First-principles investigation of magnetic and transport properties in hole-doped shandite compounds Co$_3$In$_x$Sn$_{2-x}$S$_2$

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Co-based shandite Co$_3$Sn$_2$S$_2$ is a representative example of magnetic Weyl semimetals showing rich transport phenomena. We thoroughly investigate magnetic and transport properties of hole-doped shandites Co$_3$In$_x$Sn$_{2-x}$S$_2$ by first-principles calculations. The calculations reproduce nonlinear reduction of anomalous Hall conductivity with doping In for Co$_3$Sn$_2$S$_2$, as reported in experiments, against the linearly decreased ferromagnetic moment within virtual crystal approximation. We show that a drastic change in the band parity character of Fermi surfaces, attributed to the nodal rings lifted energetically with In-doping, leads to strong enhancement of anomalous Nernst conductivity with reversing its sign in Co$_3$In$_x$Sn$_{2-x}$S$_2$.

I. INTRODUCTION

Novel charge and spin transports have attracted growing interests in the contexts of topological phases of matter. The anomalous Hall effect (AHE) and anomalous Nernst effect (ANE) are classical examples of such phenomena and have been studied for many years [1]. The AHE (ANE) is characterized by a transverse charge current flow $j$ induced by an applied electric field $E$ (thermal gradient $\nabla T$) in the absence of an external magnetic field as follows,

$$j_a = \sum_b \left[ \sigma_{ab}^A E_b + \alpha_{ab}^A (-\nabla_a T) \right],$$  \hspace{1cm} (1)

where antisymmetric tensors $\sigma_{ab}^A$ and $\alpha_{ab}^A$ are anomalous Hall conductivities and anomalous Nernst conductivities (ANC), respectively, with $a, b = x, y, z$. Since the AHC and ANC are closely related to topological properties of electronic structures via Berry curvature [1-5], significant effort has been devoted to exploring such anomalous transports in topological quantum matters with time-reversal symmetry breaking. Recently, large anomalous Hall and Nernst responses have been observed in magnetic Weyl semimetals including Co$_3$Sn$_2$S$_2$ and Co$_2$MnGa [6,10].

Shandite compound Co$_3$Sn$_2$S$_2$ is a half-metallic ferromagnet with transition temperature $T_c \sim 177$ K and saturated moment $M \sim 0.3\, \mu_B$ per Co atom [11,14]. This material is a representative example of magnetic Weyl semimetals since, according to the angle resolved photoemission spectroscopy (ARPES) and electronic structure calculations, Weyl nodes are located near the Fermi energy [6,7,15]. In Weyl semimetals, the divergent behavior of the Berry curvature at the Weyl nodes can give rise to characteristic physics, e.g., the chiral magnetic effect and the emergence of the anomalous surface states called Fermi arcs [3]. The existence of the anomalous surface states in Co$_3$Sn$_2$S$_2$ has been confirmed by the ARPES and scanning tunneling spectroscopy (STS) measurements [15,17], supporting the existence of the Weyl nodes near the Fermi energy.

Co$_3$Sn$_2$S$_2$ is expected to be a potential candidate for the thermoelectric devise applications due to the characteristic transport phenomena with the large AHC and ANC, reaching $\sigma_{xy}^A \sim 500$-1130 S cm$^{-1}$ [6,7] and $\alpha_{xy}^A \sim 2$-10 A K$^{-1}$ m$^{-1}$ [8,18], respectively. Previous theoretical studies imply the close relation between these anomalous transports and topological bands such as Weyl nodes and nodal rings [1,3,5,7,19,21]. Controlling pressure, temperature and chemical composition often affect transport properties. It is known that, in Co$_3$Sn$_2$S$_2$, applying pressure suppresses the AHE, leading to the AHC and Hall angle comparable to those in conventional ferromagnetic metals [22,24].

It has also been shown experimentally that the chemical substitution have a considerable impact on the magnetic and transport properties. So far, the effects of substitution of Fe and Ni for Co and of In for Sn have been investigated [11,25,29], where Ni substitution corresponds to the electron doping, while Fe and In substitutions correspond to the hole doping. Irrespective of doped elements, similar doping dependence of magnetic properties has been confirmed, that is, the monotonic decrease of the transition temperature and magnetic moment with increasing doping content. The doping effects on transport properties, on the other hand, show more complicated behaviors. In the case of the Ni substitution, the AHC decreases monotonically with the doping content [28], while in the cases of Fe and In substitutions, AHC is enhanced for relatively small doping and decreases for large doping [27,29]. From the theoretical side, the effects of substitution atoms on magnetic properties and/or electric transport properties have been previously investigated based on the first-principles calculations with the supercell approach for specific doping concentrations [26,28,30]. A systematic investigation of the atom substitution effects on the thermoelectric transport, i.e., Nernst effect has not been performed. Here, we present a systematic investigation of the effects of In-doping into Sn sites on the thermoelectric transports as well as magnetic properties based on the first-principles method.
II. METHODS

We perform the density functional calculation for Co$_3$In$_x$Sn$_{2-x}$S$_2$ by using the WIEN2K code [31, 32]. Sn/In substitution effects are treated within the virtual crystal approximation (VCA) and with the lattice parameters adopted from the experimental values of Co$_3$Sn$_2$S$_2$ in ref. [26], independently of In content $x$. Sn atoms in Co$_3$Sn$_2$S$_2$ occupy two inequivalent Wyckoff positions, intra and inter Co Kagomé layer sites, and in the present study, Sn atoms at the inter-layer sites are substituted by In atoms for the proper description of the paramagnetic insulating phase at $x = 1.0$ [30]. We generate the maximally localized Wannier function to construct an effective tight-binding Hamiltonian from the obtained electronic structures with WANNIER90 package [33, 34] through the WIEN2WANNIER interface [35]. We explicitly include Co-3$d$, Sn/In-5$s$, 5$p$, and S-3$p$ orbitals for the Wannier model. Based on the Wannier models, we investigate the intrinsic contributions to electric and thermoelectric transports, which are determined from purely electronic band structures, in Co$_3$In$_x$Sn$_{2-x}$S$_2$ by calculating the AHC and ANC with use of the following Kubo formulae [1, 36–38],

\[
\sigma_{ab}^\Delta (\mu, T) = -\frac{e^2}{h} \int_{BZ} \frac{dk}{(2\pi)^3} \sum_n f(\varepsilon_{nk}) \Omega_{n,ab}(k), \tag{2}
\]

\[
\alpha_{ab}^\Delta (\mu, T) = \frac{e k_B}{h} \int_{BZ} \frac{dk}{(2\pi)^3} \sum_n s(\varepsilon_{nk}) \Omega_{n,ab}(k), \tag{3}
\]

where $e$, $k_B$, $h$ and $\varepsilon_{nk}$ are the positive elementary charge, Boltzmann constant, reduced Planck constant and one-particle energy with band index $n$ and wave vector $k$, respectively. The Fermi distribution function $f(\varepsilon)$ and the entropy density $s(\varepsilon)$ are given as $f(\varepsilon) = (\exp(\frac{\varepsilon - \mu}{k_B T}) + 1)^{-1}$ and $s(\varepsilon) = -f(\varepsilon) \log f(\varepsilon) - [1 - f(\varepsilon)] \log [1 - f(\varepsilon)]$. $\Omega_{n,ab}(k)$ is the Berry curvature for band $n$, which is expressed as follows:

\[
\Omega_{n,ab}(k) = -2h^2 \text{Im} \sum_{m(\neq n)} \frac{\langle nk | v_a | mk \rangle \langle mk | v_b | nk \rangle}{(\varepsilon_{nk} - \varepsilon_{mk})^2}, \tag{4}
\]

where $v_a$ is the velocity operator along $a$-direction, and $|nk\rangle$ is the Bloch state with band index $n$ and wave vector $k$. In the actual numerical calculation, we perform the $k$-integration in Eqs. (2) and (3) as the discrete $k$-summation on 250$^3$ grids in the first Brillouin zone.

III. RESULTS

First, we show the results for $x = 0$, i.e., Co$_3$Sn$_2$S$_2$. Figure 1(a) shows the density of states (DOS) for Co$_3$Sn$_2$S$_2$ both in the paramagnetic and ferromagnetic states. The DOS in the paramagnetic state has a gap between $-0.31$ eV to $-0.17$ eV and the states from $-0.17$ eV to the Fermi energy $E_F$ are occupied by one electron per unit cell, resulting in the fully-polarized magnetic moment $\sim 1 \mu_B$ per unit cell in the ferromagnetic calculation. The exchange splitting pushes down the up-spin DOS, leading to the Fermi energy around the dip of the up-spin DOS, and pushes up the down-spin DOS, resulting in the Fermi energy in a gap of down-spin DOS. As a consequence, the half-metallic state is realized.

The electric and thermoelectric transport properties in Co$_3$Sn$_2$S$_2$ are now discussed. Since the Berry curvature and ferromagnetic moment have the same symmetry properties under the magnetic point group, the AHC and ANC can be finite in the ferromagnetic state [37, 41–45]. In the present case, since the magnetic point group of the ferromagnetic phase is $3m$, only $\sigma_{xy}^\Delta = -\sigma_{yx}^\Delta$ and $\alpha_{xy}^\Delta = -\alpha_{yx}^\Delta$ can be finite and the other components vanish. It is instructive to rewrite ANC in Eq. (3) by the generalized Mott formula as follows [38],

\[
\alpha_{ab}^\Delta (\mu, T) = \frac{1}{eT} \int d\varepsilon (\varepsilon - \mu) \frac{\partial f(\varepsilon, T = 0)}{\partial \varepsilon} \sigma_{ab}(\varepsilon, T = 0) \tag{5}
\]

\[
= -\frac{k_B}{e} \int d\varepsilon s(\varepsilon) \frac{\partial \sigma_{ab}(\varepsilon, T = 0)}{\partial \varepsilon}. \tag{6}
\]

The well-known Mott relation is obtained as $\alpha_{ab}^\Delta \sim \frac{\sigma_{ab}(\varepsilon, T = 0)}{\varepsilon}$, assuming that $\sigma_{ab}^\Delta(\varepsilon, T = 0) \sim \varepsilon - \mu$ for $\varepsilon \sim \mu$ at low temperature limit.

Figures 1(b) and (c) display the $\mu$ dependence of AHC and ANC. A shift of the chemical potential corresponds to the rigid band picture, where $\mu > 0$ and $\mu < 0$ represent elec-
Figure 2. (a)-(f) Band structures for Co$_3$In$_x$S$_{2-x}$S$_2$ along high symmetry $k$-lines, where the color map represents the spin density along $z$-axis. (g) $k$-path on which the band structures are plotted in panels (a)-(f). (h) In-doping dependence of the net magnetization.

Figure 3. (a) Doping dependence of AHC $\sigma_{xy}^A$ at $k_B T = 0$ and (b) that of ANC $\alpha_{xy}^A$ at finite temperatures. (c) Temperature dependence of $\alpha_{xy}^A$ and (d) that of $\alpha_{xy}^A/T$ at various In-doping concentrations. In panel (a), experimental data extracted from refs. [29, 39] are plotted together with calculated results for comparison.
minimum at $x \approx 0.1$. With further increasing $x$, the AHC decreases and vanishes at $x = 1.0$ where the system becomes paramagnetic (see also Fig. 2). The AHC sensitively depends on the electronic structure such as the details of the Fermi surfaces and the distribution of the Berry curvature in $k$-space. As a result, the doping dependence of the AHC shows more complicated behavior than that of the magnetic moment $\langle \alpha^x y \rangle$ which linearly decreases with respect to the doping concentration. As shown in Fig. 3(b), regarding the thermoelectric transport, the rigid band picture works well for the small doping region (see also Fig. 1(c)). The ANC is negative at $x = 0$ and changes its sign into positive for the small doping content $x$. The absolute values of $\alpha^A_{xy}/T$ at low temperatures are large at $x \sim 0$ and 0.2 with values $|\alpha^A_{xy}|/T \sim 0.02$ A K$^{-2}$ m$^{-1}$. The ANC decreases with further increasing $x$, reflecting the suppression of the magnetization. To elucidate the enhancement of the ANC for these doping concentrations, the temperature dependence of the ANC is shown in Figs. 3(c) and (d). For large doping $x \geq 0.6$, $\alpha^A_{xy}$ shows linear $T$ dependence in the wide temperature range $k_B T \lesssim 0.01 \text{ eV}$, while for $x = 0 (0.2)$, that exhibits logarithmic $T$ dependence for $0.005 \text{ eV} \lesssim k_B T \lesssim 0.04 \text{ eV}$ ($0.02 \text{ eV} \lesssim k_B T \lesssim 0.05 \text{ eV}$). These behaviors could be due to the stationary points in the nodal rings as demonstrated by Minami et al. in ref. [21].

In order to get clear insight into the low temperature behavior of the ANC, let us perform the detailed analysis of the topological properties of the electronic structures which are reflected in the Berry curvature $\Omega_{n,ab}(k)$. As mentioned before, the ANC is dominated by $\frac{\partial \sigma_{ab}(\varepsilon, T = 0)}{\partial \varepsilon}$ for $|\varepsilon - \mu| \lesssim k_B T$, whose explicit form is given as follows [20],

$$
\frac{\partial \sigma_{ab}(\varepsilon, T = 0)}{\partial \varepsilon} = -\frac{e^2}{\hbar} \sum_n \int_{\varepsilon_n = \varepsilon (2\pi)^3} dS_k \frac{\Omega_{n,ab}(k)}{|\nabla k \varepsilon_{nk}|},
$$

where $\int_{\varepsilon_n = \varepsilon} dS_k$ represents the $k$-integration over the isoenergy surfaces for $\varepsilon_{nk} = \varepsilon$. From Eqs. (6) and (7), one can...
see that the qualitative behavior of the ANC at low temperatures are governed by the distribution of the $\Omega_{\text{n,ab}}(k)|\nabla_{k_{\text{F}-nk}}|^2$ near the Fermi surfaces. In Fig. 4(a), we show the Fermi surfaces with $\Omega_{\text{n,ab}}(k)|\nabla_{k_{\text{F}-nk}}|^2$. The value of $\Omega_{\text{n,ab}}(k)|\nabla_{k_{\text{F}-nk}}|^2$ is positive on the small portions of the Fermi surfaces for $x = 0$, while on more wide region, $\Omega_{\text{n,ab}}(k)|\nabla_{k_{\text{F}-nk}}|^2$ becomes negative. As a result, the $k$-integration over the Fermi surfaces of $\Omega_{\text{n,ab}}(k)|\nabla_{k_{\text{F}-nk}}|^2$ is negative, resulting in $c_{xy}^A < 0$ for Co$_3$Sn$_2$S$_2$ as shown in Fig. 3(b). On the other hand, for $x = 0.2$, the area of the Fermi surfaces on which $\Omega_{\text{n,ab}}(k)|\nabla_{k_{\text{F}-nk}}|^2$ is negative becomes small and the resulting ANC is positive. The absolute value of $\Omega_{\text{n,ab}}(k)|\nabla_{k_{\text{F}-nk}}|^2$ decreases with further increasing $x$, and the ANCs for large $x$ have small values [see also Fig. 3(b)].

We here demonstrate that the intensity of the Berry curvature on Fermi surfaces is closely related to the nodal lines. As shown in Fig. 4(b), the nodal lines appear on the mirror symmetry planes in the absence of the spin-orbit coupling. The spin-orbit coupling gaps out the nodal lines but leaves the energy $\sim 0.065$ eV, resulting in the Weyl nodes for $x = 0$ [6, 7]. In this case, the energy bands characterized by different eigen values $\pm 1$ of the mirror symmetry operator produce nodal lines due to its crossing [see Fig. 4(c)]. This origin of nodal lines is similar to those in archetypal nonmagnetic nodal line semimetals Ca$_3$P$_2$ [48, 49] and CaAgX ($X$=P, As) [50].

The hole doping decreases the Fermi energy and, as a result, shift the Weyl nodes away from the Fermi level. The nodal rings are located around the Fermi energy for small hole doping and for $x \lesssim 0.2$, the nodal lines surrounding the L-point cross the Fermi surfaces as shown in Fig. 4(b). The band at L-point near the Fermi energy with mirror eigen value $+1$ shifts upward in energy with increasing $x$ and cross with the band having mirror eigen value $-1$ for $x \sim 0.3$, as shown in Fig. 4(c). Then, the nodal lines are split into two rings, as shown in Fig. 4(b), with the annihilation of Weyl nodes in the presence of the spin-orbit coupling. The nodal lines still cross the Fermi surfaces for $x < 0.4$ and give the significant contribution to the ANC. For $x \gtrsim 0.6$, the nodal lines are located far from the Fermi level, resulting in the small Berry curvature on the whole Fermi surfaces. One can clearly see that the intensity of the Berry curvature is large near the nodal lines.

IV. SUMMARY AND DISCUSSIONS

In the present paper, we investigated the magnetic and transport properties in Co$_3$In$_x$Sn$_{2-x}$S$_2$ based on first-principles calculations in which In-doping effect is treated within the virtual crystal approximation. We show that the anomalous Hall and Nernst conductivities show complicated behaviors with varying $x$ against linearly reduced magnetization with respect to In content $x$ due to the half-metallic electronic states. The Nernst conductivity has large values for $x \sim 0$ and 0.2 with opposite signs and show logarithmic temperature dependence consistently with the previous theoretical study [21]. We also clarify that the low temperature behavior of the anomalous Nernst conductivity can be understood by the distribution of the Berry curvature divided by the Fermi velocity. The close relationships between the Berry curvature, nodal rings, and anomalous Nernst effect are explicitly demonstrated. The intensity of the Berry curvature has a large value near the nodal rings for small hole doping, leading to a large anomalous Nernst conductivity. The In-doping induces the reconstruction of the nodal rings and moves the nodal lines far away from the Fermi level, resulting in the small Berry curvature on the Fermi surfaces. Our results give a qualitative understanding of the thermoelectric transport in Co$_3$In$_x$Sn$_{2-x}$S$_2$ and encourage experimental measurements of the anomalous Nernst effect in Co$_3$In$_x$Sn$_{2-x}$S$_2$.

Lastly, we comment on the important issues which are not addressed in this study. In the present paper, we have focused on the intrinsic contribution to the anomalous transports and neglected the extrinsic effects such as side-jump and skew-scattering [11]. Effects of the structural disorder, however, is inevitable in doped compounds in general and might give considerably large extrinsic contribution to the thermoelectric transport pointed by several authors [27, 51, 52]. A quantitative study on extrinsic contributions using first-principles calculations is a remaining issue in a future work.

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