XI *AUSE* Conference
VI ALBA Users Meeting
Oviedo
2 – 6 September 2024

Universidad de Oviedo

THE ROLE OF ANHARMONICITY ON THE THERMOELECTRIC PROPERTIES OF HALF-HEUSLER ALLOYS

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Universidad de Oviedo

ESRF The European Synchrotron

UCLM Universidad de Castilla-La Mancha

SINTEF

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cinn Nanomaterials & Nanotechnology Research Center

UiO : Department of Physics University of Oslo

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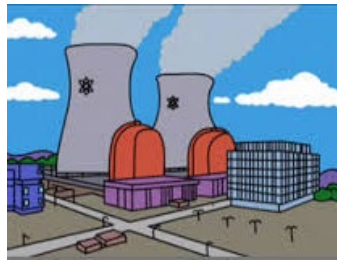
WHY THERMOELECTRIC MATERIALS?

Thermal power plant

Nuclear power plant

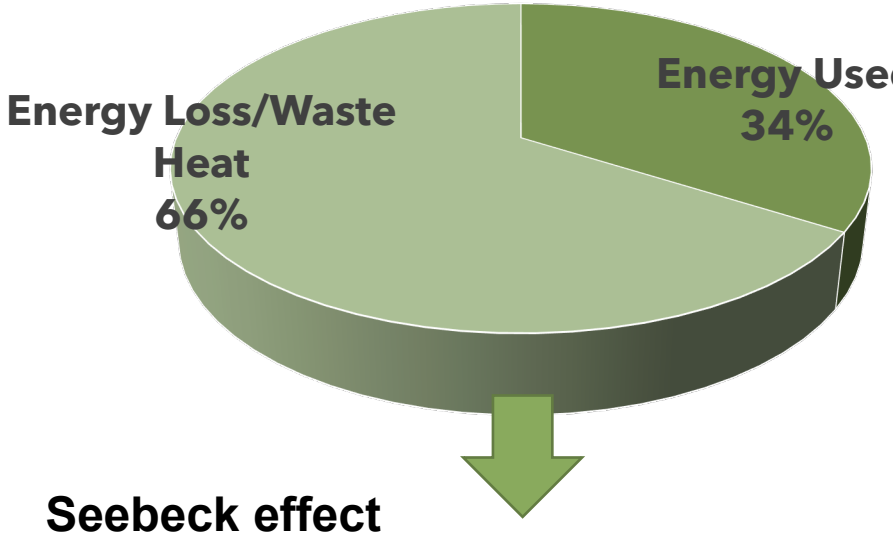


Waste incinerator

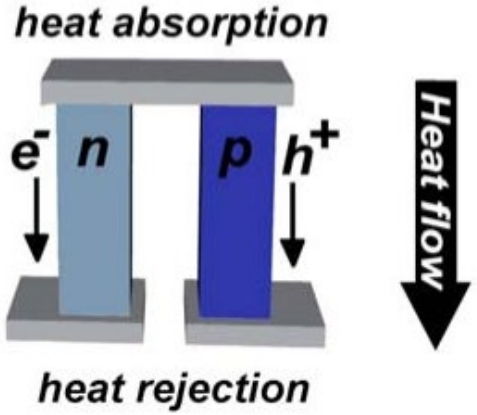
Factories

Natural gas

Automobile



Recovery

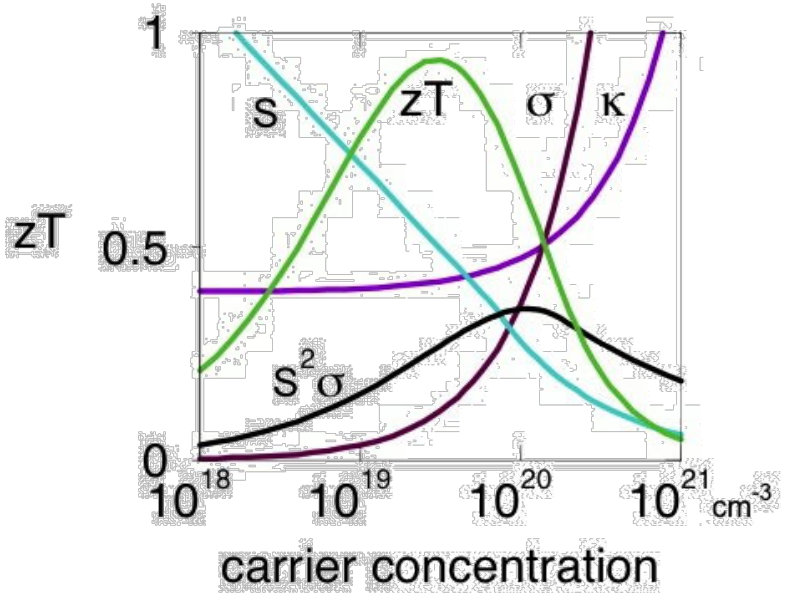


Seebeck effect

Thermoelectrics → Electric energy

MOTIVATION

To make a thermoelectric device competitive, an average ZT>2 (in the application T-range) is required.



- **Why half-Heusler alloys?**

Pb-based alloys — high ZT, but high toxicity and weak mechanical strength.

Skutterudites — high ZT, but poor thermal stability and limited supply of rare-earth elements.

Half-Heusler alloys — environmentally friendly and mechanically and thermally robust.

$$ZT = \frac{S^2\sigma}{\kappa_L + \kappa_e}T$$

OBJETIVE:

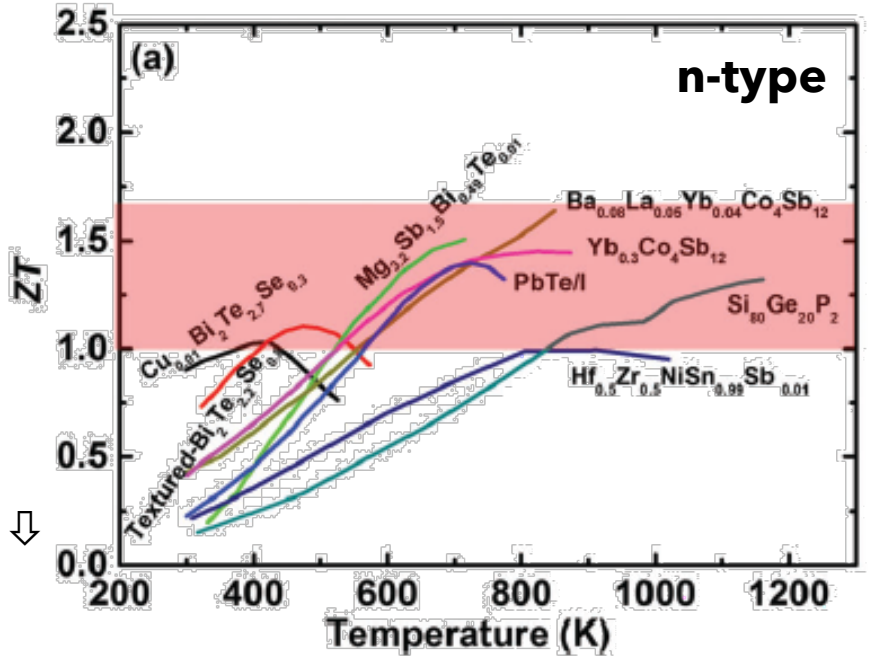
- **Increase ZT**

→ Reduction of the lattice contribution to the thermal conductivity: κ_L

→ Increase of the electrical contribution to transport: $PF = S^2\sigma$

Nanostructures → ⇧ Phonon scattering → Thermal conductivity κ_L ⇩

Doping → Modification of the charge carrier density



[Z. Liu et al., Energy Environ. Sci. **11**, 23-44 (2017)].

HALF-HEUSLER ALLOYS

Half-Heusler (HH) alloys can be derived by combining a rocksalt- and a zincblende-type crystal structures.
Wickoff positions:

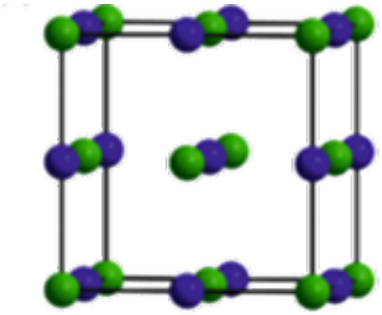
1. NaCl
   - 4a (0,0,0)
   - 4b (½, ½, ½)
2. Zn-S
   - 4a (0,0,0)
   - 4c (¼, ¼, ¼)

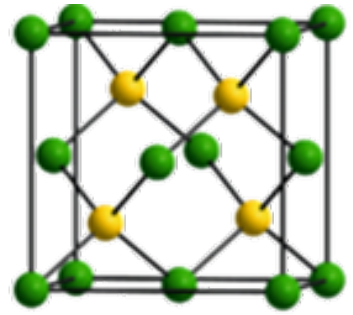
and 4d (¾, ¾, ¾) vacant.

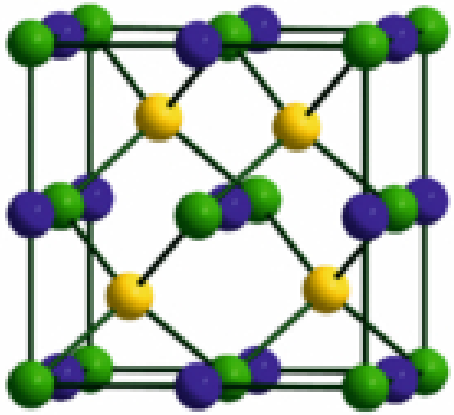
Space group: F-43m (no. 216); stoichiometry: 1:1:1 (ABC)

(A,B,C elements)
- A,B transition metals (e.g. A ≡ Ti, Zr, Hf…; B ≡ Ni, Co…)
- C metalloid or metal (e.g. C ≡ Sn, Sb…)

(Ti,Zr,Hf)NiSn


rock salt-type structure


zinc blende-type structure



Half-Heusler structure

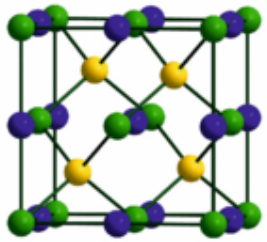
EXPERIMENTAL TECHNIQUES

(Ti,Zr,Hf)NiSn

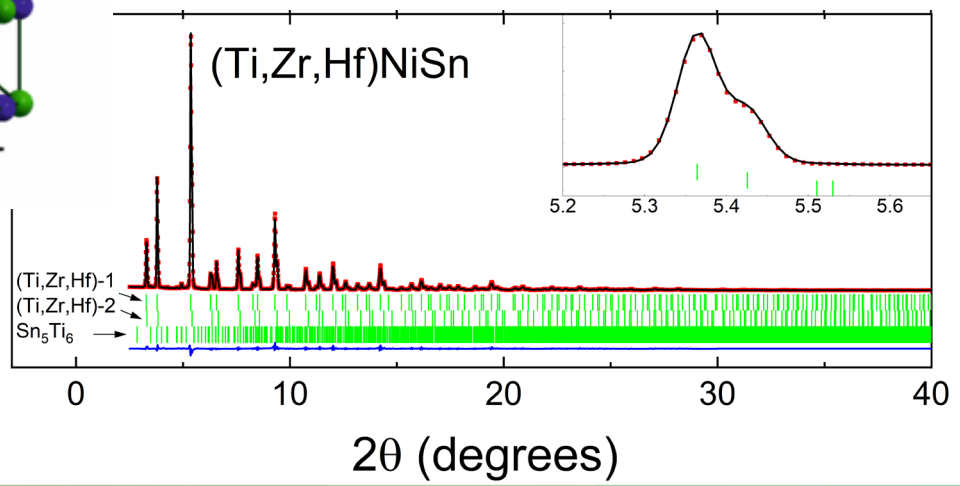
Arc melting **+** Thermal annealing @ 900°C, 1week – water quenched

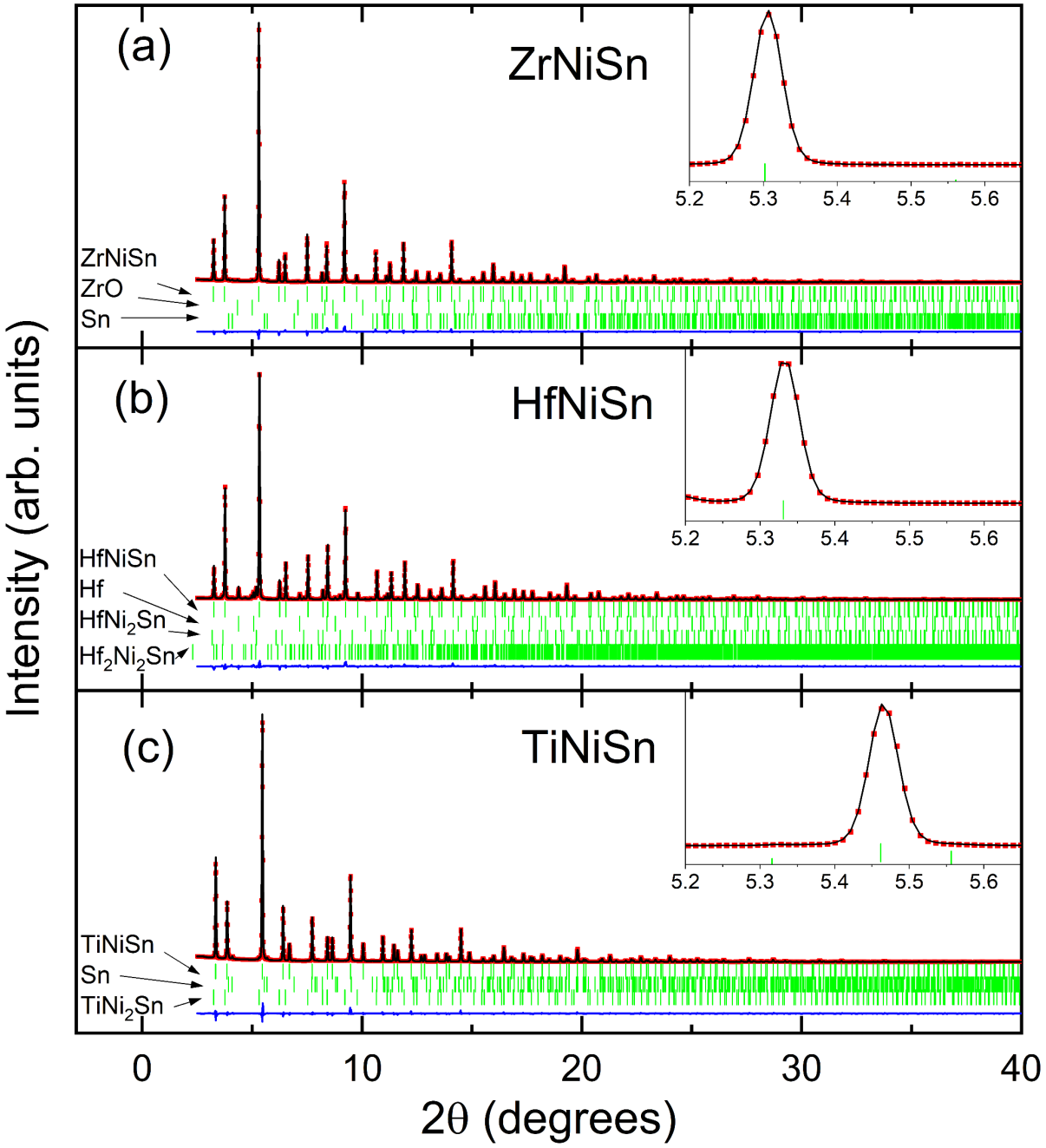
STRUCTURAL CHARACTERIZATION

- High resolution synchrotron X-ray diffraction
- **ID22@ESRF** (Grenoble, France), λ = 0.2 Å.
- Single hH phase – ternary alloys
- Segregation of hH phases – pseudoternary alloys
- Minor secondary phases (< 3 wt.%)



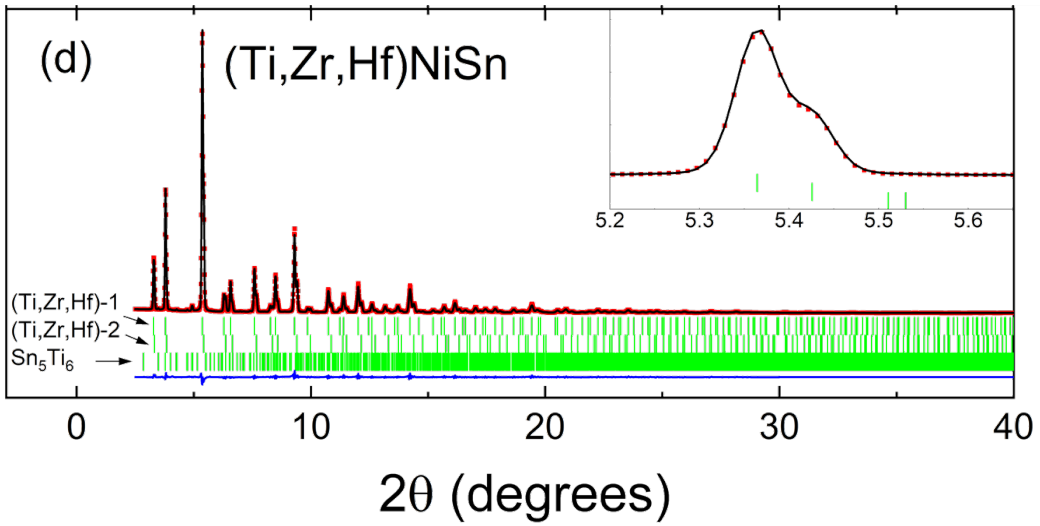
Half-Heusler structure

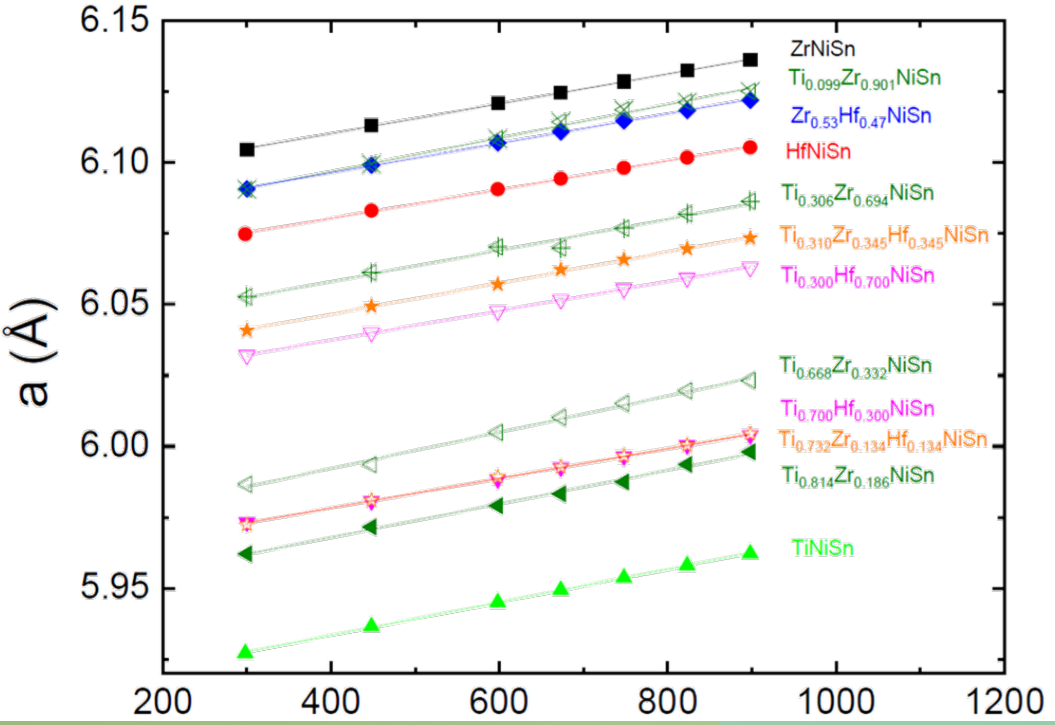


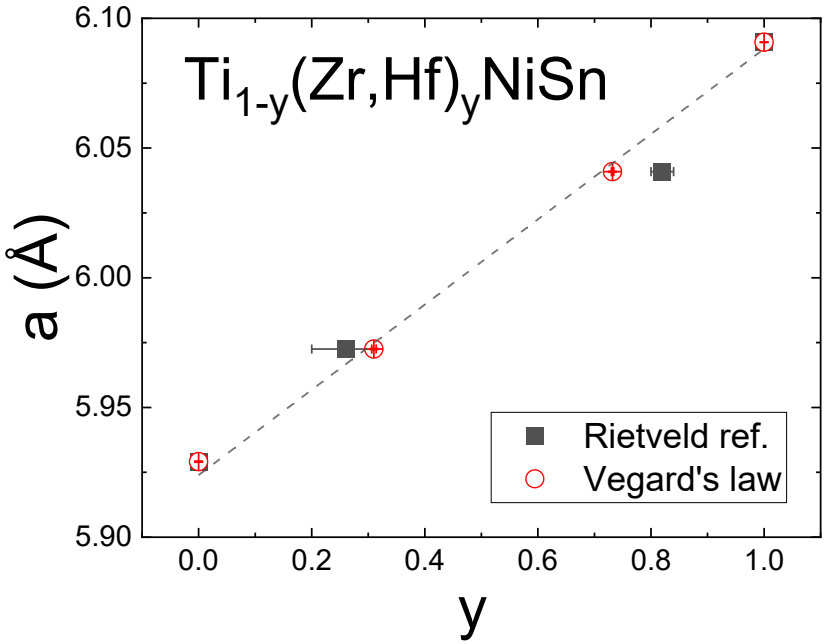


STRUCTURAL CHARACTERIZATION

- Linear coefficient of **thermal expansion** (CTE) for every hH phase.
- $\alpha = 8.4 - 9.8 \times 10^{-6}\ K^{-1}$ → small expansion with T







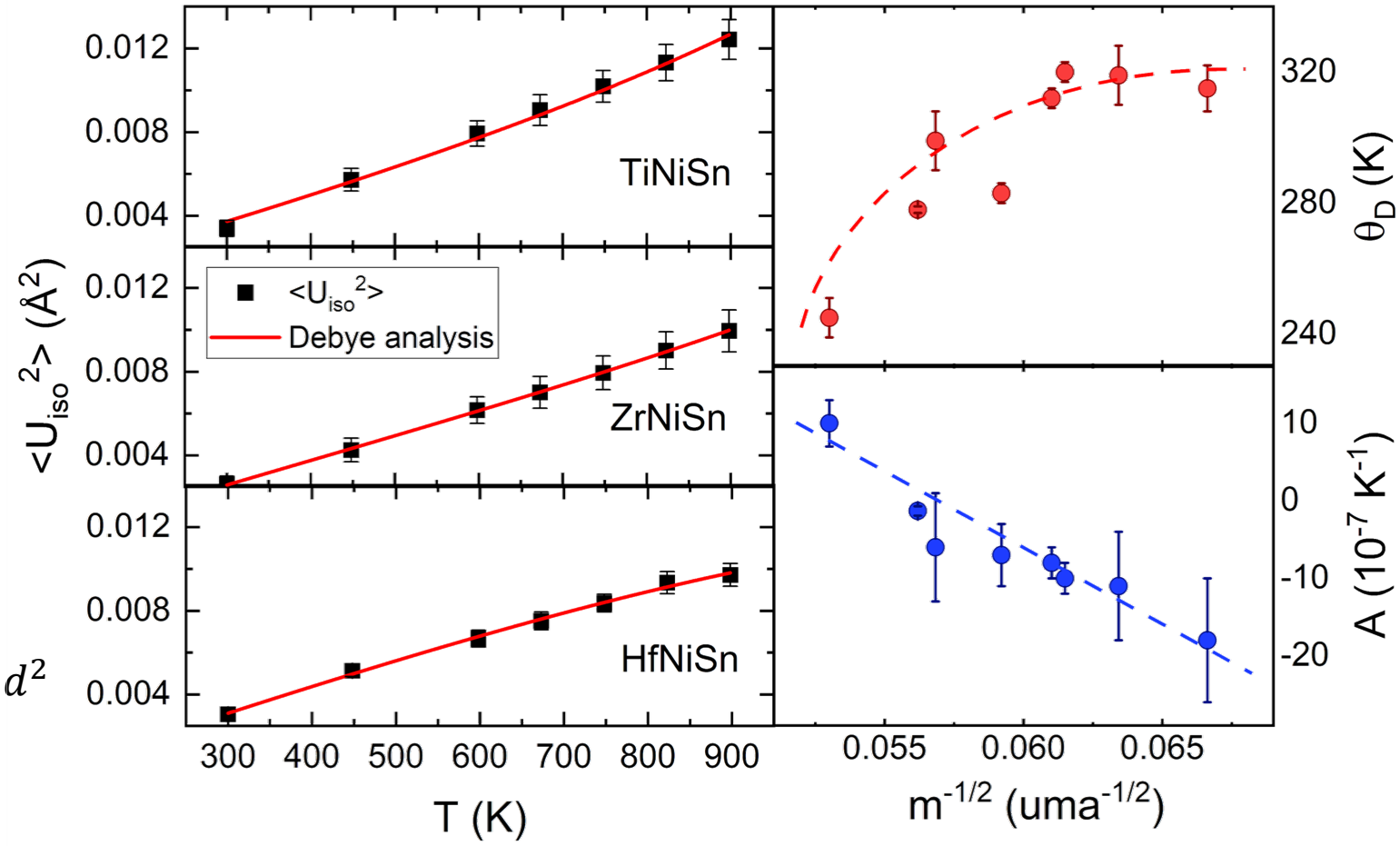
STRUCTURAL CHARACTERIZATION

- **Atomic (isotropic) displacement parameters (ADPs)**:

$$B_{iso} = 8\pi^2 < U_{iso}^2 >$$

- Debye model:
  - Simple crystal structures
  - Single mass m → weighted average of every atomic species

$$< U_{iso}^2 > = \frac{3\hbar^2 T}{m k_B \theta_D^2}\left[\frac{T}{\theta_D}\int_0^{\frac{\theta_D}{T}} \frac{x}{e^x - 1}dx + \frac{\theta_D}{4T}\right] + d^2$$



[C. Echevarria-Bonet et al., JALCOM **959**, 170583 (2023)]

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STRUCTURAL CHARACTERIZATION

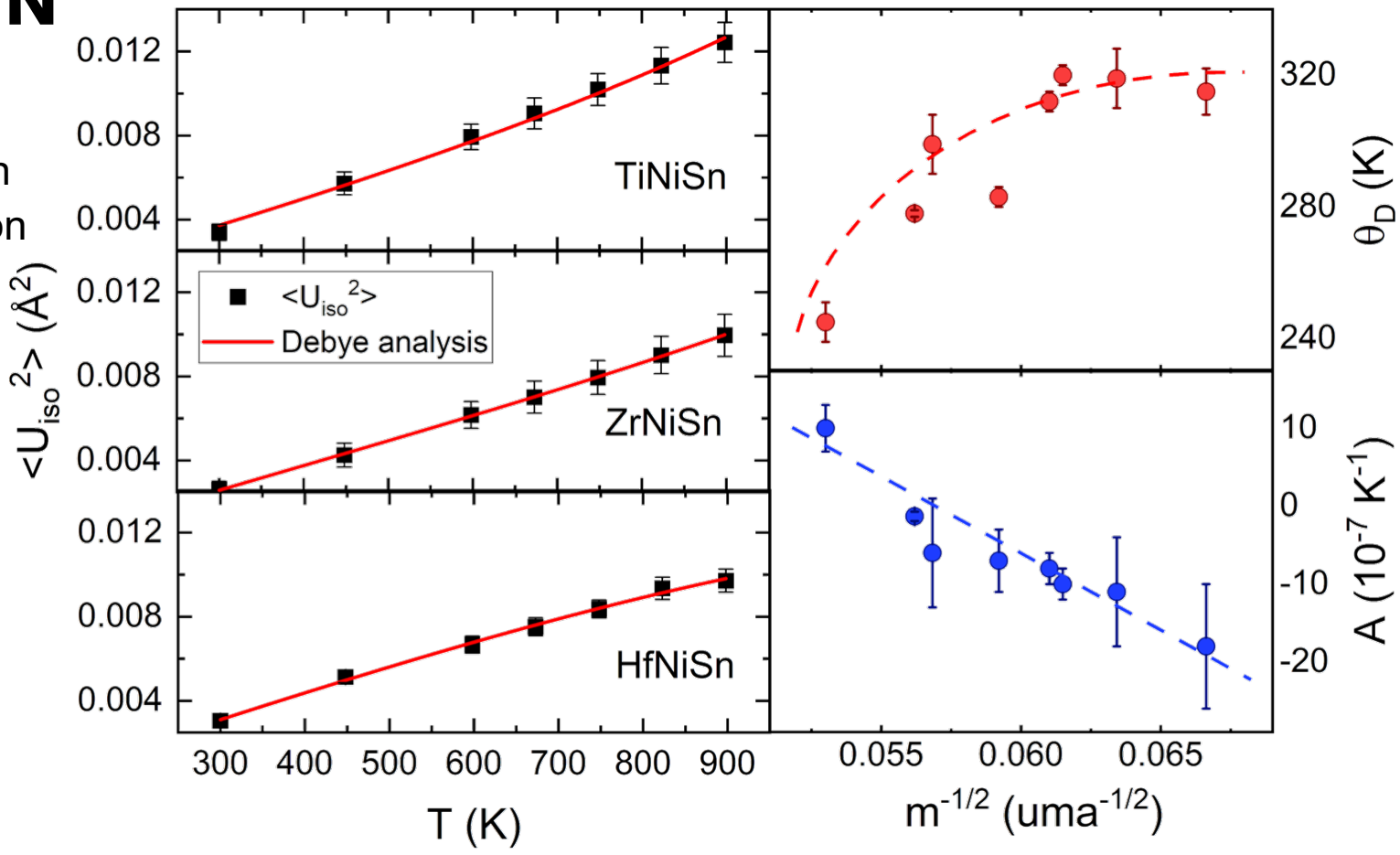
- θ_D generally depends on T
  - It can be calculated using the Thirring-Stern expansions of the quasiharmonic expression for the thermal energy θ_W^h:

$$\theta_W^h = \theta_1 + \sum_{n=1}^{\infty} b_n T^{-n}$$

(b_n coefficients)

  - Also an anharmonic contribution has to be considered, so, the T-dependent Debye temperature:

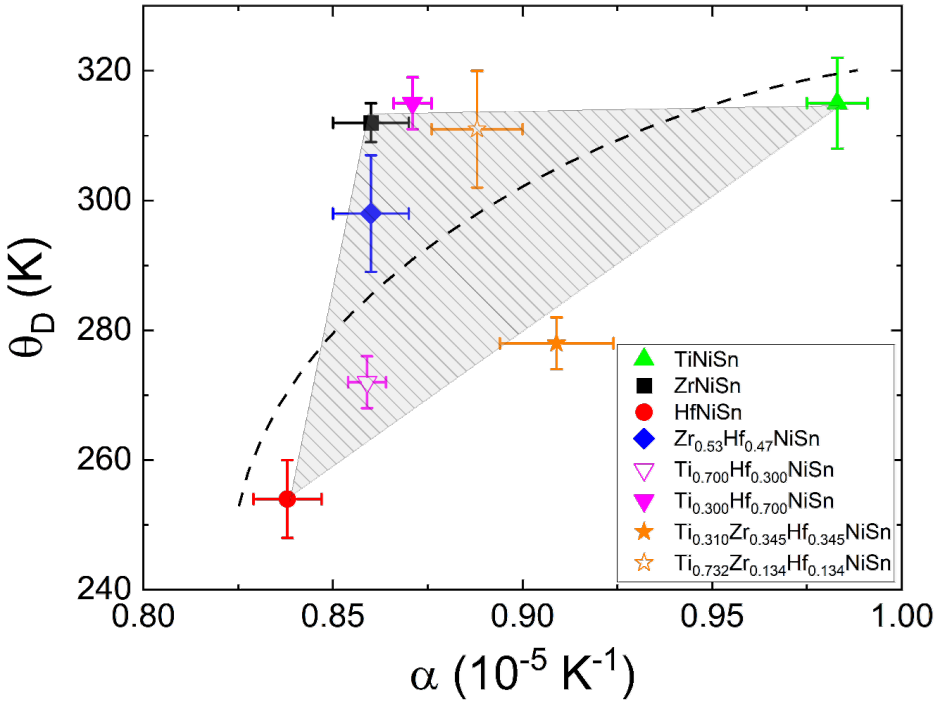
$$\theta_W = \theta_W^h + \left[\frac{1}{2} A T^2 \Big/ \frac{d\left(\frac{W_{th}^h}{3Nk_BT}\right)}{d\left(\frac{\theta_W^h}{T}\right)} \right]$$



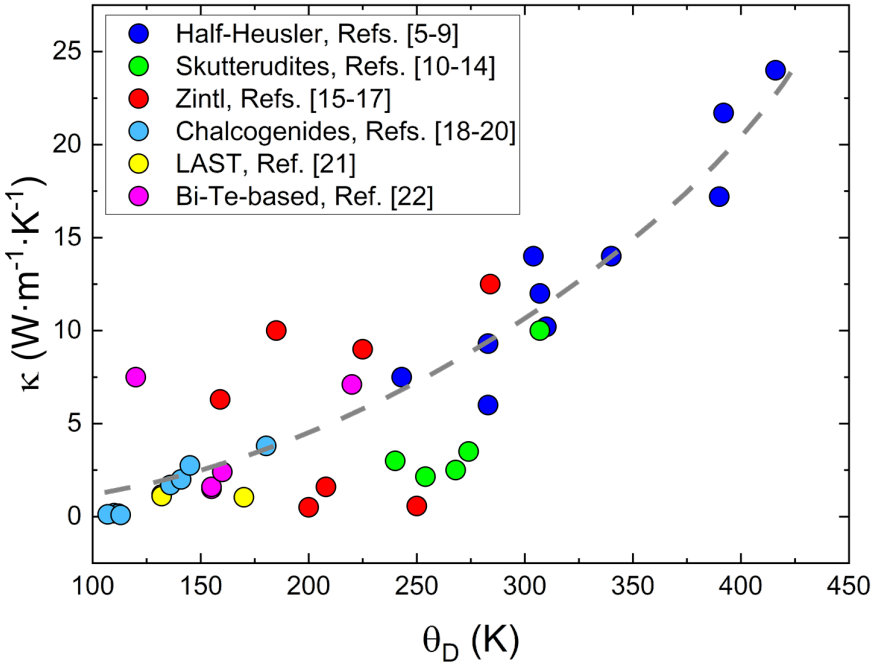
The lower θ_D → **the larger anharmonicity A**

STRUCTURAL CHARACTERIZATION

- Relationship between Debye temperature and CTE:



- Implications in the thermoelectric properties: thermal conductivity



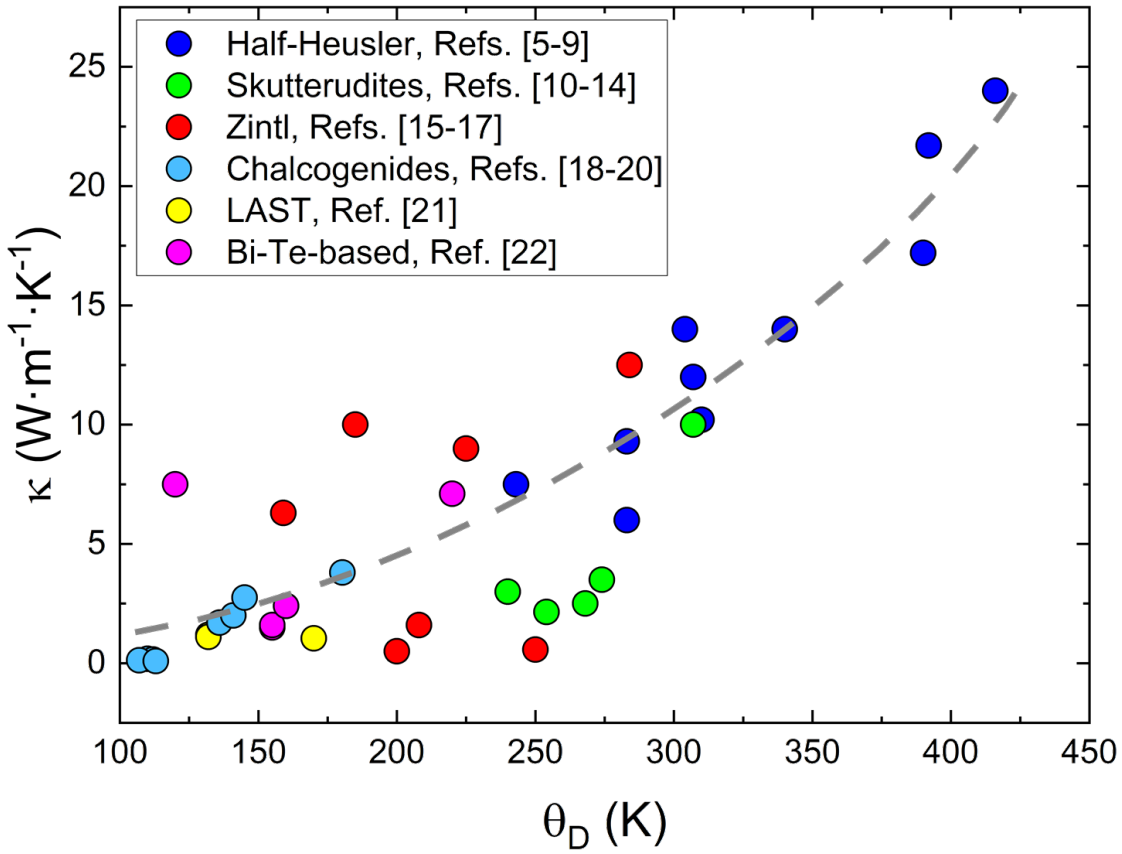
The lower CTE → the lower θ_D → the lower κ → the larger ZT

The larger anharmonicity A → the larger ZT

[C. Echevarria-Bonet et al., JALCOM **959**, 170583 (2023)]

CONCLUSIONS

- High resolution synchrotron XRD experiments give precise insight on the phase separation in isoelectronic substituted half-Heusler Alloys.
- Temperature dependent XRD can provide information of the suitability of a material to be a good thermoelectric compound.
- **The larger the anharmonicity, the larger ZT**.




THANKS