

of better exchange-correlation approximations in the context of DFT remains an important research area. In recent years, the GW method and related many-body methods have emerged as promising formalisms for obtaining better descriptions of the single-particle states (i.e., charged excitations) of nanomaterials.⁹ Although treating interactions between electrons and holes by representing electronic excitations in terms of many-particle wavefunctions is desirable, having a manifold of closely spaced excited states is a great computational challenge for studying nanomaterials with thousands of electrons. An interesting and potentially promising alternative is an approach based on the real-time propagation of the so-called Kadanoff-Baym equations, which cast the time-dependent problem in terms of Greens functions. A first-principle implementation of the Kadanoff-Baym equations has been demonstrated already for simple materials such as silicon,¹⁰ and this time-evolved non-equilibrium Green-function approach might open up exciting opportunities for studying PHET dynamics in the future.

This preview discusses the work by Zhang et al.³ in the context of recent findings by Wu et al.² and earlier theoretical work by Long and Prezhdo.¹ The work by Zhang et al. represents the current state-of-the-art in modeling PHET at complex interfaces from first-principle theory, and the simulation has greatly advanced our understanding of PHET mechanisms. At the same time, continued progress will require further advancement in theoretical and computational methodologies, and emerging, potentially promising approaches are highlighted. The development of new computational methodologies will continue to enable more scientific discoveries and help us develop a better understanding of PHET in complex systems at the molecular scale.

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Preview

Slight Symmetry Reduction in Thermoelectrics

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Thermoelectric research on germanium telluride (GeTe) has been mainly focused on the enhancement of its performance in the high-temperature cubic phase since the 1960s. Recently in *Joule*, Pei and co-workers achieved an unprecedented thermoelectric figure of merit in rhombohedral-phase GeTe by exploiting slight symmetry breaking in the structure, which simultaneously improved the electronic properties and reduced the lattice thermal conductivity.

The ever-increasing demand for energy along with a greater emphasis on increasing efficiency has led scientists

to search for clean and renewable energy sources. Heat can be contemplated as one of the most available

renewable energy sources because of its ubiquitous and ineluctable nature. It is worth noting that the combustion of coal, petroleum, and natural gas produces enormous amounts of energy for running industries and fulfilling daily needs; however, a large percentage (~65%) of the utilized energy is being lost as wasted heat. Thermoelectric materials can directly convert heat to electricity, so they should play an important

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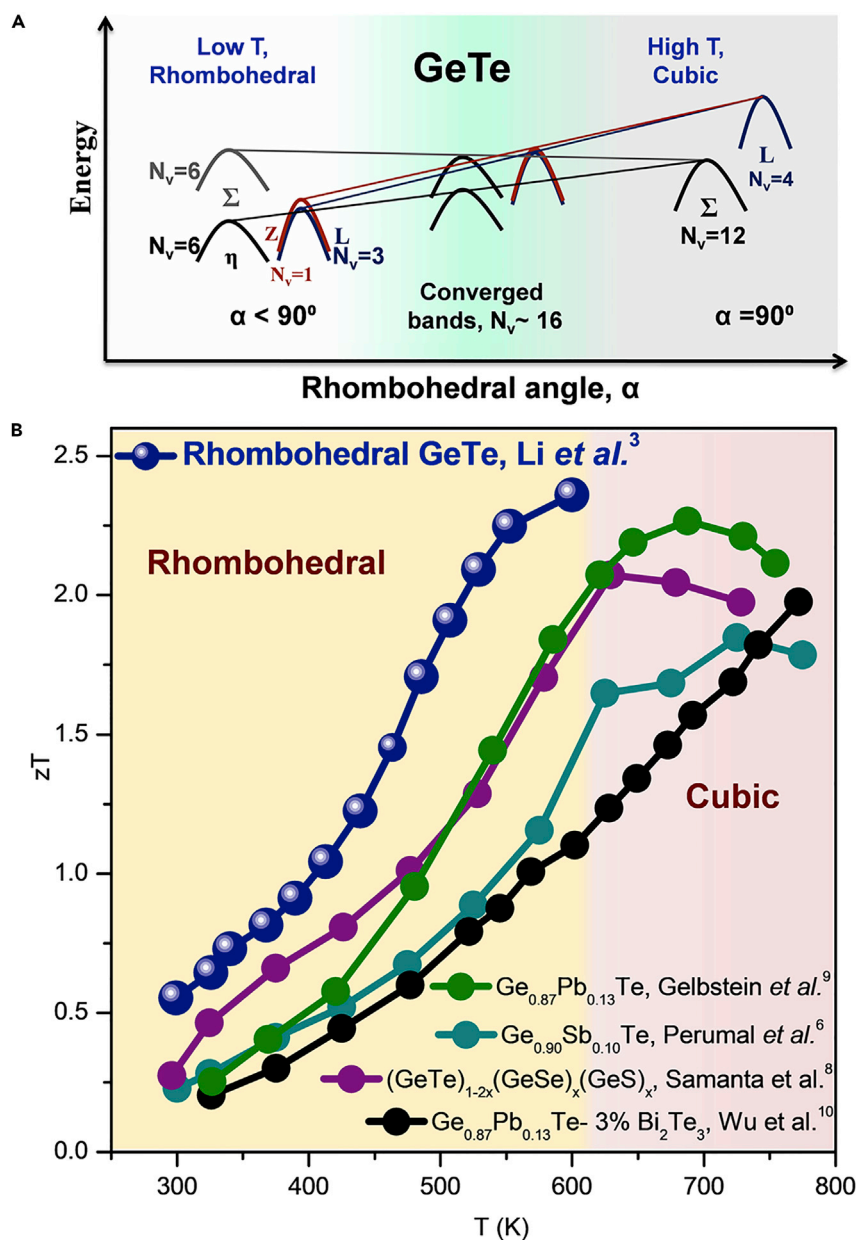


Figure 1. High Thermoelectric Performance in GeTe

(A) Schematic energy diagram of the evolution of the electronic structure of GeTe from the cubic to the rhombohedral phase depending on the extent of symmetry reduction.

(B) Temperature-dependent thermoelectric figure of merit (zT) for high-performance GeTe-based materials.

role in future energy management.^{1,2} Further, thermoelectric devices are devoid of moving parts and do not emit CO₂ or any other greenhouse gases. Hitherto, the use of thermoelectric materials and devices has been limited to niche applications, although the scope is huge. A limited thermo-

electric figure of merit (zT) motivates the unearthing of new material and the development of new strategies to enhance the zT . The recent *Joule* paper on high-performance thermoelectrics based on germanium telluride (GeTe) addresses some of the issues and demonstrates an important discovery.³

Lead chalcogenides (PbTe, PbSe, and PbS) and their alloys have been widely considered as the best performers for thermoelectric power generation at medium and high temperatures (600–900 K).^{1,2} Although their extraordinary properties make them prime candidates, the toxicity of lead (Pb) has ostracized its usefulness in mass-market applications. GeTe from the same IV-VI semiconductor family has recently been considered as an alternative to PbTe, but pristine GeTe is a less efficient thermoelectric material because of its high p -type carrier concentration resulting from its intrinsic Ge vacancies and high thermal conductivity.^{4,5} However, GeTe has been extensively alloyed with AgSbTe₂ (coined as TAGS [tellurium-antimony-germanium-silver]) to achieve high thermoelectric performance via carrier and phonon engineering. Since the 1960s, several attempts have been made to enhance its performance via different doping regimens and tailoring the composition of TAGS.⁴ Deep-space missions of NASA, namely, Viking Mars Landers (1976) and Pioneers 10 and 11 (1972–1973), mainly used TAGS-based materials for their radio-isotope thermoelectric generators as a p -type leg. With regard to the goal of optimizing the carrier concentration in GeTe, we recently found that antimony (Sb) is an effective donor dopant that can simultaneously increase the Seebeck coefficient and decrease the lattice thermal conductivity via nano- and meso-scale phonon scattering, resulting in a high zT of ~ 1.85 at 725 K.⁶ The performance of GeTe was still lower than that of PbTe ($zT \sim 2.2$ at 913 K in PbTe-SrTe doped with 2% Na).² Pei and co-workers further optimized the carrier concentration of the Sb-doped GeTe sample by Se substitution and obtained a reasonably high zT of ~ 1.95 at 725 K.⁷ Thermodynamics mainly governs a material's capacity for chemical modification, which can dramatically influence thermoelectric properties. Entropy engineering is an effective approach for enhancing the thermoelectric performance of materials

that can decrease lattice thermal conductivity to its theoretical minimum value via the formation of extensive point defects that can scatter heat-carrying phonons extensively. Recently, we achieved a significantly high zT of ~ 2.1 at 630 K in $(\text{GeTe})_{1-2x}(\text{GeSe})_x(\text{GeS})_x$ via the formation of an entropy-driven solid solution point defect.⁸ A spinodal miscibility gap in the PbTe–GeTe phase diagram limits the solubility of Pb in the GeTe matrix. Gelbstein and co-workers realized an extraordinarily high zT of ~ 2.2 at 723 K in GeTe by taking advantage of a phase separation reaction via alloying with PbTe ($\text{Ge}_{0.87}\text{Pb}_{0.13}\text{Te}$), which decreased the lattice thermal conductivity significantly as a result of extensive phonon scattering from thermodynamically driven modulations.⁹ The solubility of Pb in the GeTe matrix was further improved by the addition of Bi_2Te_3 (3 mol %), which simultaneously decreased the lattice thermal conductivity as a result of point-defect scattering and increased the Seebeck coefficient via band engineering.¹⁰ Since its discovery in 1960, thermoelectric research on GeTe has focused on the enhancement of its performance in the high-temperature cubic phase (Figure 1). Interestingly, GeTe is the only IV–VI family member that crystallizes in a rhombohedral structure near room temperature. GeTe undergoes a ferroelectric phase transition from the rhombohedral phase (α phase, $R3m$) to the cubic phase (β phase, $Fm-3m$) at ~ 700 K.⁶

The recent article published in *Joule* by Pei and co-workers demonstrates the advantage of low-symmetry rhombohedral GeTe over its conventional high-temperature cubic counterpart in achieving high thermoelectric performance.³ Decoupling electronic and thermal transport is the main challenge to enhancing the thermoelectric performance in a material. Meanwhile, an ideal thermoelectric material should have high symmetry to enhance the electronic transport, but a low-symmetry structure facilitates low thermal con-

ductivity. High band degeneracy is generally expected for a high-symmetry structure. Thus, optimization of structural symmetry is necessary for accessing the advantages of both effects.

Rhombohedral distortion in GeTe splits the four equivalent L valence bands of the cubic phase into 3L and 1Z and splits the 12 Σ bands into 6 Σ + 6 η in the Brillouin zone (Figure 1A). This provides an obstacle to achieving optimal band convergence in the rhombohedral phase, making it a poor thermoelectric candidate compared with the conventional cubic phase. Pei and co-workers achieved a favorable electronic structure of the rhombohedral phase via Bi doping by increasing the lattice distortion along the $\langle 111 \rangle$ direction.³ Slight symmetry reduction from the cubic to the rhombohedral structure of GeTe gave rise to a distortion along the $\langle 111 \rangle$ direction, leading the desired heavy mass Σ valence band to be higher in energy so that it could contribute favorably to the electronic transport and enhance the thermoelectric performance. Compositional complexity was created by Pb alloying in GeTe and optimized Bi doping, which resulted in low lattice thermal conductivity in the low-symmetry structure.

Symmetry reduction in the crystal structure generally splits the electronic bands according to the degree of symmetry reduction. The electronic transport can be enhanced significantly via proper crystal-structure engineering if many split bands with slightly different energy converge together to result in high valley degeneracy, which is even sometimes better than that of the high-symmetry structure. The symmetry reduction can simultaneously reduce the lattice thermal conductivity. In *Joule*, Pei and co-workers showed a high zT of ~ 2.4 at 600 K in rhombohedral GeTe,³ which is significantly higher than the previously reported cubic analog of GeTe (Figure 1B).

Practical application demands high zT throughout the measured temperature range, which is governed by the device figure of merit (ZT). Rhombohedral GeTe showed a record-high device ZT of 1.5 in the temperature range of 300–800 K.³ Significantly high zT_{max} and ZT values in rhombohedral Bi- and Pb-doped GeTe can be attributed to slight symmetry breaking of the crystal structure, which synergistically improves the electronic transport properties via convergence of the split valence bands and reduces the lattice thermal conductivity. Thus, an optimized low-symmetry solid will be an important candidate for next-generation thermoelectrics, which expands the possibility of a search for a new inorganic solid stabilized in a slightly low-symmetry structure.

GeTe-based materials are being considered as promising alternatives to p -type PbTe thermoelectrics because of their advanced structural, electrical, thermal, and mechanical properties. Although the exciting new approach introduced by Pei and co-workers makes rhombohedral GeTe an excellent thermoelectric material, further efforts in device technology are essential for mass-market applications. Efficient p - and n -type materials are necessary for thermoelectrics, but high performance is rarer for n -type thermoelectric materials than for their p -type counterparts, which has to be investigated with priority. Finally, we believe that the work of Pei and co-workers provides a new concept for the slight symmetry reduction in a crystal structure that can simultaneously optimize both electronic and phonon transport in a thermoelectric material, but this will require further realization in other inorganic solids.

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