

Fundamental Mathematical Formalism of DFT for Predictive Structure and Transport response of Ru-Based Intermetallics

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Abstract

The evaluation of thermoelectric transport coefficients constitutes a fundamental criterion for assessing the technological viability of a material in high-efficiency waste-heat recovery and solid-state energy conversion systems. These transport descriptors, including the Seebeck coefficient, electrical conductivity, electronic thermal conductivity, and power factor, collectively quantify the efficacy of thermal-to-electrical energy conversion under an imposed temperature gradient. Furthermore, the calculated thermal parameters provide valuable insight into the lattice dynamical behavior and anharmonic characteristics of the investigated compounds. The relatively low degree of lattice anharmonicity, together with favorable thermodynamic stability, indicates that these alloys can preserve their structural integrity and transport performance over a broad range of temperatures and external pressures. The coexistence of robust thermoelectric transport characteristics with intrinsically favorable electronic and magnetic properties further underscores the multifunctional nature of these materials, rendering them highly promising candidates for advanced spin-caloritronic, and thermoelectric energy-harvesting technologies.

Introduction

Thermoelectric (TE) materials are a class of functional materials capable of directly converting heat into electrical energy and vice versa through the Seebeck and Peltier effects, respectively shown in **Fig. 1**[1-8]. Owing to their ability to harvest waste heat without the use of moving components, thermoelectric materials have attracted considerable attention as sustainable energy-conversion systems for power generation and solid-state refrigeration. The efficiency of a thermoelectric material is primarily determined by the dimensionless figure of merit, (ZT , where (S) is the Seebeck coefficient, (σ) is the electrical conductivity, (k) is the total thermal conductivity, and (T) is the absolute temperature [9-15]. An ideal thermoelectric material simultaneously possesses a large Seebeck coefficient, high electrical conductivity, and low thermal conductivity, enabling efficient conversion of thermal gradients into electrical power. Consequently, extensive theoretical and experimental efforts have been devoted to the exploration of novel compounds, particularly Heusler alloys, owing to their tunable electronic structure, favorable transport properties, and excellent thermal stability, which render them promising candidates for next-generation thermoelectric applications.

Methodology

Density Functional Theory (DFT) has emerged as one of the most robust and extensively employed first-principles quantum-mechanical frameworks in contemporary computational materials science for investigating the ground-state properties of condensed matter systems. By reformulating the complex many-electron problem in terms of the electron density rather than the many-body wavefunction, DFT provides a computationally efficient yet highly accurate approach for elucidating the structural, electronic, magnetic, optical, mechanical, and thermodynamic characteristics of materials. Owing to its remarkable predictive capability and favorable balance between computational efficiency and accuracy, DFT has become an indispensable theoretical methodology for the rational design, characterization, and discovery of advanced functional materials, including Heusler alloys, semiconductors, superconductors,

topological materials, and energy-conversion compounds. That conception was used by Born-Oppenheimer by expending the Schrodinger equation as;

$$\hat{H}\psi = [\hat{T} + \hat{U} + \hat{V}_{ext}]\psi = [-\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 + \sum_{i<j}^N U(r_i, r_j) + \sum_{i=1}^N v_{ext}(r_i, R^\mu)]\psi = E\psi,$$

Here, the electron-electron and electron-ion interactions is defined as,

$$U(r_i, r_j) = e^2 |r_i - r_j|^{-1}$$

and

$$v_{ext}(r_i, R^\mu) = \sum_{\mu} \frac{e^2 Z^\mu}{|r_i - R^\mu|}$$

Additionally this will deliver us lowest energy as ground state energy as $E_0 = E[n_0(r, R)]$. External potential functional over all wave functions gets minimized, which defines the density $n(r, R)$.

$$E[n(r, R)] = \min_{\psi \rightarrow n} \langle \psi | \hat{T} + \hat{U} + \hat{V}_{ext} | \psi \rangle$$

The functional becomes;

$$E[n(r, R)] = F[n(r, R)] + \int n(r, R) v_{ext}(r, R) dr$$

Where, functional is well-defined as,

$$F[n(r, R)] = \min_{\psi \rightarrow n} \langle \psi | \hat{T} + \hat{U} + \hat{V}_{ext} | \psi \rangle \geq E_0$$

The minimum or optimized ground state energy is attained from variational principle demonstrated as;

$$E_0 = \min_n \left(F[n] + \int n(r, R) v_{ext}(r, R) dr \right)$$

Structural Analysis

The crystallographic architecture of a material represents the cornerstone for understanding its intrinsic physicochemical properties, since the precise atomic arrangement, site occupancy, and lattice symmetry govern the fundamental electronic, magnetic, mechanical, and thermodynamic characteristics of the system. Consequently, an accurate structural optimization constitutes the prerequisite for establishing the equilibrium ground-state configuration and assessing the structural stability of full-Heusler intermetallic compounds. Owing to their highly ordered atomic framework and exceptional compositional versatility, Ru-based full-Heusler alloys have attracted considerable attention because of their remarkable multifunctional properties, which originate from the delicate interplay between crystal symmetry and electronic hybridization.

The optimized crystal structure of the investigated Co-based full-Heusler alloy is presented in **Fig. 2**, revealing its stabilization in the conventional cubic L2₁ structure with the well defined space group. The primitive unit cell consists of four interpenetrating face-centered cubic (fcc) sublattices arranged in a highly ordered fashion. Within this crystallographic framework, the two crystallographically equivalent Co atoms occupy the 8c Wyckoff positions at fractional coordinates (¼, ¼, ¼) and (¾, ¾, ¾), while the transition-metal atom (Sc/Ti) is located at the 4a site (0, 0, 0), and the Sb atom occupies the 4b site (½, ½, ½). This well-defined atomic ordering preserves the inherent centrosymmetric nature of the L2₁ phase and promotes strong orbital hybridization among the constituent atoms, thereby giving rise to the distinctive electronic band topology, magnetic exchange interactions, and transport characteristics commonly observed in Ru-based Heusler systems.

Thermoelectric response

Thermoelectric (TE) materials constitute a class of functional energy-conversion systems capable of directly transmuting dissipated thermal energy into electrical power through the coupled transport of charge carriers and heat. Owing to their solid-state energy conversion mechanism, absence of moving components, operational reliability, and negligible environmental footprint, TE materials have emerged as promising candidates for sustainable and environmentally benign energy-harvesting technologies. The

thermoelectric performance is fundamentally governed by the intricate interplay between the electronic band topology and lattice dynamical characteristics, which collectively dictate the transport behavior of charge carriers and phonons. Consequently, the optimization of electronic and thermal transport coefficients necessitates a comprehensive understanding of the underlying electronic structure and phonon dispersion. To quantitatively evaluate the thermoelectric transport coefficients, the semi-classical Boltzmann transport formalism is employed within the framework of the constant relaxation time approximation (CRTA) and the rigid-band approximation (RBA). Within this theoretical paradigm, the perturbation induced by external electric fields and temperature gradients is assumed to preserve the equilibrium electronic band dispersion while the carrier lifetime remains invariant with respect to energy. This formalism facilitates the determination of the electrical conductivity, Seebeck coefficient, electronic thermal conductivity, and power factor directly from the first-principles electronic band structure. Accordingly, the electrical current density arising from the transport of charge carriers is generally expressed as: $J = e \sum_{\vec{k}} f_{\vec{k}} v_{\vec{k}}$

Where, $f_{\vec{k}}$ is the distribution function. The $\vec{k}$ state of Boltzmann's is designated as i.e.

$$\frac{\partial f_{\vec{k}}}{\partial t} + v_{\vec{k}} \cdot \nabla_{\vec{r}} f_{\vec{k}} + \frac{e}{\hbar} \left(\vec{E} + \frac{1}{c} v_{\vec{k}} \times \vec{H} \right) \cdot \nabla_{\vec{k}} f_{\vec{k}} = \left(\frac{\partial f_{\vec{k}}}{\partial t} \right)_{\text{scatt.}}$$

The population is given by;

$$f_{\vec{k}} = f_0(\varepsilon_{\vec{k}}) + e \left(-\frac{\partial f_0}{\partial \varepsilon} \right) \tau_{\vec{k}} v_{\vec{k}} \vec{E}$$

The conductivity tensor can be expressed as:

$$\sigma = e^2 \sum_{\vec{k}} \left(-\frac{\partial f_0}{\partial \varepsilon} \right) v_{\vec{k}} v_{\vec{k}} \tau_{\vec{k}}$$

The transport scattering is described as,

$$\Xi = \sum_{\vec{k}} v_{\vec{k}} v_{\vec{k}} \tau_{\vec{k}}$$

Using scalar coefficients,

$$\sigma = e^2 \int \Xi(\varepsilon) \left(-\frac{\partial f_0}{\partial \varepsilon} \right) d\varepsilon$$

$$S = \frac{e}{T\sigma} \int \Xi(\varepsilon) \left(-\frac{\partial f_0}{\partial \varepsilon} \right) (\varepsilon - \mu) d\varepsilon$$

$$\kappa = \frac{1}{T} \int \Xi(\varepsilon) \left(-\frac{\partial f_0}{\partial \varepsilon} \right) (\varepsilon - \mu)^2 d\varepsilon$$

Where μ is the chemical potential.

Seebeck coefficient: The Seebeck coefficient (S) constitutes one of the most pivotal thermoelectric transport parameters, as it exerts a direct and profound influence on both the power factor and the dimensionless thermoelectric figure of merit (ZT). Since the power factor exhibits a quadratic dependence on the Seebeck coefficient, an enhanced magnitude of (S) generally signifies superior thermoelectric energy-conversion efficiency, provided that the electrical conductivity remains sufficiently high. The temperature-dependent evolution of the Seebeck coefficient is illustrated in **Fig. 3(a)**, wherein a consistently positive value of (S) is observed throughout the investigated temperature regime for Co based alloy. This persistent positive thermopower unequivocally establishes holes as the predominant charge carriers governing the transport process, thereby confirming the intrinsic p-type conduction character in both spin channels over the entire temperature interval. The monotonic variation of the Seebeck coefficient further suggests that the electronic band topology in the vicinity of the Fermi level remains favorable for sustaining hole-dominated thermoelectric transport across the explored thermal range.

Power Factor: Another indispensable descriptor of thermoelectric performance is the power factor (PF), which serves as a critical electronic transport metric for assessing the efficiency of thermoelectric energy conversion. Defined as $(PF = S^2\sigma/T)$ the power factor embodies the synergistic contribution of the Seebeck coefficient (S) and the electrical conductivity thereby quantifying the capability of a material to generate electrical power from an imposed thermal gradient. Owing to its quadratic dependence on the Seebeck coefficient, any enhancement in thermopower substantially amplifies the power factor, provided that the electrical conductivity is not significantly compromised. Consequently, PF reflects the collective response of itinerant charge carriers and provides valuable insight into the optimization of carrier transport for superior thermoelectric functionality. The temperature-dependent evolution of the power factor is depicted in **Fig. 3(b)**, which reveals a progressive enhancement with increasing temperature, indicative of improved electronic transport characteristics under elevated thermal conditions. At ambient temperature, the calculated power factor demonstrating the comparatively superior thermoelectric performance of the latter compound. These observations underscore that the simultaneous realization of high electrical conductivity and a large Seebeck coefficient is indispensable for maximizing the electronic contribution to thermoelectric efficiency. Therefore, materials exhibiting an optimal balance between charge-carrier mobility and thermopower are regarded as the most promising candidates for high-performance thermoelectric applications, as they facilitate efficient conversion of thermal energy into electrical power while maximizing the attainable figure of merit.

Conclusions

High-throughput ab-initio calculations within the framework of Density Functional Theory (DFT) have been systematically performed to comprehensively elucidate the crystallographic, electronic, and magnetic characteristics of the investigated full-Heusler compounds. Rigorous structural optimization, accomplished through total-energy minimization and equation-of-state analysis, unequivocally demonstrates that the energetically preferred ground-state configuration corresponds to the highly ordered cubic $L2_1$ phase. The optimized equilibrium lattice parameters, minimum total energy, and associated structural descriptors collectively confirm the thermodynamic stability and crystallographic robustness of the compounds, thereby establishing the cubic $L2_1$ structure as the most energetically favorable phase. The excellent agreement of the calculated structural parameters with available theoretical and experimental investigations further substantiates the reliability of the adopted first-principles methodology and provides a robust foundation for the subsequent investigation of the structural and thermoelectric properties of these Ru based Heusler alloys. These alloys shows good Seebeck coefficient and power factor which lends its applicability in thermoelectric materials.

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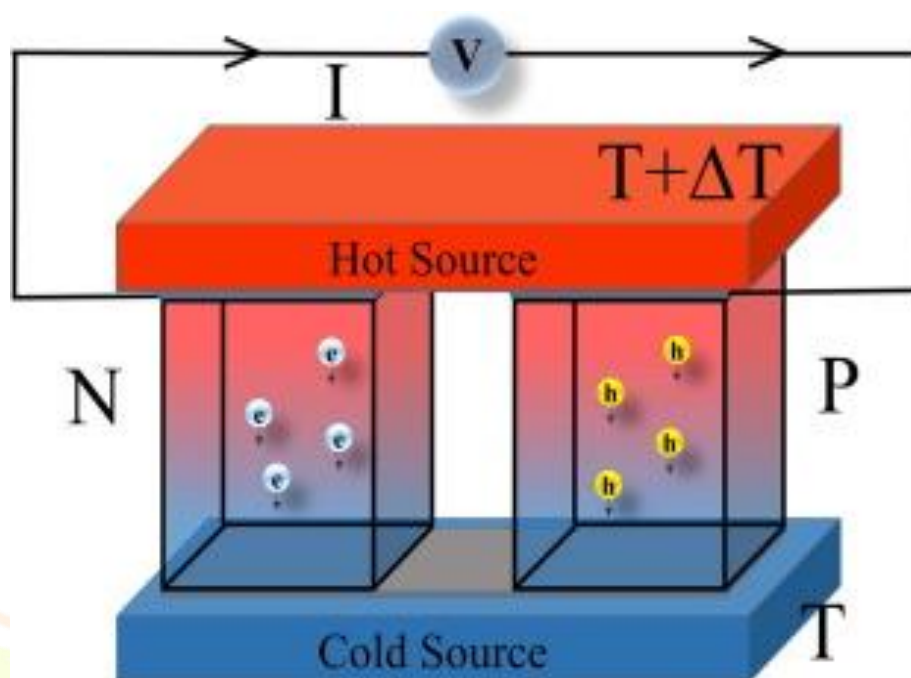


Fig. 1. Schematic diagram of the Seebeck effect.

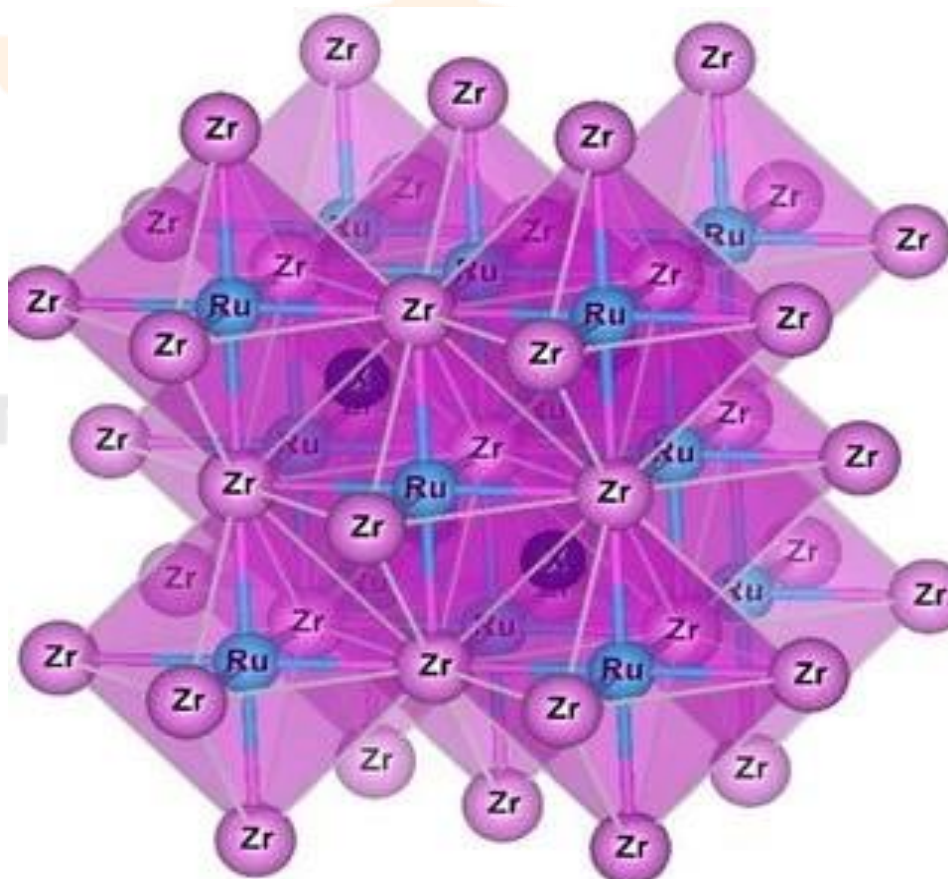


Fig. 2. Crystal structure of RuCrX (X = Si, Ge, Sn)

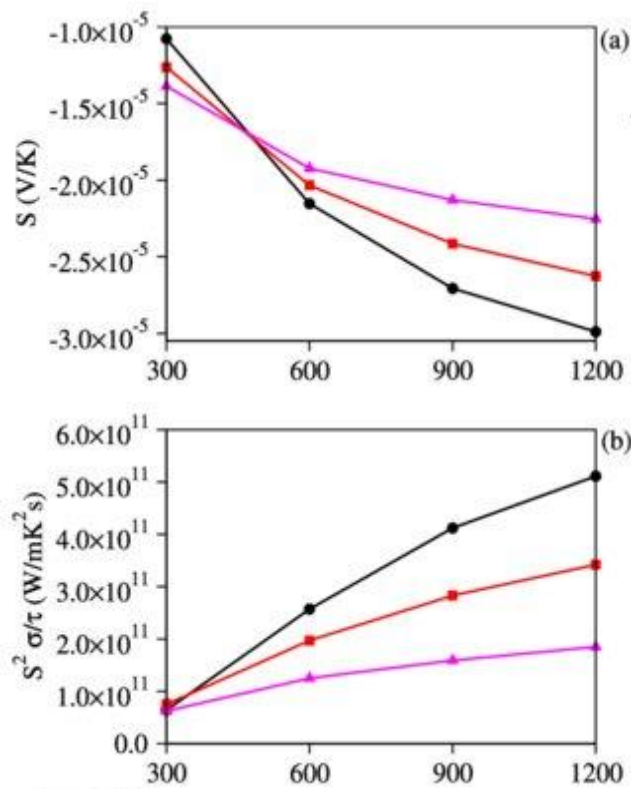


Fig 3. Variation of (a) Seebeck coefficient, (b) power factor of RuCrX (X = Si, Ge, Sn) against temperature.

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