High temperature thermoelectric properties of Zr and Hf based transition metal dichalcogenides: A first principles study

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Objective

- To study the electronic and thermal transport properties of bulk MX_2 compounds (M = Zr, Hf and X = S, Se).
- Quantify the thermoelectric figure of merit (**ZT**) at high temperature.

Introduction

- Thermoelectric effect is the generation of an electric voltage from a temperature gradient and vice versa.
- The efficiency of a thermoelectric material is determined by the figure of merit $\mathbf{ZT = S^2\sigma T/\kappa}$, where **S**, σ, κ and **T** are the thermopower, electrical conductivity, thermal conductivity and operating temperature, respectively.

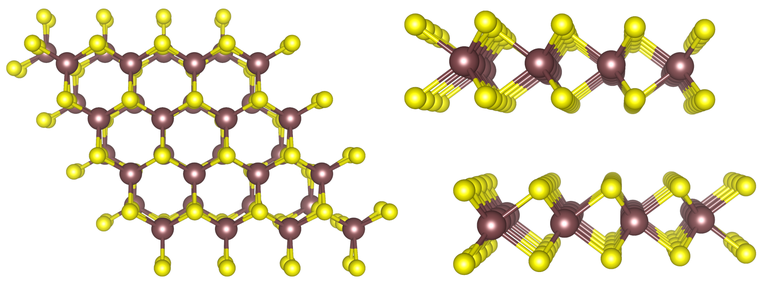


Fig. 1: A typical TMD: WS_2

- We explore the thermoelectric properties of Zr/Hf based TMDs which has much lower κ, with high thermopower, electrical conductivity.

Computational methodology

- *Ab initio* Density Functional Theory using linear augmented plane wave method including local orbitals (LAPW+lo) - WIEN2k
- Electronic transport is calculated by Boltzmann transport equations under CSTA (BoltzTraP)
- κ_{latt} (PBTE)
- IFCs - PBE-GGA (VASP)
- The linearized PBTE - ShengBTE

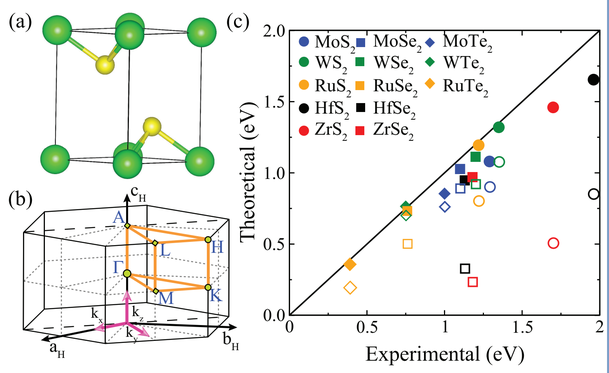


Fig. 2: (a) Unit cell (MX_2), (b) Symmetric K-path in FBZ. (c) Comparison of E_g^{theo} and E_g^{calc}.

Electronic structure (Band structure)

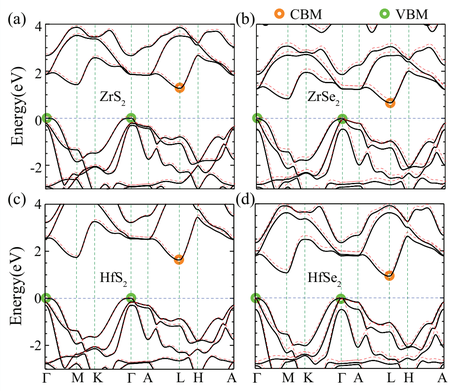


Fig. 3: Electronic band structure

- Conduction band:
  - Heavy ($\hat{z}$) - $\mathbf{d_{yz}}$, $\mathbf{d_{xz}}$
  - Light ($\hat{x}$, $\hat{y}$) - $\mathbf{d_{x^2-y^2}}$, $\mathbf{d_{z^2}}$.
- Valence band:
  - Heavy - ($\hat{x}$, $\hat{y}$) - $\mathbf{p_x}$, $\mathbf{p_y}$.
  - Light - ($\hat{z}$) - $\mathbf{p_z}$.

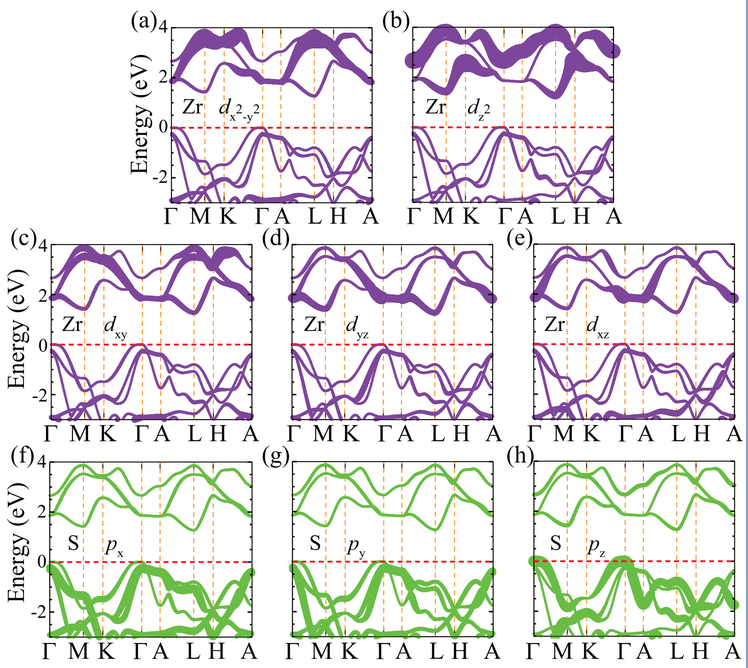
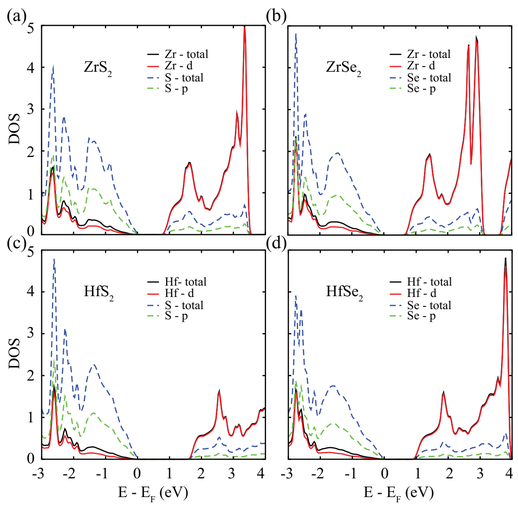


Fig. 4: Orbital-resolved band structure of ZrS_2.

Electronic structure (DOS, Fermi surface)



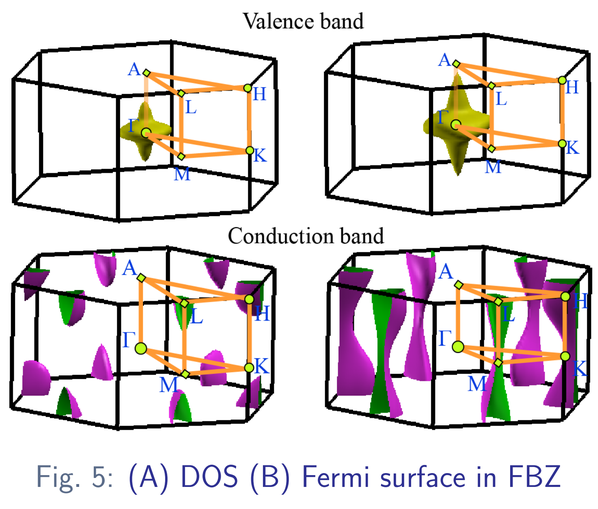


Fig. 5: (A) DOS (B) Fermi surface in FBZ

Electronic transport properties

- Huge anisotropy in the electrical conductivity provides the option of tuning the electronic transport in the desired direction.
- Large thermopower (**S**) results in very high power-factor ($\mathbf{S^2\sigma}$).

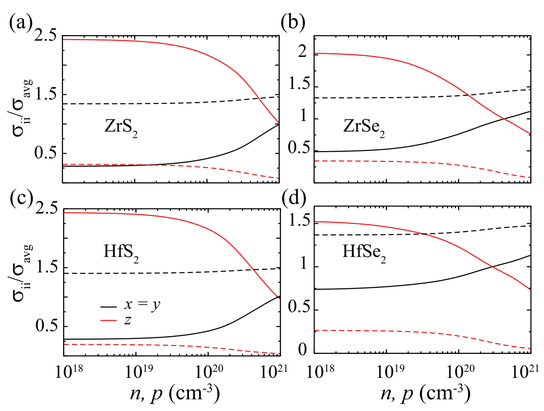


Fig. 6: Electrical conductivity

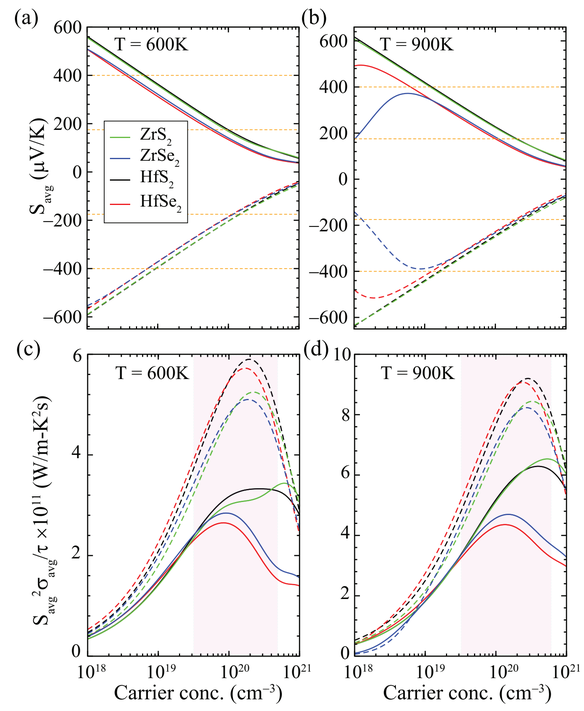


Fig. 7: (a, b) Thermopower, (c, d) Power-factor.

Lattice dynamics and thermal conductivity

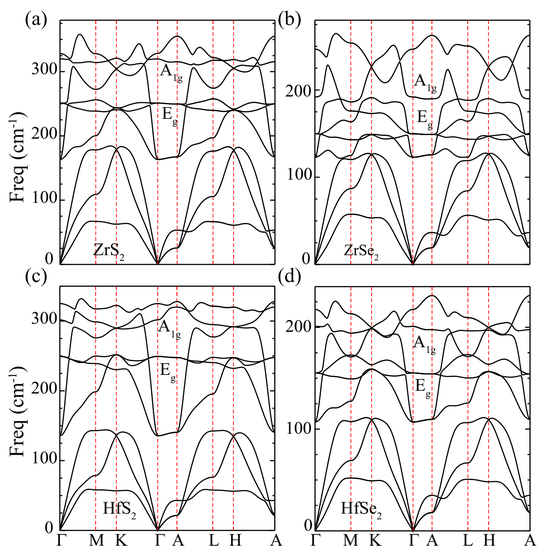


Fig. 8: Phonon dispersion curve

- Ultra low lattice thermal conductivities arises from the low group velocity and high phonon scattering rates.

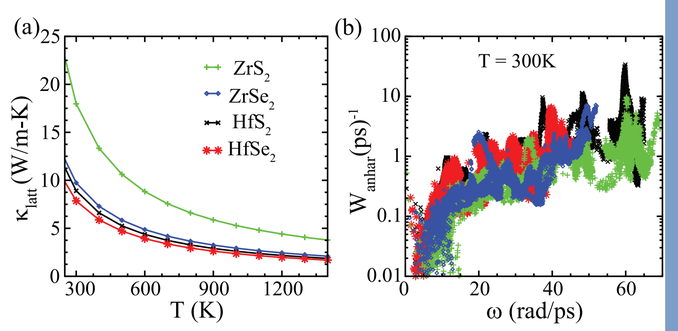


Fig. 9: (a) Lattice thermal conductivity (b) Anharmonic scattering rate at room temperature.

- Less anisotropy in κ_{latt} due to isotropic group velocity.

Conclusion

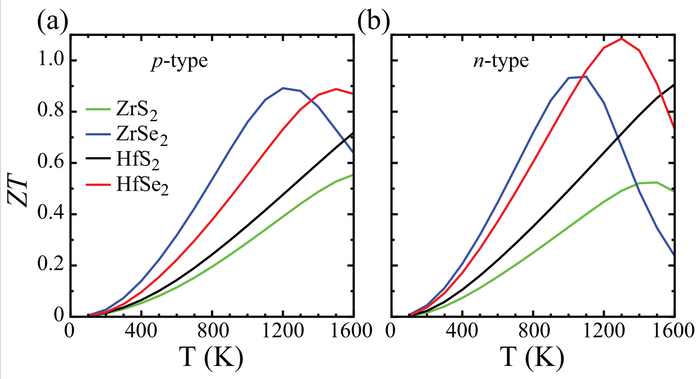


Fig. 10: Figure of merit (**ZT**)

- The **n**-type doping exhibits $\mathbf{ZT > 1}$ at T > 1200 K (Bi_2Te_3 - ZT$\sim$ 1, T$\sim$ 300 K)
- **n**-type doped $HfSe_2$ emerge as an efficient material for high temperature thermoelectric application, with $\mathbf{ZT = 1.1}$ at T=1300 K.
- This confirms the suitability of the **n**-type doping of these TMDs for high temperature thermoelectric application.

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Reference

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