

Tunable band-filling effects on thermoelectric properties and anomalous Hall conductivity in Weyl semimetal $\text{Co}_3\text{Sn}_2\text{S}_2$

Y. H. Chang¹, P. J. Sun¹, H. J. Chen¹, D. Chandrasekhar Kakarla¹, P. C. Wang¹, S. M. Huang¹, P. Y. Yang¹,
Y. J. Tsai², M. N. Ou², R. H. Jhang², S. F. Lee², C.-C. Chang³, J. Y. Huang³, C. M. Cheng^{3,1}, W. H. Huang³,
H. L. Meng⁴, P. Bag⁴, Y. K. Kuo⁴, C. N. Kuo^{5,6}, C. S. Lue^{5,6}, H. D. Yang^{1,*} and H. C. Wu^{1,†}

¹Department of Physics, National Sun Yat-sen University, Kaohsiung 80424, Taiwan

²Institute of Physics, Academia Sinica, Taipei 11529, Taiwan

³National Synchrotron Radiation Research Center, Hsinchu City, Taiwan

⁴Department of Physics, National Dong Hwa University, Hualien 97401, Taiwan

⁵Department of Physics, National Cheng Kung University, Tainan 70101, Taiwan

⁶Taiwan Consortium of Emergent Crystalline Materials, National Science and Technology Council, Taipei 10622, Taiwan



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The magnetic Weyl semimetal $\text{Co}_3\text{Sn}_2\text{S}_2$ has garnered significant experimental and theoretical interest, particularly regarding its electronic structure and transport properties. In this study, we comprehensively investigated the effects of Fe and Ni substitution in $\text{Co}_3\text{Sn}_2\text{S}_2$. The temperature-dependent Seebeck coefficient (S) implies that the reduction of the band gap and the shift in the Fermi level (E_F) due to Fe and Ni substitution, which was supported by angle-resolved photoemission spectroscopy results. These band-structure modifications influence not only thermoelectric (TE) performance but also the anomalous Hall conductivity (σ_{xy}^A). Specifically, Fe substitution increases σ_{xy}^A via skew scattering, while Ni substitution increases σ_{xy}^A via intrinsic deflection with minor skew scattering. Additionally, the Fe and Ni dopant-induced changes in the c/a ratio were demonstrated using high-resolution powder synchrotron x-ray diffraction, which explains the different modulation in the magnetic anisotropy of $\text{Co}_3\text{Sn}_2\text{S}_2$ due to the magnetostriction effect. Notably, the oxidation states of Co, Fe, and Ni in each single crystal were confirmed as 0 using x-ray absorption near-edge structure analysis, further explaining the dopant-induced suppression in ferromagnetism of $\text{Co}_3\text{Sn}_2\text{S}_2$. These findings provide deeper insight into the band-filling effects on both TE and anomalous Hall transport in $\text{Co}_3\text{Sn}_2\text{S}_2$, offering perspectives for topological spintronics and TE applications.

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I. INTRODUCTION

Geometrically frustrated magnets, arising from competing interactions in specific lattice geometries such as triangular, kagome, pyrochlore, or hyperkagome lattices, have emerged as a fertile ground for discovering exotic quantum states and physical phenomena. These include spin liquids, spin ice, multiferroicity, and topologically nontrivial electronic structures [1–11]. Among these, topologically nontrivial electronic states have received particular attention for their rich transport properties, such as the intrinsic anomalous Hall effect (AHE), which originates from the Berry curvature in momentum space [12–15]. As a result, the AHE serves as a hallmark of nontrivial band topology in magnetic systems and has recently garnered considerable attention due to its contribution to fundamental physics and potential in practical applications [12,16,17].

In this context, the layered shandite compound $\text{Co}_3\text{Sn}_2\text{S}_2$, with a two-dimensional kagome layer formed by magnetic Co atoms, is a well-established magnetic Weyl semimetal and half-metal that has been experimentally identified [18–26]. Notably, $\text{Co}_3\text{Sn}_2\text{S}_2$, with a Curie temperature (T_C) of 178 K, has a giant σ_{xy}^A of $1130 \Omega^{-1} \text{cm}^{-1}$ and an anomalous Hall angle ($\sigma_{xy}^A/\sigma_{xx}$) of approximately 20%. Furthermore, the measured σ_{xy}^A closely matches the theoretical prediction, indicating that the σ_{xy}^A of $\text{Co}_3\text{Sn}_2\text{S}_2$ primarily originates from intrinsic mechanisms and the doping-induced shifts in the Fermi energy (E_F) are not expected to further increase the σ_{xy}^A of $\text{Co}_3\text{Sn}_2\text{S}_2$ within the rigid band framework [24,27]. However, based on the Kubo formula [28], the intrinsic σ_{xy}^A can be manipulated not only by the electron distribution defined by the E_F but also by the characteristics of the topological bands around E_F . Therefore, it is crucial to experimentally confirm the effect on intrinsic AHE in $\text{Co}_3\text{Sn}_2\text{S}_2$ induced by changes in band structure and E_F shifting due to extrinsic doping, such as doping Fe or Ni at the Co site [29–31], In or Sb at the Sn site [32,33], and Cl at the S site [34]. Most existing studies have primarily focused on theoretical investigations to explore the doping-induced effects on σ_{xy}^A of doped $\text{Co}_3\text{Sn}_2\text{S}_2$; however, only a limited number of these studies have incorporated experimental approaches.

*Contact author: yang@mail.nsysu.edu.tw

†Contact author: tedwu@mail.nsysu.edu.tw

Additionally, unlike extensive research on the transport properties, magnetic structure/properties, or topological electronic structure of $\text{Co}_3\text{Sn}_2\text{S}_2$ [29–39], studies exploring its thermal properties remain relatively limited. Previous literature has offered detailed references on the thermal behavior of Fe-doped and pristine $\text{Co}_3\text{Sn}_2\text{S}_2$, including temperature (T)-dependent heat capacity, Seebeck coefficient, and thermal conductivity [40]. These investigations facilitate the exploration of the potential for further applications of the present sample. Additionally, the Seebeck coefficient can also provide valuable insights into the E_F and the energy gap (E_g) of a material, thereby offering a means to understand electronic-structure-related phenomena [41]. As a result, in this study, we employed various experimental tools, such as powder synchrotron x-ray diffraction, x-ray absorption spectroscopy (XAS), angular-resolved photoemission spectroscopy, resistivity, Hall resistivity, Seebeck coefficient, and thermal conductivity measurements in Fe- and Ni-doped $\text{Co}_3\text{Sn}_2\text{S}_2$ samples to investigate the band-filling effects on both thermoelectric (TE) and AHE properties in $\text{Co}_3\text{Sn}_2\text{S}_2$.

II. RESEARCH METHODS

Polycrystal samples of $(\text{Co}_{1-y}\text{Fe}_y)_3\text{Sn}_2\text{S}_2$ ($0.0000 < y < 0.0500$) and $(\text{Co}_{1-z}\text{Ni}_z)_3\text{Sn}_2\text{S}_2$ ($0.0000 < z < 0.0500$) were synthesized via the solid-state reaction method. X-ray diffraction (XRD) and electron probe microanalysis (EPMA) were conducted to confirm the phase purity and chemical composition of the polycrystalline samples, and the full characterization details are described in our previous work [35]. Single-crystal samples of $\text{Co}_3\text{Sn}_2\text{S}_2$, $(\text{Co}_{0.95}\text{Fe}_{0.05})_3\text{Sn}_2\text{S}_2$, and $(\text{Co}_{0.95}\text{Ni}_{0.05})_3\text{Sn}_2\text{S}_2$ were synthesized by the modified Bridgman method. Stoichiometric amounts of high-purity sulfur pieces, tin pellets, cobalt powder, iron powder, and nickel powder were mixed and loaded into an alumina crucible, which was then sealed in a quartz tube under vacuum. The sealed tube was placed in a vertical tube furnace and heated to 1000°C over a 24-h period, followed by a 20-h dwell time. The system was then cooled slowly to 700°C at a rate of 1.5°C/h , and finally cooled naturally to room temperature by turning off the furnace power. The quality of the cleaved single-crystal surface, corresponding to the ab plane, was verified by Laue diffraction patterns. The phase purity of the single crystals was confirmed using a room-temperature high-resolution powder synchrotron x-ray diffraction (SXRD) measurement, conducted at the Taiwan Photon Source (TPS) 19A beamline of the National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan, utilizing x-rays with a wavelength of $0.619\,92\,\text{\AA}$. The energy-dispersive x-ray spectroscopy (EDS) was measured to confirmed elemental contents of Co, Fe, Ni, Sn, and S in the single crystals using a multifunctional environmental field-emission scanning electron microscope (EFE-SEM; SU-5000, HITACHI), equipped with an EDS (ELITE, EDAX). T -dependent magnetic susceptibility (χ) of single crystals was performed using a superconducting quantum interference device (SQUID)-based magnetic property measurement system (Quantum Design). The T -dependent longitudinal electrical resistivity (ρ_{xx}) measurements on polycrystal samples were performed using the standard four-probe method in a closed-cycle helium

refrigerator. For the single crystals, T -dependent ρ_{xx} and Hall resistivities were carried out using a physical property measurement system (Quantum Design) with standard four-probe and five-probe methods, respectively. The current was applied along the a axis, while the magnetic field (H) was applied along the c axis. Simultaneous measurements of T -dependent Seebeck coefficient and thermal conductivity were performed using a direct heat-pulse technique in the closed-cycle helium refrigerator. X-ray absorption spectroscopy measurements were carried out at the Co, Fe, and Ni K edges at the TPS 44A beamline of NSRRC, Hsinchu, Taiwan. Angle-resolved photoemission spectroscopy (ARPES) measurements were completed at NSRRC, utilizing the Taiwan Light Source (TLS) 21B1 U9 beamline and the micro-ARPES endstation at TPS 39A1. The samples were cleaved *in situ* under ultrahigh vacuum conditions, with a base pressure of 8.5×10^{-11} Torr and measured at room temperature. Photoemission spectra were acquired using a Scienta R4000 electron analyzer, with an angular resolution of 0.5° . Photon energies ranging from 110 to $124\,\text{eV}$ were employed, resulting in an overall energy resolution of approximately $25\,\text{meV}$. The T -dependent ARPES measurements were performed at the TPS 39A1 beamline of the NSRRC in Hsinchu, Taiwan, using a photon energy of $120\,\text{eV}$ with an energy resolution better than $20\,\text{meV}$. For the polycrystalline samples, multiple specimens were measured and showed consistent results. For the single crystals, the transport data were taken on different pieces cut from the same crystal, and consistent behavior was observed among them. According to the following data, the obtained T_C , residual resistivity, and anomalous Hall effect are also in good agreement with previous literature reports [24,29–31].

III. RESULTS AND DISCUSSIONS

A. Crystal structure and magnetic structure

The crystal structure and magnetic structure of $\text{Co}_3\text{Sn}_2\text{S}_2$ are shown in Fig. 1(a). The Co and Sn(2) atoms form quasi2D kagome layers, with the Sn(1) and S atoms distributed between these layers. Due to its strong magnetic anisotropy, the magnetic moment of Co atoms, fixed in the ab plane, aligns along the c axis. Room-temperature powder SXRD patterns and corresponding Rietveld refinement profiles for ground single crystals of $\text{Co}_3\text{Sn}_2\text{S}_2$, $(\text{Co}_{0.95}\text{Fe}_{0.05})_3\text{Sn}_2\text{S}_2$, and $(\text{Co}_{0.95}\text{Ni}_{0.05})_3\text{Sn}_2\text{S}_2$ are shown in Figs. 1(b)–1(d). Structural analysis of the pristine sample confirms a predominantly single-phase rhombohedral structure with space group $R\bar{3}m$, along with minor impurity phase of SnO_2 , which is the oxidized flux used during crystal growth. In contrast, both Fe- and Ni-doped samples exhibit a pure single-phase structure. The orientations of the single crystals were determined by x-ray Laue diffraction on a cleavage plane, where the sharp, well-defined diffraction spots confirmed the sample's high quality, and the six-fold symmetry in the Laue pattern indicated that the cleavage plane was identified as (001), as shown in Figs. 2(a)–2(c).

The refined lattice parameters, Wyckoff positions, and relevant structural details are summarized in Table I. The refined lattice parameters reveal that Fe and Ni substitutions exert opposite effects on the crystal structure of $\text{Co}_3\text{Sn}_2\text{S}_2$. Fe

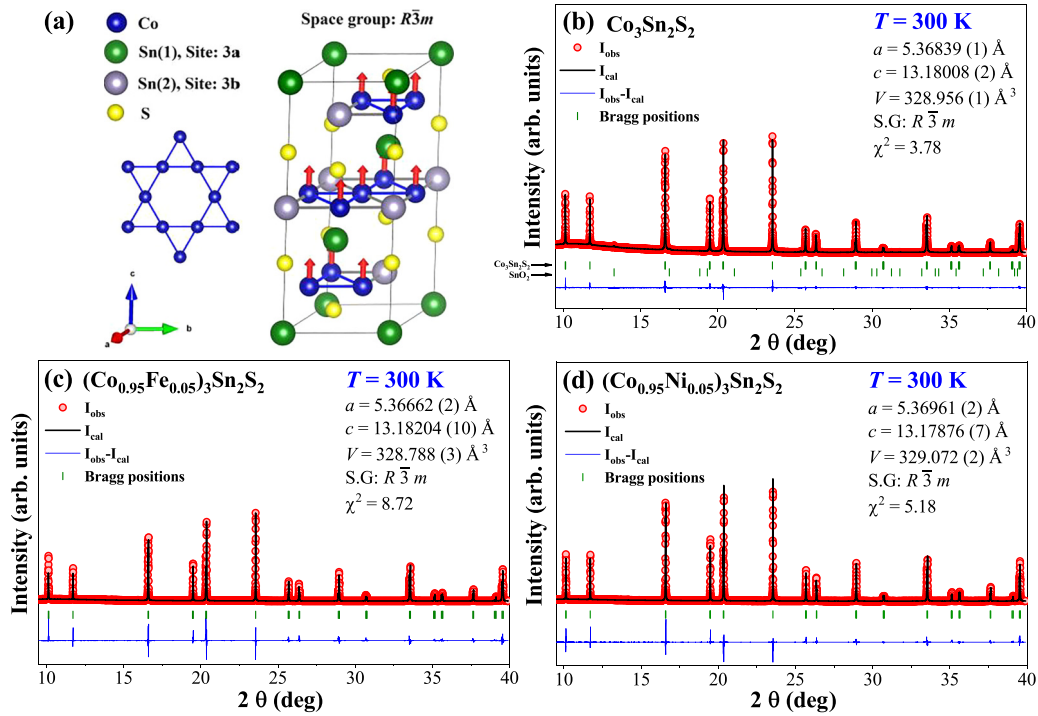


FIG. 1. (a) The crystal structure and magnetic structure. Blue, green, gray, and yellow spheres represent Co, Sn(1), Sn(2), and S atoms, respectively. The Sn(1) and Sn(2) atoms occupy the 3a and 3b Wyckoff positions, respectively. Co atoms form a ferromagnetic kagome lattice, and the red arrows penetrating the Co atoms indicate the magnetic moments, which is oriented perpendicular to the ab plane. Rietveld refinement plots of SXRD data for (b) $\text{Co}_3\text{Sn}_2\text{S}_2$, (c) $(\text{Co}_{0.95}\text{Fe}_{0.05})_3\text{Sn}_2\text{S}_2$, and (d) $(\text{Co}_{0.95}\text{Ni}_{0.05})_3\text{Sn}_2\text{S}_2$ single crystals, which were ground to powder. The observed data, refined data, difference, and Bragg position are represented by red circles, black solid lines, blue bottom line, and green mark, respectively. For the pristine sample, the upper green marks correspond to the $\text{Co}_3\text{Sn}_2\text{S}_2$ phase, while the lower green marks indicate the impurity phase, which is SnO_2 .

substitution decreases the lattice parameter a from 5.368 39(1) to 5.366 62(2) Å, while increasing c from 13.180 08(2) to 13.182 04(10) Å. In contrast, Ni substitution results in an increase in a to 5.369 61(2) Å and a decrease in c to 13.178 76(7) Å. As a result, the c/a ratio is modified in opposite directions by these dopants, with Fe substitution increasing it from 2.455 13(1) to 2.456 30(2) and Ni substitution decreasing it to 2.454 32(2). Notably, after calculating the c/a ratio, the proportion of the standard uncertainty relative to the numerical value increased, which can be attributed to uncertainty propagation. It is worth mentioning that although the changes in lattice parameters and the c/a ratio are on the orders of 10^{-3} and 10^{-4} , their maximum 95% confidence limits (CL) are on the orders of 10^{-5} , where 95%

CL = $1.96 \times$ standard uncertainty. Therefore, these small variations can still be considered reliable within refinement accuracy. This trend aligns with previous reports [42], and its implications for the AHE measurements are discussed in the section of AHE. Additionally, the detailed XRD analyses and chemical compositions on $(\text{Co}_{1-y}\text{Fe}_y)_3\text{Sn}_2\text{S}_2$ and $(\text{Co}_{1-z}\text{Ni}_z)_3\text{Sn}_2\text{S}_2$ polycrystals, based on EPMA results, have been reported in detail in our previous study [35]. The elemental contents of Fe and Ni dopants in the single-crystal samples were verified by the EDS measurements in multiple regions of each single crystal. The final elemental contents are the average value of EDS of multiple regions, which indicates that the doping levels were determined to be approximately 0.048(9) for the Fe-doped sample and 0.046(4) for the

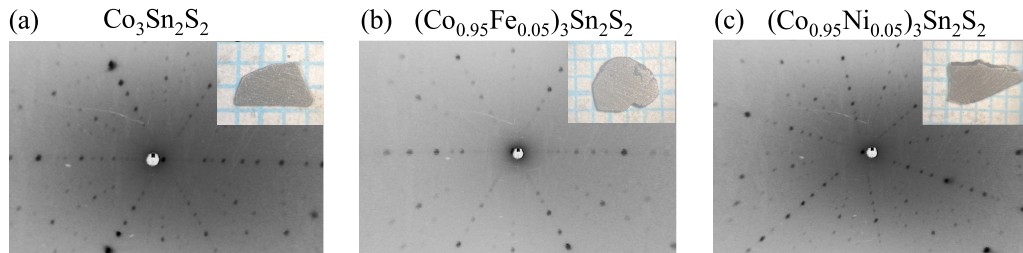


FIG. 2. The single-crystal Laue diffraction pattern of (a) $\text{Co}_3\text{Sn}_2\text{S}_2$, (b) $(\text{Co}_{0.95}\text{Fe}_{0.05})_3\text{Sn}_2\text{S}_2$, and (c) $(\text{Co}_{0.95}\text{Ni}_{0.05})_3\text{Sn}_2\text{S}_2$, which confirms the high-quality crystal structure of the sample. The Laue x-ray patterns with the six-fold symmetry of the hexagon structure indicated that the cleavage plane (as shown in the top-right insets) is (001).

TABLE I. The Wyckoff positions and other structural parameters collected from the Rietveld refinement of the SXRD data at 300 K for $\text{Co}_3\text{Sn}_2\text{S}_2$, $(\text{Co}_{0.95}\text{Fe}_{0.05})_3\text{Sn}_2\text{S}_2$, and $(\text{Co}_{0.95}\text{Ni}_{0.05})_3\text{Sn}_2\text{S}_2$.

Space group:	$R\bar{3}m$		
Parameters	$\text{Co}_3\text{Sn}_2\text{S}_2$	$(\text{Co}_{0.95}\text{Fe}_{0.05})_3\text{Sn}_2\text{S}_2$	$(\text{Co}_{0.95}\text{Ni}_{0.05})_3\text{Sn}_2\text{S}_2$
a (Å)	5.368 39(1)	5.366 62(2)	5.369 61(2)
b (Å)	5.368 39(1)	5.366 62(2)	5.369 61(2)
c (Å)	13.180 08(2)	13.182 04(10)	13.178 76(7)
c/a ratio	2.455 13(1)	2.456 30(2)	2.454 32(2)
V (Å ³)	328.956(1)	328.788(3)	329.072(2)
α	90°	90°	90°
β	90°	90°	90°
γ	120°	120°	120°
Co, Fe, and Ni			
x	0.500 00	0.5000	0.5000
y	0.000 00	0.0000	0.0000
z	0.500 00	0.5000	0.5000
Sn(1)			
x	0.000 00	0.0000	0.0000
y	0.000 00	0.0000	0.0000
z	0.000 00	0.0000	0.0000
Sn(2)			
x	0.000 00	0.0000	0.0000
y	0.000 00	0.0000	0.0000
z	0.500 00	0.5000	0.5000
S			
x	0.000 00	0.0000	0.0000
y	0.000 00	0.0000	0.0000
z	0.282 55(9)	0.282 18(51)	0.285 34(31)
χ^2, R_p, R_{wp}	3.78, 2.05%, 3.04%	8.72, 8.20%, 13.90%	5.18, 6.37%, 10.10%

Ni-doped sample, as shown in Table SI in the Supplemental Material [43]. The doping levels are also supported by substituting their T_C values into the correlation between T_C and the EPMA results obtained from the polycrystalline samples, which are illustrated in Figs. S1 and S2 in the Supplemental Material [43].

The oxidation state of Co, Fe, and Ni in ground single crystals of $\text{Co}_3\text{Sn}_2\text{S}_2$, $(\text{Co}_{0.95}\text{Fe}_{0.05})_3\text{Sn}_2\text{S}_2$, and $(\text{Co}_{0.95}\text{Ni}_{0.05})_3\text{Sn}_2\text{S}_2$ was further studied by XAS measurements. The normalized Co, Fe, and Ni K -edge x-ray absorption near-edge structure (XANES) spectra are presented in Fig. 3. For Co K -edge spectra, the edge positions of $\text{Co}_3\text{Sn}_2\text{S}_2$, $(\text{Co}_{0.95}\text{Fe}_{0.05})_3\text{Sn}_2\text{S}_2$, and $(\text{Co}_{0.95}\text{Ni}_{0.05})_3\text{Sn}_2\text{S}_2$ are aligned with that of Co foil as shown in Fig. 3(a), suggesting that Co in all three single crystal samples is in the oxidation state of Co^{0+} . For Fe and Ni K -edge spectra, Figs. 3(b) and 3(c) show that the edge positions of $(\text{Co}_{0.95}\text{Fe}_{0.05})_3\text{Sn}_2\text{S}_2$ and $(\text{Co}_{0.95}\text{Ni}_{0.05})_3\text{Sn}_2\text{S}_2$ are aligned with that of Fe foil and Ni foil, respectively. These indicate that Fe in $(\text{Co}_{0.95}\text{Fe}_{0.05})_3\text{Sn}_2\text{S}_2$ and Ni in $(\text{Co}_{0.95}\text{Ni}_{0.05})_3\text{Sn}_2\text{S}_2$ are both in the oxidation state of Fe^{0+} and Ni^{0+} , respectively. Recent publication have also confirmed the oxidation state of Co in $\text{Co}_3\text{Sn}_2\text{S}_2$ as Co^{0+} using XPS [44], and a number of research groups have indicated that Co in $\text{Co}_3\text{Sn}_2\text{S}_2$ exhibits a valency close to Co^{0+} [45,46], sometimes denoted as $\text{Co}^{\delta+}$ to represent a minor positive valency [47,48]. These findings support the reliability of our result of the oxidation state of Co. Notably, to the best of our knowledge, the oxidation states

of Fe and Ni in $\text{Co}_3\text{Sn}_2\text{S}_2$ with minor Fe and Ni substitution have not been previously reported in the literature. The oxidation state results of Co, Fe, and Ni can give us better insights into the dopants-induced modulations in ferromagnetism, electrical transport, and thermoelectric properties of $\text{Co}_3\text{Sn}_2\text{S}_2$, which are discussed in the following sections.

B. Electric transport properties

Figures 4(a) and 4(b) show T -dependent $\rho_{xx}/\rho_{300\text{K}}$ of $(\text{Co}_{1-y}\text{Fe}_y)_3\text{Sn}_2\text{S}_2$ ($0.0000 < y < 0.0500$) and $(\text{Co}_{1-z}\text{Ni}_z)_3\text{Sn}_2\text{S}_2$ ($0.0000 < z < 0.0500$) polycrystal samples, respectively. Figure 4(c) displays T -dependent ρ_{xx} of $\text{Co}_3\text{Sn}_2\text{S}_2$, $(\text{Co}_{0.95}\text{Fe}_{0.05})_3\text{Sn}_2\text{S}_2$, and $(\text{Co}_{0.95}\text{Ni}_{0.05})_3\text{Sn}_2\text{S}_2$ single crystal samples. The $\rho_{xx}(T)$ curves of all samples show a positive T dependence, exhibiting metallic behavior, which is consistent with the zero-valent oxidation state of Co confirmed by XANES analysis. A noticeable kink is observed at the corresponding T_C for each sample, which is also evident in other measurements such as T -dependent ac magnetic susceptibility [35], Seebeck coefficient, and anomalous Hall conductivity, as shown in Fig. 4(d). With increasing concentrations of Fe and Ni dopants, the T_C decreases, indicating a dopant-induced suppression of ferromagnetism in $\text{Co}_3\text{Sn}_2\text{S}_2$. This suppression of ferromagnetism has also been both experimentally and theoretically observed in previous studies [49–52].

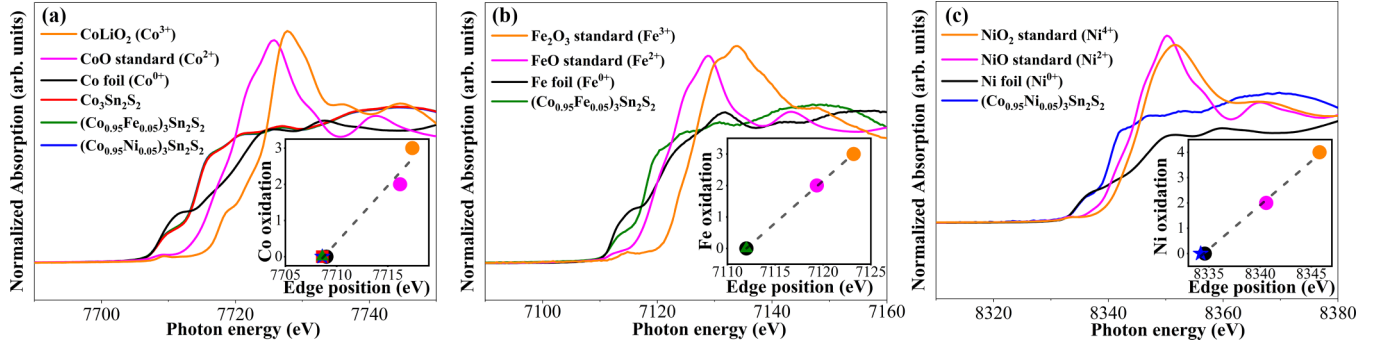


FIG. 3. (a) XANES spectra at the Co K edge of Co foil (Co^{0+}), CoO (Co^{2+}) standard, CoLiO₂ (Co^{3+}) standard, and XANES spectra of $\text{Co}_3\text{Sn}_2\text{S}_2$, $(\text{Co}_{0.95}\text{Fe}_{0.05})_3\text{Sn}_2\text{S}_2$, and $(\text{Co}_{0.95}\text{Ni}_{0.05})_3\text{Sn}_2\text{S}_2$ single crystals, which were ground to powder. (b) XANES spectra at the Fe K edge of Fe foil (Fe^{0+}), FeO (Fe^{2+}) standard, Fe_2O_3 (Fe^{3+}) standard, and XANES spectrum of $(\text{Co}_{0.95}\text{Fe}_{0.05})_3\text{Sn}_2\text{S}_2$ single crystal, which were ground to powder. (c) XANES spectra at the Ni K edge of Ni foil (Ni^{0+}), NiO (Ni^{2+}) standard, NiO_2 (Ni^{4+}) standard, and XANES spectrum of $(\text{Co}_{0.95}\text{Ni}_{0.05})_3\text{Sn}_2\text{S}_2$ single crystal, which were ground to powder. Insets: The edge positions for each oxidation state of Co, Fe, and Ni.

This dopant-induced suppression of ferromagnetism may be attributed to changes in the electronic structure due to the substitutions at the Co site, which is responsible for ferromagnetism of $\text{Co}_3\text{Sn}_2\text{S}_2$. To be more specific, a previous study suggested that $\text{Co}_3\text{Sn}_2\text{S}_2$ exhibits weak itinerant ferromagnetism, where the magnetic state arises from exchange splitting in the Co $3d$ orbitals [49]. This splitting creates

an imbalance in electron occupancy between majority and minority bands just above the pseudogap, stabilizing ferromagnetism. This pseudogap is a partial reduction of the density of states (DOS) at E_F . Our ARPES measurements (see Sec. III F and Fig. 8) confirm that this pseudogap is situated around the K point in the Brillouin zone. It primarily involves the Co- $3d$ derived bands that form the kagome lat-

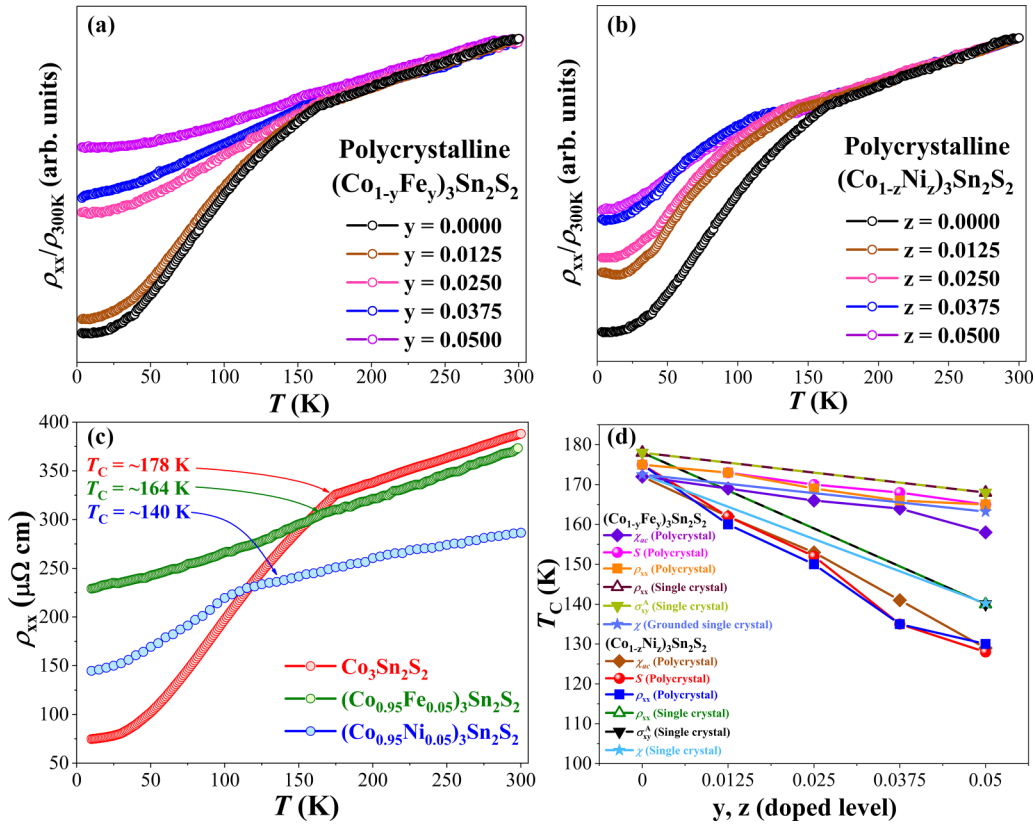


FIG. 4. T dependence of $\rho_{xx}/\rho_{300\text{K}}$ of (a) $(\text{Co}_{1-y}\text{Fe}_y)_3\text{Sn}_2\text{S}_2$ and (b) $(\text{Co}_{1-z}\text{Ni}_z)_3\text{Sn}_2\text{S}_2$ polycrystalline samples ($y, z = 0.0000, 0.0125, 0.0250, 0.0375$, and 0.0500). (c) T dependence of ρ_{xx} of $\text{Co}_3\text{Sn}_2\text{S}_2$, $(\text{Co}_{0.95}\text{Fe}_{0.05})_3\text{Sn}_2\text{S}_2$, and $(\text{Co}_{0.95}\text{Ni}_{0.05})_3\text{Sn}_2\text{S}_2$ single crystals with $I \parallel a$ in the absence of H . (d) The comparison of T_C obtained from various measurements, including ac magnetic susceptibility (in polycrystal samples), Seebeck coefficient (in polycrystal samples), resistivity measurement (in polycrystal and single samples), magnetic susceptibility (in single crystal samples), and anomalous Hall conductivity (in single crystal samples). These results indicate that both Fe doping and Ni doping suppress the ferromagnetism of $\text{Co}_3\text{Sn}_2\text{S}_2$.

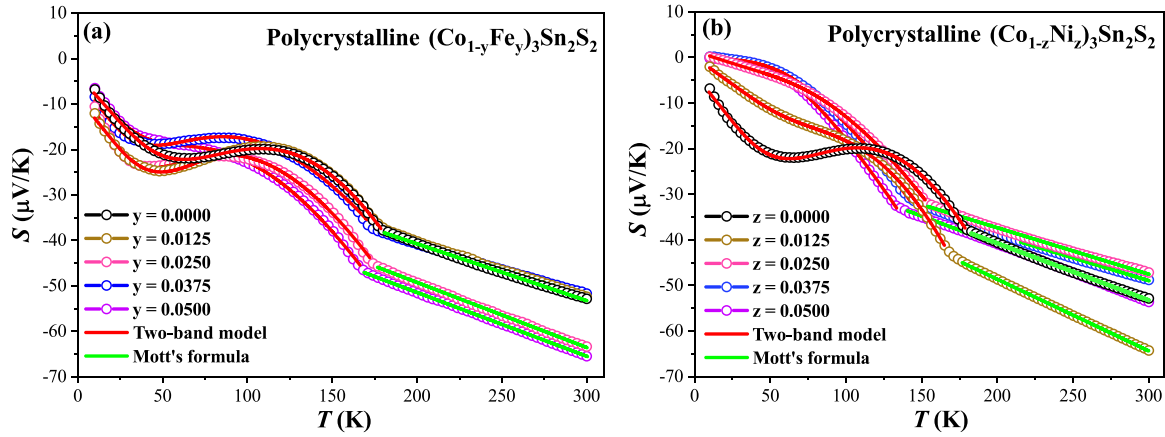


FIG. 5. The T -dependent S curves of (a) $(\text{Co}_{1-y}\text{Fe}_y)_3\text{Sn}_2\text{S}_2$ and (b) $(\text{Co}_{1-z}\text{Ni}_z)_3\text{Sn}_2\text{S}_2$ polycrystal samples ($y, z = 0.0000, 0.0125, 0.0250, 0.0375$, and 0.0500). Above T_C , the linear curve indicating a metallic behavior was fitted by Mott's formula, as illustrated by the green line. Below T_C , the nonlinear curve suggesting the complete contribution of hole and electron carriers was fitted by the two-band model, as demonstrated by the red line. The fitting parameters are presented in Table II and Table SII in the Supplemental Material [43].

tice. This gapping occurs in the minority-spin channel and is driven by the magnetic order below T_C , consistent with the first-principles calculations [39,53,54]. Based on the XANES analysis in the previous section, because Co, Fe, and Ni are all in the same valence state (zero-valent state) in this system, Fe has one less $3d$ electron than Co, and Ni has one more. As a result, Fe substitution reduces the $3d$ electron population in the majority band, located just above the pseudogap, thereby reducing the exchange splitting and suppressing ferromagnetism. On the other hand, Ni substitution increases the $3d$ electron count, predominantly filling the minority band, thereby suppressing ferromagnetism, as well. Notably, the suppression effect of Fe substitution is weaker than that of Ni substitution. Similarly, a weak effect on T_C was observed in $\text{Co}_3\text{Sn}_2\text{S}_2$ when In substitutes for Sn, where In also has fewer electrons than Sn [55]. This suggests that hole doping induces a smaller shift in the electronic DOS around the E_F compared to electron doping in $\text{Co}_3\text{Sn}_2\text{S}_2$.

C. Seebeck coefficient

To investigate the change in electronic structure of $\text{Co}_3\text{Sn}_2\text{S}_2$, the T -dependent Seebeck coefficient (S) measurements were performed. These measurements can provide complementary insights into the E_F and E_g of a material. Figures 5(a) and 5(b) show the $S(T)$ curves of $(\text{Co}_{1-y}\text{Fe}_y)_3\text{Sn}_2\text{S}_2$ ($0.0000 < y < 0.0500$) and

$(\text{Co}_{1-z}\text{Ni}_z)_3\text{Sn}_2\text{S}_2$ ($0.0000 < z < 0.0500$) polycrystal samples, respectively. The values of S for all samples are negative, indicating that electrons are the dominant charge carriers. This is consistent with previous reports [24,56] and our Hall effect measurements, which are discussed in the following section. The absolute value of S at 300 K for the pristine sample is $53 \mu\text{V/K}$, which is quite large compared to the elemental metals. Additionally, the value for $y/z = 0.0125, 0.0250, 0.0375$, and 0.0500 are approximately $52/64, 63/47, 52/48$, and $65/53 \mu\text{V/K}$, respectively, where each pair corresponds to Fe- and Ni-doped samples. This variation of S can be attributed to the modulation of E_F and the DOS near E_F in $\text{Co}_3\text{Sn}_2\text{S}_2$ alloys, as discussed below. Notably, these values are comparable to well-known TE Heusler alloys, such as the metallic half-metals Ni_2MnGa and Co_2TiSi , as well as semimetallic alloys like $\text{Fe}_2\text{VGa/Al}$ and $\text{Ru}_2\text{NbGa/Al}$ [57–62]. It suggests that the materials investigated could be potential candidates for TE applications, which are further discussed in the following sections.

As T decreases, sudden slope changes in the $S(T)$ curves appear near the corresponding T_C , indicating changes in magnetic scattering that influence TE transport in $\text{Co}_3\text{Sn}_2\text{S}_2$. This behavior is primarily attributed to a modification of the electronic structure due to the opening of a pseudogap below T_C , rather than a full Fermi surface reconstruction. Above T_C , the quasilinear increase in the absolute value of

TABLE II. The E_g and E_F obtained from the T -dependent Seebeck coefficient of $\text{Co}_3\text{Sn}_2\text{S}_2$, $(\text{Co}_{0.95}\text{Fe}_{0.05})_3\text{Sn}_2\text{S}_2$, and $(\text{Co}_{0.95}\text{Ni}_{0.05})_3\text{Sn}_2\text{S}_2$ polycrystal samples: The $S(T)$ curves below T_C are fitted by Eq. (2): $S = a + bT + (c\lambda + dT)e^{-\lambda/T}$, where $\lambda = E_g/2k_B$. The $S(T)$ curves above T_C are fitted by Mott's formula for ordinary metals with $S = [(\pi k_B)^2/2eE_F]T = mT$. The detail fitting parameters for all doped polycrystal samples are illustrated in Table SII in the Supplemental Material [43].

$(\text{Co}_{1-y}\text{Fe}_y)_3\text{Sn}_2\text{S}_2$	Two-band model		Mott's formula	
	λ (K)	E_g (meV)	m ($\mu\text{V/K}^2$)	E_F (meV)
$(\text{Co}_{1-z}\text{Ni}_z)_3\text{Sn}_2\text{S}_2$				
$y/z = 0.0000$	233(1)	40.2(2)	−0.1250(3)	292.8(1)
$y/z = 0.0500$ (Fe/Ni)	152(2)/79(2)	26.2(3)/13.7(2)	−0.1401(1)/−0.1242(1)	261.3(2)/294.7(3)

$S(T)$ is a typical characteristic of metals and semimetals, suggesting a diffusivelike TE transport, which is consistent with the $\rho_{xx}(T)$ measurements. This quasilinear curve can also provide complementary information about the E_F through fitting with Mott's formula for ordinary metals, which can be expressed as

$$S = [(\pi k_B)^2 / 2eE_F]T = mT, \quad (1)$$

where e represents the elementary charge, assuming a single-band model with an energy-independent relaxation time. The fitted lines of Eq. (1) are shown in Figs. 5(a) and 5(b) as a solid green line. The fitting parameter, m , is shown in Table SII in the Supplemental Material [43], which is inversely proportional to E_F . The variations in the E_F for $(\text{Co}_{1-y}\text{Fe}_y)_3\text{Sn}_2\text{S}_2$ and $(\text{Co}_{1-z}\text{Ni}_z)_3\text{Sn}_2\text{S}_2$ ($y, z = 0.0000$ and 0.0500) are summarized in Table II. The results of E_F indicate a trend that Fe substitution causes a more significant modulation in E_F compared to Ni substitution.

Below T_C , the nonlinear $S(T)$ curves for all samples are qualitatively similar to those observed in various half-metallic ferromagnetic alloys, such as $\text{Co}_2\text{Ti}(\text{Si}/\text{Ge}/\text{Sn})$ and BaFe_2As_2 [63,64]. The conduction mechanism of $S(T)$ can be explained using a phenomenological two-band model; however, the underlying physical origins differ fundamentally from those in systems like BaFe_2As_2 . The BaFe_2As_2 compound exhibits Fermi surface reconstruction and requires T -dependent electron scattering rates for accurate modeling. Nevertheless, $\text{Co}_3\text{Sn}_2\text{S}_2$ does not show such reconstruction, since our ARPES data confirm only the formation of a pseudogap and shifts in E_F . The $S(T)$ curve in the two-band model by the Nordheim-Gorter rule can be simplified for semimetals and expressed as

$$S = a + bT + (c\lambda + dT)e^{-\lambda/T}, \quad (2)$$

where a, b, c, d , and λ are the fitting parameters. Here, $\lambda = E_g/2k_B$, E_g is the effective pseudogap energy scale, related to a partial suppression of DOS near the Fermi level in the spin-up channel [24], and k_B is the Boltzmann constant [41,57]. This phenomenological model assumes approximately constant electron scattering rates as a simplification. This assumption is justified for $\text{Co}_3\text{Sn}_2\text{S}_2$, as the primary TE transport is governed by electronic structure changes rather than complex scattering mechanisms, similar to those in the $\text{Co}_2\text{Ti}(\text{Si}/\text{Ge}/\text{Sn})$ compounds. The dominant features of $S(T)$ are well captured by this electronic model, emphasizing the primary role of pseudogap formation and Fermi-level shifts. The inherently weak phonon-drag contribution in our samples, evidenced by their high-residual resistivity, further supports this electronic interpretation. The fitted line of Eq. (2) is shown in Figs. 5(a) and 5(b) as a solid red line. The fitting parameters obtained are summarized in Table SII in the Supplemental Material [43]. The estimated E_g of about 40.2 meV supports that the $\text{Co}_3\text{Sn}_2\text{S}_2$ alloy has a pseudogap near the E_F . The variations in the E_g for $(\text{Co}_{1-y}\text{Fe}_y)_3\text{Sn}_2\text{S}_2$ and $(\text{Co}_{1-z}\text{Ni}_z)_3\text{Sn}_2\text{S}_2$ ($y, z = 0.0000$ and 0.0500) are summarized in Table II, as well. Regarding Fe substitution, E_g narrows from 40.2 meV at $y = 0.0000$ to 26.2 meV at $y = 0.0500$. Regarding Ni substitution, E_g narrows from 40.2 meV at $z = 0.0000$ to 13.7 meV

at $z = 0.0500$. These results suggest that the dopants-induced modulation in the band structure of $\text{Co}_3\text{Sn}_2\text{S}_2$ can effectively affect the behaviors of $S(T)$. This is further discussed in the direct observations of band structure using ARPES measurements in the following section. Furthermore, to understand the band-filling effect on thermal transport properties and the potential for TE applications, the T dependence of thermal conductivity curves and TE performance are analyzed in the following sections.

D. Thermal conductivity

To understand the thermal transport properties in $(\text{Co}_{1-y}\text{Fe}_y)_3\text{Sn}_2\text{S}_2$ ($0.0000 < y < 0.0500$) and $(\text{Co}_{1-z}\text{Ni}_z)_3\text{Sn}_2\text{S}_2$ ($0.0000 < z < 0.0500$) polycrystal samples, T -dependent thermal conductivity (κ) measurements were performed, as illustrated in Figs. 6(a) and 6(b), respectively. Upon cooling, the $\kappa(T)$ curves in both Fe- and Ni-doped series of $\text{Co}_3\text{Sn}_2\text{S}_2$ alloys exhibit a weak T dependence until the corresponding T_C , where a sudden rise in κ is observed, which can be attributed to the scattering of phonons by critical spin fluctuations in the ferromagnetic state. Below T_C , $\kappa(T)$ gradually increases with decreasing T and exhibits a pronounced peak in the region between 30 and 50 K. Overall, the $\kappa(T)$ curves exhibit typical T -dependence characteristics for crystalline narrow-gap semiconductors, and the phonon peak feature at low T indicates a reduction of thermal scattering in solids [65]. The maximum takes place at the T where the phonon mean-free path is approximately equal to the crystal site/interatomic distance, ascribed to the generalized Umklapp process. The room-temperature values of κ ($\kappa_{300\text{K}}$) for the Fe- and Ni-doped $\text{Co}_3\text{Sn}_2\text{S}_2$ alloys is comparable, between 1.8 and 2.4 W/mK, which are lower than those of some Heusler alloys, such as Fe_2VGa , Ru_2NbGa , and NbFeSb [58–60,66], and even comparable with the state-of-art TE materials, such as SiGe , Bi_2Te_3 , and PbTe [67–70].

In general, the total κ in ordinary metals and semimetals is usually expressed as the sum of the electronic thermal conductivity (κ_e) and lattice thermal conductivity (κ_L), i.e., $\kappa(T) = \kappa_e(T) + \kappa_L(T)$. The electronic part can be calculated using the Wiedemann-Franz law $\kappa_e = L_0 T / \rho_{xx}$, where L_0 ($= 2.45 \times 10^{-8} \text{ W } \Omega / \text{K}^2$) is the Lorentz number. Deviations from L_0 can occur in various metallic systems due to inelastic scattering. We computed the $L(T)$ curves using the relation proposed by Kim *et al.* [71]: $L = 1.5 + \exp(-|S|/116)$, where L is measured in $10^{-8} \text{ W } \Omega / \text{K}^2$ and S is in $\mu\text{V}/\text{K}$, as shown in Fig. S3 in the Supplemental Material [43]. We found that $L(T)$ converges to L_0 at low T , confirming the validity of using a constant L_0 in this temperature regime [71]. Consequently, the $\kappa_L(T)$ was obtained by subtracting the measured $\kappa(T)$ from $\kappa_e(T)$. The decomposed $\kappa_L(T)$ and $\kappa_e(T)$ are displayed in the main panel and the inset in Figs. 6(c) and 6(d), respectively. This estimation shows that κ_e at 300 K contributes approximately 30–50% of the total κ across all samples. However, at low T , the κ_e contribution is much smaller (about 10–25%) than the total κ . This finding can be attributed to the relatively high-residual resistivity observed in both series of samples, which range from 0.1 to 0.6 m Ω cm at 2 K. This high resistivity leads to a low κ_e as observed. Consequently, at low T ,

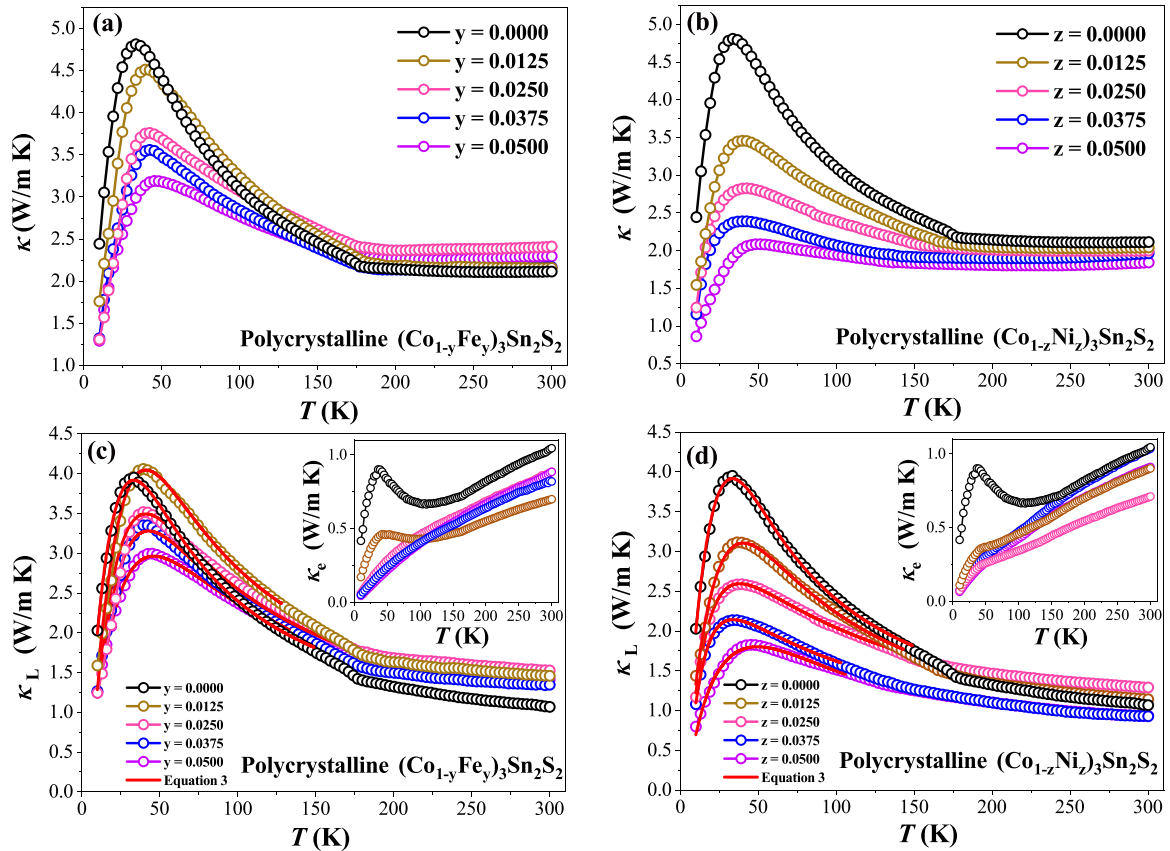


FIG. 6. T -dependent thermal conductivity of (a) $(\text{Co}_{1-y}\text{Fe}_y)_3\text{Sn}_2\text{S}_2$ and (b) $(\text{Co}_{1-z}\text{Ni}_z)_3\text{Sn}_2\text{S}_2$ polycrystal samples ($y, z = 0.0000, 0.0125, 0.0250, 0.0375$, and 0.0500). T -dependent lattice thermal conductivity of (c) $(\text{Co}_{1-y}\text{Fe}_y)_3\text{Sn}_2\text{S}_2$ and (d) $(\text{Co}_{1-z}\text{Ni}_z)_3\text{Sn}_2\text{S}_2$ polycrystalline samples ($y, z = 0.0000, 0.0125, 0.0250, 0.0375$, and 0.0500). The solid red line represents the fits at low T using Eq. (3). Insets: The electronic thermal conductivity of these alloys.

heat conduction is primarily governed by phonons rather than electrons. This behavior, where phonons effectively carry heat in metallic systems with high-residual disorder, has also been documented in various disordered alloys, such as Heusler alloys and high-entropy alloys [63,72,73].

The T -dependent κ_L curves exhibit variations in the height and sharpness of the phonon peak, which are sensitive to doping concentrations y and z . In the case of Fe-doped samples, the phonon peak height first increases when $y = 0.0125$, and it decreases systematically with increasing y . On the other hand, for the Ni-doped samples, the phonon peak is suppressed systematically with increasing z . Such a finding suggests a substantial enhancement in the phonon scattering with Fe and Ni substitutions. To examine the effect of Fe/Ni substitution on the phonon scattering processes, such as defects, imperfections, Umklapp scattering of phonons, etc., the $\kappa_L(T)$ for $T < T_C$ is analyzed by using the Debye-Callaway approximation [74]. Accordingly, the $\kappa_L(T)$ can be expressed as

$$\kappa_L(T) = \frac{k_B}{2\pi^2 v_s} \left(\frac{k_B T}{\hbar} \right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{\tau_p^{-1}(e^x - 1)^2} dx, \quad (3)$$

where k_B , Θ_D , v_s , $\hbar$, and τ_p are the Boltzmann constant, the Debye temperature, the phonon velocity, the reduced Planck's constant, and the phonon scattering relaxation time, respec-

tively, and $x = \hbar\omega/k_B T$ (ω = the phonon frequency) is a dimensionless quantity. Here, the $1/\tau_p$ can be described as the sum of three scattering contributions:

$$1/\tau_p = v_s/l + p\omega^4 + q\omega^2 T e^{-r/T}, \quad (4)$$

where l is the grain size and the coefficient p is the point-defects-scattering constant, q is the Umklapp scattering parameter, and r is the Umklapp scattering temperature coefficient. The terms in Eq. (4), from left to right, represent the phonon scattering rates due to grain-boundary scattering, point defects, and phonon-phonon Umklapp scattering, respectively. It is important to note that the Debye model is formulated for 3D crystals. Applying it to $\text{Co}_3\text{Sn}_2\text{S}_2$, which exhibits a quasi2D character, is a simplification. However, the Debye-Callaway framework remains a well-established approach for analyzing phonon transport in polycrystalline materials, as it explicitly incorporates grain-boundary scattering [the v_s/l term in Eq. (4)]. The value of $\Theta_D = 428$ K is determined from the reported specific heat data of $\text{Co}_3\text{Sn}_2\text{S}_2$ alloy [75]. The value of v_s was thus estimated to be 2815 m/s using the Debye model $v_s = \frac{k_B \Theta_D}{\hbar(6\pi^2 N)^{1/3}}$, where N is the density of atoms [76]. The best fit of the $\kappa_L(T)$ data for $T < T_C$ is illustrated as solid red lines in Figs. 6(c) and 6(d), and the parameters obtained from the fit are listed in Table III. It indicates that the low-temperature $\kappa_L(T)$ of Fe- and Ni-doped

TABLE III. Parameters obtained from the thermal conductivity analysis: Grain-boundary scattering coefficient (v_s/l), grain size (l), point-defect-scattering constant (p), Umklapp scattering parameter (q), Umklapp scattering temperature coefficient (r).

$(\text{Co}_{1-y}\text{Fe}_y)_3\text{Sn}_2\text{S}_2$ $(\text{Co}_{1-z}\text{Ni}_z)_3\text{Sn}_2\text{S}_2$	v_s/l (10^9 s^{-1})	l (10^{-6} m)	p (10^{-42} s^3)	q (10^{-19} s/K)	r (K)
$y/z = 0.0000$	1.41(3)	1.99(4)	14.5(2)	217(2)	89(1)
$y/z = 0.0125$	3.56(17)/2.66(7)	0.79(4)/1.06(3)	9.3(3)/16.5(3)	237(4)/218(2)	104(3)/100(2)
$y/z = 0.0250$	3.80(33)/2.87(3)	0.74(7)/0.98(1)	11.1(9)/18.2(2)	210(8)/145(9)	91(5)/53(1)
$y/z = 0.0375$	4.02(27)/3.20(11)	0.70(5)/0.88(3)	12.3(7)/20.1(7)	222(7)/196(4)	99(5)/40(1)
$y/z = 0.0500$	4.20(12)/5.52(20)	0.67(2)/0.51(2)	14.6(3)/28.7(8)	182(2)/251(1)	98(2)/112(6)

alloys can be described satisfactorily by the Debye approximation. We have also attempted to include electron-phonon interaction in the calculations, but such an effort yielded no significant improvement to the overall fit. We thus conclude that electron-phonon scattering has a minor influence on the κ_L in the present Fe- and Ni-doped systems.

From this analysis, it appears that the Umklapp parameter q , which is generally the dominant factor at high T , shows no systematic variation with the concentrations of Fe or Ni. This lack of a clear trend is mainly attributed to the material's intrinsic quasi2D anisotropy, a characteristic that the isotropic 3D Debye-Callaway model fails to adequately describe. Other factors, such as unknown Θ_D for these materials and unavoidable radiation losses during the measurements, may also play a role. However, the model successfully yielded systematic doping-dependent trends for the point-defect (p) and grain-boundary (l) scattering parameters, which dominate at low T . The parameter l shows a decreasing trend for both series of samples as the concentrations of Fe or Ni increase, as illustrated in Table III. This indicates that the substituents induce local lattice distortions in $\text{Co}_3\text{Sn}_2\text{S}_2$, which is consistent with the ρ_{xx} of the Fe- and Ni-doped $\text{Co}_3\text{Sn}_2\text{S}_2$ alloys, as the smaller grain size increases the ρ_{xx} of crystalline solids. Furthermore, the p parameter in the Fe-doped samples decreases slightly for the $y = 0.0125$ sample and then increases with increasing y . In contrast, the parameter p in the Ni-doped samples increased with increasing z . This variation is well consistent with the interpretation of the height in the phonon peak at low T . It indicated that the height of the phonon peak with Fe or Ni substitution is mainly influenced by the phonon-point-defect-scattering mechanism, as the mean free path of the phonon is expected to decrease with increasing doping concentration y/z . Since Co, Fe, and Ni are in a zero-valent state in this system, as discussed in the previous section, the atomic mass and size differences between these atoms are less than 5%. Therefore, the point-defect scattering in the present samples may be induced by the other lattice imperfections, such as vacancies, dislocations, etc.

E. Thermoelectric performance

The moderate value of S and relatively small ρ_{xx} observed in both Fe- and Ni-doped $\text{Co}_3\text{Sn}_2\text{S}_2$ polycrystals lead to a high TE power factor $\text{PF} = S^2/\rho_{xx}$, a prerequisite for good TE material. In the insets of Figs. 7(a) and 7(b), we displayed the T dependence of PF of the Fe- and Ni-doped $\text{Co}_3\text{Sn}_2\text{S}_2$ polycrystals, respectively. For both series of alloys, above T_C , the value of PF increases nearly linearly with T . At

300 K, the maximum PF values of about $5.16 \mu\text{W}/\text{cm K}^2$ for $y = 0.0500$ and $5.06 \mu\text{W}/\text{cm K}^2$ for $z = 0.0125$ were obtained for Fe- and Ni-doped $\text{Co}_3\text{Sn}_2\text{S}_2$ systems, respectively. These values are comparable with those theoretically and experimentally obtained for In-substituted $\text{Co}_3\text{Sn}_2\text{S}_2$ alloys and the previously published reports on Fe- and Ni-doped $\text{Co}_3\text{Sn}_2\text{S}_2$ alloys at high T [42,45,75]. Interestingly, in Fe-doped samples, enhanced PF values are observed near T_C at $y = 0.0250$ and 0.0500 , whereas for Ni-doped samples, similar enhancements appear at $y = 0.0125$, 0.0375 , and 0.0500 . Due to the squared dependence of PF on S , this variation is primarily attributed to changes in S due to E_g narrowing and E_F shifts induced by Fe and Ni substitution. These results highlight the tunability of TE performance near T_C in $\text{Co}_3\text{Sn}_2\text{S}_2$ through band-filling effect.

The figure of merit ZT ($= S^2 T / \rho_{xx} \kappa = \text{PF} / \kappa$), which represents a dimensionless quantity to assess the performance of a TE material, was calculated and presented in Figs. 7(a) and 7(b). Due to the large PF and relatively low thermal conductivity, the ZT value of these Fe- and Ni-doped $\text{Co}_3\text{Sn}_2\text{S}_2$ samples is reasonably high. In all compositions of Fe and Ni, ZT increases quite linearly with T above T_C . The maximum ZT is about 0.067 and 0.074 for Fe- and Ni-doped samples with $y = 0.0500$ and $z = 0.0125$, respectively, at room temperature, which are comparable to those found in other sulfur-based alloys such as Bi_2S_3 , Cu_xMoS_8 , and Cu_2S [77–79]. Given the relatively small change in κ near T_C , the variation of ZT around T_C is mainly governed by the behavior of the PF. These results suggest that the $\text{Co}_3\text{Sn}_2\text{S}_2$ alloys could be a potential tunable TE material both at high T and in the vicinity of the T_C via chemical substitution.

F. Angle-resolved photoemission spectroscopy

To further examine the modulation in the E_F of $\text{Co}_3\text{Sn}_2\text{S}_2$ due to the Fe and Ni substitution, ARPES measurements were performed on $\text{Co}_3\text{Sn}_2\text{S}_2$, $(\text{Co}_{0.95}\text{Fe}_{0.05})_3\text{Sn}_2\text{S}_2$, and $(\text{Co}_{0.95}\text{Ni}_{0.05})_3\text{Sn}_2\text{S}_2$ single crystals. The evolution of the band structure of $(\text{Co}_{0.95}\text{Fe}_{0.05})_3\text{Sn}_2\text{S}_2$ at various T , including 300, 110, and 25 K is shown in Fig. S4 in the Supplemental Material [43], showing only minor band shifts. Furthermore, photon energy dependence of the band structure of $(\text{Co}_{0.95}\text{Fe}_{0.05})_3\text{Sn}_2\text{S}_2$ at 300 K is shown in Fig. S5 in the Supplemental Material [43], indicating that the photon energy of 122 eV gives the best resolution. Additionally, the significant change in the band structure with varying incident photon energies suggests a three-dimensional, bulk-originated nature of the measured bands [80]. Based on these results, the band

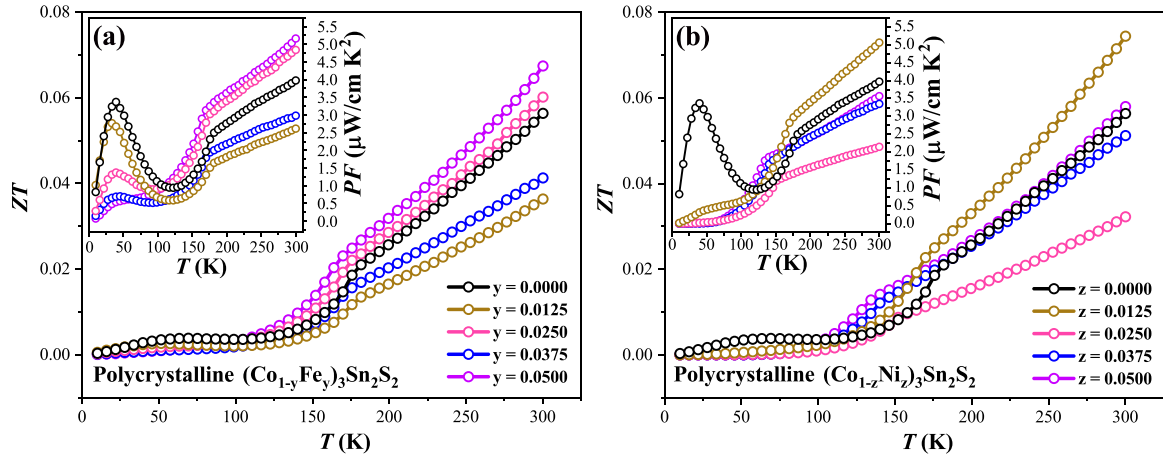


FIG. 7. The T variation of the thermoelectric figure of merit (ZT) values of (a) $(\text{Co}_{1-y}\text{Fe}_y)_3\text{Sn}_2\text{S}_2$ and (b) $(\text{Co}_{1-z}\text{Ni}_z)_3\text{Sn}_2\text{S}_2$ polycrystalline samples ($y, z = 0.0000, 0.0125, 0.0250, 0.0375$, and 0.0500). Insets: The T variation of the thermoelectric power factor PF for each sample.

mapping results of the single crystal samples measured at 300 K using a photon energy of 122 eV along the Γ - K direction are shown in Fig. 8. To explore the location of E_F of each sample by comparing similar features in their electronic structures, the band mapping results of $(\text{Co}_{0.95}\text{Ni}_{0.05})_3\text{Sn}_2\text{S}_2$ and $\text{Co}_3\text{Sn}_2\text{S}_2$ are extended to higher binding energy as shown in Figs. 8(a) and 8(c), respectively.

In Fig. 8(a), the electron band near K point and the depletion of spectral weight around a binding energy of 0.28 eV indicate a gapped region. The band broadening effect observed on the electron band supports the expected reduction in the band gap derived from the $S(T)$ fittings. Notably, since

this gapped region lies below E_F , the electronic states at the E_F exhibit metallic, which is consistent with the metallic behavior of the $S(T)$ curves above T_C as shown in Figs. 5(a) and 5(b). The two intensity patches around K points also appear in the band mapping result of the pristine sample at similar positions, as shown in the inset of Fig. 8(a). By comparing these two graphs, the E_F of the pristine sample can be inferred to lie near the valence band edge, whereas that of the Ni-doped sample is approximately 350 meV higher, lying closer to the conduction band edge. Based on these experimental observations and the data of E_g in Table II, a schematic illustration of the band structure change induced by Ni doping is shown

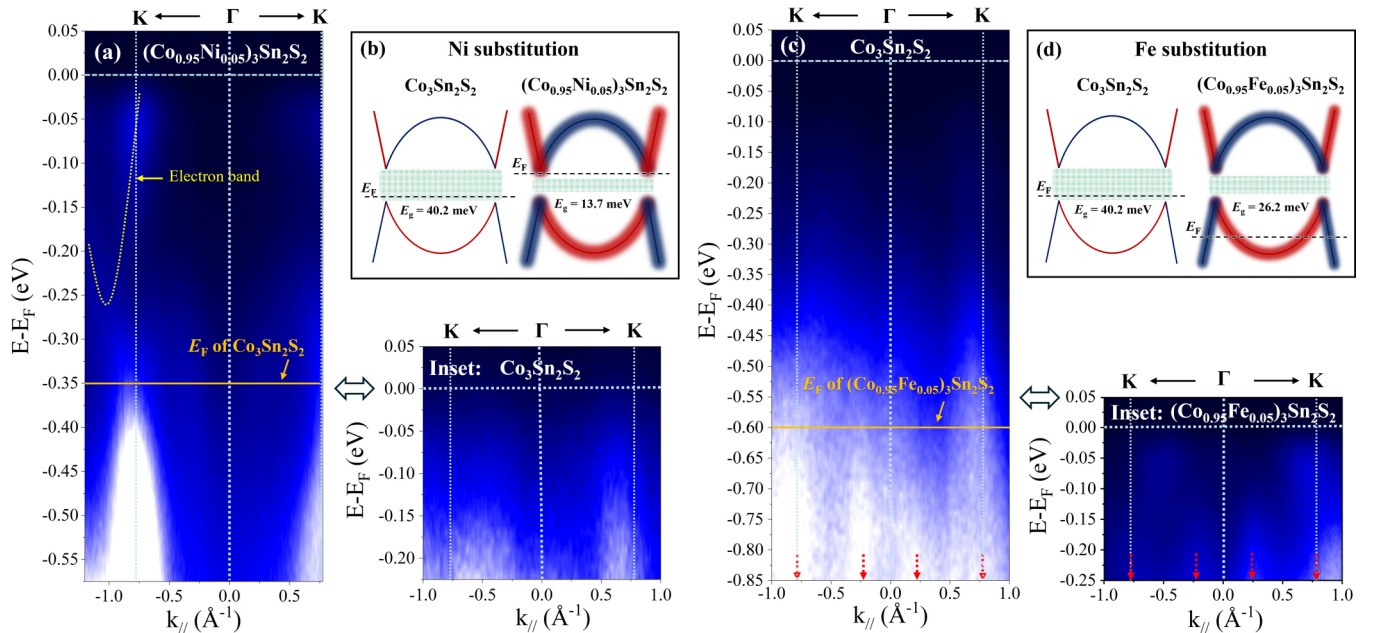


FIG. 8. High-symmetry Γ - K cuts taken at 300 K with a photon energy of 122 eV for each single-crystal sample. (a) Band mapping result of $(\text{Co}_{0.95}\text{Ni}_{0.05})_3\text{Sn}_2\text{S}_2$ single crystal, extended to higher binding energies. Inset: Band mapping result of $\text{Co}_3\text{Sn}_2\text{S}_2$ single crystal. (b) The schematic model of the band structure for Ni substitution, in which the narrowing of the E_g due to band broadening is based on data in Table II. (c) Band mapping result of $\text{Co}_3\text{Sn}_2\text{S}_2$ single crystal, extended to higher binding energies. Inset: Band mapping result of $(\text{Co}_{0.95}\text{Fe}_{0.05})_3\text{Sn}_2\text{S}_2$ single crystal. (d) Modified schematic model of the band structure for Fe substitution, in which the narrowing of the E_g due to band broadening is based on data in Table II.

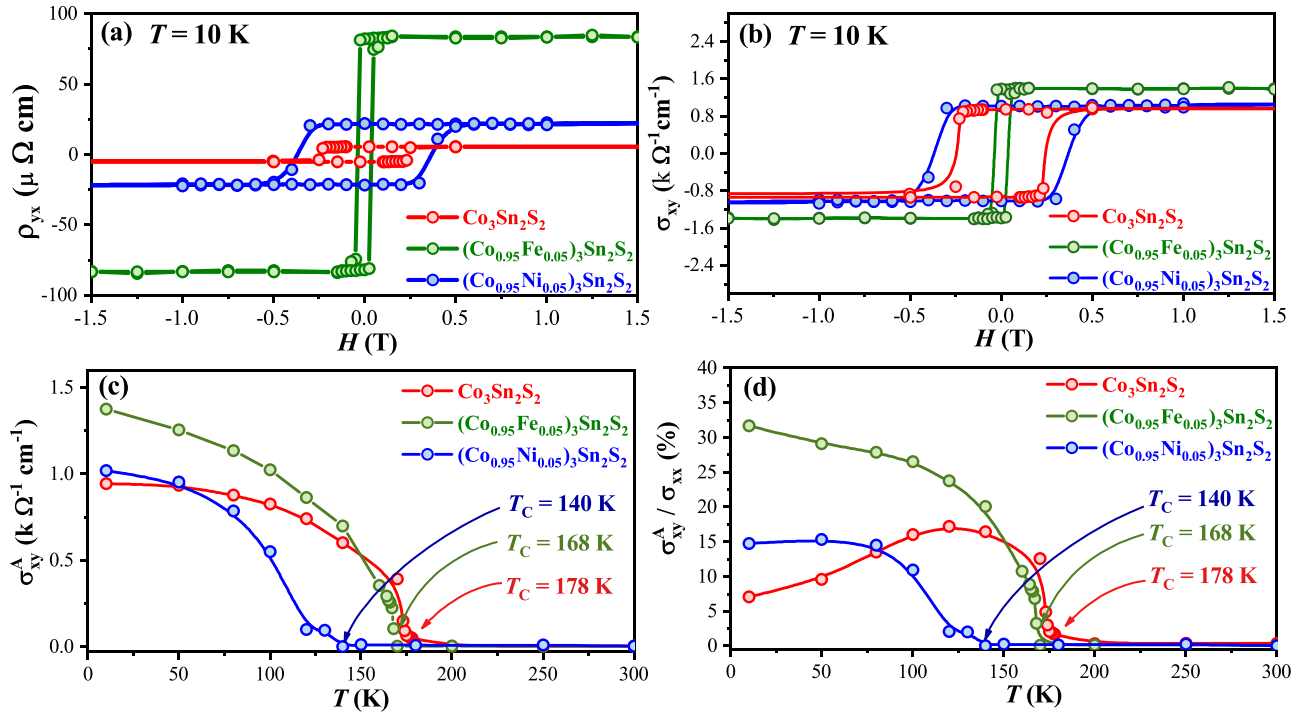


FIG. 9. (a) H dependence of ρ_{yx} on the single crystals with $H//c$ and $I//a$, where $\rho_{yx} = -\rho_{xy}$. The negative Hall voltage signal indicates the main carrier is electrons, which is consistent with the negative signal in our $S(T)$ measurement. (b) H dependence of σ_{xy} on the single crystals with $H//c$ and $I//a$. (c) T dependence of σ_{xy}^A on the single crystals with $H//c$ and $I//a$. (d) T dependence of $\sigma_{xy}^A / \sigma_{xx}$ on the single crystals with $H//c$ and $I//a$.

in Fig. 8(b). In Fig. 8(c), the four broad intensity patches at higher binding energies in the band structure of the pristine sample also appear at similar $k_{//}$ values in the band structure of the Fe-doped sample, as shown in the inset of Fig. 8(c). Similarly, comparison of these two graphs suggests that the E_F of the Fe-doped sample can be inferred to lie approximately 600 meV below that of the pristine sample. A schematic illustration of the band structure change induced by Fe doping is shown in Fig. 8(d). By comparing Figs. 8(b) and 8(d), the greater difference in the location of the E_F induced by Fe substitution, compared to Ni substitution, is consistent with the trend observed in the $S(T)$ fitting results.

Interestingly, intrinsic AHE is dominated by the band anticrossings from topological band inversion [24]. The Kubo formula indicates that the intrinsic σ_{xy}^A arises from two competing effects: the electron occupation, governed by E_F , and the topological band characteristic around E_F , such as the magnitude of E_g [28,31]. According to the formula, intrinsic σ_{xy}^A tends to be suppressed as E_F lies further from the gapped region, while a gap narrowing contributes to its increase. For the Fe-doped sample, the gap narrowing due to band broadening can increase σ_{xy}^A . However, its E_F lies further away from the band gap region. These two opposing effects may compensate each other, suggesting that the intrinsic contribution of σ_{xy}^A would not significantly change or even be suppressed under small-scale Fe doping. For the Ni-doped sample, the gap narrowing can lead to an increase in σ_{xy}^A . Additionally, its E_F does not lie far from the gapped region, indicating that the suppression of σ_{xy}^A is not expected to be significant. Therefore, Ni substitution may preserve or slightly increase the intrinsic σ_{xy}^A . This expectation is further discussed in the subsequent section.

G. Anomalous Hall effect

To verify the anticipated changes in AHE, as suggested by Figs. 8(b) and 8(d), isothermal Hall resistivity (ρ_{yx}) measurements on $\text{Co}_3\text{Sn}_2\text{S}_2$, $(\text{Co}_{0.95}\text{Fe}_{0.05})_3\text{Sn}_2\text{S}_2$, and $(\text{Co}_{0.95}\text{Ni}_{0.05})_3\text{Sn}_2\text{S}_2$ single crystals were conducted at various T . Figure 9(a) displays the $\rho_{yx}(H)$ curves for each sample at 10 K. The observed hysteresis loops exhibit the typical behavior of the AHE, where ρ_{yx} is proportional to the magnetization. Notably, Fe substitution reduces the coercivity of $\text{Co}_3\text{Sn}_2\text{S}_2$, whereas Ni substitution increases it. As discussed in Sec. III A, Fe and Ni substitutions have opposite effects on the c/a ratio, as illustrated in Table I. Additionally, the increase of the c/a ratio in the Fe-doped sample could be analogous to apply a tensile strain along the c axis. Similarly, the decrease of that in Ni-doped sample could be analogous to apply a compressive strain along the c axis. This interpretation may suggest a magnetostriction for the modulation of coercivity. For instance, the tensile strain from Fe substitution could lower the anisotropy energy along the easy axis (c axis), making magnetization reversal easier and thus reducing coercivity, whereas compressive strain from Ni substitution could enhance anisotropy energy and thereby increase coercivity [81]. Nevertheless, coercivity changes cannot be simply attributed to magnetostriction based solely on the observation of the lattice modification. The influence of strain on anisotropy critically depends on the sign of magnetostriction constant, which has not yet been determined for the best of our knowledge. Additionally, other possible mechanism regarding the increased coercivity in Ni-doped $\text{Co}_3\text{Sn}_2\text{S}_2$, such as the

pinning of the spin, has also been proposed [29]. Therefore, even though our results indicate that the modulation in coercivity of $\text{Co}_3\text{Sn}_2\text{S}_2$ upon Fe and Ni substitution may involve a magnetostriction mechanism, further studies are still needed to clarify this point.

Figure 9(b) shows H dependence of the Hall conductivity (σ_{xy}) at 10 K, where $\sigma_{xy} = -\sigma_{yx} = \rho_{yx}/(\rho_{yx}^2 + \rho_{xx}^2)$. The T -dependence of σ_{xy}^A curves is presented in Fig. 9(c), where σ_{xy}^A is extrapolated from the high- H regime to zero field in the $\sigma_{xy}(H)$ curves. The σ_{xy}^A of the Ni-doped sample at 10 K ($\sigma_{xy}^A = 1020 \Omega^{-1} \text{cm}^{-1}$) is larger than that of the pristine sample ($\sigma_{xy}^A = 944 \Omega^{-1} \text{cm}^{-1}$), which is consistent with the anticipation. However, contrary to expectations, the σ_{xy}^A of the Fe-doped samples at 10 K is also larger than that of the pristine sample, reaching a value of $1376 \Omega^{-1} \text{cm}^{-1}$. To gain further insight into this unexpected increase, it is crucial to discuss the contribution of AHE in the Fe-doped sample. As shown in Fig. 9(c), as T decreases, the σ_{xy}^A of each sample remains negligible above T_C , due to disordered magnetic moments in the paramagnetic phase for each sample. Below T_C , the pristine sample exhibits an increase in σ_{xy}^A as T decreases with the slope gradually becoming less steep, indicating an intrinsic behavior at low T . For the Ni-doped sample, σ_{xy}^A behaves similarly, though the decrease in slope is less pronounced, suggesting that the intrinsic mechanism dominates yet with a minor extrinsic contribution. The σ_{xy}^A of the Fe-doped sample continues to increase almost linearly at low T , suggesting an extrinsic contribution. To illustrate this more clearly, Fig. 9(d) displays the T dependence of the anomalous Hall angle ($\sigma_{xy}^A/\sigma_{xx}$). For the pristine sample, $\sigma_{xy}^A/\sigma_{xx}$ increases with T and peaks around 120 K, due to the constant of intrinsic AHE and thermally decreasing σ_{xx} , indicating the intrinsic AHE gradually becomes dominant at lower T . In the Ni-doped sample, $\sigma_{xy}^A/\sigma_{xx}$ remains nearly constant at low T and slightly decreases below 50 K, suggesting the intrinsic AHE gradually becomes dominant over the extrinsic contribution at lower T . In contrast, the Fe-doped sample exhibits a significantly increasing $\sigma_{xy}^A/\sigma_{xx}$ at low T , reaching a maximum of 31.7% at 10 K, which reflects a strong correlation between σ_{xy}^A and thermal scattering, supporting the presence of an extrinsic contribution induced by Fe substitution.

To further elucidate the origin of the enhanced σ_{xy}^A in each sample, Fig. 10 presents a log-log plot of the σ_{xx} -dependence of σ_{xy}^A in the framework of a unified model [82,83]. The σ_{xx} values for all samples are located at the intrinsic regime where σ_{xy}^A is expected to be dominated by the Berry curvature and remain independent of σ_{xx} , as σ_{xx} is primarily related to thermal scattering. The pristine sample starts showing a σ_{xx} -independent σ_{xy}^A below 100 K, consistent with the model prediction. Similarly, the Ni-doped sample exhibits an almost constant σ_{xy}^A below 50 K, indicating that its σ_{xy}^A mainly originates from the Berry curvature with a minor extrinsic contribution from Ni substitution. In contrast, the Fe-doping sample displays a clear dependence of σ_{xy}^A on σ_{xx} , suggesting that the σ_{xy}^A of the Fe-doped sample is predominantly governed by extrinsic mechanisms. To quantitatively analyze the contribution to σ_{xy}^A , the TYJ model was applied [84], as shown in

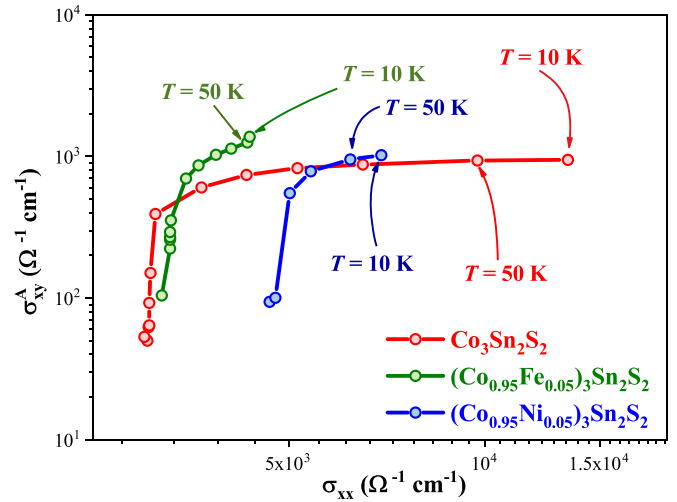


FIG. 10. σ_{xy}^A vs σ_{xx} curves in the framework of a unified model. For Fe-doped $\text{Co}_3\text{Sn}_2\text{S}_2$, the σ_{xy}^A increases as σ_{xx} increases even at lower T , suggesting that the increase in σ_{xy}^A originates from the skew-scattering effect. For Ni-doped $\text{Co}_3\text{Sn}_2\text{S}_2$, the σ_{xy}^A has the trend to become constant at lower temperatures, indicating that the increase in σ_{xy}^A at 10 K originates from intrinsic deflection with a small contribution of the skew-scattering effect.

Fig. 11. The TYJ scaling can be expressed in the conductivity form as

$$\sigma_{xy}^A = -(\alpha\sigma_{xx0}^{-1} + \beta\sigma_{xx0}^{-2})\sigma_{xx}^2 - b, \quad (5)$$

where σ_{xx0} denotes the residual conductivity. The first term on the right-hand side represents the extrinsic contributions, in which α and β correspond to skew scattering and side-jump mechanisms, respectively. The second term b corresponds to the intrinsic contribution. In the present case, the TYJ model fitting was performed for every two adjacent data points to extract the intercept, which represent the estimated intrinsic contribution by the TYJ model (σ_{xy}^A). The difference between σ_{xy}^A and the measured σ_{xy}^A was then used to evaluate the contribution of the AHE. This difference is large when T is close to T_C , since the magnetic disorder near T_C suppresses the measured σ_{xy}^A . Consequently, a decreasing difference with decreasing T and a smaller difference observed at low T , indicate that the AHE is predominantly governed by the intrinsic mechanism.

For the pristine sample, the difference decreases as T decreases, and at 10 K, the σ_{xy}^A ($923 \Omega^{-1} \text{cm}^{-1}$) is in good agreement with the σ_{xy}^A ($944 \Omega^{-1} \text{cm}^{-1}$). This result indicates that the AHE is predominantly intrinsic in origin. For the Ni-doped sample, although the difference also decreases with decreasing T , the σ_{xy}^A ($740 \Omega^{-1} \text{cm}^{-1}$) at 10 K shows a deviation from the σ_{xy}^A ($1020 \Omega^{-1} \text{cm}^{-1}$). This suggests that, in addition to the intrinsic contribution, an extrinsic component is also present in the Ni-doped sample. According to the schematic plot in Fig. 8(b), the E_F of Ni-doped sample is located near the edge of the conduction band. The relatively slight suppression in intrinsic σ_{xy}^A due to the location of E_F suggests that the σ_{xy}^A of Ni-doped sample observed at 10 K might come from the E_g narrowing and minor extrinsic mechanisms, which support the results of TYJ model analysis.

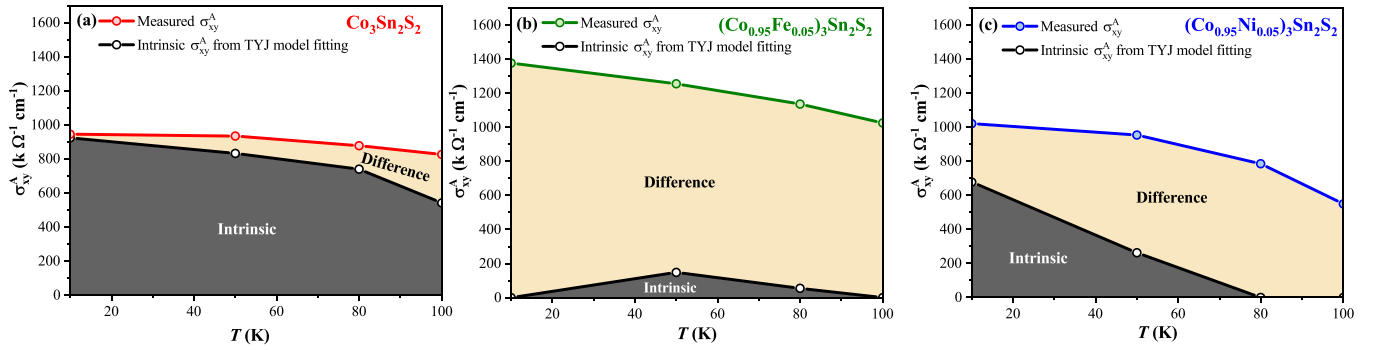


FIG. 11. Comparison between the measured σ_{xy}^A and the intrinsic contribution obtained from the TYJ model fitting (σ_{TYJ}^A) for (a) $\text{Co}_3\text{Sn}_2\text{S}_2$, (b) $(\text{Co}_{0.95}\text{Fe}_{0.05})_3\text{Sn}_2\text{S}_2$, and (c) $(\text{Co}_{0.95}\text{Ni}_{0.05})_3\text{Sn}_2\text{S}_2$. The gray region represents the σ_{TYJ}^A , and the beige region denotes the difference between the σ_{xy}^A and σ_{TYJ}^A . The detail fitting parameters for the TYJ model are illustrated in Table SIII in the Supplemental Material [43].

However, since the T_C of the Ni-doped sample is relatively low (approximately 140 K), the data near 10 K may only begin to exhibit the scattering-independent behavior, as reported in previous literature [29]. Therefore, it is difficult to draw a definitive conclusion regarding the relative proportions of intrinsic and extrinsic contributions in the Ni-doped sample due to the relatively larger range of T , which is 10 and 40 K in the present case. In contrast, for the Fe-doped sample, σ_{TYJ}^A remains at a low level as the T decreases, while σ_{xy}^A continues to increase with decreasing T . This behavior indicates that the AHE in the Fe-doped sample is primarily dominated by the extrinsic contribution. This interpretation is consistent with the schematic plot in Fig. 8(d), where the E_F lies far from the gapped region, thereby suppressing the intrinsic contribution. To be more specific to the origin of the extrinsic contribution, since the side-jump contribution to the AHE in $\text{Co}_3\text{Sn}_2\text{S}_2$ has been reported to be negligible [23], the extrinsic component in both Fe- and Ni-doped samples is most likely attributed to skew-scattering effect. These results are consistent with previous literature [24,30,31], and successfully demonstrate that the combined use of ARPES and thermopower measurements can corroborate the findings of AHE and TE experiments, offering an indirect yet powerful experimental method to support AHE and TE conclusions. Such enhanced understanding may accelerate the development of next-generation topological spintronic and TE devices.

IV. SUMMARY

We systematically investigated the Fe and Ni doping effects in the magnetic Weyl semimetal $\text{Co}_3\text{Sn}_2\text{S}_2$, focusing on their effects on TE properties and AHE. The key results are as follows: (1) XANES analysis confirmed that the oxidation number of Co, Fe, and Ni in single crystal samples presented as 0, further explaining the isotropic suppression of T_C , which was observed in T -dependent ρ_{xx} , σ_{xy}^A , and S measurements. (2) $S(T)$ analysis and ARPES measurements revealed that the

Fe and Ni doping cause a gap narrowing while introducing a shift in E_F to different extents, in which Fe doping lowers it by ~ 600 meV, while Ni doping raises E_F by ~ 350 meV. (3) Based on the Kubo formula, the change in band structure induced by Fe and Ni doping can well support the increase in σ_{xy}^A and their contribution. (4) H -dependent σ_{xy} at 10 K shows that Fe doping weakens, while Ni doping enhances, the magnetic anisotropy, respectively, which could be attributed to magnetostriction effect. (5) The comparison among the model of band structure, the dependence of σ_{xy}^A on σ_{xx} , and the analysis of the TYJ model suggests that skew scattering prevails in the σ_{xy}^A of the Fe-doped $\text{Co}_3\text{Sn}_2\text{S}_2$, while intrinsic deflection with minor skew scattering contributes to that of the Ni-doped $\text{Co}_3\text{Sn}_2\text{S}_2$. Overall, this study provides a comprehensive understanding of the doping-induced modifications in band structure of magnetic Weyl semimetal $\text{Co}_3\text{Sn}_2\text{S}_2$, revealing the interplay among electronic structure, TE properties, and AHE. These findings contribute to advancements in topological spintronics and TE applications.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

[1] L. Balents, Spin liquids in frustrated magnets, *Nature (London)* **464**, 199 (2010).

[2] Y. Guo, H. Liu, O. Janson, I. C. Fulga, J. van den Brink, and J. I. Facio, Spin-split collinear antiferromagnets: A

large-scale *ab initio* study, *Mater. Today Phys.* **32**, 100991 (2023).

[3] Y. H. Chang, A. Pal, P. T. W. Yen, C. W. Wang, S. Giri, G. R. Blake, J. Gainza, M. J. Hsieh, J. Y. Lin, C. Y. Huang,

- Y. J. Chen, T. W. Kuo, A. Tiwari, D. Chandrasekhar Kakarla, and H. D. Yang, Field-induced transformation of complex spin ordering and magnetodielectric and magnetoelastic coupling in MnGeTeO_6 , *Phys. Rev. B* **110**, 064405 (2024).
- [4] H. C. Wu, J. K. Yuan, K. D. Chandrasekhar, C. H. Lee, W. H. Li, C. W. Wang, J. M. Chen, J. Y. Lin, H. Berger, T. W. Yen, S. M. Huang, C. W. Chu, and H. D. Yang, Observation of charge-transfer-driven antiferroelectricity in 3d-pyroxene multiferroic Cu_2OCl_2 , *Mater. Today Phys.* **8**, 34 (2019).
- [5] W. Shon, D. C. Ryu, K. Kim, B. I. Min, B. Kim, B. Kang, B. K. Cho, H. J. Kim, and J. S. Rhyee, Magnetic field-induced type II Weyl semimetallic state in geometrically frustrated Shastry-Sutherland lattice GdBi_4 , *Mater. Today Phys.* **11**, 100168 (2019).
- [6] H. C. Wu, K. D. Chandrasekhar, J. K. Yuan, J. R. Huang, J. Y. Lin, H. Berger, and H. D. Yang, Anisotropic spin-flip-induced multiferroic behavior in kagome $\text{Cu}_3\text{Bi}(\text{SeO}_3)_2\text{O}_2\text{Cl}$, *Phys. Rev. B* **95**, 125121 (2017).
- [7] M. K. Dasoundhi, S. Baral, I. Rajput, D. Kumar, and A. Lakhani, Extremely large magnetoresistance and non-trivial band topology in YSb semimetal, *Mater. Today Phys.* **40**, 101310 (2024).
- [8] H. C. Wu, Y. C. Chung, T. W. Yen, H. J. Chen, T. W. Kuo, D. C. Kakarla, S. M. Huang, Y. Y. Wang, J. Y. Lin, J. J. Lee, Y. C. Lai, C. L. Chen, J. F. Lee, T. L. Chou, Y. C. Lai, M. W. Chu, M. M. C. Chou, and H. D. Yang, Evidence of a structural phase transition in the triangular-lattice compound CuIr_2Te_4 , *Phys. Rev. B* **103**, 104111 (2021).
- [9] A. P. Ramirez, Strongly geometrically frustrated magnets, *Annu. Rev. Mater. Res.* **24**, 453 (1994).
- [10] H. J. Chen, C. H. Yeh, T. W. Kuo, D. C. Kakarla, H. C. Wu, T. W. Yen, S. M. Huang, H. Chou, M. C. Chou, H. W. Chen, S. W. Kuo, Y. C. Chuang, C. K. Chang, U. Eckstein, N. H. Khansur, K. G. Webber, and H. D. Yang, Unique multiferroics with tunable ferroelastic transition in antiferromagnet $\text{Mn}_2\text{V}_2\text{O}_7$, *Mater. Today Phys.* **23**, 100623 (2022).
- [11] A. Pal, C. H. Huang, T. W. Yen, P. H. Lee, Y. H. Chang, C. H. Yeh, T. W. Kuo, A. Tiwari, D. C. Kakarla, S. M. Huang, M. C. Chou, H. S. Kunwar, S. Rana, V. G. Sathe, B. H. Chen, Y. C. Chuang, and H. D. Yang, Spin-induced strongly correlated magnetodielectricity, magnetostriction effect, and spin-phonon coupling in helical magnet $\text{Fe}_3(\text{PO}_4)_2\text{O}_3$, *Phys. Rev. B* **106**, 094404 (2022).
- [12] N. Nagaosa, J. Sinova, S. Onoda, A. H. MacDonald, and N. P. Ong, Anomalous Hall effect, *Rev. Mod. Phys.* **82**, 1539 (2010).
- [13] Z. Fang, N. Nagaosa, K. S. Takahashi, A. Asamitsu, R. Mathieu, T. Ogasawara, H. Yamada, M. Kawasaki, Y. Tokura, and K. Terakura, The anomalous Hall effect and magnetic monopoles in momentum space, *Science* **302**, 92 (2003).
- [14] D. Xiao, M.-C. Chang, and Q. Niu, Berry phase effects on electronic properties, *Rev. Mod. Phys.* **82**, 1959 (2010).
- [15] F. D. M. Haldane, Berry curvature on the Fermi surface: Anomalous Hall effect as a topological Fermi-liquid property, *Phys. Rev. Lett.* **93**, 206602 (2004).
- [16] E. Vilanova Vidal, G. Stryganyuk, H. Schneider, C. Felser, and G. Jakob, Exploring Co_2MnAl Heusler compound for anomalous Hall effect sensors, *Appl. Phys. Lett.* **99**, 132509 (2011).
- [17] C.-Z. Chang, J. Zhang, M. Liu, Z. Zhang, X. Feng, K. Li, L.-L. Wang, X. Chen, X. Dai, Z. Fang, X.-L. Qi, S.-C. Zhang, Y. Wang, K. He, X.-C. Ma, and Q.-K. Xue, Thin films of magnetically doped topological insulator with carrier-independent long-range ferromagnetic order, *Adv. Mater.* **25**, 1065 (2013).
- [18] K. Manna, L. Muechler, T.-H. Kao, R. Stinshoff, Y. Zhang, J. Gooth, N. Kumar, G. Kreiner, K. Koepf, R. Car, J. Kübler, G. H. Fecher, C. Shekhar, Y. Sun, and C. Felser, From colossal to zero: Controlling the anomalous Hall effect in magnetic Heusler compounds via Berry curvature design, *Phys. Rev. X* **8**, 041045 (2018).
- [19] D. F. Liu, A. J. Liang, E. K. Liu, Q. N. Xu, Y. W. Li, C. Chen, D. Pei, W. J. Shi, S. K. Mo, P. Dudin, T. Kim, C. Cacho, G. Li, Y. Sun, L. X. Yang, Z. K. Liu, S. S. P. Parkin, C. Felser, and Y. L. Chen, Magnetic Weyl semimetal phase in a Kagomé crystal, *Science* **365**, 1282 (2019).
- [20] N. Morali, R. Batabyal, P. K. Nag, E. Liu, Q. Xu, Y. Sun, B. Yan, C. Felser, N. Avraham, and H. Beidenkopf, Fermi-arc diversity on surface terminations of the magnetic Weyl semimetal $\text{Co}_3\text{Sn}_2\text{S}_2$, *Science* **365**, 1286 (2019).
- [21] S. Rathod, M. Malasi, A. Lakhani, and D. Kumar, Electron-magnon scattering in an anisotropic Half-metallic ferromagnetic Weyl semimetal $\text{Co}_3\text{Sn}_2\text{S}_2$, *Phys. Rev. Mater.* **6**, 084202 (2022).
- [22] R. Wehrich and I. Anusca, Half antiperovskites. III. Crystallographic and electronic structure effects in $\text{Sn}_{2-x}\text{In}_x\text{Co}_3\text{S}_2$, *Z. Anorg. Allg. Chem.* **632**, 1531 (2006).
- [23] Q. Wang, Y. Xu, R. Lou, Z. Liu, M. Li, Y. Huang, D. Shen, H. Weng, S. Wang, and H. Lei, Large intrinsic anomalous Hall effect in half-metallic ferromagnet $\text{Co}_3\text{Sn}_2\text{S}_2$ with magnetic Weyl fermions, *Nat. Commun.* **9**, 3681 (2018).
- [24] E. Liu, *et al.*, Giant anomalous Hall effect in a ferromagnetic Kagome-lattice semimetal, *Nat. Phys.* **14**, 1125 (2018).
- [25] R. K. Gopal Shama and Y. Singh, Observation of planar Hall effect in the ferromagnetic Weyl semimetal $\text{Co}_3\text{Sn}_2\text{S}_2$, *J. Magn. Magn. Mater.* **502**, 166547 (2020).
- [26] M. Tanaka, Y. Fujishiro, M. Mogi, Y. Kaneko, T. Yokosawa, N. Kanazawa, S. Minami, T. Koretsune, R. Arita, S. Tarucha, M. Yamamoto, and Y. Tokura, Topological kagome magnet $\text{Co}_3\text{Sn}_2\text{S}_2$ thin flakes with high electron mobility and large anomalous hall effect, *Nano Lett.* **20**, 7476 (2020).
- [27] E. A. Stern, Rigid-band model of alloys, *Phys. Rev.* **157**, 544 (1967).
- [28] D. J. Thouless, M. Kohmoto, M. P. Nightingale, and M. den Nijs, Quantized Hall conductance in a two-dimensional periodic potential, *Phys. Rev. Lett.* **49**, 405 (1982).
- [29] G. S. Thakur, P. Vir, S. N. Guin, C. Shekhar, R. Wehrich, Y. Sun, N. Kumar, and C. Felser, Intrinsic anomalous Hall effect in Ni-substituted magnetic Weyl semimetal $\text{Co}_3\text{Sn}_2\text{S}_2$, *Chem. Mater.* **32**, 1612 (2020).
- [30] J. Shen, Q. Zeng, S. Zhang, H. Sun, Q. Yao, X. Xi, W. Wang, G. Wu, B. Shen, Q. Liu, and E. Liu, 33% giant anomalous Hall current driven by both intrinsic and extrinsic contributions in magnetic Weyl semimetal $\text{Co}_3\text{Sn}_2\text{S}_2$, *Adv. Funct. Mater.* **30**, 2000830 (2020).
- [31] J. Shen, Q. Yao, Q. Zeng, H. Sun, X. Xi, G. Wu, W. Wang, B. Shen, Q. Liu, and E. Liu, Local disorder-induced elevation of intrinsic anomalous Hall conductance in an electron-doped magnetic Weyl semimetal, *Phys. Rev. Lett.* **125**, 086602 (2020).
- [32] H. Zhou, G. Chang, G. Wang, X. Gui, X. Xu, J.-X. Yin, Z. Guguchia, S. S. Zhang, T.-R. Chang, H. Lin, W. Xie, M. Z. Hasan, and S. Jia, Enhanced anomalous Hall effect in the

- magnetic topological semimetal $\text{Co}_3\text{Sn}_{2-x}\text{In}_x\text{S}_2$, *Phys. Rev. B* **101**, 125121 (2020).
- [33] Y. Li, W. Li, J. Lin, Z. Guo, F. Sun, X. Chen, Y. Luo, J. Yang, and W. Yuan, Electron doping and physical properties in the ferromagnetic semimetal $\text{Co}_3\text{Sn}_{2-x}\text{Sb}_x\text{S}_2$, *J. Phys. Chem. C* **126**, 7230 (2022).
- [34] B. He, M. Yao, Y. Pan, K. E. Arpino, D. Chen, F. M. Serrano-Sanchez, S. Ju, M. Shi, Y. Sun, and C. Felser, Enhanced Weyl semimetal signature in $\text{Co}_3\text{Sn}_2\text{S}_2$ kagome ferromagnet by chlorine doping, *Commun. Mater.* **5**, 275 (2024).
- [35] H. C. Wu, P. J. Sun, D. J. Hsieh, H. J. Chen, D. C. Kakarla, L. Z. Deng, C. W. Chu, and H. D. Yang, Observation of skyrmion-like magnetism in magnetic Weyl semimetal $\text{Co}_3\text{Sn}_2\text{S}_2$, *Mater. Today Phys.* **12**, 100189 (2020).
- [36] S. Rathod, M. Malasi, A. Lakhani, and D. Kumar, How to enhance anomalous Hall effects in magnetic Weyl semimetal $\text{Co}_3\text{Sn}_2\text{S}_2$? *Chem. Mater.* **36**, 7418 (2024).
- [37] M. Kanagaraj, J. Ning, and L. He, Topological $\text{Co}_3\text{Sn}_2\text{S}_2$ magnetic Weyl semimetal: From fundamental understanding to diverse fields of study, *Rev. Phys.* **8**, 100072 (2022).
- [38] Z. Shen, X. D. Zhu, R. R. Ullah, P. Klavins, and V. Taufour, Anomalous depinning of magnetic domain walls within the ferromagnetic phase of the Weyl semimetal $\text{Co}_3\text{Sn}_2\text{S}_2$, *J. Phys. Condens. Matter* **35**, 045802 (2023).
- [39] A. Rossi, V. Ivanov, S. Sreedhar, A. L. Gross, Z. Shen, E. Rotenberg, A. Bostwick, C. Jozwiak, V. Taufour, S. Y. Savrasov, and I. M. Vishik, Electronic structure and topology across T_c in the magnetic Weyl semimetal $\text{Co}_3\text{Sn}_2\text{S}_2$, *Phys. Rev. B* **104**, 155115 (2021).
- [40] Y. Zhang, Z. Li, and C. Uher, Low-temperature thermal properties of Fe-doped $\text{Co}_3\text{Sn}_2\text{S}_2$, *Mater. Today Commun.* **34**, 105100 (2023).
- [41] Y. Xin, K. W. Wong, C. X. Fan, Z. Z. Sheng, and F. T. Chan, Thermoelectric power of the thallium-based superconductor $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10-\delta}$, *Phys. Rev. B* **48**, 557 (1993).
- [42] P. Mangelis, P. Vaqueiro, J.-C. Jumas, I. da Silva, R. I. Smith, and A. V. Powell, The effect of electron and hole doping on the thermoelectric properties of shandite-type $\text{Co}_3\text{Sn}_2\text{S}_2$, *J. Solid State Chem.* **251**, 204 (2017).
- [43] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/71sm-3r2x> for the details of the additional data of $\text{Co}_3\text{Sn}_2\text{S}_2$.
- [44] J. Liu, Y. Yang, J. Shen, D. Liu, G. S. Thakur, C. Guillemard, A. Smekhova, H. Chen, D. Biswas, M. Valvidares, E. Liu, C. Felser, T.-L. Lee, T. Hesjedal, Y. Chen, and G. van der Laan, Unusually high occupation of Co 3d state in magnetic Weyl semimetal $\text{Co}_3\text{Sn}_2\text{S}_2$, *ACS Nano* **19**, 8561 (2025).
- [45] J. Corps, P. Vaqueiro, A. Aziz, R. Grau-Crespo, W. Kockelmann, J.-C. Jumas, and A. V. Powell, Interplay of metal-atom ordering, Fermi level tuning, and thermoelectric properties in cobalt shandites $\text{Co}_3\text{M}_2\text{S}_2$ ($M = \text{Sn}, \text{In}$), *Chem. Mater.* **27**, 3946 (2015).
- [46] M. Yan, Y. Jin, X. Hou, Y. Guo, A. Tsaturyan, A. Makarova, D. Smirnov, Y. Dedkov, and E. Voloshina, Topological quasi-2D semimetal $\text{Co}_3\text{Sn}_2\text{S}_2$: Insights into electronic structure from NEXAFS and resonant photoelectron spectroscopy, *J. Phys. Chem. Lett.* **12**, 9807 (2021).
- [47] G. Li, Q. Xu, W. Shi, C. Fu, L. Jiao, M. E. Kamminga, M. Yu, H. Tüysüz, N. Kumar, V. Süß, R. Saha, A. K. Srivastava, S. Wirth, G. Auffermann, J. Gooth, S. Parkin, Y. Sun, E. Liu, and C. Felser, Surface states in bulk single crystal of topological semimetal $\text{Co}_3\text{Sn}_2\text{S}_2$ toward water oxidation, *Sci. Adv.* **5**, eaaw9867 (2019).
- [48] Y. Zhao, Y. Zhu, F. Jiang, Y. Li, Y. Meng, Y. Guo, Q. Li, Z. Huang, S. Zhang, R. Zhang, J. C. Ho, Q. Zhang, W. Liu, and C. Zhi, Vacancy modulating $\text{Co}_3\text{Sn}_2\text{S}_2$ topological semimetal for aqueous zinc-ion batteries, *Angew. Chem. Int. Ed.* **61**, e202111826 (2022).
- [49] T. Kubodera, H. Okabe, Y. Kamihara, and M. Matoba, Ni substitution effect on magnetic and transport properties in metallic ferromagnet $\text{Co}_3\text{Sn}_2\text{S}_2$, *Phys. B Condens. Matter* **378-380**, 1142 (2006).
- [50] P. Gütlisch, K. J. Range, C. Felser, C. Schultz-Münzenberg, W. Tremel, D. Walcher, and M. Waldeck, The valence states of nickel, tin, and sulfur in the ternary chalcogenide $\text{Ni}_3\text{Sn}_2\text{S}_2$ -XPS, ^{61}Ni , and ^{119}Sn Mössbauer investigations, and band structure calculations, *Angew. Chem. Int. Ed.* **38**, 2381 (1999).
- [51] Y. Sakai, R. Tanakadate, M. Matoba, I. Yamada, N. Nishiyama, T. Irifune, K. Funakoshi, T. Kunimoto, Y. Higo, and Y. Kamihara, Magnetic properties of shandite-phase $\text{Co}_{3-x}\text{Fe}_x\text{Sn}_2\text{S}_2$ ($x = 0-1.0$) obtained with high pressure synthesis, *J. Phys. Soc. Jpn.* **84**, 044705 (2015).
- [52] Y. Zhang and C. Uher, Magnetic and transport properties of Fe-doped Weyl semimetal $\text{Co}_3\text{Sn}_2\text{S}_2$, *J. Alloys Compd.* **911**, 165089 (2022).
- [53] F. Sun, T. Zhang, C. J. Yi, Y. L. Wu, H. Zhao, Q. Wu, Y. G. Shi, H. Weng, and J. Zhao, Spin-polarized gap in the magnetic Weyl semimetal $\text{Co}_3\text{Sn}_2\text{S}_2$, *Phys. Rev. B* **104**, L100301 (2021).
- [54] W. Schnelle, A. Leithe-Jasper, H. Rosner, F. M. Schappacher, R. Pöttgen, F. Pielnhofer, and R. Wehrich, Ferromagnetic ordering and half-metallic state of $\text{Sn}_2\text{Co}_3\text{S}_2$ with the shandite-type structure, *Phys. Rev. B* **88**, 144404 (2013).
- [55] M. A. Kassem, Y. Tabata, T. Waki, and H. Nakamura, Single crystal growth and characterization of kagomé-lattice shandites $\text{Co}_3\text{Sn}_{2-x}\text{In}_x\text{S}_2$, *J. Cryst. Growth* **426**, 208 (2015).
- [56] S. N. Guin, P. Vir, Y. Zhang, N. Kumar, S. J. Watzman, C. Fu, E. Liu, K. Manna, W. Schnelle, J. Gooth, C. Shekhar, Y. Sun, and C. Felser, Zero-field Nernst effect in a ferromagnetic Kagome-lattice Weyl-semimetal $\text{Co}_3\text{Sn}_2\text{S}_2$, *Adv. Mater.* **31**, 1806622 (2019).
- [57] M. B. Brodsky, Thermoelectricity in metals and alloys, *Phys. Bull.* **24**, 620 (1973).
- [58] P. Bag, W. Z. Liu, Y.-K. Kuo, C. N. Kuo, and C. S. Lue, Thermoelectric properties of chemically substituted Heusler-type $\text{Ru}_{2-x}\text{Nb}_{1+x}\text{Ga}$ and $\text{Ru}_2\text{NbGa}_{1-x}\text{M}_x$ ($M = \text{In}, \text{Ge}, \text{and Sn}$) alloys, *J. Alloys Compd.* **849**, 156617 (2020).
- [59] C. S. Lue and Y. K. Kuo, Thermoelectric properties of the semimetallic Heusler compounds $\text{Fe}_{2-x}\text{V}_{1+x}\text{M}$ ($M = \text{Al}, \text{Ga}$), *Phys. Rev. B* **66**, 085121 (2002).
- [60] S. Mondal, C. Mazumdar, R. Ranganathan, E. Alleno, P. C. Sreeparvathy, V. Kanchana, and G. Vaitheeswaran, Ferromagnetically correlated clusters in semimetallic Ru_2NbAl Heusler alloy and its thermoelectric properties, *Phys. Rev. B* **98**, 205130 (2018).
- [61] Y. K. Kuo, K. M. Sivakumar, H. C. Chen, J. H. Su, and C. S. Lue, Anomalous thermal properties of the Heusler alloy $\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Ga}$ near the martensitic transition, *Phys. Rev. B* **72**, 054116 (2005).

- [62] J. Bhattacharya, P. Sadhukhan, S. Sarkar, V. K. Singh, A. Gloskovskii, S. R. Barman, and A. Chakrabarti, Bulk electronic structure of Ni_2MnGa studied by density functional theory and hard x-ray photoelectron spectroscopy, *Phys. Rev. B* **108**, L121114 (2023).
- [63] J. Barth, G. H. Fecher, B. Balke, S. Ouardi, T. Graf, C. Felser, A. Shkabko, A. Weidenkaff, P. Klaer, H. J. Elmers, H. Yoshikawa, S. Ueda, and K. Kobayashi, Itinerant half-metallic ferromagnets Co_2TiZ ($Z = \text{Si}, \text{Ge}, \text{Sn}$): *Ab initio* calculations and measurement of the electronic structure and transport properties, *Phys. Rev. B* **81**, 064404 (2010).
- [64] S. Arsenijević, R. Gaál, A. S. Sefat, M. A. McGuire, B. C. Sales, D. Mandrus, and L. Forró, Pressure effects on the transport coefficients of $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$, *Phys. Rev. B* **84**, 075148 (2011).
- [65] T. M. Tritt, *Thermal Conductivity: Theory, Properties, and Applications* (Springer Science+Business Media, Berlin/Heidelberg, Germany, 2005).
- [66] J. W. Yan, F. Liu, G.-h. Ma, B. Gong, J. Zhu, X. G. Wang, W. Ao, C. Zhang, Y. Li, and J. Li, Suppression of the lattice thermal conductivity in NbFeSb -based half-Heusler thermoelectric materials through high entropy effects, *Scr. Mater.* **157**, 129 (2018).
- [67] D. M. Rowe, *CRC Handbook of Thermoelectrics* (CRC Press, Boca Raton, Florida, 1995).
- [68] G. J. Snyder and E. S. Toberer, Complex thermoelectric materials, *Nat. Mater.* **7**, 105 (2008).
- [69] C.-C. Chang, C.-H. Liu, C.-C. Wu, P. Bag, and Y.-K. Kuo, Thermoelectric properties of $(\text{HgTe})_{0.55}(\text{PbTe})_{0.45}$ eutectic composite with In doping, *Mater. Res. Bull.* **129**, 110916 (2020).
- [70] B. Ramachandran, K. K. Wu, Y. K. Kuo, L. S. Guo, and L. M. Wang, Compositional effects on the low-temperature transport properties of non-stoichiometric $\text{Bi}_2\text{Te}_{x-y}\text{Se}_y$ -based crystals, *J. Phys. D Appl. Phys.* **50**, 025302 (2017).
- [71] H.-S. Kim, Z. M. Gibbs, Y. Tang, H. Wang, and G. J. Snyder, Characterization of Lorenz number with Seebeck coefficient measurement, *APL Mater.* **3**, 041506 (2015).
- [72] P. Bag, Y. H. Lin, Y. K. Kuo, C. N. Kuo, and C. S. Lue, Physical properties of the full Heusler-type $\text{Ru}_{2-x}\text{Fe}_x\text{NbAl}$ ($x = 0.00\text{--}0.50$) alloys, *J. Alloys Compd.* **945**, 169318 (2023).
- [73] P. Bag, Y.-C. Su, Y.-K. Kuo, Y.-C. Lai, and S.-K. Wu, Physical properties of face-centered cubic structured high-entropy alloys: Effects of NiCo, NiFe, and NiCoFe alloying with Mn, Cr, and Pd, *Phys. Rev. Mater.* **5**, 085003 (2021).
- [74] J. Callaway, Model for lattice thermal conductivity at low temperatures, *Phys. Rev.* **113**, 1046 (1959).
- [75] A. Saadi, L. e. H. Omari, and A. Boudali, Sn replacement influence on magnetic, electronic, thermodynamic, thermoelectric and transport properties in shandite compounds of $\text{Co}_3\text{In}_{2-x}\text{Sn}_x\text{S}_2$, *Eur. Phys. J. B* **93**, 180 (2020).
- [76] K. Ciesielski, K. Synoradzki, I. Veremchuk, P. Skokowski, D. Szymański, Y. Grin, and D. Kaczorowski, Thermoelectric performance of the half-Heusler phases RNiSb ($R = \text{Sc}, \text{Dy}, \text{Er}, \text{Tm}, \text{Lu}$): High mobility ratio between majority and minority charge carriers, *Phys. Rev. Appl.* **14**, 054046 (2020).
- [77] M. Ohta, H. Obara, and A. Yamamoto, Preparation and thermoelectric properties of chevreel-phase $\text{Cu}_x\text{Mo}_6\text{S}_8$ ($2.0 \leq x \leq 4.0$), *Mater. Trans.* **50**, 2129 (2009).
- [78] D. Guo, C. Hu, and C. Zhang, First-principles study on doping and temperature dependence of thermoelectric property of Bi_2S_3 thermoelectric material, *Mater. Res. Bull.* **48**, 1984 (2013).
- [79] M. R. Burton, S. Mehraban, J. McGettrick, T. Watson, N. P. Lavery, and M. J. Carnie, Earth abundant, non-toxic, 3D printed Cu_{2-x}S with high thermoelectric figure of merit, *J. Mater. Chem. A* **7**, 25586 (2019).
- [80] A. Damascelli, Probing the electronic structure of complex systems by ARPES, *Phys. Scr.* **2004**, 61 (2004).
- [81] J. M. D. Coey, *Magnetism and Magnetic Materials* (Cambridge University Press, Cambridge, 2010).
- [82] S. Onoda, N. Sugimoto, and N. Nagaosa, Intrinsic versus extrinsic anomalous Hall effect in ferromagnets, *Phys. Rev. Lett.* **97**, 126602 (2006).
- [83] T. Miyasato, N. Abe, T. Fujii, A. Asamitsu, S. Onoda, Y. Onose, N. Nagaosa, and Y. Tokura, Crossover behavior of the anomalous Hall effect and anomalous Nernst effect in itinerant ferromagnets, *Phys. Rev. Lett.* **99**, 086602 (2007).
- [84] Y. Tian, L. Ye, and X. Jin, Proper scaling of the anomalous Hall effect, *Phys. Rev. Lett.* **103**, 087206 (2009).