sub>2</sub> powders were thoroughly ground and sintered into pellets by a hot-press method at 500 °C for 10 min. All reagents and products were handled in a glove box filled with dry Ar gas (dew point < -80 °C and oxygen concentration < 1 ppm).

## 2.2 Characterization

Crystalline phases were examined by X-ray diffraction (XRD) in the Bragg–Brentano geometry using a Cu K $\alpha$  radiation source (MiniFlex600, Rigaku Co.). The lattice parameters were refined by the Pawley method using the TOPAS ver. 4.2 program (Bruker AXS GmbH). The microstructure and chemical compositions (*i.e.*, atomic ratios of Tl, Fe, and Se) of the samples were characterized using an electron probe micro-analyzer (EPMA).

$\sigma$  and  $S$  were simultaneously measured using a ZEM-3 (ULVAC-RIKO, Inc.) under a He atmosphere.  $S$  was obtained from the thermoelectric voltage generated under an applied temperature difference ( $\Delta T$ ); the thermoelectromotive force ( $\Delta V$ ) and  $\Delta T$  were measured simultaneously, and  $S$  was determined from the slope of the  $\Delta V$ - $\Delta T$  plots. Pt electrodes deposited by sputtering were used to form ohmic contacts.  $\kappa$  was obtained from  $\kappa = D \times C \times d$ , where the thermal diffusivity ( $D$ ) was measured in an Ar atmosphere by the laser flash method (LFA 457, NETZSCH), the specific heat capacity ( $C$ ) was measured by differential scanning calorimetry (DSC), and the sample density ( $d$ ) was determined from the mass and geometric dimensions of the pellets.  $\kappa_{\text{ele}}$  was calculated using  $\kappa_{\text{ele}} = LT\sigma$ .  $L$  was calculated based on a single-parabolic-band model as follows:<sup>21</sup>

$$L = \left(\frac{k_{\text{B}}}{e}\right)^2 \left( \frac{\left(r + \frac{7}{2}\right) F_{r+5/2}(\eta)}{\left(r + \frac{3}{2}\right) F_{r+1/2}(\eta)} - \left[ \frac{\left(r + \frac{5}{2}\right) F_{r+3/2}(\eta)}{\left(r + \frac{3}{2}\right) F_{r+1/2}(\eta)} \right]^2 \right), \quad (1)$$

where  $k_{\text{B}}$  is the Boltzmann constant. Here, the reduced Fermi energy ( $\eta$ ) was obtained based on the free carrier model using the measured  $S$  as

$$S = \frac{k_{\text{B}}}{e} \left( \frac{\left(r + \frac{5}{2}\right) F_{r+3/2}(\eta)}{\left(r + \frac{3}{2}\right) F_{r+1/2}(\eta)} - \eta \right) \quad (2)$$

with the Fermi integral defined as

$$F_n(\eta) = \int_0^{\infty} \frac{\chi^n}{1 + e^{\chi - \eta}} d\chi, \quad (3)$$

where  $r = -1/2$  is the scattering factor.<sup>22</sup>  $\kappa_{\text{lat}}$  was obtained by subtracting  $\kappa_{\text{ele}}$  from the total  $\kappa$ , *i.e.*,  $\kappa_{\text{lat}} = \kappa - \kappa_{\text{ele}}$ .  $\sigma$  and  $S$  were measured in the in-plane direction of the hot-pressed pellets, while  $\kappa$  was measured along the out-of-plane direction.

## 2.3 Theoretical analysis

First-principles calculations were conducted using the projector-augmented wave (PAW) method as implemented in the Vienna *Ab initio* Simulation Package (VASP).<sup>23,24</sup> Tl [5d 6s 6p], Fe [3d 4s], and Se [4s 4p] orbitals were treated as valence states. Variable-cell structural optimizations were performed using the Perdew–Burke–Ernzerhof functional adapted for solids (PBEsol) functional,<sup>25</sup> with a plane-wave cutoff energy of 550 eV, the convergence criteria of  $10^{-6}$  eV for the energy and  $0.01 \text{ eV } \text{\AA}^{-1}$  for the force, and a  $\Gamma$ -centered  $k$ -mesh with a  $k$ -spacing of  $0.1 \text{ \AA}^{-1}$ . Phonon calculations were performed using the ALAMODE codes.<sup>26,27</sup> For FeSe, a  $4 \times 4 \times 2$  supercell containing 192 atoms was employed to compute the interatomic force constants (IFCs). For TlFe<sub>1.6</sub>Se<sub>2</sub>, a  $2 \times 2 \times 2$  supercell with 368 atoms was used to obtain the harmonic IFCs, whereas a  $1 \times 1 \times 1$  unit-cell with 46 atoms was used to evaluate the anharmonic IFCs. The harmonic IFCs were fixed to the values determined by the finite-displacement approach,<sup>28,29</sup> and the anharmonic IFCs up to the sixth order were estimated by the compressive sensing lattice dynamics. We included all allowed interactions for the harmonic IFCs, all third-order IFCs within a 12-bohr cutoff radius, and all fourth-to-sixth-order IFCs within an 8-bohr cutoff radius. Density functional theory (DFT) calculations to obtain energies and forces were performed using the PBEsol functional with a plane-wave energy cutoff of 400 eV and an energy convergence criterion of  $10^{-8}$  eV. Finite-temperature phonon dispersions were computed by using the self-consistent phonon (SCPH) approach.<sup>30</sup>  $\kappa_{\text{lat}}$  was determined by considering the Peierls term, obtained by solving the Peierls–Boltzmann transport equation (PBTE) under the single-mode relaxation time approximation, and the coherent term using the unified formula.<sup>31</sup> The phonon-isotope scatterings were considered.<sup>32</sup> The convergence of  $\kappa_{\text{lat}}$  with respect to the  $q$ -point mesh was verified using a  $7 \times 7 \times 7$  grid for TlFe<sub>1.6</sub>Se<sub>2</sub> and a  $15 \times 15 \times 10$  grid for FeSe in the PBTE calculations.

## 3 Results and discussion

### 3.1 Electrical transport properties

Crystal structures and microstructure characterizations are summarized in Fig. 2, S1 and S2 in the SI. It was confirmed that TlFe<sub>1.6</sub>Se<sub>2</sub> adopted the  $V_{\text{Fe}}$ -ordered crystal structure with a space group of  $I4/m$  (Fig. 2a) and FeSe crystallized in a PbO-type  $\alpha$ -phase with a space group of  $P4/nmm$  at RT (Fig. S2). Upon heating the TlFe<sub>1.6</sub>Se<sub>2</sub> bulk sample, a transition from the  $V_{\text{Fe}}$ -ordered structure to the  $V_{\text{Fe}}$ -disordered structure (space group:  $I4/mmm$ ) was observed in the  $T$  range of 100 °C–200 °C (Fig. 2b). At higher  $T$ , the  $V_{\text{Fe}}$ -disordered phase became stable.<sup>33</sup> When cooled back to RT, the  $V_{\text{Fe}}$ -ordered phase reappeared, indicating a reversible structural transition. The relative density of the sintered bulk samples was  $\sim 96\%$ . A minor secondary phase of Fe<sub>7</sub>Se<sub>8</sub> ( $\sim 2.6 \text{ mol}\%$ ) was detected in the FeSe sample (Fig. S2). Although Fe<sub>7</sub>Se<sub>8</sub> is a ferromagnetic metallic phase with a vacancy-ordered NiAs-type crystal structure<sup>34</sup> and may, in principle, contribute to electrical transport, its small fraction



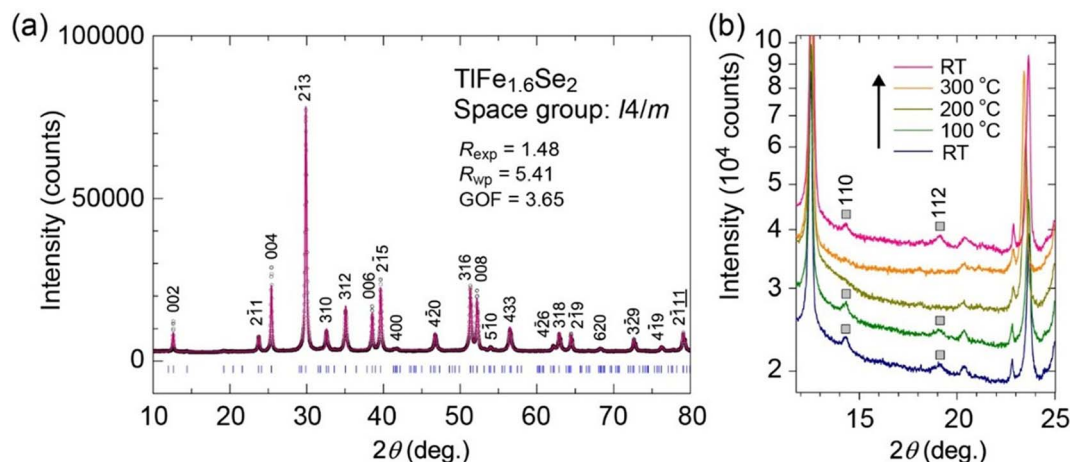


Fig. 2 (a) XRD pattern of the  $\text{TlFe}_{1.6}\text{Se}_2$  bulk sample at RT. (b) Enlarged view of the XRD patterns measured at different  $T$ . In the  $T$  range from RT to 100 °C, superlattice diffraction peaks of 110 and 112, originating from  $V_{\text{Fe}}$  ordering, were clearly observed. On the other hand, these peaks disappeared between 200 °C and 300 °C, indicating that  $V_{\text{Fe}}$  disordering occurred in the  $T$  range. Upon cooling back to RT, the superlattice reflections reappeared, demonstrating that the  $V_{\text{Fe}}$  ordered structure reversibly recovered.

suggests that its influence on the overall transport properties is expected to be limited.

Fig. 3 compares the  $T$  dependences of electrical transport properties of  $\text{TlFe}_{1.6}\text{Se}_2$  and FeSe bulk polycrystals. FeSe tends to transform to the NiAs-type  $\beta$ -phase at  $\sim 300$  °C,<sup>35</sup> and accordingly, all measurements were performed below this temperature to retain the  $\alpha$ -phase FeSe. For FeSe,  $\sigma$  exhibited only a slight  $T$  dependence; it increased from  $1.7 \times 10^5 \text{ S cm}^{-1}$  at 50 °C to  $1.9 \times 10^5 \text{ S cm}^{-1}$  at 290 °C (upper panel of Fig. 3a). At 50 °C, FeSe showed a small positive  $S$  of  $10 \mu\text{V K}^{-1}$  (Fig. 3b), which is consistent with the previously reported p-type conduction inferred from Hall-effect measurements.<sup>36</sup> Upon heating, however, the absolute value of  $S$  ( $|S|$ ) gradually decreased and the sign eventually became negative around 200 °C, reaching  $-4 \mu\text{V K}^{-1}$  at 290 °C. This sign reversal suggests that the dominant carrier type changes with  $T$ , which is reasonable given that metallic FeSe is a multiple-band system.<sup>36</sup> In contrast,  $\text{TlFe}_{1.6}\text{Se}_2$  showed a significant increase in  $\sigma$  in the  $T$  range of 150 °C–200 °C, rising from  $402 \text{ S cm}^{-1}$  in the  $V_{\text{Fe}}$ -ordered phase at 50 °C to  $1064 \text{ S cm}^{-1}$  at 595 °C upon transition to the  $V_{\text{Fe}}$ -disordered phase (lower panel of Fig. 3a). Upon cooling,  $\sigma$  reversibly returned to its original value, reflecting the reversibility of the  $V_{\text{Fe}}$  order-disorder transitions. The sign of  $S$  in  $\text{TlFe}_{1.6}\text{Se}_2$  was negative over the entire  $T$  range, indicating dominant electron conduction (Fig. 3b). In  $\text{TlFe}_{1.6}\text{Se}_2$ ,  $V_{\text{Fe}}$  ordering induces a reconstruction of the electronic structure, associated with antiferromagnetic ordering and the opening of a band gap. The n-type behavior should not be attributed solely to Tl intercalation because the nominal composition is charge-balanced. Rather, it is more likely related to the reconstructed electronic structure associated with  $V_{\text{Fe}}$  ordering, possibly together with slight off-stoichiometry such as reduced  $V_{\text{Fe}}$  concentration or Se deficiency. At 50 °C,  $\text{TlFe}_{1.6}\text{Se}_2$  exhibited a large  $|S|$  value of  $110 \mu\text{V K}^{-1}$ ; however, once the  $V_{\text{Fe}}$  order was lost through phase transition,  $|S|$  decreased substantially around 150 °C and remained almost constant at  $\sim 34 \mu\text{V K}^{-1}$

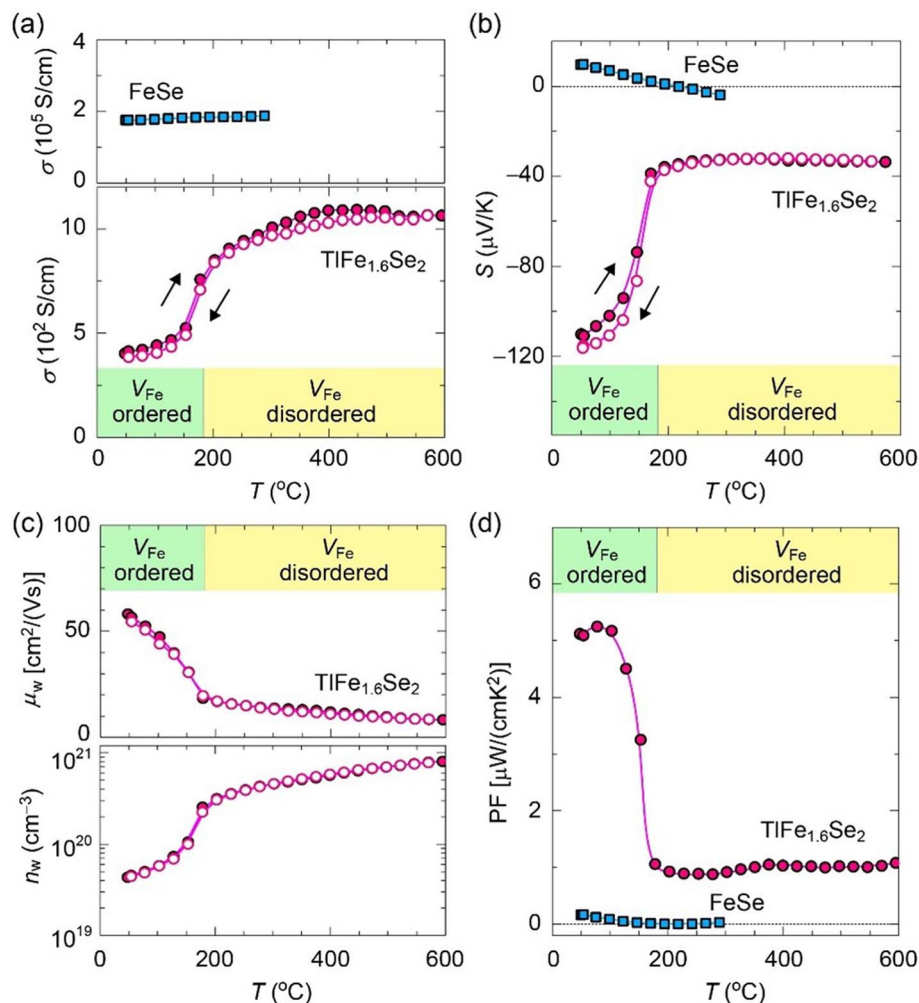
above 200 °C. This behavior can be attributed to the collapse of the Mott gap upon  $V_{\text{Fe}}$  disordering, which leads to partial compensation between the electron and hole contributions and consequently reduces the  $S$ .

As a reliable Hall voltage could not be obtained by Hall effect measurements, the carrier mobility was estimated as the weighted mobility ( $\mu_w$ ), calculated from  $\sigma$  and  $S$  using the following formula:

$$\mu_w = \frac{3h^3\sigma}{8\pi e(2m_e k_B T)^{3/2}} \left[ \frac{\exp\left[\frac{|S|}{k_B/e} - 2\right]}{1 + \exp\left[-5\left(\frac{|S|}{k_B/e} - 1\right)\right]} + \frac{\frac{3}{\pi^2} \frac{|S|}{k_B/e}}{1 + \exp\left[5\left(\frac{|S|}{k_B/e} - 1\right)\right]} \right], \quad (4)$$

where  $m_e$  is the free electron mass,  $k_B$  is the Boltzmann constant,  $h$  is the Planck constant, and  $e$  is the elementary charge.<sup>37</sup> The  $\mu_w$  is related to the drift mobility ( $\mu$ ) through  $\mu_w \approx \mu \left(\frac{m_{\text{DOS}}^*}{m_e}\right)^{3/2}$ , where  $m_{\text{DOS}}^*$  is the effective mass of the density of state. Using  $\mu_w$ , the weighted carrier concentration was calculated as  $n_w = \frac{\sigma}{e\mu_w}$ . In the  $V_{\text{Fe}}$ -ordered phase,  $\text{TlFe}_{1.6}\text{Se}_2$  exhibited a high  $\mu_w$  of  $60 \text{ cm}^2 (\text{V}^{-1} \text{ s}^{-1})$  at 50 °C, whereas  $\mu_w$  markedly decreased through transition to the  $V_{\text{Fe}}$ -disordered phase, reaching  $8 \text{ cm}^2 (\text{V}^{-1} \text{ s}^{-1})$  at 595 °C. This reduction is likely associated with enhanced carrier scattering induced by the  $V_{\text{Fe}}$  disorder. The  $n_w$  in the  $V_{\text{Fe}}$ -ordered phase was  $\sim 4.3 \times 10^{19} \text{ cm}^{-3}$ , but it increased sharply during the phase-transition and then continued to increase gradually in the  $V_{\text{Fe}}$ -disordered phase, reaching  $\sim 8.0 \times 10^{20} \text{ cm}^{-3}$ . This behavior is consistent with the collapse of the Mott gap upon  $V_{\text{Fe}}$  disordering. These results suggest that both  $\sigma$  and  $S$  undergo pronounced changes in response to the transition between the  $V_{\text{Fe}}$  ordered and





**Fig. 3**  $T$  dependence of the (a) electrical conductivity ( $\sigma$ ) and (b) Seebeck coefficient ( $S$ ) for the FeSe and TlFe<sub>1.6</sub>Se<sub>2</sub> polycrystals. (c)  $T$  dependence of the weighted mobility ( $\mu_w$ ) and weighted carrier concentration ( $n_w$ ) for the TlFe<sub>1.6</sub>Se<sub>2</sub> polycrystal. (d)  $T$  dependence of the power factor (PF) for the TlFe<sub>1.6</sub>Se<sub>2</sub> and FeSe polycrystals. The green and yellow regions indicate the  $T$  ranges where the  $V_{\text{Fe}}$ -ordered and  $V_{\text{Fe}}$ -disordered phases are stabilized in TlFe<sub>1.6</sub>Se<sub>2</sub>, respectively.

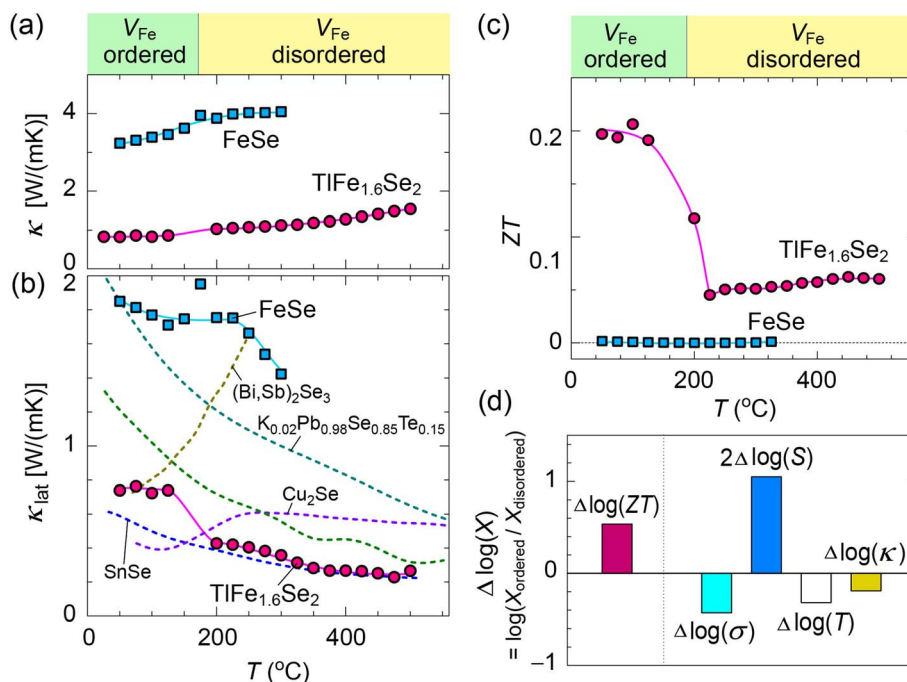
disordered states, accompanied by changes in the electronic structure. Fig. 3d summarizes the  $T$  dependences of PF ( $=S^2\sigma$ ) for TlFe<sub>1.6</sub>Se<sub>2</sub> and FeSe bulk samples. Bulk FeSe exhibited a small  $S$ , resulting in low PF over the entire  $T$  range. In contrast, TlFe<sub>1.6</sub>Se<sub>2</sub> showed a pronounced increase in PF in the  $V_{\text{Fe}}$ -ordered phase, reaching  $5.2 \mu\text{W} (\text{cm}^{-1} \text{K}^{-2})$  at  $50^\circ\text{C}$ , which is 30 times higher than that of bulk FeSe. Above  $200^\circ\text{C}$ , where the  $V_{\text{Fe}}$ -disordered phase was stabilized, PF was reduced to  $\sim 1.0 \mu\text{W} (\text{cm}^{-1} \text{K}^{-2})$ . These results demonstrate that TlFe<sub>1.6</sub>Se<sub>2</sub>, which contains FeSe monolayers embedded within the bulk crystal, can realize a substantially larger PF than bulk FeSe, with its electrical transport properties strongly modulated by the transition between  $V_{\text{Fe}}$  ordered and disordered states.

### 3.2 Thermal and thermoelectric properties

Next, we investigated the thermal transport properties of TlFe<sub>1.6</sub>Se<sub>2</sub> and FeSe polycrystals. The  $T$  dependences of thermal diffusivity and specific heat capacity are summarized in Fig. S3a

and b, SI. Because the specific heat capacity in TlFe<sub>1.6</sub>Se<sub>2</sub> exhibited a peak near the phase-transition temperature ( $125^\circ\text{C}$ – $200^\circ\text{C}$ ), data in this region were excluded from the analysis of  $\kappa$ . Fig. 4a shows the  $T$  dependence of the total  $\kappa$ . FeSe exhibited a  $\kappa$  value of  $3.2 \text{ W} (\text{m}^{-1} \text{K}^{-1})$  at  $50^\circ\text{C}$ , which gradually increased with increasing  $T$  and reached  $4.1 \text{ W} (\text{m}^{-1} \text{K}^{-1})$  at  $300^\circ\text{C}$ . In contrast, TlFe<sub>1.6</sub>Se<sub>2</sub> showed a much lower  $\kappa$  of  $0.8 \text{ W} (\text{m}^{-1} \text{K}^{-1})$  at  $50^\circ\text{C}$ , remaining nearly constant up to  $\sim 125^\circ\text{C}$ . After the transition to the  $V_{\text{Fe}}$ -disordered phase,  $\kappa$  slightly increased to  $1.0 \text{ W} (\text{m}^{-1} \text{K}^{-1})$  and then increased gradually, reaching  $1.5 \text{ W} (\text{m}^{-1} \text{K}^{-1})$  at  $500^\circ\text{C}$ . We next discuss the thermal transport properties by separating electronic and lattice contributions. As shown in Fig. S3c in the SI,  $\kappa_{\text{ele}}$  is very large in FeSe than TlFe<sub>1.6</sub>Se<sub>2</sub> due to its higher  $\sigma$ , and therefore plays a dominant role in determining  $\kappa$ . Fig. 4b compares the  $T$  dependence of  $\kappa_{\text{lat}}$  ( $=\kappa - \kappa_{\text{ele}}$ ), in comparison with the typical high-performance thermoelectric materials, including (Bi<sub>0.5</sub>Sb<sub>1.5</sub>)Te<sub>3</sub>,<sup>38</sup> (Pb<sub>0.98</sub>-K<sub>0.02</sub>)(Te<sub>0.15</sub>Se<sub>0.85</sub>),<sup>39</sup> (Ge<sub>0.9</sub>In<sub>0.015</sub>Cu<sub>0.125</sub>)Te,<sup>40</sup> Cu<sub>2</sub>Se,<sup>41</sup> and SnSe<sup>42</sup> polycrystals. FeSe exhibited a  $\kappa_{\text{lat}}$  value of  $1.8 \text{ W} (\text{m}^{-1}$





**Fig. 4**  $T$  dependence of (a)  $\kappa$  and (b)  $\kappa_{\text{lat}}$  for the TlFe<sub>1.6</sub>Se<sub>2</sub> and FeSe polycrystals. For comparison, the  $\kappa_{\text{lat}}$  vs.  $T$  curves of typical high-performance thermoelectric materials, including the (Bi<sub>0.5</sub>Sb<sub>1.5</sub>)Te<sub>3</sub>,<sup>38</sup> (Pb<sub>0.98</sub>K<sub>0.02</sub>)(Te<sub>0.15</sub>Se<sub>0.85</sub>),<sup>39</sup> (Ge<sub>0.9</sub>In<sub>0.015</sub>Cu<sub>0.125</sub>)Te,<sup>40</sup> Cu<sub>2</sub>Se,<sup>41</sup> and SnSe<sup>42</sup> polycrystals, are also shown in (b). (c)  $T$  dependence of the dimensionless figure of merit ( $ZT$ ) for the TlFe<sub>1.6</sub>Se<sub>2</sub> and FeSe polycrystals. (d) Decomposition of contributions in the  $ZT$  change across the  $V_{\text{Fe}}$  order-disorder transition, evaluated between the  $V_{\text{Fe}}$ -ordered phase at 50 °C and the  $V_{\text{Fe}}$ -disordered phase at 400 °C. Here,  $\Delta \log(X) = \log(X_{\text{ordered}}/X_{\text{disordered}})$ ; the positive (negative) values indicate parameters that enhance (reduce)  $ZT$  in the  $V_{\text{Fe}}$ -ordered phase.

$\text{K}^{-1}$ ) at 50 °C, which gradually decreased with increasing  $T$  and reached  $1.4 \text{ W (m}^{-1} \text{ K}^{-1}\text{)}$  at 300 °C. In contrast, TlFe<sub>1.6</sub>Se<sub>2</sub> showed an extremely low  $\kappa_{\text{lat}}$  of  $0.7 \text{ W (m}^{-1} \text{ K}^{-1}\text{)}$  at 50 °C in the  $V_{\text{Fe}}$ -ordered phase, where  $\kappa_{\text{lat}}$  exhibited a weak  $T$  dependence and remained nearly constant. After the transition to the  $V_{\text{Fe}}$ -disordered phase,  $\kappa_{\text{lat}}$  decreased further to  $0.4 \text{ W (m}^{-1} \text{ K}^{-1}\text{)}$  at 200 °C and  $\sim 0.2 \text{ W (m}^{-1} \text{ K}^{-1}\text{)}$  at 500 °C. In addition, these values are lower than those of high-performance thermoelectric materials with intrinsically low  $\kappa_{\text{lat}}$ , and are comparable to the lowest  $\kappa_{\text{lat}}$  values reported for layered SnSe polycrystals.<sup>42</sup> Therefore, TlFe<sub>1.6</sub>Se<sub>2</sub>, containing FeSe layers with  $V_{\text{Fe}}$  order-disorder structures, is demonstrated to achieve extremely low  $\kappa_{\text{lat}}$ .

Here, the Lorenz number ( $L$ ) for  $\kappa_{\text{ele}}$  was estimated using a single-parabolic-band model with a scattering parameter of  $r = -1/2$ . Since TlFe<sub>1.6</sub>Se<sub>2</sub> is a multiband Mott system with strong electron correlations,  $L$  depends on the Fermi level, effective mass and  $r$ , which are difficult to determine uniquely because of the complex electronic structure and the uncertainty in the dominant scattering mechanism. Then, we evaluated  $L$  over a broad physically reasonable range of  $r$  ( $-1/2$  to  $2$ ) and Fermi level. For the  $V_{\text{Fe}}$ -ordered phase ( $n = 4.2 \times 10^{19} \text{ cm}^{-3}$ ),  $L$  varies within  $1.5\text{--}2.8 \times 10^{-8} \text{ W}\Omega \text{ K}^{-2}$ , corresponding to an uncertainty of  $\pm 30\text{--}40\%$ . This leads to a variation of  $\kappa_{\text{ele}}$  from  $0.05$  to  $0.11 \text{ W (m}^{-1} \text{ K}^{-1}\text{)}$  (nominal value:  $0.084 \text{ W (m}^{-1} \text{ K}^{-1}\text{)}$ ), resulting in  $\kappa_{\text{lat}}$  ranging from  $0.71$  to  $0.79 \text{ W (m}^{-1} \text{ K}^{-1}\text{)}$  (nominal value:  $0.74 \text{ W (m}^{-1} \text{ K}^{-1}\text{)}$ ), indicating a relatively limited uncertainty. In

contrast, for the  $V_{\text{Fe}}$ -disordered phase with a higher carrier concentration ( $n = 6.0 \times 10^{20} \text{ cm}^{-3}$ ),  $L$  becomes much less sensitive to model parameters and converges to a narrow range of  $2.4\text{--}2.5 \times 10^{-8} \text{ W}\Omega \text{ K}^{-2}$ , close to the degenerate limit. In this case,  $\kappa_{\text{ele}}$  is  $\sim 1.01 \text{ W (m}^{-1} \text{ K}^{-1}\text{)}$ , with a variation of less than  $\pm 0.05 \text{ W (m}^{-1} \text{ K}^{-1}\text{)}$ , leading to only minor alternations in  $\kappa_{\text{lat}}$  ( $\sim 0.27 \text{ W (m}^{-1} \text{ K}^{-1}\text{)}$ ). Although the exact value of  $L$  depends on the model assumptions, the resulting uncertainty in  $\kappa_{\text{lat}}$  remains limited. Therefore, even when this uncertainty is taken into account, TlFe<sub>1.6</sub>Se<sub>2</sub> exhibits intrinsically low  $\kappa_{\text{lat}}$ .

Based on the electronic and thermal transport properties discussed above, we evaluated the overall thermoelectric performance of TlFe<sub>1.6</sub>Se<sub>2</sub> and FeSe (Fig. 4b). Bulk FeSe exhibited both a small  $S$  and a high  $\kappa$ , resulting in low  $ZT$  over the entire  $T$  range, consistent with its metallic electronic structure. In contrast, TlFe<sub>1.6</sub>Se<sub>2</sub> showed a pronounced increase of  $ZT$  in the  $V_{\text{Fe}}$ -ordered phase, reaching  $\sim 0.2$  at 50 °C, which is two orders of magnitude higher than that of bulk FeSe, whereas  $ZT$  was limited to  $\sim 0.05$  in the  $V_{\text{Fe}}$ -disordered phase at  $T > 200$  °C. To clarify the origin of this strong contrast in  $ZT$  between the  $V_{\text{Fe}}$ -ordered and  $V_{\text{Fe}}$ -disordered phases, the relative change in  $ZT$  across the transition was analyzed by decomposing  $ZT$  into contributions from individual transport parameters. Taking the logarithm of  $ZT = S^2\sigma T/\kappa$ , we obtain  $\Delta \log(ZT) = \Delta \log(\sigma) + 2\Delta \log(S) + \Delta \log(T) - \Delta \log(\kappa)$ , which are the approximations of relative differences,  $\frac{\Delta ZT}{ZT} \approx \frac{\Delta \sigma}{\sigma} + \frac{2\Delta S}{S} + \frac{\Delta T}{T} - \frac{\Delta \kappa}{\kappa}$ . Here, the



contributions are evaluated using logarithmic differences, defined as  $\Delta \log(X) = \log(X_{\text{ordered}}) - \log(X_{\text{disordered}})$ , which represents the change in each parameter across the transition. Fig. 4c summarizes the changes in each transport parameter between the  $V_{\text{Fe}}$ -ordered phase at 50 °C and the  $V_{\text{Fe}}$ -disordered phase at 400 °C. These temperatures were chosen because they lie sufficiently far from the order–disorder transition, ensuring high phase purity in the fully  $V_{\text{Fe}}$ -ordered and fully  $V_{\text{Fe}}$ -disordered states, respectively. This allows us to compare the intrinsic transport properties of the pure phases. Positive values indicate quantities that are enhanced in the  $V_{\text{Fe}}$ -ordered phase and therefore contribute positively to the increase in  $ZT$ , whereas negative values indicate factors that reduce  $ZT$ . Note that  $\kappa$  appears in the denominator of  $ZT$ , an increase of  $\kappa$  (*i.e.*, positive  $\Delta \log(\kappa)$ ) contributes negatively to  $ZT$ . Although  $\kappa_{\text{lat}}$  is effectively reduced in the  $V_{\text{Fe}}$ -disordered phase, the overall contribution of the total  $\kappa$  to  $ZT$  is only slightly negative. This is because the transition to a metallic state simultaneously leads to a substantial increase in  $\kappa_{\text{ele}}$ , which compensates for the benefit of the reduced  $\kappa_{\text{lat}}$ . In contrast,  $S$  exhibits the largest positive contribution, indicating that the enhancement of  $ZT$  in the  $V_{\text{Fe}}$ -ordered phase is predominantly driven by the large  $S$  associated with the opening of the Mott gap. To assess possible effects arising from the large temperature difference in the above comparison, the  $ZT$  decomposition analysis was also performed with a closer temperature difference of 125 °C for the ordered phase and 225 °C for the disordered phase (Fig. S4). The results confirm that the overall conclusion remains unchanged; the dominant contribution to the  $ZT$  enhancement arises from the increase in  $S$ . These results demonstrate that  $V_{\text{Fe}}$  ordering in layered  $\text{TlFe}_{1.6}\text{Se}_2$  enables a favorable balance between electronic and thermal transport, allowing relatively large PF and  $ZT$  values to be realized in the bulk form.

To further elucidate the underlying mechanism responsible for the low  $\kappa_{\text{lat}}$  in  $\text{TlFe}_{1.6}\text{Se}_2$ , we conducted first-principles anharmonic lattice dynamics (ALD) calculations, as implemented in the ALAMODE code.<sup>26,27</sup> We first calculated the harmonic phonon dispersion of  $\text{TlFe}_{1.6}\text{Se}_2$ , shown as the dotted black lines in Fig. 5a. Imaginary modes appear at the  $X$  and  $R$  points, indicating that the structure is dynamically unstable at  $T = 0$  K within the harmonic approximation. To account for the temperature effect, SCPH calculations were performed. At  $T = 300$  K, as shown by the solid blue lines in Fig. 5a, all phonon frequencies become positive, meaning that the previously imaginary modes are stabilized after including the temperature-induced anharmonic correction.  $\text{TlFe}_{1.6}\text{Se}_2$  exhibits a large number of phonon branches with strong mode entanglement (left panel of Fig. 5a). The acoustic phonons and the low-frequency optical phonons up to  $\sim 2.5$  THz exhibit relatively flat dispersions, indicating low phonon group velocities and the suppression of heat transport. The partial phonon density of states (DOSs) projected on each element for the  $V_{\text{Fe}}$ -ordered  $\text{TlFe}_{1.6}\text{Se}_2$  at  $T = 300$  K is shown in the right panel of Fig. 5a. The phonon DOS reveals that vibrations of the heavy Tl atoms predominantly contribute to the low-frequency phonon modes below  $\sim 2$  THz. These Tl-derived optical modes exhibit extremely flat dispersions and strongly overlap with the acoustic

branches, indicating highly localized vibrations associated with weak coupling between the Tl atoms and the Fe–Se framework. In contrast, the higher-frequency phonon branches are mainly associated with vibrations of Fe and Se atoms. For comparison, the phonon dispersion and partial phonon DOS of FeSe at  $T = 300$  K are shown in Fig. 5b. FeSe exhibits a much simpler phonon spectrum with fewer but strongly dispersive branches (left panel of Fig. 5b), consistent with its relatively simple crystal structure. While the phonon dispersions along the out-of-plane  $\Gamma$ – $Z$  direction are relatively weak, much stronger dispersions are observed along the in-plane  $\Gamma$ – $X$  and  $\Gamma$ – $M$  direction, extending up to  $\sim 5$  THz. The broad frequency distribution of the Fe–Se vibrational modes in the partial phonon DOSs (right panel of Fig. 5b) reflects the strong Fe–Se bonding and is consistent with the highly dispersive phonon branches. Compared with bulk FeSe, the Fe–Se phonon branches in  $\text{TlFe}_{1.6}\text{Se}_2$  exhibit reduced dispersion and stronger mode entanglement, reflecting the reduced symmetry and structural complexity of FeSe layers caused by  $V_{\text{Fe}}$  and interlayer Tl atoms.

We subsequently calculated  $\kappa_{\text{lat}}$  by solving the Peierls–Boltzmann transport equation (PBTE) within the relaxation time approximation. Fig. 5c and d present the anisotropic  $\kappa_{\text{lat}}$  components along the in-plane ( $xx$  and  $yy$ ) and the out-of-plane ( $zz$ ) directions for  $\text{TlFe}_{1.6}\text{Se}_2$  and FeSe as a function of  $T$ , considering the contribution from the coherent term. The effect of the coherent contribution on the  $T$  dependence of  $\kappa_{\text{lat}}$  is shown in Fig. S5 in the SI.  $\kappa_{\text{lat}}$  for  $\text{TlFe}_{1.6}\text{Se}_2$  was calculated based on the ordered structure and is therefore shown only at low temperatures. In layered FeSe, the pronounced structural anisotropy leads to a strong crystallographic-direction dependence of  $\kappa_{\text{lat}}$  (Fig. 5d). At 27 °C, the in-plane  $\kappa_{\text{lat},xx}$  ( $\kappa_{\text{lat},yy}$ ) reaches an exceptionally high value of 33.74 W ( $\text{m}^{-1} \text{K}^{-1}$ ) within the FeSe layers, whereas  $\kappa_{\text{lat},zz}$  is only 1.09 W ( $\text{m}^{-1} \text{K}^{-1}$ ), resulting in an extremely large anisotropy ratio of  $\sim 33$ . In contrast,  $\text{TlFe}_{1.6}\text{Se}_2$  exhibits intrinsically suppressed  $\kappa_{\text{lat}}$  even along the in-plane direction (Fig. 5c). At 27 °C,  $\kappa_{\text{lat},xx}$  ( $\kappa_{\text{lat},yy}$ ) is only 1.43 W ( $\text{m}^{-1} \text{K}^{-1}$ ), more than an order of magnitude lower than that of FeSe, while  $\kappa_{\text{lat},zz}$  is further reduced to 0.42 W ( $\text{m}^{-1} \text{K}^{-1}$ ).

To facilitate comparison with the experimental data for anisotropic polycrystalline materials, we evaluated orientation-averaged  $\kappa_{\text{lat}}$  values using both a harmonic-mean (series-type) average,  $\kappa_{\text{lat}}^{\text{series}} = \left( \frac{1}{\kappa_{xx}} + \frac{1}{\kappa_{yy}} + \frac{1}{\kappa_{zz}} \right)^{-1} \times 3$ , and an arithmetic-mean (parallel-type) average,  $\kappa_{\text{lat}}^{\text{parallel}} = \frac{\kappa_{xx} + \kappa_{yy} + \kappa_{zz}}{3}$ , which are plotted together with the measured  $\kappa_{\text{lat}}$  of  $V_{\text{Fe}}$ -ordered  $\text{TlFe}_{1.6}\text{Se}_2$  and FeSe polycrystals (Fig. 5c and d). The parallel-type average corresponds to a transport regime in which heat flows independently along different crystallographic directions, whereas the series-type average represents a transport regime largely controlled by the lowest  $\kappa_{\text{lat}}$  component. Both  $\text{TlFe}_{1.6}\text{Se}_2$  and FeSe polycrystals exhibit  $\kappa_{\text{lat}}$  close to  $\kappa_{\text{lat}}^{\text{series}}$ , indicating that heat transport in the polycrystalline form is largely governed by the low out-of-plane component. In FeSe, the intrinsically high in-plane  $\kappa_{\text{lat}}$  is strongly suppressed in the polycrystal, whereas in



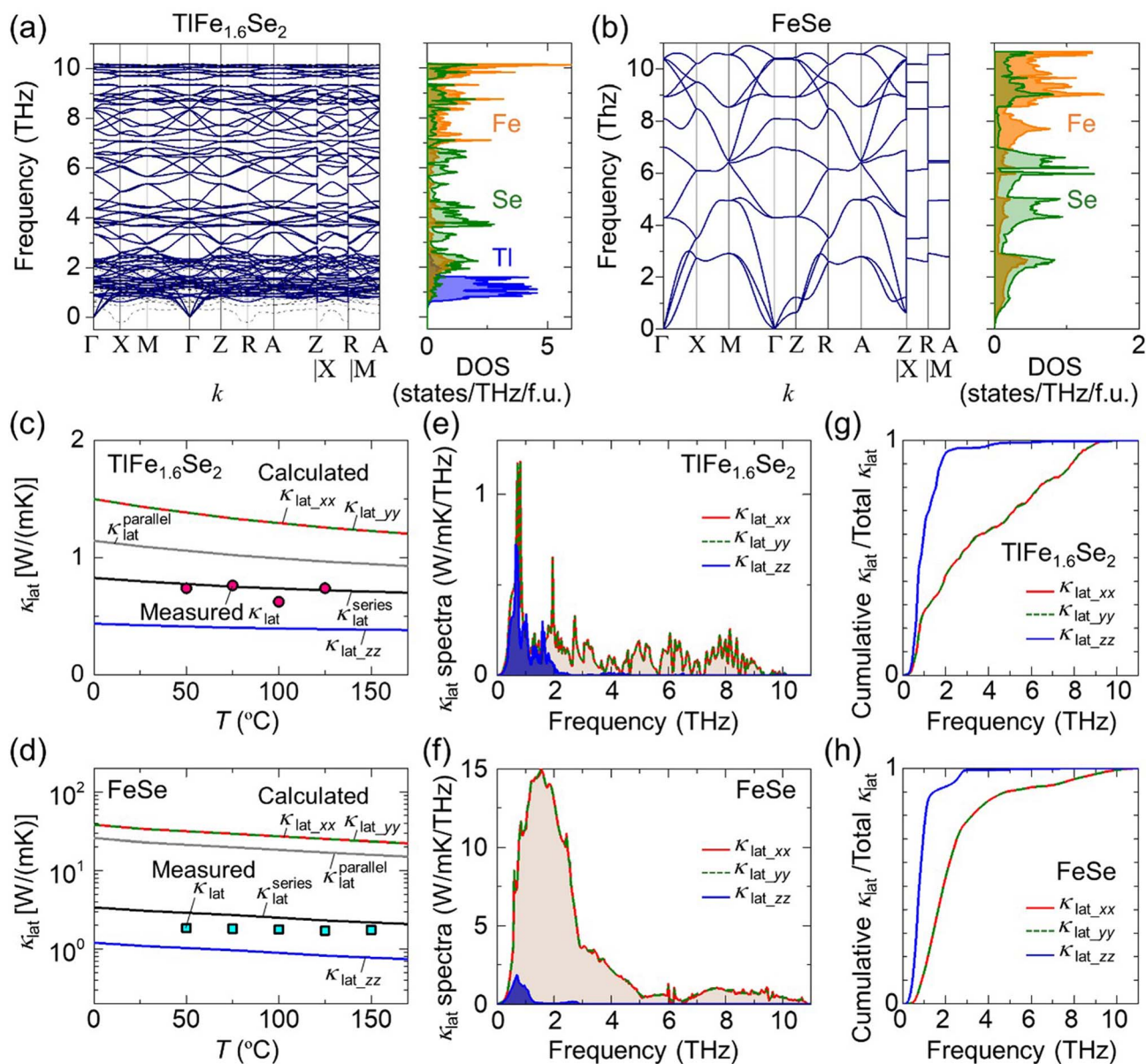


Fig. 5 Anharmonic phonon dispersions (left panels) and partial phonon density of states (DOS) projected on each element (right panels) for (a)  $\text{TlFe}_{1.6}\text{Se}_2$  and (b)  $\text{FeSe}$  at  $T = 300$  K. The dotted black lines in (a) represent the phonon dispersion calculated within the harmonic approximation. The  $k$ -path is  $\Gamma$  (0.0, 0.0, 0.0),  $X$  (0.0, 0.5, 0.0),  $M$  (0.5, 0.5, 0.0),  $Z$  (0.0, 0.0, 0.5),  $R$  (0.0, 0.5, 0.5), and  $A$  (0.5, 0.5, 0.5).  $T$  dependence of the calculated  $\kappa_{\text{lat}}$  along the  $xx$  and  $yy$  (parallel to  $\text{FeSe}$  layer) and  $zz$  (perpendicular to  $\text{FeSe}$  layer) axes for (c)  $\text{TlFe}_{1.6}\text{Se}_2$  and (d)  $\text{FeSe}$ . The averaged  $\kappa_{\text{lat}}$  values obtained using the series  $\left(\kappa_{\text{lat}}^{\text{series}} = \left(\frac{1}{\kappa_{xx}} + \frac{1}{\kappa_{yy}} + \frac{1}{\kappa_{zz}}\right)^{-1} \times 3\right)$  and parallel  $\left(\kappa_{\text{lat}}^{\text{parallel}} = \frac{\kappa_{xx} + \kappa_{yy} + \kappa_{zz}}{3}\right)$  conduction models are also shown. The experimentally measured  $\kappa_{\text{lat}}$  for the  $V_{\text{Fe}}$ -ordered  $\text{TlFe}_{1.6}\text{Se}_2$  and  $\text{FeSe}$  polycrystals are also plotted for comparison. Comparison of the  $\kappa_{\text{lat}}$  spectra for (e)  $\text{TlFe}_{1.6}\text{Se}_2$  and (f)  $\text{FeSe}$  at  $T = 300$  K. Frequency-dependent cumulative  $\kappa_{\text{lat}}$  for (g)  $\text{TlFe}_{1.6}\text{Se}_2$  and (h)  $\text{FeSe}$  at  $T = 300$  K.

$\text{TlFe}_{1.6}\text{Se}_2$ , the already low in-plane  $\kappa_{\text{lat}}$  is further reduced by the out-of-plane contribution.

Fig. 5e and f compare the anisotropic frequency-resolved  $\kappa_{\text{lat}}$  at  $T = 300$  K for  $\text{TlFe}_{1.6}\text{Se}_2$  and  $\text{FeSe}$ , while the frequency-dependent cumulative  $\kappa_{\text{lat}}$  are shown in Fig. 5g and h. In  $\text{FeSe}$ , the in-plane  $\kappa_{\text{lat},xx}$  ( $\kappa_{\text{lat},yy}$ ) exhibits a pronounced peak around  $\sim 1.5$  THz, whereas the out-of-plane  $\kappa_{\text{lat},zz}$  shows a small peak at  $\sim 0.5$  THz (Fig. 5f). As shown in Fig. 5h, phonons below  $\sim 5$  THz account for about 90% of the total  $\kappa_{\text{lat},xx}$  ( $\kappa_{\text{lat},yy}$ ),

indicating that heat transport is dominated by acoustic phonon modes. The contribution to  $\kappa_{\text{lat},zz}$  is confined to frequencies below  $\sim 1.5$  THz and arises almost exclusively from acoustic phonons, reflecting the intrinsically inefficient thermal transport along the out-of-plane direction. This anisotropic behavior is consistent with the steep phonon branches along the  $\Gamma$ - $X$  and  $\Gamma$ - $M$  directions, arising from highly dispersive in-plane acoustic phonons of the  $\text{Fe}$ - $\text{Se}$  framework, and the much less dispersive



phonon branches along the  $T$ - $Z$  direction, reflecting the layered structural characteristic (Fig. 5b).

For  $\text{TlFe}_{1.6}\text{Se}_2$ , the frequency-resolved  $\kappa_{\text{lat}}$  shows a clear directional contrast (Fig. 5e). The in-plane  $\kappa_{\text{lat}_{xx}}$  ( $\kappa_{\text{lat}_{yy}}$ ) spans a much broader frequency range extending up to  $\sim 10$  THz, mainly associated with the vibration of the Fe-Se framework (left panel of Fig. 5a). In contrast, the out-of-plane  $\kappa_{\text{lat}_{zz}}$  is dominated by phonons below  $\sim 2$  THz, primarily arising from the vibrations of the heavy Tl atoms (right panel of Fig. 5a). The cumulative  $\kappa_{\text{lat}}$  (Fig. 5g) further clarifies this difference. Below 2.5 THz, only  $\sim 49\%$  of  $\kappa_{\text{lat}_{xx}}$  ( $\kappa_{\text{lat}_{yy}}$ ) is accumulated, whereas more than  $\sim 96\%$  of  $\kappa_{\text{lat}_{zz}}$  is contributed within this range. This indicates that higher-frequency optical modes contribute to more than half of the in-plane heat transport in  $\text{TlFe}_{1.6}\text{Se}_2$ . Such behavior is markedly different from that of FeSe, where the in-plane heat transport is dominated almost entirely by low-frequency phonons. Consequently, the contribution of low-

frequency phonons to  $\kappa_{\text{lat}_{xx}}$  ( $\kappa_{\text{lat}_{yy}}$ ) is strongly suppressed in  $\text{TlFe}_{1.6}\text{Se}_2$ .

Fig. 6 compares the phonon group velocity ( $\nu_{\text{ph}}$ ), phonon lifetime ( $\tau_{\text{ph}}$ ), and phonon mean free path ( $l_{\text{ph}}$ ) as functions of phonon frequency.  $\text{TlFe}_{1.6}\text{Se}_2$  exhibits much lower  $\nu_{\text{ph}}$  than FeSe over a wide frequency range (Fig. 6a), reflecting the flatter acoustic and optical phonon branches shown in Fig. 5a. This reduction in  $\nu_{\text{ph}}$  originates from the weak coupling between the heavy Tl atoms and the Fe-Se framework, which effectively softens the lattice vibrations and limits phonon propagation. More importantly,  $\tau_{\text{ph}}$  in  $\text{TlFe}_{1.6}\text{Se}_2$  is reduced over a broad frequency range, with an exceptionally strong suppression observed for phonons below  $\sim 4$  THz (Fig. 6b). In the lowest-frequency region below  $\sim 1.5$  THz, this reduction is primarily associated with Tl-related vibrational modes, whereas in the higher-frequency region up to  $\sim 4$  THz, it mainly affects phonons derived from the Fe-Se framework. As a result,  $l_{\text{ph}}$  in  $\text{TlFe}_{1.6}\text{Se}_2$  is strongly suppressed, particularly because the  $\tau_{\text{ph}}$  of phonon modes below  $\sim 4$  THz become extremely short (Fig. 6c). These results indicate that two distinct scattering mechanisms operate in different frequency regimes: low-frequency phonon scattering induced by the weakly bound heavy Tl atoms, and the additional scattering of the Fe-Se framework phonons in  $\text{TlFe}_{1.6}\text{Se}_2$ .

To further clarify the microscopic origin of the enhanced phonon scattering in the Fe-Se framework, we evaluated the Fe-Se bonding characteristics in  $\text{TlFe}_{1.6}\text{Se}_2$  and FeSe by estimating their bonding energies using crystal orbital Hamilton population (COHP)<sup>43</sup> analysis, as implemented in the LOBSTER code.<sup>44</sup> The  $-\text{ICOHP}$  values, obtained by integrating  $-\text{COHP}$  up to the Fermi level and corresponding to the bond strength, are 2.35 eV per bond for the Fe-Se bonds in FeSe and range from 2.17 to 2.51 eV per bond in  $\text{TlFe}_{1.6}\text{Se}_2$ , with an average value of 2.34 eV per bond. The Fe-Se bond length in FeSe is 2.278 Å, while that in  $\text{TlFe}_{1.6}\text{Se}_2$  spans a range of 2.242–2.290 Å, yielding an average bond length of 2.272 Å (Fig. S6 in SI). These results indicate that the average Fe-Se bond strength and bond length are nearly identical in  $\text{TlFe}_{1.6}\text{Se}_2$  and FeSe. In contrast,  $\text{TlFe}_{1.6}\text{Se}_2$  exhibits a pronounced distribution of Fe-Se bond strengths, reflecting bond heterogeneity induced by  $V_{\text{Fe}}$  ordering. Such bond heterogeneity provides an additional phonon-scattering channel, particularly for intermediate- and high-frequency Fe-Se vibrational modes, and plays a key role in shortening  $\tau_{\text{ph}}$  and suppressing  $\kappa_{\text{lat}}$ . This is further supported by the interatomic force constant (IFC) distributions (Fig. S7 in SI), showing the broadened force-constant distribution in  $\text{TlFe}_{1.6}\text{Se}_2$  compared to FeSe. In addition, the three-phonon scattering phase space (SPS) is significantly enhanced, particularly in the 1.5–4 THz region (Fig. S8 in SI), indicating an increased number of scattering channels in this frequency range. This frequency range is dominated by the Fe-Se vibrational modes with strong acoustic-optical mixing (Fig. 5a), making them sensitive, especially to the bond heterogeneity. The dominance of force-constant disorder is also inferred from the frequency-selective reduction of phonon lifetimes between 1.5 and 4 THz (Fig. 6b). Therefore, the lifetime reduction in this frequency window is primarily driven by emission channels activated by

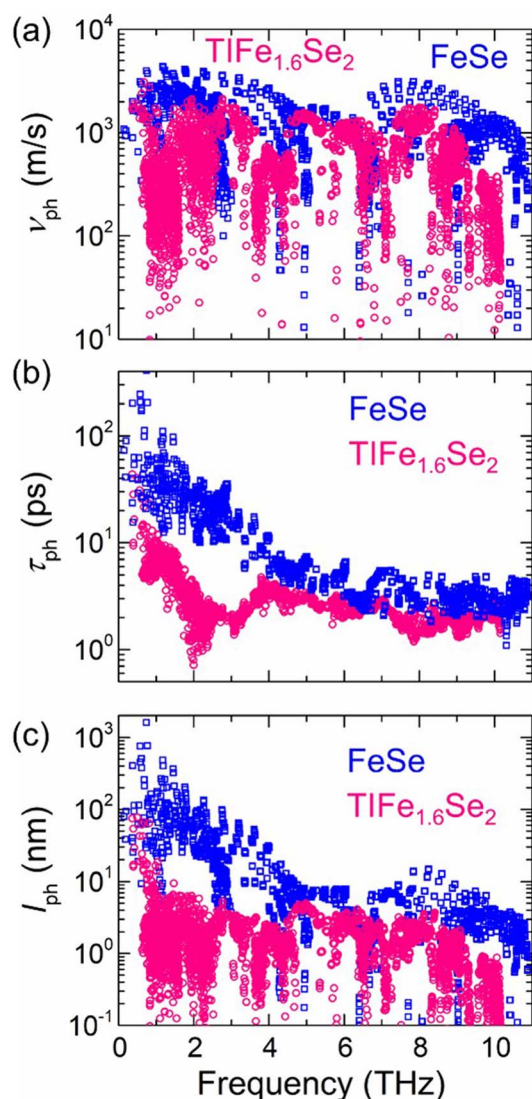


Fig. 6 (a) Phonon group velocity ( $\nu_{\text{ph}}$ ), (b) phonon lifetime ( $\tau_{\text{ph}}$ ), and (c) phonon mean free path ( $l_{\text{ph}}$ ) in terms of the phonon frequency for  $\text{TlFe}_{1.6}\text{Se}_2$  (pink plots) and FeSe (blue plots) at  $T = 300$  K.



the force-constant disorder, while mass disorder provides a secondary background contribution. Such bond-heterogeneity-induced phonon scattering has also been reported in a variety of complex crystalline materials, where local fluctuations in bonding strength or force constants give rise to enhanced anharmonic phonon scattering and reduced  $\kappa_{\text{lat}}$ .<sup>45–49</sup> In the  $V_{\text{Fe}}$ -disordered phase, this bond heterogeneity is further amplified by the random distribution of  $V_{\text{Fe}}$ , introducing additional mass and force-constant disorder. This disorder-driven enhancement of phonon scattering accounts for the further reduction of  $\kappa_{\text{lat}}$  observed experimentally at elevated temperatures. Direct first-principles calculations for the  $V_{\text{Fe}}$  disordered phases were not performed due to the large configurational space associated with random vacancy distributions and the limitation of our computational resources. Random  $V_{\text{Fe}}$  distributions are expected to introduce spatially uncorrelated force-constant disorder, which is likely more effective in scattering phonons than the ordered structure, leading to additional suppression of  $\kappa_{\text{lat}}$ .

## 4 Conclusions

We investigated the thermoelectric properties of layered  $\text{TlFe}_{1.6}\text{Se}_2$ , motivated by the expectation that its embedded two-dimensional FeSe transport layers, together with the  $V_{\text{Fe}}$  order-disorder transition, could provide a unique combination of enhanced PF and suppressed  $\kappa_{\text{lat}}$ .  $\text{TlFe}_{1.6}\text{Se}_2$  exhibited an exceptionally low  $\kappa_{\text{lat}}$ , reaching  $\sim 0.7 \text{ W (m}^{-1} \text{ K}^{-1})$  in the  $V_{\text{Fe}}$ -ordered phase at 50 °C and further decreasing to  $\sim 0.2 \text{ W (m}^{-1} \text{ K}^{-1})$  in the  $V_{\text{Fe}}$ -disordered phase at 500 °C, which is comparable to or even lower than those of high-performance thermoelectric materials with intrinsically low  $\kappa_{\text{lat}}$ . Notably, unlike layered FeSe, which shows extremely high in-plane  $\kappa_{\text{lat}}$  and strong anisotropy,  $\kappa_{\text{lat}}$  in  $\text{TlFe}_{1.6}\text{Se}_2$  is intrinsically suppressed even along the in-plane direction. This ultralow  $\kappa_{\text{lat}}$  originates from the combined effects of weakly bound heavy Tl atoms, which reduce phonon group velocities, and enhanced phonon scattering caused by the  $V_{\text{Fe}}$ -induced bond heterogeneity within the Fe–Se framework.

The electronic transport properties are strongly modulated across the transition between the  $V_{\text{Fe}}$  ordered and disordered states. In the  $V_{\text{Fe}}$ -disordered phase,  $\text{TlFe}_{1.6}\text{Se}_2$  exhibits a metallic state with enhanced  $\sigma$  and ultralow  $\kappa_{\text{lat}}$ ; however, strong carrier compensation significantly reduces  $S$ , limiting the  $ZT$  value to  $\sim 0.05$ . In contrast, in the  $V_{\text{Fe}}$ -ordered phase, the opening of a Mott gap leads to a large  $S$  of  $\sim 110 \mu\text{V K}^{-1}$  at 50 °C, resulting in an enhanced PF of  $5.2 \mu\text{W (cm}^{-1} \text{ K}^{-2})$  and a  $ZT$  of  $\sim 0.2$ . These results demonstrate that the confinement of FeSe layers within bulk  $\text{TlFe}_{1.6}\text{Se}_2$  enables a substantial PF enhancement compared with bulk FeSe, while  $V_{\text{Fe}}$  ordering and disordering play complementary roles by tuning carrier transport and strongly suppressing  $\kappa_{\text{lat}}$ . Looking forward, further enhancement of  $ZT$  may be achieved by optimizing carrier concentration in the  $V_{\text{Fe}}$ -ordered phase and by tuning the  $V_{\text{Fe}}$  concentration.

Although the incorporation of two-dimensional FeSe layers suggested the possibility of achieving a high PF comparable to that of FeSe monolayers, the obtained PF is substantially lower. This

difference is primarily attributed to the much lower carrier mobility in  $\text{TlFe}_{1.6}\text{Se}_2$ , which is about four orders of magnitude smaller than that of FeSe monolayers, likely due to the polycrystalline nature and enhanced carrier scattering arising from  $V_{\text{Fe}}$  ordering/disordering and interactions involving Tl atoms. In contrast, the exceptionally high mobility in FeSe monolayers is realized for in-plane transport in the two-dimensional electronic structure. To clarify the intrinsic transport properties and to potentially realize higher PF in  $\text{TlFe}_{1.6}\text{Se}_2$ , studies using single crystals or epitaxial thin films will be essential, as they enable selective probing of in-plane transport in the embedded FeSe layers.

Extending this concept to other alkali-based  $\text{A}_{1-x}\text{Fe}_{2-y}\text{Se}_2$  ( $\text{A} = \text{K, Rb, and Cs}$ ) is an attractive direction, as they consist of FeSe layers with  $V_{\text{Fe}}$ , forming quasi-two-dimensional frameworks, and exhibit high electrical conductivity. Moreover, these systems show high- $T_c$  superconductivity, reminiscent of FeSe monolayers, suggesting a close connection between their electronic structures. In addition, the  $V_{\text{Fe}}$  concentration in these systems can be tuned over a wide range,<sup>16,17</sup> providing a versatile platform for controlling carrier concentration and optimizing thermoelectric performance. However, their poor air stability, precise control of vacancy ordering, and suppression of phase separation remain significant challenges.<sup>15</sup> The growth of high-quality single crystals or epitaxial thin films will also be essential to clarify the intrinsic transport properties. A possible strategy to address air stability is partial substitution or solid-solution formation with air-stable Tl-based compounds,<sup>50</sup> which may enable simultaneous control of environmental stability and thermoelectric performance.

Taken together, the present study highlights the confinement of two-dimensional FeSe layers, combined with vacancy-order control, as a promising design strategy for bulk thermoelectric materials that combine large PF with intrinsically low  $\kappa_{\text{lat}}$ .

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data supporting this study are included within the article and its supplementary information (SI). Supplementary information: the SI includes the bulk synthesis, characterization, and theoretical calculations for  $\text{TlFe}_{1.6}\text{Se}_2$  and FeSe. See DOI: <https://doi.org/10.1039/d6ta02075e>.

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