Topological Ferromagnets



Zero-Field Nernst Effect in a Ferromagnetic Kagome-Lattice Weyl-Semimetal Co₃Sn₂S₂

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The discovery of magnetic topological semimetals has recently attracted significant attention in the field of topology and thermoelectrics. In a thermoelectric device based on the Nernst geometry, an external magnet is required as an integral part. Reported is a zero-field Nernst effect in a newly discovered hard-ferromagnetic kagome-lattice Weyl-semimetal $Co_3Sn_2S_2$. A maximum Nernst thermopower of $\approx 3 \ \mu V \ K^{-1}$ at 80 K in zero field is achieved in this magnetic Weyl-semimetal. The results demonstrate the possibility of application of topological hard magnetic semimetals for low-power thermoelectric devices based on the Nernst effect and are thus valuable for the comprehensive understanding of transport properties in this class of materials.

The advantages such as the absence of moving parts and noise make the thermoelectric technology promising for energy conversion and solid-state cooling.^[1-6] Its progress largely relies on the Seebeck effect, i.e., the generation of an electrical voltage longitudinal to a temperature gradient. In contrast, configurations based on the Nernst effect, which is the generation of a transverse electrical signal in a magnetic field, have been significantly less studied,^[7–9] partly as an external magnetic field is usually required to observe a Nernst signal. In conventional thermoelectric devices based on the Seebeck effect, the heat reservoir

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is required to be a part of the electrical circuit (**Figure 1**a). In contrast, the multiterminal thermoelectric devices based on the Nernst effect enable spatial separation of the heat reservoir from the electric circuitry.^[10] Moreover, in Nernst devices, there is no need for both p- and n-type materials as the polarity of the voltage can be reversed by reversing the magnetic field direction.^[8,11] Therefore, Nernst devices overcome certain problems of Seebeck devices, where the different thermal expansion coefficients of p- and n-type materials lead to compatibility issues.

In a ferromagnetic material, the genera-

tion of an additional electric voltage orthogonal to the applied temperature gradient due to the internal magnetization is referred to as the anomalous Nernst effect (ANE).^[11,12] In general, the Nernst thermopower (S_{xy}) of a soft magnetic material is zero once the magnetic field is removed. Therefore, a part generating an external magnetic field needs to be integrated in devices based on the Nernst effect, which is a big obstacle for the thermomagnetic devices. A possible solution could be the use of a hard magnetic material, where an anomalous Nernst signal (S_{xy}^{A}) can be obtained in zero field. Such a permanent magnetic material remains in a magnetized state even when the external magnetic field is removed.^[13,14] Magnetic ferrites and rare-earth-based hard magnets have been extensively studied owing to their wide range of functional applications including magnetic motors, magnetic recording media, magnetic fluids, and electromagnetic wave filters.^[13-16] A novel potential application with hard magnets is energy conversion based on the Nernst effect, which has not attracted significant attention. Few examples of such materials include thin films of the alloys FePt, FePd, L10-MnGa, D022-Mn2Ga, Co/Ni, dilute magnetic semiconductor (DMS) Ga1-xMnxAs, and recently Mn₃Sn.^[17-20] Therefore, novel hard-magnetic materials are required. Studies on their thermomagnetic properties are of significance in terms of both technological application and fundamental understanding. A promising approach is to search for a new candidate from the library of topological materials as they share many mutual features with the thermoelectric materials.

In the current decade, topological materials attract significant research interest. These newly discovered materials exhibit various physical properties such as chiral anomaly, high carrier mobility, giant magnetoresistance, and mixed axial-gravitational anomaly due to the topological band structure.^[21–26] They are

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Figure 1. Schematics of thermoelectric modules, crystal structure, and magnetization of $Co_3Sn_2S_2$. a,b) Thermoelectric modules in the Seebeck and Nernst geometries, respectively. In the conventional Seebeck device, both n- and p-type legs are required. In contrast, in the Nernst device, a single type of thermopile can be used and the polarity of the voltage can be altered by changing the magnetization direction. c) Crystal structure of $Co_3Sn_2S_2$. Sn atoms are distributed over the interlayer (marked as Sn(1)) and in the kagome layers (marked as Sn(2)). The structure consists of the flat hexagonal kagome unit composed of Co and Sn(2) (see the *c*-axis view). The Sn(1) atoms are surrounded by a couple of Co_3 triangles in a trigonal-antiprismatic configuration. S atoms capped the Co_3 triangles above or below the kagome sheets. d) Field-dependent magnetization of $Co_3Sn_2S_2$ at different temperatures. The inset shows a magnified plot.

also potential candidates for functional applications in quantum computing, infrared sensors, and heterogenous catalysis.^[27–29] In this context, the discovery of magnetic topological materials created a new frontier in the field.^[30–37] These exotic magnetic topological materials provide a new scope in the thermoelectric research as the topological band structure effect can enhance the thermoelectric response.

Here, we show that the topological ferromagnets with large coercive fields (H_c) could be potential candidates for observation of the Nernst effect in zero field. As a case study material, we choose Co3Sn2S2, a newly discovered hard-magnetic kagome-lattice Weyl-semimetal. Recently, a large intrinsic anomalous Hall conductivity (AHC) and giant anomalous Hall angle (AHA) have been observed in Co₃Sn₂S₂, originating from the topological band structure.^[38,39] We show that a singlecrystalline Co₃Sn₂S₂ exhibits a maximum S_{xy}^{A} value of $\approx 3 \,\mu V \, K^{-1}$ at 80 K in zero field, which is significantly high considering its magnetic moment of $\approx 0.89 \ \mu_B \ f.u.^{-1}$. We employed a combined approach including electrical and thermoelectric measurements and first-principles calculations to elucidate this observation. Our complementary electrical transport measurement and density functional theory (DFT)-based calculations indicate that the high Nernst signal in Co₃Sn₂S₂ originates from the topological band structure.

The ternary chalcogenide $Co_3Sn_2S_2$ is a member of the shandite family $A_3M_2X_2$ (A = Ni, Co, Rh, Pd; M = Pb, In, Sn, Tl; X = S, Se) and crystallizes in a rhombohedral structure (space group: $R\overline{3}m$).^[40,41] In this structure, Sn atoms are

distributed over interlayers (Sn1) and in the kagome layers (Sn2). The Sn(1) atoms are surrounded by two Co₃ triangles in a trigonal-antiprismatic configuration, whereas the Sn(2) atoms form a hexagonal planar layer with the magnetic Co atoms arranged on a kagome lattice in the *ab*-plane (Figure 1c). Each of the Co₃ triangles is capped above or below the kagome sheets by an S atom. The material is a type-IA half-metallic ferromagnet with a Curie temperature of $T_c = 177$ K and magnetic moment of 0.29 $\mu_{\rm B}/{\rm Co.}^{[40,41]}$ The strong magnetic anisotropy leads to a long-range quasi-2D type of magnetism with a spontaneous out-of-plane magnetization.^[40,41]

The single crystals of $\text{Co}_3\text{Sn}_2\text{S}_2$ were synthesized from the elements using a melting reaction followed by slow cooling. The asgrown crystal was characterized by Laue X-ray diffraction (XRD) and powder XRD (see the Experimental Section, and Figure S1, Supporting Information). For the electrical and thermoelectric measurements, the crystal was oriented and cut into a bar shape. As the material exhibits a highly anisotropic out-of-plane magnetization, we used the following configuration: magnetic field (μ_0H) || *c*-axis and electrical current (*I*) or thermal gradient (ΔT) || *ab*-plane.

Figure 1d shows the magnetization (*M*) as a function of the magnetic field ($\mu_0 H$) for Co₃Sn₂S₂ at different temperatures. Distinct rectangular-shaped hysteresis loops with large coercive fields H_c of \approx 3650 and \approx 570 Oe are observed at 2 and 100 K, respectively. The origin of the large coercivity is attributed to the strong magnetic anisotropy of the compound (see Discussion, Supporting Information).^[42] This distinct hysterics loop is observed up to \approx 100 K; it becomes less pronounced with the further increase in

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Figure 2. Nernst thermopower data. a) Temperature (*T*)-dependent anomalous Nernst thermopower (S_{xy}^{A}) of $Co_3Sn_2S_2$ in zero field, measured using a magnetized sample. b) Magnetic field dependences of the Nernst thermopower (S_{xy}) of $Co_3Sn_2S_2$ at different temperatures. The extracted zero-field anomalous Nernst thermopower (S_{xy}) as a function of *T* is presented in the inset.

temperature and vanishes as the temperature approaches T_c . The temperature-dependent magnetization measurement indicates a magnetic transition at \approx 177 K (Figure S2, Supporting Information). Overall, the magnetic measurement data indicate that Co₃Sn₂S₂ exhibits a sizable H_c up to \approx 120 K.

After we demonstrated the hard-magnetic nature of $Co_3Sn_2S_2$, we investigated the anomalous Nernst thermopower (S_{w}^{A}) in zero magnetic field. We magnetized the sample by applying a field of $\pm 1 \text{ T}$ (>*H*_c) to orient the magnetic moments along the *c*-axis and then switched off the field. Figure 2a presents S_{xy}^{A} of $Co_3Sn_2S_2$ in zero field as a function of the temperature. S_{xy}^{A} increases with the temperature and reaches a peak value of $\approx 3 \,\mu\text{V}$ K⁻¹ at ≈ 80 K. The further increase in the temperature leads to a decrease in S_{xy}^{A} ; above ≈ 120 K, the signal is almost zero as the compound loses its hard-magnetic structure. The observed maximum value of S_{xy}^{A} for Co₃Sn₂S₂ is remarkable considering the magnetic moment of ${\approx}0.89~\mu_B$ f.u.^-1 (see Discussion in the Supporting Information). Further, we investigated the magnetic-field dependence of the Nernst thermopower $S_{xy}(\mu_0 H)$ at different temperatures (Figure 2b and Figure S4, Supporting Information). As discussed in the introduction that ferromagnets exhibit ANE below their $T_{\rm C}$, this system starts to exhibit an anomalous behavior in S_{xy} . The effect of the large magnetocrystalline anisotropy of this compound is evident in the $S_{xy}(\mu_0 H)$ data. The anomalous behavior in $S_{xy}(\mu_0 H)$ (Figure 2b and Figure S4, Supporting Information) can be observed up to the Curie temperature of the compound ($T_{\rm C} = 177$ K). Above $T_{\rm C}$ the Co₃Sn₂S₂ does not show any ANE as it is no longer magnetic in nature. Below 100 K, a rectangular-shaped hysteresis loop was observed in the $S_{xy}(\mu_0 H)$ data; S_{xy} maintains a plateau value after a certain field. The change of the sign of S_{xy} is due to the flipping of the magnetic moment of the Co atoms with the direction of $\mu_0 H$ (positive to negative). This observation is consistent with the zero-field measurement of a magnetized sample. The finite H_{c} in the data below ≈ 120 K enables to estimate the zero-field S_{xy} , i.e., S_{xy}^{A} . The temperature-dependent estimated values of S_{xy}^{A} from the field sweep data are in good agreement with the temperature-dependent zero-field measurement results (inset in Figure 2b). In the $S_{xy}(\mu_0 H)$ data, we observed S_{xy}^A up to ≈ 170 K by extrapolating the slope of the high-field data; however, estimated S_{xy}^{A} above ≈ 120 K is not a true zero-field anomalous value, as the hard-magnetic nature disappears above ≈120 K.

In order to understand the origin of the large S_{xy}^A of $Co_3Sn_2S_2$, we measured the electrical resistivity (ρ_{xx}) , longitudinal thermoelectric response, i.e., the Seebeck coefficient (S_{xx}) , and Hall resistivity (ρ_{yx}) . The temperature dependence of the electrical resistivity (ρ_{xx}) is presented in **Figure 3a**. ρ_{xx} decreases with the decrease in the temperature reaching a value of $\approx 55 \ \mu\Omega$ cm at 2 K, indicating the metallic nature of the compound. The anomaly at $T_c = 177 \ K$ in ρ_{xx} reflects the onset of a magnetic transition. The negative sign of S_{xx} is attributed to the dominant n-type charge carriers in $Co_3Sn_2S_2$ (Figure 3b). S_{xx} linearly increases with the temperature and becomes approximately constant in the range of 50–120 K. Above 120 K, S_{xx} increases with the temperature and exhibits an anomaly near T_c .

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It is known that the intrinsic band structure effect from the Berry curvature can lead to a large anomalous Hall effect (AHE) in a topological material (see the Experimental Section). Therefore, we estimated the Hall conductivity (σ_{xy}) of Co₃Sn₂S₂ from the measured electrical resistivity (ρ_{xx}) and Hall resistivity (ρ_{yx})

$$\sigma_{xy} = \frac{\rho_{yx}}{\rho_{yx}^2 + \rho_{xx}^2} \tag{1}$$

Figure 3c presents $\sigma_{x\gamma}$ of $Co_3Sn_2S_2$ as a function of the magnetic field at different temperatures. The trend and values of the AHC ($\sigma_{\rm H}^{\rm A}$) are fully consistent with previous observations.^[38] Below 100 K, a large AHE is observed with a sharp rectangular-shaped loop, which arises from the topological-band-structure-enhanced Berry curvature effect.^[38] This observation indicates the topological-band-structure-related origin of the large $S_{x\gamma}^{\rm A}$ of $Co_3Sn_2S_2$ as the transverse thermoelectric response is associated with the Berry curvature, as discussed below.

The notion of the topological band structure effect in transverse thermoelectric responses can be understood by analyzing the temperature dependence of the anomalous transverse thermoelectric conductivity (α_N^A). Therefore, we estimated the transverse thermoelectric conductivity (α_{yx}) using the measured components of resistivity (ρ_{xx} , ρ_{yx}) and Seebeck and Nernst thermopowers (S_{xx} and $S_{xy} = -S_{yx}$)

$$\alpha_{yx} = \frac{S_{yx}\rho_{xx} - S_{xx}\rho_{yx}}{\rho_{xx}^2 + \rho_{yx}^2}$$
(2)

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Figure 3. Electrical transport, Seebeck coefficient, and thermoelectric conductivity. a) *T*-dependent electrical resistivity (ρ_{xx}). The change in slope in ρ_{xx} around \approx 177 K corresponds to a magnetic transition (marked with an arrow). b) *T* dependence of the Seebeck coefficient (S_{xx}) of Co₃Sn₂S₂. c) Magnetic field dependence of the Hall conductivity (σ_{xy}). The *T* dependence of the AHC (σ_{H}^{A}) is shown in the inset. d) *T* dependence of the experimentally determined anomalous transverse thermoelectric conductivity (α_{N}^{A}). The dotted line indicates magnetic transition temperature.

Figure 3d shows the anomalous part of α_{yx} of Co₃Sn₂S₂. The S_{xy} and ρ_{yx} exhibit anomalous behavior below $T_{\rm C}$. Therefore, a nonzero $\alpha_{\rm N}^{\rm A}$ value can be observed only below $T_{\rm C}$. In Co₃Sn₂S₂, the $\alpha_{\rm N}^{\rm A}$ shows a peak value around 150 K and decreases upon cooling, although the saturation magnetization increases. A similar observation was reported in an anomalous Hall resistance measurement.^[38] The observation is an evidence that the anomalous Nernst signal originates from a different source, rather than from the magnetization.

For a deeper understanding, we carried out DFT- and abinitio-based electronic structure calculations and numerical simulations of $\sigma_{\rm H}^{\rm A}$ and $\alpha_{\rm N}^{\rm A}$ using the Kubo formula. Figure 4a shows the calculated electronic structures of Co₃Sn₂S₂ with and without spin-orbit coupling (SOC). The spin-down channel of the bands has a gap of ≈ 0.35 eV, while the spin-up channel is semimetallic (see also Figure S6, Supporting Information). Moreover, for the spin-up channel along the Γ -L and L-U paths, linear band crossings can be observed near the charge-neutral Fermi point (E_0). In the absence of SOC, the full Hamiltonian could be split into the direct product of a spinless Hamiltonian and spin-Hamiltonian, in which the band degeneracy of each spin channel is determined by the spinless Hamiltonian. Owing to the mirror symmetry of the lattice, the band inversion of the spin-up channel forms a nodal line in the mirror plane (M_y) . Considering the combination of inversion and C3 rotational symmetries, there are six nodal lines in total (Figure 4b). The application of SOC breaks the mirror symmetry and lifts the degeneracy of the nodal lines, with one pair of Weyl points remaining on it.

Figure 4c shows the computed $\alpha_{\rm N}^{\rm A}$ as a function of the position of the Fermi level $(E_{\rm F})$ at 80 K. We would like to note that unlike intrinsic AHE, the intrinsic part of α_{N}^{A} depends on the strength of the Berry curvature near $E_{\rm F}$ rather than on the Berry curvature of all of the occupied bands (see the Experimental Section).^[43,44] The anomalous Nernst conductivity (ANC) of $Co_3Sn_2S_2$ exhibits a strong E_F dependence, which is not observed for $\sigma_{\rm H}^{\rm A}$ (Figure S7, Supporting Information). $\sigma_{\rm H}^{\rm A}$ maintains a plateau value (≈ 1000 S cm⁻¹) over an energy window of ≈ 100 meV around $E_{\rm F}$. In contrast, $\alpha_{\rm N}^{\rm A}$ has a peak value slightly away from $E_{\rm F}$ and then rapidly decreases away from $E_{\rm F}$ due to the modulation of the Berry curvature strength. This finding was further supported by our temperaturedependent $\sigma_{\rm H}^{\rm A}$ and $\alpha_{\rm N}^{\rm A}$ data. The experimental $\sigma_{\rm H}^{\rm A}$ exhibits a small change below ≈ 100 K. In contrast, $\alpha_{\rm N}^{\rm A}$ exhibits a monotonous decreasing trend with the decrease in temperature.

In a previous study, angle-resolved photoelectron spectroscopy and low-temperature Shubnikov–de Haas quantum oscillation analysis indicated that $E_{\rm F}$ was slightly shifted toward the valence bands in Co₃Sn₂S₂.^[38] In this study, we use a sample with a similar quality to that for the AHE, indicating a similar position of $E_{\rm F}$. We calculated the temperature dependence of $\alpha_{\rm N}^{\rm A}$ below ordering temperature using different positions of $E_{\rm F}$ of Co₃Sn₂S₂ (Figure S8, Supporting Information). $\alpha_{\rm N}^{\rm A}$ exhibits a monotonous increase with *T* for $E_{\rm F} = E_0 - 0.07$ eV to $E_0 - 0.10$ eV and well agrees with the experimental value when $E_{\rm F} = E_0 - 0.08$ eV (Figure 4d). Moreover, the temperature-modified Berry curvature distributions ($\Omega_{\rm N}$) at 80 and 150 K for $E_{\rm F} = E_0 - 0.08$ eV







Figure 4. Electronic structure and calculated transverse thermoelectric conductivity. a) Electronic structures of $Co_3Sn_2S_2$ with and without SOC. The application of SOC breaks the mirror symmetry leading to gapping of the nodal lines due to the degeneracy lifting of the bands. b) Temperature-modified Berry curvature distribution (Ω_N) at 80 K in the Brillouin zone with the magnetization along the *c*-axis for $E_F = E_0 - 0.08$ eV. The green lines indicate the nodal rings. c) Theoretically calculated ANC (α_N^A) as a function of the chemical potential with respect to the charge neutrality point E_0 at T = 80 K. d) Theoretically estimated temperature-dependent α_N^A with $E_F = E_0 - 0.08$ eV below ordering temperature. The calculated value is in good agreement with the measured value.

also have large nonzero values (Figure 4b and Figure S9, Supporting Information), suggesting a topological band structure contribution in the transverse thermoelectric transport.

Figure 5 compares the absolute value of peak $S_{x\gamma}^A$ of different class of materials from the literature with Co₃S n_2S_2 .^[17–19,34,45–49] A maximum $S_{x\gamma}^A$ of $\approx 3 \ \mu V \ K^{-1}$ at $T = 80 \ K$ is measured in the case of Co₃Sn₂S₂. In addition, Co₃Sn₂S₂



Figure 5. Absolute value of anomalous Nernst thermopowers (S_{xy}^A) for ferromagnetic metals, antiferromagnet Mn₃Sn, DMS Ga_{0.93}Mn_{0.07} As from the literature and Co₃Sn₂S₂. The shaded region indicates hard and soft ferromagnetic metals.^[17–19,34,45–49]

exhibits a zero-field signal, which is not the case for nonmagnetic and soft-ferromagnetic metals. Although the maximum S_{xy}^{A} of Co₃Sn₂S₂ (\approx 3 μ V K⁻¹ at T = 80 K) is lower than that of topological ferromagnet Co₂MnGa ($\approx 6 \mu V K^{-1}$ at T = 300 K) and DMS $Ga_{0.93}Mn_{0.07}As$ ($\approx 8.1 \text{ }\mu\text{V} \text{ } \text{K}^{-1}$ at T = 10 K), but the present results provide a possible guiding principle for the observation of large zero-field anomalous Nernst thermopower in a hard-ferromagnetic topological semimetal at elevated temperature. Moreover, considering the magnetic moments of $\approx 0.79 \ \mu_B \ f.u.^{-1}$ for $Co_3Sn_2S_2$ (*T* = 80 K) and $\approx 3.7 \mu_B$ f.u.⁻¹ for Co_2MnGa (*T* = 300 K), the present result is more interesting and due to lower magnetic moment the inherent stray field for Co₃Sn₂S₂ will be low. Figure S10 in the Supporting Information compares the ratios of the strengths of the anomalous Nernst signals to their saturation magnetizations of different hard and soft ferromagnetic metals and antiferromagnet Mn₃Sn.^[17,19,34,45-49] The Y-axis of the plot $(S_{xy}^{A}/\mu_0 M)$ represents the ratio of S_{xy}^{A} to the magnetic moment $(\mu_0 M)$. The values of $S_{xv}^{A}/\mu_0 M$ for the topological ferromagnets are higher than those of the trivial ferromagnetic materials. A similar result was observed for the topological chiral antiferromagnet Mn₃Sn; however, it exhibited a lower Nernst signal than that of Co₃Sn₂S₂ (Figure S10, Supporting Information).^[19] $S_{xy}^{A}/\mu_0 M$ indicates that the strength of the transverse signal is significantly higher in Co₃Sn₂S₂ and indeed highest among those of ferromagnetic metals. This implies that the anomalous transport properties originate from the topological band structure effect and are independent of the strength of the magnetic moments.



In conclusion, magnetic topological semimetals are potential candidates for the observation of exotic anomalous transport properties. We showed that the hard ferromagnetic kagome-lattice Weyl-semimetal Co₃Sn₂S₂ from the shandite family exhibited a large ANE in zero field. Our experimental and DFT calculation results showed that the large ANE originated from the strong Berry curvature was associated with the nodal lines and Weyl points. Although the magnitude of the zero-field transverse signal of Co₃Sn₂S₂ was not sufficiently high for applications, this study shows that the topological material with a large H_c could be a potential candidate for a transverse thermoelectric and that the large signal can be achieved in zero field. Therefore, it is of interest to search for new hard magnets with high Curie temperatures from the library of magnetic topological materials.

Experimental Section

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Single-Crystal Growth of $Co_3Sn_2S_2$ and Characterization: The single crystals of $Co_3Sn_2S_2$ were grown using an elemental melting reaction followed by a slow cooling. As-purchased high-quality elemental cobalt (99.999%), tin (99.999%), and sulfur (99.999%) were used for the synthesis. Stoichiometric amounts of the elements (Co:Sn:S = 3:2:2) were loaded in an alumina crucible and then sealed in a quartz tube. The tube was heated to 1323 K over a period of 48 h, soaked for 24 h, and then slowly cooled down to 873 K over 7 days. The power XRD measurement was performed at room temperature using a Huber Image Plate Guinier Camera G670 operated with Cu K_{\alpha} radiation (λ = 1.54056 Å). The single crystallinity of the as-grown crystal was evaluated by the white-beam backscattering Laue XRD method. Well-characterized and aligned crystals were cut into bar shapes for transport and magnetization measurements. The typical dimensions of the crystals used for the electrical and thermal transport measurements were $\approx 7 \times 1.3 \times 0.4$ mm³.

Electrical Transport and Magnetization Measurements: The electrical transport properties were measured using a PPMS9 instrument (ACT option, Quantum Design). The standard four-probe method was used in all of the measurements. In order to correct for contact misalignment, the measured data were field-symmetrized and antisymmetrized. The magnetization measurement was performed using a Quantum Design MPMS3 instrument.

Thermoelectric Transport Measurements: All of the thermal transport experiments were performed in a physical property measurement system (PPMS) cryostat. The Seebeck and Nernst thermoelectric measurements were carried out in the one-heater two-thermometer configuration. In the field sweep experiments in a temperature range of 13-310 K, the PPMS as well as an external nanovoltmeter and current source (Keithley) were controlled using LabVIEW. The temperature gradient was generated using a resistive heater, connected to a gold-coated flat copper wire at one end of the sample. The thermal gradient ΔT was applied along the *ab*-plane of the sample, while the magnetic field was applied along the *c*-axis. Another gold-plated flat copper wire was attached to the puck clamp for the heat sink. In order to measure the temperature gradient, two gold-plated copper leads were attached directly to the sample using a silver-filled epoxy along the thermal gradient direction. The distance between the thermometers was ≈3.5 mm. In the Seebeck and Nernst measurements, ΔT was typically set to ${\approx}1{-}3\%$ of the base temperature. Two copper wires were attached using the silver epoxy, orthogonal to the thermal gradient direction, to measure the transverse voltage. In order to correct the data for contact misalignment, the measured data were field-symmetrized and antisymmetrized. The thermal conductivity measurement was carried out in the PPMS using the thermal transport option.

Anomalous Nernst Thermopower of Different Class of Materials from the Literature: The highest absolute value of anomalous Nernst thermopowers (S_{xy}^A) were used for the different soft and hard ferromagnets, antiferromagnet Mn₃Sn, and DMS Ga_{0.93}Mn_{0.07}As well below their Curie temperatures. Their magnetizations ($\mu_0 M$ in Tesla) were used to calculate the ratios (Co/Ni film (300 K; ref. [17]), L1₀-FePt (300 K; ref. [17]), D0₂₂-Mn₂Ga (300 K; ref. [17]), L1₀-MnGa (300 K; ref. [17]), L1₀-FePd (300 K; ref. [17]), Ga_{0.93}Mn_{0.07}As (10 K, ref. [18]), Mn₃Sn (200 K; ref. [19]), Co₂MnGa (300 K; refs. [34,36]), Nd₂Mo₂O₇ ($T < T_c = 73$ K, B = 1 T [111]; ref. [45]), Fe (300 K; ref. [46]), Co (300 K; ref. [46]), Fe₃O₄ (300 K, B < 0.8 T; ref. [47]), MnGe (100 K, B > 5 T; ref. [48]), and Pt/Fe multilayer (N = 9, 300 K, B < 5 T; ref. [49]).

Ab Initio Calculations: For ab initio calculations, the DFT was employed using the Vienna ab initio simulation package,^[50] including the exchange–correlation energy through the Perdew–Burke–Ernzerhof functional. For the integrations in the *k*-space, a grid of $19 \times 19 \times 19$ points was used. The Wannier functions from the resulting band structure was extracted using WANNIER90^[51] to set up a tight-binding Hamiltonian, which reproduced the DFT band structure within a few millielectronvolts. With this Hamiltonian, the Berry curvature Ω_n was calculated

$$\Omega_{n,jj} = Im \sum_{m \neq n} \frac{\left\langle n \left| \frac{\partial H}{\partial k_i} \right| m \right\rangle \left\langle m \left| \frac{\partial H}{\partial k_j} \right| n \right\rangle - (i \leftrightarrow j)}{(\varepsilon_n - \varepsilon_m)^2}$$
(3)

where *m* and *n* are the eigenstates and ε are the eigenenergies of the Hamiltonian *H*.

Subsequently, the AHC $\sigma_{
m H}^{
m A}$ was calculated as

$$\sigma_{\rm H}^{\rm A} = -\frac{e^2}{\hbar} \sum_n \int \frac{\mathrm{d}k}{(2\pi)^3} \Omega_{n,xy}(k) f_{nk} \tag{4}$$

where f_{nk} is the Fermi–Dirac distribution for a band n at a k-point. The ANC $\alpha^{\rm A}_{\rm A}$ below ordering temperature is[^{43]}

$$\alpha_{\rm N}^{\rm A} = \frac{e}{T\hbar} \int \frac{dk}{(2\pi)^3} \Omega_{\rm N} \tag{5}$$

If $\beta = k_{\rm B}T$ was defined, where $k_{\rm B}$ is the Boltzmann constant, the temperature-modified Berry curvature distribution can be expressed as

$$\Omega_{\rm N} = \sum_{n} \Omega_{n, yx} \left(k \right) \left\{ \left(\varepsilon_{nk} - \mu \right) f_{nk} + k_{\rm B} T \ln \left[1 + e^{-\beta(\varepsilon_{nk} - \mu)} \right] \right\}$$
(6)

 Ω_N has a finite value only around the Fermi energy. Therefore, σ_H^A is related to the summation of the Berry curvatures of all of the occupied bands below the Fermi energy. In contrast, α_N^A is related to the Berry curvature of the occupied bands near the Fermi energy. For the integrations over the whole Brillouin zone in the AHE and ANE calculations, a mesh of 251 \times 251 \times 251 k-points was employed, providing converged results. Discussion on finite-temperature DFT calculation has been given in the Supporting Information.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

hard magnets, magnetic Weyl-semimetals, Nernst effect, thermoelectrics, zero-field Nernst thermopower

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- D. M. Rowe, CRC Handbook of Thermoelectrics, CRC Press, Boca Raton, FL, USA 1995.
- [2] J. He, T. M. Tritt, Science 2017, 357, 1369.
- [3] G. J. Snyder, E. S. Toberer, Nat. Mater. 2008, 7, 105.
- [4] G. Tan, L.-D. Zhao, M. G. Kanatzidis, Chem. Rev. 2016, 116, 12123.
- [5] T. Zhu, Y. Liu, C. Fu, J. P. Heremans, G. J. Snyder, X. Zhao, Adv. Mater. 2017, 29, 1605884.
- [6] K. Biswas, J. He, I. D. Blum, C.-I. Wu, T. P. Hogan, D. N. Seidman, V. P. Dravid, M. G. Kanatzidis, *Nature* **2012**, *489*, 414.
- [7] K. Behnia, H. Aubin, Rep. Prog. Phys. 2016, 79, 046502.
- [8] S. J. Watzman, T. M. McCormick, C. Shekhar, S.-C. Wu, Y. Sun, A. Prakash, C. Felser, N. Trivedi, J. Heremans, *Phys. Rev. B* 2018, 97, 161404.
- [9] C. Fu, S. N. Guin, S. J. Watzman, G. Li, E. Liu, N. Kumar, V. Süß, W. Schnelle, G. Auffermann, C. Shekhar, Y. Sun, J. Gooth, C. Felser, *Energy Environ. Sci.* 2018, *11*, 2813.
- [10] H. Thierschmann, R. Sánchez, B. Sothmann, F. Arnold, C. Heyn, W. Hansen, H. Buhmann, L. W. Molenkamp, *Nat. Nanotechnol.* 2015, *10*, 854.
- [11] S. R. Boona, R. C. Myers, J. P. Heremans, Energy Environ. Sci. 2014, 7, 885.
- [12] T. Miyasato, N. Abe, T. Fujii, A. Asamitsu, S. Onoda, Y. Onose, N. Nagaosa, Y. Tokura, *Phys. Rev. Lett.* **2007**, *99*, 086602.
- [13] J. M. D. Coey, IEEE Trans. Magn. 2011, 47, 4671.
- [14] S. Hirosawa, M. Nishino, S. Miyashita, Adv. Nat. Sci. Nanosci. Nanotechnol. 2017, 8, 013002.
- [15] A. Namai, M. Yoshikiyo, K. Yamada, S. Sakurai, T. Goto, T. Yoshida, T. Miyazaki, M. Nakajima, T. Suemoto, H. Tokoro, S. I. Ohkoshi, *Nat. Commun.* **2012**, *3*, 1035.
- [16] J. Jin, S. I. Ohkoshi, K. Hashimoto, Adv. Mater. 2004, 16, 48.
- [17] K. Hasegawa, M. Mizuguchi, Y. Sakuraba, T. Kamada, T. Kojima, T. Kubota, S. Mizukami, T. Miyazaki, K. Takanashi, *Appl. Phys. Lett.* 2015, *106*, 252405.
- [18] Y. Pu, D. Chiba, F. Matsukura, H. Ohno, J. Shi, Phys. Rev. Lett. 2008, 101, 117208.
- [19] M. Ikhlas, T. Tomita, T. Koretsune, M. T. Suzuki, D. Nishio-Hamane, R. Arita, Y. Otani, S. Nakatsuji, *Nat. Phys.* 2017, 13, 1085.
- [20] X. Li, L. Xu, L. Ding, J. Wang, M. Shen, X. Lu, Z. Zhu, K. Behnia, *Phys. Rev. Lett.* **2017**, *119*, 056601.
- [21] M. Hirschberger, S. Kushwaha, Z. Wang, Q. Gibson, S. Liang, C. A. Belvin, B. A. Bernevig, R. J. Cava, N. P. Ong, *Nat. Mater.* 2016, *15*, 1161.
- [22] T. Liang, Q. Gibson, M. N. Ali, M. Liu, R. J. Cava, N. P. Ong, *Nat. Mater.* 2015, 14, 280.
- [23] C. Shekhar, A. K. Nayak, Y. Sun, M. Schmidt, M. Nicklas, I. Leermakers, U. Zeitler, Y. Skourski, J. Wosnitza, Z. Liu, Y. Chen, W. Schnelle, H. Borrmann, Y. Grin, C. Felser, B. Yan, *Nat. Phys.* 2015, *11*, 645.
- [24] F. Arnold, C. Shekhar, S. C. Wu, Y. Sun, R. D. Dos Reis, N. Kumar, M. Naumann, M. O. Ajeesh, M. Schmidt, A. G. Grushin, J. H. Bardarson, M. Baenitz, D. Sokolov, H. Borrmann, M. Nicklas, C. Felser, E. Hassinger, B. Yan, *Nat. Commun.* **2016**, *7*, 11615.
- [25] N. Kumar, Y. Sun, N. Xu, K. Manna, M. Yao, V. Süß, I. Leermakers, O. Young, T. Förster, M. Schmidt, H. Borrmann, B. Yan, U. Zeitler, M. Shi, C. Felser, C. Shekhar, *Nat. Commun.* **2017**, *8*, 1642.



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- [26] J. Gooth, A. C. Niemann, T. Meng, A. G. Grushin, K. Landsteiner, B. Gotsmann, F. Menges, M. Schmidt, C. Shekhar, V. Süß, R. Hühne, B. Rellinghaus, C. Felser, B. Yan, K. Nielsch, *Nature* 2017, 547, 324.
- [27] L. M. Schoop, F. Pielnhofer, B. V. Lotsch, Chem. Mater. 2018, 30, 3155.
- [28] C. R. Rajamathi, U. Gupta, N. Kumar, H. Yang, Y. Sun, V. Süß, C. Shekhar, M. Schmidt, H. Blumtritt, P. Werner, B. Yan, S. Parkin, C. Felser, C. N. R. Rao, Adv. Mater. 2017, 29, 1606202.
- [29] C.-K. Chan, N. H. Lindner, G. Refael, P. A. Lee, Phys. Rev. B 2017, 95, 41104.
- [30] Z. Wang, M. G. Vergniory, S. Kushwaha, M. Hirschberger, E. V. Chulkov, A. Ernst, N. P. Ong, R. J. Cava, B. A. Bernevig, *Phys. Rev. Lett.* **2016**, *117*, 236401.
- [31] K. Kuroda, T. Tomita, M.-T. Suzuki, C. Bareille, A. A. Nugroho, P. Goswami, M. Ochi, M. Ikhlas, M. Nakayama, S. Akebi, R. Noguchi, R. Ishii, N. Inami, K. Ono, H. Kumigashira, A. Varykhalov, T. Muro, T. Koretsune, R. Arita, S. Shin, T. Kondo, S. Nakatsuji, *Nat. Mater.* **2017**, *16*, 1090.
- [32] K. Manna, L. Muechler, T.-H. Kao, R. Stinshoff, Y. Zhang, N. Kumar, G. Kreiner, K. Koepernik, R. Car, J. Kübler, G. H. Fecher, C. Shekhar, Y. Sun, C. Felser, *Phys. Rev. X* 2018, *8*, 041045.
- [33] I. Belopolski, D. S. Sanchez, G. Chang, K. Manna, B. Ernst, S.-Y. Xu, S. S. Zhang, H. Zheng, J. Yin, B. Singh, G. Bian, D. Multer, X. Zhou, S.-M. Huang, B. Wang, A. Bansil, H. Lin, C. Felser, M. Z. Hasan, 2017, arXiv:1712.09992.
- [34] S. N. Guin, K. Manna, J. Noky, S. J. Watzman, C. Fu, N. Kumar, W. Schnelle, C. Shekhar, Y. Sun, J. Gooth, C. Felser, NPG Asia Mater. 2019, 11, 16.
- [35] J. Noky, J. Gooth, C. Felser, Y. Sun, Phys. Rev. B 2018, 98, 241106(R).
- [36] A. Sakai, Y. P. Mizuta, A. A. Nugroho, R. Sihombing, T. Koretsune, M. T. Suzuki, N. Takemori, R. Ishii, D. Nishio-Hamane, R. Arita, P. Goswami, S. Nakatsuji, *Nat. Phys.* **2018**, *14*, 1119.
- [37] G. Chang, S. Y. Xu, H. Zheng, B. Singh, C. H. Hsu, G. Bian, N. Alidoust, I. Belopolski, D. S. Sanchez, S. Zhang, H. Lin, M. Z. Hasan, *Sci. Rep.* **2016**, *6*, 38839.
- [38] E. Liu, Y. Sun, N. Kumar, L. Muechler, A. Sun, L. Jiao, S. Y. Yang, D. Liu, A. Liang, Q. Xu, J. Kroder, V. Süß, H. Borrmann, C. Shekhar, Z. Wang, C. Xi, W. Wang, W. Schnelle, S. Wirth, Y. Chen, S. T. B. Goennenwein, C. Felser, *Nat. Phys.* **2018**, *14*, 1125.
- [39] Q. Wang, Y. Xu, R. Lou, Z. Liu, M. Li, Y. Huang, D. Shen, H. Weng, S. Wang, H. Lei, *Nat. Commun.* **2018**, *9*, 3681.
- [40] R. Weihrich, I. Anusca, Z. Anorg. Allg. Chem. 2006, 632, 1531.
- [41] P. Vaqueiro, G. G. Sobany, Solid State Sci. 2009, 11, 513.
- [42] R. Weihrich, W. Yan, J. Rothballer, P. Peter, S. M. Rommel, S. Haumann, F. Winter, C. Schwickert, R. Pöttgen, *Dalton Trans.* 2015, 44, 15855.
- [43] D. Xiao, Y. Yao, Z. Fang, Q. Niu, Phys. Rev. Lett. 2006, 97, 026603.
- [44] D. Xiao, M. C. Chang, Q. Niu, Rev. Mod. Phys. 2010, 82, 1959.
- [45] N. Hanasaki, K. Sano, Y. Onose, T. Ohtsuka, S. Iguchi, I. Kézsmárki, S. Miyasaka, S. Onoda, N. Nagaosa, Y. Tokura, *Phys. Rev. Lett.* 2008, 100, 106601.
- [46] J. Weischenberg, F. Freimuth, S. Blügel, Y. Mokrousov, Phys. Rev. B 2013, 87, 060406.
- [47] R. Ramos, M. H. Aguirre, A. Anadón, J. Blasco, I. Lucas, K. Uchida, P. A. Algarabel, L. Morellón, E. Saitoh, M. R. Ibarra, *Phys. Rev. B* 2014, 90, 054422.
- [48] Y. Shiomi, N. Kanazawa, K. Shibata, Y. Onose, Y. Tokura, Phys. Rev. B 2013, 88, 064409.
- [49] K. I. Uchida, T. Kikkawa, T. Seki, T. Oyake, J. Shiomi, Z. Qiu, K. Takanashi, E. Saitoh, Phys. Rev. B 2015, 92, 094414.
- [50] G. Kresse, J. Furthmüller, Phys. Rev. B 1996, 54, 11169.
- [51] A. A. Mostofi, J. R. Yates, Y.-S. Lee, I. Souza, D. Vanderbilt, N. Marzari, Comput. Phys. Commun. 2008, 178, 685.