Berry-Phase Effect in Anomalous Thermoelectric Transport

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We develop a theory of the Berry-phase effect in anomalous transport in ferromagnets driven by statistical forces such as the gradient of temperature or chemical potential. Here a charge Hall current arises from the Berry-phase correction to the orbital magnetization rather than from the anomalous velocity, which does not exist in the absence of a mechanical force. A finite-temperature formula for the orbital magnetization is derived, which enables us to provide an explicit expression for the off-diagonal thermoelectric conductivity, to establish the Mott relation between the anomalous Nernst and Hall effects, and to reaffirm the Onsager relations between reciprocal thermoelectric conductivities. A first-principles evaluation of our expression is carried out for the material $CuCr_2Se_{4-x}Br_x$, obtaining quantitative agreement with a recent experiment.

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The phenomena of transport fall into two categories: those due to a mechanical force, such as the electric field on charges, and those driven by a statistical force, such as the gradient of temperature or chemical potential. The mechanical force exists on the microscopic level and can be described by a perturbation to the Hamiltonian for the carriers, while the statistical force manifests on the macroscopic level and makes sense only through the statistical distribution of the carriers. It has been established [1,2] that the Berry phase of Bloch states has a profound effect on transport driven by a mechanical force. This is through the mechanism that the group velocity of a Bloch electron acquires an anomalous term proportional to the mechanical force, i.e.,

$$\dot{\boldsymbol{r}} = \frac{1}{\hbar}\frac{\partial \varepsilon_n(\boldsymbol{k})}{\partial \boldsymbol{k}} + \frac{e}{\hbar}\boldsymbol{E} \times \boldsymbol{\Omega}_n(\boldsymbol{k}), \tag{1}$$

where $\varepsilon_n(\boldsymbol{k})$ is the band energy, $-e\boldsymbol{E}$ is the mechanical force due to the external electric field, and $\boldsymbol{\Omega}_n(\boldsymbol{k})$ is the Berry curvature, the Berry phase per unit area in the $\boldsymbol{k}$ space. Evaluation of the Hall current from the anomalous term reproduces the Karplus-Luttinger formula [3] for the anomalous Hall conductivity. Calculations based on the Berry-phase effect have found much success in explaining anomalous Hall effects (AHE) in ferromagnets of semiconductors [4], oxides [5], and transition metals [6]. Recent experiments [7,8] give further convincing evidence in support of this theory.

A natural question is whether and how the Berry phase also manifests in transport driven by a statistical force. On the one hand, the anomalous velocity vanishes in the absence of a mechanical force, eliminating the obvious cause for a Berry-phase effect in this case. On the other hand, this conclusion would introduce a number of basic contradictions to the standard transport theory. First, a chemical potential gradient would be distinct from the electrical force, violating the basis for the Einstein relation for transport. Second, a temperature gradient would not induce an intrinsic charge Hall current, violating the Mott relation [see Eq. (10) below] between the AHE and the anomalous Nernst effect (ANE), where a transverse current is produced by a temperature gradient in ferromagnets. Third, as will be made clear below, it would be impossible to establish the Onsager relation between cross transport coefficients connecting thermoelectric Hall currents and forces. In addition, a recent experiment on the ANE in the spinel ferromagnet $CuCr_2Se_{4-x}Br_x$ [9] found weak dependence on scattering, suggesting that there should indeed be a Berry-phase-induced intrinsic mechanism.

In this Letter, we solve the puzzle by showing how the Berry-phase effect manifests in thermoelectric transport driven by a statistical force. It turns out that the local current of carriers acquires an extra term from the carrier magnetic moment in the presence of a nonuniform distribution which arises from the gradient of temperature or chemical potential. However, the complete theory also relies on a proper deduction of magnetization current [10] and requires a deeper understanding of the orbital magnetization. It was found that there is a Berry-phase correction to the magnetization [11,12], and here we generalize it to the case of finite temperatures which is needed for thermoelectric transport. This Berry-phase correction eventually enters into the transport current produced by the statistical force, playing the counterpart as the anomalous velocity term due to a mechanical force.

We have thus found perfect harmony between statistical and mechanical forces even in the presence of a Berry-phase effect. The basic transport relations of Einstein, Mott, and Onsager continue to hold, which gives strong support for the validity of our theory. Finally, we also provide a reality check on the Berry-phase effect in the ANE by calculating the intrinsic anomalous Nernst conductivity α_{xy} [13] for $CuCr_2Se_{4-x}Br_x$ using a first-principles method. The obtained doping dependence curve agrees

well with available experimental data [9]. Our calculation also predicts a peak-valley structure between the data points, at a place where the anomalous Hall conductivity has a sudden sign and magnitude change.

Local and transport currents.—In the conventional Boltzmann transport theory, one considers a statistical distribution $g(\boldsymbol{r}, \boldsymbol{k})$ of carriers in the phase space of position and crystal momentum. The distribution function satisfies the Boltzmann equation with a collision integral whose form depends on the details of the collision process. The current density is given by $\boldsymbol{J} = -e \int [d\boldsymbol{k}] g(\boldsymbol{r}, \boldsymbol{k}) \dot{\boldsymbol{r}}$, where $\int [d\boldsymbol{k}]$ is shorthand for $\int d\boldsymbol{k}/(2\pi)^3$, and a summation over the band index has been omitted for simple notation. In the absence of a mechanical force, the electron velocity is simply $\dot{\boldsymbol{r}} = \partial \varepsilon(\boldsymbol{k})/\hbar \partial \boldsymbol{k}$. It is then apparent that the anomalous velocity term due to the Berry phase drops out of the expression for the current.

However, the above picture is naïve in that the carrier is treated as a structureless point particle. The quantum representation of the carrier is, in fact, a wave packet, which has a finite spread in the phase space. The wave packet generally rotates about its center position, as illustrated in Fig. 1, giving rise to an orbital magnetic moment $\boldsymbol{m}(\boldsymbol{k}) = -(e/2)\langle W|(\hat{\boldsymbol{r}} - \boldsymbol{r}_c) \times \hat{\boldsymbol{v}}|W\rangle$, where $|W\rangle$ is the wave packet and $\hat{\boldsymbol{v}}$ is the velocity operator [1,2]. A careful coarse graining analysis [14] shows that the correct expression for the *local* current has an extra term:

$$\boldsymbol{J} = -e \int [d\boldsymbol{k}] g(\boldsymbol{r}, \boldsymbol{k}) \dot{\boldsymbol{r}} + \boldsymbol{\nabla} \times \int [d\boldsymbol{k}] f(\boldsymbol{r}, \boldsymbol{k}) \boldsymbol{m}(\boldsymbol{k}), \quad (2)$$

where the magnetic moment enters explicitly. In the extra term, we have replaced $g(\boldsymbol{r}, \boldsymbol{k})$ with the local equilibrium Fermi-Dirac distribution $f(\boldsymbol{r}, \boldsymbol{k})$ for a linear-order calculation. When the temperature or chemical potential varies in space, the extra term will be proportional to the gradient of these thermodynamic quantities and is therefore non-negligible.

For transport studies, it is important to discount the contribution from the magnetization current, a point which has attracted much discussion in the past. It was argued that the magnetization current cannot be measured by conventional transport experiments. (For a recent most comprehensive work, see Ref. [10].) Therefore, one introduces the concept of *transport* current, defined by

$$\boldsymbol{j} = \boldsymbol{J} - \boldsymbol{\nabla} \times \boldsymbol{M}(\boldsymbol{r}), \quad (3)$$

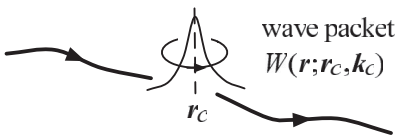

FIG. 1. The wave packet description of a charge carrier whose center is $(\boldsymbol{r}_c, \boldsymbol{k}_c)$. A wave packet generally possesses two kinds of motion: the center of mass motion and the self-rotation around its center. Both of them contribute to the local current density as given in Eq. (2).

where $\boldsymbol{M}(\boldsymbol{r})$ is the magnetization density. This is entirely analogous to the classic distinction between microscopic current and free current [15].

It is also important to realize that the magnetization density is not simply a statistical sum of the carrier magnetic moments. It has been shown recently that there is a Berry-phase correction to the magnetization [11,12]. The contribution from the carrier magnetic moments to the local current will be subtracted out in the transport current, but the Berry-phase correction to the magnetization will give rise to an extra term in the transport current. Earlier work concentrated on the zero temperature magnetization, and we provide an extension to the finite-temperature case below. Using Eq. (6) for the magnetization, we find that the transport current is given by

$$\boldsymbol{j} = -e \int [d\boldsymbol{k}] g(\boldsymbol{r}, \boldsymbol{k}) \dot{\boldsymbol{r}} - \boldsymbol{\nabla} \times \frac{1}{\beta} \int [d\boldsymbol{k}] \frac{e}{\hbar} \boldsymbol{\Omega}(\boldsymbol{k}) \times \log(1 + e^{-\beta(\varepsilon - \mu)}), \quad (4)$$

where $\beta = 1/k_B T$, and the Berry curvature is defined by $\boldsymbol{\Omega}(\boldsymbol{k}) = \boldsymbol{\nabla}_{\boldsymbol{k}} \times \langle u | i \boldsymbol{\nabla}_{\boldsymbol{k}} | u \rangle$, with $|u\rangle$ being the periodic amplitude of the Bloch wave.

The above expression gives a complete account of the transport current in ferromagnets and for crystals with nonzero Berry curvatures, in general. The first term is the usual expression for the charge current, which vanishes at local equilibrium (assuming the absence of a mechanical force), i.e., $g(\boldsymbol{r}, \boldsymbol{k}) = f(\boldsymbol{r}, \boldsymbol{k})$. Nonequilibrium correction to first order in the gradient of temperature or chemical potential yields a result strongly depending on the relaxation process, and a transverse current can result from skew scattering due to spin-orbit coupling [16]. The second term is new, which results from the Berry-phase correction to the magnetization. It is also first-order in the statistical force but is independent of the relaxation time and is, therefore, an intrinsic property of the system.

Orbital magnetization at finite temperatures.—The orbital magnetization of Bloch electrons has been an outstanding problem in solid state physics. Recently, different approaches [11,12] have been used to derive a formula at zero temperature, where the Berry phase is found to play an important role. In order to study thermoelectric transport, we need to generalize it to finite temperatures. Our derivation is made easy by using the field-dependent density of states introduced in Ref. [11], where it was shown that, in the weak-field limit, a quantum-state summation $\sum_{\boldsymbol{k}} \mathcal{O}(\boldsymbol{k})$ of some physical quantity $\mathcal{O}(\boldsymbol{k})$ should be converted to a $\boldsymbol{k}$-space integral according to $\int [d\boldsymbol{k}](1 + e\boldsymbol{\Omega} \cdot \boldsymbol{B}/\hbar)\mathcal{O}(\boldsymbol{k})$.

The equilibrium magnetization density can be obtained from the grand canonical potential, which, within first order in the magnetic field, may be written as

$$F = -\frac{1}{\beta} \sum_{\boldsymbol{k}} \log(1 + e^{-\beta(\varepsilon_M - \mu)}) = -\frac{1}{\beta} \int [d\boldsymbol{k}] \left(1 + \frac{e}{\hbar} \boldsymbol{B} \cdot \boldsymbol{\Omega}\right) \log(1 + e^{-\beta(\varepsilon_M - \mu)}), \quad (5)$$

where the electron energy $\varepsilon_M = \varepsilon(\boldsymbol{k}) - \boldsymbol{m}(\boldsymbol{k}) \cdot \boldsymbol{B}$ includes a correction due to the orbital magnetic moment $\boldsymbol{m}(\boldsymbol{k})$. The magnetization is then the field derivative at fixed temperature and chemical potential, $\boldsymbol{M} = -(\partial F/\partial \boldsymbol{B})_{\mu,T}$, with the result

$$\boldsymbol{M}(\boldsymbol{r}) = \int [d\boldsymbol{k}] f(\boldsymbol{r}, \boldsymbol{k}) \boldsymbol{m}(\boldsymbol{k}) + \frac{1}{\beta} \int [d\boldsymbol{k}] \frac{e}{\hbar} \boldsymbol{\Omega}(\boldsymbol{k}) \log(1 + e^{-\beta(\varepsilon-\mu)}). \quad (6)$$

For generality, we have included a position dependence to cover the situation of local equilibrium with a position-dependent temperature and chemical potential.

We have thus derived a general expression for the equilibrium orbital magnetization density, valid at zero magnetic field but at arbitrary temperatures. The first term is just a statistical sum of the orbital magnetic moments of the carriers originating from self-rotation of the carrier wave packets. It has been derived in Refs. [1,2] with the expression $\boldsymbol{m}(\boldsymbol{k}) = -i(e/2\hbar)\langle \boldsymbol{\nabla}_{\boldsymbol{k}} u| \times [\hat{H}(\boldsymbol{k}) - \varepsilon(\boldsymbol{k})] |\boldsymbol{\nabla}_{\boldsymbol{k}} u\rangle$, where $\hat{H}(\boldsymbol{k})$ is the crystal Hamiltonian acting on $|u\rangle$. It has the same symmetry properties as the Berry curvature. The second term of Eq. (6) is the Berry-phase correction to the orbital magnetization. It is of topological nature, arising from a bulk consideration, on the one hand, as in the above derivation, and being connected to a boundary current circulation on the other [17]. Interestingly, it is this second term that eventually enters the transport current.

Anomalous thermoelectric transport.—With the aid of Eq. (4), it is straightforward to calculate various thermoelectric responses to statistical forces. For example, a chemical potential gradient will produce, through the second term, a Hall current given by $-\boldsymbol{\nabla}\mu \times (e/\hbar) \int [d\boldsymbol{k}] f(\boldsymbol{k}) \boldsymbol{\Omega}(\boldsymbol{k})$. This is the same as the Berry-phase-induced anomalous Hall current in response to an electric field if one substitutes $\boldsymbol{\nabla}\mu/e$ for the field. It is gratifying to see that the Einstein relation continues to hold in the presence of the Berry-phase effect.

In the presence of a temperature gradient, an intrinsic Hall current also results from the second term of Eq. (4),

$$\boldsymbol{j}_{\text{in}} = -\frac{\boldsymbol{\nabla} T}{T} \times \frac{e}{\hbar} \int [d\boldsymbol{k}] \boldsymbol{\Omega} \Big[(\varepsilon - \mu) f + k_B T \log(1 + e^{-\beta(\varepsilon-\mu)}) \Big]. \quad (7)$$

One can then extract an anomalous Nernst conductivity α_{xy} defined by $j_x = \alpha_{xy}(-\nabla_y T)$. On a different route, we can also obtain the same result by invoking a fictitious gravitational field [18], establishing the Einstein relation between this mechanical force and the temperature gradient.

Interestingly, by integration by parts, α_{xy} can be written into the following more suggestive form:

$$\alpha_{xy} = -\frac{1}{e} \int d\varepsilon \frac{\partial f}{\partial \mu} \sigma_{xy}(\varepsilon) \frac{\varepsilon - \mu}{T}, \quad (8)$$

where $\sigma_{xy}(\varepsilon)$ is the intrinsic anomalous Hall conductivity at zero temperature with Fermi energy ε, given by

$$\sigma_{xy}(\varepsilon) = -\frac{e^2}{\hbar} \int [d\boldsymbol{k}] \Theta(\varepsilon - \varepsilon_{\boldsymbol{k}}) \Omega_z(\boldsymbol{k}). \quad (9)$$

At low temperatures, the above relation reduces to

$$\alpha_{xy} = \frac{\pi^2}{3} \frac{k_B^2 T}{e} \sigma'_{xy}(\varepsilon_F). \quad (10)$$

Such relations between the electrical and thermoelectric conductivities are known as Mott relations. They were proved for nonmagnetic materials without or with a magnetic field [19,20]. Our result extends the validity of this relation to ferromagnets and other systems with a Berry curvature and justifies the usage of Eq. (10) in Ref. [9].

The reciprocal of the ANE is the generation of a transverse heat current by an electric field. The Onsager relation dictates that the Berry phase should also affect the latter. To show this explicitly, we consider the energy current carried by a wave packet $\langle W|(\hat{H}\hat{\boldsymbol{r}} + \hat{\boldsymbol{r}}\hat{H})/2|W\rangle = \varepsilon \dot{\boldsymbol{r}} - \boldsymbol{E} \times \boldsymbol{m}(\boldsymbol{k})$, where the second term is from the field correction to the local Hamiltonian. Assuming a uniform temperature and chemical potential [21], we obtain the *local* energy current to first order in the electric field:

$$\boldsymbol{J}^E = \int [d\boldsymbol{k}] g(\boldsymbol{k}) \varepsilon \dot{\boldsymbol{r}} - \boldsymbol{E} \times \int [d\boldsymbol{k}] f(\boldsymbol{k}) \boldsymbol{m}(\boldsymbol{k}), \quad (11)$$

where the electron velocity $\dot{\boldsymbol{r}}$ is given by Eq. (1). However, the energy current also has a magnetization part from an "energy" magnetization [10]. In the present case, it is given by $-\boldsymbol{E} \times \boldsymbol{M}$, which is nothing but the material-dependent part of the Poynting vector $\boldsymbol{E} \times \boldsymbol{H}$ describing the energy flow (with $\boldsymbol{H} = \boldsymbol{B}/\mu_0 - \boldsymbol{M}$) [15]. Since this energy flow exists in an equilibrium state, it does not correspond to a transport current and thus must be subtracted from $\boldsymbol{J}^E$ to yield the *transport* energy current $\boldsymbol{j}^E = \boldsymbol{J}^E + \boldsymbol{E} \times \boldsymbol{M}$. Based on our expression (6) for the magnetization density, we finally find the Berry-phase correction to the heat current (defined by $\boldsymbol{j}^Q \equiv \boldsymbol{j}^E - \mu \boldsymbol{j}$):

$$\boldsymbol{j}^Q_{\text{in}} = \boldsymbol{E} \times \frac{e}{\hbar} \int [d\boldsymbol{k}] \boldsymbol{\Omega} [(\varepsilon - \mu) f + k_B T \log(1 + e^{-\beta(\varepsilon-\mu)})], \quad (12)$$

while the usual expression for the heat current is $\int [d\boldsymbol{k}] g(\boldsymbol{k}) (\varepsilon - \mu) \boldsymbol{v}$, where $\boldsymbol{v}$ is the usual group velocity determined by the band energy. In this case, the Berry-phase correction comes from both the anomalous velocity and the orbital magnetization. Comparison with Eq. (7) shows that the Onsager relation is indeed satisfied, providing strong evidence for the validity of our theory.

Comparison with experiment.—The intrinsic anomalous Nernst conductivity α_{xy} depends only on the band structure and Berry curvature, so it can be evaluated for crystals based on first-principles methods. Here we report our result for $CuCr_2Se_{4-x}Br_x$ and compare with the experiment [9].

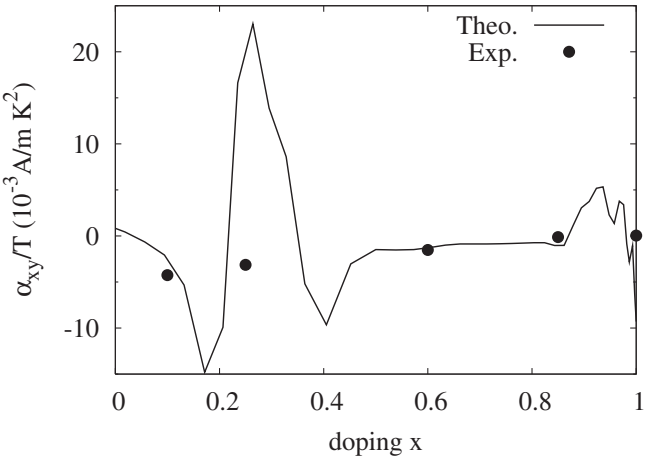

FIG. 2. The intrinsic anomalous Nernst conductivity α_{xy} (divide by the temperature T) of $CuCr_2Se_{4-x}Br_x$ as a function of the Br content x. The calculated curve is compared with experimental results (●) extracted from Ref. [9].

The band structure and Berry curvature are calculated following the procedures in Ref. [6], using the generalized gradient approximation for the exchange-correlation potential. Such calculations are very extensive, and, to reduce the work load, we assume that doping affects the Fermi energy but not the band structure, which is justified for the present compounds [22].

The calculated α_{xy} is plotted in Fig. 2 as a function of doping x together with the experimental data from Ref. [9]. The comparison is *quantitatively* good, except for the data point at $x = 0.25$. This is, however, a rather special point, because it was reported [9] that, for unknown reasons, α_{xy} is not really proportional to T for $x = 0.25$. At low temperatures, a proportional relation is expected from the Mott relation, which is followed strictly by all the data points at other doping densities.

We also note that, while our theory predicts a pronounced peak-valley structure around $x = 0.3$, the available experimental data at present is too sparse to confirm or disprove it. The oscillatory behavior results from the complicated band structure of this material and occurs when the Fermi energy (which depends on doping) goes through a region of spin-orbit-induced energy gap. A detailed explanation based on the numerical calculations will be presented elsewhere [22]. An indirect experimental evidence for this peak is that it occurs at a place where the anomalous Hall conductivity has a sudden change of sign and magnitude around $x = 0.3$ according to Ref. [7]. Such a correlation is expected from the Mott relation (10) and the fact that the Fermi energy changes approximately linearly with the doping density [22]. Nevertheless, more direct experimental results are clearly needed for a careful comparison with our theory.

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