Enhanced Thermoelectric Performance and Anomalous Seebeck Effects in Topological Insulators

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Improving the thermoelectric figure of merit zT is one of the greatest challenges in material science. The recent discovery of topological insulators (TIs) offers new promise in this prospect. In this work, we demonstrate theoretically that zT is strongly size dependent in TIs, and the size parameter can be tuned to enhance zT to be significantly greater than 1. Furthermore, we show that the lifetime of the edge states in TIs is strongly energy dependent, leading to large and anomalous Seebeck effects with an opposite sign to the Hall effect. These striking properties make TIs a promising material for thermoelectric science and technology.

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The search of high-performance thermoelectric (TE) materials for efficient heat-electricity interconversion is a long-sought goal of material science [1–3]. The recent discovery of topological insulators (TIs) [4–6] sheds new light on this pursuit. TIs are new quantum states of matter characterized by an insulating bulk gap and gapless edge or surface states, which are protected by time-reversal symmetry [7–9]. TIs share similar material properties, namely, heavy elements and narrow bulk gaps, with TE materials. Consequently many currently known TIs (like Bi_2Te_3, Sb_2Te_3, and Bi_xSb_{1-x}) are also excellent TE materials [10–13]. The nontrivial TI edge and surface states, which were unknown in the earlier research of TE materials, might be advantageous in improving the thermoelectric figure of merit zT.

TIs are interesting for thermoelectrics due to their unique electronic structure. Distinct from conventional materials, TIs support topologically protected boundary (surface or edge) states together with bulk states, and the two types of charge carriers exhibit distinct transport properties in different dimensions. However, the approximate particle-hole symmetry near the gapless Dirac point implies a vanishing Seebeck coefficient, and previous works introduced a truncation [14–16] or opened a gap [17] in the band structure of boundary states so that a sizable Seebeck coefficient can be recovered. In contrast to all previous work, we utilize the intrinsic properties of the boundary states, and show that the strong energy dependence of the lifetime naturally leads to large and anomalous Seebeck effects. Furthermore, we show that TE properties are strongly size dependent in TIs, and this size parameter, mostly ignored in previous works, can be tuned to greatly enhance zT. In this work, we theoretically investigated TE transport in TIs from ballistic to diffusive regions using the Landauer transport approach. We find that zT of TIs changes from nearly zero to significantly larger than 1 by varying the geometric size. The finding fundamentally changes our common belief that zT is an intrinsic material property. We also predict that the boundary states of TIs can have the opposite signs for the Seebeck and Hall coefficients. These striking predictions, if confirmed experimentally, can open new directions for the science and technology of thermoelectrics.

To understand TE properties of TIs, we will first discuss the definition of zT that determines the TE efficiency of a material. In a typical definition, zT is written as

$$zT = \frac{\sigma S^2 T}{\kappa}, \tag{1}$$

where σ is the electrical conductivity, S is the Seebeck coefficient, T is the absolute temperature, and the thermal conductivity κ is the sum of contributions from electrons κ_e and lattice vibrations κ_l [1]. The use of this definition inexplicitly assumes that zT is an intrinsic material property, independent of the geometric size. However, this basic assumption does not always hold, as we will demonstrate in TIs.

We present a general definition of zT that can describe the general geometric size dependence. Using simple derivations based on thermodynamics [18], zT is described as

$$zT = \frac{GS^2 T}{K}, \tag{2}$$

where G is the electrical conductance and $K = K_e + K_l$ is the thermal conductance. According to Ohm's scaling law in the diffusive transport regime, $G = \sigma A/L$ and Fourier's scaling law $K = \kappa A/L$, where A is the cross section area and L is the length of a material. The geometry factor A/L

cancels between G and K. Then if S is size independent, so would be zT. In this sense, the two definitions, Eqs. (1) and (2), are equivalent.

However, generally zT can be size dependent as caused by two mechanisms: (i) Ohm's scaling law and Fourier's scaling law fail; (ii) S depends on the geometric size. Both mechanisms take effect in TIs. First, Ohm's scaling law does not apply to TIs, because boundary and bulk states distribute in different physical dimensions. In addition, as boundary states have mean free paths significantly longer than bulk states, it is possible to see unusual length-dependent transport behaviors, such as ballistic transport of the boundary states and diffusive transport of the bulk states. Second, the total S is described as [18]

$$S = \frac{G_1 S_1 + G_2 S_2}{G_1 + G_2}. \tag{3}$$

We use subscripts "1" and "2" to denote the contributions of boundary and bulk states, respectively. The size dependence of S always exists in TIs. For nondiffusive transport, all individual TE quantities (including G_1, G_2, S_1, and S_2) change with increasing L. Even if transport becomes diffusive, varying A would modify the relative contribution of boundary and bulk states, and thus change the total S. Therefore, we expect a strong size dependence of zT in TIs. A previous work [16], which makes a truncation in the band structure of edge states, observed important changes in zT when varying the inelastic scattering length of edge states and the cross section of the transport system.

We apply the Landauer transport formalism to study TE properties of TIs (see details in the Supplemental Material [19]). We will focus on two-dimensional (2D) TIs. Similar discussion can be applied for three-dimensional (3D) TIs, which will be presented elsewhere. As a prominent feature of 2D TIs, the edge states are gapless with bands dispersing inside the bulk gap and helical with spin-momentum locking, as schematically depicted in Fig. 1. Without losing generality, we assume a linear dispersion for 1D edge states and a parabolic dispersion for 2D bulk states: $E_1(k) = \pm\hbar k v - \Delta$ and $E_2(k) = \hbar^2 k^2/(2m^*)$, where "±" denotes up (down) spins, $\hbar$ is the reduced Planck constant, k is the wave vector, v is the velocity of edge states, the bulk conduction band minimum (CBM) is selected as the energy reference, $-\Delta$ is the energy of the Dirac point, and m^* is the effective mass.

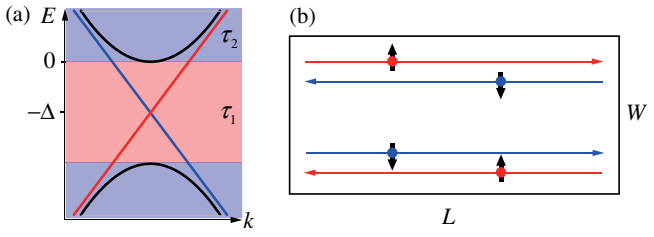

FIG. 1 (color online). (a) Schematic band structure and (b) schematic drawing depicting helical edge states of 2D TIs. τ_1 and τ_2 denote the scattering times within and outside the bulk gap, respectively. Red (blue) colored lines represent edge states of up (down) spins.

Transport calculations usually use the constant scattering time approximation. The approximation does not rely on any assumption about the possible dependence on doping and temperature of the scattering time τ, and has been successfully applied to study various TE materials [27]. If assuming that the scattering rate $1/\tau$ is proportional to the density of states (DOS), like for electron-phonon scattering [1], the feature that one-dimensional (1D) linear bands and 2D parabolic bands have constant DOS also suggests to use constant τ. However, care has to be taken for TIs. There are two important facts that must be considered: (i) when the Fermi level E_F is within the bulk gap, boundary states are protected by the time-reversal symmetry against back-scattering and thus have large τ; (ii) when E_F is outside the bulk gap, backscatterings become allowed for the boundary states due to interactions with bulk states, which decreases τ considerably.

As a generalization of the constant scattering time approximation, we introduce a dual scattering time (DST) model for TIs, as schematically depicted in Fig. 1(a). In the DST model, we assume two different constant scattering times, τ_1 and τ_2, for edge states with energies within and outside the bulk gap, respectively. τ_1 is much greater than τ_2. Meanwhile, we assume a constant scattering time of τ_2' for bulk states. τ_2', similar as τ_2, is significantly smaller than τ_1. For simplicity we take $\tau_2' = \tau_2$. Note the scattering-time ratio $r_\tau = \tau_1/\tau_2$ is system dependent. In the HgTe quantum well, a well-known 2D TI system [8,9], r_τ is on the order of 10^3 as deduced from existing experiments [28,29]. In principle r_τ can be enhanced, for instance, by introducing nonmagnetic defects or disorders into the system. References [14–16] truncate the band structure of edge states, which can be mathematically viewed as the limiting case of $r_\tau = \infty$.

Let us first focus on edge states. Herein L is scaled by the inelastic mean free path of edge states $\lambda_1 = v\tau_1$, E_F is scaled by $k_B T$, Δ is unimportant to calculations, and r_τ is the only remaining parameter. The length dependence of S_1 (S of edge states) is visualized in Fig. 2(a) for a specified Fermi level of $E_F = 0$ and varying r_τ. S_1 is nearly zero in the ballistic limit (small L), gradually increases with L, and finally becomes saturated in the diffusive limit (L on the order of λ_1). This basic trend is independent of the selection of r_τ, which only affects the results quantitatively. Increasing r_τ from 10^2 to 10^4 leads to a larger slope in the S_1-L curve and similar diffusive S_1 of about 120 μV/K. The results are consistent with previous ones [14–16] which were calculated for the limiting case of $r_\tau = \infty$ and $L = \lambda_1$. The optimization of E_F further enhances S_1. As presented in Fig. 2(b) for $r_\tau = 10^3$, the diffusive S_1 can be enhanced to 450 μV/K when choosing $E_F \sim 5k_B T$.

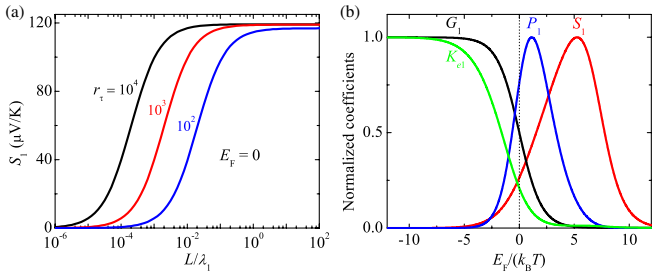

FIG. 2 (color online). (a) The length dependence of S_1 (S of edge states) for $E_F = 0$ and varying scattering-time ratio $r_\tau = \tau_1/\tau_2$ (see τ_1 and τ_2 in Fig. 1). (b) The Fermi level dependence of TE quantities of edge states for diffusive transport and $r_\tau = 10^3$. S_1, G_1, P_1, and K_{e1} are normalized by 450 μV/K, $(2e^2/h)(\lambda_1/L)$, $(2.5k_B^2/h)(\lambda_1/L)$, and $(6.6k_B^2T/h)(\lambda_1/L)$, respectively, where λ_1 is the inelastic mean free path of edge states and L is the transport length.

As E_F shifts upwards across the bulk CBM, G_1 and K_{e1} sharply decrease, and the power factor $P_1 = G_1S_1^2$ shows a peaked shape centered at $E_F \sim 1k_BT$. At the optimal E_F of P_1, S_1 is about 200 μV/K , which is comparable to the best S of around 250 μV/K in bulk Bi_2Te_3 systems [1].

At this point, it is important to emphasize novel aspects of the Seebeck effects of edge states. S is usually small for gapless band structures, since both electrons and holes are thermally excited and contribute opposite Seebeck coefficients which cancel with each other. This explains the vanishingly small S_1 in the ballistic limit. However, the extraordinarily large S_1 obtained in the diffusive limit seems illusive. Furthermore, there exists an anomaly in the sign of S_1. It is well known that the type of charge carriers, n or p, is defined by the sign of S or the Hall coefficient. As far as we know, previous work always found the same sign in the two coefficients at least for a single type of charge carriers. In contrast, we show a counterexample here. For E_F around the bulk CBM, edge states with energies above the Dirac point are mostly unoccupied (see band structures of realistic systems [6,30]). The corresponding charge carriers are obviously n type in the sense of Hall measurement, yet they contribute a p-type Seebeck effect, as evidenced by the positive sign of S_1.

To understand the anomalous sign of the Seebeck effects, we first explain generally how the sign of S is defined. The Seebeck effect represents the response of electrons to the external temperature gradient. When increasing the temperature, the occupation of electrons gets larger or smaller, depending on whether the energy of the electrons is above or below E_F. Electrons above or below E_F thus have opposite contribution to S. The Landauer formula of S brings in the contribution of states within around $5k_BT$ of E_F [27]. When electrons above E_F have dominating contribution to the Seebeck effect, the sign of S is negative, and vice versa. Now let us consider the case of edge states for $E_F = 0$ (as referenced to the bulk CBM). The ballistic transmission of edge states is energy independent [19]. Electrons below and above E_F have the same contribution to S, leading to a zero ballistic S_1. As L increases, electrons above the E_F experience more scatterings than those below the E_F due to the edge-bulk interactions. As a result, S_1 becomes nonzero and positive. We thus conclude that the anomalous sign in S_1 originates from the unique energy dependence of the scattering time in TIs. An anomalous sign in S_1 may also appear when E_F is around the bulk valence band maximum (VBM).

A simple way to estimate S is to use the Sommerfield expansion [31]

$$S = -\frac{\pi^2 k_B^2 T}{3e} \frac{\partial \ln[\bar{\mathcal{T}}(E)]}{\partial E}\bigg|_{E=E_F}, \tag{4}$$

which is obtained from the Landauer formula by assuming a smooth transmission function $\bar{\mathcal{T}}(E)$ and low T. $\bar{\mathcal{T}}(E)$ is determined by the distribution of conduction modes $M(E)$ and the mean free path $\lambda(E)$ [19]. The formula states that S is determined by the slope of the transmission function at E_F, which suggests two mechanisms to enhance S: (i) an increased energy dependence of $M(E)$, for instance by a local increase in the density of states [32]; (ii) an increased energy dependence of $\lambda(E)$. The later mechanism, usually thought to be unimportant, is ignored in most theoretical studies. However, it plays a crucial role in TIs. The strong energy dependence of $\lambda(E)$ [or $\tau(E)$], caused by edge-bulk interactions, makes a dominating contribution to S_1. This explains the large magnitude of S_1 obtained from the gapless band structure of the boundary states. A previous study [17] suggests to tune a hybridization gap in boundary states for increasing S with decreasing mobility as a sacrifice. In contrast, we show that edge states can contribute large S by optimizing E_F with no need for opening the band gap. Thus edge states can simultaneously have large S and superior mobility, advantageous for TE applications.

The improvement of zT requires suppressing thermal conduction while keeping electrical conduction less affected. Edge states are quite promising for this purpose, since their low physical dimension and excellent transport ability enable an effective decoupling between electrons and phonons. Specifically, as the width of 2D TIs decreases, transport of edge states remains unchanged but the lattice thermal conductance lowers; when nonmagnetic perturbations (e.g., defects or disorders) are introduced into the transport system, edge states are topologically protected against scattering while phonons are significantly scattered.

What is the maximum possible zT ($zT_{\max}$) a 2D TI can have? To answer this question, we consider the limiting case that edge states contribute all electrical conductance and lattice thermal conductance is negligible, which gives the best zT. Edge states are treated in the diffusive transport region for improving S and zT. Then the optimization of the Fermi level gives $zT_{\max}$ as a function of r_τ. As shown in

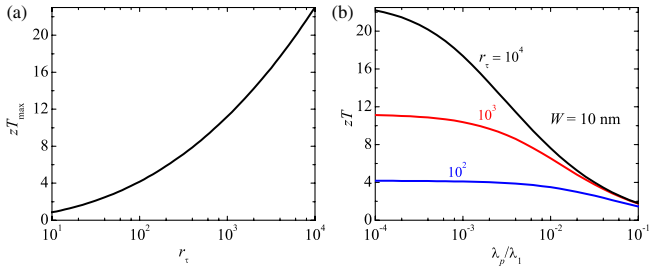

FIG. 3 (color online). (a) The maximum possible zT of 2D TIs, $zT_{\max}$, as a function of the scattering-time ratio r_τ. (b) zT including contributions of edge states and phonons as a function of λ_p/λ_1 for varying r_τ, where λ_p is the phonon mean free path and λ_1 is the inelastic mean free path of edge states. The width of transport system W is selected to be 10 nm.

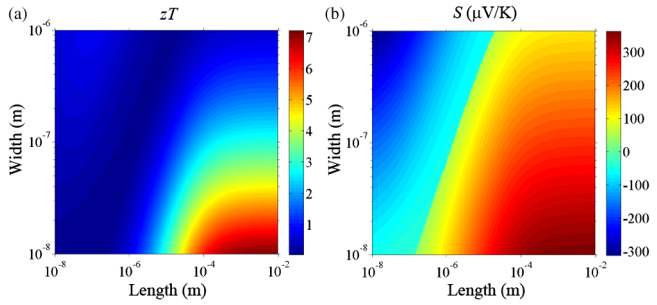

FIG. 4 (color online). The size dependence of (a) zT and (b) S for the 2D TI fluorinated stanene at 300 K.

Fig. 3(a), $zT_{\max}$ increases monotonically with increasing r_τ. When varying r_τ from 10^2 to 10^3, $zT_{\max}$ enhances from 4 to 11, shifting the optimized E_F from $2.0k_BT$ to $3.3k_BT$. Importantly, $zT_{\max}$ is temperature independent and much larger than 1.

It is interesting to see how $zT_{\max}$ changes when including the contribution of lattice thermal conduction. In our discussion, the width of the transport system (W) is selected to be on the order of 2 times the localization width ξ of edge states to minimize K_l and to avoid hybridization between edge states [19]. Note that inelastic scatterings of edge states can happen at finite temperatures, and the temperature dependence of λ_1 could be important. In TE calculations, the relevant quantities are the ratios r_τ and λ_p/λ_1 (λ_p is the phonon mean free path). The ratios can vary with temperature for a given transport system. They can also be tuned at a fixed temperature, for instance by the control over disorders. To account for these effects, we calculate zT for different ratio values. As presented in Fig. 3(b), an increased λ_p/λ_1 leads to a decreased zT, and such a trend looks more obvious for larger r_τ. For instance, when changing λ_p/λ_1 from 10^{-3} to 10^{-2}, zT decreases from 4.1 to 3.5 for $r_\tau = 10^2$ and from 10.4 to 6.5 for $r_\tau = 10^3$. As discussed above, a small λ_p/λ_1 is in principle feasible in 2D TIs, for instance, by using nonmagnetic defects or disorders. Our results thus indicate that zT can stay much larger than 1 when K_l is included.

Finally we take the electrical conduction of bulk states into account. We perform an example study on a realistic 2D TI material, fluorinated stanene as described in the Supplemental Material [19], which has a nontrivial bulk gap of 0.3 eV, suitable for room temperature operation [30]. Figure 4 presents the size dependence of zT and S, whose values are maximized by optimizing E_F. For small L and large W, bulk states dominate TE transport, resulting in small zT and negative S. When increasing L and decreasing W, edge states becomes increasingly important, leading to a bulk-edge crossover. Consequently, zT improves noticeably, and S has a sign change from positive to negative. The contribution of edge states is maximized by choosing L on the order of λ_1 and W on the order of 2ξ (~10 nm). At this optimized geometry, a maximal zT of 7 is realized. In practice, $\tau(E)$ may not change sharply from τ_1 to τ_2 as described by the DST model. We considered a smooth decrease of $\tau(E)$ from τ_1 to τ_2 in the form of $\exp[E/(k_BT)]$. The predicted zT slightly decreases but still remains extremely large (about 6).

It has been theoretically predicted [33,34] and then experimentally confirmed [35–39] that low-dimensional and nanostructured materials can have zT much larger than their bulk counterparts. However, in those previous works a subtle control of material composition and structure is required to get an overall balance between electrical conduction and thermal conduction for optimizing zT. Here we propose to use TIs for thermoelectrics, for which the optimization of the geometric size can suppress thermal conduction while keeping the electrical conduction little affected. In comparison, our approach of improving zT is simpler and more effective, which could greatly prompt the development of TE science and technology.

In summary, we present the basic design principles to optimize zT for TI materials. We show that zT is no longer an intrinsic material property, but strongly depends on the geometric size in TIs. This new tuning parameter can dramatically increase zT of topological materials, including quantum anomalous Hall insulators and topological crystal insulators. In 2D TIs, we show that zT could be improved to be significantly larger than 1 by optimizing the geometric size. Moreover, we predict that the gapless edge states can contribute large and anomalous Seebeck effects with an opposite sign to the Hall effect. This striking prediction can be used to experimentally test the theoretical framework presented in this work.

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