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Large, nonsaturating thermopower in a quantizing magnetic field

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The thermoelectric effect is the generation of an electrical voltage from a temperature gradient in a solid material due to the diffusion of free charge carriers from hot to cold. Identifying materials with a large thermoelectric response is crucial for the development of novel electric generators and coolers. We theoretically consider the thermopower of Dirac/Weyl semimetals subjected to a quantizing magnetic field. We contrast their thermoelectric properties with those of traditional heavily doped semiconductors and show that, under a sufficiently large magnetic field, the thermopower of Dirac/Weyl semimetals grows linearly with the field without saturation and can reach extremely high values. Our results suggest an immediate pathway for achieving record-high thermopower and thermoelectric figure of merit, and they compare well with a recent experiment on $Pb_{1-x}Sn_xSe$.

INTRODUCTION

When a temperature gradient is applied across a solid material with free electronic carriers, a voltage gradient arises as carriers migrate from the hot side to the cold side. The strength of this thermoelectric effect is characterized by the Seebeck coefficient S, defined as the ratio between the voltage difference ΔV and the temperature difference ΔT; the absolute value of S is referred to as the thermopower. Finding materials with a large thermopower is vital for the development of thermoelectric generators and thermoelectric coolers—devices that can transform waste heat into useful electric power or electric current into cooling power (*1*–*3*).

The effectiveness of a thermoelectric material for power applications is quantified by its thermoelectric figure of merit

$$ZT = S^2\sigma T/\kappa \quad (1)$$

where σ is the electrical conductivity, T is the temperature, and κ is the thermal conductivity. To design a material with a large thermoelectric figure of merit, one can try in general to use either an insulator, such as an intrinsic or lightly doped semiconductor, or a metal, such as a heavily doped semiconductor. In an insulator, the thermopower can be large, of the order $E_0/(eT)$, where e is the electron charge and E_0 is the difference in energy between the chemical potential and the nearest band mobility edge (*4*). However, obtaining such a large thermopower comes at the expense of an exponentially small, thermally activated conductivity, $\sigma \propto \exp(-E_0/k_BT)$, where k_B is the Boltzmann constant. Because the thermal conductivity in general retains a power-law dependence on temperature due to phonons, the figure of merit ZT for insulators is typically optimized when E_0 and k_BT are of the same order of magnitude. This yields a value of ZT that can be of order unity but no larger (*5*).

On the other hand, metals have a robust conductivity, but usually only a small Seebeck coefficient S. In particular, in the best-case scenario where the thermal conductivity due to phonons is much smaller than that of electrons, the Wiedemann-Franz law dictates that the quantity $\sigma T/\kappa$ is a constant of order $(e/k_B)^2$. The Seebeck coefficient, however, is relatively small in metals, of order $k_B^2T/(eE_F)$, where $E_F \gg k_BT$ is the metal's Fermi energy. If the temperature is increased to the point that $k_BT > E_F$, then the Seebeck coefficient typically saturates at a constant of order k_B/e. The maximum value of the figure of merit in metals is therefore obtained when k_BT is of the same order as E_F and, once again, one arrives at the conclusion that ZT is of order unity at best. Of course, real thermoelectric materials are often far from the "best-case scenario" of negligible thermal conductivity due to phonons so that even achieving an order-unity value of ZT is difficult. Finding materials with low thermal conductivity is often the bottleneck for optimizing thermoelectric performance (*2*, *3*).

Here, we show that these limitations on the figure of merit can be circumvented by considering the behavior of doped nodal semimetals in a strong magnetic field, for which $ZT \gg 1$ is, in fact, possible. Crucial to our proposal is a confluence of three effects. First, a sufficiently high magnetic field produces a large enhancement of the electronic density of states and a reduction in the Fermi energy E_F. Second, a quantizing magnetic field assures that the transverse $\mathbf{E} \times \mathbf{B}$ drift of carriers plays a dominant role in the charge transport, and this allows both electrons and holes to contribute additively to the thermopower, rather than subtractively as in the zero-field situation. Third, in materials with a small band gap and electron-hole symmetry, the Fermi level remains close to the band edge in the limit of large magnetic field, and this allows the numbers of thermally excited electrons and holes to grow with magnetic field even while their difference remains fixed. These three effects together allow the thermopower to grow without saturation as a function of magnetic field.

RESULTS

Relation between Seebeck coefficient and entropy

The Seebeck coefficient is usually associated, conceptually, with the entropy per charge carrier. In a large magnetic field, and in a generic system with some concentrations n_e of electrons and n_h of holes, the precise relation between carrier entropy and thermopower can be derived using the following argument. Let the magnetic field $\mathbf{B}$ be oriented in the z direction and suppose that an electric field $\mathbf{E}$ is directed along the y direction. Suppose also that the magnetic field is strong enough that $\omega_c\tau \gg 1$, where ω_c is the cyclotron frequency and τ is the momentum scattering time so that carriers complete many cyclotron orbits without scattering. In this situation, charge carriers acquire an $\mathbf{E} \times \mathbf{B}$ drift velocity in the x direction, with magnitude $v_d = E/B$. The direction of

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drift is identical for both negatively charged electrons and positively charged holes so that drifting electrons and holes contribute additively to the heat current but oppositely to the electrical current. This situation is illustrated schematically in Fig. 1.

To understand the Seebeck coefficient S_{xx} in the x direction, one can exploit the Onsager symmetry relation between the coefficients S_{ij} of the thermoelectric tensor and the coefficients Π_{ij} of the Peltier heat tensor $S_{ij}(B) = \Pi_{ji}(-B)/T$. The Peltier heat is defined by $J_i^Q = \Pi_{ij}J_j^e$, where $\mathbf{J}^Q$ is the heat current density at a fixed temperature and $\mathbf{J}^e$ is the electrical current density. In the setup we are considering, the electrical current in the x direction is given simply by $J_x^e = ev_d(n_h - n_e)$.

In sufficiently large magnetic fields, the flow of carriers in the x direction is essentially dissipationless. In this case, the heat current in the x direction is related to the entropy current J_x^s by the law governing reversible processes: $J_x^Q = TJ_x^s$. This relation is valid in general when the Hall conductivity σ_{xy} is much larger in magnitude than the longitudinal conductivity σ_{xx}; for a system with only a single sign of carriers, this condition is met when $\omega_c\tau \gg 1$. If we define s_e and s_h as the entropy per electron and per hole, respectively, then $J_x^s = v_d(n_e s_e + n_h s_h)$, because electrons and holes both drift in the x direction. Putting these relations together, we arrive at a Seebeck coefficient $S_{xx} = \Pi_{xx}/T = (J_x^Q)/(TJ_x^e)$ that is given by

$$S_{xx} = \frac{n_h s_h + n_e s_e}{e(n_h - n_e)} \equiv \frac{\mathbb{S}}{en} \tag{2}$$

In other words, the Seebeck coefficient in the x direction is given simply by the total entropy density $\mathbb{S}$ divided by the net carrier charge density en. This relation between entropy and thermopower in a large transverse magnetic field has been recognized for over 50 years and explained by a number of authors (*6*–*10*), but it is usually applied only to systems with one sign of carriers. As we show below, it has marked implications for the thermopower in three-dimensional (3D) nodal semimetals, where both electrons and holes can proliferate at small $E_F \ll k_B T$.

In the remainder of this paper, we focus primarily on the thermopower S_{xx} in the directions transverse to the magnetic field, which can be described simply according to Eq. 2. At the end of the paper, we comment briefly on the thermopower along the direction of the magnetic field, which has less marked behavior and saturates in all cases at ~ (k_B/e) in the limit of a large magnetic field.

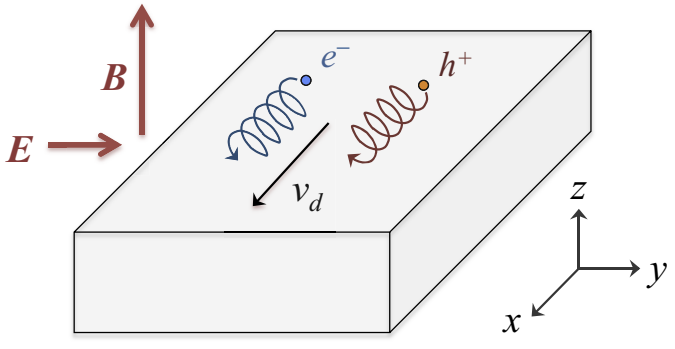

Fig. 1. Schematic depiction of the E × B drift of carriers in a strong magnetic field. Electrons (labeled e^-) and holes (labeled h^+) drift in the same direction under the influence of crossed electric and magnetic fields. Both signs of carrier contribute additively to the heat current in the x direction and subtractively to the electric current in the x direction, which leads to a large Peltier heat Π_{xx} and therefore to a large thermopower S_{xx}.

We also neglect the contribution to the thermopower arising from phonon drag. This is valid provided that the temperature and Fermi energy E_F are low enough that $(k_B T/E_F) \gg (T/\Theta_D)^3$, where Θ_D is the Debye temperature (*11*). These low-temperature and low-E_F systems are the primary focus of this paper [although it should be noted that phonon drag tends to increase the thermopower (*12*)].

When the response coefficients governing the flow of electric and thermal currents have finite transverse components, as introduced by the magnetic field, the definition of the figure of merit ZT should be generalized from the standard expression of Eq. 1. This generalized definition can be determined by considering the thermodynamic efficiency of a thermoelectric generator with generic thermoelectric, thermal conductivity, and resistivity tensors. The resulting generalized figure of merit is derived in the Supplementary Text and is given by

$$Z_B T = \frac{S_{xx}^2 T}{\kappa_{xx}\rho_{xx}} \frac{\left(1 - \frac{S_{xy}}{S_{xx}}\frac{\kappa_{xy}}{\kappa_{xx}}\right)^2}{\left(1 + \frac{\kappa_{xy}^2}{\kappa_{xx}^2}\right)\left(1 - \frac{S_{xy}^2 T}{\kappa_{xx}\rho_{xx}}\right)} \tag{3}$$

where ρ_{xx} is the longitudinal resistivity. Similarly, the thermoelectric power factor, which determines the maximal electrical power that can be extracted for a given temperature difference, is given by

$$\mathrm{PF} = \frac{S_{xx}^2}{\rho_{xx}} \frac{\left(1 - \frac{S_{xy}}{S_{xx}}\frac{\kappa_{xy}}{\kappa_{xx}}\right)^2}{1 - \frac{S_{xy}^2 T}{\kappa_{xx}\rho_{xx}}} \tag{4}$$

In the limit of $\omega_c\tau \gg 1$ that we are considering, $S_{xy} \ll S_{xx}$, and therefore, for the remainder of this paper, we restrict our analysis to the case $S_{xy} = 0$.

In situations where phonons do not contribute significantly to the thermal conductivity, we can simplify Eq. 3 by exploiting the Wiedemann-Franz relation $\hat{\kappa} = c_0(k_B/e)^2 T\hat{\sigma}$, where c_0 is a numeric coefficient of order unity, and $\hat{\kappa}$ and $\hat{\sigma}$ represent the full thermal conductivity and electrical conductivity tensors. This relation remains valid even in the limit of large magnetic field as long as electrons and holes are good quasiparticles (*9*). In the limit of strongly degenerate statistics, where either $E_F \gg k_B T$ or the band structure has no gap, c_0 is given by the usual value $c_0 = \pi^2/3$ corresponding to the Lorenz number. In the limit of classical, nondegenerate statistics, where $E_F \ll k_B T$ and the Fermi level reside inside a band gap, c_0 takes the value corresponding to classical thermal conductivity $c_0 = 4/\pi$. Inserting the Wiedemann-Franz relation into Eq. 3 and setting $S_{xy} = 0$ gives

$$Z_B T = \frac{S_{xx}^2}{c_0(k_B/e)^2} \tag{5}$$

In other words, when the phonon conductivity is negligible, the thermoelectric figure of merit is given to within a multiplicative constant by the square of the Seebeck coefficient, normalized by its natural unit k_B/e. As we show below, in a nodal semimetal, $S_{xx}/(k_B/e)$ can be parametrically large under the influence of a strong magnetic field, and thus, the

figure of merit Z_BT can far exceed the typical bound for heavily doped semiconductors.

In situations where phonons provide a dominant contribution to the thermal conductivity so that the Wiedemann-Franz law is strongly violated, one generically has $\kappa_{xx} \gg \kappa_{xy}$, and Eq. 3 becomes

$$Z_BT = \frac{S_{xx}^2 T}{\kappa_{xx}\rho_{xx}} \tag{6}$$

Heavily doped semiconductors

In this subsection, we present a calculation of the thermopower S_{xx} for a heavily doped semiconductor, assuming for simplicity an isotropic band mass m and a fixed carrier concentration n [in other words, we assume sufficiently high doping that carriers are not localized onto donor/acceptor impurities by magnetic freeze-out (*13*)]. This classic problem has been considered in various limiting cases by previous authors (*6*, *8*, *12*, *14*). Here, we briefly present a general calculation and recapitulate the various limiting cases, both for the purpose of conceptual clarity and to provide contrast with the semimetal case.

Full details of the thermopower calculation at arbitrary B and T are presented in the Supplementary Text, and an example of this calculation is shown in Fig. 2. This plot considers a temperature $T \ll E_F^{(0)}/k_B$, where $E_F^{(0)}$ is the Fermi energy at zero magnetic field. The asymptotic behaviors evidenced in this figure can be understood as follows.

In the limit of vanishing temperature, the chemical potential μ is equal to the Fermi energy E_F, and the entropy per unit volume

$$\mathbb{S} \simeq \frac{\pi^2}{3} k_B^2 T \nu(\mu) \tag{7}$$

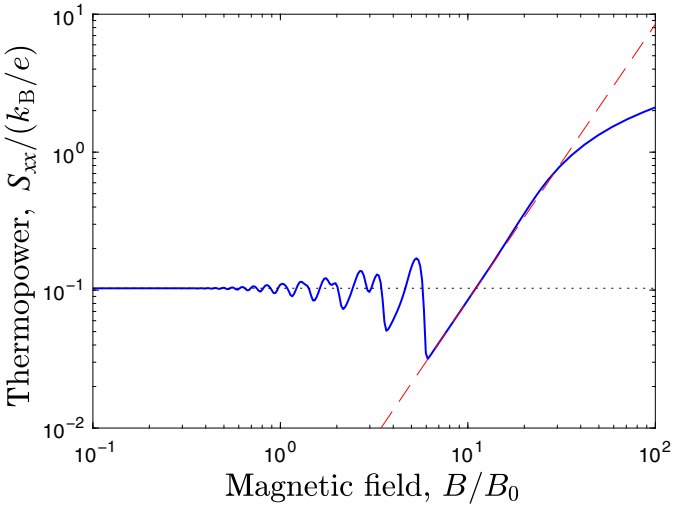

Fig. 2. Thermopower in the transverse direction, S_{xx}, as a function of magnetic field for a degenerate semiconductor with parabolic dispersion relation. The magnetic field is plotted in units of $B_0 = \hbar n^{2/3}/e$. The temperature is taken to be $T = 0.02E_F^{(0)}/k_B$, and for simplicity, we have set $N_v = 1$ and $g = 2$. The dotted line shows the limiting result of Eq. 8 for small B, and the dashed line shows the result of Eq. 11 for the extreme quantum limit. At a very large magnetic field, the thermopower saturates at ~ k_B/e, with only a logarithmic dependence on B and T, as suggested by Eq. 12.

where $\nu(\mu)$ is the density of states at the Fermi level. At weak enough magnetic field that $\hbar\omega_c \ll E_F$, the density of states is similar to that of the usual 3D electron gas, and the corresponding thermopower is

$$S_{xx} \simeq \frac{k_B}{e}\left(\frac{\pi}{3}N_v\right)^{2/3}\frac{k_B T m}{\hbar^2 n^{2/3}} \tag{8}$$

where N_v is the degeneracy per spin state (the valley degeneracy), m is the effective mass, and $\hbar$ is the reduced Planck constant. As the magnetic field is increased, the density of states undergoes quantum oscillations that are periodic in $1/B$, which are associated with individual Landau levels passing through the Fermi level. These oscillations are reflected in the thermopower, as shown in Fig. 2.

Of course, Eq. 8 assumes that impurity scattering is sufficiently weak that $\omega_c\tau \gg 1$. For the case of a doped and uncompensated semiconductor where the scattering rate is dominated by elastic collisions with donor/acceptor impurities, this limit corresponds to (*15*) $\ell_B \ll a_B^*$, where $\ell_B = \sqrt{\hbar/eB}$ is the magnetic length and $a_B^* = 4\pi\epsilon\hbar^2/(me^2)$ is the effective Bohr radius, with ϵ denoting the permittivity. In the opposite limit of small $\omega_c\tau$, the thermopower at $k_BT \ll E_F$ is given by the Mott formula (*9*)

$$S = \frac{k_B}{e}\frac{\pi^2}{3}\frac{k_B T}{\sigma}\left(\frac{d\sigma(E)}{dE}\right)\Big|_{E=\mu}, (\text{at } B = 0) \tag{9}$$

where $\sigma(E)$ is the low-temperature conductivity of a system with Fermi energy E. In a doped semiconductor with charged impurity scattering, the conductivity $\sigma \propto E_F^3$, and Eq. 9 gives a value that is twice larger than that of Eq. 8.

When the magnetic field is made so large that $\hbar\omega_c \gg E_F$, electrons occupy only the lowest Landau level, and the system enters the extreme quantum limit. At these high magnetic fields, the density of states rises strongly with increased B, as more and more flux quanta are threaded through the system and more electron states are made available at low energy. As a consequence, the Fermi energy falls relative to the energy of the lowest Landau level, and E_F and $\nu(\mu)$ are given by

$$\begin{aligned} E_F(B) - \frac{\hbar\omega_c}{2} &= \frac{2\pi^4\hbar^2 n^2 \ell_B^4}{m N_s^2 N_v^2} \propto 1/B^2 \\ \nu(\mu) &= \frac{m N_s^2 N_v^2}{4\pi^4\hbar^2 n \ell_B^4} \propto B^2 \end{aligned} \tag{10}$$

Here, N_s denotes the spin degeneracy at high magnetic field; $N_s = 1$ if the lowest Landau level is spin split by the magnetic field, and $N_s = 2$ otherwise. As long as the thermal energy k_BT remains smaller than E_F, Eq. 7 gives a thermopower

$$S_{xx} = \frac{k_B}{e}\frac{N_s^2 N_v^2}{12\pi^2}\frac{me^2B^2k_BT}{\hbar^4 n^2} \tag{11}$$

However, if the magnetic field is so large that k_BT becomes much larger than the zero-temperature Fermi energy, then the distribution of electron momenta p in the field direction is well described by a

classical Boltzmann distribution: $f \propto \exp\left[-p^2/(2mk_BT)\right]$. Using this distribution to calculate the entropy gives a thermopower

$$S_{xx} \simeq \frac{1}{2}\frac{k_B}{e}\ln\left(\frac{mk_BTN_v^2N_s^2}{\hbar^2n^2\ell_B^4}\right) \tag{12}$$

In other words, in the limit where the magnetic field is so large that $\hbar\omega_c \gg k_BT \gg E_F$, the thermopower saturates at a value $\sim k_B/e$ with only a logarithmic dependence on the magnetic field [the argument of the logarithm in Eq. 12 is proportional to $k_BT/E_F(B)$]. This result is reminiscent of the thermopower in nondegenerate (lightly doped) semiconductors at high temperature (*16*), where the thermopower becomes $\sim (k_B/e)\ln(T)$.

Dirac/Weyl semimetals

Let us now consider the case where quasiparticles have a linear dispersion relation and no band gap (or, more generally, a band gap that is smaller than k_BT), as in 3D Dirac or Weyl semimetals. Here, we assume, for simplicity, that the Dirac velocity v is isotropic in space so that, in the absence of magnetic field, the quasiparticle energy is given simply by $\varepsilon = \pm vp$, where p is the magnitude of the quasiparticle momentum. The net charge density en is constant as a function of magnetic field, because the gapless band structure precludes the possibility of magnetic freeze-out of carriers. A generic calculation of the thermopower S_{xx} is presented in the Supplementary Text, and an example of our result is plotted in Fig. 3.

The limiting cases for the thermopower can be understood as follows. In the weak-field regime $\hbar\omega_c \ll E_F$, the electronic density of states is relatively unmodified by the magnetic field, and one can use Eq. 7 with the zero-field density of states $\nu(\mu) = (9N_v/\pi^2)^{1/3}n^{2/3}/\hbar v$. This procedure gives a thermopower

$$S_{xx} \simeq \frac{k_B}{e}\left(\frac{\pi^4}{3}\right)^{1/3}\frac{k_BT}{\hbar v}\left(\frac{N_v}{n}\right)^{1/3} \tag{13}$$

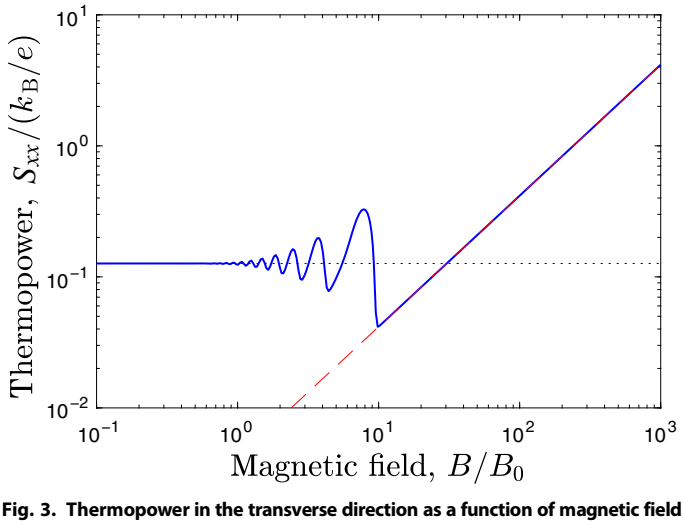

Fig. 3. Thermopower in the transverse direction as a function of magnetic field for a gapless Dirac/Weyl semimetal. Units of magnetic field are $B_0 = \hbar n^{2/3}/e$. In this example, the temperature is taken to be $T = 0.01E_F^{(0)}/k_B$ and $N_v = 1$. The dotted line is the low-field limit given by Eq. 13, and the dashed line is the extreme quantum limit result of Eq. 15. Unlike the semiconductor case, at a large magnetic field, the thermopower continues to grow with increasing B without saturation.

Here, N_v is understood as the number of Dirac nodes; for a Weyl semimetal, N_v is equal to half the number of Weyl nodes. Equation 13 applies only when $\omega_c\tau \gg 1$. If the dominant source of scattering comes from uncompensated donor/acceptor impurities (*17*), then the condition $\omega_c\tau \gg 1$ corresponds to $B \gg e^3n^{2/3}/[(4\pi\epsilon)^2\hbar v^2]$. In the opposite limit of small $\omega_c\tau$, one can evaluate the thermopower using the Mott relation (Eq. 9). A Dirac material with Coulomb impurity scattering has $\sigma(E) \propto E^4$ (*17*), so in the limit $\omega_c\tau \ll 1$, the thermopower is larger than Eq. 13 by a factor of 4/3.

As the magnetic field is increased, the thermopower undergoes quantum oscillations as higher Landau levels are depopulated. At a large enough field that $\hbar v/\ell_B > E_F$, the system enters the extreme quantum limit, and the Fermi energy and density of states become strongly magnetic field–dependent. In particular

$$\begin{aligned}\mu &\simeq \frac{2\pi^2}{N_v}\hbar v n\ell_B^2 \propto 1/B\\ \nu(\mu) &\simeq \frac{N_v}{2\pi^2\hbar v\ell_B^2} \propto B\end{aligned} \tag{14}$$

The rising density of states implies that the thermopower also rises linearly with magnetic field. From Eq. 7

$$S_{xx} \simeq \frac{k_B}{e}\frac{N_v}{6}\frac{k_BTeB}{\hbar^2 vn} \tag{15}$$

Remarkably, this relation does not saturate when μ becomes smaller than k_BT. Instead, Eq. 15 continues to apply up to arbitrarily high values of B, as μ declines and the density of states continues to rise with increasing magnetic field. One can think that this lack of saturation comes from the gapless band structure, which guarantees that there is no regime of temperature for which carriers can be described by classical Boltzmann statistics, unlike in the semiconductor case when the chemical potential falls below the band edge.

In more physical terms, the nonsaturating thermopower is associated with a proliferation of electrons and holes at large $(k_BT)/\mu$. Unlike in the case of a semiconductor with a large band gap, for a Dirac/Weyl semimetal, the number of electronic carriers is not fixed as a function of magnetic field. As μ falls and the density of states rises with increasing magnetic field, the concentrations of electrons and holes both increase even as their difference $n = n_e - n_h$ remains fixed. Because both electrons and holes contribute additively to the thermopower (as depicted in Fig. 1) in a strong magnetic field, the thermopower S_{xx} increases without bound as the magnetic field is increased. This is notably different from the usual situation of semimetals at $B = 0$, where electrons and holes contribute oppositely to the thermopower (*18*).

The unbounded growth of S_{xx} with the magnetic field also allows the figure of merit Z_BT to grow, in principle, to arbitrarily large values. For example, in situations where the Wiedemann-Franz law holds, Eq. 5 implies a figure of merit that grows without bound in the extreme quantum limit as B^2T^3. On the other hand, if the phonon thermal conductivity is large enough that the Wiedemann-Franz law is violated, then the behavior of the figure of merit depends on the field and temperature dependence of the resistivity. As we discuss below, in the common case of a mobility that declines inversely with temperature, the figure of merit grows as B^2T^2 and can easily become significantly larger than unity in experimentally accessible conditions.

DISCUSSION

Thermopower in the longitudinal direction

So far, we have concentrated on the thermopower S_{xx} in the direction transverse to the magnetic field; let us now briefly comment on the behavior of the thermopower S_{zz} in the field direction. At low temperature $k_BT \ll E_F$, the thermopower S_{zz} can be estimated using the usual zero-field expression (Eq. 9), where σ is understood as σ_{zz}. This procedure gives the usual thermopower $S_{zz} \sim k_B^2 T/(eE_F)$. Such a result has a weak dependence on magnetic field outside the extreme quantum limit, $\hbar\omega_c \ll E_F$, and rises with magnetic field when the extreme quantum limit is reached in the same way that S_{xx} does. That is, $S_{zz} \propto B^2$ for the semiconductor case (as in Eq. 11) and $S_{zz} \propto B$ for the Dirac semimetal case (as in Eq. 15), provided that $E_F \gg k_BT$.

However, when the magnetic field is made so strong that $E_F(B) \ll k_BT$, the thermopower S_{zz} saturates. This can be seen by considering the definition of thermopower in terms of the coefficients of the Onsager matrix $S = L^{12}/L^{11}$, where $L^{11} = -\int dE f'(E)\sigma(E)$ and $L^{12} = -1/(eT)\int dE f'(E)(E-\mu)\sigma(E)$ (*19*). In the limit where $k_BT \gg |\mu|$, the coefficient L^{11} is equal to σ, whereas L^{12} is of order $k_B\sigma/e$. Thus, unlike the behavior of S_{xx}, the growth of the thermopower in the field direction saturates when S_{zz} becomes as large as $\sim k_B/e$. As alluded to above, this difference arises because in the absence of a strong Lorentz force, electrons and holes flow in opposite directions under the influence of an electric field and thereby contribute oppositely to the thermopower. It is only the strong $\mathbf{E}\times\mathbf{B}$ drift, which works in the same direction for both electrons and holes, that allows the Dirac semimetal to have an unbounded thermopower S_{xx} in the perpendicular direction.

Experimental realizations

In semiconductors, achieving a thermopower of order k_B/e is relatively common, particularly when the donor/acceptor states are shallow and the doping is light. Nonetheless, we are unaware of any experiments that demonstrate the B^2 enhancement of S_{xx} implied by Eq. 11 for heavily doped semiconductors. Achieving this result requires a semiconductor that can remain a good conductor even at low electron concentration and low temperature so that the extreme quantum limit is achievable at not-too-high magnetic fields. This condition is possible only for semiconductors with a relatively large effective Bohr radius a_B^*, because of either a small electron mass or a large dielectric constant. For example, the extreme quantum limit has been reached in 3D crystals of HgCdTe (*20*), InSb (*21*), and $SrTiO_3$ (*22*, *23*). $SrTiO_3$, in particular, represents a good platform for observing large-field enhancement of the thermopower, because its enormous dielectric constant allows one to achieve metallic conduction with extremely low Fermi energy. For example, using the conditions of the experiments in the study of Bhattacharya *et al.* (*23*), where $n \sim 5\times10^{16}$ cm^{-3} and $T = 20$ mK, the value of S_{xx} can be expected to increase ≈ 50 times between $B = 5$ T and $B = 35$ T. The corresponding increase in the figure of merit is similarly large, although at these low temperatures, the magnitude of Z_BT remains relatively small.

More interesting is the application of our results to nodal semimetals, where S_{xx} does not saturate at $\sim k_B/e$, but continues to grow linearly with B without saturation. Similar behavior was recently seen by Liang *et al.* (*24*). These authors measured S_{xx} in the Dirac material $Pb_{1-x}Sn_xSe$ as a function of magnetic field and observed a result strikingly similar to that of Fig. 3, with quantum oscillations in S_{xx} at low field followed by a continuous linear increase with B upon entering the extreme quantum limit. Our theoretical results for S_{xx} agree everywhere with their measured value to within a factor 2 (the slight disagreement may be due to spatial anisotropy of the Dirac velocity). The experiments of Liang *et al.* (*24*) were performed in the degenerate limit, $E_F \gg k_BT$, where the magnitude of the thermopower is relatively small, but our results show that the linear increase in S_{xx} with B should continue without bound as one enters the nondegenerate limit, $k_BT \gg E_F$, by increasing B and/or T. We emphasize that, while our theory for Dirac/Weyl semimetals has formally assumed a vanishing band gap, the theory can still be applied in situations where there is a finite gap whose magnitude is much smaller than either k_BT or E_F. In $Pb_{1-x}Sn_xSe$, for example, the band gap is a function of both the alloy composition x and the temperature T, and experiments suggest that there is a line in the space of x and T at which the band gap vanishes (*25*, *26*). Points along this line represent ideal conditions for realizing a large, field-enhanced thermopower.

Given such a small band gap, one can quantitatively estimate the expected thermopower and figure of merit for $Pb_{1-x}Sn_xSe$ under generic experimental conditions using Eq. 15. Inserting the measured value of the Dirac velocity (*24*) gives

$$S_{xx} \approx \left(0.4\frac{\mu V}{K}\right)\times\frac{(T[K])(B[T])}{n[10^{17}\mathrm{cm}^{-3}]}$$

So, for example, a $Pb_{1-x}Sn_xSe$ crystal with a doping concentration $n = 10^{17}$ cm^{-3} at temperature $T = 300$ K and subjected to a magnetic field $B = 30$ T can be expected to produce a thermopower $S_{xx} \approx 3600$ μV/K. At this low doping, the Wiedemann-Franz law is strongly violated due to a phonon contribution to the thermal conductivity that is much larger than the electron contribution, and κ_{xx} is of order 3 W/(m K) (*27*). The value of ρ_{xx} can be estimated from the measurements of Liang *et al.* (*24*), which show a B-independent mobility μ_e that reaches $\approx 10^5$ cm^{2}V^{-1} s^{-1} at zero temperature, and which at temperatures above $T \approx 20$ K is limited by phonon scattering and declines as $\mu_e \approx \frac{1.5\times10^6\mathrm{cm}^2\mathrm{V}^{-1}\mathrm{s}^{-1}}{T[\mathrm{K}]}$. [This result for ρ_{xx} is consistent with previous measurements (*26*, *28*).] The large magnetic field limit $\omega_c\tau \gg 1$ is equivalent to $\mu_eB \gg 1$ so that, for $Pb_{1-x}Sn_xSe$ at temperatures above ≈ 20 K, our theory is applicable at all fields $B \gg 1/\mu_e \approx (7\times10^{-3}\,\mathrm{T})\times(T[\mathrm{K}])$. This corresponds to $B \gg 2$ T at room temperature. Inserting the experimental result for mobility into Eq. 6, and using $\rho_{xx} = 1/(ne\mu_e)$, gives a figure of merit

$$Z_BT \approx 1.3\times10^{-7}\times\frac{(T[K])^2(B[T])^2}{n[10^{17}\mathrm{cm}^{-3}]}$$

So, for example, at $n = 10^{17}$ cm^{-3}, $T = 300$ K, and $B = 30$ T, the figure of merit can apparently reach an unprecedented value $Z_BT \approx 10$. These experimental conditions are already achievable in the laboratory so that our results suggest an immediate pathway for arriving at record-large figure of merit. The sample studied by Liang *et al.* (*24*) has $n \approx 3.5\times10^{17}$ cm^{-3} so that, at $B = 30$ T and $T = 300$ K, this sample should already exhibit $Z_BT \approx 3$. If the doping concentration can be reduced as low as $n = 3\times10^{15}$ cm^{-3} [as has been achieved, for example, in the Dirac semimetals $ZrTe_5$ (*29*, *30*) and $HfTe_5$ (*31*)], then one can expect the room temperature figure of merit to be larger than unity already at $B > 1$ T. The corresponding power factor is also enormously enhanced by the magnetic field

$$\mathrm{PF} \approx \left(4\times10^{-3}\frac{\mu W}{\mathrm{cm}\ K^2}\right)\times\frac{(T[K])(B[T])^2}{n[10^{17}\mathrm{cm}^{-3}]}$$

reaching PF ≈ 1000 μW/(cm K^2) at $n = 10^{17}$ cm^{-3}, $T = 300$ K, and $B = 30$ T.

Note that the numerical estimates in this section have used a B-independent mobility, as reported by Liang *et al.* (*24*). Experiments probing transport in other Dirac and Weyl semimetals, however, have reported a nonsaturating linear magnetoresistance at large magnetic field, $\rho_{xx} \propto B$ [see, for example, the studies of Shekhar *et al.* (*32*) and Liang *et al.* (*33*)]. This linear magnetoresistance tends to blunt the growth of the figure of merit ZT at large B, reducing the dependence $ZT \propto B^2$ implied by Eqs. 6 and 15 to $ZT \propto B$. We emphasize, however, that even in the presence of a large, linear magnetoresistance, the figure of merit continues to grow without saturation as B is increased.

Finally, note that Eq. 15 implies a thermopower that is largest in materials with low Dirac velocity and high valley degeneracy. In this sense, there appears to be considerable overlap between the search for effective thermoelectrics and the search for novel correlated electronic states.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/4/5/eaat2621/DC1

Supplementary Text

section S1. Generalized expression for the thermoelectric figure of merit and power factor

section S2. General expression for the thermopower of heavily doped semiconductors

section S3. General expression for the thermopower of Dirac/Weyl semimetals

fig. S1. Setup of a thermodynamic generator, used to derive the generalized expression for figure of merit.

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