# **Controlling Spin Orientation and Metamagnetic Transitions** in Anisotropic van der Waals Antiferromagnet CrPS<sub>4</sub> by Hydrostatic Pressure HPSTAR

Yuxuan Peng, Zhongchong Lin, Guang Tian, Jie Yang, Peijie Zhang, Fanggui Wang, Pingfan Gu, Xingyu Liu, Chin-Wei Wang, Maxim Avdeev, Fuyang Liu, Dong Zhou, Rui Han, Peng Shen, Wenyun Yang,\* Shunguan Liu, Yu Ye, and Jinbo Yang

Controlling the phases of matter is a central task in condensed matter physics and materials science. In 2D magnets, manipulating spin orientation is of great significance in the context of the Mermin-Wagner theorem. Herein, a systematic study of temperature- and pressure-dependent magnetic properties up to 1 GPa in van der Waals CrPS<sub>4</sub> is reported. Owing to the temperature-dependent change of the magnetic anisotropy energy, the material undergoes a first-order spin reorientation transition with magnetic moments realigning from being almost parallel with the c axis in the ac plane to the quasi-1D chains of  $CrS_6$  octahedra along the *b* axis upon heating. The spin reorientation temperature is suppressed after applying pressure, shifting the high-temperature phase to lower temperatures with the emergence of spinflop transitions under magnetic fields applied along the *b* axis. The saturation field increases with pressure, indicating the enhancement of interlayer antiferromagnetic coupling. However, the Néel temperature is slightly reduced, which is ascribed to the suppression of intralayer ferromagnetic coupling. The work demonstrates the control of spin orientation and metamagnetic transitions in layered antiferromagnets, which may provide new perspectives for exploring 2D magnetism and related spintronic devices.

## vdW materials with diverse ground states and potential applications in spintronics have sparked intense interest in fundamental research.<sup>[3,4]</sup> Controlling the phases and magnetism of these 2D magnets has always been a key issue.<sup>[3,5]</sup> Compared to 3D magnetic materials, the magnetism of 2D magnets can be manipulated more easily<sup>[5]</sup> owing to their layered nature and vdW gap between layers. Several methods have been utilized to tune the magnetism of these 2D magnets, including electrostatic doping,<sup>[6-8]</sup> electric-field control,<sup>[9]</sup> different substrates,<sup>[10,11]</sup> proximity coupling,<sup>[12]</sup> and pressure.<sup>[13,14]</sup> In particular, the application of pressure offers an effective way to tune the electronic and magnetic properties by modifying the bond lengths and angles of the lattice continuously without changing the chemical composition or inducing disorder. For instance, hydrostatic pressure alters the stacking order and induces antiferromagnetic (AFM) to FM phase transition

# 1. Introduction

Since the discovery of 2D intrinsic ferromagnetism (FM) in atomically thin van der Waals (vdW) magnets,<sup>[1,2]</sup> 2D magnetic

Y. Peng, Z. Lin, G. Tian, J. Yang, F. Wang, P. Gu, X. Liu, W. Yang, S. Liu, Y. Ye, J. Yang State Key Laboratory for Artificial Microstructure & Mesoscopic Physics School of Physics Peking University Beijing 100871, P. R. China E-mail: yangwenyun@pku.edu.cn P. Zhang, F. Liu Center for High Pressure Science and Technology Advanced Research (HPSTAR) Beijing 100094, P. R. China C.-W. Wang National Synchrotron Radiation Research Center Hsinchu 30076, Taiwan The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adfm.202106592.

#### DOI: 10.1002/adfm.202106592

in bilayer CrI<sub>2</sub>.<sup>[13,14]</sup> It also controls the shape of the hysteresis loop and decreases the coercive field as well as the Curie temperature (T<sub>C</sub>) in Fe<sub>3</sub>GeTe<sub>2</sub> flakes.<sup>[15]</sup> The application of pressure also yields different  $T_{\rm C}$  in bulk crystals, with  $T_{\rm C}$ 

M. Avdeev Australian Nuclear Science and Technology Organisation (ANSTO) New Illawarra Road, Lucas Heights, NSW 2234, Australia
M. Avdeev School of Chemistry The University of Sydney Sydney, NSW 2006, Australia
D. Zhou, R. Han, P. Shen Division of Functional Material Central Iron & Steel Research Institute Beijing 100081, P. R. China
J. Yang Collaborative Innovation Center of Quantum Matter Beijing 100871, P. R. China
j. rang Beijing Key Laboratory for Magnetoelectric Materials and Devices Beijing 100871, P. R. China

enhanced in Cr1<sub>3</sub><sup>[16]</sup> and V1<sub>3</sub>,<sup>[17,18]</sup> unchanged in Cr<sub>2</sub>Si<sub>2</sub>Te<sub>6</sub><sup>[19]</sup> but suppressed in Cr<sub>2</sub>Ge<sub>2</sub>Te<sub>6</sub>,<sup>[20]</sup> CrBr<sub>3</sub>,<sup>[21]</sup> and Fe<sub>3-x</sub>GeTe<sub>2</sub>.<sup>[22,23]</sup> Surprisingly, spin reorientation transition (SRT) with uniaxial anisotropy switching to easy-plane anisotropy has been observed in Cr<sub>2</sub>Ge<sub>2</sub>Te<sub>6</sub> crystals under hydrostatic pressures up to 2 GPa.<sup>[24]</sup> Together, these studies demonstrate that the application of pressure is a universal and clean way to manipulate magnetic properties, and also to comprehend lattice-related magnetic exchange coupling regardless of the physical form of 2D magnets.

IDVANCED

SCIENCE NEWS \_\_\_\_\_\_

Notably, studies on pressure-induced magnetic property changes in 2D magnets focus mainly on ferromagnets, leaving most of the antiferromagnets less well explored. In this study, we focus on the AFM semiconductor CrPS<sub>4</sub>, which has been proven to be a promising 2D magnet with a number of intriguing properties, including photoluminescent Fano resonance,<sup>[25]</sup> good photoconductivity,<sup>[26]</sup> synaptic effect,<sup>[27]</sup> giant tunneling magnetoresistance,<sup>[28]</sup> and exchange bias effect.<sup>[29]</sup> In particular, CrPS<sub>4</sub> is air-stable, making it a practical alternative for h-BN in protecting 2D materials and assembling vdW heterostructures.<sup>[30]</sup> It has an A-type AFM structure of out-of-plane FM monolayers coupled antiferromagnetically with a Néel temperature  $T_{\rm N} = 38$  K,<sup>[31,32]</sup> and can be exfoliated into an FM monolayer.<sup>[34]</sup>

In our previous study, the low-field metamagnetic transition of CrPS<sub>4</sub> was identified as a spin-flop transition.<sup>[31]</sup> During the spin-flop transition, magnetic moments realign from the ac plane (at a small angle from the c axis) to the quasi-1D chains of  $CrS_6$  octahedra along the *b* axis, showing both in-plane and out-of-plane magnetic anisotropy in CrPS<sub>4</sub>. Strong in-plane optical anisotropy has also been observed in CrPS<sub>4</sub> flakes,<sup>[33]</sup> confirming the inherent anisotropy of CrPS<sub>4</sub>. Notably, the spin-flop field is very low (less than 1 T at 2 K) and disappears at 35 K, indicating that CrPS<sub>4</sub> has small magnetic anisotropy energy (MAE) and a potential SRT<sup>[32]</sup> with the sign change of MAE. The low magnetic anisotropy and weak interlayer AFM exchange coupling<sup>[31,32]</sup> enable the effective tuning of SRT and metamagnetic transitions using external pressure. In particular, manipulating the spin orientation in 2D magnets is crucial for current information technology and applications of spintronic devices. Manipulating Néel vector by uniaxial strain has recently been realized in MnPSe<sub>3</sub>,<sup>[35]</sup> questioning whether similar phenomena could occur in CrPS4 with a smaller MAE. The first high-pressure experiment of CrPS4 mainly studied electronic and optical properties under pressures up to 31 GPa, yet leaving magnetic properties unclear.<sup>[36]</sup> A recent study investigated the magnetism in CrPS<sub>4</sub> under pressure by direct measurements of temperature-dependent magnetization along the *b* axis and specific heat. SRT was found to be rapidly suppressed by pressure, whereas Néel temperature  $T_N$  decreased only slightly.<sup>[37]</sup> However, the precise determination of the change of the Néel vector during SRT and the underlying mechanisms of pressure-tuned transitions remain unsolved.

Here, we investigated the magnetic properties of  $CrPS_4$  at hydrostatic pressures up to 1 GPa under magnetic fields along all three crystallographic axes. The anomaly observed in the *M*–*T* curves is identified as an SRT with spin realigning from the *ac* plane to the *b* axis upon heating. When *H* // *c*,

the spin-flop transition field decreases with increasing pressure, which results from the decrease of MAE. With a further increase in pressure, a spin-flop transition emerges with H // b when the sign of MAE changes. The saturation field ( $H_S$ ) of AFM to FM increases due to the reduced vdW gap with enhanced interlayer exchange coupling under pressure. However,  $T_N$  is slightly suppressed, which is ascribed to the suppression of intralayer FM coupling. The pressure-dependent X-ray diffraction (XRD) and first-principles calculations were further performed to comprehend pressure-dependent magnetic properties.

# 2. Results and Discussion

#### 2.1. Spin Reorientation Transition

The magnetic ground state of CrPS<sub>4</sub> is an A-type AFM consisting of out-of-plane FM monolayers coupled antiferromagnetically, as shown in Figure 1e. The magnetic moments lie in the *ac* plane with a small deviation of 8.94° from the c axis. According to our previous study, the disappearance of the spin-flop transition with H // c and an anomaly in M-Tat approximately 35 K indicate a potential spin configuration change with MAE close to zero, namely an SRT. Therefore, we conducted a temperature-dependent neutron diffraction experiment with the two typical diffraction patterns shown in Figure 1a,b at 20 and 35 K, respectively. The magnetic reflections at 20 and 35 K can both be indexed with the k = (0, 1)0, 0.5) propagation vector in the nonmagnetic unit cell of C2 space group<sup>[31,32,38,39]</sup> (Note S1, Supporting Information), consistent with that of 1.7 K, indicating no magnetic group change. However, two magnetic structures are symmetryallowed with spins in the *ac* plane or along the *b* axis.<sup>[32]</sup> Owing to the disappearance of the spin-flop transition with *H* // *c* at 35 K (Figure 1c), the magnetic moments are unlikely in the *ac* plane. Meanwhile, the boundary between the A-type AFM and the spin-flop state in the magnetic phase diagram of  $CrPS_4$  with H // c approaches the spin-reorientation temperature in the zero field,<sup>[31,37]</sup> which also indicates that the high-temperature spin-reorientation and spin-flop phases are identical with magnetic moments along the b axis. In contrast, a spin-flop transition is observed with  $H \parallel b$  at 35 K (Figure 1d), thereby confirming that magnetic moments turn from the *ac* plane to the *b* axis during SRT upon heating. Therefore, the spin is determined to be along the b axis in refinement for 35 K, giving an ordered moment of  $1.47\mu_{\rm B}/$ Cr using the Rietveld analysis with the FullProf suite,<sup>[40,41]</sup> which is smaller than that obtained at a lower temperature due to the more substantial thermal fluctuation near  $T_{\rm N}$ . The temperature-dependent lattice parameters and magnetic moments are summarized in Figure S2, Supporting Information. Notably, the *b* axis where the quasi-1D chains of  $CrS_6$ octahedra lie along is abnormally elongated upon cooling, which is consistent with an earlier study<sup>[32]</sup> and will be discussed later. In brief, the SRT in CrPS<sub>4</sub> is realized by the rearrangement of moments from antiferromagnetically aligned in the *ac* plane  $(AFM_{ac})$  to antiferromagnetically aligned along the b (AFM<sub>b</sub>) axis upon heating.





**Figure 1.** a,b) Neutron diffraction patterns of CrPS<sub>4</sub> at 20 and 35 K, respectively. c,d) Field-dependent magnetizations at 31 (black line) and 35 K (red line) of (c) H / / c and (d) H / / b, respectively. Red arrows highlight the disappearance (appearance) of the spin-flop transition at 35 K for H / / c (H / / b). e) The refined magnetic structure at 20 K with magnetic moments lying in the *ac* plane with a small deviation of 8.94° with respect to the *c* axis. f) The refined magnetic structure at 35 K with magnetic moments along the *b* axis.

#### 2.2. Pressure-Dependent Magnetic Properties

After understanding the change of spin orientation during SRT, we conducted magnetization measurements of CrPS<sub>4</sub> under hydrostatic pressure up to approximately 1 GPa. The samples were made of CrPS<sub>4</sub> single crystals stacked together with the same orientation. The magnetic properties of the samples with magnetic fields along each crystallographic axis without pressure are consistent with those of the pristine CrPS<sub>4</sub>, indicating the negligible misalignments of crystals. The temperaturedependent magnetizations under different pressures with magnetic fields along the *c* and *b* axis are shown in **Figure 2a**,b.  $T_{\rm N}$ is slightly suppressed with increasing pressure, as evidenced by the kinks of both the M-T curves (dashed lines). In contrast, the spin reorientation temperature  $T_{SF}$  decreases evidently, which can be traced by the sudden-drop (H // c) or sudden-rise (H // b) anomaly of magnetization when cooling from  $T_N$ , indicated by the black arrows. The evolution of  $T_{\rm N}$  and  $T_{\rm SF}$  under pressure is basically consistent with an earlier report.<sup>[37]</sup> On the other hand, the magnetizations around  $T_{\rm N}$  also become smaller with the application of pressure, indicating the enhancement of AFM exchange coupling. Temperature-dependent magnetizations at a specific pressure are shown in Figure 2c,d. The saturation field  $H_{\rm S}$  from AFM to FM (indicated by black arrows), which is directly connected to the AFM coupling, decreases at a higher temperature where thermal fluctuation weakens the exchange coupling as expected. With increasing pressure,  $H_{\rm S}$  continuously shifts to higher values, as shown in Figure 2e,f. This confirms that the AFM coupling is enhanced with increasing pressure, consistent with the reduced magnetizations in M-T curves.

In addition to the AFM to FM transition, the spin-flop transition occurs as a sharp and nonlinear increase of magnetization when the magnetic field is parallel with the magnetic easy *c* axis. At a fixed pressure, the signature of spin-flop transition reduces with increasing temperature and finally vanishes at 25 K due to the linear decrease of MAE  $K_{\mu}$  (Figure 2c).<sup>[31]</sup> In pristine CrPS<sub>4</sub>, the spin-flop transition vanishes at 35 K when  $K_{\mu}$  decreases to zero with  $H_{SF} \propto \sqrt{K_{\mu}}$  due to the change of spin orientation. Therefore, the disappearance of the spin-flop transition with  $H \parallel c$  can be regarded as a hallmark of SRT. As the pressure increases, the spin-flop transition under H // c also gradually disappears with decreasing  $H_{SF}$  (Figure 2e), indicating that SRT moves to a lower temperature (between 20 and 25 K for 0.40(4) GPa in Figure 2c). Since increasing temperature also lowers the  $H_{\rm SF}$ , the pressure and temperature may have the same effect on the MAE and SRT. The pressure reduces  $K_{\mu} = E_{AFM_b} - E_{AFM_{ac}}$  and turns it from positive to negative, thereby driving spin orientation from  $AFM_{ac}$  to  $AFM_b$ . Owing to the increase of  $|K_{\mu}|$  induced by pressure in the  $AFM_h$  phase, the spin-flop transition with *H* // *b* becomes more remarkable at higher pressures compared to that in Figure 1d (Figure 2d,2f). At a given pressure with H // b (0.38(4) GPa in Figure 2d), the spin-flop hump emerges at 15 K and gradually expands with increasing temperature. A similar phenomenon is observed when increasing pressure at a given temperature (15 K in Figure 2f), confirming the same influence of temperature and pressure on the MAE change. In short, the pressure lowers  $T_{SR}$  with the decrease (increase) of  $H_{SF}$  under  $H \parallel c (H \parallel b)$ . When the pressure is up to 0.64(3) GPa, the AFM<sub>h</sub> can be stabilized at the lowest temperature (2 K) of the experiment. The complete data, including those of H // a, are shown in Figures S3-S6, Supporting Information.



**Figure 2.** a,b) Temperature-dependent magnetizations with H // c and H // b at an applied magnetic field of 0.1 T under zero-field cooling, respectively. c,d) Field-dependent magnetizations with H // c of 0.40(4) GPa and H // b of 0.38(4) GPa at different temperatures, respectively. e,f) Field-dependent magnetizations with H // c and H // b of 0.40(4) GPa and H // b of 0.38(4) GPa at different temperatures, respectively. e,f) Field-dependent magnetizations with H // c and H // b at 15 K of different pressures, respectively. The black arrows highlight the  $T_{SR}$  in (a) and (b) as well as  $H_{S}$  in (c–e).

#### 2.3. Pressure-Temperature Phase Diagram

The pressure dependences of characteristic temperatures  $T_{SR}$  and  $T_N$  are summarized in the pressure-temperature phase diagram in **Figure 3**a. The  $T_{SR}$  points are extracted from both M-T and M-H curves. For M-T curves,  $T_{SR}$  points are obtained from dM/dT with H // c. Since the temperature interval for measuring M-H curves is 5 K,  $T_{SR}$  is determined to be  $T_{critical}$ -2.5, where  $T_{critical}$  is the critical temperature when spin-flop transition disappears (H // c) or appears (H // b), which captures the actual spin orientation better than that of M-T curves.

Therefore, the phase regions are divided by the  $T_{\rm SR}$  obtained from M–H. By linear fitting of the  $T_{\rm SR}$ , pressure-tuning  $T_{\rm SF}$ rates of –24.3(20) K GPa<sup>-1</sup> for H // c (disappearance of AFM<sub>ac</sub>) and –44.4(65) K GPa<sup>-1</sup> for H // b (appearance of AFM<sub>b</sub>) are obtained. The negative slopes verify that temperature and pressure have a similar effect on the MAE, that is, SRT can be driven by increasing temperature or increasing pressure individually.

There is an unexpected discrepancy between the  $T_{SR}$  obtained from *M*–*H* curves of *H* // *c* and *H* // *b*, indicating the coexistence of spin components both in the *ac* plane and along



**Figure 3.** a) Temperature-pressure magnetic phase diagram of CrPS<sub>4</sub>, determined from *M*-*T* (open symbols) and *M*-*H* (open symbols) curves. The blue region between AFM<sub>ac</sub> and AFM<sub>b</sub> phase represents the phase coexistence of both phases (AFM<sub>ac</sub>+AFM<sub>b</sub>).  $T_{SR}$  estimated from *M*-*T* are all located in the phase-coexistence region, showing the consistency of our data. b) Pressure-dependent saturation field at different temperatures with *H* // *c* and *H* // *b*.

the *b* axis. We also checked the temperature-dependent magnetizations of a single CrPS<sub>4</sub> crystal, which confirmed the coexistence of both spin components between 32 and 34 K by tracing the spin-flop transition (Figure S7, Supporting Information), indicating that it is an intrinsic property of CrPS<sub>4</sub>. However, this can be either a gradual change of the easy magnetic axis in a single phase during the SRT with spin components both in the *ac* plane and along the *b* axis, or an abrupt change with phase coexistence of the AFM<sub>ac</sub> and AFM<sub>b</sub> phase, depending on whether the SRT is second- or first-order. To explore the nature of SRT, we measured temperature-dependent magnetizations during both cooling and heating processes at a prolonged temperature change rate of 0.1 K min<sup>-1</sup>. The curve shows an apparent thermal hysteresis around T<sub>SR</sub> (see Figure S8, Supporting Information), indicative of a first-order transition, as suggested by a previous study.<sup>[37]</sup> As the SRT can be regarded as a spontaneous spin-flop transition without magnetic field and the spin-flop transition is usually first-order, it is not surprising that SRT is also first-order. Therefore, the area between AFM<sub>ac</sub> and  $AFM_h$  phase region is the phase coexistence region of  $AFM_{ac}$  and  $AFM_{b}$  phase. Phase coexistence can be realized by the coexistence of different types of magnetic domains, which has been observed in the Kagome ferromagnet Fe<sub>3</sub>Sn<sub>2</sub>.<sup>[42,43]</sup> Surface reconstructions could also be a cause, which induces phase coexistence of FM and AFM phase in bulk vdW CrI<sub>3</sub>.<sup>[44]</sup> Further experiments are needed to understand the phase coexistence in CrPS<sub>4</sub>. It's worth noting that the determined phase coexistence region is not very accurate due to the large temperature interval (5 K) between each M-H curve. By extrapolating the intercept of fitting lines with the pressure axis, the critical pressure for appearance and complete stabilization of AFM<sub>h</sub> at 0 K is obtained, which is 0.67(38) GPa and 1.41(50) GPa, respectively. In contrast to  $T_{SR}$ ,  $T_N$  is slightly suppressed by pressure even though the interlayer AFM coupling is enhanced, as inferred from the  $H_{s}$ .

The saturation fields  $H_{\text{S-}c}$  (H // c) and  $H_{\text{S-}b}$  (H // b) of the sample at various temperatures and pressures are summarized in Figure 3b. At a fixed temperature,  $H_{\text{S}}$ , which can be roughly considered as interlayer AFM coupling, increases linearly with pressure. The increased rate, obtained by linearly fitted H // c data points, is higher at a lower temperature due to the stronger AFM coupling with minor thermal perturbation and can be up to 2.87 T GPa<sup>-1</sup> at 10 K. In pristine CrPS<sub>4</sub> without pressure,  $H_{\text{S-}c}$  is the smallest because the magnetic moments are almost near the *c* axis. As pressure increases,  $H_{\text{S-}b}$  is the smallest when SRT occurs (Figure 3b). This confirms the conclusion that magnetic moments realign from being almost parallel with the *c* axis to being along the *b* axis during SRT upon increasing pressure.

# 2.4. Origin of Magnetocrystalline Anisotropy Revealed by In Situ XRD

The large tunability of SRT in  $CrPS_4$  can be ascribed to the small magnetocrystalline anisotropy. The spin-orbit coupling, which is the main source of MAE, is weak in  $CrPS_4$  with all constituent elements of small atomic numbers. The chromium in  $CrPS_4$  is in the oxidation state of +3 with an electronic configuration  $3s^03d^3$ . Owing to the octahedral crystal field effect (distorted S



octahedral environment around the Cr<sup>3+</sup>), 3d orbitals of Cr split into a lower-energy  $t_{2g}$  triplet ( $d_{xy}$ ,  $d_{yz}$ , and  $d_{xz}$ ) and a higherenergy doublet  $e_g$  state ( $d_{x2-y2}$  and  $d_{z2}$ ). The remaining three electrons of Cr<sup>3+</sup> (3d<sup>3</sup>) fill the  $t_{2g}$  state, complying with Hund's rule. The lack of orbital degeneracy results in an orbital singlet with a quenched orbital moment.<sup>[45]</sup> The neutron diffraction and saturated magnetization give a magnetic moment of  $\approx 3 \mu_B/$ Cr,<sup>[31,32]</sup> confirming that the orbital moment is fully quenched. When the orbital moment is quenched, the lowest order nonzero contribution of MAE arises from quantum fluctuations of the orbital moments,<sup>[45]</sup> which is quadratic and vanishes in a perfect octahedral environment. However, the distorted S octahedral environment around the Cr<sup>3+</sup> yields a nonzero small single-ion anisotropy of 0.0058 meV, as revealed by inelastic neutron scattering,<sup>[32]</sup> which is the source of MAE in CrPS<sub>4</sub>.

To gain insight into the pressure-tuned MAE, we performed in situ XRD under different hydrostatic pressures. The pressure-dependent XRD patterns and related lattice parameters are shown in Figure 4. All peak positions gradually shift to higher angles due to the compression of unit cells induced by pressure. Refinements exhibit monotonic decreases of a, b, and c with increasing pressure. In contrast,  $\beta$  becomes larger and gradually deviates from 90°. No structural phase transition is observed under pressures up to 11.4 GPa, which is in agreement with previous Raman spectroscopy.<sup>[36]</sup> As discussed above, temperature and pressure have the same influence on MAE change. By comparing temperature- and pressure-dependent lattice parameters, b and b/a are found to both decrease with increasing temperature and pressure (Figure 4b and Figure S2, Supporting Information), indicating that the compression of bplays a major role. Considering the 1D chains of edge-sharing  $CrS_6$  octahedra running along the *b* axis, the SRT from  $AFM_{ac}$ to  $AFM_h$  is likely driven by the shrinkage of the 1D  $CrS_6$  chain along the *b* axis. The reduction of MAE is realized by distorting the octahedral environment around the Cr<sup>3+</sup> during the compression of the *b* axis. The SRT will occur when the sign of MAE changes at high temperatures or pressures. Experiments applying uniaxial tensile strain along the b axis with flexible substrates<sup>[35,46,47]</sup> are needed to further explore the interplay between 1D CrS<sub>6</sub> chains and the magnetic properties of CrPS<sub>4</sub>.

#### 2.5. Pressure-Tuned Exchange Couplings from DFT Calculations

Interlayer and intralayer exchange couplings, which determine the magnetic ground state of the CrPS<sub>4</sub>, are further investigated by DFT calculations based on the pressure-dependent lattice parameters obtained from XRD. The strength of the interlayer and intralayer exchange coupling can be calculated by the energy difference between different magnetic configurations, that is,  $E_{\rm FM}-E_{\rm A.AFM}$  and  $E_{\rm G.AFM}-E_{\rm A.AFM}$ , respectively. As shown in **Figure 5**, the interlayer exchange coupling increases linearly with pressure. Considering the molecular field approximation based on a semiclassical model,  $H_{\rm S}$  is proportional to the AFM exchange field.<sup>[48,49]</sup> Therefore,  $H_{\rm S}$  can be expressed by  $E_{\rm FM}-E_{\rm A.AFM}$ , increasing linearly with pressure (Figure 5b), which agrees well with the experimental results shown in Figure 3b. In contrast, pressure weakens intralayer FM exchange coupling with smaller  $E_{\rm G.AFM}-E_{\rm A.AFM}$  at higher





Figure 4. a) XRD patterns of CrPS<sub>4</sub> under different hydrostatic pressures. b) Pressure-dependent lattice parameters obtained from Rietveld refinements of XRD patterns.

pressures (Figure 5c). While enhanced interlayer AFM exchange coupling increases  $T_N$ , the decrease of  $T_N$  can only be attributed to the reduced intralayer exchange coupling. The intralayer exchange couplings are determined by the competition between direct and super-exchange interactions.<sup>[50]</sup> The intralayer superexchange interactions in CrPS<sub>4</sub> are mediated by the S anions between Cr ions, which are all ferromagnetic with Cr-S-Cr angles close to 90° according to the Goodenough-Kanamori rules.<sup>[51–53]</sup> In contrast, the direct exchange interactions of Cr  $t_{2g}$ states are AFM. Owing to the large Cr-Cr distance (Figure 5a) in CrPS<sub>4</sub>, super-exchange interactions are stronger than direct exchange interactions, resulting in intralayer FM exchange coupling. With increasing pressure, Cr-S-Cr bond angles stay almost unchanged whereas Cr-Cr distance decreases by about 1.1% and 1.5% for Cr1-Cr2 and Cr2-Cr3, respectively (Table S2, Supporting Information). As the direct exchange interactions are more sensitive to the distance ( $\approx 1/d_{Cr-Cr}^5$ ),<sup>[54,55]</sup> the enhancement of AFM direct exchange interactions will be

dominant under pressure, leading to the reduction of intralayer FM coupling. Therefore,  $T_{\rm N}$  is slightly suppressed upon increasing pressure due to such AFM/FM competition, which has also been observed in MnBi<sub>2</sub>Te<sub>4</sub> with the same A-type magnetic structure.<sup>[56]</sup> The undiminished  $T_{\rm C}$  in monolayer CrPS<sub>4</sub> without AFM interlayer coupling in recent theoretical calculations<sup>[34,57,58]</sup> also confirms the importance of intralayer FM coupling in determining the ordering temperature.

# 3. Conclusion

In summary, we have combined various magnetization measurements, pressure-dependent XRD, and first-principles calculations to study the pressure-dependent magnetism of  $CrPS_4$ . A first-order SRT with magnetic moments rotating from the *ac* plane to the *b* axis is observed on warming, which can be traced by the field-induced spin-flop transition. The



**Figure 5.** a) In-plane crystal structure of CrPS<sub>4</sub>. Black solid lines highlight the direct exchange interactions between adjacent Cr atoms. Red dashed lines highlight the super-exchange interactions between Cr ions meditated by the S anions. b) The energy difference of FM and A-type AFM magnetic structures at different pressures. c) The energy difference of G-type AFM and A-type AFM magnetic structures at different pressures. c)





spin reorientation temperature can be tuned by hydrostatic pressure, offering an effective way to control the Néel vector in CrPS<sub>4</sub>. Such tunable magnetic anisotropy between easyaxis and easy-plane anisotropy makes perfect platforms for producing and studying 2D Ising-type magnetism as well as the Berezinskii-Kosterlitz-Thouless (BKT) regime of 2D magnetism, which has recently been predicted in monolayer CrCl<sub>3</sub>.<sup>[59]</sup> In particular, CrPS<sub>4</sub> opens up a pathway to reveal the evolution of these major universality classes of magnetism with dimensionality by reducing thicknesses. In addition, interlayer AFM exchange coupling is enhanced by pressure, leading to the increase of the saturation field. However,  $T_{\rm N}$  is slightly suppressed, which is ascribed to the reduced intralayer FM exchange coupling. Our complementary study demonstrates the rare experimental realization and understanding of controlling spin orientation and metamagnetic transitions in a vdW antiferromagnet, which may shed light on the comprehension and tuning of magnetism in the 2D limit as well as stimulate 2D AFM spintronics in the future.

# 4. Experimental Section

*Crystal Growth*: CrPS<sub>4</sub> single crystals were synthesized through chemical vapor transport. Stoichiometric mixtures of Cr, P, and S powders with iodine as the transport agent were sealed in a quartz tube. The tube was then loaded into a two-zone furnace with a temperature gradient of 953–873 K and kept for 8 days. The crystals of CrPS<sub>4</sub> were formed on the cold side of the tube. The crystal was usually strip-like with the long side of the crystal being the crystallographic *b* axis.

Magnetization Measurements: Pressure-dependent magnetizations were measured using a Quantum Design Physical Properties Measurement System (PPMS-9T). The pressure cell used was a commercial clamp-type cell made of nonmagnetic BeCu alloy. Samples were made of single crystals stacked with the same crystallographic orientation to investigate the magnetic properties under magnetic fields parallel to crystallographic axes. Then, they were immersed in the pressure-transmitting medium (Daphne 7373 oil) with pure Pb as the manometer. The background signal from the cell was negligible because of the large mass of the samples.

*Neutron and* X-*Ray Diffraction*: Neutron powder diffraction measurement was performed on the ECHIDNA high-resolution powder diffractometer ( $\lambda = 2.4395(2)$  Å) at the Australian Nuclear Science and Technology Organisation (ANSTO).<sup>[60]</sup> Pressure dependence of XRD patterns was performed on a Bruker D8 VENTURE PHOTON II system (Mo K $\alpha$ ,  $\lambda = 0.71073$  Å). A diamond anvil cell was used for applying pressures with pressure estimated from the ruby fluorescence.<sup>[61]</sup> A standard CeO<sub>2</sub> sample was used for calibrating the diffraction data. All preliminary data reductions were performed using Dioptas program.<sup>[62]</sup> In the experiment below 1.5 GPa, the powder sample was pressed into a sheet and filled into the sample chamber with a pressure-transmitting medium (mineral oil). In the experiment under 11.4 GPa, the powder sample was directly filled into the sample chamber with no pressure medium.

Theoretical Calculations: The first-principles calculations were carried out based on the density functional theory in the Vienna ab initio simulation package (VASP),<sup>[63]</sup> applying the exchange-correlation description of GGA.<sup>[64]</sup> An on-site Hubbard term U = 2 eV was used for Cr-*d* orbitals.<sup>[36]</sup> The supercells containing 48 atoms were constructed, and the crystal was optimized until the forces put on ions were smaller than 10<sup>-3</sup> eV Å<sup>-1</sup>. The plane-wave cut-off energy was taken as 450 eV, and a 4×4×4 k-points sampling was set to ensure that the total energy difference in self-consistency was less than 10<sup>-5</sup> eV.

# **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

# Acknowledgements

Y.P. and Z.L. contributed equally to this work. This work was supported by the National Natural Science Foundation of China (Grant Nos. 11975035, 51731001, 11805006, 11675006, 22022101, 21875006, and 21771011), the National Key R&D Program of China (Grant Nos. 2017YFA0206303, 2017YFA0403701, and 2019YFA0708502), and High-Performance Computing Platform of Peking University.

# **Conflict of Interest**

The authors declare no conflict of interest.

# Data Availability Statement

Research data are not shared.

## Keywords

2D material, hydrostatic pressure, spin reorientation transition, van der Waals magnet

Received: August 31, 2021 Revised: October 21, 2021 Published online:

- [1] C. Gong, L. Li, Z. Li, H. Ji, A. Stern, Y. Xia, T. Cao, W. Bao, C. Wang, Y. Wang, Z. Q. Qiu, R. J. Cava, S. G. Louie, J. Xia, X. Zhang, *Nature* 2017, 546, 265.
- [2] B. Huang, G. Clark, E. Navarro-Moratalla, D. R. Klein, R. Cheng, K. L. Seyler, D. Zhong, E. Schmidgall, M. A. McGuire, D. H. Cobden, W. Yao, D. Xiao, P. Jarillo-Herrero, X. Xu, *Nature* 2017, 546, 270.
- [3] K. S. Burch, D. Mandrus, J. G. Park, Nature 2018, 563, 47.
- [4] C. Gong, X. Zhang, Science 2019, 363, eaav4450.
- [5] K. F. Mak, J. Shan, D. C. Ralph, Nat. Rev. Phys. 2019, 1, 646.
- [6] S. Jiang, L. Li, Z. Wang, K. F. Mak, J. Shan, Nat. Nanotechnol. 2018, 13, 549.
- [7] B. Huang, G. Clark, D. R. Klein, D. MacNeill, E. Navarro-Moratalla, K. L. Seyler, N. Wilson, M. A. McGuire, D. H. Cobden, D. Xiao, W. Yao, P. Jarillo-Herrero, X. Xu, *Nat. Nanotechnol.* **2018**, *13*, 544.
- [8] Y. Deng, Y. Yu, Y. Song, J. Zhang, N. Z. Wang, Z. Sun, Y. Yi, Y. Z. Wu, S. Wu, J. Zhu, J. Wang, X. H. Chen, Y. Zhang, *Nature* **2018**, *563*, 94.
- [9] S. Jiang, J. Shan, K. F. Mak, Nat. Mater. 2018, 7, 406.
- [10] H. Idzuchi, A. E. Llacsahuanga Allcca, X. C. Pan, K. Tanigaki, Y. P. Chen, Appl. Phys. Lett. 2019, 115, 232403.
- [11] L. Zhang, L. Song, H. Dai, J.-H. Yuan, M. Wang, X. Huang, L. Qiao, H. Cheng, X. Wang, W. Ren, X. Miao, L. Ye, K.-H. Xue, J.-B. Han, *Appl. Phys. Lett.* **2020**, *116*, 042402.
- [12] L. Zhang, X. Huang, H. Dai, M. Wang, H. Cheng, L. Tong, Z. Li, X. Han, X. Wang, L. Ye, J. Han, *Adv. Mater.* **2020**, *32*, 2002032.
- [13] T. Song, Z. Fei, M. Yankowitz, Z. Lin, Q. Jiang, K. Hwangbo, Q. Zhang, B. Sun, T. Taniguchi, K. Watanabe, M. A. McGuire,

## **ADVANCED** SCIENCE NEWS

www.advancedsciencenews.com

D. Graf, T. Cao, J. H. Chu, D. H. Cobden, C. R. Dean, D. Xiao, X. Xu, *Nat. Mater.* **2019**, *18*, 1298.

- [14] T. Li, S. Jiang, N. Sivadas, Z. Wang, Y. Xu, D. Weber, J. E. Goldberger, K. Watanabe, T. Taniguchi, C. J. Fennie, K. Fai Mak, J. Shan, *Nat. Mater.* 2019, *18*, 1303.
- [15] H. Wang, R. Xu, C. Liu, L. Wang, Z. Zhang, H. Su, S. Wang, Y. Zhao, Z. Liu, D. Yu, J. W. Mei, X. Zou, J. F. Dai, J. Phys. Chem. Lett. 2020, 11, 7313.
- [16] S. Mondal, M. Kannan, M. Das, L. Govindaraj, R. Singha, B. Satpati, S. Arumugam, P. Mandal, *Phys. Rev. B* 2019, *99*, 180407.
- [17] E. Gati, Y. Inagaki, T. Kong, R. J. Cava, Y. Furukawa, P. C. Canfield, S. L. Bud'ko, *Phys. Rev. B* **2019**, *100*, 094408.
- [18] J. Valenta, M. Kratochvílová, M. Míšek, K. Carva, J. Kaštil, P. Doležal, P. Opletal, P. Čermák, P. Proschek, K. Uhlířová, J. Prchal, M. J. Coak, S. Son, J. G. Park, V. Sechovský, *Phys. Rev. B* **2021**, *103*, 054424.
- [19] W. Cai, H. Sun, W. Xia, C. Wu, Y. Liu, H. Liu, Y. Gong, D.-X. Yao, Y. Guo, M. Wang, Phys. Rev. B 2020, 102, 144525.
- [20] Y. Sun, R. C. Xiao, G. T. Lin, R. R. Zhang, L. S. Ling, Z. W. Ma, X. Luo, W. J. Lu, Y. P. Sun, Z. G. Sheng, *Appl. Phys. Lett.* **2018**, *112*, 072409.
- [21] H. Yoshida, J. Chiba, T. Kaneko, Y. Fujimori, S. Abe, *Phys. B* **1997**, 237, 525.
- [22] D. J. O'Hara, Z. E. Brubaker, R. L. Stillwell, E. F. O'Bannon, A. A. Baker, D. Weber, L. B. B. Aji, J. E. Goldberger, R. K. Kawakami, R. J. Zieve, J. R. Jeffries, S. K. McCall, *Phys. Rev. B* **2020**, *102*, 054405.
- [23] S. Ding, Z. Liang, J. Yang, C. Yun, P. Zhang, Z. Li, M. Xue, Z. Liu, G. Tian, F. Liu, W. Wang, W. Yang, J. Yang, *Phys. Rev. B* **2021**, *103*, 094429.
- [24] Z. Lin, M. Lohmann, Z. A. Ali, C. Tang, J. Li, W. Xing, J. Zhong, S. Jia, W. Han, S. Coh, W. Beyermann, J. Shi, *Phys. Rev. Mater.* 2018, 2, 051004.
- [25] P. Gu, Q. Tan, Y. Wan, Z. Li, Y. Peng, J. Lai, J. Ma, X. Yao, S. Yang, K. Yuan, D. Sun, B. Peng, J. Zhang, Y. Ye, ACS Nano 2020, 14, 1003.
- [26] A. K. Budniak, N. A. Killilea, S. J. Zelewski, M. Sytnyk, Y. Kauffmann, Y. Amouyal, R. Kudrawiec, W. Heiss, E. Lifshitz, *Small* **2020**, *16*, 1905924.
- [27] M. J. Lee, S. Lee, S. Lee, K. Balamurugan, C. Yoon, J. T. Jang, S.-H. Kim, D.-H. Kwon, M. Kim, J.-P. Ahn, D. H. Kim, J.-G. Park, B. H. Park, NPG Asia Mater 2018, 10, 23.
- [28] J. Yang, S. Fang, Y. Peng, S. Liu, B. Wu, R. Quhe, S. Ding, C. Yang, J. Ma, B. Shi, L. Xu, X. Sun, G. Tian, C. Wang, J. Shi, J. Lu, J. Yang, *Phys. Rev. Appl.* **2021**, *16*, 024011.
- [29] S. Ding, Y. Peng, M. Xue, Z. Liu, Z. Liang, W. Yang, Y. Sun, J. Zhao, C. Wang, S. Liu, J. Han, J. Yang, J. Phys.: Condens. Matter 2020, 32, 405804.
- [30] S. Son, Y. J. Shin, K. Zhang, J. Shin, S. Lee, H. Idzuchi, M. J. Coak, H. Kim, J. Kim, J. H. Kim, M. Kim, D. Kim, P. Kim, J.-G. Park, 2D *Mater.* **2020**, *7*, 041005.
- [31] Y. Peng, S. Ding, M. Cheng, Q. Hu, J. Yang, F. Wang, M. Xue, Z. Liu, Z. Lin, M. Avdeev, Y. Hou, W. Yang, Y. Zheng, J. Yang, *Adv. Mater.* 2020, 32, 2001200.
- [32] S. Calder, A. V. Haglund, Y. Liu, D. M. Pajerowski, H. B. Cao, T. J. Williams, V. O. Garlea, D. Mandrus, *Phys. Rev. B* 2020, 102, 024408.

[33] J. Lee, T. Y. Ko, J. H. Kim, H. Bark, B. Kang, S. G. Jung, T. Park, Z. Lee, S. Ryu, C. Lee, ACS Nano 2017, 11, 10935.

FUNCTIONAL

www.afm-iournal.de

- [34] Q. Chen, Q. Ding, Y. Wang, Y. Xu, J. Wang, J. Phys. Chem. C 2020, 124, 12075.
- [35] Z. Ni, A. V. Haglund, H. Wang, B. Xu, C. Bernhard, D. G. Mandrus, X. Qian, E. J. Mele, C. L. Kane, L. Wu, *Nat. Nanotechnol.* **2021**, *16*, 782.
- [36] R. A. Susilo, B. G. Jang, J. Feng, Q. Du, Z. Yan, H. Dong, M. Yuan, C. Petrovic, J. H. Shim, D. Y. Kim, B. Chen, *npj Quantum Mater.* 2020, 5, 58.
- [37] S. L. Bud'ko, E. Gati, T. J. Slade, P. C. Canfield, Phys. Rev. B 2021, 103, 224407.
- [38] S. Kim, J. Lee, C. Lee, S. Ryu, J. Phys. Chem. C 2021, 125, 2691.
- [39] S. N. Neal, K. R. O'Neal, A. V. Haglund, D. G. Mandrus, H. A. Bechtel, G. L. Carr, K. Haule, D. Vanderbilt, H.-S. Kim, J. L. Musfeldt, 2D Mater. 2021, 8, 035020.
- [40] H. M. Rietveld, Acta Crystallogr. 1967, 22, 151.
- [41] J. Rodríguez-Carvajal, Phys. B 1993, 192, 55.
- [42] N. Kumar, Y. Soh, Y. Wang, Y. Xiong, Phys. Rev. B 2019, 100, 214420.
- [43] K. Heritage, B. Bryant, L. A. Fenner, A. S. Wills, G. Aeppli, Y. A. Soh, Adv. Funct. Mater. 2020, 30, 1909163.
- [44] S. Li, Z. Ye, X. Luo, G. Ye, H. H. Kim, B. Yang, S. Tian, C. Li, H. Lei, A. W. Tsen, K. Sun, R. He, L. Zhao, *Phys. Rev. X* **2020**, *10*, 011075.
- [45] J. L. Lado, J. Fernández-Rossier, 2D Mater. 2017, 4, 035002.
- [46] Y. Wang, C. Wang, S. J. Liang, Z. Ma, K. Xu, X. Liu, L. Zhang, A. S. Admasu, S. W. Cheong, L. Wang, M. Chen, Z. Liu, B. Cheng, W. Ji, F. Miao, Adv. Mater. 2020, 32, 2004533.
- [47] F. An, K. Qu, G. Zhong, Y. Dong, W. Ming, M. Zi, Z. Liu, Y. Wang, B. Qi, Z. Ding, J. Xu, Z. Luo, X. Gao, S. Xie, P. Gao, J. Li, *Adv. Funct. Mater.* **2020**, *30*, 2003495.
- [48] L. J. De Jongh, A. R. Miedema, Adv. Phys. 1974, 23, 1.
- [49] Y. Zhang, K. Deng, X. Zhang, M. Wang, Y. Wang, C. Liu, J.-W. Mei, S. Kumar, E. F. Schwier, K. Shimada, C. Chen, B. Shen, *Phys. Rev. B* 2020, 101, 205126.
- [50] M. Blei, J. L. Lado, Q. Song, D. Dey, O. Erten, V. Pardo, R. Comin, S. Tongay, A. S. Botana, *Appl. Phys. Rev.* 2021, *8*, 021301.
- [51] J. B. Goodenough, Phys. Rev. 1955, 100, 564.
- [52] J. B. Goodenough, J. Phys. Chem. Solids 1958, 6, 287.
- [53] J. Kanamori, J. Phys. Chem. Solids 1959, 10, 87.
- [54] A. N. Yaresko, Phys. Rev. B 2008, 77, 115106.
- [55] X. Li, J. Yang, J. Mater. Chem. C 2014, 2, 7071.
- [56] K. Y. Chen, B. S. Wang, J. Q. Yan, D. S. Parker, J. S. Zhou, Y. Uwatoko, J. G. Cheng, *Phys. Rev. Mater.* **2019**, *3*, 094201.
- [57] S. Lu, Q. Zhou, Y. Guo, Y. Zhang, Y. Wu, J. Wang, Adv. Mater. 2020, 32, 2002658.
- [58] J. Deng, J. Guo, H. Hosono, T. Ying, X. Chen, Phys. Rev. Mater. 2021, 5, 034005.
- [59] M. Dupont, Y. O. Kvashnin, M. Shiranzaei, J. Fransson, N. Laflorencie, A. Kantian, Phys. Rev. Lett. 2021, 127, 037204.
- [60] M. Avdeev, J. R. Hester, J. Appl. Crystallogr. 2018, 51, 1597.
- [61] H. K. Mao, J. Xu, P. M. Bell, J. Geophys. Res. 1986, 91, 4673.
- [62] C. Prescher, V. B. Prakapenka, High Pressure Res. 2015, 35, 223.
- [63] G. Kresse, J. Furthmüller, Phys. Rev. B 1996, 54, 11169.
- [64] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, A. P. Sutton, *Phys. Rev. B* **1998**, *57*, 1505.