Rashba-driven anomalous Nernst conductivity of lead chalcogenide films
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The presence of a finite Berry curvature ($\Omega (k)$) leads to anomalous thermal effects. In this letter, we compute the coefficients for the anomalous Nernst effect (ANE) and its spin analogue, the spin Nernst effect (SNE) in lead chalcogenide ($PbX; X = S, Se, Te$) films. The narrow gapped $PbX$ films with a large spin-orbit coupling ($soc$) offer a significant Rashba interaction that gives rise to $\Omega (k)$ and the attendant anomalous thermal behaviour. In presence of a temperature gradient, the ANE and SNE establish a thermal and spin current and are characterized by their respective coefficients which acquire higher values for a stronger Rashba interaction. We further show that an extrinsic $soc$ generated by an in-plane electric field offers a gate-like mechanism to control (and turn-off) the anomalous thermal currents. Finally, we conclude by deriving the efficiency of an ANE-driven low-temperature Carnot heat engine and demonstrate that it can be gainfully optimized in systems with a robust intrinsic $soc$ resulting in low carrier effective masses.

The Nernst effect (NE) describes the generation of a transverse electric field by a longitudinal temperature gradient in presence of an out-of-plane magnetic field. The related Nernst coefficient is nominally expressed as $N = E_y / (\nabla T_x)$. The Nernst-induced electric field and the temperature gradient exist along the $y$- and $x$-axes, respectively. A variant of NE in absence of a real-space magnetic field has also been observed\textsuperscript{2}, the magnetic field, instead, is supplied by an analogous quantity - the Berry curvature\textsuperscript{2}. The Berry curvature ($\Omega (k)$) as an effective magnetic field in momentum space ($k$) imparts a Lorentz force on carrier electrons giving rise to an ‘anomalous’ velocity that is the precursor to a variety of observed effects, an illustration of which is the anomalous Nernst effect (ANE). The ANE has been theoretically predicted in a wide selection of materials including the $d$-density wave state in cuprate superconductors\textsuperscript{4}, illuminated graphene\textsuperscript{5}, and monolayer group-VI dichalcogenides\textsuperscript{2}. In each of these family of materials, it is possible to write a prototypical Hamiltonian transformable along a closed contour in momentum space in a cyclic adiabatic process giving rise to the non-zero Berry connection ($\mathbf{A} (k)$) from which an equivalent magnetic field ($\Omega (k) = \nabla \times \mathbf{A} (k)$) can be defined. For the case of graphene-like materials and the dichalcogenides, in the presence of either broken inversion or time-reversal symmetry (TRS), the form of Hamiltonian that sets up a finite $\Omega (k)$ is of a massive Dirac-type: $\mathcal{H}_{eff} = \nu (\sigma_z k_y - \sigma_y k_z) + \Delta \sigma_z$. The constant $\nu$ has units of $eV\AA$ and $\Delta$ is the generalized Dirac mass. The Pauli matrices ($\sigma_i$) may act on the lattice or spin sub-space.

It is easy to note, however, that the form of the $k$-dependent part of the Hamiltonian that permits a finite $\Omega (k)$ also describes the linear Rashba spin-orbit coupling (RSOC) for Bloch conduction electrons. For a set of conduction electrons in a thin film (quantum well) that follow a quadratic dispersion and spill into the linear RSOC-induced spin-polarized sub-bands, it is reasonable to anticipate the occurrence of a similarly definable $\Omega (k)$. The $\Omega (k)$ in this case would be solely an outcome of the linear RSOC Hamiltonian; the quadratic term does not contribute. A non-vanishing $\Omega (k)$ therefore alludes to the appearance of a concomitant ANE, the analytic estimation of which is the chief purpose here. We quantitatively estimate the strength of ANE in thin films whose Bloch conduction bands are split by RSOC in spin-polarized ensembles and examine underlying dependencies that enhance this thermomagnetic process. An additional purposed aim is also to uncover avenues that potentially optimize the efficiency of ANE via changes to strength of RSOC, the band curvature (tied to film dimensions), and external impurities. In fact, since an avowed goal in recent times hinges on the design of ‘energy-harvesting’ techniques, a large ANE can complement the ANE in miniaturized magnetoe-thermal devices.

It is worthwhile though to clarify that while a definite $\Omega (k)$ is derivable from a RSOC Hamiltonian and assumes an identical form to that obtained for gapped graphene-like materials and chalcogenides\textsuperscript{2}, the genesis of it lies in the spin degree of freedom unlike an inversion breaking mixing of orbitals in the latter. This disparity in the origin of the emergence of $\Omega (k)$ aside, it is significant to observe that RSOC is only operational when inversion symmetry is lost, which essentially constitutes one of the prerequisites (the other is $TRS$ and at least one must be satisfied) for a non-vanishing $\Omega (k)$ and fulfilled by the graphene family and dichalcogenides. Evidently, for a discernible $\Omega (k)$ (and ANE), a primary requirement centers around a large RSOC, a quantity generally pronounced in confined structures of compounds with narrow band gaps and high intrinsic spin-orbit coupling. While several sets of materials display a robust RSOC, it is beneficial to recall the thermal basis of the parent NE and thus select a candidate system that also combines favourable thermoelectric behaviour. The lead chalcogenides\textsuperscript{2} - PbX ($X = S/Se/Te$) - conform well in this regard, possessing the necessary material attributes for a large RSOC and a high thermoelectric figure of merit (ZT). PbTe and its alloyed derivatives have been widely researched for achieving an enhanced ZT\textsuperscript{10}.

In an $n$-doped PbTe sample under an out-of-plane magnetic field (causing a Zeeman split) and a temperature gradient (Fig.\textsuperscript{1}), we show that the ANE responds to a Rashba-controlled Berry curvature distribution in momentum space and can be further modulated with an in-plane electric field. A complete cessation of ANE (van-
lishing $\Omega (k)$ happens when the in-plane electric field initiated spin-orbit coupling (soc) exactly annihilates the Zeeman splitting. An accompanying quantifiable spin current - the anomalous spin Nernst effect - also flows mirroring the pattern observed for ANE. In the last part, we develop the idea of an ANE-driven Carnot engine whose efficiency is shown to be optimized by low carrier effective masses - the hallmark of high soc that also greatly influences RSO\textit{C.}

For an analytic formulation, we begin by writing the expression for ANE which is $J_y = N' (-\nabla_x T)$. The primed coefficient $N'$ distinguishes from $N$, the corresponding notation for NE. The ANE coefficient is

$$N' = \frac{e k_B}{h} \sum_{\pm} \int \frac{d^2 k}{4\pi^2} \Omega (k) S (k),$$

where $S (k)$ is the entropy density. The entropy density is defined as: $S (k) = - f_k \ln f_k - (1 - f_k) \ln (1 - f_k)$. Here $f_k$ is the usual Fermi distribution function. The summation over the spin-split bands is indicated by $\pm$ under the $\sum$ operator. As a brief insight into the particular form of the ANE coefficient (Eq. 1), we simply note that a finite $\Omega (k)$ lets the electron carriers (of charge ‘e’ and in presence of an electric field $\mathbf{E}$) acquire an additional velocity $v_{ane} = (e \mathbf{E}/h) \times \Omega (k)$. Multiplying $v_{ane}$ by the entropy density furnishes the coefficient for the transverse heat current from which we obtain $N'$ in Eq. 1. The primary task, therefore, to proceed further with ANE calculations is a determination of $\Omega (k)$. To do so, we first write down the minimal Hamiltonian that describes the Rashba and Zeeman spin-split parabolic conduction bands in a PbX quantum well. It is simply given by

$$H_0 = \frac{p^2}{2m^*} + \alpha_R (\sigma_z k_y - \sigma_y k_x) + \Delta \sigma_z.$$

The Pauli matrices in Eq. 2 act on the spin-space and the parameter $\Delta$ is the the out-of-plane magnetic field governed Zeeman splitting. The Rashba coupling pa-

rameter is $\alpha_R$ with adjustable strength via a gate electrode while the effective mass is $m^*$, which here are for the L-valley conduction electrons of a PbX film (quantum well confined along the z-axis). The corresponding eigen states are $\varepsilon_{\pm} = p^2/2m^* \pm \alpha_R k \pm \Delta$. The upper (lower) sign is for the spin-up (down) band. Additionally, we consider only conduction electrons (CE) of the PbX film (rock salt crystal structure) that belong to the L-valley and whose axis coincides with the [111] direction. Note that there exist three other oblique valleys with axes mis-aligned to the [111] vector. We make use of a $4 \times 4 k.p$ Hamiltonian\textsuperscript{11} that captures the dispersion around the high-symmetry L-valley; substituting for the confined $k_z = -i\partial_z$ in the Hamiltonian and followed by a numerical diagonalization supplies the quantum well CE effective mass\textsuperscript{12} The presented calculations use PbTe as the representative PbX.

For a quantum well, which is a two-dimensional system whose Hamiltonian (disregarding the quadratic component that does not contribute to $\Omega (k)$) is expressible as

$$H (k) = \mathbf{d} (k) \cdot \sigma, \text{the Berry curvature is defined as}^\text{15}$$

$$\Omega_{\mu\nu} = \frac{1}{2} \varepsilon_{\alpha\beta\gamma} d_{\alpha} (k) \partial_{k_\mu} d_{\beta} (k) \partial_{k_\nu} (k), \text{ (3)}$$

where $\mathbf{d} (k) = (d (k))$. Applying this formalism in the case of Rashba Hamiltonian (Eq. 2), the $\Omega (k)$ takes the form:

$$\Omega (k) = \pm \frac{\alpha^2 R \Delta}{2 \left( (\alpha R k)^2 + \Delta^2 \right)^{3/2}} \hat{z}. \hspace{1cm} (4)$$

In Eq. 4, $k^2 = k_x^2 + k_y^2$. The upper (lower) sign is for the spin-down (up) band. The $\Omega$ is a momentum-dependent magnetic field points out-of-plane (the z-axis). The $\Omega (k)$ vanishes as $\Delta \rightarrow 0$; the quenching of $\Delta$ (the Zeeman splitting) in this case restores TRS from which follows the relation, $\Omega (k) = 0$. A simple inspection of Eqs. 1 and 2 reveals that for a significant ANE a large $\Omega (k)$ is desirable which in turn requires a sizable Rashba splitting determined via the strength of the coefficient, $\alpha_R$. The Rashba coefficient is strong in narrow band gap materials with considerable intrinsic soc, such as those belonging to the PbX family. The Rashba coupling coefficient is expressed as: $\alpha_R = \lambda_0 \langle F (z) \rangle$, where $\langle F (z) \rangle$ is the average out-of-plane (z-axis) electric field. The average value for $\langle F (z) \rangle$ is $en/\epsilon$. Here, $e$ is the electronic charge, the dopant density is $n$, and $\epsilon$ identifies the dielectric constant. The material-dependent $\lambda_0$ is given as\textsuperscript{16}

$$\lambda_0 = \frac{\hbar^2 \Delta_{so}}{2m^* E_g} \frac{2 E_g + \Delta_{so}}{(2 E_g + 2 \Delta_{so})}. \hspace{1cm} (5)$$

For the specific case of PbX quantum wells, the parameters in Eq. 5 are defined at the L-valley; here, $E_g$ is the direct band gap, the intrinsic soc is $\Delta_{so}$, and $m^*$ denotes the conduction band effective mass. The tuning of $\alpha_R$ is therefore, unlike, the intrinsic soc possible via changes to the band gap and effective mass in confined structures.
Before we carry out a quantitative analysis of the anomalous thermal behaviour, a set of remarks are in order: Firstly (1), the dielectric constant \(d_{	ext{c}}\) of PbTe is abnormally large \((\approx 400)\), an outcome attributed to the high-polarizability of the chemical bond. This high \(d_{	ext{c}}\) in addition to determining \(\alpha_R\) via \(F(z)\) also couples with the low effective electron masses (in part, attributed to a substantial intrinsic \(\text{soc}\)) to set up a significant Bohr radius and thus enhancing carrier mobility. While thermoelectric applications require a pronounced mobility (and low thermal conductivity) for an optimized thermoelectric figure-of-merit \((ZT)\), for the Rashba-driven \(\text{ANE}\), a change in \(d_{	ext{c}}\) is reflected in \(\alpha_R\) which clearly revises \(\Omega(k)\) and consequently the thermal anomalous effects. The \(dc\) has been shown to be adjustable via simple lattice deformations of the rock salt crystal. In passing, it is useful to mention that polarizable \(\text{PbX}\) bonds also typically scupper the thermal conductivity to improve \(ZT\). The second comment (2) pertains to additional \(\text{soc}\) terms that may occur in the Hamiltonian (Eq. 2). An extra \(\text{soc}\)-term (besides Rashba) for an in-plane electric field \((F_{ip})\) can be of the form \(e\beta F_{ip} k_y\). For an \(x\)-axis directed \(F_{ip}\), the Hamiltonian receives a contribution expressed as \(e\beta F_{ip} k_y \sigma_z\). The corresponding expression for \(\Omega(k)\) by a direct application of the formula in Eq. 3 gives

\[
\Omega(k) = \pm \frac{\alpha_R^2 \left( \Delta + e\beta F_{ip} k_y \right)}{2 \left( \alpha_R k^2 + \left( \Delta + e\beta F_{ip} k_y \right)^2 \right)^{3/2}}. \tag{6}
\]

A more appealing situation emerges for an in-plane electric field solely directed along the \(y\)-axis; the \(\text{soc}\) in this case is simply \(-e\beta F_{ip} k_x \sigma_z\) and manifestly counteracts \(\Delta\), the Zeeman splitting. For values of the \(y\)-directed \(F_{ip}\) such that \(\Delta - e\beta F_{ip} k_x \rightarrow 0\), the out-of-plane \((z\)-axis\) magnetic field induced broken \(\text{TRS}\) is restored. The fulfillment of \(\text{TRS}\) to which we pointed out before leads to a ceasing of \(\Omega(k)\) and the attendant \(\text{ANE}\). It is therefore also apparent (from Eq. 3) that a union of the spin-orbit Hamiltonians through their respective coupling coefficients, \(\alpha_R\) and \(\beta\), allows a more detailed measure of control over the \(\text{ANE}\)-governed charge current (in a closed circuit). In fact, \(\mathcal{F}_{ip}\) can be considered applied from a gate terminal and serve as a threshold bias; for the correct polarity and magnitude, as \(\Omega(k) \rightarrow 0\), it describes a complete turnoff setting unique to the material system. The final remark (3) considers the overall contribution of the two spin-split bands. Noting that \(\Omega_{\uparrow}(k) = -\Omega_{\downarrow}(k)\), the complete \(\text{ANE}\) coefficient becomes \(\mathcal{N}_{\text{ANE}} = e k_B / (4\pi^2 h) \int d^2 k \Omega_{\uparrow}(k) |\mathcal{S}_{\uparrow}(k) - \mathcal{S}_{\downarrow}(k)|\). It is therefore straightforward to see that a spin-up band placed energetically above its spin-down counterpart when empty (or zero entropy) maximizes the \(\text{ANE}\). Further, in connection to the spin-split bands and analogous to \(\text{ANE}\), following Ref. 3, a spin Nernst coefficient \((\text{SNE})\) can be defined as

\[
\mathcal{N}' = \frac{k_B}{2} \int \frac{d^2 k}{4\pi^2} \left[ \Omega_{\uparrow}(k) \mathcal{S}_{\uparrow}(k) - \Omega_{\downarrow}(k) \mathcal{S}_{\downarrow}(k) \right]. \tag{7}
\]

**FIG. 2.** The numerically obtained \(L\)-valley dispersion of a 6.0 \(\text{nm}\) wide [111] PbTe film along the high-symmetry path \(\overrightarrow{K} - \overrightarrow{L} - \overrightarrow{\Gamma}\) is shown on the left panel (a). The right figure (b) plots (using Eq. 3) the Rashba-aided Berry curvature at the conduction band minimum \((|k| = 0)\) where the upper (lower) branch is for the spin-down (up) conduction state. The asymmetry-inducing electric field \((\text{out-of-plane})\) necessary for the Rashba splitting arises from an \(n\)-doping concentration; for purpose of numerical calculation, \(n\) was varied between \(1 \times 10^{12} \text{cm}^{-2}\) and \(4 \times 10^{12} \text{cm}^{-2}\). The dielectric constant of PbTe was set to 400 (see note below). The Zeeman splitting is treated as an external parameter and set to \(\Delta = 2.0 \text{meV}\) throughout.

It is, however, useful to reiterate that the \(\Omega(k)\) in Ref. 3 strictly arises from the broken inversion symmetry of the monolayer transition metal dichalcogenide, unlike the Rashba-governed case here.

For numerical estimate of \(\alpha_R\), from which follows the \(\Omega(k)\) and coefficients for \(\text{ANE}\) and \(\text{SNE}\), a 6.0 \(\text{nm}\) wide PbTe film grown along the [111] axis is selected as the model structure. The \(L\)-valley band gap and effective mass (transverse) of this film from a \(k.p\) calculation are 0.0565\(m_0\) and 0.33\(eV\). The free electron mass is \(m_0 = 9.1 \times 10^{-31} \text{kg}\). The dispersion of the 6.0 \(\text{nm}\) wide PbTe film and the accompanying Rashba-induced \(\Omega(k)\) is shown in Fig. 2. Note that \(\Omega(k)\) is plotted as a function of \(\alpha_R\), which is a function of material parameters and the film’s Bloch conduction electrons effective mass. To proceed further a number of other parameters useful in determination of \(\mathcal{N}'\) and \(\mathcal{N}_{\text{SNE}}\) must be defined: We begin by assigning the temperature \(T\) a pair of values: \(T = \{125, 300\} \text{K}\). The Fermi level is set to \(E_f = 0.15 \text{eV}\) from the bottom of the conduction band while the charge/dopant density is assumed to lie between \(10^{12} \text{cm}^{-2}\) and \(8 \times 10^{12} \text{cm}^{-2}\). This dopant density furnished electric field lets \(\alpha_R\) acquire values from 5.0 \(\text{meV}\) – 30.0 \(\text{meV}\). Inserting these numbers in Eqs. 1 and 7 and numerically integrating for \(|k| \leq 0.31 / \text{A}\), we plot \(\mathcal{N}'\) and \(\mathcal{N}_{\text{SNE}}\) in Fig. 3 in units of \(e k_B / \hbar\) and \(k_B / 4\pi\), respectively. We only show the \(\text{ANE}\) coefficient for the spin-down band since the contribution of the spin-up band differs marginally from the former and carries a reversed sign. The closeness is simply a consequence of the moderate energy difference between the spin-split bands. Separately, the plot clearly reveals a more forceful display of \(\text{ANE}\) and \(\text{SNE}\) for weightier \(\alpha_R\), which expressly influences and enlarges \(\Omega(k)\) - the engine behind anomalous effects. We make a note here
that the parameter $\alpha_R$, in addition to dopant density changes is also amenable to further modification via adjustments to $m^*$, the band gap ($E_g$), and the intrinsic soc. While the soc, admittedly, is harder to modulate; however, $m^*$ and $E_g$ through varying degrees of confinement, layered-heterostructure design, and strain-like perturbation can substantially augment $\alpha_R$. In line with schemes that may reinforce the anomalous thermal behaviour, it is also expedient to identify regions in momentum-space where $\Omega(k)$ and $\mathcal{S}(k)$ attain their highest values. The $\Omega(k)$ from Eq. 11 has a Lorentzian sprawl centered around the $|k| = 0$ point, which is the conduction band origin and reaches its maximum; likewise, the entropy has peaks on the Fermi surface and tails off away from it. For these two variables to amplify ANE and SNE, an intersecting region of momentum space must therefore be chosen to locate carriers with energy closely aligned to the Fermi surface while simultaneously ensuring that it isn’t too far away from $|k| = 0$ for a reasonable $\Omega(k)$.

As a more definitive guide that ascertains the efficiency ($\eta = \text{output/input}$ of ANE, we can construct a paradigmatic Carnot engine like abstraction into which heat is pumped and ‘useful’ work extracted as power in a closed circuit. The power (‘output’) is $\left(\mathcal{N} \left(-\nabla_x T\right)^2 R\right)$. The electric resistance of the closed circuit is $\mathcal{R}$. We consider a low temperature regime to ignore any phonon-driven thermal currents. A Carnot engine modeled on the $NE$ must proceed by establishing a temperature gradient, where the desired heat current (‘input’) to maintain a temperature difference is given by the Fourier law: $J_Q = -\kappa \nabla_x T$. Here, $\kappa$ is the thermal conductivity which is connected via the Wiedemann-Franz law (WFL) to its electric counterpart. Briefly, the electric conductivity (for energy $\varepsilon$) using the linearized Boltzmann equation is $\sigma = e^2 v_f^2/2 \int d\varepsilon D(\varepsilon) \tau(\varepsilon)(-\partial_x f)$. The density-of-states, $D(\varepsilon)$, ignoring the linear Rashba and Zeeman term is $m^* / (\pi \hbar^2)$ and the Fermi velocity ($v_f$) is $\hbar k/m^*$. The scattering time is $\tau(\varepsilon)$. A direct application of WFL therefore gives the thermal conductivity as $\kappa = L \sigma T$. Here, $L = 2.44 \times 10^{-8} W \Omega K^{-2}$ is the Lorentz number. By following the outlined sequence of steps, the quantity $\eta$ for the proposed Carnot engine is

$$\eta_{Carnot} = \frac{2\pi \hbar^2 \left[N^2 \nabla_x T \right] R}{L e^3 v_f^2 m^* \tau T}. \quad (8)$$

It is clearly noticeable from Eq. 8 that a low-effective mass improves efficiency - a result that ties well with the requirement of a strong Rashba coupled material, as both arise in compounds with a large intrinsic soc.

To summarize, we obtained analytic expressions for anomalous Nernst and spin Nernst coefficients tunable through the Rashba-created Berry curvature in PbTe films. Similarly, it is expected that narrow-gap and strongly spin-orbit coupled III-V materials such as InAs or InSb can give rise to comparable anomalous thermal currents. Besides, the SNE-origin anomalous spin current may find applications in spin caloritronics\textsuperscript{22} for a more diverse set of PbTe-like materials, rather than being limited, as it is hitherto, to mostly magnetic systems.

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