Electronic Supplementary Information for

Intrinsic Giant Magnetoresistance due to Exchange-bias-type Effects at the Surface of Single-crystalline NiS_2 Nanoflakes

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Experimental methods

Fabrication and exfoliation of NiS_2 nanoflakes

NiS_2 single crystals were synthesized via the chemical vapor transport (CVT) method, as already reported in ref.[1]. The CVT growth was carried out using precursor powders of Ni (Alfa Aesar, 99.999% purity), S (CERAC, 99.9995% purity), and $NiBr_2$ (Sigma-Aldrich, 99.999% purity) which were placed in evacuated ($\sim 10^{-6}$ Torr), sealed quartz ampoules. The growth of the NiS_2 single crystals was carried out for 16 days using a two-zone tube furnace with hot and cold-zone temperatures of 700 and 650 °C, respectively. At the beginning of the growth process, the hot and cold zones were inverted for 3 days. After growth, the NiS_2 crystals were cleaned in solvent to remove any residual S and $NiBr_2$.

Single-crystalline NiS_2 nanoflakes were obtained via cleaving and mechanical exfoliation of the CVT-grown NiS_2 single crystals inside a glovebox with inert N_2 atmosphere. From the exfoliation tape (Ultron Systems Inc.), the NiS_2 nanoflakes were then transferred onto a SiO_2(300 nm)/Si substrate with pre-patterned Au(50 nm)/Ti (5 nm) markers. The markers were used to identify the positions of the nanoflakes on the substrate whilst mapping the samples under an optical microscope of a transfer system placed inside the glovebox (HQ graphene). The same markers were also used for alignment during the EBL patterning of the devices.

The NiS_2 nanoflakes used for diamond quantum magnetometry were also capped with hexagonal boron nitride to prevent their oxidation during shipment. For magnetotransport measurements, capping was not necessary since the deposition of the electrical contacts was carried out right after development of the polymer resist patterned by EBL. Low-T magnetotransport measurements were also performed right after the fabrication of the devices to minimize exposure of the devices to air.

SEM, EDX and EELS

The scanning electron microscope (SEM) micrographs of the NiS_2 nanoflakes were collected using a Zeiss Gemini 500 SEM with an acceleration voltage of 10 kV. Elemental composition analysis and crystallographic orientation were carried out in the same SEM setup by EDX and EBDS using Oxford Instruments ULTIM MAX and Oxford Instrument SYMMETRY detectors, respectively.

Micro-XRD

The XRD measurements for the characterization of the crystallographic structure and orientation of the NiS_2 nanoflakes were carried out using a Rigaku Smartlab diffractometer. The primary arm of the diffractometer is equipped with a double-bounce channel cut Ge(220) monochromator, which provide a monochromatic CuKα1(λ = 1.5406 Å) radiation. To perform micro-XRD (µ-XRD) measurements, the diffractometer is equipped with a Cross beam optical (CBO) capillary optics with an incident-limiting slit of 0.5 mm which reduces the beam diameter to ~ 400 µm at the nanoflake position.

Device fabrication and magnetotransport

Magnetotransport measurements were performed using electrical contacts of Au (250 nm)/Pd (50 nm) or of Au (250 nm)/Ti (50 nm). The nanoscale contacts were patterned by EBL into a double-layer polymethyl methacrylate A4/methyl methacrylate EL11 (PMMA A4/MMA EL 11) resist mask, which was spin-coated onto the SiO_2/Si substrates with the pre-selected NiS_2 nanoflakes. After the development of the EBL-patterned polymer mask, the material of the contact electrodes was deposited by direct current magnetron sputtering in an ultrahigh vacuum sputtering chamber (AJA international Inc.). Once the devices were fabricated, wire-bonded contacts were made to pads connected to the nanoscale electrodes. Magnetotransport measurements were carried out down to low temperatures (~ 1.5 K) in a cryogen-free system with an applied field (in-plane or out-of-plane) of up to 7 Tesla (Cryogenic Ltd.).

Diamond quantum magnetometry

The diamond quantum magnetometry (DQM) setup is a cryogenic atomic force microscope (Attocube system, attoDry1000) integrated with a custom confocal setup. The DQM employs commercially available diamond probes with a single nitrogen vacancy (NV) center (Qzabre AG). The NV is excited, and its spin state is read out via the confocal microscope mounted on top of a closed-cycle cryostat, which houses the sample. The NV axis direction defined by the angles (ϕ_{NV} and θ_{NV}) and its distance from the sample surface (d_{NV}) were determined with independent measurements[2] yielding ϕ_{NV} = 90° and θ_{NV} = 120°, and $d_{NV} \sim 70$ nm. All DQM measurements were performed with the same diamond probe. The DQM raster scans the NV across the sample surface and measures the projection of the emitted stray field onto the NV axis. During DQM imaging, we applied an out-of-plane bias field of approximately 4.3 mT – equivalent of 2.5 mT along the NV axis – which allowed us to determine the direction of the stray field.

Supplementary Table

Device ID	**Thickness (nm)**	**Resistivity at *T* = 293 K (Ω cm)**	**Magnetic field (*H*) orientation with respect to nanoflake**	**Contacts across step edges**	**Corresponding Figure in manuscript**
Device 1	380	0.10	in plane	No	Fig. 3 and Fig. 4
Device 2	790	0.09	out-of-plane	No	Fig. 4 and Fig. S1
Device 3	400	0.33	out-of-plane	No	Fig. 4 and Fig. S2
Device 4	280	414	in-plane	Yes	Fig. 6
Device 5	780	31	out-of-plane	Yes	Fig. S3

Table S1. List of NiS_2 devices with magnetotransport properties measured and reported in the manuscript with some corresponding values of physical parameters.

Supplementary Figures

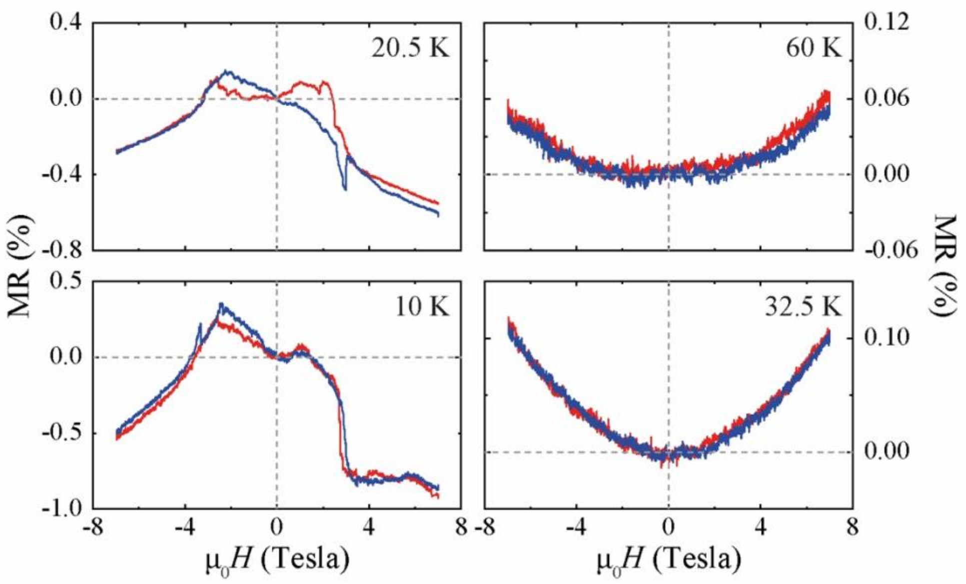

Fig. S1. Magnetotransport measurements at a few representative temperatures performed on a 790-nm-thick NiS$_2$ nanoflake labelled as device 2 in Figure 4 of the main text with the magnetic field *H* applied out of plane. Ascending and descending *H* sweeps are shown in blue and red, respectively.

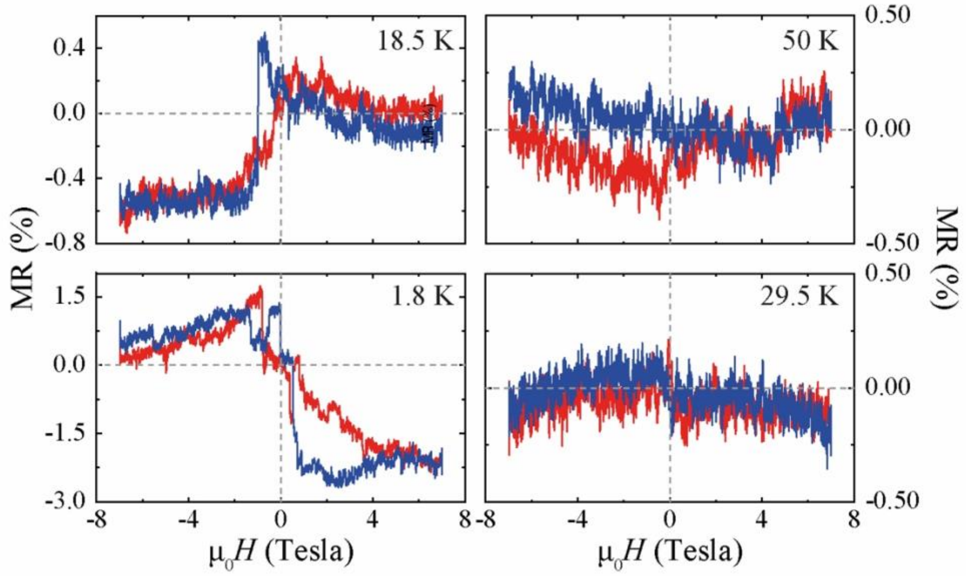

Fig. S2. Magnetotransport measurements at a few representative temperatures performed on a 400-nm-thick NiS$_2$ nanoflake labelled as device 3 in Figure 4 of the main text with the magnetic field *H* applied out of plane. Ascending and descending *H* sweeps are shown in blue and red, respectively.

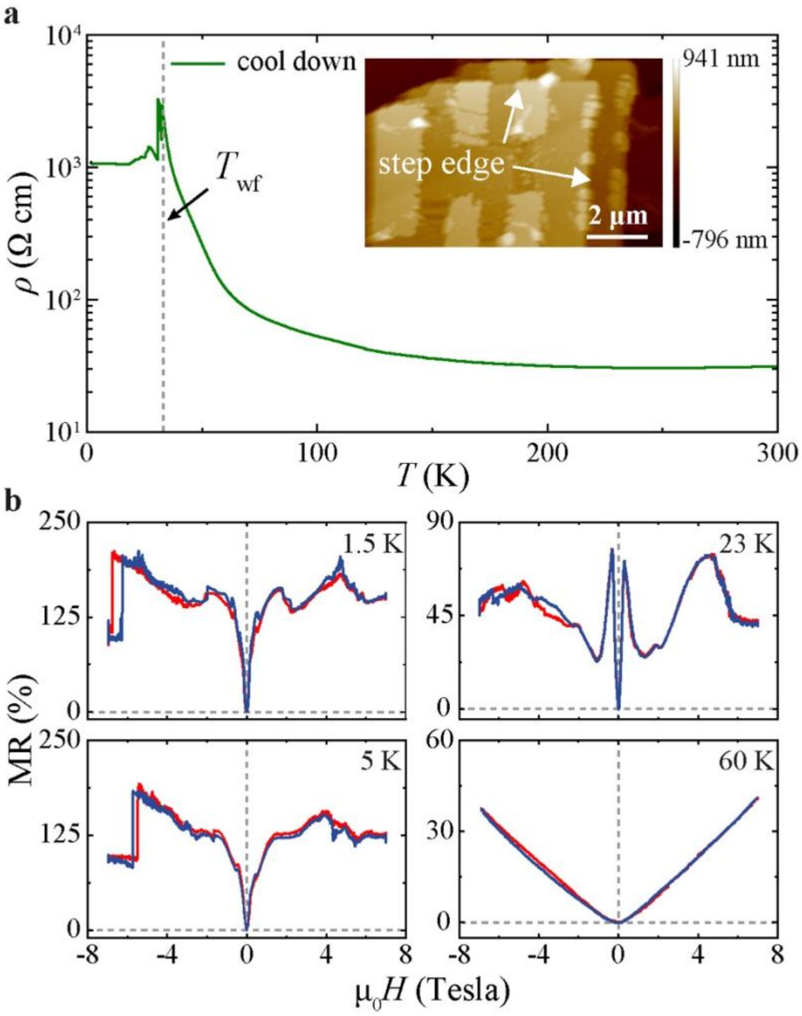

Fig. S3. Additional magnetotransport measurements on a NiS_2 nanoflake with high step edges (device 5). (a) Resistivity versus temperature, $\rho(T)$, curves measured for a 780-nm-thick nanoflake. Atomic force microscopy image highlighting the step edges of the nanoflakes is shown as inset to panel (a), with the dashed lines in the same panel (a) marking the onset temperature of weak ferromagnetism T_{wf} for NiS_2. (b) Magnetoresistance (MR) change as a function of the applied field H, MR(H), at a few representative temperatures for the NiS_2 nanoflake in (a). Ascending and descending H sweeps are shown in blue and red, respectively.

Supplementary References

1. S. El-Khatib, B. Voigt, B. Das, A. Stahl, W. Moore, M. Maiti and C. Leighton, *Phys. Rev. Mater*. 2021, **5**, 115003.https://doi.org/10.1103/PhysRevMaterials.5.115003
2. L. Stefan, A. K. C. Tan, B. Vindolet, M. Högen, D. Thian, H. K. Tan, L. Rondin, H. S. Knowles, J. F. Roch, A. Soumyanarayanan and M. Atatüre, *Phys. Rev. Appl*. 2021, **16**, 014054. https://doi.org/10.1103/PhysRevApplied.16.014054