First-principles calculation of anomalous Hall and Nernst conductivity by local Berry phase

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In this study, we implemented a finite-difference algorithm for computing anomalous Hall and Nernst conductivity. Based on the expression to evaluate the Berry curvature in an insulating system [J. Phys. Soc. Jpn. 74 1674(2005)], we extended the methods to a metallic system. We calculated anomalous Hall conductivity and Nernst conductivity in a two-dimensional ferromagnetic material FeCl$_2$ and three-dimensional ferromagnetic transition metals bcc-Fe, hcp-Co, and fcc-Ni. Our results are comparable to previously reported results computed by Kubo-formula or Wannier representation. To evaluate anomalous Nernst coefficients, the detailed Fermi-energy dependence of the anomalous Hall conductivity is required. Nonetheless, previous methods based on Wannier representation or Kubo-formula have numerical instability due to the k-space Dirac monopole. The present method will open an efficient thermoelectric material design based on the high-throughput first-principles screening.

I. INTRODUCTION

Anomalous Hall effect (AHE) shows Hall conductivity induced by broken time-reversal symmetry based on spontaneous magnetization$^{[12]}$. AHE has an extrinsic mechanism, which originates from impurities$^{[33]}$ and an intrinsic mechanism induced by the Berry curvature$^{[23]}$. The Berry curvature is a gauge invariant due to the topology of the electron wave function, and AHE occurs in simple ferromagnetic materials and materials with spin chirality$^{[35]}$. Therefore, the relation between anomalous Hall conductivity and magnetic structure in materials is non-trivial. In an insulating system, AHE has attracted much research attention as a topological effect because it is quantized as a Chern number, which is a topological invariant$^{[10,11]}$.

Anomalous Nernst effect (ANE), which originates from AHE, has attracted renewed interest. ANE generates a transverse voltage from a longitudinal temperature gradient due to a transverse electric conductivity through AHE$^{[2,7,12]}$. It can be utilized in developing energy-harvesting technology which may provide a simple layout$^{[5–7]}. Experimental and theoretical studies of ANE have been reported in various magnetic materials$^{[15–40]}$. Among them, theoretical work predicted large AHE and ANE in the Skyrmion crystal, which has a spin chirality$^{[23]}$. In addition, topological magnets, such as Mn$_2$Sn$^{[41–43]}$, Co$_2$MnGa$^{[25–27,13]}$, Fe$_3$X (X=Al, Ga, Si$^{[23]}$, Co$_3$Si$_2$S$^{[26,28,41]}$, and UCo$_3$$^{[23]}$, are particularly interesting due to their large ANE signal and characteristic low-energy electronics structure including Weyl points.

Anomalous Nernst conductivity (transverse thermoelectric conductivity), which indicates anomalous Nernst thermoelectric conversion efficiency can be evaluated from the chemical potential dependence of anomalous Hall conductivity. The intrinsic component of anomalous Hall conductivity $\sigma_{xy}$ can be obtained from the Berry curvature $\mathbf{F}^n(\mathbf{k})$:

$$\sigma_{xy}(\mu) = -\frac{e^2}{h} \sum_n \int \frac{d^2k}{2\pi} F_{xy}^n(\mathbf{k}) f(\varepsilon_{nk} - \mu).$$

Here, $N, \varepsilon, h, f, \varepsilon_{nk}$ and $\mu$ are the electron occupation number, elementary charge, Planck constant, Fermi-Dirac distribution function, band energy with the band index $n$, wave vector $\mathbf{k}$, and Fermi energy, respectively. The Berry curvature $\mathbf{F}^n(\mathbf{k})$ is given as,

$$\mathbf{F}^n(\mathbf{k}) = \nabla \times \mathbf{A}^n, \quad (2)$$

$$\mathbf{A}^n(\mathbf{k}) = -i \left\langle u^n(\mathbf{k}) | \nabla_{\mathbf{k}} | u^n(\mathbf{k}) \right\rangle, \quad (3)$$

where $\mathbf{A}^n$ and $u^n(\mathbf{k})$ are the Berry connection and the periodic part of the Bloch states, respectively. In an insulating system, Eq. (1) should be quantized, and it can be described as follows: $\sigma_{xy}(\varepsilon_F) = -e^2 C / h \ (C = 0, \pm 1, \pm 2, \cdots)$. Here, $\varepsilon_F$ is the Fermi energy, and the integer $C$ is “Chern number”. Anomalous Nernst conductivity $\alpha_{xy}$ can be calculated from the chemical potential dependence of $\sigma_{xy}$ as follows:

$$\alpha_{xy}(\mu, T) = \frac{1}{e} \mathcal{E} \left( \frac{\partial f(\mu)}{\partial \varepsilon} \right).$$

An efficient and simple method to evaluate the chemical potential dependence of $\sigma_{xy}$ is required for the design of thermoelectric materials based on high-throughput first-principles screening. Previous studies were mainly performed by evaluating the off-diagonal Hall conductivities with Wannier representation$^{[13,19]}$, or the Kubo formula$^{[20]}$. The former method was implemented in the Wannier90 code$^{[22]}$ and has been widely used in conjunction with many first-principles electronic structure packages. However, some empirical and technical procedures such as choice of bases and energy window range are required to
construct Wannier functions, which are material dependent.

In this paper, we introduce an efficient method for calculating anomalous Hall conductivity $\sigma_{xy}$ and anomalous Nernst conductivity $\alpha_{xy}$. We apply the finite-differences expression for Berry curvature on the two-dimensional Brillouin zone and defined its grid Suzuki'sulating system, which was proposed by Fukui-Hatsugai-Suzuki code and input files are publicly available on GitHub.

High-throughput first-principles screening. The source code and input files are publicly available on GitHub.

II. METHODS

First, we explain a method of computing $\sigma_{xy}$ in an insulating system, which was proposed by Fukui-Hatsugai-Suzuki.

We set the wave vector $\mathbf{k} = (k_1, k_2)$ at the lattice point on the two-dimensional Brillouin zone and defined its grid interval as $\delta k_1$ and $\delta k_2$ along the $k_1$ and $k_2$ directions, respectively. The $N \times N$ overlap matrix on the Brillouin zone is defined as follows:

$$
(M_{\mathbf{k}, \mathbf{k} + \delta \mathbf{k}})_{mn} = \langle u_m(\mathbf{k}) | u_n(\mathbf{k} + \delta \mathbf{k}) \rangle
$$

and we defined $U(1)$ link variable as follows:

$$
U_{\delta \mathbf{k}}(\mathbf{k}) = \det M_{\mathbf{k}, \mathbf{k} + \delta \mathbf{k}}.
$$

The non-abelian Berry curvature on the Brillouin zone, the local Berry phase, can be computed using $U_{\delta \mathbf{k}}(\mathbf{k})$ as follows:

$$
F(\mathbf{k}) = \text{Im} \ln U_{\delta \mathbf{k}_1}(\mathbf{k})U_{\delta \mathbf{k}_2}(\mathbf{k} + \delta \mathbf{k}_1) \times U_{\delta \mathbf{k}_1}(\mathbf{k} + \delta \mathbf{k}_2)^{-1}U_{\delta \mathbf{k}_2}(\mathbf{k})^{-1}.
$$

The value of $F(\mathbf{k})$ varies in the range of $-\pi \leq F(\mathbf{k}) < \pi$ because $\text{Im} \ln$ is an operation to take the argument of a complex number. To compute the Berry curvature $F$, we carried out the contour integration at four wave numbers on the vertices of a plaquette as shown in Fig. 1(a). The anomalous Hall conductivity, $\sigma_{xy}$ in the insulating system is computed by obtaining the Berry curvature on the Brillouin zone $F(\mathbf{k})$

$$
\sigma_{xy}(\mu) = -\frac{e^2}{h} \frac{1}{2\pi} \sum_{\mathbf{k}} F(\mathbf{k}) = -\frac{e^2}{h} C
$$

For computing $\sigma_{xy}(\mu)$, the matrix size of $U$ must be equal to that in another vertex, i.e., the all occupied number $N$ on vertices of a plaquette must be equal. Therefore, this method can apply only in the insulating system which all occupation numbers $N$ on the vertices of a plaquette are equal.

Next, we expanded the Fukui-Hatsugai-Suzuki method to metallic system. As shown in Fig. 1(b), we consider the case in which any band intersects the Fermi energy.

(i) In the case of occupation numbers $N$ on four vertices of a plaquette are equal, we can compute Berry curvature similarly to the case of an insulating system. As shown in Fig. 1(c), we can compute $U$ on each plaquette and obtain Berry curvature $F$.

(ii) In the case that even one occupation number $N$ is different from one of the plaquette, we approximate the Berry curvature $F$ by computing the average. Figure 1(d) illustrates the approximation concept for determining the average $F$. For example, in the case where the occupation numbers on four vertexes are $N_1, N_2, N_3, N_4$, we can obtain the four Berry curvatures $F_1(\mathbf{k}), F_2(\mathbf{k}), F_3(\mathbf{k}), F_4(\mathbf{k})$ which are calculated assuming that the all occupation numbers on the four vertexes are $N_1, N_2, N_3$ and $N_4$. The approximated Berry curvature $\bar{F}$ on this plaquette is approximated by the following equation:

$$
\bar{F}(\mathbf{k}) \approx \frac{1}{4} (F_1(\mathbf{k}) + F_2(\mathbf{k}) + F_3(\mathbf{k}) + F_4(\mathbf{k})).
$$

Through this approximation, we can compute $\bar{F}(\mathbf{k})$ on all plaquette, and we can obtain $\sigma_{xy}$ as

$$
\sigma_{xy}(\mu) = -\frac{e^2}{h} \sum_{\mathbf{k}} \bar{F}(\mathbf{k}).
$$

To approximate $\alpha_{xy}$, we need to calculate the $\mu$ dependence of $\sigma_{xy}$. If we set the occupation number $N$ corresponding to a chemical potential height, we can compute the chemical potential dependence of $\sigma_{xy}$ immediately by computing the overlap matrices until the occupation number $N$ in Eq. (7). If $\mu$ is changed, it is only necessary to recalculate the Eq. (6) in each plaquette needs to be calculated. Because the computational cost of Eq. (6) is much smaller than that of Eq. (5), it is possible to calculate $\alpha_{xy}$ efficiently.

Finally, in the case of a three-dimensional system, $\sigma_{xy}$ are defined on each $\mathbf{k}_3$. Thus, $\sigma_{xy}$ in a bulk system is computed by the average along the $\mathbf{k}_3$ direction as follows:

$$
\sigma_{xy}(\mu) = \frac{1}{N_3} \sum_{\mathbf{k}_3} \sigma_{xy}(\mu, \mathbf{k}_3).
$$

Here, $N_3$ is the mesh number along the $\mathbf{k}_3$ direction. Through this, $\sigma_{xy}$ in a three-dimensional system can be computed by applying our method on each $\mathbf{k}_3$. 
FIG. 1. (a) Computing $\sigma_{xy}$ in insulating system. (b) Fermi energy intersecting energy bands. (c) Carrying out contour integration on each plaquette. Except for the plaquette intersecting the Fermi surface, Berry curvature can be computed the same as insulating system because the occupation numbers $N$ on four vertexes are equal to one another. (d) The schematic diagram of an approximation in computing the Berry curvature on the plaquette intersecting the Fermi surface. Assuming occupation numbers on four vertexes are equal, one can take the average of the computed Berry curvature.

III. COMPUTATIONAL CONDITION

We conducted first-principles calculations based on the noncollinear density functional theory (DFT) based using the OpenMX code\cite{51}. DFT calculations were performed through the exchange-correlation functional within the generalized gradient approximation\cite{57} and norm-conserving pseudopotentials\cite{58}. The wave functions were expanded by a linear combination of multiple pseudoatomic orbitals\cite{59,60}. The spin-orbit inter-
action was included by using total-angular-momentum-dependent pseudopotential. For FeCl₂, the cutoff energy for a charge density of 500 Ry, a k-point sampling of \(20 \times 20 \times 1\), and lattice constant of 3.475 Å were used. A set of pseudo atomic orbital basis functions was specified as Fe6.0S-s3p3d3f1 and Cl7.0-s3p3d2, where 6.0 and 7.0 are the cutoff radii (in bohrs) of each element, respectively. 

TABLE I. Comparison of this work and previous ones for the \(\sigma_{xy}\) in bcc-Fe.

| Refs.          | \(\sigma_{xy}\) (S/cm) |
|---------------|----------------------|
| This work (700 \(\times\) 200) | 788                  |
| This work (600 \(\times\) 200) | 790                  |
| This work (500 \(\times\) 200) | 785                  |
| This work (400 \(\times\) 200) | 786                  |
| This work (300 \(\times\) 200) | 782                  |
| This work (200 \(\times\) 200) | 788                  |
| This work (100 \(\times\) 100) | 770                  |
| Exp         | 1032                  |
| C-C. Lee et al  | 750                  |
| X. Wang et al  | 756.76                |
| Y. Yao et al   | 751                   |

Next, let us perform our method in a three-dimensional ferromagnetic system. We calculated the \(\sigma_{xy}\) and \(\alpha_{xy}\) for bcc-Fe, hcp-Co, and fcc-Ni as a typical example. Here, we focused on bcc-Fe [Fig. 2(a)] (for hcp-Co and fcc-Ni, see Appendix A). In table II, we compared the \(\sigma_{xy}\) for bcc-Fe at the Fermi energy for the present work with a previous study. We can see that our calculation results converge to approximately \(\sigma_{xy} \approx 750\) S/cm as similarly reported in previous theoretical calculation.

Figure 3(b) shows the k-mesh dependence of the \(\sigma_{xy}\) at the Fermi energy. The \(\sigma_{xy}\) converged with at least the k-mesh of \(200 \times 200 \times 200\) and its value converged within about 10% with \(100 \times 100 \times 100\) k-mesh. Our results differ in value from those reported by Wannier90’s with less than 0.86 S/cm, where the k-mesh is finer than \(200 \times 200 \times 200\) at the Fermi energy. We can conclude that our method could reproduce the \(\sigma_{xy}\) at a specific chemical potential.

Finally, we discuss the chemical potential dependence of the \(\sigma_{xy}\) and \(\alpha_{xy}\) for bcc-Fe. Figures 3(c) and (d) show the band structure of bcc-Fe and the chemical potential dependence of the \(\sigma_{xy}\) at 0 K and \(\alpha_{xy}\) at 100 K, respectively. Compared to the two-dimensional system, the correspondence of the \(\sigma_{xy}\) between our method and the Wannier representation is slightly lowered at the specific energy region from -1.0 eV to -0.5 eV. This numerical error may originate from an entangled or degenerate electronic structure because the bcc-Fe system has many degenerate points stemming from point nodes. However, due to the smearing of the Fermi-Dirac distribution function, this inconsistency decreases as the temperature increases. In fact, the shown in Fig. 3 shows that our \(\alpha_{xy}\) of bcc-Fe at 100 K results are almost consistent with those calculated by Wannier90. We safely conclude that our method has enough accuracy for evaluating \(\alpha_{xy}\) in a finite temperature.
FIG. 2. (a) Crystal structure of FeCl$_2$. (b) $k$-mesh dependence of the $\sigma_{xy}$ at the Fermi energy. (c) Band structure of FeCl$_2$. (d) Chemical potential dependence of the $\sigma_{xy}$ and $\alpha_{xy}$. Blue and Red solid line points correspond to the present calculation results and results obtained from the Wannier90, respectively.

FIG. 3. (a) Crystal structure of bcc-Fe. (b) $k$-mesh dependence of the $\sigma_{xy}$ at the Fermi energy. (c) Band structure of bcc-Fe. (d) Chemical potential dependence of the $\sigma_{xy}$ and $\alpha_{xy}$. Blue and Red solid line points correspond to the present calculation results and results obtained from the Wannier90, respectively.

V. CONCLUSION

In this study, we expanded the Fukui-Hatsugai-Suzuki method to a metallic system to improve the efficiency in calculation of $\sigma_{xy}$ and $\alpha_{xy}$ in magnetic materials. Calculating an average of the Berry curvature on the all $k$-mesh plaquette, with respect to each vertex, makes it possible to estimate the $\sigma_{xy}$ in partially occupied cases. We also demonstrated the calculations of $\sigma_{xy}$ and $\alpha_{xy}$ by using this method in a typical two-dimensional ferromagnetic material FeCl$_2$ and three-dimensional magnetic transition metal bcc-Fe, hcp-Co, and fcc-Ni. The $\sigma_{xy}$ in FeCl$_2$ with a simple band structure completely reproduced the calculation results obtained from the Wannier representation and exhibited fast conversion with a rough $k$-mesh. Whereas, in three-dimensional transition metal cases, the consistency is slightly dropped in a specific energy range because of a complicated band structure; however, we find a good agreement for anomalous Nernst conductivity at a finite temperature. The present study will give us a more efficient calculation method for the AHE and ANE without some technical and empirical procedures such as those constructing Wannier functions. High-throughput first-principles screening based on this method will be a useful tool for thermoelectric materials design.

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FIG. 4. Chemical potential dependence of $\sigma_{xy}$ for (a) hcp-Co, and (b) fcc-Ni. Blue, green and red solid lines correspond to the $k$-mesh of $100 \times 100 \times 100$, $300 \times 300 \times 300$ and $500 \times 500 \times 500$, respectively.

Appendix A: Anomalous Hall conductivity for hcp-Co and fcc-Ni

We also calculated the $\sigma_{xy}$ for typical transition metal ferromagnetic materials of hcp-Co and fcc-Ni. For fcc-Ni, the cutoff energy for a charge density of 300 Ry, a $k$-point sampling of $32 \times 32 \times 32$, and lattice constant of $a = 3.56$ Å were used. A set of pseudo atomic orbital basis functions was specified as Ni6.0-s3p2d2f1. For hcp-Co, the cutoff energy for a charge density of 300 Ry, a $k$-point sampling of $24 \times 24 \times 18$, and lattice constant of $a = 2.50$ Å and $c = 4.07$ Å were used. A set of pseudo atomic orbital basis functions was specified as Co6.0-s3p2d2f1. Figure 4 shows the chemical potential dependence of the $\sigma_{xy}$ for hcp-Co and fcc-Ni. We found that the $k$-point mesh of $300 \times 300 \times 300$ converged enough. Our calculation results well reproduce the previous studies one.

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