

Spontaneous Hall effect induced by collinear antiferromagnetic order at room temperature

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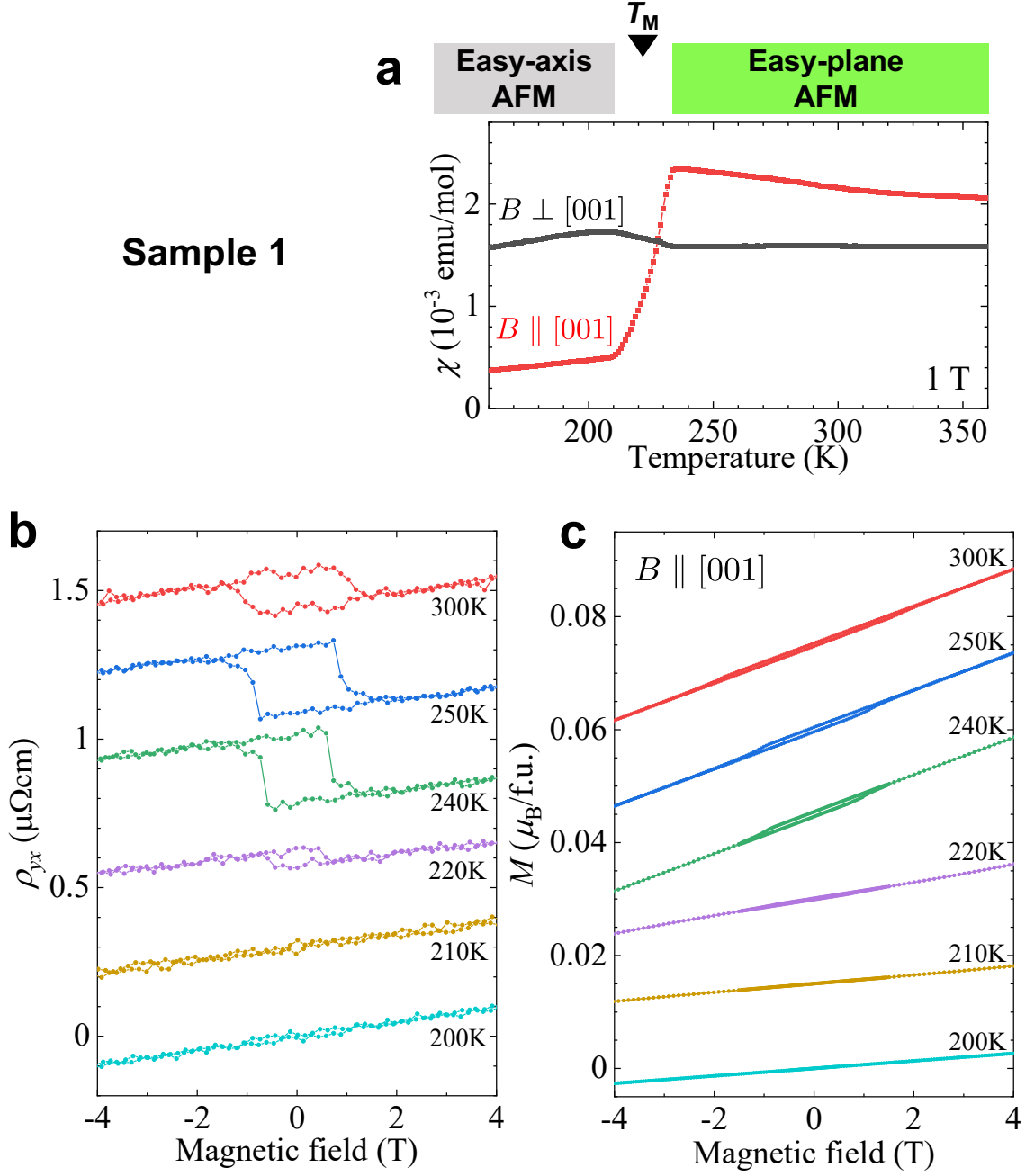
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I. HALL RESISTIVITY AND MAGNETIZATION MEASURED AT VARIOUS TEMPERATURES FOR DIFFERENT CRYSTAL PIECES

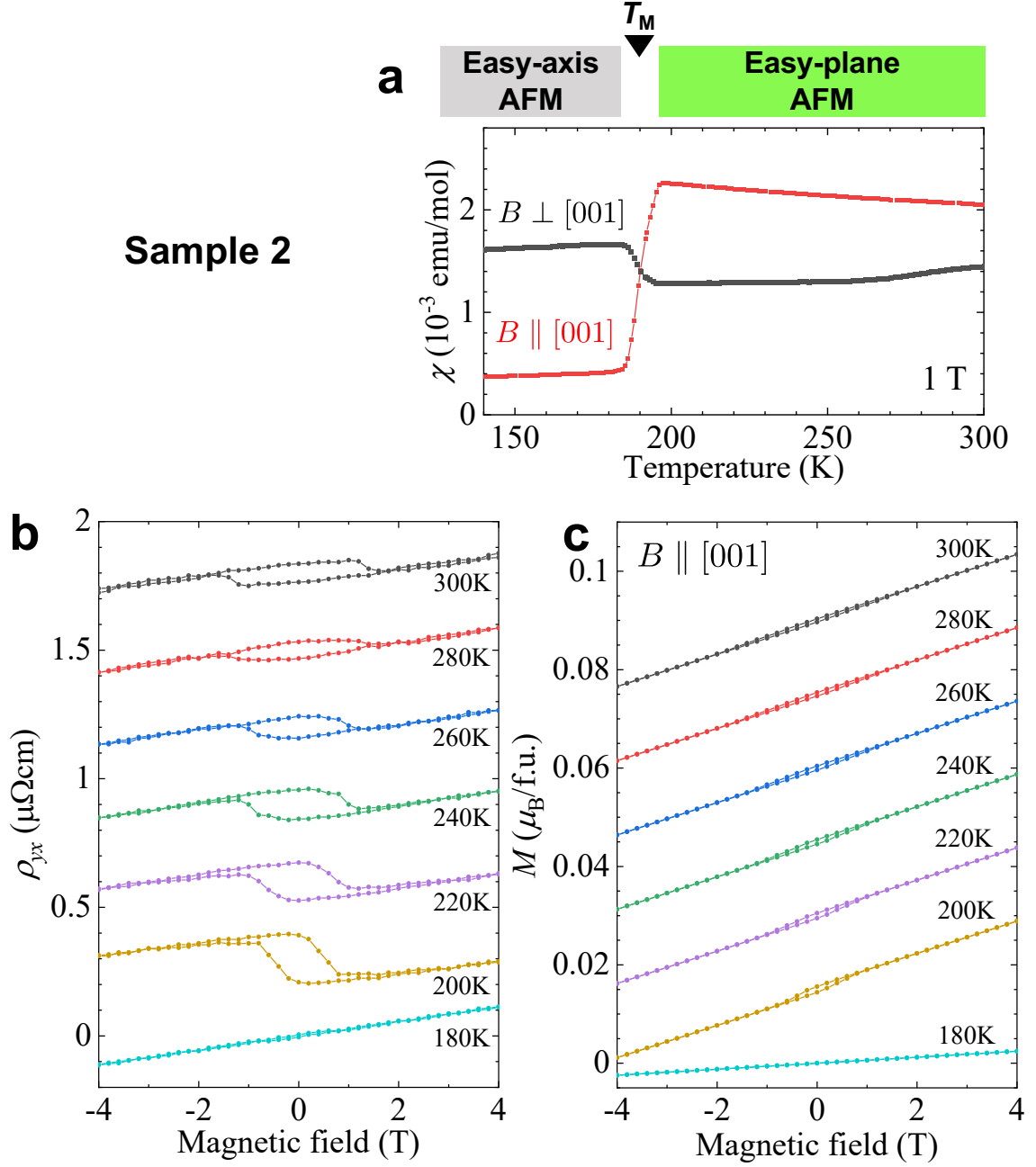
In the main text, we focused on the single crystal sample with the Morin transition temperature $T_M \sim 220$ K (i.e. the sample 1), which has been identified from the anomaly in the χ - T profile (Supplementary Fig. 1a). Supplementary Figs. 1b and c indicate magnetic field dependence of Hall resistivity ρ_{yx} and magnetization M for the sample 1, measured with $B \parallel [001]$ at various temperatures. In the easy-plane antiferromagnetic state above the Morin temperature $T_M \sim 220$ K, clear spontaneous Hall signal at zero field and associated hysteresis loop are always observed in ρ_{yx} profiles. The corresponding M profile is almost B -linear, but tiny spontaneous magnetization ΔM_{cant} can be identified. The amplitude of spontaneous Hall signal is gradually enhanced at lower temperature, which is probably related with the development of antiferromagnetic order parameter (Similar behavior has also been reported in Mn_3Sn [S1]). In the easy-axis antiferromagnetic state below T_M , on the other hand, spontaneous Hall signal and ΔM_{cant} disappear. It reflects the change of magnetic symmetry as summarized in Fig. 3e in the main text.

We have also performed the similar measurement for several different single crystal pieces grown by the same conditions. Previous studies reported that the Morin transition temperature T_M sensitively depends on the composition x for FeS_{1+x} [S2]. T_M of our samples ranges from 230 K to 190 K, corresponding to $x = 0.05 \sim 0.06$ according to Ref. [S2]. As mentioned in Methods section in the main text, the additional SEM/EDS (scanning electron microscope with an energy dispersive X-ray spectroscopy) measurement revealed that the sample 1 with $T_M \sim 220$ K is characterized by the chemical composition $x = 0.045 \pm 0.009$, in good agreement with the aforementioned estimation.

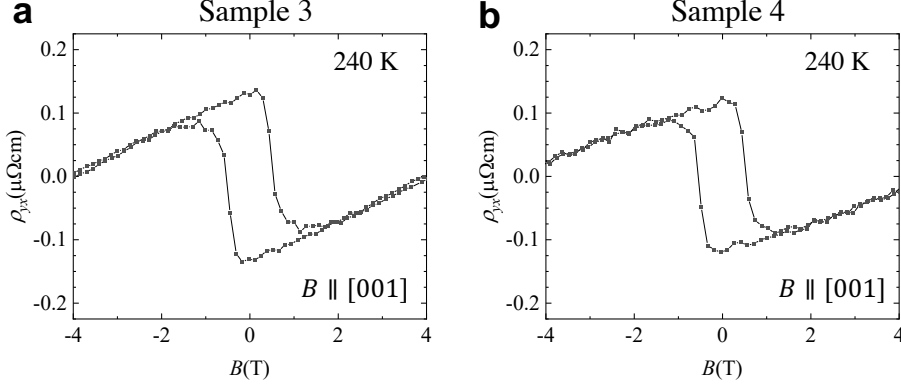
We confirmed that all samples show the similar behaviors, i.e. the existence (absence) of prominent spontaneous Hall signal $\Delta\rho_{yx}$ and weak spontaneous magnetization $\Delta M_{\text{cant}} \parallel [001]$ in the easy-plane (easy-axis) antiferromagnetic state above (below) T_M . As an example, we plotted the corresponding data for the sample 2 with $T_M \sim 190$ K in Supplementary Fig. 2 (In this manuscript, the data for the sample 1 are presented unless specified). Since the presence/absence of spontaneous Hall signal and weak spontaneous magnetization is clearly correlated with Morin transition as well as crystallographic orientation (Figs. 2 and 3 in the main text), the observed features should reflect the intrinsic properties of this compound.



Supplementary Fig. 1: **Hall resistivity and magnetization profiles measured at various temperatures for FeS (Sample 1).** **a**, Temperature dependence of magnetic susceptibility, measured at 1 T for $B \parallel [001]$ and $B \parallel [1\bar{1}0]$ ($\perp [001]$). **b,c**, Magnetic field dependence of Hall resistivity ρ_{yx} and magnetization M measured with $B \parallel [001]$ and $I \parallel [110]$ at various temperatures. Each data is arbitrarily shifted along the vertical direction for clarify.



Supplementary Fig. 2: **Hall resistivity and magnetization profiles measured at various temperatures for FeS (Sample 2).** **a**, Temperature dependence of magnetic susceptibility, measured at 1 T for $B \parallel [001]$ and $B \parallel [1\bar{1}0]$ ($\perp [001]$). **b,c**, Magnetic field dependence of Hall resistivity ρ_{yx} and magnetization M measured with $B \parallel [001]$ and $I \parallel [110]$ at various temperatures. Each data is arbitrarily shifted along the vertical direction for clarify.



Supplementary Fig. 3: **Hall resistivity data for the samples 3 and 4.** Magnetic field dependence of Hall resistivity ρ_{yx} measured at 240 K for the samples 3 (a) and 4 (b), which are characterized by the Morin transition temperature $T_M \sim 222$ K and 225 K, respectively.

In Supplementary Fig. 3, the Hall resistivity profile at 240 K measured for the two additional samples (i.e. the samples 3 and 4 characterized by $T_M \sim 222$ K and 225 K) are also plotted. All samples 1, 2, 3 and 4 are confirmed to host the similar amplitude of spontaneous Hall resistivity in the order of $0.1\mu\Omega\text{cm}$ at 240 K.

In general, the small amount of excess atoms due to off-stoichiometry are randomly distributed within a crystal, and don't affect the overall symmetry and selection rule of conductivity tensor. The experimentally observed selection rules (i.e. anisotropy and spin-orientation dependence) of spontaneous Hall effect are fully consistent with the symmetry analysis in Fig. 3 in the main text and Supplementary Fig. 9, which supports the validity of this assumption.

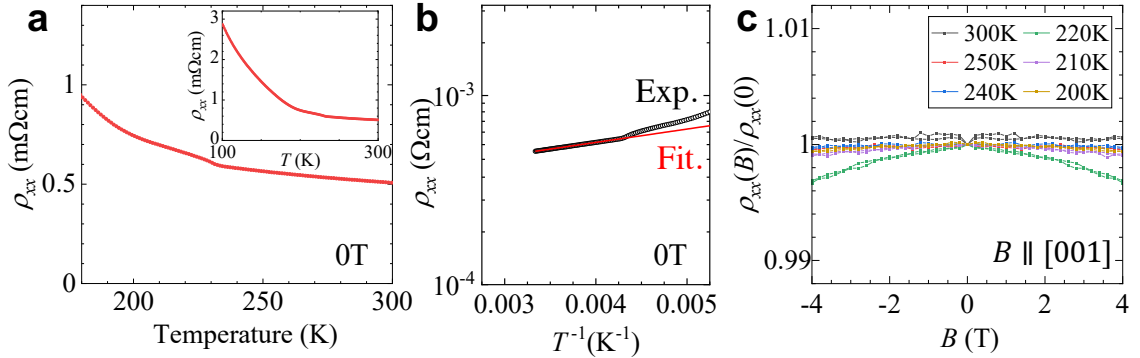
According to Ref. [S3], the relative phase stability of the easy-plane and easy-axis anti-ferromagnetic phases is governed by the delicate balance between the two-types of magnetic anisotropy terms. This is probably the reason why the Morin transition temperature sensitively depends on the chemical composition x . On the other hand, the overall electron band structure in each phase is generally expected to be rigid against the off-stoichiometry, because the magnetic and crystal structures are retained. Here, the main consequence of excess S ions would be the slight shift of Fermi-energy position, and our DFT calculation suggests that 5 % of excess S corresponds to the shift of E_F by 0.068 eV. Since our calculation provides the Fermi-energy-dependence of Hall conductivity (Fig. 4g in the main

text), the properties of such off-stoichiometric samples can be reasonably discussed within the preset theoretical framework.

II. TEMPERATURE AND MAGNETIC FIELD DEPENDENCE OF RESISTIVITY

Supplementary Fig. 4a indicates the temperature dependence of longitudinal resistivity ρ_{xx} measured at 0 T for FeS (Sample 1). We obtained $\rho_{xx} \sim 526 \mu\Omega\text{cm}$ at 300 K, and its value slightly increases at lower temperature. By fitting the experimental data with the Arrhenius equation $\rho_{xx} \propto \exp[-E_g/2k_B T]$ (Supplementary Fig. 4b), the energy gap E_g is estimated to be 0.03 eV. Previous studies reported that FeS is a narrow gap semiconductor with $E_g \sim 0.04$ eV[S4], and the observed behavior is consistent with this picture. The Morin transition does not have much influence on ρ_{xx} .

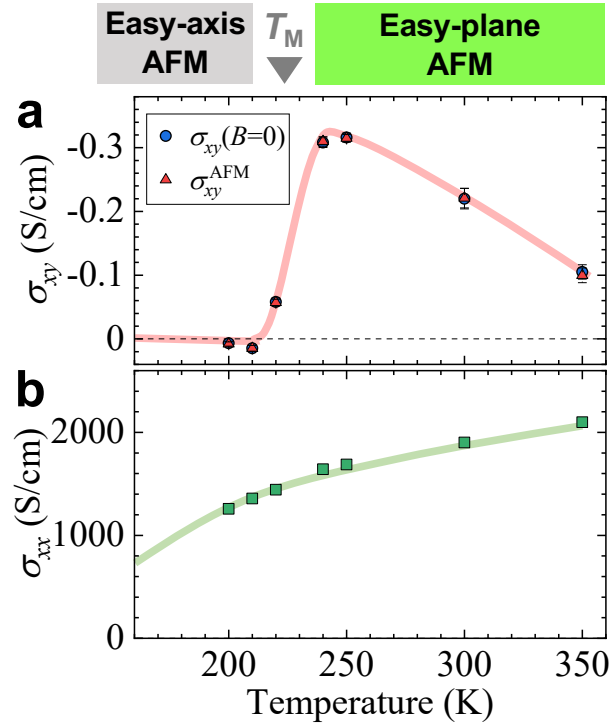
In Supplementary Fig. 4c, magnetoresistance $\rho_{xx}(B)/\rho_{xx}(0)$ for $B \parallel [001]$ measured at various temperatures are summarized. At any temperature, B -induced relative change of resistivity is much smaller than 1 % for $B < 4$ T, while its amplitude slightly increases around



Supplementary Fig. 4: **Temperature and magnetic field dependence of longitudinal resistivity ρ_{xx} for FeS (Sample 1).** **a**, Temperature dependence of ρ_{xx} at 0 T. The inset shows the data for wider temperature range. **b**, ρ_{xx} plotted against T^{-1} . Black dots and a red solid line indicate the experimental data (identical with the one plotted in **a**) and the result of fitting by the Arrhenius equation $\rho_{xx} \propto \exp[-E_g/2k_B T]$, respectively (See text). **c**, Magnetoresistance $\rho_{xx}(B)/\rho_{xx}(0)$ (i.e. the ratio between the values of ρ_{xx} with and without external magnetic field) measured with $B \parallel [001]$ and $I \parallel [110]$ at various temperatures.

the Morin transition temperature. In general, the spin fluctuation and associated electron scattering is enhanced at temperature near the magnetic transition, and the magnetic-field-induced suppression of such a spin fluctuation may be the origin of the observed negative magneto-resistance. The absence of hysteresis is probably due to the smallness of the resistivity difference between the two possible time-reversal domains (i.e. the $\uparrow\downarrow$ and $\downarrow\uparrow$ spin states).

Supplementary Fig. 5 indicates the temperature-dependence of spontaneous Hall conductivity σ_{xy} and longitudinal conductivity σ_{xx} measured at $B = 0$. When the scattering rate $1/\tau (\propto \sigma_{xx})$ is the only variable parameter, the relationship $\sigma_{xy} \propto \sigma_{xx}^0$ (i.e. constant) is expected for the intrinsic (Berry curvature) mechanism of spontaneous Hall effect[S5]. Experimentally, the increase of temperature leads to the gradual suppression of σ_{xy} . It



Supplementary Fig. 5: **Temperature dependence of σ_{xy} and σ_{xx} at $B = 0$ in FeS (Sample 1).** Temperature dependence of (a) spontaneous Hall conductivity σ_{xy} and (b) longitudinal conductivity σ_{xx} measured at $B = 0$. In a, the estimated $\sigma_{xy}^{\text{AFM}} (= \rho_{yx}^{\text{AFM}} / (\rho_{xx}^2 + \rho_{yy}^2))$ value at each temperature is also plotted. The error bars in a represent the standard deviations of the linear fits of $\sigma_{xy}^{\text{AFM}}-B$ profiles between 0 and 4 T for each temperature.

probably reflects the temperature-dependent change of antiferromagnetic order parameter. Note that the relationship $\sigma_{xy} \propto \sigma_{xx}^\beta$ ($1.0 \leq \beta \leq 1.6$) has been predicted for the extrinsic mechanism of spontaneous Hall effect[S5]. In this case, the increase of σ_{xx} at higher temperature should lead to the increase of σ_{xy} , while the experimental σ_{xy} is rather suppressed. It means that the scattering rate $1/\tau (\propto \sigma_{xx})$ alone cannot explain the observed suppression of σ_{xy} at higher temperature in either case, and T -dependent change of antiferromagnetic order parameter should be also considered.

III. ANALYSIS OF HALL RESISTIVITY DATA

As discussed in Ref. [S1], Hall resistivity of TtS-broken antiferromagnets can be generally described as

$$\rho_{yx} = \rho_{yx}^N + \rho_{yx}^A + \rho_{yx}^{\text{AFM}} = R_0 B + S_H \rho_{xx}^2 M + \rho_{yx}^{\text{AFM}}, \quad (\text{S1})$$

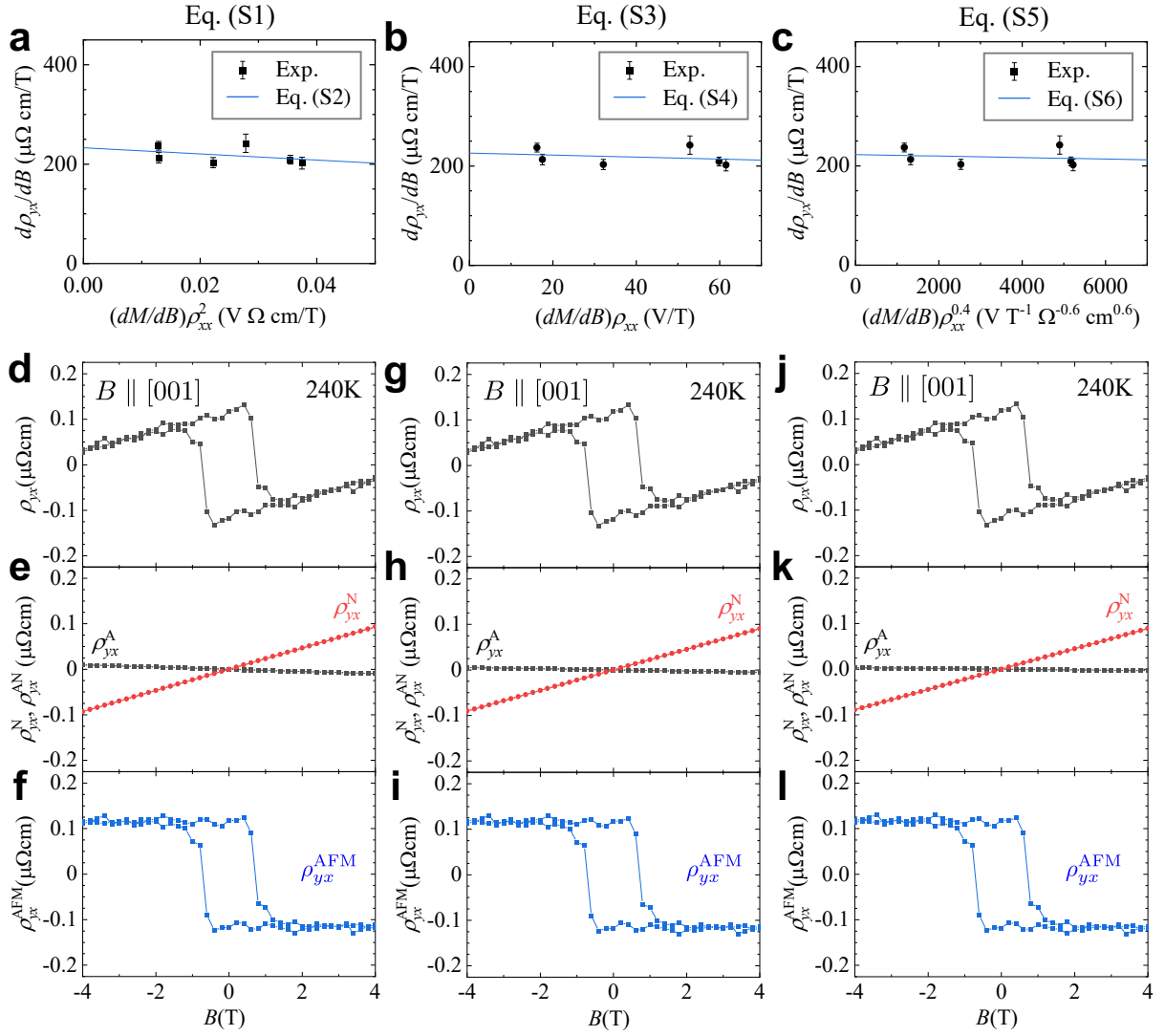
where the first and second terms represent the normal Hall term ρ_{yx}^N proportional to external magnetic field B and anomalous Hall term ρ_{yx}^A proportional to magnetization M , respectively (R_0 and S_H are the coefficients for each term). For magnetic conductors with relatively high resistivity, the relation $\rho_{yx}^A = S_H \rho_{xx}^2 M$ is usually expected from the intrinsic mechanism of anomalous Hall effect[S5]. The third term ρ_{yx}^{AFM} represents the additional Hall contribution from the TtS-broken antiferromagnetic order, which is governed by antiferromagnetic order parameter and usually insensitive to B .

In case of FeS, B -induced relative change of resistivity is much smaller than 1 % for $B < 4$ T at any temperature (Supplementary Fig. 4c). When we assume ρ_{xx} and ρ_{yx}^{AFM} as B -independent, the relationship

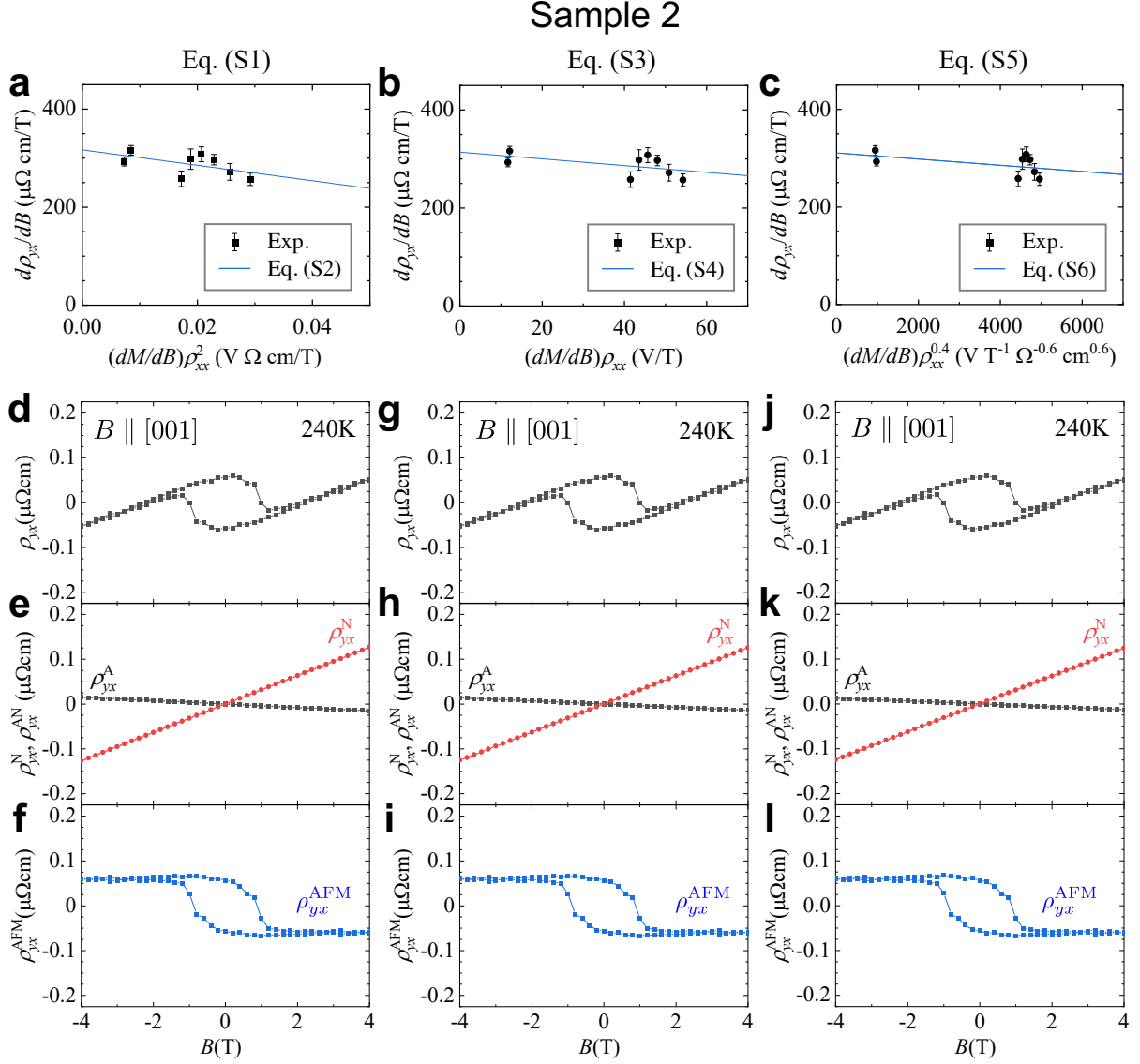
$$\frac{d\rho_{yx}}{dB} = R_0 + S_H \rho_{xx}^2 \frac{dM}{dB} \quad (\text{S2})$$

is obtained by taking the derivative of Eq. (S1) with respect to B . To estimate the coefficient R_0 and S_H , we extract the linear slope of experimental ρ_{yx} - B and M - B profiles (i.e. $d\rho_{yx}/dB$ and dM/dB) at each temperature (Supplementary Figs. 1b and c), and plotted $d\rho_{yx}/dB$ against $(dM/dB)\rho_{xx}^2$ in Supplementary Fig. 6a. The data can be well fitted by Eq. (S2), and its linear slope and intercept provide $S_H = -6.2 \times 10^{-4} \text{ V}^{-1}$ and $R_0 = 2.3 \times 10^{-10} \text{ m}^3/\text{C}$, respectively. The good fit of the data, both above and below T_M by a single set of parameters, indicates that our assumption of temperature independent R_0 and S_H is

Sample 1



Supplementary Fig. 6: **Analysis of Hall resistivity profiles for FeS (Sample 1).** **a-c**, The plot of $d\rho_{yx}/dB$ against $(dM/dB)\rho_{xx}^2$, $(dM/dB)\rho_{xx}$ and $(dM/dB)\rho_{xx}^{0.4}$, respectively, where the values of $d\rho_{yx}/dB$ and dM/dB are taken from the slope of ρ_{yx} - B and M - B profiles measured at various temperatures in Supplementary Figs. 1b and c. The error bars represent the standard deviations of the linear fits to estimate the slopes. The blue lines in **a-c** represent the fitting by Eq. (S2), Eq. (S4) and Eq. (S6), respectively. **d-f**, Magnetic field dependence of **(d)** Hall resistivity ρ_{yx} experimentally measured at 240 K in the easy-plane antiferromagnetic state, and the corresponding **(e)** ρ_{yx}^N , ρ_{yx}^A and **(f)** ρ_{yx}^{AFM} components deduced based on Eq. (S1) with the fitting results in **a**. **g-i**, The corresponding data deduced based on Eq. (S3) with the fitting results in **b**. **j-l**, The corresponding data deduced based on Eq. (S5) with the fitting results in **c**.



Supplementary Fig. 7: **Analysis of Hall resistivity profiles for FeS (Sample 2).** **a-c**, The plot of $d\rho_{yx}/dB$ against $(dM/dB)\rho_{xx}^2$, $(dM/dB)\rho_{xx}$ and $(dM/dB)\rho_{xx}^{0.4}$, respectively, where the values of $d\rho_{yx}/dB$ and dM/dB are taken from the slope of ρ_{yx} - B and M - B profiles measured at various temperatures in Supplementary Figs. 2b and c. The error bars represent the standard deviations of the linear fits to estimate the slopes. The blue lines in **a-c** represent the fitting by Eq. (S2), Eq. (S4) and Eq. (S6), respectively. **d-f**, Magnetic field dependence of (d) Hall resistivity ρ_{yx} experimentally measured at 240 K in the easy-plane antiferromagnetic state, and the corresponding (e) ρ_{yx}^N , ρ_{yx}^A and (f) ρ_{yx}^{AFM} components deduced based on Eq. (S1) with the fitting results in **a**. **g-i**, The corresponding data deduced based on Eq. (S3) with the fitting results in **b**. **j-l**, The corresponding data deduced based on Eq. (S5) with the fitting results in **c**.

a reasonable approximation. It is consistent with the weak temperature dependence of ρ_{xx} and $d\rho_{yx}/dB$ (i.e. the slope of ρ_{yx} - B profiles governed by R_0 and S_H) as observed in Supplementary Figs. 4a and 1b. Similar fitting also worked well for Mn_3Sn as reported in Ref. [S1].

On the basis of these S_H and R_0 values, we can estimate ρ_{yx}^N and ρ_{yx}^A in Eq. (S1). By subtracting the above two terms from the experimental ρ_{yx} profile, ρ_{yx}^{AFM} can be also obtained. In Supplementary Figs. 6d-f, magnetic field dependence of ρ_{yx} measured at 240 K (i.e. the easy-plane antiferromagnetic state), as well as its decomposed ρ_{yx}^N , ρ_{yx}^A and ρ_{yx}^{AFM} profiles, are plotted. It indicates that the linear slope of ρ_{yx} - B profile is mainly governed by the normal Hall term, and the contribution of M -linear anomalous Hall term is negligibly small (Supplementary Fig. 6e). The smallness of M -linear ρ_{yx}^A term is consistent with the fact that $d\rho_{yx}/dB$ (Supplementary Figs. 1b) is nearly temperature independent across the easy-plane and easy-axis antiferromagnets states, despite the large change of dM/dB (Supplementary Figs. 1c) between these two magnetic states. Importantly, the present analysis revealed that the spontaneous Hall signal at $B = 0$ is dominated by ρ_{yx}^{AFM} (Supplementary Fig. 6f), which demonstrates that its origin is TtS-broken collinear antiferromagnetic order itself, rather than tiny spontaneous magnetization ΔM_{cant} .

Note that the M -linear anomalous Hall term ρ_{yx}^A can also originate from extrinsic skew scattering mechanism, which is expected to satisfy the relationship $\rho_{yx}^A = C_H \rho_{xx} M$ (C_H is the coefficient)[S5]. In this case, Eq. (S1) and Eq. (S2) are replaced by

$$\rho_{yx} = \rho_{yx}^N + \rho_{yx}^A + \rho_{yx}^{\text{AFM}} = R_0 B + C_H \rho_{xx} M + \rho_{yx}^{\text{AFM}} \quad (\text{S3})$$

and

$$\frac{d\rho_{yx}}{dB} = R_0 + C_H \rho_{xx} \frac{dM}{dB}, \quad (\text{S4})$$

respectively. While this picture is usually valid for metals in the clean limit rather than semiconducting materials like FeS, we attempted to analyze the present experimental data based on Eqs. (S3) and (S4) as a trial. In Supplementary Fig. 6b, we have plotted $d\rho_{yx}/dB$ against $(dM/dB)\rho_{xx}$. By fitting them with Eq. (S4), C_H and R_0 can be estimated from its linear slope and intercept, respectively. On the basis of Eq. (S3) and the obtained C_H and R_0 values, we can decompose the experimental ρ_{yx} into ρ_{yx}^N , ρ_{yx}^A and ρ_{yx}^{AFM} as summarized in Supplementary Figs. 6g-i. This analysis leads to the same conclusion that the spontaneous

Hall signal at $B = 0$ is dominated by ρ_{yx}^{AFM} , and the contribution of M -linear ρ_{yx}^{A} is negligibly small.

In the system with very low conductivity (i.e. the dirty limit), another scaling relationship $\sigma_{xy}^{\text{A}} \propto \sigma_{xx}^{1.6}$ has been proposed[S5, S6, S7], which corresponds to $\rho_{yx}^{\text{A}} = D_{\text{H}}\rho_{xx}^{0.4}M$ (D_{H} is the coefficient). In this case, Eq. (S1) and Eq. (S2) are replaced by

$$\rho_{yx} = \rho_{yx}^{\text{N}} + \rho_{yx}^{\text{A}} + \rho_{yx}^{\text{AFM}} = R_0B + D_{\text{H}}\rho_{xx}^{0.4}M + \rho_{yx}^{\text{AFM}} \quad (\text{S5})$$

and

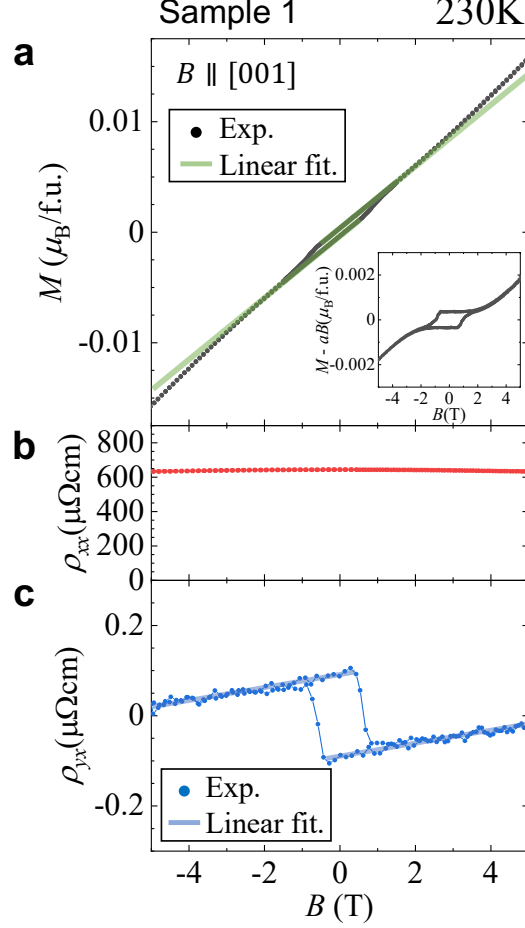
$$\frac{d\rho_{yx}}{dB} = R_0 + D_{\text{H}}\rho_{xx}^{0.4}\frac{dM}{dB}, \quad (\text{S6})$$

respectively. In Supplementary Fig. 6c, we have plotted $d\rho_{yx}/dB$ against $(dM/dB)\rho_{xx}^{0.4}$ as a trial. By fitting them with Eq. (S6), D_{H} and R_0 can be estimated from its linear slope and intercept, respectively. On the basis of Eq. (S5) and the obtained D_{H} and R_0 values, we can decompose the experimental ρ_{yx} into ρ_{yx}^{N} , ρ_{yx}^{A} and ρ_{yx}^{AFM} as summarized in Supplementary Figs. 6j-l. This analysis also leads to the same conclusion that the spontaneous Hall signal at $B = 0$ is dominated by ρ_{yx}^{AFM} , and the contribution of M -linear ρ_{yx}^{A} is negligibly small.

In Supplementary Fig. 7, the similar analysis has been performed for the sample 2, which also confirms that its spontaneous Hall signal is dominated by ρ_{yx}^{AFM} as in case of the sample 1 (Supplementary Fig. 6).

The negligibly small nature of M -linear ρ_{yx}^{A} term can be also confirmed from the Hall resistivity profile at 230 K in the sample 1. Supplementary Figs. 8a-c indicate the magnetic field dependence of M , ρ_{xx} and ρ_{yx} measured at 230 K under $B \parallel [001]$ for the sample 1. Unlike other temperatures, this temperature is close to $T_{\text{M}} \sim 220$ K, and the M - B profile shows non-linear behavior at high- B region. Here, we fitted the magnetization data at the low- B region with a linear function ($M = aB + b$), and the nonlinear magnetization component ($M - aB$ obtained by the subtraction of B -linear slope from the raw experimental data) is plotted as the inset. If the Hall resistivity profile is dominated by the M -linear ρ_{yx}^{A} and B -linear ρ_{yx}^{N} terms, it should show a non-linear B -dependence in the similar manner as the $M - aB$ profile (the inset of Supplementary Fig. 8a). Nevertheless, the experimental Hall resistivity profile (Supplementary Fig. 8c) shows B -linear behavior even at high- B region. It indicates that the contribution of M -linear ρ_{yx}^{A} term is very small, and rather the contribution of ρ_{yx}^{AFM} and ρ_{yx}^{N} terms is significant in the present compound.

As detailed in Supplementary Note IV and IX, the microscopic origin of ρ_{yx}^{AFM} can be ascribed to the fictitious magnetic field associated with TtS-broken collinear antiferromagnetic order. Note that some materials with non-coplanar spin texture (such as $\text{Nd}_2\text{Mo}_2\text{O}_7$) are known to host large fictitious magnetic field associated with scalar spin chirality (i.e. solid angle spanned by three neighboring spins)[S5], while the latter scenario would be irrel-



Supplementary Fig. 8: **Analysis of Hall resistivity profile at 230 K (Sample 1).** Magnetic field dependence of Magnetization M (a), longitudinal resistivity ρ_{xx} (b) and Hall resistivity ρ_{yx} (c) measured for FeS (sample 1) at 230 K with $B \parallel [001]$. In a, the experimental data (closed circles) at low- B region is fitted by a linear function $M = aB + b$ (green solid line), with a and b being the fitting parameters. The inset in a represents the B -dependence of $M - aB$, where the B -linear component is subtracted from the raw experimental data. In c, the experimental data (closed circles) is fitted by a linear function (blue solid line).

evant to the present case because FeS is characterized by coplanar spin texture even under $B \parallel [001]$.

IV. MAGNETIC SYMMETRY AND CONDUCTIVITY TENSOR

In this section, we discuss a general method for the derivation of symmetry-imposed shape of electrical conductivity tensor σ (defined by $\mathbf{j} = \sigma \mathbf{E}$ with $\mathbf{j}$ and $\mathbf{E}$ representing electric current and electric field, respectively). As detailed in Ref. [S8], the transformation rules of conductivity tensor under symmetry operations are governed by the Neumann's principle and Onsager relationship. When the system is invariant under the primed symmetry operation $R' = R1'$ (i.e. the symmetry operation R followed by time-reversal operation $1'$), the conductivity tensor should satisfy the relation

$$\sigma_{ij} = \sum_{m,n} R_{im} R_{jn} \sigma_{nm}. \quad (\text{S7})$$

On the other hand, for the symmetry operation R that doesn't contain time-reversal,

$$\sigma_{ij} = \sum_{m,n} R_{im} R_{jn} \sigma_{mn} \quad (\text{S8})$$

should be satisfied[S8].

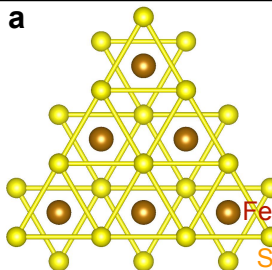
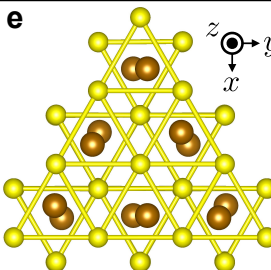
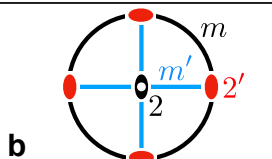
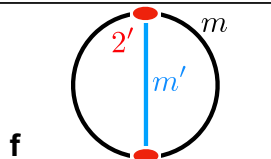
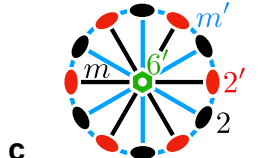
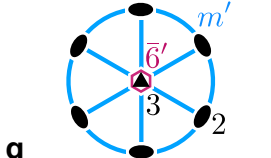
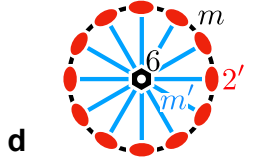
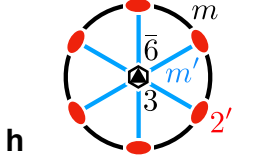
For example, when the magnetic point group of the target system contains the mirror (m) plane normal to the z -axis or the two-fold rotation (2) axis parallel to the z -axis, the relationship

$$\begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ -\sigma_{xy} & \sigma_{yy} & \sigma_{yz} \\ -\sigma_{xz} & -\sigma_{yz} & \sigma_{zz} \end{pmatrix} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & -\sigma_{xz} \\ -\sigma_{xy} & \sigma_{yy} & -\sigma_{yz} \\ \sigma_{xz} & \sigma_{yz} & \sigma_{zz} \end{pmatrix} \quad (\text{S9})$$

should hold. In this case, the appearance of σ_{xy} is allowed, while σ_{xz} and σ_{yz} should be zero. On the other hand, when there is the m' plane normal to the z -axis or the $2'$ axis parallel to the z -axis,

$$\begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ -\sigma_{xy} & \sigma_{yy} & \sigma_{yz} \\ -\sigma_{xz} & -\sigma_{yz} & \sigma_{zz} \end{pmatrix} = \begin{pmatrix} \sigma_{xx} & -\sigma_{xy} & \sigma_{xz} \\ \sigma_{xy} & \sigma_{yy} & \sigma_{yz} \\ -\sigma_{xz} & -\sigma_{yz} & \sigma_{zz} \end{pmatrix} \quad (\text{S10})$$

should hold. It allows the appearance of σ_{xz} and σ_{yz} , while σ_{xy} should be zero. By performing the similar analysis for all symmetry elements in the target system, the symmetry-imposed

	High- T structure	Low- T structure	
Crystal structure	$P6_3/mmc$	$P\bar{6}2c$	Conductivity tensor
	a 	e 	
Easy-plane AFM 	$m'm'm$ b 	$2'm'm$ f 	i $\begin{pmatrix} \sigma_{xx} & \sigma_{xy} & 0 \\ -\sigma_{xy} & \sigma_{yy} & 0 \\ 0 & 0 & \sigma_{zz} \end{pmatrix}$
Easy-axis AFM 	$6'/m'm'm$ c 	$\bar{6}'2m'$ g 	j $\begin{pmatrix} \sigma_{xx} & 0 & 0 \\ 0 & \sigma_{yy} & 0 \\ 0 & 0 & \sigma_{zz} \end{pmatrix}$
Easy-axis FM 	$6/mm'm'$ d 	$\bar{6}2'm'$ h 	k $\begin{pmatrix} \sigma_{xx} & \sigma_{xy} & 0 \\ -\sigma_{xy} & \sigma_{yy} & 0 \\ 0 & 0 & \sigma_{zz} \end{pmatrix}$

Supplementary Fig. 9: **Magnetic symmetry and symmetry-imposed shape of conductivity tensor in FeS.** **a-d**, (a) High-temperature (T) crystal structure of FeS characterized by space group $P6_3/mmc$, and the corresponding magnetic point group in the (b) easy-plane AFM (antiferromagnetic), (c) easy-axis AFM, and (d) easy-axis FM (ferromagnetic) states. Here, the crystal structure is viewed from the z -axis (i.e. $[001]$ axis), and the stereographic projection of the symmetry elements in each magnetic point group is also provided. Small white circles at the center of **b**, **c** and **d** represent the inversion center, which do not affect the extinction rule of conductivity tensor components. **e-h**, The corresponding plots for the low-temperature crystal structure characterized by space group $P\bar{6}2c$, which is obtained by removing the 2_1 screw axis along the z -axis in the high- T crystal structure. **i-k**, Symmetry-imposed shapes of conductivity tensor in the (i) easy-plane AFM, (j) easy-axis AFM, and (k) easy-axis FM states. The selection rules are common between the high- T and low- T crystal structures.

shape of electrical conductivity tensor (i.e. the presence/absence of each tensor component) can be deduced. The exhaustive list of the correspondence between the magnetic point group and the symmetry-imposed shape of conductivity tensor is provided in Ref. [S10, S11].

In case of the high-temperature ($P6_3/mmc$) crystal structural phase of FeS (Supplementary Fig. 9a), the easy-plane and easy-axis antiferromagnetic states are characterized by the magnetic point group $m'm'm$ and $6'/m'm'm$, respectively. Here, the easy-plane antiferromagnetic state is characterized by the m plane and $2'$ -axis normal to the z -axis, as well as the m' plane and 2 -axis parallel to the z -axis, which allows the appearance of σ_{xy} but prohibits σ_{yz} and σ_{xz} (Supplementary Figs. 9b and i). On the other hand, the easy-axis antiferromagnetic state is characterized by the m' planes normal and parallel to the z -axis, where any off-diagonal component of conductivity tensor is prohibited (Supplementary Figs. 9c and j).

In the low-temperature crystal structural phase of FeS (characterized by the space group $P\bar{6}2c$, i.e. the subgroup of $P6_3/mmc$ in the high-temperature phase), the 2_1 screw axis along the z -axis in the high-temperature phase is broken due to the slight shift of Fe atom positions (Supplementary Fig. 9e). Since the selection rules are generally relaxed for lower symmetry systems, the conductivity tensor component allowed for the high-temperature crystal structure should be also permitted in the low-temperature one. For the low-temperature crystal structural phase of FeS, the easy-plane and easy-axis antiferromagnetic states are characterized by the magnetic point group $2'm'm$ and $\bar{6}'2m'$, respectively. The easy-plane antiferromagnetic state is characterized by the m plane and $2'$ -axis normal to the z -axis, as well as the m' plane parallel to the z -axis, which allows the appearance of σ_{xy} but prohibits σ_{yz} and σ_{xz} (Supplementary Figs. 9f and i). On the other hand, the easy-axis antiferromagnetic state is characterized by the m' planes normal and parallel to the z -axis, where any off-diagonal component of conductivity tensor is prohibited (Supplementary Figs. 9g and j). The above analysis suggests that the symmetry-imposed shape of electrical conductivity tensor remains unchanged[S10, S11] between the high temperature ($P6_3/mmc$) and low temperature ($P\bar{6}2c$) crystal structures of FeS, and we can expect the same selection rule of spontaneous Hall effect for both crystal structures (Supplementary Figs. 9i and j).

Note that the presence of σ_{xy} is associated with the fictitious magnetic field $\mathbf{b}_f \parallel z$. In general, the fictitious magnetic field $\mathbf{b}_f$ changes its direction for $1'$, $m \parallel \mathbf{b}_f$, $m' \perp \mathbf{b}_f$, $n \perp \mathbf{b}_f$, and $n' \parallel \mathbf{b}_f$ (with $n = 2, 3, 4$ or 6 representing the n -fold rotation axis), and therefore the

existence of $\mathbf{b}_f \parallel z$ is allowed only when these symmetry elements are absent in the target system[S9]. By analyzing the presence/absence of such symmetry elements in each magnetic point group, the selection rule of the off-diagonal component of conductivity tensor can be also derived as well.

When the magnetic point group of the target system allows the appearance of σ_{xy} , it also allows the appearance of net magnetization ΔM_{cant} along the direction of $\mathbf{b}_f \parallel z$ (due the slight tilting of antiferromagnetically aligned moments) as discussed in Supplementary Note V. In case of the easy-plane antiferromagnetic state on the FeS crystal lattice, the collinear antiferromagnetic order without spin tilting is already characterized by the magnetic point group compatible with spontaneous Hall effect, and the introduction of additional spin tilting doesn't change the magnetic point group. It means that the spin tilting is not essential for the appearance of spontaneous Hall effect in this system, and non-zero Hall conductivity can be allowed even in the limit of $\Delta M_{\text{cant}} = 0$. This symmetry-based prediction is also supported by the additional DFT calculation in Supplementary Note IX.

In Supplementary Figs. 9d, h, and k, the similar symmetry analysis has also been performed for the uniform ferromagnetic state with magnetic moments parallel to the z -axis, where the appearance of non-zero σ_{xy} component is allowed.

Here, we would like to emphasize that TtS-breaking is a necessary condition, but not sufficient condition for the emergence of spontaneous Hall effect associated with the off-diagonal component of electrical conductivity tensor (σ_{xy}). For its presence, not only TtS-breaking, but also some additional symmetry breaking is required[S9]. In the present case, both easy-plane and easy-axis antiferromagnetic orders in FeS break the TtS symmetry. Nevertheless, they are characterized by different magnetic point group and conductivity tensor shape, and only the former easy-plane one is allowed to host non-zero σ_{xy} component (Supplementary Fig. 9).

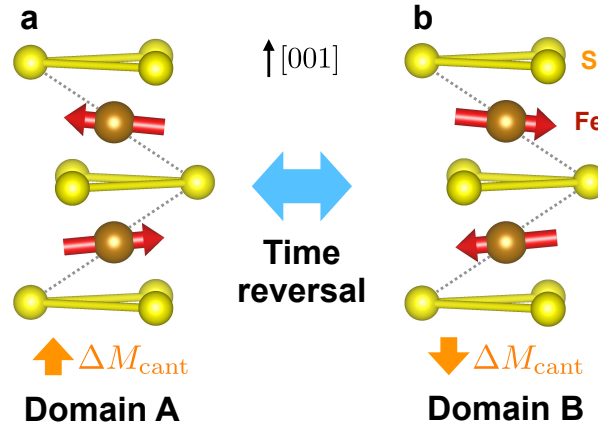
Recently, the term “altermagnet” is often used to describe the collinear antiferromagnets with TtS-breaking, where spin splitting (i.e. degeneracy lifting of up-spin and down-spin electron bands) is allowed even without spin-orbit interaction[S12, S13]. Spin group is the framework to describe the symmetry of the spin system without spin-orbit interaction, and it was used to classify the selection rule of spin splitting in altermagnets. On the other hand, spontaneous Hall effect induced by collinear magnetic order requires spin-orbit coupling[S9], and its selection rule should be discussed based on magnetic point group, rather

than spin group. As already discussed, not all altermagnets, but only a part of them with additional symmetry breaking (such as FeS with easy-plane antiferromagnetic order) can host spontaneous Hall effect.

V. ORIGIN OF WEAK SPONTANEOUS MAGNETIZATION IN THE EASY-PLANE ANTIFERROMAGNETIC STATE

When the magnetic point group of TtS-broken antiferromagnetic order permits the presence of σ_{xy} , the emergence of fictitious magnetic field along the $[001]$ axis can be expected. In such a situation, the magnetic symmetry also allows the appearance of tiny spontaneous magnetization ΔM_{cant} along the $[001]$ direction.

In case of FeS, the appearance of $\Delta M_{\text{cant}} \parallel [001]$ can be well explained in terms of local magneto-crystalline anisotropy. Here, each Fe ion is sandwiched by a pair of oppositely oriented triangular plaquettes of S ions (Supplementary Fig. 10). The site symmetry of



Supplementary Fig. 10: **Weak spontaneous magnetization in the easy-plane antiferromagnetic state.** **a,b**, The magnetic domains A and B in the easy-plane antiferromagnetic state, which are converted into each other by the time-reversal operation. Here, each local magnetic moment slightly tilts from the original $[110]$ direction toward the closest Fe-S bond (represented by the dashed lines) to obtain the energy gain by the trigonal magnetocrystalline anisotropy term given by Eq. (S11). It leads to the appearance of weak spontaneous magnetization ΔM_{cant} along the $[001]$ direction, and the sign of ΔM_{cant} is opposite between the domains A and B. Note that the amplitude of spin tilting is exaggerated in these figures for clarity.

Fe ion is characterized by the trigonal point group $\bar{3}m$ for the $P6_3/mmc$ structure, or the point group 1 for the $P\bar{6}2c$ structure. In both cases, the phenomenological expression of local magneto-crystalline anisotropy energy will include the term[S14]

$$\Delta E_{\text{trigonal}} = K \sin^3 \theta \cos \theta \cos 3\phi. \quad (\text{S11})$$

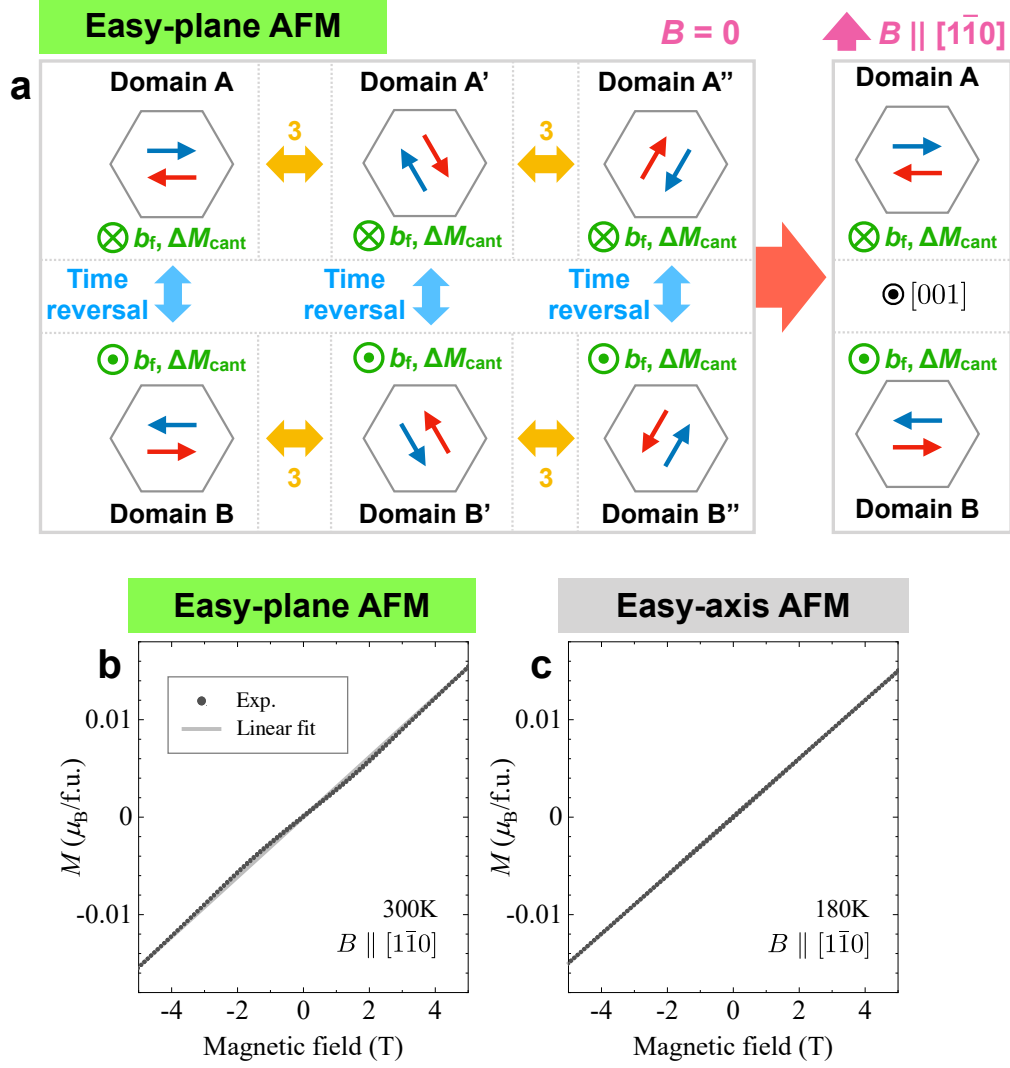
K is the coefficient, and θ (ϕ) represents the angle between the local magnetic moment and the $[001]$ ($[110]$) axis. Intuitively, this term favors to align the local magnetic moment toward the direction of Fe-S bond. The sign of K is opposite between the neighboring Fe layers, because of the alternate stacking manner of sulfur triangular plaquettes (Supplementary Fig. 10).

In the easy-plane antiferromagnetic state, the in-plane component of local magnetic moment ($\parallel \langle 110 \rangle$) is antiparallel between the neighboring Fe layer. To maximize the energy gain by $\Delta E_{\text{trigonal}}$, each local magnetic moment tilts toward the closest Fe-S bond direction (represented by the dashed lines in Supplementary Fig. 10). As a result, the local moments in the neighboring Fe layers tilt toward the same out-of-plane direction, which leads to the appearance of net magnetization along the $[001]$ axis. Between the $\uparrow\downarrow$ and $\downarrow\uparrow$ spin states (i.e. the domains A and B that are converted into each other by the time-reversal operation), the sign of ΔM_{cant} is opposite (Supplementary Figs. 10a and b). It means that the domain A or B can be selected by the sign of external magnetic field applied along the $[001]$ direction.

For the easy-axis antiferromagnetic state, this $\Delta E_{\text{trigonal}}$ term doesn't induce net magnetization.

VI. MAGNETIC DOMAINS IN THE EASY-PLANE ANTIFERROMAGNETIC STATE AND THEIR SELECTION BY EXTERNAL MAGNETIC FIELD

When the magnetic order breaks the symmetry of original crystal structure, there should appear multiple equivalent magnetic domains that are converted into each other by the broken symmetry elements. In case of FeS, the easy-plane antiferromagnetic order breaks the three-fold rotational symmetry and time-reversal symmetry, and it leads to the appearance of six possible antiferromagnetic domains (i.e. the domains A, B, A', B', A'', and B'' in the left panel of Supplementary Fig. 11a). While these six domains are expected to coexist with the equal population at $B = 0$, the application of $B \parallel [\bar{1}10]$ should lead to the selection of



Supplementary Fig. 11: **Magnetization profiles for the in-plane magnetic field.** **a**, Left panel illustrates six possible magnetic domains in the easy-plane antiferromagnetic state at $B = 0$, which are converted into each other by either three-fold rotation (3) or time-reversal operation. The red and blue arrows pointing along the in-plane direction represents the orientation of local magnetic moment in the first and second Fe layer, respectively. The green arrows pointing along the out-of-plane direction indicate the orientation of fictitious magnetic field $\mathbf{b}_f$ and tiny spontaneous magnetization ΔM_{cant} . Right panel illustrates the selection of magnetic domains by $B \parallel [1\bar{1}0]$. **b,c**, Magnetic field dependence of magnetization measured for $B \parallel [1\bar{1}0]$ at **(b)** 300 K in the easy-plane antiferromagnetic state and **(c)** 180 K in the easy-axis antiferromagnetic state. Black dots and gray bold lines represent the experimental data and the fitting by $M = \chi B$, respectively. The small anomalies in **b** originates from the B -induced selection of three-fold rotational domains as described in **a**.

domains A and B (right panel of Supplementary Fig. 11a). This is because the collinear antiferromagnetic order generally hosts larger (smaller) magnetic susceptibility χ for the direction normal (parallel) to their spin orientation. Supplementary Fig. 11b indicates the M - B profile measured for $B \parallel [1\bar{1}0]$ at 300 K in the easy-plane antiferromagnetic state. The slope of magnetization profile gradually changes at around 2 T, and the M - B profile above 4 T can be well fitted by the relationship $M = \chi B$ (bold gray line in Supplementary Fig. 11b) with no spontaneous magnetization component. The observed anomaly reflects the B -induced selection of three-fold rotational magnetic domains as considered in Supplementary Fig. 11a. Note that the absence of hysteresis is due to the small potential barrier among the domains A, A' and A'', where the thermal fluctuation leads to the recovery of these three domains at $B = 0$.

At 180 K in the easy-axis antiferromagnetic state, on the other hand, just a linear M - B profile is observed for $B \parallel [1\bar{1}0]$ as shown in Supplementary Fig. 11c. Since the easy-axis collinear antiferromagnetic structure sustains the three-fold rotational symmetry, there's no rotational magnetic domains and associated B -induced domain selection.

In the easy-plane antiferromagnetic state, each magnetic domain hosts the fictitious magnetic field $\mathbf{b}_f$ along the $[001]$ direction, as discussed in the main text and Supplementary Note IV. In Supplementary Fig. 11a, the direction of fictitious magnetic field $\mathbf{b}_f$ for each domain is shown by the green arrow pointing along the out-of-plane orientation. Here, the domains A, A' and A'' are converted into each other by three-fold rotation, and characterized by the same orientation and amplitude of fictitious magnetic field $\mathbf{b}_f \parallel [001]$. On the other hand, the domains B, B' and B'' are related with the domains A, A' and A'' by the time-reversal operation, respectively, and therefore characterized by the opposite direction of $\mathbf{b}_f$. Since these domains host tiny spontaneous magnetization ΔM_{cant} along the direction of fictitious magnetic field $\mathbf{b}_f$ as discussed in Supplementary Note V, the application of the positive (negative) sign of external magnetic field $B \parallel [001]$ induces the selection of the domains A, A' and A'' (B, B' and B'') with equal population ratio. For the B -induced switching from the domain A to domain B, large potential barrier has to be overcome, since it requires the reversal of antiferromagnetic order parameter. This switching process usually involves the nucleation and successive expansion of the domain B, and large amplitude of external magnetic field and associated Zeeman energy gain are required to overcome the potential barrier. It leads to the appearance of hysteresis loop in the ρ_{yx} - B and M - B pro-

files for $B \parallel [001]$ as experimentally observed in Supplementary Figs. 1b and c. In such Hall measurements, we did not apply any in-plane magnetic field, since the domains A, A' and A'' host the same sign and amplitude of $\mathbf{b}_f \parallel [001]$ and σ_{xy} . (Note that the in-plane conductivity tensor for the Hall effect is generic (similarly to what a Hall effect would be for a real magnetic field along the z -direction) and not tied to any in-plane crystallographic direction.) The coercive field is determined by the balance of several factors, such as the amplitudes of potential barrier, thermal fluctuation, Zeeman energy gain, and the pinning strength of magnetic domain wall. The dynamics of magnetic domain wall is generally governed by the intricate non-equilibrium excitation process, and the quantitative evaluation of potential barrier and pinning strength is not straightforward. For the better understanding of domain wall dynamics, various additional information, such as the stable spin texture at the domain wall region, the nucleation process of magnetic domains, and the manner of domain wall propagation under external magnetic field and crystallographic defects, are required.

For the easy-plane antiferromagnetic state, the simplest magnetic Hamiltonian to describe the domain rearrangement process under in-plane magnetic field $\mathbf{B}$ is[S14]

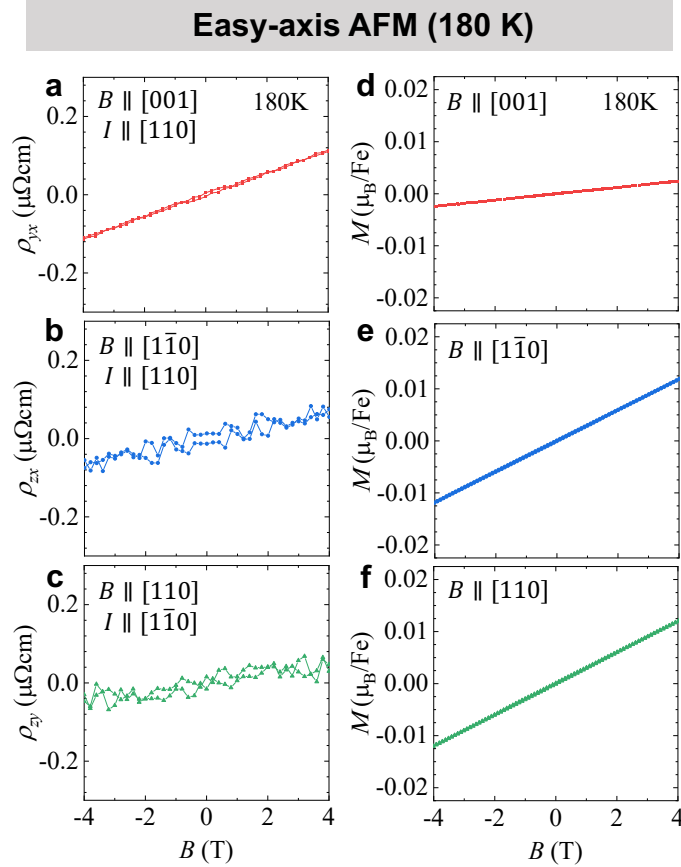
$$\mathcal{H} = \sum_{i,j} J_{ij}(\mathbf{S}_i \cdot \mathbf{S}_j) + \mathbf{B} \sum_i \mathbf{S}_i + K_1 \sum_i (\sin \theta_i)^2 + K_2 \sum_i (\sin \theta_i)^6 \cos 6\phi_i, \quad (\text{S12})$$

where $\mathbf{S}_i = (S_i^x, S_i^y, S_i^z) = |\mathbf{S}_i|(\sin \theta_i \cos \phi_i, \sin \theta_i \sin \phi_i, \cos \theta_i)$ is the local magnetic moment at the site i on the stacked triangular lattice. The first and second terms represent the (intra-plane ferromagnetic and inter-plane antiferromagnetic) exchange and Zeeman energy terms, respectively, which favor to make spins normal to the external magnetic field. The third and fourth terms represent the easy-plane and in-plane six-fold magnetic anisotropy, which favor to make spins parallel to one of the $\langle 110 \rangle$ directions. When the external magnetic field $\mathbf{B}$ is applied along the generic in-plane direction, the competition between the former and latter types of interactions leads to the following spin reorientation process. (1) When the amplitude of magnetic field is small, the spins favor to remain parallel to one of the $\langle 110 \rangle$ direction to maximize the energy gain by anisotropy terms, and the one of three possible rotational domains (A, A' or A'') is selected. The degeneracy of these rotational domains are lifted, since the energy gain by the first and second terms becomes larger when the angle between the magnetic field and spins is closer to 90° . (2) When the amplitude of magnetic field is large, the spin orientation becomes normal to external magnetic field. This is because

the energy gain by the first and second terms becomes larger than the anisotropy terms, and spin orientations are no longer confined along the $\langle 110 \rangle$ directions. Such a spin reorientation process under in-plane magnetic field has commonly been observed in easy-plane triangular lattice antiferromagnets[S15].

VII. ANISOTROPY OF HALL RESISTIVITY AND MAGNETIZATION PROFILES IN THE EASY-AXIS ANTIFERROMAGNETIC STATE

Supplementary Fig. 12 indicates magnetic field dependence of Hall resistivity and magnetization measured with various directions of B and I at 180 K (i.e. easy-axis antiferro-

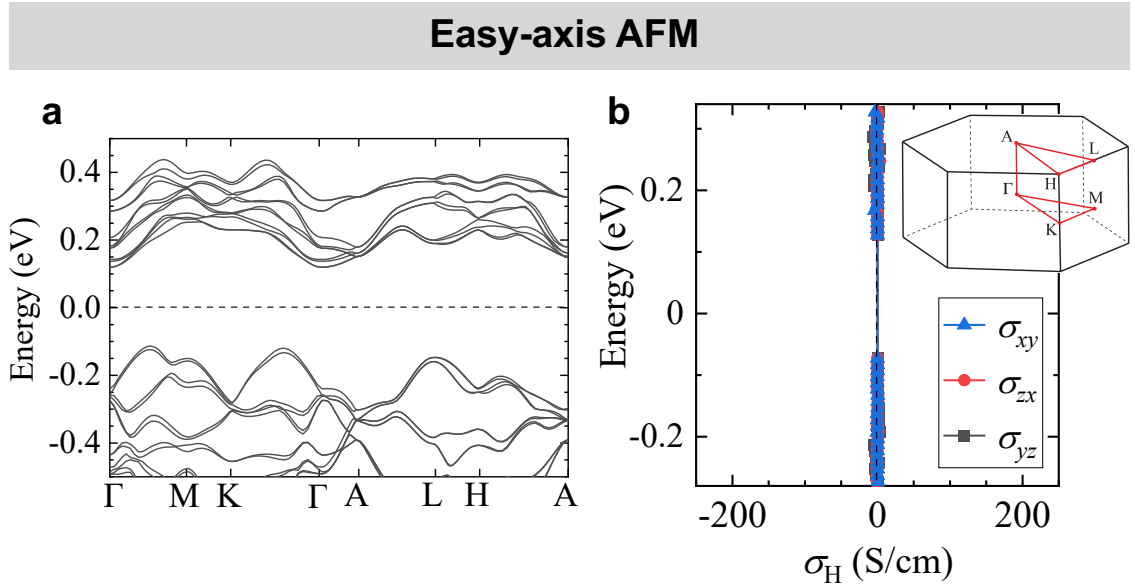


Supplementary Fig. 12: **Anisotropy of Hall resistivity and magnetization profiles in the easy-axis antiferromagnetic state at 180 K.** **a-c**, Magnetic field dependence of Hall resistivity ρ_{yx} , ρ_{zx} , and ρ_{zy} measured with $B \parallel [001]$, $B \parallel [1\bar{1}0]$ and $B \parallel [110]$, respectively. **d-f**, Magnetic field dependence of magnetization measured with $B \parallel [001]$, $B \parallel [1\bar{1}0]$ and $B \parallel [110]$, respectively.

magnetic state). For all configurations, the spontaneous Hall/magnetization components are absent at $B = 0$, and just simple B -linear profiles are observed. Such behaviors are consistent with the magnetic symmetry of easy-axis antiferromagnetic state, which doesn't allow the existence of any off-diagonal conductivity tensor component as summarized in Fig. 3e in the main text and Supplementary Fig. 9.

VIII. FIRST PRINCIPLES CALCULATION OF HALL CONDUCTIVITY IN THE EASY-AXIS COLLINEAR ANTIFERROMAGNETIC STATE

Supplementary Fig. 13 indicates the electronic band structure and E_F -dependence of Hall conductivity σ_H , calculated for the easy-axis collinear antiferromagnetic state of FeS with low-temperature crystal structure ($P\bar{6}2c$). It confirms the absence of spontaneous Hall conductivity in the easy-axis antiferromagnetic state, which is in contrast with the easy-plane

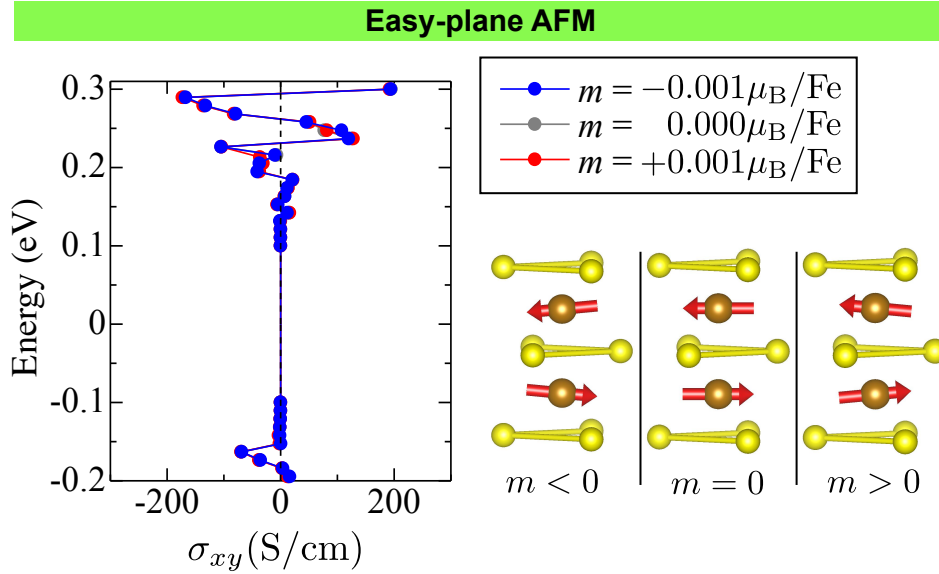


Supplementary Fig. 13: **First principles calculation of Hall conductivity in the easy-axis antiferromagnetic state of FeS.** **a**, Electronic band structure of FeS in the easy-axis collinear antiferromagnetic state, theoretically estimated based on DFT calculation. Each letter symbol represents the position in Brillouin zone as shown in the inset of **b**. In this calculation, the $P\bar{6}2c$ crystal structure and $U = 0$ is assumed. **b**, Fermi-energy dependence of intrinsic spontaneous Hall conductivity σ_H , theoretically calculated based on the Berry curvature mechanism.

antiferromagnetic state hosting non-zero σ_{xy} component (Figs. 4f and g in the main text). These results are consistent with the selection rule of conductivity tensors predicted by the symmetry analysis (Middle and left panels of Fig. 3e in the main text and Supplementary Fig. 9).

IX. FIRST PRINCIPLES CALCULATION OF HALL CONDUCTIVITY WITH AND WITHOUT ADDITIONAL SPIN CANTING.

According to the symmetry analysis in Supplementary Note IV, the easy-plane antiferromagnetic order on FeS crystal lattice is allowed to host spontaneous Hall effect even without



Supplementary Fig. 14: **First principles calculation of Hall conductivity in the easy-plane antiferromagnetic state of FeS with and without additional spin canting.** Fermi-energy dependence of intrinsic spontaneous Hall conductivity σ_{xy} , calculated for the easy-plane antiferromagnetic state with various amplitudes of additional spin canting toward the [001] direction. Here, we fixed the antiferromagnetic order parameter (i.e. assumed the $\uparrow\downarrow$ spin state). The calculation has been performed with $m = -0.001, 0.000$ and $+0.001 \mu_B/\text{Fe}$, where m represents the tiny net magnetization along the [001] direction due to spin canting as schematically illustrated in the bottom right panel. Note that the amplitude of spin tilting is exaggerated in these figures for clarity. In the above calculation, the $P\bar{6}2c$ crystal structure with $U = 0$ is assumed.

net magnetization. To confirm this feature, we performed the additional DFT calculation in the easy-plane antiferromagnetic state with and without small spin canting toward the [001] direction, as summarized in Supplementary Fig. 14. In this calculation, the $P\bar{6}2c$ crystal structure with $U = 0$ is assumed, in the similar manner as Figs. 4f and g in the main text and Supplementary Fig. 13.

Here, we fixed the antiferromagnetic order parameter (i.e. assumed the $\uparrow\downarrow$ spin state) and introduced various amplitudes of additional spin canting toward the [001] direction. In Supplementary Fig. 14, $\sigma_{xy}(E_F)$ profiles are calculated for $m = -0.001, 0.000$ and $+0.001 \mu_B/\text{Fe}$, where m represents the tiny net magnetization along the [001] direction due to spin canting. The results demonstrate that sizable $\sigma_{xy}(E_F)$ can be obtained even without net magnetization, which is rarely affected by the sign and amplitude of small spin canting. It indicates that the calculated σ_{xy} in FeS originates from the TtS-broken easy-plane collinear antiferromagnetic order itself, rather than the tiny net magnetization. Experimentally, the easy-plane antiferromagnetic state is characterized by tiny spontaneous magnetization $m \sim 0.0005\mu_B/\text{Fe}$ along the [001] direction (Fig. 2c in the main text), which is within the range of m -value considered in the present theoretical calculation.

X. AMPLITUDE OF SPONTANEOUS HALL CONDUCTIVITY

Experimentally, FeS in the low-temperature crystal structural phase ($P\bar{6}2c$) is reported to be a narrow gap p -type semiconductor with band-gap 0.04 eV[S4]. It suggests that the present DFT calculation (Fig. 4f in the main text) slightly overestimates the band gap, and the actual Fermi energy (E_F) is located around the upper limit of valence band. Our DFT calculation for the easy-plane collinear antiferromagnetic state suggests that the amplitude of spontaneous Hall conductivity σ_{xy} depends on the Fermi-energy position (Fig. 4g in the main text). As discussed in the main text, the intrinsic spontaneous Hall conductivity σ_{xy} is described as[S5, S9]

$$\sigma_{xy} = \frac{e^2}{\hbar} \sum_n \int_{\text{BZ}} \frac{d^3k}{(2\pi)^3} f_n(\mathbf{k}) \Omega_n^z(\mathbf{k}), \quad (\text{S13})$$

where the integral is taken over the Brillouin zone. $f_n(\mathbf{k})$ is the Fermi-Dirac distribution and $\Omega_n^z(\mathbf{k})$ is the z -component of Berry curvature of the n -th band. It means that σ_{xy} can be interpreted as the integral of Berry curvature over occupied electron states. In general, Berry curvature contribution cancels out for the fully occupied band ($\int \Omega_n^z(\mathbf{k}) d^3k = 0$), and

σ_{xy} becomes smaller as the Fermi energy approaches the upper limit of valence band. This trend is actually confirmed in the $\sigma_{xy}(E_F)$ profile calculated for FeS (Fig. 4g in the main text).

In the case of *p*-type semiconductor, the associated valence band is almost fully occupied, which causes the cancelation of Berry curvature and relatively small value of σ_{xy} . To avoid such a cancelation and realize larger amplitude of σ_{xy} , the employment of metallic compounds with partially filled band structure would be effective. The experimental spontaneous Hall conductivity of semiconducting FeS is $\sigma_{xy} \sim 0.3$ S/cm at 240 K, i.e., considerably smaller than the case of metallic Mn₃Sn[S1], which is consistent with the above theoretical prediction. Here, the amplitude of fictitious magnetic field $|\mathbf{b}_f|$ can be estimated as $|\mathbf{b}_f| = \rho_{xy}^{\text{AFM}}/R_0 \sim 5$ T, based on $\rho_{xy}^{\text{AFM}} \sim 0.12 \mu\Omega\text{cm}$ and $R_0 \sim 2.3 \times 10^{-8} \Omega\text{cm/T}$ obtained from the experimental data at 240 K (Fig. 4d in the main text). Estimated carrier density is $n = 1/(eR_0) \sim 2.7 \times 10^{22} \text{ cm}^{-3}$, in consistent with the previous report[S16].

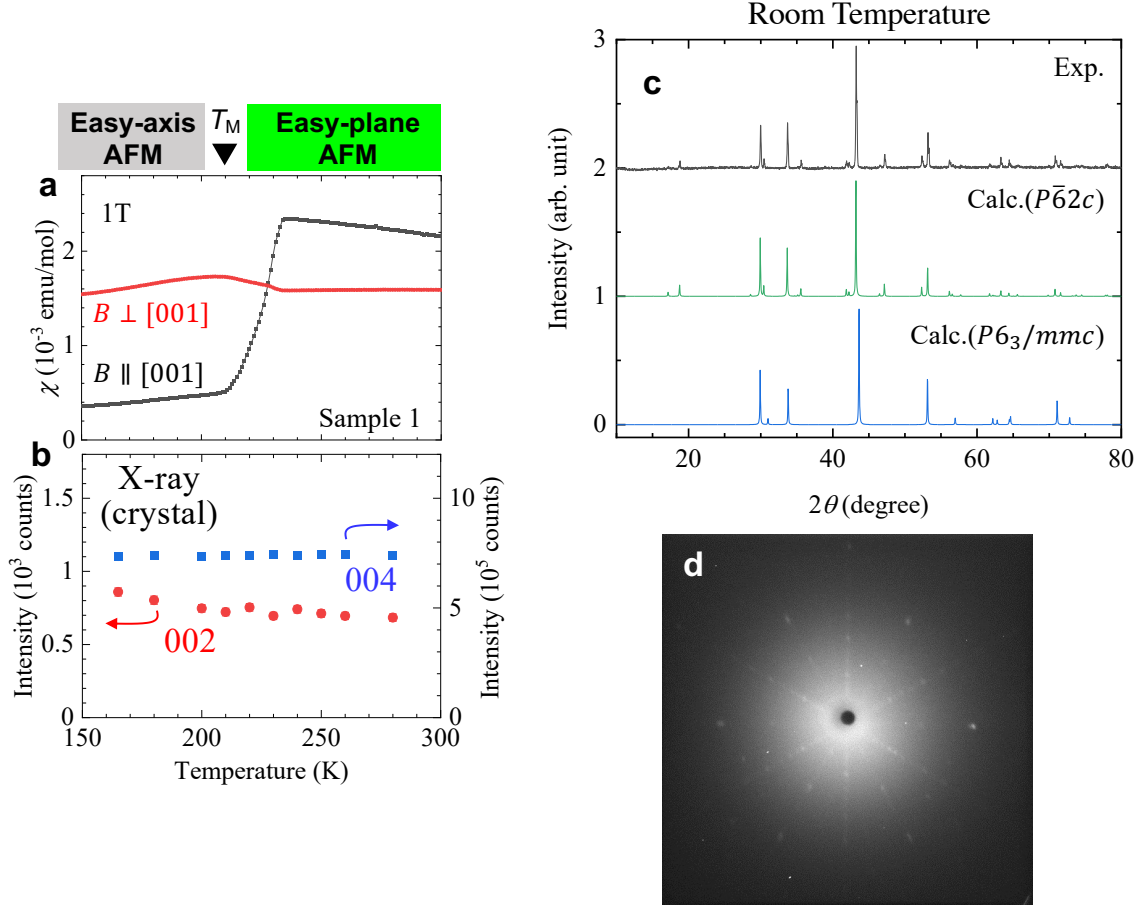
According to recent studies, large Berry curvature often emerges from the band crossing at the Weyl points[S17], nodal lines[S18] or nodal planes[S19]. In this context, to achieve larger spontaneous Hall conductivity, the metallic band structure with characteristic band crossing features, as well as the tuning of Fermi energy position, would be promising. In general, the theoretically calculated E_F -dependence of spontaneous Hall conductivity σ_{xy} is governed by the subtle detail of band structure, such as the location of band crossing points. The direct experimental confirmation of electron band structure and its comparison with the theory are the issue for future study. While there is still room for improvement with Hall signal amplitude, the present experimental discovery of spontaneous Hall effect induced by collinear $\uparrow\downarrow$ spin order at room temperature would be an important step toward further material development.

XI. CRYSTAL AND MAGNETIC STRUCTURE ANALYSIS BASED ON X-RAY AND NEUTRON SCATTERING EXPERIMENTS

According to the previous studies, FeS_{1+x} hosts a crystal structural transition between the high-temperature phase ($P6_3/mmc$) and low-temperature phase ($P\bar{6}2c$), as well as a magnetic transition (i.e. Morin transition) between the easy-plane antiferromagnetic state and easy-axis antiferromagnetic state, as a function of temperature. For $x = 0$, these

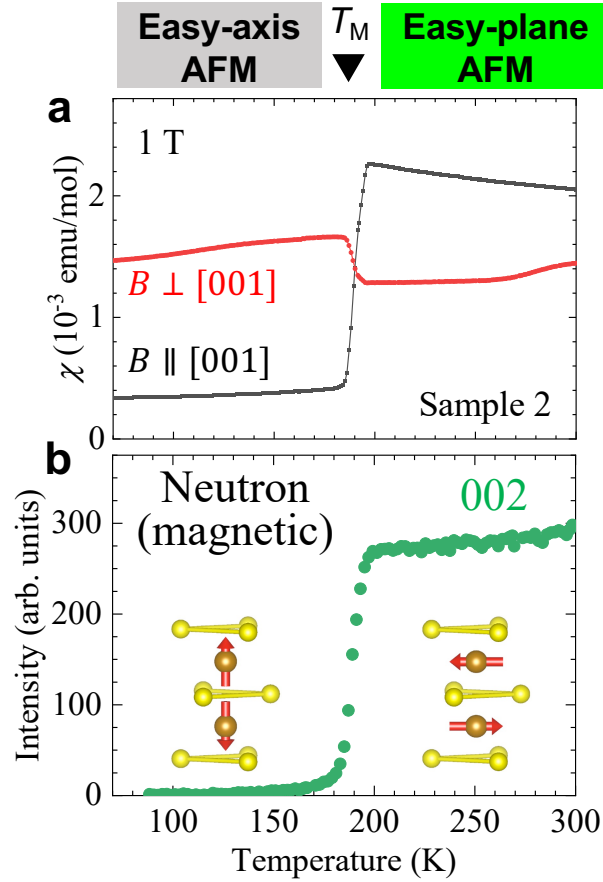
transitions appear at around 400 K[S20]. On the other hand, in case of $x \sim 0.05$, the structural and magnetic transitions were reported to take place at different temperatures, where the Morin transition temperature T_M sensitively depends on the composition x [S2].

To investigate the crystal structure of the present sample, we have performed the X-ray diffraction experiments. For this purpose, the powder X-ray diffraction pattern was measured at room temperature as shown in Supplementary Fig. 15c, where the powder sample



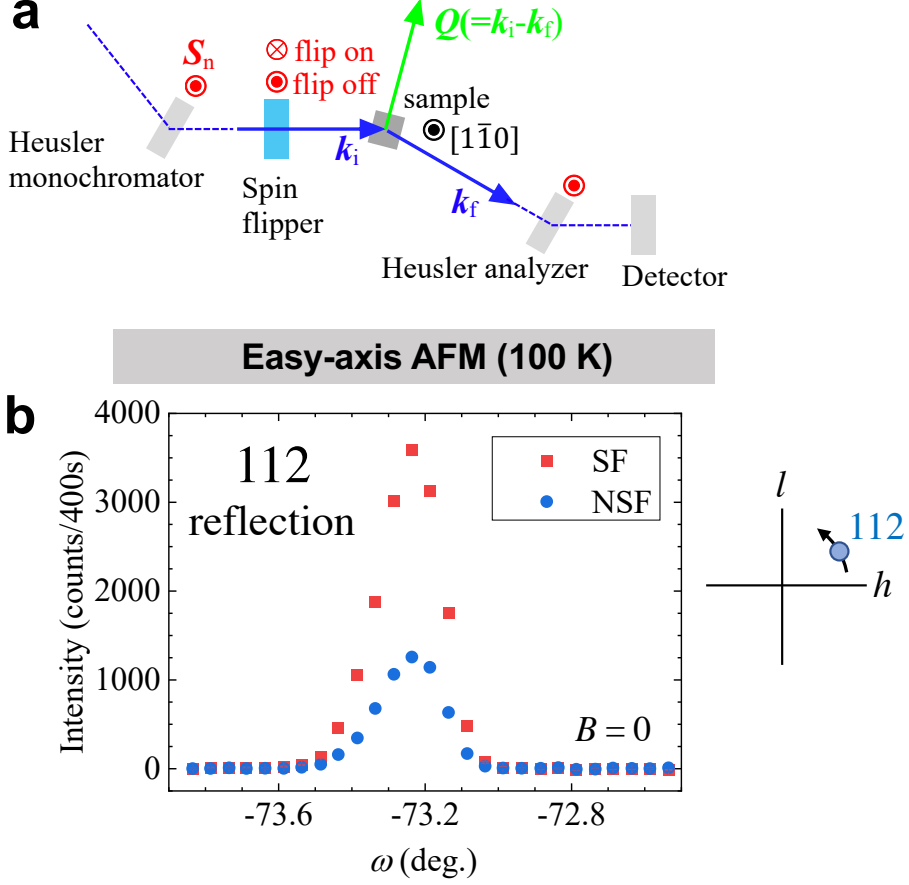
Supplementary Fig. 15: **Crystal structure analysis based on the X-ray scattering experiments.** **a,b** Temperature dependence of magnetic susceptibility at 1 T for $B \parallel [001]$ and $B \parallel [1\bar{1}0]$ ($\perp [001]$), and X-ray scattering intensity for the 002 and 004 Bragg reflections at 0 T, measured for the sample 1 with $T_M \sim 220$ K. **c**, Experimentally observed powder X-ray diffraction pattern, compared with the calculated ones for the crystal structure of FeS with the space group $P\bar{6}2c$ and $P6_3/mmc$. **d**, X-ray Laue diffraction pattern for the (001) plane of the single crystal sample, taken in the back reflection geometry.

was prepared by grinding the single crystal pieces. The observed diffraction pattern indicates that the low-temperature structural phase ($P\bar{6}2c$) is realized at room temperature. There is no discernible additional peak, which confirms the purity of our sample. Supplementary Fig. 15d indicates the X-ray Laue back reflection patterns observed for the (001) plane of the crystal, which indicates the good single-crystalline nature of our sample. We also investigated the temperature dependence of X-ray scattering intensity for the sample 1 with $T_M \sim 220$ K, as summarized in Supplementary Figs. 15a and b. The X-ray scattering intensity for the 002 and 004 Bragg reflections remains constant as a function of tempera-



Supplementary Fig. 16: **Magnetic phase transition investigated by the neutron scattering experiments.** **a,b** Temperature dependence of magnetic susceptibility at 1 T for $B \parallel [001]$ and $B \parallel [1\bar{1}0]$ ($\perp [001]$), and neutron scattering intensity for the 002 magnetic reflection at 0 T, measured for the sample 2 with $T_M \sim 190$ K. Here, the 002 neutron scattering intensity reflects the in-plane spin component normal to the $[001]$ axis (See text).

ture, which suggests that the Morin transition does not affect the crystal structure in the present sample. Note that the crystal structure factor of the 002 reflection is much smaller than the 004 reflection.



Supplementary Fig. 17: **Polarized neutron scattering experiments in the easy-axis anti-ferromagnetic state.** **a**, Schematic illustration of measurement setup for the polarized neutron scattering experiment. The neutron polarization direction $\mathbf{S}_n$ is aligned along the $[1\bar{1}0]$ direction, which is normal to the (hhl) scattering plane. **b**, ω -scan profile of (112) Bragg reflection measured for the sample 2 at 100 K (i.e. easy-axis antiferromagnetic state). SF and NSF represent the spin-flip and non-spin-flip scattering, the former of which purely reflects the contribution from magnetic scattering (See text). For polarized neutron, Fourier-transformed spin components parallel and perpendicular to $\mathbf{S}_n$ contribute to NSF and SF channels, respectively[S21]. The right panel indicates the trajectory of ω -scan in the reciprocal space. The error bars represent one standard deviation.

Next, to investigate the magnetic structure, we have further performed (unpolarized) neutron scattering experiments for the sample 2 with $T_M \sim 190$ K. Supplementary Fig. 16 indicates the temperature dependence of neutron scattering intensity for the 002 magnetic reflection (I_{002}). In general, the magnetic scattering originates from the spin components normal to the scattering vector[S21], and I_{002} reflects the in-plane spin component normal to the [001] axis. The observed presence (absence) of I_{002} confirms the realization of the easy-plane (easy-axis) antiferromagnetic order above (below) T_M . Here, the possible contribution from the nuclear scattering should be negligibly small, considering the temperature independent behavior of X-ray scattering intensity at the 002 position in Supplementary Fig. 15b.

To confirm the presence of antiferromagnetic order below T_M , polarized neutron scattering experiment has also been performed with the measurement setup as shown in Supplementary Fig. 17a. The direction of the neutron spin polarization $\mathbf{S}_n$ was set to be parallel to the $[1\bar{1}0]$ direction. In this configuration, the intensities in non-spin-flip (NSF) channel reflect nuclear scattering and magnetic scattering arising from the Fourier-transformed spin components parallel to $\mathbf{S}_n$. On the other hand, those in spin-flip (SF) channel are attributed to pure magnetic scattering arising from the spin components perpendicular to $\mathbf{S}_n$ [S21], which include the contribution from [001] spin component in the present setup. Supplementary Fig. 17b indicates the polarized neutron scattering profile for the 112 reflection at 100 K (i.e. the easy-axis AFM phase), where a clear peak structure is identified in the SF channel. Since the SF channel purely reflects the contribution from magnetic scattering, the above results demonstrate the existence of antiferromagnetic order at this temperature. The finite intensity in the NSF channel is ascribed to the nuclear scattering. Combined with the aforementioned absence of 002 magnetic reflection (indicating the absence of in-plane spin component), the present polarized neutron scattering results establish the realization of the easy-axis antiferromagnetic order below T_M , which has the same periodicity as that of crystal structure (i.e. $q = 0$ magnetic order) with the magnetic moments parallel and antiparallel to the [001] axis.

Based on the above analysis, we concluded that the low temperature structural phase ($P\bar{6}2c$) is realized for the whole temperature region below room temperature, and the magnetization anomalies observed at T_M reflects the magnetic transition between the easy-plane and easy-axis antiferromagnetic states in the present samples.

XII. COMPARISON WITH OTHER RELEVANT MATERIALS

As discussed in the main text, the emergence of spontaneous Hall effect has recently been reported for several helimagnets with broken $\mathcal{T}t$ symmetry. Typical examples are Mn_3Sn with non-collinear 120° spin texture[S1] and CoM_3S_6 ($M = \text{Ta}, \text{Nb}$) with non-coplanar all-in-all-out spin texture[S22, S23, S24], both of which host large spontaneous Hall effect despite its negligibly small net magnetization (Note that some early studies proposed the collinear antiferromagnetic order for CoNb_3S_6 [S9, S25, S26], while the latest polarized neutron scattering experiments confirmed the realization of non-coplanar spin texture in this compound[S22, S24]). These compounds are characterized by the metallic band structure, and their spontaneous Hall conductivity σ_{xy} and spontaneous Hall angle $\theta_H = \sigma_{xy}/\sigma_{xx}$ at $B = 0$ are $\sigma_{xy} \sim 30$ S/cm and $\theta_H \sim 1\%$ for Mn_3Sn at 300 K and $\sigma_{xy} \sim 27$ S/cm and $\theta_H \sim 0.7\%$ for CoNb_3S_6 at 23 K.

On the other hand, experimentally it remains a controversy whether the simple collinear antiferromagnetic order can induce spontaneous Hall effect or not. According to the recent theoretical studies, the collinear antiferromagnet RuO_2 is predicted to host spontaneous Hall effect, if the Néel vector is aligned perpendicular to the c -axis[S9]. Nevertheless, the Néel vector is rather aligned parallel to the c -axis in the zero-field ground state of RuO_2 [S27], and its magnetic symmetry doesn't allow the emergence of spontaneous Hall effect at $B = 0$. As a result, the application of extremely strong magnetic field is required to observe unconventional Hall signal in this compound[S28].

Very recently, the appearance of spontaneous Hall effect has been reported for a thin-film form of antiferromagnetic semiconductor MnTe [S29]. However, this signal was observable only at low temperature, and its amplitude was very small compared with B -linear normal Hall term. In this compound, the spontaneous Hall signal at $B = 0$ was much smaller than the B -induced saturated value, which suggests that the population ratio of two possible time-reversal domains couldn't be maintained at 1 to 0 after the removal of external magnetic field.

Toward the potential application as an information medium, the experimental identification of clear zero-field spontaneous Hall signal induced by collinear antiferromagnetic order at room temperature, as well as the search of appropriate materials to enable the full non-volatile switching of $\uparrow\downarrow$ and $\downarrow\uparrow$ spin states, should be an important challenge. In this

study, we experimentally demonstrated their realization in a collinear antiferromagnet FeS at room temperature. It must be a significant step toward the possible information device application of TtS-broken collinear antiferromagnets.

According to the analysis in Supplementary Note III and Supplementary Fig. 6, the zero-field spontaneous Hall signal in FeS mostly originates from TtS-broken antiferromagnetic order itself (rather than tiny net magnetization), in consistent with the associated DFT calculation in Supplementary Note IX and Supplementary Fig. 14. The observed spontaneous Hall signal is characterized by $\sigma_{xy} = 0.3$ S/cm and $\theta_H = 0.02\%$, and this σ_{xy} value is two order of magnitude smaller than metallic helimagnets Mn_3Sn and CoNb_3S_6 , but one order of magnitude larger than the semiconducting antiferromagnet MnTe with $\sigma_{xy} = 0.02$ S/cm. As detailed in Supplementary Note X, the relatively small value of σ_{xy} in FeS is probably due to its semiconducting character, since the Berry curvature contribution generally cancels out for the fully occupied band. To achieve larger spontaneous Hall conductivity, the metallic band structure with characteristic band crossing features, as well as the tuning of Fermi energy position, would be promising. While there is still room for improvement with Hall signal amplitude, the present experimental discovery of spontaneous Hall effect induced by collinear $\uparrow\downarrow$ spin order at room temperature would be an important step toward further material exploration.

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