Finite-temperature violation of the anomalous transverse Wiedemann-Franz law

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The Wiedemann-Franz (WF) law has been tested in numerous solids, but the extent of its relevance to the anomalous transverse transport and the topological nature of the wave function, remains an open question. Here, we present a study of anomalous transverse response in the noncollinear antiferromagnet Mn$_3$Ge extended from room temperature down to sub-kelvin temperature and find that the anomalous Lorenz ratio remains close to the Sommerfeld value up to 100 K but not above. The finite-temperature violation of the WF correlation is caused by a mismatch between the thermal and electrical summations of the Berry curvature and not by inelastic scattering. This interpretation is backed by our theoretical calculations, which reveals a competition between the temperature and the Berry curvature distribution. The data accuracy is supported by verifying the anomalous Bridgman relation. The anomalous Lorenz ratio is thus an extremely sensitive probe of the Berry spectrum of a solid.

INTRODUCTION

The Berry curvature of electrons can give rise to the anomalous Hall effect (AHE) (1, 2). This happens if the host solid lacks time-reversal symmetry, which impedes cancellation after integration over the whole Fermi surface. Explored less frequently (3–5), the thermoelastic and thermal counterparts of the AHE (the anomalous Nernst and anomalous Righi-Leduc effects) also arise by the same fictitious magnetic field (6–8). How do the magnitudes of these anomalous off-diagonal coefficients correlate with each other? Do the established correlations between the ordinary transport coefficients hold? Satisfactory answers to these questions are still missing. A semiclassical formulation of AHE (9) is laborious because the concept of Berry connection [or the “anomalous velocity” (10)] is based on off-diagonal matrix elements linking adjacent Bloch functions and not wave packets of semiclassical transport theory (9). This makes any intuitive picture of how Berry curvature combined to a longitudinal thermal gradient can produce a transverse electric field (an anomalous thermoelectric or the “anomalous velocity” of microscopic details. Last, we quantify the anomalous transverse thermoelectric response $\sigma_{ij}^A$ and find that the ratio of $\sigma_{ij}^A/\sigma_{ij}^B$ tends to saturate toward a value close to $k_B/e$ in the high-temperature limit.

We argue that this observation implies a hitherto unnoticed mechanism for finite-temperature violation of the Wiedemann-Franz (WF) law and points to a small (10 meV) energy scale in the Berry spectrum of Mn$_3$Ge that is absent in Mn$_3$Sn. This experimental observation is backed by theoretical calculations identifying the source of the Berry curvature in this family. By directly measuring the anomalous Ettingshausen and anomalous Nernst effects, we verify the validity of the Bridgman relation connecting the two transverse thermoelectric coefficients to each other. This confirms that the Bridgman relation, a consequence of Onsager reciprocity and based on thermodynamics of irreversible processes (14), holds regardless of microscopic details. Last, we quantify the anomalous transverse thermoelectric response $\sigma_{ij}^A$ and find that the ratio of $\sigma_{ij}^A/\sigma_{ij}^B$ tends to saturate toward a value close to $k_B/e$ in the high-temperature limit.

Following theoretical propositions (15, 16), a large AHE was found in Mn$_3$X (X = Sn and Ge) family of noncollinear antiferromagnets (17–19) below a high Néel temperature (20–22). These newcomers to the emerging field of antiferromagnetic spintronics (23) present a distinct profile of the Hall resistivity in which the extraction of the anomalous Hall conductivity becomes straightforward. An anomalous thermoelastic (Nernst) (24–26) and Righi-Leduc (25), counterparts of AHE, were also observed in Mn$_3$Sn. In the case of Mn$_3$Sn, the triangular order is destroyed at finite temperature (17, 24, 25). This is not the case for Mn$_3$Ge where the fate of these signals can be followed down to sub-kelvin temperatures.

RESULTS

Basic properties

The room temperature field dependence of the three transport properties in Mn$_3$Ge is shown in Fig. 1. Like in Mn$_3$Sn, a hysteretic jump is triggered at a well-defined magnetic field, marking the nucleation of domains of opposite polarity induced by magnetic field (27). The large jump, the small magnetic field required for inverting polarity, and the weakness of the ordinary Hall response lead to step-like profiles contrasting with other topological solids exhibiting AHE (28–30). A step-like profile of anomalous transverse response
[for other varieties (31, 32)] makes the extraction of the anomalous component straightforward. The panels of Fig. 1 show the measured Hall resistivity, Nernst signal, and thermal Hall resistivity, which were used to extract electric, thermoelectric, and thermal Hall conductivities.

Figure 2 presents a number of basic properties of the system under study. The spin texture (17, 20, 21) is shown in Fig. 2A. This magnetic order is stabilized thanks to the combination of Heisenberg and Dzyaloshinskii-Moriya interactions (33). As seen in Fig. 2B, which shows the magnetization, it emerges below $T_N = 370$ K. The small residual ferromagnetism has been attributed to the residual magnetic moment of octupole clusters of Mn atoms (34) in this pseudo-Kagomé lattice.

A carrier density of $n = 3.1 \times 10^{22}$ cm$^{-3}$ is extracted from the magnitude of the ordinary Hall number (Supplementary Materials) in agreement with a previous report (19). The electrical resistivity shows little variation with temperature (Fig. 2C), and its magnitude of 150 $\mu$Ω-cm implies a mean free path as short as 0.9 nm, compatible with the fact that Mn$_3$X crystals are not stoichiometric (19, 21). In our crystals, we found the Mn:Ge ratio ranges from 3.32:1 to 3.35:1 (Supplementary Materials). Since one-tenth of Ge sites are occupied by Mn atoms, the average distance between these defects is $\sqrt{3}$ times the average lattice parameter ($a = 0.53$ and $c = 0.43$ nm) and comparable to the short electronic mean free path.

The Seebeck coefficient (Fig. 2D) has a nonmonotonic temperature dependence with a peak around 60 K, a sign change above 200 K, and a large low-temperature slope indicative of electronic correlations. The $T$-linear electronic specific heat (Fig. 2E) is as large as $\gamma = 24.3$ mJ mol$^{-1}$ K$^{-2}$, 30 times larger than copper and 5 times larger than iron (35). Assuming a single spherical Fermi surface corresponding to the known carrier density, such a $\gamma$ implies an effective mass as large as $m^* = 14.5$ $m_e$, which should not be taken literally given that the system is multiband. The slope of the Seebeck coefficient at low temperature ($S/T \sim -0.2 \mu$V K$^{-1}$) correlates with $\gamma$, yielding $q = \frac{S_{\text{Hall}}}{T_{\text{Av}}} \sim 1$, as observed in other correlated systems (Fig. 2F) (36). On the other hand, the low-temperature resistivity presents a weak upturn impeding the detection of any $T^2$-square term, and the Wilson ratio [of the specific heat and magnetic susceptibility (37)] implies that mobile electrons do not play any notable role in the magnetic response (Supplementary Materials).

**The anomalous transverse WF law**

For each temperature, we measured $\sigma_{xx}$ and $\kappa_{xx}$, identified as jumps in $\sigma_{xx}(B)$ and $\kappa_{xx}(B)$. This led to the determination of $L_A^{xx}$ at each temperature and a comparison with $L_0$ to check the WF law.

Our main finding is presented in Fig. 3. Below 100 K, the anomalous Lorenz ratio, $L_A^{xx}$, was found to be flat, with a magnitude slightly larger than the Sommerfeld value, equal to it within the experimental margin. The results were reproduced by two different measuring methods [with resistive sensors and thermocouples (Supplementary Materials)] and in two different samples. In one of them, we checked the persistent validity of this equality below 1 K down to 0.3 K. As seen also in the figure, $L_A^{xx}$ begins a steady downward deviation from $L_0$ above 100 K. Interestingly, $\sigma_{xx}$ begins a steady decrease itself above 100 K. The temperature dependence of $\sigma_{xx}$ is similar to what was reported in previous reports (18, 19), and its zero-temperature magnitude [which depends on stoichiometry (19)] is in agreement with
what was reported for a similar Mn content (Supplementary Materials). As seen in Fig. 3D, the anomalous Lorenz ratio in Mn₃Ge and in Mn₃Sn behave very differently despite the fact that resistivity in both shows only a slight change with temperature (Fig. 3E), in contrast to elemental ferromagnets.

**The Bridgman relation**

Several previous reports of the violation of WF law have been refuted afterward. One may therefore wonder whether our data can be validated by independent criteria. The answer is affirmative. Their validity is supported by the verification of the Kelvin relation (for normal longitudinal transport coefficients) and the Bridgman relation (for anomalous transverse coefficients). According to the thermodynamics of irreversible processes, these relations should remain valid irrespective of microscopic details.

The same data (namely, the electric field and the thermal gradient produced by imposing a heat current) and the same setup were used for both thermal and thermoelectric studies. Therefore, the validity of Kelvin and Bridgman relations is a guarantee of the validity of the collected thermal data.

To check the Bridgman relation, we directly measured both the Nernst (Fig. 4A) and the Ettingshausen (Fig. 4B) effects. The former is the transverse electric field generated by a longitudinal thermal gradient, \( S_{xx} = \frac{E_x}{T} \), and the latter is the transverse thermal gradient produced by a longitudinal charge current, \( \epsilon_{xx}^A = \frac{\nabla T}{I_x} \). The anomalous Ettingshausen effect (Fig. 4B) is easily invertible by a small magnetic field, similar to other anomalous transverse responses. We measured \( S_{xx}^A \) and \( \epsilon_{xx}^A \) at several different temperatures. Combined with longitudinal thermal conductivity data \( \kappa_{xx}(T) \), this allowed us to check the Bridgman relation (38), which links these three quantities

\[
\epsilon_{xx}^A = \frac{T S_{xx}^A}{\kappa_{xx}}
\]

As seen in Fig. 4C, the two sides of the equation remain close to each other in the whole temperature range. The Bridgman relation, derivable by a thermodynamic argument (39), is based on Onsager reciprocity (14). Its experimental validity has been confirmed in semiconductors (40) and in superconductors hosting mobile vortices (41). While there is a previous report on simultaneous measurements of anomalous Nernst and Ettingshausen coefficients (42), the present study is the first experimental confirmation of the validity of Bridgman relation in the context of topological transverse response. We also verified the Kelvin relation linking the Seebeck and Peltier coefficients (Supplementary Materials).

The temperature dependence of the anomalous transverse thermoelectric conductivity, \( \alpha_{xx}^A \), extracted from anomalous Nernst coefficient, is presented in Fig. 4 (D and E). As expected, it vanishes in the zero-temperature limit but is remarkably large at room temperature. This can be seen by noting that the ratio of \( \alpha_{xx}^A \) to \( \alpha_0^A \) is close to \( k_B/e \) at room temperature (see Fig. 4F). This contrasts with the ordinary longitudinal counterpart of this ratio, which includes a \( T/T_F \) damping factor, inversely scaling with the Fermi temperature \( T_F \) (43).

**DISCUSSION**

**Origin of the finite-temperature violation**

Having discussed the thermoelectric response, let us now turn back to the thermal transport. The zero-temperature validity of the WF law implies that the transverse flow of charge and entropy caused by Berry curvature conforms to a ratio of \( \frac{A_1}{A_2} \). This confirms Haldane’s argument (48) that AHE is a property of the topological quasiparticles of the Fermi surface. As argued previously (25), only the states within the thermal window of the Fermi surface can be affected by a temperature gradient and give rise to a finite \( \kappa_{xx}^A \).

To identify the origin of the observed drop in the anomalous transverse Lorenz number, let us begin by recalling what is known about ordinary transport and Lorenz number. The WF law ceases to be valid in the presence of inelastic scattering. This is because small-angle inelastic collisions decay the momentum flow less efficiently than the energy flow (45). In the semiclassical picture of electronic transport, charge and heat conductivity are set by the mean free path and the Fermi radius averaged over the whole Fermi surface with different pondering factors (45, 46, 47)

\[
F_{\beta}(\epsilon_k) = \left[ \frac{\epsilon_k - \mu}{k_B T} \right]^{a} \frac{\partial f(\epsilon_k)}{\partial \epsilon_k}
\]
of their in-plane resistivity. The large deviation from the WF law in Mn3Ge occurs despite the fact that the temperature dependence of its resistivity is even more modest than that in Mn3Sn.

Fig. 3. Anomalous transverse WF law. Temperature dependence of the anomalous Hall conductivity $\sigma_{H}^{A}$ (A), the anomalously thermal Hall conductivity divided by temperature $\kappa_{T}^{A}/T$ (B), and (C) the anomalously Lorenz ratio $\kappa_{L}^{A}/\kappa_{T} T$. Different symbols are used for data obtained with two different setups: resistive thermometers (diamonds) and thermocouples (circles). Star symbols refer to a third set of data obtained on another sample measured down to sub-kelvin temperatures. The horizontal solid line marks $L_0 = 2.44 \times 10^{-8}$ V$^2$ K$^{-2}$. The deviation between $L$ and $L_0$ starts at $T \geq 100$ K and is concomitant with the decrease in $\sigma_{H}^{A}$. (D) Temperature dependence of the anomalous Lorenz ratio in Mn3Ge and in Mn3Sn (25, 41). Mn3Ge #3 shows an upturn at high temperature. The Hall data can be found in the Supplementary Materials. (E) Comparison of their in-plane resistivity. The large deviation from the WF law in Mn3Ge occurs despite the fact that the temperature dependence of its resistivity is even more modest than that in Mn3Sn.

This expression has been obtained for both Boltzmann (45) and Landauer (46) formalisms. It has been shown that $n = 0$ for charge transport, $n = 1$ for thermoelectric transport, and $n = 2$ for thermal transport (see Fig. 5A).

One can see that in the presence of energy-dependent scattering, the difference between the electric and the thermal pondering functions can give rise to a difference between thermal and electrical conductivities. Electron-phonon scattering is expected to give rise to electric and thermal resistivities with different exponents in their temperature dependence [45, 48]. Different symbols are used for data obtained with two different setups: resistive thermometers (diamonds) and thermocouples (circles). Star symbols refer to a third set of data obtained on another sample measured down to sub-kelvin temperatures. The horizontal solid line marks $L_0 = 2.44 \times 10^{-8}$ V$^2$ K$^{-2}$. The deviation between $L$ and $L_0$ starts at $T \geq 100$ K and is concomitant with the decrease in $\sigma_{H}^{A}$. (D) Temperature dependence of the anomalous Lorenz ratio in Mn3Ge and in Mn3Sn (25, 41). Mn3Ge #3 shows an upturn at high temperature. The Hall data can be found in the Supplementary Materials. (E) Comparison of their in-plane resistivity. The large deviation from the WF law in Mn3Ge occurs despite the fact that the temperature dependence of its resistivity is even more modest than that in Mn3Sn.

The pondering functions plotted in Fig. 5A remain relevant to the anomalous transverse transport. They imply that states probed by each transport coefficient are centered at a given location in the $k$-space. In this context, the summation of the Berry curvature over the Fermi sheets with these pondering factors can potentially generate a mismatch between $\sigma_{H}^{A}$ and $\kappa_{T}^{A}$ (in a manner similar to an energy-dependent scattering matrix). As the temperature rises, the summations extend over a broader interval in the $k$-space inversely proportional to the thermal de Broglie length of electrons ($\Lambda = \frac{h}{\sqrt{2\pi m_e k_B T}}$) (47).

The electrical and thermal summations of the Berry curvature depend on these two length scales and the fine details of the spectrum, i.e., the size of the Berry curvature sources (and sinks) and their position (see Fig. 5B). One can see that the validity of the WF correlation depends on temperature. The higher the temperature, the larger the $k$-space area swept by the two different pondering functions and the easier it becomes to find a mismatch between $\sigma_{H}^{A}$ and $\kappa_{T}^{A}$. We note that our picture of the violation of the anomalous WF law shares a formal similarity with the well-established route toward violation of the ordinary WF law in a degenerate Fermi liquid (where $T < T_F$). In the latter case, it is caused by a sufficiently large energy dependence in the scattering time near the Fermi energy. In our interpretation, it is caused by a sufficiently large energy dependence...
The anomalous Hall conductivity

Theoretical calculations of

identically near the Fermi level. By the fact that thermal and electric conductivities do not average the overall contribution of the Berry curvature sources and sinks. Disorder makes these functions step-like in k-space. Note four distinct length scales in the k-space relevant to these summations: the inverse of the thermal wavelength ($\lambda$), the inverse of the mean free path ($L$) and anomalous thermal and Nernst signals ($A$, $D$) co-

Fig. 4. Anomalous Nernst and Ettingshausen effects and the Bridgman relation. (A) The transverse electric field created by a finite longitudinal temperature gradient as a function of magnetic field (the Nernst effect). (B) The transverse thermal gradient produced by a finite longitudinal charge current (the Ettingshausen effect) at the same temperature. Insets show experimental configurations. (C) The temperature dependence of the anomalous Nernst ($\sigma_{xx}$) and anomalous Ettingshausen ($\sigma_{xx}$) coefficients. $\sigma_{xx}$ and $\sigma_{xx}$/$\kappa_{xx}$ remain equal as expected by the Bridgman relation. (D) and (E) Temperature dependence of $\sigma_{xx}$ and $\sigma_{xx}$ extracted from the Hall signal and Nernst signal $\sigma_{xx}$. (F) The evolution of the ratio of $\sigma_{xx}$/$\sigma_{xx}$ with temperature.

in the Berry curvature near the Fermi energy. The driving source of violation is totally different, but in both cases, the departure is caused by the fact that thermal and electric conductivities do not average identically near the Fermi level.

Theoretical calculations of the anomalous Lorenz ratio

The anomalous Hall conductivity $\sigma_{xx}^A$ and anomalous thermal Hall conductivity $\kappa_{xx}^A$ are expressed in the form of the Berry curvature $\Omega_{xx}^A(k)$ (49)

$$\sigma_{xx}^A(\mu) = e^2 \hbar \int_{-\infty}^{\infty} d\xi \left( -\frac{\partial f(\xi - \mu)}{\partial \xi} \right) \sigma_{xx}(\xi)$$

(5)

$$\kappa_{xx}^A(\mu) = \frac{1}{\mu} \int_{-\infty}^{\infty} d\xi \left( -\frac{(\xi - \mu)^2}{\mu} \frac{\partial f(\xi - \mu)}{\partial \xi} \right) \sigma_{xx}(\xi)$$

(6)

$$\sigma_{xx}(\xi) = \frac{\partial f(\xi - \mu)}{\partial \xi} \sum_{\epsilon,\delta} \Omega_{xx}^A(k)$$

(7)

Here, $f(\xi - \mu) = 1/(e^{\frac{\xi - \mu}{T}} + 1)$ is the Fermi-Dirac function, $m$ and $n$ are band indices, $\nu_{xx}$ is the velocity operator, and $\sigma_{xx}(\xi)$ is actually the zero-temperature anomalous Hall conductivity (divided by $\hbar$). We point out that the electric and thermal coefficients are mainly different in the pondering factors for $\sigma_{xx}(\xi)$. As shown in Fig. 5, the pondering factor $-\frac{\partial f(\xi - \mu)}{\partial \xi}$ in Eq. 5 is a $\delta$-function, while $-(\xi - \mu)^2 \frac{\partial f(\xi - \mu)}{\partial \xi}$ in Eq. 6 displays a double-peak profile. The double-peak distance is in the order of magnitude of $k_BT$, where $T$ is the temperature. This is the essential cause to violate the anomalous WF law at finite $T$. It is clear that the anomalous Lorenz ratio $L_{xx}^A = \frac{\kappa_{xx}^A}{\sigma_{xx}^A}$ remains as a constant $L_0 = \frac{\pi^2}{3} \left( \frac{\mu}{T} \right)^2 = 2.44 \times 10^{-8}$ $\Omega$ $WK^{-2}$ at exact zero $T$ because two pondering functions summarize at the same Fermi energy, $\mu$. At finite $T$, for example, if $\sigma_{xx}(\xi)$ is a constant or a linear function of $\xi$, then $L_{xx}^A$ also remains $L_0$.

Here, we summarize general rules about the anomalous WF law. At zero temperature, $L_{xx}^A = L_0$ is valid, as long as the total Berry curvature is smooth to energy, which is commonly true. At finite $T$, $L_{xx}^A$ is close to $L_0$ if $e\sigma_{xx}(\xi)$ has an approximately antisymmetric profile with respect to $\mu$ in the energy window of several $k_BT$ because two pondering factors contribute the same summation of the Berry curvature in this case. Otherwise, $L_{xx}^A$ can vary strongly from $L_0$. Such a violation of the anomalous WF law is caused by the distribution of the Berry curvature, instead of the extrinsic scattering.

\[ \Omega_{xx}^A(k) = \frac{1}{i} \sum_{m \neq n} \langle n | \sigma_{xx} | m \rangle < \langle n | \sigma_{xx} | m \rangle > \left( 2\pi \hbar \right)^2 \]
The total Berry curvature $\tilde{\sigma}_{zx}(\xi)$ is determined by the intrinsic band structure of a given material. It is expected that $L_{zx}^A$ depends sensitively on the position of $\mu$ because $\kappa_{zx}^A(\mu)$ and $\sigma_{zx}^A(\mu)$ do. In experiment, Mn$_3$Ge(Sn) is usually off-stoichiometric, as discussed in the above section, and such an off-stoichiometry can shift up the chemical potential in energy compared to the charge neutral point.

By shifting $\mu$ slightly above, we can reproduce the general trend of $T$ dependence of $L_{zx}^A$ for both Ge and Sn compounds in Fig. 6. For Mn$_3$Ge at $\mu = 180$ meV above the charge neutral point, $L_{zx}^A$ drops quickly from 100 to 250 K and goes up again after 250 K, qualitatively consistent with the experiment. The first drop is induced by dips of $\sigma_{zx}^A$ at $\sim 0.1$ and $\sim 0.3$ eV because the $\kappa_{zx}^A(T)$ sums smaller Berry curvature than $\sigma_{zx}^A(T)$ does in this case (see Eqs.5 and 6). We note that the dip at $\sim 0.1$ eV is induced by an anticrossing gap, while the dip (and sign change) at $\sim 0.3$ eV is caused by a Weyl point (see fig. S9). The following upturn is related to the increase of $L_{zx}^A$ after these dips. For Mn$_3$Sn at $\mu = 140$ meV, however, $L_{zx}^A$ remains close to $L_0$ in a large temperature range. For completeness, we show the temperature dependence of $\kappa_{zx}^A$ and $\sigma_{zx}^A$ in fig. S10.

We note that the theoretical violation for Mn$_3$Ge is smaller than the experimental one. Let us recall that electronic correlations are neglected in the density functional theory used to calculate the band structure of the system and are absent in Eqs. 5 to 8. In addition, calculations that were performed for an ideal clean system may cause quantitative discrepancies when comparing to the dirty metal in the experiment. Given these deviations, our theory qualitatively demonstrates the different Berry spectrum in Mn$_3$Sn and Mn$_3$Ge, which leads to different behaviors of $L_{zx}^A$ at finite temperature for two compounds.

Different behaviors between two materials originate in their different Berry curvature $\tilde{\sigma}_{zx}(\xi)$, as shown in Fig. 6 (A and B). In the energy window investigated, the chemical potential dependence of $\tilde{\sigma}_{zx}$ looks smoother for the Sn compound compared to the Ge one. There are abrupt dips and even sign changes of $\tilde{\sigma}_{zx}$ for the Ge compound. This difference can be understood by the fact that Sn displays stronger spin-orbit coupling (SOC) than Ge. Stronger SOC tends to smear the Berry curvature more uniformly in energy and separate the Weyl points further away from each other, as shown in Fig. 6 (E and F). Therefore, it is more possible to find energy regions of antisymmetric $\tilde{\sigma}_{zx}$ distribution, which gives the conservation of $L_{zx}^A$ in the smoother Berry curvature (Sn compound) than the rougher one (Ge compound). For Mn$_3$Sn, $\tilde{\sigma}_{zx}(\xi)$ is approximately antisymmetric with respect to $\mu = 140$ meV in an energy window of nearly 200 meV, inducing $L_{zx}^A \approx L_0$ up to 400 K and even above. However, $\mu$ may vary from such an ideal antisymmetric point in different samples. This explains the observed deviation of $L_{zx}^A$ in a different Mn$_3$Sn sample, as shown in fig. S7. To demonstrate the sensitive role of the chemical potential, we show $L_{zx}^A - T$ curves for different $\mu$ in Fig. 6. Because it depends on the competition of the Berry curvature [$(\tilde{\sigma}_{zx}(\xi))$] profile and the temperature ($\sim k_B T$), $L_{zx}^A \approx L_0$ at low $T$ for different $\mu$. In addition, there are interesting topological features near the chosen chemical potential [see Fig. 6 (E and F)]. Along the $\Gamma$-M line in the Brillouin zone, there are two Weyl points induced by the crossing between the lowest and second-lowest conduction bands. These Weyl points were not revealed in previous studies, which usually focus on the crossing between the lowest conduction band and the highest valence band (50, 51). For Mn$_3$Sn at $\mu = 140$ meV, a Weyl point exists and contributes large Berry curvature to the anomalous Hall conductivity. For Mn$_3$Ge at $\mu = 180$ meV, however, the Weyl cone is strongly tilted so that negative and positive Berry curvatures nearly cancel each other near the Weyl point (see more information in fig. S8).

Fig. 6. Contrasting the theoretical Berry spectrum in Mn$_3$Ge and in Mn$_3$Sn. The theoretical zero-temperature Berry curvature $\tilde{\sigma}_{zx}(\xi)$ (A and B) and the anomalous Lorenz ratio $L_{zx}^A$ (C and D). The charge neutral point is set to zero. The green, red, and blue lines represent $\mu = 0, 140$, and 180 meV, respectively. The dashed horizontal black lines represents $L_0$ in (C) and (D). In the band structure (E and F), the color indicates the Berry curvature value. The blue arrows point out two Weyl points between the lowest and second-lowest conduction bands.
MATERIALS AND METHODS

Sample preparation and transport measurement
Single crystals of Mn₃Ge were grown from polycrystalline samples using Bridgman-Stockbarger technique. The raw materials, Mn (99.99% purity) and Ge (99.999% purity), were weighed and mixed in an argon glove box with a molar ratio of 3.3:1, loaded in an alumina crucible, and sealed into another vacuum quartz ampule. The mixture was heated up to 1050°C, remained for 2 hours to ensure homogeneity of melt, and then cooled slowly down to 800°C to obtain polycrystalline samples. The polycrystalline Mn₃Ge were ground, loaded in an alumina crucible and then sealed in a vacuum quartz ampule. The growth temperature was controlled at 980° and 800°C for high-temperature and low-temperature experiment, respectively. Last, to obtain high-temperature hexagonal phase, the quartz ampule was quenched with water. The single crystals were cut by a wire saw into typical dimensions of 0.3 mm by 1.5 mm by 2 mm for transport measurements. The stoichiometry was found to be Mn₃₀.₈₈Ge₀.₉₂ (Mn₃Ge = 3.32 to 3.5:1) using energy-dispersive X-ray spectroscopy. This is close to the ratio of the raw materials and comparable to previous reports (19).

Longitudinal and Hall resistivity were measured by the standard four-probe method using a current source (Keithley 6221) with a dc nanovoltmeter (Keithley 2182A) in a commercial measurement system [Physical Property Measurement System (PPMS), Quantum Design]. The thermal conductivity and thermal Hall effect were performed using a heater and two pairs of thermocouples in the PPMS in a high-vacuum environment (25). For temperatures below 4.2 K, the measurements were performed in a dilution refrigerator inserted in a 14-T superconducting magnet using one heater–three thermometers setup, allowing the measurement of longitudinal and transverse transport coefficients with the same contacts.

Theoretical calculations

The band structure was calculated with the density functional theory in the framework of the generalized-gradient approximation (52). The Bloch wave functions were projected to atomic orbital–like Wannier functions (53). On the basis of the Wannier-projected tight-binding Hamiltonian, we calculated the Berry curvature and the anomalous Hall conductivity in the clean limit. More details can be found in (54). As shown in Fig. 6 (A and C), the Δσₓz(ξ) data are analytically fitted so that integrals in Eqs. 5 and 6 can be evaluated accurately with dense energy steps.
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C. Shekhar, N. Kumar, V. Grinenko, S. Singh, R. Sarkar, H. Luetkens, S.-C. Wu, Y. Zhang, A. C. Komarek, E. Kampert, Y. Skourski, J. Wosnitza, W. Schnelle, A. McCollam, U. Zeitler, J. Kübler, B. Yan, H.-H. Klaus, S. S. P. Parkin, C. Felser, Anomalous Hall effect in Weyl semimetal half-Heusler compounds RPtBi (R = Gd and Nd). Proc. Natl. Acad. Sci. U.S.A. 115, 9140–9144 (2018).

A. Sakai, Y. P. Mizuta, A. A. Nugroho, R. Shirombing, T. Koretsune, M.-T. Suzuki, N. Takemori, R. Ishii, D. Nishio-Hamane, R. Arita, P. Goswami, S. Nakatsuji, Giant anomalous Nernst effect and quantum-critical scaling in a ferromagnetic semimetal. Nat. Phys. 14, 1119–1124 (2018).

Liu, J., L. Balents, Anomalous Hall effect and topological defects in antiferromagnetic weyl semimetals: Mn₃Sn/Ge. Phys. Rev. Lett. 119, 087202 (2017).

M.-T. Suzuki, T. Koretsune, M. Ochi, R. Arita, Cluster multipole theory for anomalous Hall effect in antiferromagnets. Phys. Rev. B 95, 094406 (2017).

C. Kittel, Introduction to Solid State Physics (Wiley, ed. 3, 1968).

Delves, Thermomagnetic effects in semiconductors and semimetals. Rep. Prog. Phys. 28, 249–289 (1965).

P. Coleman, Heavy fermions: Electrons at the edge of magnetism, in Handbook of Magnetism and Advanced Magnetic Materials (Wiley, 2007).

P. W. Bridgman, The connections between the four transverse galvanomagnetic and thermomagnetic phenomena. Phys. Rev. 24, 644–651 (1924).

Sommerfeld, N. H. Frank, The statistical theory of thermoelectric galvanomagnetic and thermomagnetic phenomena in metals. Rev. Mod. Phys. 3, 1–42 (1931).

Delves, Thermomagnetic effects in semiconductors and semimetals. Rep. Prog. Phys. 28, 249–289 (1965).

R. P. Huebener, Superconductors in a temperature gradient. Supercond. Sci. Technol. 8, 189 (1995).

S. Seki, R. Isguchi, K. Takenashi, K. Uchida, Relationship between anomalous Etinghausen effect and anomalous Nernst effect in an FePt thin film. J. Phys.: D Appl. Phys. 51, 254001 (2018).

K. Behnia, H. Aubin, Nernst effect in metals and semiconductors: A review of concepts and experiments. Rep. Prog. Phys. 79, 046502 (2016).

M. V. Haldane, Berry curvature on the Fermi surface: Anomalous Hall effect as a topological Fermi-liquid property. Phys. Rev. Lett. 93, 206602 (2004).

J. Ziman, Principles of the Theory of Solids (Cambridge Univ. Press, 1972).

Van Houten, L. W. Molenkamp, C. W. J. Beenakker, C. T. Foxon, Thermo-electric properties of quantum point contacts. Semicond. Sci. Technol. 7, B215–B221 (1992).

K. Behnia, Fundamentals of Thermoelectricity (Oxford Univ. Press, 2015).

A. Jaou, B. Fauqué, C. Willem Rischau, A. Subedi, C. Fu, J. Gooth, N. Kumar, V. Süss, D. L. Maslov, C. Felser, K. Behnia, Departure from the Wiedemann-Franz law in WP, driven by mismatch in T-square resistivity prefactors. npj Quantum Mater. 3, 64 (2018).

O. Vafek, A. Melkýan, Z. Tesanovic, Quasiparticle Hall transport of d-wave superconductors in the vortex state. Phys. Rev. B 64, 224508 (2001).

H. Yang, Y. Sun, Y. Zhang, W.-J. Shi, S. S. P. Parkin, B. Yan, Topological Weyl semimetals in the chiral antiferromagnetic materials Mn₃Ge and Mn₃Sn. New J. Phys. 19, 015008 (2017).

K. Kuroda, T. Tomita, M.-T. Suzuki, C. Bareille, A. A. Nugroho, P. Goswami, M. Ochi, M. Ikhas, N. Nakayama, S. Akebi, R. Noguchi, R. Ishii, N. Inami, K. Ono, H. Kurnigashira, A. Varykhalov, T. Muro, T. Koretsune, R. Arita, S. Shin, T. Kondo, S. Nakatsuji, Evidence for magnetic Weyl fermions in a correlated metal. Nat. Mater. 16, 1090–1095 (2017).

J. P. Pendry, K. Burke, M. Erzerhoro, Generalized gradient approximation made simple. Phys. Rev. Lett. 77, 3865–3868 (1996).

K. Ikhas, N. Nakayama, S. Akebi, R. Noguchi, R. Ishii, N. Inami, K. Ono, H. Kurnigashira, A. Varykhalov, T. Muro, T. Koretsune, R. Arita, S. Shin, T. Kondo, S. Nakatsuji, Evidence for magnetic Weyl fermions in a correlated metal. Nat. Mater. 16, 1090–1095 (2017).

A. A. Mostofi, J. R. Yates, Y.-S. Lee, I. Souza, D. Vanderbilt, N. Marzari, Wannier90: A tool for obtaining maximally-localised wannier functions. Comput. Phys. Commun. 178, 685–699 (2008).

Y. Zhang, Y. Sun, H. Yang, J. Železny, S. P. P. Parkin, C. Felser, B. Yan, Strong anisotropic anomalous Hall effect and spin Hall effect in the chiral antiferromagnetic compounds MnₓX (X = Ge, Sn, Ga, Ir, Rh, and Pt). Phys. Rev. B 95, 075128 (2017).

S. M. Stishov, A. E. Petrova, S. Khasanov, G. K. Panova, A. A. Shikov, J. C. Lashley, D. Wu, T. A. Lograsso, Heat capacity and thermal expansion of the itinerant helimagnet Mn₃Sn. J. Phys.: Cond. Matter 20, 235222 (2008).

S. Arsenjevic, C. Petrovic, I. Forró, A. Akrap, Manifestation of the spin textures in the thermopower of Mn₃Sn. Europhys. Lett. 103, 57015 (2013).

K. Sugii, Y. Imai, M. Shimozawa, M. Ikhas, N. Kiyohara, T. Tomita, M. Suzuki, T. Koretsune, A. Ryotaro, S. Nakatsuji, M. Yamashita, Anomalous thermal Hall effect in the topological antiferromagnetic state. arXiv:1902.05601 [cond-mat.str-el] (2019).

G. Garrido, Pelletier's and Thomson's coefficients of thermoelectric phenomena in the observable formulation. J. Phys.: Cond. Matter 21, 155802 (2009).

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