Antiferromagnetic Phase Induced by Nitrogen Doping in 2D Cr$_2$S$_3$

Wenda Zhou $^{1,2}$, Mingyue Chen $^{1,2}$, Cailei Yuan $^{1,3,}$*, He Huang $^{1}$, Jingyan Zhang $^{1}$, Yanfei Wu $^{1}$, Xinqi Zheng $^{1}$, Jianxin Shen $^{1}$, Guyue Wang $^{1}$, Shouguo Wang $^{1,3,*}$ and Baogen Shen $^{1,3,}$*

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1. Introduction

As the scaling process of traditional ferromagnet-based spin device reaches the end, interest has been fueled in the development of antiferromagnetic spintronics [1–3]. In contrast to ferromagnetic materials, antiferromagnets have exhibited many distinct advantages for information manipulation and storage including robust antiferromagnetic order, absence of stray fields, and teraHertz switching frequencies [4–6]. Recently, accompanied by the discovery of two-dimensional (2D) van der Waals (vdW) magnetic materials such as the ferromagnetic Cr$_2$GeTe$_2$ insulator, ferromagnetic Fe$_2$GeTe$_2$ metal, and intralayer-ferromagnetic (interlayer-antiferromagnetic) CrI$_3$ semiconductor [7–9], the 2D antiferromagnet has attracted tremendous attention for exploring ultrathin antiferromagnetic spintronics devices with advanced functionalities [10–12]. Unfortunately, the practical application of 2D antiferromagnets is greatly limited by their air-instabilities, low ordering temperatures, and low-yield productions by exfoliation [9,13,14]. Therefore, air-stable atomically thin antiferromagnets with high-yield production are highly demanded. Except for exploring new air-stable intrinsic antiferromagnets, externally introducing antiferromagnetic ordering in existing 2D materials, such as structural regulation by virtue of the strong correlation between structural phase transition and magnetic phase transition, would be another promising strategy to modulate antiferromagnetism in the 2D limit and widen the magnetic materials systems.
In this paper, we firstly realized in situ nitrogen doping growth of 2D Cr$_3$Si nanoflakes successfully by a plasma-enhanced chemical vapor deposition (PECVD) system under N$_2$ atmosphere. X-ray diffraction (XRD) patterns at variable temperatures demonstrated that in situ nitrogen doping could induce a new phase (space group P$\overline{3}$1c), which was not observed in previously reported 2D Cr$_3$Si nanoflakes [15–18]. Theoretical calculations revealed the tendency of 2D Cr$_3$Si nanoflakes with space group P$\overline{3}$1c to exhibit an antiferromagnetic order. An anomalous peak located ~150 K was observed in the temperature dependence of magnetization (M–T curve), where a different loop shape compared with the P-Cr$_3$Si counterpart can be seen from M–H loops in nitrogen-doped Cr$_3$Si (N-Cr$_3$Si) nanoflakes. This attractive magnetic behavior can be attributed to the competition between ferromagnetic and antiferromagnetic phases in 2D N-Cr$_3$Si nanoflakes. Our work may provide a new approach to manipulate antiferromagnetism in atomically thin 2D magnets and greatly extend their applications of 2D magnets in valleytronics and spintronics.

2. Materials and Methods

The morphologies of Cr$_3$Si nanoflakes were examined using Atomic Force Microscopy (AFM, Park system XE7, Suwon, South Korea). Transmission electron microscope (TEM) characterization was carried out on a FEI Talos F200x microscope (Thermo Fisher, , San Francisco, California, USA) operated at 200 KV. The X-ray photoelectron spectroscopy (XPS) spectra were recorded employing Al Ka radiation from a XSAM800 spectrometer (Kratos, Manchester UK). The binding energy of samples was calibrated by C 1s peak. XRD patterns at variable temperatures were examined using Rigaku SmartLab (Tokyo, Japan). The magnetic properties were studied by a physical properties measurement system (PPMS, Quantum Design, San Diego, USA) with a vibrating sample magnetometer option (Ever Cool II).

3. Results and Discussion

Ultrathin N-Cr$_3$Si nanoflakes were successfully synthesized by a PECVD system. The growth configuration of N-Cr$_3$Si nanoflakes was depicted in Figure 1a. S powder (99.9%, Aladdin, China) precursor was placed in the center of low temperature zone. A powder mixed with CrCl$_3$ (99.9%, anhydrous, Alfa Aesar, Tewksbury, USA) and NaCl (99.5%, Aladdin, China) with a weight ratio of 10:1 was loaded into quartz boat in the middle of high temperature zone. The SiO$_2$/Si growth substrate (facing down) was slanted downward into the chute (~45°) of the quartz boat. The substrate tilted 45° with respect to the carrier gas flow may reduce the downstream depletion of precursors, which facilitates the nanoflake growth. The S and CrCl$_3$ powders were heated up concurrently to 240 and 760 °C at a N$_2$ flow rate of 60 sccm. A radio frequency plasma reactor (CHY, China, input power 100 W) was turned on to generate nitrogen plasma, as shown in Figure 1b. After 15 minutes, the plasma reactor was turned off and the PECVD system was cooled down naturally to room temperature under N$_2$ atmosphere. The growth conditions of pristine Cr$_3$Si (P-Cr$_3$Si) nanoflakes were kept as same as those of N-Cr$_3$Si nanoflakes, except without turning on the plasma reactor. Moreover, to control the level of nitrogen doping in Cr$_3$Si nanoflakes, by adjusting the input power (50 W) of plasma reactor, low-density nitrogen-doped Cr$_3$Si nanoflakes can be synthesized (see Figure S1 and S2, Supporting Information). However, with too high input power of the plasma reactor, Cr$_3$Si nanoflakes cannot be produced (see Figure S3, Supporting Information).

Figure 1c,d show optical microscope images of P-Cr$_3$Si and N-Cr$_3$Si nanoflakes grown on SiO$_2$/Si substrate, respectively, indicating a hexagonal shape with an average size of around 10 micrometers. These typical microscopic images confirmed that no obvious morphological change was observed in P-Cr$_3$Si nanoflakes after nitrogen plasma doping. Furthermore, the thickness of P-Cr$_3$Si and N-Cr$_3$Si nanoflakes on SiO$_2$/Si substrate was determined to be ~1.79 and ~1.68 nm, respectively, by AFM shown in Figure 1 e, f, h, and i.
Above results indicate that we have fulfilled the one-unit-cell thickness synthesis of Cr₂S₃ nanoflakes [18]. Moreover, a little thickness difference between P-Cr₂S₃ and N-Cr₂S₃ nanoflakes may be due to the smaller atomic size of N atoms compared with S atoms [19]. To further resolve the crystallinity and detailed lattice structure of the as-grown Cr₂S₃ nanoflakes, TEM characterization was performed. A typical high-resolution TEM (HRTEM) image of the P-Cr₂S₃ was shown in Figure 1g, and the interplanar spacing was measured to be 0.341 nm referring to the (120) plane, in good agreement with previous reports [17]. It is worth noting that there is a slight difference between the interplanar spacing of N-Cr₂S₃ (0.332 nm) and P-Cr₂S₃, which is mainly due to the incorporation of nitrogen into the one-unit-cell Cr₂S₃ nanoflakes, which is well supported by AFM results [19]. More importantly, no defects or grain boundaries were observed, revealing the uniformity and high quality characteristics of P-Cr₂S₃ and N-Cr₂S₃ samples. Such high-crystal-quality features are consistent with the fast Fourier transform (FFT) mode, with a single set of hexagonal diffraction spots (inset of Figures 1g and 3j). The AFM and TEM observations demonstrate that the nitrogen plasma doping has no significant effect on the surface morphology and crystallinity of one-unit-cell Cr₂S₃ nanoflakes.

The elemental composition and bonding state of the as-grown Cr₂S₃ nanoflakes were identified by XPS (Figure 2). As manifested in Figure 2a, two strong peaks at about 574.8
and 584.1 eV can be clearly observed in Cr 2p spectra of P-CrS₃ nanoflakes, which are ascribed to the doublet Cr 2pₓ/y and Cr 2pₓ/z, respectively. The peaks of S 2pₓ/y and S 2pₓ/z orbits corresponding to divalent sulfide ions (S²⁻) located at about 160.8 and 161.9 eV (Figure 2b). These featuring peaks are in good agreement with the reported results of Cr:S₃ nanoflakes synthesized by CVD method [15,17]. For N-CrS₃ nanoflakes shown in Figures 2d and 2e, the 2pₓ/y and 2pₓ/z states of Cr were confirmed by the peaks at about 575.2 and 584.4 eV, and the S 2pₓ/y and S 2pₓ/z states at about 161.1 and 162.3 eV, respectively. In comparison with P-CrS₃, the binding energies of Cr 2p and S 2p regions of N-CrS₃ exhibit a negative shift of about 0.3 eV in the XPS spectra. This negative shift indicates the Fermi level moves to the maximum of valence band, a characteristic feature of p-type doping caused by nitrogen doping, which is well consistent with previous reports [19]. For N 1s spectra, in contrast to the P-CrS₃, an emerging peak at 397.1 eV was observed in N-CrS₃, which was attributed to Cr-N bonds in CrN (397.0 eV) as reported previously [20], demonstrating the successful doping of nitrogen into P-CrS₃. Furthermore, no clear N peak was observed in the S 2p region, suggesting that there was no reaction between sulfur and nitrogen. Additionally, the atomic ratio of S:Cr is determined according to the equation

\[
\frac{C_{S}}{C_{Cr}} = \frac{(I_{S}/ASF_{S})}{(I_{Cr}/ASF_{Cr})}
\]

[19, 21], where ASFₜ and Iₜ are the atomic sensitivity factor and integrated areas of S 2pₓ/z, respectively. Similarly, ASFₜ and Iₜ are the atomic sensitivity factor and integrated areas of Cr 2pₓ/z, respectively. According to the XPS spectra of P-CrS₃ and N-CrS₃, the atomic ratio of S:Cr is estimated to be 1.52:1 and 1.33:1, respectively, further indicating the replacement of sulfur atoms by nitrogen atoms in P-CrS₃.

![Figure 2](image-url)

**Figure 2.** XPS spectra of (a) and (d) Cr 2p, (b) and (e) S 2p, (c) and (f) N 1s of P-CrS₃ and N-CrS₃ nanoflakes, respectively.

To clarify the crystal structure of as-grown CrS₃ nanoflakes, XRD patterns at various temperatures were collected. As shown in Figure 3a (top), the XRD peaks of P-CrS₃ at 300 K can be well indexed by the standard rhombohedral CrS₃ (PDF #10-0340) with space group (R₃̅₃̅) [16]. Interestingly, as manifested in Figure 3a (bottom), the XRD peaks of N-CrS₃ at 300 K can be indexed by two sets of standard rhombohedral CrS₃ structures including PDF #10-0340 and PDF #11-0007, indicating the coexistence of space group R₃̅ and space group P31c in N-CrS₃ nanoflakes. Those results demonstrate that in situ nitrogen doping could induce a structural phase transition in 2D CrS₃ nanoflakes. Moreover, there is no obvious change in XRD patterns of P-CrS₃ and N-CrS₃ with the temperature variation (from 123 K to 300 K), respectively.

Based on XRD results, theoretical calculations were performed to explore the magnetic properties of the new phase (space group P31c) of N-CrS₃. All the spin theoretical
simulations in this work were conducted on a Vienna ab initio Simulation Package (VASP) [22]. The electron–electron exchange and correlation interactions were evaluated by the generalized gradient approximation (GGA) with the Perdew–Burke–Emzerhof (PBE) functional form, while the core-electron (valence electron) interactions were represented by implanted the projector augmented-wave (PAW) methods [23]. Plane-Wave basis function was set with a kinetic cut-off energy of 550 eV. Relaxing the force below 0.02 eV/Å was used to optimize the ground-state atomic geometries, and the convergence criteria for energy set as $1.0 \times 10^{-5}$ eV/cell. By using a Monkhorst–Pack meshes with $4 \times 4 \times 2$, the Brillouin zone was sampled. Electronic structures, total energy of models, and stress or force relaxations were calculated by the Gaussian method. In order to better depict the intermolecular interaction, DFT-D3 method of Grimme was employed to describe van der Waal (vdw) interactions [24]. The equation is $E_{\text{bonding energy}} = (E_{\text{total}} - N_{\text{CrS}} - N_{\text{Si}})/(N_{\text{CrS}} + N_{\text{Si}})$.

In this work, the bonding energy was calculated to evaluate the stability of our structure with different magnetic configurations. Various possible magnetic configurations of N-CrS$_3$ with space group P31c were investigated, including ferromagnetic (Figure 3b) and two types of antiferromagnetic configurations, as shown in Figures 3c and 3d. The Antiferromagnetic-1 ($-0.83$ eV) would be the most stable configuration due to its lowest bonding energy, compared to Ferromagnetic ($-0.80$ eV) and Antiferromagnetic-2 ($-0.81$ eV). Thus, our calculations indicate the tendency of N-Cr$_2$S$_3$ with space group P31c to exhibit antiferromagnetic order. Based on XRD data and theoretical calculations, a new phase with an antiferromagnetic order could be induced in 2D CrS$_3$ by nitrogen doping.

**Figure 3.** (a) XRD patterns at variable temperatures for P-CrS$_3$ (top) and N-CrS$_3$ (bottom) nanoflakes. Diffraction peaks marked with stars in N-CrS$_3$ indicate rhombohedral CrS$_3$ (PDF #10-0340) with space group (R3) still exist in N-CrS$_3$. (b) Schematic structure of N-CrS$_3$ with ferromagnetic configuration. (c) and (d) Schematic structures of N-CrS$_3$ with two possible antiferromagnetic configurations. Orange and green arrows denote opposite spin orientations.
In order to check the prediction by theoretical calculations, magnetic properties of as-synthesized Cr$_2$S$_3$ nanoflakes were studied in a PPMS with a vibrating sample magnetometer under a parallel magnetic field due to its in-plane magnetic easy axis [17,18]. As shown in Figure 4a, zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves exhibit that P-Cr$_2$S$_3$ nanoflakes have an obvious ferromagnetic behavior with the Curie temperature TC $\sim$ 120 K and a maximum magnetic susceptibility at $\sim$ 73 K. The upturn of magnetization below 20 K maybe attribute to the interaction of magnetic sublattices [25]. As shown in Figure 4b, obvious hysteresis can be found in M–H curves of P-Cr$_2$S$_3$ nanoflakes with the temperature below 120 K (T$_C$), and the hysteresis vanished when the temperature was increased above T$_C$, indicating the emergence of paramagnetic property. These results are well consistent with the previous results for CVD-derived Cr$_2$S$_3$ nanoflakes [17,18]. For N-Cr$_2$S$_3$ nanoflakes, an anomalous peak at $\sim$150 K can be clearly observed in M–T curves (see Figure 4c). It is deduced that this anomaly of temperature can be attributed to the emerging structural phase (space group P$\bar{3}$1c) of N-Cr$_2$S$_3$ nanoflakes. Moreover, the irreversibility behavior observed in M–T curves of N-Cr$_2$S$_3$ may come from domain wall pinning effect, spin reorientation phase transition or glassy state [26]. As manifested in Figure 4d, the M–H curve of N-Cr$_2$S$_3$ nanoflakes at $\sim$ 73 K exhibits different loop shape compared with the P-Cr$_2$S$_3$ counterpart, with magnetic hysteresis expanding under higher applied field while pinching under lower applied field, which indicates the coexistence of ferromagnetic and canted antiferromagnetic ordering [27]. Additionally, low-density nitrogen doping in Cr$_2$S$_3$ nanoflakes cannot trigger the new phase (proved by XRD results, Figure S2), which exhibit similar magnetic behaviors with P-Cr$_2$S$_3$ nanoflakes (Figure S4). Therefore, magnetic ground states with an increase of temperature in N-Cr$_2$S$_3$ can be defined as coexistence of ferromagnetic and antiferromagnetic (below $\sim$ 120 K), antiferromagnetic (120–150 K), and paramagnetic (150–300 K). These attractive magnetic behaviors prove that antiferromagnetic phase in 2D Cr$_2$S$_3$ nanoflakes can be triggered by an in situ nitrogen doping-induced new phase (space group P$\bar{3}$1c), which is in line with our theoretical calculations.

Figure 4. (a) and (c) Temperature—dependent magnetization, (b) and (d) magnetic hysteresis loop measurements at different temperatures for P-Cr$_2$S$_3$ and N-Cr$_2$S$_3$ nanoflakes, respectively. The inset of (b) and (d) are the corresponding magnified images of M–H curve at 150 K.
4. Conclusions

In summary, based on the large-scale synthesis of air-stable 2D ferromagnetic Cr$_2$S$_3$ nanoflakes, we successfully realized in situ nitrogen doping by PECVD. Variable temperature XRD results demonstrated that in situ nitrogen doping could induce a new phase in 2D N-Cr$_2$S$_3$ nanoflakes. Theoretical calculations and magnetic measurements prove the achievement of antiferromagnetic ordering in Cr$_2$S$_3$ by nitrogen doping induced a new phase (space group P$ar{3}$1c). Our work opens up a new route for the manipulation of antiferromagnetism in the 2D limit and widens the magnetic materials systems.

Supplementary Materials: The following supporting information can be downloaded at: www.mdpi.com/article/10.3390/ma15051716/s1, Figure S1 XPS spectra of (a) Cr 2p, (b) S 2p, (c) N 1s of low-density nitrogen doped Cr$_2$S$_3$ nanoflakes.; Figure S2 XRD pattern for low-density nitrogen doped Cr$_2$S$_3$ nanoflakes.; Figure S3 Optical microscope image of N-Cr$_2$S$_3$ nanoflakes with high input power of plasma reactor (120 W).; Figure S4 (a) M-T and (b) M-H curves at different temperatures for low-density nitrogen doped Cr$_2$S$_3$ nanoflakes, respectively. The inset of (b) is the corresponding magnified image of M-H curve at 150 K.

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