Surface Ferromagnetism in Superconducting and Non-superconducting Fe-chalcogenide

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We report direct evidence of Time-reversal symmetry breaking (TRSB) in superconducting (SC) Fe-chalcogenide Fe\(_{1-x}\)Se\(_x\) by surface-magneto-optic-Kerr effect (SMOKE) measurements using a high precision Sagnac interferometer at zero magnetic field. Bulk magnetic susceptibility measurements show clear diamagnetic signatures of SC but no sign of any ferromagnetic (FM) transition, allowing us to pinpoint the observed TRSB to the surface, where we observe a Dirac gap in the topological surface state (TSS). We find surface TRSB in the non-SC Fe\(_{0.55}\)Se\(_{0.45}\), indicating that TRSB arises from surface FM that is a competing order to SC. The observed surface FM bears striking similarities to the two-dimensional (2D) FM found in 2D van der Waals crystals. It is highly sensitive to the exact chemical composition, thereby providing a means for optimizing the conditions for Majorana particles that are useful for robust quantum computing.

The quest for a robust quantum computer that is immune to external perturbations has stimulated intense searches for topologically protected quantum phases of matter where quasiparticles obey non-Abelian exchange rules [1]. One such example, the Majorana zero modes (MZM), have been reported in Fe-chalcogenide superconductors Fe\(_{1-x}\)Se\(_x\) as bound states in magnetic vortex cores [2–5] and as propagating 1D modes [6] by scanning tunnelling microscopy (STM) that performs spectroscopic imaging of the surface state. However, the imperfect conductance quantization [5] and the unexpected field dependence of MZM’s occurrence [4] highlight the need for a deeper understanding of Fe\(_{1-x}\)Se\(_x\), towards the optimization of material conditions for MZM. The hallmark of topological superconductivity [7], the topological surface state (TSS) has been reported [8,9] in Fe\(_{1-x}\)Se\(_x\) by angle-resolved photo emission spectroscopy (ARPES) that probes the energy dispersions of surface electrons. Photoemission spectra reveal [8,9] a topologically protected TSS characterized by a linear dispersion centered at the Dirac point at chemical potential \(\mu\) below \(E_F\), and below the superconducting critical temperature \(T_c\), a superconducting gap at the Fermi energy \(E_F\). It is this superconducting TSS, when subjected to a magnetic field, that hosts the reported MZM that is potentially useful for topologically protected quantum computing. Without the magnetic field, the TSS is expected to obey time-reversal symmetry (TRS) and remain massless.

Therefore, it came as a surprise when in a low temperature ARPES study at zero magnetic field [10] the above linear dispersion was interrupted by the opening of a Dirac gap as temperature is lowered across \(T_c\) in Fe\(_{1-x}\)Se\(_x\). The associated mass acquisition points to symmetry breaking. To explain this observation, a phenomenological Weiss field \(h\) was introduced to the surface Hamiltonian, which fits well to the observed photoemission spectra [10]. A Weiss field in the absence of an external magnetic field represents spontaneous time-reversal symmetry breaking (TRSB), which could arise from ferromagnetism (FM) or an intrinsic TRSB superconducting (SC) state [11]. So far, the results of magnetic characterizations of Fe\(_{1-x}\)Se\(_x\) remain mixed. While nitrogen vacancy center (NV) magnetometry has detected static magnetic fields that are best described by a combination of SC supercurrents and FM in micron-sized exfoliated flakes [12], high resolution magnetic neutron scattering measurements of bulk crystals have revealed instead antiferromagnetic (AFM) orders of either double or single stripe spin arrangements [13]. Since ARPES is surface sensitive while NV magnetometry and neutron scattering probe predominantly the bulk, a critical step to solve this mystery is to separately identify the TRSB properties of the bulk and surface in Fe\(_{1-x}\)Se\(_x\). Another central issue is to resolve the relation between the possible TRSB and the SC order: is TRSB from a FM phase that competes with the SC; or does the SC state in Fe\(_{1-x}\)Se\(_x\) have an intrinsically TRSB order parameter analogous to the superfluidity [14] in \(^3\)He? If it is the first case, one might be able to separately control the FM and SC orders in the surface and engineer the optimal conditions for MZM in vortex cores. And the second scenario points to a new unconventional SC state. Based on ARPES spectra taken at discrete temperatures [10], the Dirac gap in TSS opens at a temperature close to \(T_c\). Therefore the second scenario was favored in prior theoretical treatments [11], but needs to be tested by stringent experiments.

Surface-magneto-optic-Kerr effect (SMOKE) [15,16] measurements performed by a zero-area loop fiber optic Sagnac interferometer [17] are ideally suited to provide answers to the aforementioned central questions. In a conventional SMOKE setup, a linearly polarized light beam interacts with the surface magnetic moment \(M\) through spin-orbit coupling and will experience a rotation \(\theta_k\) of the polarization plane [18]. The Kerr rotation \(\theta_k\) is proportional to \(M\), and thus provides a direct measurement of surface magnetization. It has proven to be a powerful probe for surface magnetization within an optimal penetration depth \(\delta\), typically a few nanometers for conductors [15,16]. Primarily for detecting even smaller Kerr signals that
arise in unconventional superconductors, we have introduced a zero-area loop [17] fiber optic Sagnac interferometer [19] that measures directly the non-reciprocal phase difference between counter-propagating circularly polarized light beams. This approach fundamentally rejects polarization rotations due to non-TRSB effects such as linear and circular dichroism [20]. By reducing the Sagnac loop to zero area within a single fiber, it also rejects a background Sagnac signal from earth rotation, which breaks time-reversal symmetry and is the basis for fiber gyroscopes [21].

Fig. 1. (a) Sagnac setup (b) Scanning images of reflected optical power $P_0$ and Kerr signal ($\theta_K$) of a FeTe$_{0.55}$Se$_{0.45}$ sample (type B) at 1.8 $K$ and zero magnetic field.

As illustrated in Fig. 1a, for this study we utilize a scanning Sagnac microscope with 2 $\mu$m lateral spatial resolution [22,23], inside a cryostat with 1.8 $K$ base temperature and 9 $T$ magnetic field capability. The interferometer itself is maintained at room temperature. And a polarization maintaining fiber delivers light beams of orthogonal linear polarizations into the high vacuum sample space inside the cryostat. A cryogenic quarter wave ($\lambda/4$) plate converts the polarization of these light beams to circular polarization of opposite chirality that will interact with the sample surface and detect TRSB in the form of the non-reciprocal phase difference $\phi_{nr} = 2 \theta_K$ when they finish the Sagnac loop and interfere at the detector. The Kerr resolution is at the ten nanoradian (nrad) level [24,25] that is about a thousand times better than conventional SMOKE [15,16]. The ARPES studies were carried out using the frequency quadrupled output of a 3-ps pulse width, 76-MHz repetition rate Coherent Mira 900P Ti:sapphire laser. The photoemission spectra were obtained using a Scienta SES 2002 electron spectrometer with an effective energy resolution of 2.5 meV. Bulk magnetic characterizations are performed using an AC susceptometer. Instrumentation details are presented in the Supplementary Information (FIG. S1-S3).

Single crystals of FeTe$_{1-x}$Se$_x$ with nominal x values of 0.3 and 0.45 were grown by a unidirectional solidification method (Supplementary Information FIG. S5). Flat $ab$ plane surface regions of tens of microns in size can be found in as-grown crystals (Fig. 1a inset) for optical measurements. We locate such flat regions with uniform reflected optical power ($P_0$) before performing spatial Kerr ($\theta_K$) scans at a fixed temperature or temperature scans at a fixed location. Fig. 1b demonstrates an example of this experimental procedure for a FeTe$_{0.55}$Se$_{0.45}$ sample. In the flat region inside the white square with a uniform $P_0 = 6 \mu W$, the Kerr scan shows a signal of up to $\theta_K = 500$ nrad at the base temperature of 1.8 $K$ and zero magnetic field, indicating spontaneous TRSB. As is typical of spontaneous symmetry breaking, the sign and size of $\theta_K$ at zero magnetic field normally varies as a function of location and temperature, which agrees with the Kerr scan in Fig. 1b.
Fig. 2. Superconducting FeTe\(_{0.7}\)Se\(_{0.3}\) (a) Kerr \(\theta_K\) (left axis) up to 150 \(\text{mrad}\) during zero field warmups (ZFW) indicate onset of spontaneous TRSB at \(T_{Kerr}\); bulk magnetic susceptibility \(\chi'\) (right axis) indicates onset of SC at \(T_c\) without any sign of bulk FM. (b) \(\theta_K\) during ZFW after zero field cooldown. (c) \(\theta_K\) during ZFW after +/- 0.1T trainings during cooldown. (d) ARPES spectral intensity measured in the vicinity of the \(\Gamma\)-point \((k_f = 0)\), using s-polarized light and with the sample in the superconducting state at 7 K.

To pinpoint the location of the observed TRSB, we first focus on a FeTe\(_{0.7}\)Se\(_{0.3}\) sample that was studied by ARPES in the prior publication [10] where a Dirac gap opens below the superconducting critical temperature \(T_c = 14\) K. This Dirac gap in the TSS can be seen in the 7 K ARPES spectral intensity map with s-polarized light in Fig. 2d. Bulk superconductivity is verified in AC susceptibility measurements (right axis, blue line) shown in Fig. 2a, where \(\chi'\) displays a pronounced sharp diamagnetic Meisner drop when the sample is cooled below \(T_c = 14\) K. There is no sign in \(\chi'(T)\) of any bulk FM transition, which agrees with magnetic neutron scattering [13]. In contrast, the surface Kerr signal measured during zero magnetic field warmups (ZFW), as shown (left axis, lines with dots of various colors) in Fig. 2a, display clear onsets of \(\theta_K\) at \(T_{Kerr} = 12.5\) K. This serves as direct evidence of TRSB on the surface. In exfoliated flakes with a large surface-to-volume ratio, the TRSB surface might generate a magnetic field that is comparable in size to that from bulk SC, and account for the detected static field by nitrogen vacancy center (NV) magnetometry [12]. The AC susceptibility and surface Kerr measurements are consistent with ARPES spectra taken at 7 K (Fig. 2d) that shows the coexistence of the SC gap at \(E_F = 0\) meV and the Dirac gap at the Dirac point of \(-0.008\) eV. We note that \(T_{Kerr}\) and \(T_c\) are close to each other within \(1.5\) K, and are difficult to distinguish in prior experiments [10,13]. We shall describe a decisive experiment later in this paper to tell them apart.

As explained earlier, the sign and size of spontaneous \(\theta_K\) are normally not fixed during ZFW. This is evident in Fig. 2b where ZFW takes place after cooling down in zero magnetic field and \(\theta_K\) fluctuates between \(\pm 50\) \(\text{mrad}\) below \(T_{Kerr} = 12.5\) K. The sign of \(\theta_K\) can be trained by cooling down in a symmetry-breaking magnetic field \(B_{\text{Cooling}}\) before the measurements during subsequent ZFWs. This is demonstrated in Fig. 2c where \(B_{\text{Cooling}} = \pm 0.1\) T during cooldowns result in \(\pm 100\) \(\text{mrad}\) of spontaneous Kerr signal in subsequent ZFWs. In the case of FM, this is the well-known alignment of FM domains by an external magnetic field [26]. This training effect has also been demonstrated in TRSB superconductors [24,25,27,28], but with an important caveat. In a type II superconductor such as FeTe\(_{1-x}\)Se\(_x\), magnetic vortices form when \(B_{\text{Cooling}}\) is larger than the...
lower critical field $H_{c1}$ and penetrates the superconductor. After removal of $B_{cooling}$, a small fraction of vortices can still be trapped at pinning sites. The trapped vortices break time-reversal symmetry and would result in a spontaneous Kerr signal during ZFW. In fact, we speculate that motions of trapped vortices under thermal gradients may account for the reported spontaneous Nernst signal [29] in FeTe$_{1-x}$Se$_x$. To test this possibility, we have performed training with a cooling field of 0.01 $T$ that is much smaller than $H_{c1} \sim 0.035$ $T$ [30], and the resulting spontaneous $\theta_K$ is shown as the red curve in Fig. 2a. The clear onset of $\theta_K$ at $T_{Kerr}$ with a magnitude of 100 mrad at the base temperature rules out the source of the observed surface TRSB being trapped vortices. Instead, TRSB arises either due to the formation of surface FM, or an unconventional TRSB SC state.

Now we have experimentally established that TRSB occurs only on the surface, we turn to experiments on samples with the nominal chemical composition of FeTe$_{0.55}$Se$_{0.45}$ to identify the origin of this surface TRSB. Recently neutron scattering, ARPES, and resistivity measurements have been carried out to establish that FeTe$_{0.55}$Se$_{0.45}$ is located very close to phase boundaries in a complex phase diagram [13]. By a few percent change of the Fe concentration, at $T = 0$ a nominal FeTe$_{0.55}$Se$_{0.45}$ can be a non-superconductor (Type A), a SC with TSS (Type B), or a trivial SC without TSS [13]. In a Type A sample, neutron scattering has revealed a double stripe spin arrangement for the bulk AFM order, and the APRES spectra are featureless; while in a Type B sample, a single stripe spin arrangement is found, and the APRES spectra show both SC and TSS states.

![Fig. 3. Non-superconducting FeTe$_{0.55}$Se$_{0.45}$ Type A](a) Resistivity $\rho$ and bulk magnetic susceptibility $\chi'$ show no sign of SC or bulk FM transitions; (b) $\theta_K$ up to 400 mrad during ZFW indicates onset of surface FM at $T_{Kerr}$; (c) $\theta_K$ during ZFW after $\pm 0.1$ $T$ trainings. (d) $\theta_K$ during ZFW after $\pm 0.5$ $T$ trainings.

We have performed measurements on both types of FeTe$_{0.55}$Se$_{0.45}$ samples. The experimental results on a Non-SC (Type A) FeTe$_{0.55}$Se$_{0.45}$ sample are summarized in Fig. 3, where the ARPES spectra are featureless indicating the absence of TSS. And those on a SC+TSS (Type B) FeTe$_{0.55}$Se$_{0.45}$ sample are summarized in Fig. 4, with a Dirac gap in TSS and a SC gap at $E_F$ in the ARPES spectra (Fig. 4d) at $T \sim 5$ $K$. 
Fig. 4. Superconducting FeTe\textsubscript{0.55}Se\textsubscript{0.45} (Type B) (a) \(\theta_K\) (left axis) up to 600 nrad during ZFW indicates onset of TRSB at \(T_{Kerr}\); bulk magnetic susceptibility \(\chi'\) (right axis) indicates onset of SC at \(T_C\) without any sign of bulk FM. (b) \(\theta_K\) during ZFW after ±0.1 \(T\) trainings. (c) \(\theta_K\) during ZFW after ±0.5 \(T\) trainings. (d) ARPES spectral intensity measured in the vicinity of the Γ-point (\(k_\parallel = 0\)), using p-polarized light, showing TSS at all temperatures, and the opening of a SC gap below \(T^*\).

As shown in Fig. 3a, in the non-SC type A sample, the resistivity \(\rho\) shows no sign of SC either in the bulk or on the surface. Magnetic susceptibility \(\chi'\) confirms that there is no bulk SC, and it shows no sign of any bulk FM transition. Comparing the size of \(\chi'\) in this non-SC sample to the drop of \(\chi'\) across \(T^*\) in the SC type B sample (Fig. 4a), we can estimate an upper bound of 1\% for superconducting volume fraction, indicating that this type A sample is indeed deep in the non-SC region of the phase diagram [13]. Therefore, the onsets of the surface Kerr signal up to \(\theta_K = 400\) nrad (Fig. 3b) during ZFW undoubtably indicate that the observed surface TRSB is not due to a TRSB order parameter of the SC state. Instead, it originates from a competing surface FM order. In a non-SC sample (Fig. 3), \(T_{Kerr}\) and \(T_C\) are not necessarily identical, but they are close to each other. The observed closeness between \(T_{Kerr}\) and \(T_C\), being a mere coincidence or not, puts the competing FM and SC orders very close in energy, and may be partially responsible for the complex phase diagram [13].

The temperature dependences of the spontaneous Kerr signal \(\theta_K\) (Fig. 2a, Fig. 3a, and Fig. 4a) in FeTe\textsubscript{1-x}Se\textsubscript{x} bare striking similarities to what we have discovered in the intrinsic two-dimensional (2D) ferromagnetism in 2D van der Waals (vdW) crystals of Cr\textsubscript{2}Ge\textsubscript{2}Te\textsubscript{6}, especially the bilayer case [22] (Supplementary Information FIG. S4). Namely, \(\theta_K(T)\) doesn’t saturate quickly with a reduced temperature following the well-known \(\tanh(\frac{B_E}{k_B T})\) function of the 3D Heisenberg model [26], where \(B_E\) is the molecular field. Instead, like in the exfoliated bilayers of Cr\textsubscript{2}Ge\textsubscript{2}Te\textsubscript{6}, \(\theta_K(T)\) appears to keep growing at the lowest temperatures [22], which is a direct consequence of the fact that 2D magnetism is stabilized by magnetic anisotropy instead of magnetic exchange coupling [22], even though the surface FM in FeTe\textsubscript{1-x}Se\textsubscript{x} is semi-2D due to couplings to the bulk. Just as the FM in bilayers of Cr\textsubscript{2}Ge\textsubscript{2}Te\textsubscript{6} is sensitive to magnetic anisotropy [22], the surface FM in FeTe\textsubscript{1-x}Se\textsubscript{x} is sensitive to the exact chemical composition, which in principle could modify the magnetic anisotropy. Indeed, the amplitude of observed spontaneous \(\theta_K\) in FeTe\textsubscript{0.55}Se\textsubscript{0.45} of both type A and B are four times larger than in FeTe\textsubscript{0.7}Se\textsubscript{0.3}. In addition, while a training
field of a mere 0.01 \( T \) is enough to achieve a saturating \( \theta_k \) in FeTe\(_{0.7}Se_{0.3}\), 0.5 \( T \) is needed in FeTe\(_{0.55}Se_{0.45}\) samples. The fifty times difference in coercivity suggests a large difference in the magnetic anisotropy between FeTe\(_{0.55}Se_{0.45}\) and FeTe\(_{0.7}Se_{0.3}\). In contrast, the SC and FM onset temperatures \( T_c \) and \( T_{Kerr} \) only shift by a few Kelvin between FeTe\(_{0.7}Se_{0.3}\) and SC FeTe\(_{0.55}Se_{0.45}\). It is unclear at this stage whether this is a coincidence, but it keeps the FM and SC orders in close competition when tuning the surface FM order via chemical doping.

In summary, we have unambiguously identified TRSB in FeTe\(_{1-x}Se_x\). We pinpoint its origin to be surface ferromagnetism, which displays clear 2D features similar to the 2D FM in exfoliated vdW crystals [22] where the FM can be tuned by magnetic anisotropy. While it is premature to speculate on the origin of the surface FM, we note that magnetism could occur at surfaces and interfaces where inversion symmetry is broken [31]. The surface FM in FeTe\(_{1-x}Se_x\) is highly sensitive to the exact chemical composition, and it adds a new dimension of surface FM to the already complex phase diagram of SC and TSS [13]. By tuning the surface FM, we could explore the optimal conditions for stabilizing MZM in magnetic vortex cores [2–5] and 1D modes [6] that are potentially useful for topologically protected quantum computing [1].

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Author Contributions
J.X. designed and directed the study. C.F., J.W. and J.X. constructed the Sagnac microscope, carried out Sagnac, susceptibility and resistivity measurements. N.Z. and P.J. carried out the ARPES measurements. G.D.G. grew the crystals. The manuscript is mainly written by J.X. and C.F. with input from all authors.

Data availability
All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Information. Additional data are available from the corresponding author upon reasonable request.

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(A) Zero-area-loop Sagnac interferometer for SMOKE measurements

The surface magneto-optic Kerr effect measurements were carried out with a zero-area-loop fiber optic Sagnac interferometer that was introduced by us in 2006 for detecting nano-radian level magneto-optic Kerr effects [1,2]. The optical fiber of the interferometer is connected to piezo-based scanner to allow Kerr measurements at locations of interest and spatial imaging as described in previous publications [3,4]. In this project, the scanner and sample are housed in a cryostat with 1.8 K base temperature and up to 9 Tesla magnetic field. The operation of the Sagnac interferometer and its performance are summarized below.

![Sagnac interferometer](image)

**FIG. S1. Sagnac interferometer and its performance:** (a) Schematics of zero-area-loop fiber-optic interferometer. (b) Drift of the Sagnac interferometer over 25 hours. The -800 nrad offset is due to imperfections in the alignment and is subtracted in all measurements.
As shown in FIG. S1 (a), the beam of light centered at 1552 nm is routed by a fiber circulator to a polarizer, which polarizes the beam. The circulator transmits light from port 1 to port 2 and port 2 to port 3 with better than 30 dB isolation in the reverse direction. After the polarizer the polarization of the beam is at 45° to the axis of an electro-optic modulator (EOM), which generates 4.590 MHz time-varying phase shifts with an amplitude of $\phi_m = 0.92 \text{ rad}$ between the two orthogonal polarizations that are then launched into the fast and slow axes of a PM fiber that is fed into the cryostat. Upon exiting the fiber, the two orthogonally polarized beams are converted into right- and left-circularly polarized light by a quarter-wave plate and are then focused by a numerical aperture $\text{NA} = 0.3$ aspheric lens onto the sample. The nonreciprocal phase shift $\varphi_{nr}$ between the two circularly polarized beams upon reflection from the magnetic sample is twice the Kerr rotation $\theta_K$. The same quarter-wave plate converts the reflected beams back into linear polarization, but with a net 90° rotation of the polarization axis. The two beams then pass through the PM fiber and EOM but with exchanged polarization axis. At this point, the two beams have gone through the same path but in opposite directions, except for a phase difference of $\varphi_{nr}$ from reflection off of the magnetic sample and another time-varying phase difference by the modulation of EOM. The two beams are once again combined at the detector and interfere to produce an optical signal. Lock-in detection was used to measure both first (P1) and second (P2) harmonics of this optical signal. The Kerr rotation can then be extracted using the formula: 

$$\theta_K = \frac{1}{2} \tan^{-1} \left[ \frac{J_1(2\phi_m)P_1}{J_1(2\phi_m)P_2} \right],$$

where $J_1(2\phi_m)$ and $J_2(2\phi_m)$ are Bessel functions.

The noise in Kerr signal is shot-noise-limited to $10^{-7} \text{ rad}/\sqrt{\text{Hz}}$ with 10 $\mu$W of optical power, which is small enough not to heat up the sample at low temperatures. By averaging over 100 seconds, 10 nanoradian (nrad) Kerr resolution can be achieved. In practice, the bias offset in our system drifts about 20 nrad per 25 hours (FIG.S1 (b)), which limits the ultimate resolution we can achieve in experiments.

**(B) Calibration of Low Temp Piezo Scanner of Sagnac microscope**

A low temp Piezo scanner was constructed for integration with the Sagnac interferometer to allow spatial scanning and to target reflective areas on samples to maximize the sensitivity in measurements. The scanner follows the basic S-bender piezo bimorph scanner design [5], and can operate at cryogenic temperatures in limited space, with a scan range as high as 0.25mm at 2K, and nm spatial resolution. Scanner position is controlled using a DAQ device and high voltage amplifier to apply voltage to the piezo.

![S-Bender Scanner 1.8K Calibration Scan](image)

**FIG. S2. Cryogenic scanner calibration:** Scan at 1.8K of copper TEM grid for scanner calibration.

The piezo voltage was calibrated in a cryostat at 1.8K with a copper transmission electron microscope (TEM) grid of 16.5 micro pitch size on top of a mirror, to determine the scan range.
voltage/distance conversion factor for the scan at 1.8 K shown in Fig. 1b the main text. Calibration for
different temperatures is necessary since the piezo coercive field increases at lower temperature, and
therefore requires greater voltage to move the same distance at low temperature as at high temperature (~
6X). A scan image for voltage calibration at 1.8 K is shown in FIG.S2.

(C) Angle-resolved photoemission spectroscopy (ARPES) measurements

Single-crystal samples were cleaved in situ at T≤ 5 K and base pressure of ≤2 × 10−11 Torr. The
photoemission studies were carried out using a 3-ps pulse width, 76-MHz repetition rate Coherent Mira
900P Ti:sapphire laser, the output of which was quadrupled to provide 6.0-eV incident light, focused into a
spot on the sample ~20 μm in diameter. The polarization of the latter could be varied with the use of quarter
and/or half-wave plates to provide linear or circularly polarized light of arbitrary orientation on the Poincaré
sphere. Photoemission spectra were obtained using a Scienta SES 2002 electron spectrometer. The
effective energy resolution is ~2.5 meV full width at half maximum as determined by the width of the
sharpest features in the measured spectra. The angular resolution was ~0.002 Å-1 at the low photon energy
used. The value of EF is determined by reference to a gold sample in contact with the FeTexSe1-x (FTS)
samples.

(D) Magnetic susceptibility measurements

Magnetic susceptibility measurements were done with a homemade AC susceptometer [6]. The
AC susceptometer is composed of two concentric coils, A primary coil (excitation) and secondary (pickup)
coil made from 15-micron copper wire. The primary coil has a diameter of ~0.5 mm and is ~60 turns by 3
layers, and the secondary coil has a diameter of ~0.25mm respectively with 60 turns by 3 layers with
winding direction switched halfway up the coil to reduce the background signal. The AC susceptorometer is
driven and measured by a lock-in amplifier supplying a 1017 Hz and 1 mA excitation current to the primary
coil. The lock-in phase is set at room temperature to maximize out of phase component (with respect to the
primary coil voltage phase) of the secondary coil voltage, referred to as V_y in Fig.2a of the main text.

The magnetic susceptibility $\chi^\prime$ of a material in an AC magnetic field can be measured by detecting
a change in the magnetic field when the primary coil of an ac susceptometer is put near the materials
surface. If $c^\prime >0$ the magnetic field near the primary coil will increase, and if $c^\prime <0$ the magnetic field will
decrease. This change in AC field can be detected through the secondary coil which will “pickup” an AC
voltage across it's ends which is 180 degrees out of phase with the AC field produced by the primary coil
due to Faraday's law of Induction $V = −d\Phi/dt$, where $\Phi$ is the magnetic flux through the secondary coil.
If the AC field produced by the primary coil and applied to the secondary coil is given by $B(t) = B_{app} \cos(\omega t)$,
then V across the secondary coil will have the form $V(t) = \sqrt{2} V_y \sin(\omega t + \phi)$, with $\phi$ being a small phase
shift due to lag in the circuit and the $\sqrt{2}$ factor to account for $V_y$ being an rms voltage from the lockin. When
$c^\prime$ of a material changes, the ac field around it is either increased or decreased and $V_y$ measured by the
lockin will change as well. In the main text, $c^\prime$ as a function of temperature and voltage is represented as
$\Delta V_y(T) = V_y(T) − V_y(T = 2K)$, the difference in the voltage of the secondary coil at T and it’s voltage at 2K.
The value of this voltage is arbitrary for our measurement since we are only looking for a drop in $c^\prime$. We see
for the SC samples that $\Delta V_y$ has a clear change from a positive value to zero, where $c^\prime=-1$.

(E) Resistivity measurements

Electrical transport was measured by a lock-in amplifier using 4-probe measurement technique with
5mA excitation current at 13 Hz. The voltage and current leads are attached as shown in FIG. S3.
Contacts were made on the 4 corners of a thin square sheet-like FeTe_{0.55}Se_{0.45} Type A sample using
silver epoxy and attached to 25-micron thick platinum wires. Voltage measured by the lockin in converted
to resistance dividing the lockin voltage signal by the excitation current. The resistance is calculated by
$R = V/I$. Sheet resistance $R_s$ was estimated using the Van der Pauw formula [7] for a uniform square
sample $R_s = \pi R / \ln 2$, and resistivity was calculated as $\rho = R_s \cdot t$, where t is the thickness of the sample,
30 mm.
(F) 2D Ferromagnetic order in vdW Cr$_2$Ge$_2$Te$_6$

The temperature dependences of the spontaneous Kerr signal $\theta_K$ in main text Fig. 2a, Fig. 3a, and Fig. 4a in FeTe$_{1-x}$Se$_x$ bare striking similarities to what we have discovered previously [3] in the intrinsic two-dimensional (2D) ferromagnetism in 2D van der Waals (vdW) crystals of Cr$_2$Ge$_2$Te$_6$, especially the bilayer case as shown. Sagnac measurements on of Cr$_2$Ge$_2$Te$_6$ various thicknesses from bilayer to bulk are shown in Fig. S4 below. In bulk Cr$_2$Ge$_2$Te$_6$ (right inset), $\theta_K(T)$ saturates quickly with a reduced temperature following the well-known $\tanh(\frac{\mu B}{k_B T})$ function of 3D Heisenberg model [8], where $B$ is the molecular field. In bilayer Cr$_2$Ge$_2$Te$_6$ (left inset) $\theta_K(T)$ appears to keep growing at the lowest temperatures [3], which is a direct consequence of the fact that 2D magnetism is stabilized by magnetic anisotropy instead of magnetic exchange coupling [3].

FIG. S4. Ferromagnetic order in vdw Cr$_2$Ge$_2$Te$_6$ measured at zero magnetic field by Sagnac interferometer: As the thickness of the crystals thin down from bulk to bilayer, the Curie temperature monotonically drops from ~68 K to ~33 K. Insets show Kerr signal $\theta_K$ as function of temperature for bilayer and bulk cases, showing very different temperature dependences. The temperature dependences of the spontaneous Kerr signal $\theta_K$ in FeTe$_{1-x}$Se$_x$ bare striking similarities to that in bilayer exfoliated Cr$_2$Ge$_2$Te$_6$. Details of this study can be found in our prior publication [3].
Synthesis and mounting of FeTe$_{1-x}$Se$_x$ crystals

Single crystals of FeTe$_{1-x}$Se$_x$ were grown by a unidirectional solidification method. The nominal compositions had no excess Fe, and Te. Photos of the crystals used in this work can be found below on 1-mm grid papers. During the experiment, crystals are mounted on the cryogenic sample stage using either silver paste or Ge-varnish. Flat $ab$ plane surface regions of tens of microns in size can be found in as-grown crystals for optical measurements. We locate such flat regions with Sagnac scanning imaging.

![Images of crystals](image1.png)

**FIG. S5.** FeTe$_{1-x}$Se$_x$ crystals used in this work

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