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Thermal disorder driven magnetic phases in van der Waals magnet CrI₃

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Magnetic phase transitions often occur spontaneously at specific critical temperatures and are instrumental to understand the origin of long-range spin order in condensed matter systems. The presence of more than one critical temperature (T_c) has been observed in several compounds^{1–5} where the coexistence of competing magnetic orders highlights the importance of phase separation driven by different factors such as pressure, temperature and chemical composition. However, it is unknown whether recent discovered two-dimensional (2D) van der Waals (vdW) magnetic materials^{6,7} show such intriguing phenomena that can result in

rich phase diagrams with novel magnetic features to be explored. Here we show the existence of three magnetic phase transitions at different T_c 's in 2D vdW magnet CrI_3 revealed by a complementary suite of muon spin relaxation-rotation (μSR), superconducting quantum interference device (SQUID) magnetometry, and large-scale micromagnetic simulations including higher-order exchange interactions and dipolar fields⁸. We find that the traditionally identified Curie temperature of bulk CrI_3 at 61 K⁹ does not correspond to the long-range order in the full volume (V_M) of the crystal but rather a partial transition with less than $\sim 25\%$ of V_M being magnetically spin-ordered. This transition is composed of highly disordered domains with the easy-axis component of the magnetization (S_z) not being fully spin-polarized but disordered by in-plane components (S_x , S_y) over the entire layer. As the system cools down, two additional phase transitions at 50 K and 25 K drive the system to 80% and nearly 100% of the magnetically ordered volume, respectively, where the ferromagnetic ground state has a marked S_z character yet also displaying finite contributions of S_x and S_y to the total magnetization. Our results indicate that volume-wise competing electronic phases play an important role in the magnetic properties of CrI_3 which set a much lower threshold temperature for exploitation in magnetic device-platforms than initially considered.

Competing electronic phases underlie a number of unusual physical phenomena in condensed matter^{10–12}. From superconductivity up to ferromagnetism, when the competition is sizeable the conventional outcome is phase separation. Compounds that have shown such behaviour are mostly of complex magnetic structures including cuprates¹⁰, iron-based superconductors¹²,

41 ruthenates¹¹, topological kagome magnets³ and manganites^{13,14}. A contrasting case is found in
 42 the layered transition metal halides¹⁵ where the presence of heavy halide atoms like in CrI₃ sta-
 43 bilises pronounced anisotropy constants resulting in long-range magnetic order in what appears
 44 to be a single ferromagnetic transition at a relatively high temperature^{6,16}. Nevertheless, recent
 45 experiments¹⁷⁻²⁰ have unveiled the presence of many subtleties in the magnetism of this compound
 46 which a single transition fails to capture. Firstly, CrI₃ exhibits both antiferromagnetic and fer-
 47 romagnetic orders in thin layers driven by hydrostatic pressure^{17,18}. These phases occur at the
 48 same critical temperature with a spatial separation of a few hundreds of nanometers and conse-
 49 quently there is no prelude of thermally-activated spin ordering. Secondly, multiple anomalies can
 50 be observed in the temperature dependence of the magnetic susceptibility below T_c ^{9,19,20}. Such
 51 anomalies imply that a more complex magnetic ordering involving spins not directly aligned with
 52 the easy-axis can emerge. Whether different magnetic phases may exist or competition occurs
 53 between them is largely unknown. However, these observations establish a much more intricate
 54 scenario than originally pictured for CrI₃ with many hidden features that have important implica-
 55 tions in the ordering of the magnetic domains in the system. Here we use high-resolution μ SR
 56 spectroscopy, complemented by SQUID magnetometry and large scale micromagnetic simulations,
 57 to systematically study the thermal evolution of magnetic states in CrI₃. Such suite is instrumental
 58 to identify, characterize and understand distinct macroscopic ground states with any competing
 59 magnetic phases.

60 In a μ SR experiment, positive muons implanted into a sample serve as extremely sensitive
 61 local microscopic probes to detect small internal magnetic fields and ordered magnetic volume

fractions in the bulk of magnetic systems. See details in *Methods* and Supplementary Sections S1-S2. Zero-field μ SR time-spectra are recorded in a powder sample of CrI_3 below (5 K, 30 K, 54 K and 60 K) and above (65 K and 80 K) the magnetic ordering temperature (Fig. 1a-b). A paramagnetic state is generally characterised by a small Gaussian Kubo-Toyabe depolarization of the muon spin originating from the interaction with randomly oriented nuclear magnetic moments. Conversely, the spectra from the highest measured temperature from 150 K down to 62 K, exhibit a relatively high transverse depolarization rate $\lambda_T \simeq 4.9(2) \mu\text{s}^{-1}$. This reflects the occurrence of dense electronic Cr moments and indicates strong interactions between them. In this scenario a novel correlated paramagnetic state may be present in the system at temperatures above the actual Curie temperature. As the crystal is cooled down, in addition to the paramagnetic signal, an oscillating component with a single well defined frequency is observed at $T \lesssim 62$ K (Fig. 1a-b). Below 50 K, a spontaneous muon spin precession with two well-separated distinct precession frequencies is observed in the μ SR spectra and persists down to 5 K. The temperature dependences of the internal fields ($\mu_0 H_\mu = \omega/\gamma_\mu^{-1}$) for the two components are shown in Fig. 2a. The low frequency component shows a monotonous decrease with increasing temperature and disappears at $T_{C2} \simeq 50$ K. The high frequency component decreases down to 50 K, above which it keeps a constant value within a few Kelvin's range and then decreases again to disappear at $T_{C1} \simeq 62$ K. Thus, the two oscillatory components have clearly different transition temperatures. This implies the presence of two distinct magnetic transitions in CrI_3 . We also notice that an upturn on both $\mu_0 H_{\mu,1}$ and $\mu_0 H_{\mu,2}$ is seen below $T_{C3} \simeq 30$ K. Moreover, a strongly damped component appears below T_{C3} which is seen as some lost of initial asymmetry of the ZF- μ SR signal. This suggests

the presence of another magnetic transition at this temperature. The temperature dependences of the relative weights of the individual components in the total μ SR signal are shown in Fig. 2b. The weight of the high frequency component (component I) ω_1 gradually increases below T_{C1} and reaches maximum at T_{C2} , below which the second frequency appears. The third component raises below $T_{C3} \simeq 30$ K. The components I and II share the weight of (30 - 70) % in the temperature range between 30 K and 50 K. These results portray the existence of a clear phase diagram in the temperature domain, in excellent agreement with the magnetic singularities observed by SQUID measurements performed in a single crystal of CrI_3 (see Supplementary Figure S2).

Fig. 2c-d show the temperature dependences of the transverse λ_T and the longitudinal λ_L depolarisation rates, respectively, of components I and II. The λ_T is a measure of the width of the static magnetic field distribution at the muon site, and also reflects dynamical effects (spin fluctuations). The λ_L is determined by dynamic magnetic fluctuations only. For both components, λ_T is higher than λ_L in the whole temperature range, indicating that magnetism is mostly static in origin. However, λ_{L1} has a higher overall value than λ_{L2} , implying that the magnetic order with $T_{C1} \simeq 62$ K contains more dynamics. The presence of three transitions are clearly substantiated by the anomalies, seen in λ_T and λ_L (Fig. 2c-d). Namely, the $\lambda_{T,1}$ starts to increase below T_{C1} and peaks at T_{C2} , then decreases and tends to saturate. Nevertheless, it increments again below T_{C3} . $\lambda_{T,2}$ also exhibits an increase below T_{C3} . Similarly, $\lambda_{L,1}$ goes to high values for $T < T_{C1}$, saturates at $T < T_{C2}$ and then enlarges again for $T < T_{C3}$, followed by a peak at lower temperature. We note that it is not possible to discriminate in the analysis the contribution of strongly damped components and a high frequency component into λ_{L1} below 30 K and thus the peak in λ_{L2} at low

temperatures could be due to the contribution from component III. Overall, these results point to the complex, unconventional thermal evolution of the magnetic states in CrI_3 .

The behaviour observed involves a volume-wise interplay between various states, providing an important constraint on theoretical models. One possible interpretation of the data is that below T_{C1} there is an evolution of the magnetic order in specific volumes of the crystal, which coexists with a correlated paramagnetic state. The second magnetic order thereby occurs within the paramagnetic regions below T_{C2} . This interpretation is supported by the temperature dependent measurements of the total magnetic fraction V_m (Fig. 3). The magnetic fraction V_m does not acquire the full volume below $T_{C1} \simeq 62$ K. Instead, it gradually increases below T_{C1} and reaches $\simeq 80$ % at $T_{C2} \simeq 50$ K. An additional increase of V_m takes place below $T_{C3} \simeq 25$ K, at which the third strongly damped component appears and reaches nearly $\simeq 100$ %. The volume wise evolution of magnetic order across T_{C1} , T_{C2} and T_{C3} in CrI_3 strongly suggests the presence of distinct magnetic states in the separate volumes of the sample. In addition, we propose that while the frequency of the second component disappears above 50 K, this component exhibits a precursor correlated state up to the highest temperature investigated 150 K.

To understand the microscopic mechanism of these phase transitions, we undertake macroscale spin dynamics which incorporated atomistic (several $\text{\AA}$'s) and micromagnetic (μm -level) underlying details of the magnetic and electronic structure of CrI_3 . We modelled the atomistic part using strongly correlated density functional theory based on Hubbard- U methods²¹ whereas the micromagnetic interactions are described through the Landau-Lifshitz-Gilbert (LLG) equation

techniques²². We have also taken into account dipolar fields and higher-order exchange interactions at the level of biquadratic exchange since its sizeable magnitude is important in the magnetic features of 2D magnets⁸. These approaches have been shown to be critical in the description of the spin properties of halide magnets at high-accuracy of critical temperatures, magnetic domains, and topological spin textures^{23,24}. See further details in Ref.⁸. We simulated the zero-field cooling processes for a large square flake of bulk CrI₃ of dimensions $0.4\ \mu\text{m} \times 0.4\ \mu\text{m}$ with a thickness above 200 nm thickness to avoid any coexistence of ferro- and anti-ferromagnetic phases in the system²⁵. As a descriptor of the spin dynamics of the system we utilize the ratio between the number of spins along the z -direction or easy-axis $N(S_z)$, relative to the total number $N(S_{\text{total}})$, that is, $N(S_z)/N(S_{\text{total}})$. This allows us to access the number of sites with a specific spin-polarization into the volume of the material which provides information about the disorder caused by thermal fluctuations.

We find that three main phases emerge in CrI₃ as function of the temperature, which we name them as Disordered-I, Ordered, and Disordered-II (Figure 4). Each phase is labelled according to the degree of deviation relative to the easy-axis of the magnetization S_z (Fig. 4a). For instance, the Ordered phase is characteristic of magnitudes of $|S_z|$ with high spin polarization along z , whereas Disordered-II indicates the opposite. The Disordered-I however sets an intermediate phase between both states with different amount of disorder (Fig. 4b). Surprisingly, the number of spins in the volume of CrI₃ with $|S_z| > 0.99$, corresponding to the full orientation along the easy-axis, is largely a minority ($N(S_z)/N(S_{\text{total}}) \sim 1.8 - 3.0\%$) at the first ($T_{C1} = 62\ \text{K}$) and second ($T_{C2} = 50\ \text{K}$) transitions. Most of the sites have a substantial amount of disorder with spins not completely fol-

145 lowing the easy-axis of the CrI_3 but rather stabilising orientations with in-plane orientations (S_x
 146 and S_y). Such contributions only become negligible as the temperature drops down below 10 K
 147 where a sharp increment of $N(S_z)/N(S_{\text{total}})$ appears which coincides with the antagonistic response
 148 of the Disordered-I phase. Spin sites with larger amount of disorder (e.g. Disordered-II) tend to
 149 disappear as the system cools down below 40 K. A spatial visualization of the spin orientations,
 150 shown in Fig. 4c for different temperatures confirm this description. Remarkably, it shows that
 151 mutually exclusive spatial magnetic regions with distinct projection of the magnetization exist in
 152 a wide temperature range, which is in perfect agreement with μSR results. However, in μSR the
 153 inhomogeneous and mutually exclusive spatial regions exist even at the base- T of 5 K, while the
 154 calculations show a sharp increment of the homogeneous S_z -axis oriented structure below 10 K
 155 (Figure 4b). The reason for this discrepancy could be that: (i) there is not a one-to-one corre-
 156 spondence in the temperature values between experiment and theory. (ii) In reality, much lower
 157 temperatures than 5 K are most likely required to get homogeneous magnetic states. It is worth
 158 mentioning that even when the system reached 0 K, where thermal fluctuations are inexistent, the
 159 spins still evolve in time as an effect due to high magnetic anisotropy and meta-stability of the
 160 magnetic domains in CrI_3 ²³ (Fig. 4c). Our results suggest that the magnetic structure of bulk
 161 CrI_3 is markedly composed by thermal disorder with no apparent formation of anti-ferromagnetic
 162 phases as observed in few layers^{6,17,18,25}.

Supplementary Materials

Materials and Methods.

Supplementary sections S1 to S5, and Figures S1-S2.

0.0.1 Data Availability

The data that support the findings of this study are available within the paper and its Supplementary Information.

0.0.2 Competing interests

The Authors declare no conflict of interests.

0.0.3 Acknowledgments

μ SR experiments were performed at the π M3 beam line (low background GPS instrument) of the Swiss Muon Source (SmuS) of the Paul Scherrer Institute, Villigen, Switzerland, under proposal ID: 20190297 with EJGS as the PI. GT thank Prof. Alexander Shengelaya and the Georgian National Science Foundation (grant PHDF-19-060) for funding support to participate in μ SR experiments led by ZG and EJGS. EJGS acknowledges computational resources through the UK Materials and Molecular Modelling Hub for access to THOMAS supercluster, which is partially

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Figure 1: **μ SR spectroscopy applied to CrI_3 .** **a-b**, Zero-field μ SR spectra, recorded at various temperatures for the polycrystalline sample of CrI_3 , shown in the low and extended time interval. The solid lines are the fit of the data using the methods of Supplementary Sections S3-S4. Error bars are the standard error of the mean in about 10^6 events. The error of each bin count is given by the standard deviation of n . The errors of each bin in the μ SR asymmetry are then calculated by statistical error propagation.

Figure 2: **Temperature dependent μ SR parameters.** **a**, The temperature dependence of the internal magnetic fields for the observed two components in CrI_3 . **b**, The temperature dependence of the relative weights of the three components in the total signal for CrI_3 , determined from zero-field μ SR experiments. **c-d**, The temperature dependence of transverse depolarization rates λ_{T1} , λ_{T2} and the longitudinal depolarization rates λ_{L1} , λ_{L2} for two components. The error bars represent the standard deviation of the fit parameters.

Figure 3: **Thermal evolution of various magnetic phases in CrI_3 .** **a**, The temperature dependence of the total magnetic volume fraction V_M , determined from precise weak transverse field (weak-TF) μ SR measurements. In this weak-TF experiment, a small magnetic field of 30 G is applied nearly perpendicular to the muon spin polarisation. The different components seen in Fig. 2 are highlighted in each region of the temperature range with the paramagnetic phase above the Curie temperature. The error bars represent the standard deviation of the fit parameters.

Figure 4: **Micromagnetic analysis of the spin dynamics in CrI₃.** **a**, Diagram of the different magnitudes of $|S_z|$ relative to the unit sphere in the range of $|S_z| = 1$ (full polarized along z) and $|S_z| = 0$ (only in-plane xy -projections). The orientations of the spins are assigned randomly following the Monte Carlo moves. The plot only shows a schematic of possible projections over the sphere with others (not shown) with the same $|S_z|$ equally probable. **b**, Magnetic fraction (in %) of the out-of-plane spins ($N(S_z)/N(S_{\text{total}})$) as a function of the temperature. The calculation of $N(S_z)$ and $N(S_{\text{total}})$ take into account the volumetric amount of spins over the entire system for S_z and S_{total} , respectively. Three main phases were identified in bulk CrI₃ which are named: Disordered-I (faint black), with values of $N(S_z)/N(S_{\text{total}})$ between the curves of $0.01 < |S_z| < 0.99$ and $0.20 < |S_z| < 0.80$; Ordered (faint red), within $|S_z| > 0.80$ and $|S_z| > 0.99$; and, Disordered-II (faint blue), within $|S_z| < 0.01$ and $|S_z| < 0.20$. The solid curves showed in each phase provide a sample of a specific variation of $N(S_z)/N(S_{\text{total}})$ for a given range of $|S_z|$. The vertical dashed line sets the time of 2 ns required to achieve 0 K in the spin dynamics. The magnitudes of $N(S_z)/N(S_{\text{total}})$ showed after 0 K demonstrated that even when the thermal fluctuations are zero, the system is still evolving to stabilize its ground state. The critical temperatures ($T_{C1,C2,C3}$) are also highlighted. **c**, Snapshots of the dynamical spin configurations of bulk CrI₃ during field cooling from 80 K down to 0 K. Magnetisation is projected along of in-plane components (S_x, S_y) and S_z at different temperatures: 68 K, 60 K, 50 K, 20 K and 0 K. Each column and row corresponds to a specific projection of the magnetization at a given temperature provided at the far left. The colour scale shows the variation of the three magnetization components (S_x, S_y, S_z) throughout the system.

Figure 1

Figure 2

Figure 3

a **b** **c**

Supplementary Information:

Thermal disorder driven magnetic phases in van der Waals magnet CrI_3

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21	1 CrI₃ bulk crystal growth
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22 Chromium triiodide crystals were grown using the chemical vapour transport technique. Chromium
23 powder (99.5% Sigma-Aldrich) and anhydrous iodine beads (99.999% Sigma-Aldrich) were mixed
24 in a 1:3 ratio in an argon atmosphere inside a glovebox. 972 mg of the mixture were loaded into
25 a silica ampoule with a length, inner diameter and outer diameter of 500 mm, 15 mm and 16 mm
26 respectively (Supplementary Figure S1a). The ampoule was extracted from the glovebox with a
27 ball valve covering the open end to prevent air exposure and then it was immediately was evacuated
28 using a turbo-molecular pump down to 6×10^{-6} . Once the pressure stabilised, the closed end was
29 dipped in liquid nitrogen to prevent the sublimation of the iodide beads. The ampoule was then
30 flame sealed and introduced into a three-zone furnace. An initial inverted gradient step was used
31 to minimize nucleation sites in the growth zone. The gradient was then inverted so that the source
32 zone would remain at 650 °C, the middle growth zone at 550 °C and the third zone at 600 °C for
33 3 days. Crystal growth takes place in the centre and source zones. The single crystals and the
34 microcrystalline powder were both extracted from the ampoule and stored in an argon atmosphere
35 inside the glovebox to prevent oxidation and hydration. A sample of the bigger single crystals was

296 ground into a powder using a razor blade. X-Rays diffraction analysis was performed on samples
 37 of the powder and single crystalline CrI_3 by loading the material into a capillary and flame-sealing
 38 it inside the glove box. The powder pattern of both samples were consistent with the monoclinic
 39 AlCl_3 -type structure (C2/m) reported for CrI_3 (Supplementary Figure S1b).

Figure S1: **a**, Picture of the ampoule used for sample fabrication. **b**, X-Ray diffraction pattern of the CrI_3 microcrystalline powder studied in the μSR experiment. The most prominent peaks of the orange trace (experiment) have been labelled (Miller indices) and marked (grey lines) with peaks positions of the monoclinic (room temperature) crystalline phase of CrI_3 .

2 μ SR experiment

The μ SR method is based on the observation of the time evolution of the spin polarization $\vec{P}(t)$ of the muon ensemble. In a μ SR experiments an intense beam ($p_\mu = 29$ MeV/c) of 100 % spin-polarized muons is stopped in the sample. Currently available instruments allow essentially a background free μ SR measurement at ambient conditions¹. The positively charged muons thermalize in the sample at interstitial lattice sites, where they act as magnetic microprobes. In a magnetic material the muons spin precess in the local field B_μ at the muon site with the Larmor frequency $\nu_\mu = \gamma_\mu/(2\pi)B_\mu$ (muon gyromagnetic ratio $\gamma_\mu/(2\pi) = 135.5$ MHz T⁻¹). The muons μ^+ implanted into the sample will decay after a mean life time of $\tau_\mu = 2.2$ μ s, emitting a fast positron e^+ preferentially along their spin direction. Various detectors placed around the sample track the incoming μ^+ and the outgoing e^+ . When the muon detector records the arrival of a μ in the specimen, the electronic clock starts. The clock is stopped when the decay positron e^+ is registered in one of the e^+ detectors, and the measured time interval is stored in a histogramming memory. In this way a positron-count versus time histogram is formed. A muon decay event requires that within a certain time interval after a μ^+ has stopped in the sample a e^+ is detected. This time interval extends usually over several muon lifetimes (*e.g.* 10 μ s).

56

The GPS (π M3 beamline) μ SR instrument at the Paul Scherrer Institute, Switzerland, was used to study the CrI₃ sample. The specimen was mounted in a He gas-flow cryostat and the temperature was varied between 5 and 200 K.

61 **3 Analysis of Weak TF- μ SR data**

62 The weak TF asymmetry spectra were analyzed^{2,3} using the function:

$$A_S(t) = A_p \exp(-\lambda t) \cos(\omega t + \phi). \quad (1)$$

63 where t is the time after muon implantation, $A(t)$ is the time-dependent asymmetry, A_p is the ampli-
 64 tude of the oscillating component (related to the paramagnetic volume fraction), λ is an exponential
 65 damping rate due to paramagnetic spin fluctuations and/or nuclear dipolar moments, $\omega = 2\pi\nu_\mu$ is
 66 the Larmor precession frequency set by the strength of the transverse magnetic field, and ϕ is a
 67 phase offset. The zero for $A(t)$ was allowed to vary for each temperature to deal with the asymmetry
 68 baseline shift occurring for magnetically ordered samples. From these refinements, the magneti-
 69 cally ordered volume fraction at each temperature T was obtained by $V_M = 1 - A_p(T)/A_p(T_{max})$,
 70 where $A_p(T_{max})$ is the amplitude in the paramagnetic phase at high temperature.

283 4 Analysis of ZF- μ SR data

73 In the paramagnetic state, the μ SR spectra are described by the combination of Lorentzian and
 74 Gaussian Kubo-Toyabe depolarization function:

$$A_{\text{ZF,PM}}(t) = (1 - V_M)A_0 \left(\frac{1}{3} + \frac{2}{3} (1 - (\sigma t)^2 - \Lambda t) e^{-\frac{1}{2}(\sigma t)^2 - \Lambda t} \right)$$

75 Here, the depolarisation rates σ and Λ are due to the nuclear dipole moments and randomly
 76 oriented diluted local electronic moments, respectively. A_0 is the initial asymmetry. $V_{PM} = 1 - V_M$
 77 is the paramagnetic fraction, which acquires maximum value of 1 above 60 K.

78 In the ordered state, the response of the sample consists of three magnetic components, de-
 79 pending on temperature:

$$A_{\text{ZF,M}}(t) = V_M A_0 \omega_1 \left(f_{T1} \cos(\gamma_\mu B_{\mu 1} t + \phi) e^{-\lambda_{T1} t} + f_{L1} e^{-\lambda_{L1} t} \right) + \dots \quad (2)$$

$$V_M A_0 \omega_2 \left(f_{T2} \cos(\gamma_\mu B_{\mu 2} t + \phi) e^{-\lambda_{T2} t} + f_{L2} e^{-\lambda_{L2} t} \right) + \dots \quad (3)$$

$$V_M A_0 \omega_3 \left(f_{T3} e^{-\lambda_{T3} t} + f_{L3} e^{-\lambda_{L3} t} \right) \quad (4)$$

80 Here, ω_1 , ω_2 , and ω_3 are the relative fractions of the magnetic components. The first and
 81 second terms describe the high and low frequency magnetic components, respectively. The com-
 82 ponents are characterised by an oscillating “transverse” component and a slowly relaxing “lon-

283 gitudinal” component. The longitudinal component arises due to muons experiencing local field
 84 components which are parallel to the initial muon spin polarization. In polycrystalline samples
 85 with randomly oriented fields the orientational averaging results in a so-called “one-third tail” with
 86 $f_L = \frac{1}{3}$ ($f_T = \frac{2}{3}$). For single crystals, f_L varies between zero and unity as the orientation between
 87 field and polarization changes from being perpendicular to parallel. λ_T and λ_L are the transverse
 88 and longitudinal depolarisation rates of the μ SR signals, respectively. $B_{\mu 1}$ and $B_{\mu 2}$ are the internal
 89 magnetic fields at the muon site, corresponding to high and low frequency components, respec-
 90 tively. The third term describes the strongly damped magnetic component, which occurs below 30
 91 K only. We note that it is not possible to separate λ_{L3} from λ_{L1} and λ_{L2} and thus it is fixed to 0 in
 92 the analysis.

5 SQUID magnetometry

Sample preparation In order to measure the magnetization of CrI_3 in the presence of in-plane and out-of-plane external magnetic fields, two different samples were prepared. For the out-of-plane orientation, various single crystals were stacked one on top of the other and placed onto the surface on the end of a polyethylene rod. This was carefully placed inside a silica tube with the crystals facing upwards and another polyethylene rod placed on top trapping the crystal in between. For the in-plane orientation, a polyethylene rod was cut longitudinally and a single crystal was glued to the flat using Apiezon-N grease. These preparations were performed in an argon atmosphere to avoid crystal degradation. The samples were then inserted inside an outer silica tube and flame sealed at a pressure lower than 10^{-3} mbar.

Magnetization and magnetic susceptibility of CrI_3 crystals Magnetization curves and zero-field-cooled/field-cooled susceptibility sweeps were carried out in a SQUID magnetometer (Quantum Design MPMS-XL-7) on single crystals of CrI_3 where the relative orientation of the basal plane of the sample with the external magnetic field (both AC and DC) is controlled. We find signatures of three independent magnetic phase transitions consistent with the μSR experiments (Supplementary Fig.S2). The most prominent feature in the thermal variation of the magnetic susceptibility onsets at 61 K as shown by the DC measurements reflected in Supplementary Fig. S2a-b, in good agreement with recent experiments performed on this material ⁴. The real part of the AC measurements shows that this transition is independent of the AC drive frequency (Supplementary Fig.S2c-d). Interestingly, there is no peak in the imaginary component of the AC magnetization

in both orientations. A second feature at 50 K is particularly visible in the thermal dependence of the in-plane magnetic moment of the crystal shown in Supplementary Fig. S2b, d. This can be attributed to a second magnetic phase transition as discussed in the main text. The presence of this additional peak was mentioned in previous experiments⁵ however without any explanation or characterization. As with the main critical feature, this peak also exhibits no frequency dependence, which suggests that this phase transition is a long-range ordering. The 50 K maximum is most prominent for the in-plane orientation measurements (both AC and DC), suggesting that some component of the magnetization exists in the crystallographic *ab*-plane. This observation complements the notion of a strong magnetic anisotropy along the *c*-axis and, at the same time, reveals the presence of some in-plane magnetic moment. Finally, the fact that the imaginary component of the AC magnetisation for the in-plane orientation in Supplementary Fig. S2c exhibits an onset around 30 K marks the onset of the third phase transition.

Figure S2: **a-b**, Zero-field-cooled/field-cooled temperature dependence of the DC magnetization at different external magnetic fields, aligned parallel and perpendicular to the crystallographic c -axis respectively. The DC external magnetic field used was 10 G in **a** and 50 G in **b**, represented by the empty markers. The solid markers represent the data measured with an external field of 100 G for both orientations. The solid line is a guide to the eye. **c-d**, Zero-field temperature dependence of the AC magnetization at three different frequencies for the parallel and perpendicular orientations, respectively. The real and imaginary components are represented by the hollow and solid markers, respectively. The grey-shaded regions are a reference for the reader indicating the temperatures at which the magnetic anomalies are seen. The regions are consistent with those shaded in Figure 2 for comparison.

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Figures

Figure 1

Figure 1

μ SR spectroscopy applied to CrI_3 . a-b, Zero-field μ SR spectra, recorded at various temperatures for the polycrystalline sample of CrI_3 , shown in the low and extended time interval. The solid lines are the fit of the data using the methods of Supplementary Sections S3-S4. Error bars are the standard error of the mean in about 106 events. The error of each bin count is given by the standard deviation of n . The errors of each bin in the μ SR asymmetry are then calculated by statistical error propagation.

Figure 2

Figure 2

Temperature dependent μ SR parameters. a, The temperature dependence of the internal magnetic fields for the observed two components in CrI₃. b, The temperature dependence of the relative weights of the three components in the total signal for CrI₃, determined from zero-field μ SR experiments. c-d, The temperature dependence of transverse depolarization rates λ_{T1} , λ_{T2} and the longitudinal depolarization rates λ_{L1} , λ_{L2} for two components. The error bars represent the standard deviation of the fit parameters.

Figure 3

Figure 3

Thermal evolution of various magnetic phases in CrI₃. a, The temperature dependence of the total magnetic volume fraction V_M , determined from precise weak transverse field (weak-TF) μ SR measurements. In this weak-TF experiment, a small magnetic field of 30 G is applied nearly perpendicular to the muon spin polarisation. The different components seen in Fig. 2 are highlighted in each region of the temperature range with the paramagnetic phase above the Curie temperature. The error bars represent the standard deviation of the fit parameters.

Figure 4

Figure 4

Micromagnetic analysis of the spin dynamics in CrI₃. a, Diagram of the different magnitudes of $|S_z|$ relative to the unit sphere in the range of $|S_z| = 1$ (full polarized along z) and $|S_z| = 0$ (only in-plane xy -projections). The orientations of the spins are assigned randomly following the Monte Carlo moves. The plot only shows a schematic of possible projections over the sphere with others (not shown) with the same $|S_z|$ equally probable. b, Magnetic fraction (in %) of the out-of-plane spins ($N(S_z)/N(S_{total})$) as a function of the temperature. The calculation of $N(S_z)$ and $N(S_{total})$ take into account the volumetric

amount of spins over the entire system for S_z and S_{total} , respectively. Three main phases were identified in bulk CrI_3 which are named: Disordered-I (faint black), with values of $N(S_z)/N(S_{\text{total}})$ between the curves of $0.01 < |S_z| < 0.99$ and $0.20 < |S_z| < 0.80$; Ordered (faint red), within $|S_z| > 0.80$ and $|S_z| > 0.99$; and, Disordered-II (faint blue), within $|S_z| < 0.01$ and $|S_z| < 0.20$. The solid curves showed in each phase provide a sample of a specific variation of $N(S_z)/N(S_{\text{total}})$ for a given range of $|S_z|$. The vertical dashed line sets the time of 2 ns required to achieve 0 K in the spin dynamics. The magnitudes of $N(S_z)/N(S_{\text{total}})$ showed after 0 K demonstrated that even when the thermal fluctuations are zero, the system is still evolving to stabilize its ground state. The critical temperatures (T_{C1}, T_{C2}, T_{C3}) are also highlighted. c, Snapshots of the dynamical spin configurations of bulk CrI_3 during field cooling from 80 K down to 0 K. Magnetisation is projected along of in-plane components (S_x, S_y) and S_z at different temperatures: 68 K, 60 K, 50 K, 20 K and 0 K. Each column and row corresponds to a specific projection of the magnetization at a given temperature provided at the far left. The colour scale shows the variation of the three magnetization components (S_x, S_y, S_z) throughout the system. 15