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MINI-REVIEW ARTICLE

Strategies for discovery and optimization of thermoelectric materials: Role of real objects and local fields

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Thermoelectric materials provide a renewable and eco-friendly solution to mitigate energy shortages and to reduce environmental pollution via direct heat-to-electricity conversion. Discovery of the novel thermoelectric materials and optimization of the state-of-the-art material systems lie at the core of the thermoelectric society, the basic concept behind these being comprehension and manipulation of the physical principles and transport properties regarding thermoelectric materials. In this mini-review, certain examples for designing high-performance bulk thermoelectric materials are presented from the perspectives of both real objects and local fields. The highlights of this topic involve the Rashba effect, Peierls distortion, local magnetic field, and local stress field, which cover several aspects in the field of thermoelectric research. We conclude with an overview of future developments in thermoelectricity.

Keywords thermoelectric materials, real objects, local fields

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Contents

1 Introduction

With the increasing prominence of energy crisis, environmental pollution, and climate change, it is imperative to develop green and renewable energy. On this front, thermoelectric power generation, which offers several advantages, including no moving components, no mechanical fatigue, and high power density, is particularly gaining attention as a quiet, reliable, and environmentally friendly solid-state device [1]. As the core component of thermoelectric generators, thermoelectric materials are capable of converting waste heat into useful electricity directly and reversibly [2], whose efficiencies are characterized by a dimensionless number $ZT = S^2\sigma T/\kappa_{\rm tot} = S^2\sigma T/(\kappa_{\rm ele} + \kappa_{\rm lat})$ called the thermoelectric figure of merit, where S is the Seebeck coefficient, σ is the electrical conductivity, σ is the absolute temperature, $\kappa_{\rm ele}$ is the electronic part of the total thermal conductivity $\kappa_{\rm tot}$, and $\kappa_{\rm lat}$ is the lattice component of $\kappa_{\rm tot}$ [3–6]. It is the efficiency of the thermoelectric materials that determines the performance of the thermoelectric generations. Despite actual pressing requirements, thermoelectric materials that are sufficiently stable and efficient for large-scale commercial applications have not yet been realized because low efficiency [7] is a major disadvantage in case of thermoelectric applications, which remains near 10% of the Canoe efficiency for a long time. To be considered for practical use, high-ZT thermoelectric materials should display the following properties: (i) large Seebeck coefficient (S); (ii) high electrical conductivity (σ); and (iii) low total thermal conductivity ($\kappa_{\rm tot}$) [8, 9]. Large ZT value is quite a stringent requirement involving all three important transport coefficients; how-

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ever, the three quantities are not totally independent. Thus, it is difficult to optimize each one separately [2, 10–13]. Thereby, an urgent requirement exists but it is still a significant challenge to realize the synergistic optimization of Seebeck coefficient, electrical conductivity, and thermal conductivity. In general, to optimize the power factor, PF $= S^2\sigma$, the empirical rule is to use heavily doped narrow-band semiconductors with carrier density n approximately 10^{19}–10^{21}/cm^3 [12, 14–17]. Moreover, lattice phonons should be strongly scattered and, thus, lattice thermal conductivity can be suppressed [5, 18–22]. Driven by the potential application of thermoelectric materials, various strategies have been attempted to optimize ZT, including band engineering [2, 9, 10, 13, 23–31], phonon engineering [2–5, 32–37], defect engineering [10, 38, 39], interface engineering [40].

Real objects and fields are considered as two basic forms of substances, and are profoundly impacting globally. It is not an exaggeration to mention that real objects such as stars, mountains, materials, molecules, atoms, ions, protons, electrons, and lattice, encompass every aspect of the universe and our life. At micro-scale, electrons and lattice are the two primary components of solid matter, and the unique characteristics of the electron and lattice endue several properties to materials, including thermoelectric materials [41–43], through the interplay among the spin, charge, orbital, and lattice degree of freedom [10, 44]. In addition, field is another major component of substances, albeit more abstractly. Local field plays a critical role in manipulating the transport phenomenon when it is introduced into matrix materials via defects engineering [22, 45, 46]. The above expression suggests two strategies to discover new thermoelectric materials and optimize thermoelectric performance: (i) by employing the real objects, which is generally achieved by exploring and manipulating the behavior of electrons and lattice among multiple degrees of freedom (charge, lattice, orbital, and spin) in materials, and (ii) by incorporating the local fields, which is accomplished by introducing impurities, embedding second phase, and so on.

In this mini-review, we focus our interests on local fields (local magnetic field and local stress field), as well as the interaction among particles and quasiparticles in real objects (electron-phonon coupling and spin-orbit coupling), and explore their effect on thermoelectric materials using certain representative examples. The review will conclude with future studies to improve performance in thermoelectrics.

2 Role of electrons and lattice

A recurring theme in condensed matter physics and material sciences has been the exploration and optimization of condensed matter based on different degrees of freedom (spin, charge, lattice, and orbit [44]), all of which, indeed, endow a variety of materials with diverse nature and broad applications including thermoelectrics. The thermoelectric properties are correlated with the intrinsic properties of electrons and phonons. In the following section, we will elaborate on the Rashba effect that occurs owing to spin-orbit coupling, and the charge density wave occurring from electron-phonon coupling.

2.1 Rashba effect (spin-orbit coupling)

Spin-orbit coupling can have significant effects on transport properties of condensed matter, especially those involving relatively heavy metals (atomic number > 40). A considerable amount of the traditional interest in thermoelectrics focuses on synergistic optimization of thermoelectric parameters from the viewpoints of both charge and lattice. However, spin and orbital degrees of freedom should not be neglected in offering new possibilities for high ZT. A phenomenon known as spin-orbit coupling occurs when the spin and orbital angular moment couple with each other. Electron states with spin-up and spin-down are degenerate in the absence of spin-orbit interaction. In the presence of spin-orbit coupling (SOC), spin degeneracy (or rather total angular momentum degeneracy) occurs in crystals that possess inversion and time reversal symmetries. However, in crystals that do not possess inversion symmetry, the spin-orbit coupling can cause a momentum-dependent splitting of spin bands [Fig. 1(a)], named the Rashba effect [10, 14, 47, 48] or the Dresselhaus effect where energy bands with different spins can have different energy dispersion relations and the band extrema deviate from the high-symmetry directions in the reciprocal space.

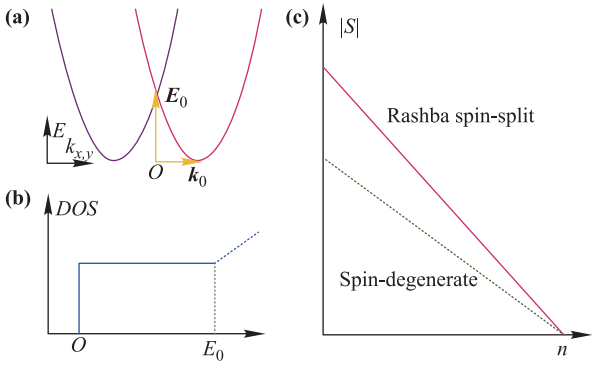

Fig. 1 **(a)** Cartoon (and much exaggerated) sketches of the Rashba effect. **(b)** Schematic behaviour of the electron density of states in the Rashba system. **(c)** Seebeck coefficient (S) as a function of carrier concentration (n) (Pisrenko plot). Reproduced with permission from Ref. [14], Copyright © 2016 Taylor & Francis.

In the early days, the study of the Rashba effect was limited to two-dimensional condensed matter systems (heterostructures and surface states) while three-dimensional (3D) bulk materials remained unexplored. Recently, bulk compounds [49–51] such as BiTeX (X = Cl, Br, or I) and GeTe have been discovered to possess large Rashba effect. The Rashba effect changes the electronic structure, and causes a sharp feature in the energy-dependent density of states (DOS) near the Fermi energy [Fig. 1(b)], which plays a critical role in defining the larger Seebeck coefficient in BiTeX compared with the traditional spin-degenerate materials [as shown in Fig. 1(c)]. It is possible that the thermoelectric properties of BiTeX could be further optimized using defect chemistry. Based on the result, a new direction has been suggested toward the search for high-performance thermoelectric materials with the Rashba effect. This has generated widespread attention ever since.

2.2 Peierls distortion (electron-phonon coupling)

A one-dimensional equally spaced chain with one electron per ion [Fig. 2(a)] was not considered to be stable according to Peierls' theorem, because it deviates from the energetically most favorable state and thus a distorted lattice with lower energy should exist. Actually, if another distorted configuration exists where every two atoms become closer within the one-dimensional chain and form a unit cell containing two electrons [Fig. 2(b)], a lower energy state will develop owing to this distorted geometry named Peierls distortion. Peierls distortion changes the lattice structure, thereby the electronic structure, and induces the charge density wave (CDW) [52], which refers to a periodic modulation of the charge density. Generally, the Peierls instability of lattice can be generalized in any arbitrary chain-like structure with partial band filling. The fundamental driving mechanism behind the charge density wave is the coupling of electrons with the lattice degree of freedom.

A low lattice thermal conductivity is an essential factor for satisfactory thermoelectric materials and reducing the lattice thermal conductivity, caused through phonon propagation, has already been used extensively for several years. In the case of In_4Se_3 [Fig. 2(c)], the Peierls instability induced a charge density wave, which is significant in scattering the heat-carrying phonons, resulting in a low thermal conductivity in the plane parallel to the charge density wave and hence high figure of merit [53]. It is notable that the thermal conductivity in the b-c plane of the charge density wave was lower than that in the a-b plane in the $In_4Se_{2.35}$ crystal, such a phenomenon is unusual because, in the canonical view of thermal transport mechanisms, the cross-plane thermal conductivity is always lower than the in-plane thermal conductivity, while in $In_4Se_{2.35}$ crystal, the opposite phenomenon occurs. The charge density wave in the chain-like structure intuitively developed a more complicated transport path for phonons, ultimately reducing the lattice thermal conductivity by increasing the phonon scattering opportunities. In case of In_4Se_3, researchers observe that the charge density wave occurring owing to electron-phonon coupling possesses the ability to endow a strong correlation system with the high ZT value. There is reason to believe that the discovery of new thermoelectric materials possessing unique electron-lattice interaction will encourage new possibilities within the thermoelectrics community.

3 Role of local field

In the previous section, we have highlighted the role of real objects in the discovery of thermoelectric materials with respect to electron-phonon coupling and spin-orbit coupling. Unlike real objects, localized field is a purely abstract notion, whereas local field in the crystal mate-

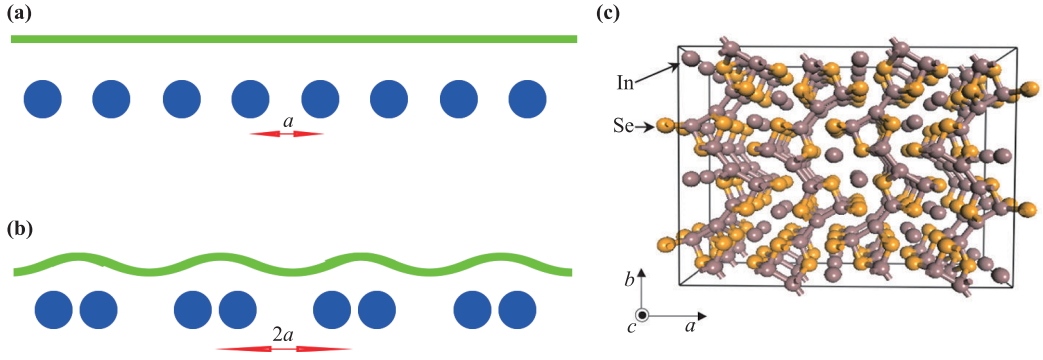

Fig. 2 **(a)** Schematic representation of a one-dimensional equally spaced chain with two atoms and two electrons per unit cell where the charge density is constant. **(b)** Schematic representation of distorted one-dimensional chain where the electron density has a periodic modulation. **(c)** Crystal structure of In_4Se_3. Figure 2(c) reproduced with permission from Ref. [53], Copyright © 2009 Springer Nature.

rial will have significant impact on the mechanical properties, transport behavior, and other physical properties of the materials [45, 46]. In addition, whether the local field is important for material performance, including the transport behavior of thermoelectric materials depends on the interaction between the matrix and the second-phase with various scale sizes. The localized field has contributed to a significant amount of recent achievements in various fields of research [54, 55]. Now let us concentrate on two examples, local magnetic field and local stress field, and investigate their effect on the improvement of thermoelectric properties.

3.1 Local magnetic field

Researchers hardly ever introduce magnetic impurities into thermoelectric materials matrix for tailoring their ZT properties, owing to poor performance of magnetic effects in improving transport properties. Bipolar effect [54], which causes a reduction of the Seebeck coefficient and a significant enhancement in the thermal conductivity when electrons are thermally excited from the valence band to the conduction band, is disadvantageous for the high temperature performance of thermoelectric materials.

Recent efforts regarding filled $CoSb_3$ have indicated how local magnetic field can work satisfactorily in maintaining a high average ZT at high temperatures; this can be understood by its suppression of the intrinsic excitation owing to the magnetic transition of permanent magnet nanoparticles from ferromagnetism to paramagnetism [56]. The local magnetic field was generated because of M-type barium ferrite ($BaFe_{12}O_{19}$) nanoparticles (BaM-NPs) that were introduced into $CoSb_3$-based thermoelectric materials as permanent magnet inclusions. The behavior of local magnetic field will change when BaM-NPs transform from the ordered ferromagnetic state to the disordered paramagnetic state (Fig. 3), and thus affect both the electric and thermal transport properties of filled $CoSb_3$. This new strategy effectively realizes exceptional suppression of the bipolar effect and hence improves the properties of the filled $CoSb_3$ at high temperatures, resulting in that the average ZT exceeds 1.52 for 675–850 K.

Another exceptional example also illustrated that the local magnetic field could manipulate the electrical and thermal characteristics, causing an increase in ZT, as a result of superparamagnetic Co, Fe, and Ni nanoparticles

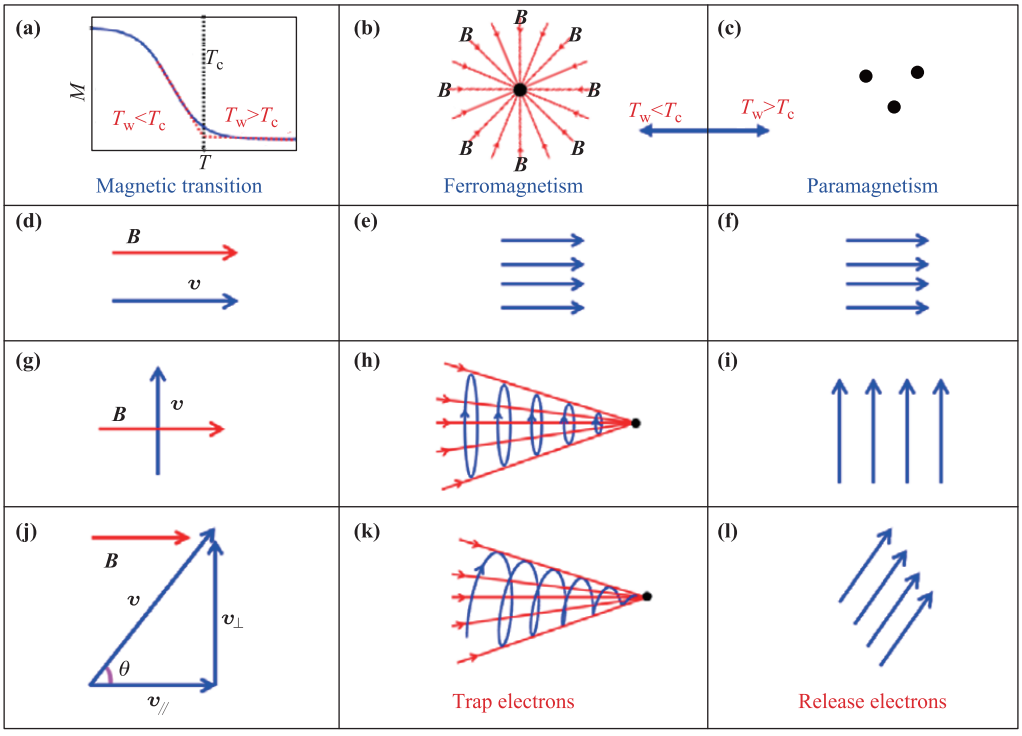

Fig. 3 **(a)** The magnetic transition of permanent magnet nanoparticles $BaFe_{12}O_{19}$. **(b)** Schematic representation of non-uniform spherical magnetic field around barium ferrite nanoparticles in the ferromagnetism state. **(c)** $BaFe_{12}O_{19}$ nanoparticles in the paramagnetism state. **(e)** and **(f)** the movement of electrons parallel to the local magnetic field as shown in **(d)**; **(h)** and **(i)** the movement of carriers perpendicular to the local magnetic field as shown in **(g)**; **(k)** and **(l)** the movement of charge carriers inclined to the local magnetic field as shown in **(j)**. Reproduced with permission from Ref. [56], Copyright © 2016 Springer Nature.

in $Ba_{0.3}In_{0.3}Co_4Sb_{12}$ [57]. Engineering the introduced local magnetic field, when electrons and phonons travel in solids under the effect of local magnetic field, their transport behavior will be further altered, which will provide a new promising avenue for optimizing the properties of thermoelectric materials.

3.2 Local stress field

The crystal structure of real crystals differs from that of ideal ones. Real crystals are never perfect, and defects always exist, which breaks the translational and/or rotational symmetry of the crystals [10]. Atomic point defects, line defects, interfacial defects, and bulk defects are all examples of defects. Despite their diversity, these defects in materials all eventually result in lattice distortion and the accompanying local stress field. Local deformation and stress have a profound impact on the physical properties of various materials systems, especially local stress field that can govern both the electrical transport behavior and thermal transport characteristics of thermoelectric materials. As a result of the difference in the arrangement of atoms between the second phase and matrix, the local stress field existing in the lattice has widely been used in reducing the lattice component of thermal conductivity by inhibiting the propagation of the heat-carrying phonons.

Moreover, it was indicated that high-efficiency thermoelectric materials require high band degeneracy near the Fermi level owing to a synergistic optimization of the Seebeck coefficient and electrical conductivity [13, 23, 25, 28, 31]. Computationally, Zhang and coworkers [58] have explored how a local stress field can realize the band convergence through orbital engineering, providing new pathways for high thermoelectric efficiencies. Considering $CaAl_2Si_2$-type thermoelectric materials [Fig. 4(a)] as an example, the local stress field was obtained when the thin film $CaAl_2Si_2$-type Zintl compounds deposited on the substrate materials, resulting in the lattice mismatch. As shown in Fig. 4, the valence band edges of $CaAl_2Si_2$-type structures consists of a doubly degenerate band and a nondegenerate band owing to the effect of the crystal field splitting, which would gradually result in convergence and even degeneracy via adjusting the local stress field, where the strain ε is characterized as $(a-a_0)/a_0\times100\%$ (a_0 and a are the in-plane lattice parameters with unstrained and strained states, respectively). Consequently, the maximum ZT increased by 50% in Mg_3Sb_2 at 800 K at the optimal strain ~3% compared with the value of Mg_3Sb_2 without the local stress field. The result indicates that band degeneracy is obtained when the local stress field works, resulting in high thermoelectric performance, and this will enable more innovative band engineering efforts.

4 Conclusion

This mini-review illustrates certain representative examples of material design and optimization via local fields,

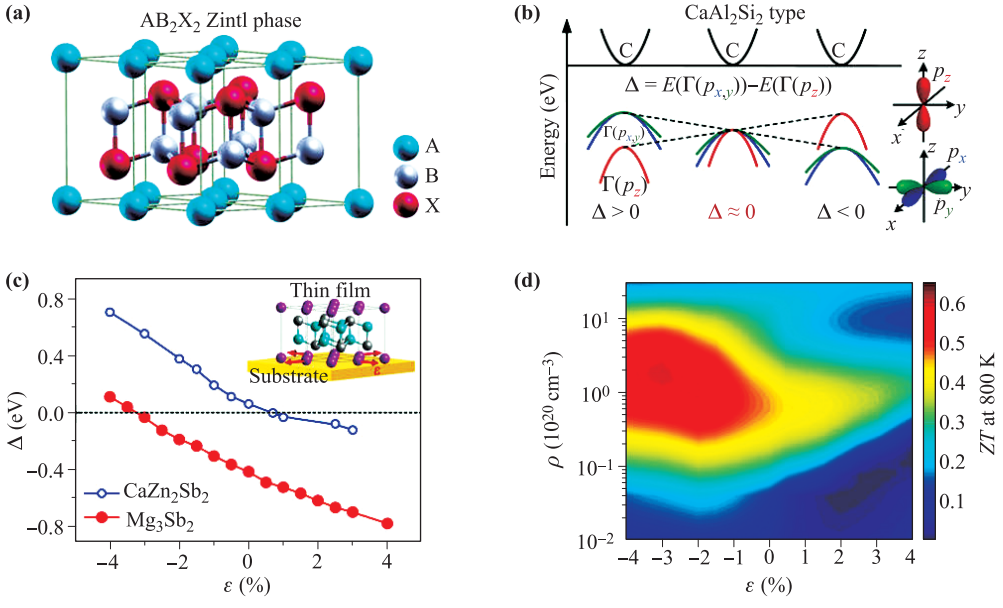

Fig. 4 **(a)** Crystal structure of $CaAl_2Si_2$-type Zintl compounds. **(b)** Schematic representation of energy bands of $CaAl_2Si_2$-type thermoelectric materials. **(c)** Crystal field induced energy split Δ versus the local stress field quantified as ε. **(d)** The contour map of the thermoelectric figure of merit of Mg_3Sb_2 at 800 K as a function of the local stress field quantified and carrier concentration. Reproduced with permission from Ref. [58], Copyright © 2016 Springer Nature.

as well as the interplay of multiple degree of freedom (charge, lattice, orbital, and spin) in real objects, all of which introduce the possibility to control and change the transport mechanisms and thus the thermoelectric performance, and provide an effective approach to develop next generation thermoelectric materials. Researchers have witnessed the exceptional development process of thermoelectric materials in the past few decades. Although we have made considerable progress in developing strategies for higher ZT, there is still a long way to go. When the ZT value reaches 3, the energy efficiency of thermoelectric materials will be comparable to conventional technologies, and that would result in a revolution for human life.

Exploring new types and characteristics of various local fields (field quantity such as force, heat, light, sound, electricity, and magnetism), and the interaction among different degrees of freedom, especially in strongly correlated electron systems, remain challenging within the thermoelectrics community, and would provide new insight into charge and heat transport, which are inseparable from the collaborations between condensed-matter physicists, materials scientists, and chemists. We are reasonably confident that these efforts would make the commercialization of thermoelectric devices a reality in the foreseeable future.

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