Electronic band splittings across the antiferromagnetic phase transition of exfoliated MnPS$_3$ probed by µ-ARPES

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Exfoliated magnetic 2D materials provide access to a versatile tuning of magnetization properties, e.g., by gating and by proximity-induced exchange interactions with other types of 2D materials. However, the electronic band structure after exfoliation has not been probed for such materials yet, mostly due to their photochemical sensitivity. Here, we provide micron-scale angle-resolved photoelectron spectroscopy of the exfoliated intralayer antiferromagnet MnPS$_3$ above and below the Néel temperature in comparison with density functional theory calculations. We demonstrate a significant splitting of parts of the Mn 3d$_z$-bands induced by the antiferromagnetic ordering. Related changes of adjacent S 3p-bands indicate a competing contribution of a ferromagnetic superexchange. The novel access to the electronic band structure is likely transferable to other MPX$_3$ materials (M: transition metal, P: phosphorus, X: chalcogenide) that provide a multitude of antiferromagnetic arrangements.

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I. INTRODUCTION

The first successful exfoliation of CrI$_3$ [1], Cr$_2$Ge$_2$Te$_6$ [2] and other layered magnetic materials [3-7] added ferromagnets to the toolbox of exfoliation-based heterostructures [8]. This enabled several magnetoelectric effects such as deliberate gate tuning of the spin-flop transition [9, 10] as well as from antiferro- to ferrimagnetism [11] or from ferro- to paramagnetism [12]. Moreover, the exchange coupling of the ferromagnet could be successfully transferred via proximity to neighboring 2D materials [13] such as graphene [14-16], WSe$_2$ [17], the topological insulator WTe$_2$ [18] and the superconductor NbSe$_2$ [19-21]. Recently, also twisted layers of 2D antiferromagnets have been prepared exhibiting distinct magnetic properties from their regularly stacked counterparts [22-24].

Nevertheless, the basic electronic band structure of exfoliated 2D magnetic materials has never been probed. This is most likely due to the extreme photochemical sensitivity of most of the flakes [25]. Previous angularly resolved photoelectron spectroscopy (ARPES) data have only been obtained on in-situ cleaved bulk materials [20-24] or in-situ after molecular beam epitaxy [25]. For this reason, the interesting class of intralayer antiferromagnetic insulators XPS$_3$ (X = Mn, Fe, Co, Ni) [36-38] that feature rather strong magnetoelastic [39, 40], magneto-electric [41, 45] and magnetically induced electron-phonon [40] couplings have not been examined, since their large band gaps prohibit ARPES of cleaved crystals below the Néel temperature [47].

Here, we investigate exfoliated MnPS$_3$, an intralayer antiferromagnet (AFM) with a honeycomb-type Néel order of Mn$^{2+}$ ions [48] and easy axis tilted by 8° from the out-of-plane direction [41] (Fig. 1a). The intralayer AFM order persists down to a monolayer [39, 49-51]. The interlayer interaction is weakly ferromagnetic [52] breaking inversion symmetry and, hence, enabling magnetoelastic (ME) coupling [43]. A sizable linear magnetoelectric coupling has indeed been found by neutron diffraction [41] and second harmonic generation [43, 53] enabling the imaging of AFM domains (≈100 µm) [54] and the determination of the critical exponent $\beta = 0.37$ [43]. The Néel temperature of the bulk material is $T_N = 78$ K [55]. Close
to the Néel temperature, the anisotropy likely changes to an in-plane XY-type AFM order \[56\]. The optical band gap of MnPS$_3$ is 2.94 eV at $T = 5$ K \[57\], \[58\] with additional localized inter-d-level transitions at lower excitation energies \[57\]. Weak interlayer van-der-Waals binding with energy density 0.25 J/m$^2$ (graphene: 0.38 J/m$^2$) enables exfoliation \[58\].

Here, we employ such exfoliation down to single layers onto a Au/Ti-covered Si/SiO$_2$ substrate to probe the insulating material by $\mu$-ARPES above and below $T_N$. We find a pronounced splitting of an occupied 3$d_{z^2}$ type Mn band for thicker flakes as identified by comparison with density functional theory (DFT+$U$) calculations. The splitting exhibits a dispersion along the $k_z$ direction. An additional sulfur band of 3$p_z$ type character also changes across $T_N$ witnessing the influence of superexchange. The band structure below $T_N$ is only slightly different for 4 layers, but strongly different for a single layer. By comparison with DFT+$U$ calculations, we conjecture that this difference is due to strain that appears on the relatively rough surface.

II. EXPERIMENTAL DETAILS

MnPS$_3$ (manganese phosphorus trisulfide) was synthesized in a quartz tube via vapor transport synthesis (VTS) – without any transporting agent, i.e. no iodine was used \[59\] \[60\]. One gram of an elements mixture of metal manganese powder (Alfa Aesar), red phosphorus (Riedel-de Haën), and sulfur (Sigma-Aldrich) with atomic ratio Mn : P : S = 1 : 1 : 3 was grounded in an agate mortar. The mixture was moved into a quartz ampoule, evacuated to the framework of the Density Functional Theory (DFT) implemented in VASP software \[62\] \[63\]. The PAW pseudopotentials \[64\] \[65\] and Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional are used \[66\]. The kinetic energy cutoff for the plane-wave expansion is set to 500 $\text{eV}$. A $\text{k}$-mesh of $10 \times 10 \times 10$ is taken to sample an irreducible first Brillouin zone of the primitive bulk cell (primitive and rectangular planar cell of a monolayer, respectively). We employ the GGA+$U$ formalism proposed by Dudarev \[67\] to properly account for on-site Coulomb repulsion between 3$d$ electrons of Mn ions, by using effective Hubbard $U$ parameters. The lattice parameters and position of the atoms are fully optimized within this approach assuming the magnetic state of AFM-Néel type. The convergence criteria for the energy and force are set to $10^{-5}$ eV and $10^{-3}$ eV/Å, respectively. In the case of the monolayer, we added 20 Å of vacuum to avoid the spurious interaction between periodic replicas. The non-local nature of dispersive forces, crucial for layered materials \[68\] \[70\], are accounted for

The bandstructure calculations are performed within the workfunction of the Density Functional Theory (DFT) implemented in VASP software \[62\] \[63\]. The PAW pseudopotentials \[64\] \[65\] and Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional are used \[66\]. The kinetic energy cutoff for the plane-wave expansion is set to 500 eV. A $\text{k}$-mesh of $10 \times 10 \times 9$ ($10 \times 10 \times 2$ and $10 \times 6 \times 2$) is taken to sample an irreducible first Brillouin zone of the primitive bulk cell (primitive and rectangular planar cell of a monolayer, respectively). We employ the GGA+$U$ formalism proposed by Dudarev \[67\] to properly account for on-site Coulomb repulsion between 3$d$ electrons of Mn ions, by using effective Hubbard $U$ parameters. The lattice parameters and position of the atoms are fully optimized within this approach assuming the magnetic state of AFM-Néel type. The convergence criteria for the energy and force are set to $10^{-5}$ eV and $10^{-3}$ eV/Å, respectively. In the case of the monolayer, we added 20 Å of vacuum to avoid the spurious interaction between periodic replicas. The non-local nature of dispersive forces, crucial for layered materials \[68\] \[70\], are accounted for
Figure 1. (a) Crystal and magnetic structure model of MnPS₃ with Mn magnetic moments depicted as arrows. Left: top view, middle: side view of two layers, right: perspective view with Mn atoms only. (b) Optical microscope image of a thick flake (violet) with several few-layer flakes at the upper left rim (darker grey areas). (c) Tapping-mode atomic force microscopy (AFMi) image of the highlighted area in b with layer thicknesses marked. (d) Optical contrast of flakes with respect to the substrate as a function of flake thickness. The green and red color filters of a Leica DFC 450 camera are used for the symbols of respective colors. The layer thicknesses are determined by AFMi. Error bars are smaller than the symbol size. (e–f) Curvature plots derived from ARPES data for exfoliated 62-layer thick MnPS₃ measured at the temperatures marked, $h\nu = 50$ eV. The Néel temperature is $T_N = 78$ K.

within semi-empirical Grimme approach [71] with a D3 parametrization [72].

IV. RESULTS

Figure 1a displays the crystal and magnetic structure of MnPS₃, the visualization was produced by using the VESTA program [74]. The Mn atoms exhibit a honeycomb lattice with a P dumbbell in the honeycomb center. Layers of S atoms on both sides terminate the single layers that are stacked by van-der-Waals forces [58]. The S atoms bridge adjacent Mn atoms, hence they contribute to their exchange path [74]. The Mn atoms show a Néel type antiferromagnetic order coupled weakly ferromagnetically between the layers. Exfoliation typically leads to relatively thick flakes with thin layers down to a monolayer at their rims (Fig. 1a-c) [58]. We found that direct exfoliation after plasma ashing of the Au substrate provides a higher yield of thin areas, e. g. an area with a thickness of two layers and a size of $\sim 150 \times 300 \mu$m² (Supplementary Information). The thickness of the layers can be determined by optical contrast [54, 75] after selecting the green or red band of a standard camera (Fig. 1d) and calibrating the respective layer thicknesses by AFMi (Fig. 1c). The existence of multiple areas of different thickness at the same flake (Fig. 1b-c) is advantageous for its investigation by $\mu$-ARPES with a possible focus down to 5 µm [76]. Figure 1e–g shows the measured band structure of a thicker sample area along the $\Gamma\bar{M}\Gamma$ direction for three different temperatures below and above $T_N = 78$ K at the identical spot (not displayed in Fig. 1b–c). The bands at $E - E_F = -3$ eV to $-5.5$ eV exhibit additional substructure below $T_N$.

Most strikingly, there is a pronounced splitting of the lower energy band around $\bar{\Gamma}$ below $T_N$, but not above $T_N$. 

This also changes the propagation of the corresponding upper energy branch showing a maximum at $\bar{\Gamma}$ below $T_N$. Moreover, two branches declining with $|k_\parallel|$ get apparent at $E - E_F = -3.6 \text{eV}$ below $T_N$ (ARPES at additional $T$ in Supplementary Information). Generally, the change of the upper band at $E - E_F = -3 \text{eV}$ to $-3.8 \text{eV}$ is more subtle. There is also a small upwards shift of the most pronounced feature around $\bar{\Gamma}$ below $T_N$. These band changes are reproduced in several cool-downs for two thicker flakes consisting of 62 layers and 13 layers, respectively.

Figure 2 shows the measured band structure along the K$\bar{\Gamma}$K direction (Fig. 2a,b) as well as ($k_x$, $k_y$) cuts at selected energies, both above and below $T_N$ (Fig. 2c–g). Moreover, the band energies of the lowest energy band belonging to b are displayed for the sake of comparison (Fig. 2h). The hexagonal surface Brillouin zone gets apparent by the symmetry that is found in all the ($k_x$, $k_y$) cuts. This symmetry does not change below $T_N$ indicating the absence of back folding and, hence, corroborating the Neél type antiferromagnetic arrangement [18].

Fig. 1f. (d) Same calculation as b, but displaying only the s, $p_z$ and $d_{xz}$ contributions as required by the photon beam geometry according to the analysis of matrix elements described in [17] (Supplementary Information).
More importantly, a transition from a ring like \((k_z, k_y)\) distribution with a local minimum in intensity at \(\Gamma\) to a structure with a local maximum at \(\Gamma\) is observed at \(E - E_F = -4.5 \pm 0.05\) eV (Fig. 2a–f). This confirms the pronounced changes of this band as observed in Fig. 1g and Fig. 2a–b. Again, the changes of the band at slightly higher energy are more subtle (Fig. 2a–d), i.e., partly, it is hard to distinguish, if only the intensity gets significantly more pronounced below \(T_N\) or if the band propagation changes (Supplementary Information).

Figure 3 shows the comparison of the ARPES data below \(T_N\) with DFT+U calculations of the antiferromagnetic Néel structure (a, c). We used the energy of the rather parabolic sulfur band of s-type character at about \(E - E_F = -7.5\) eV to calibrate \(U = 1.2\) eV, since it favorably acts as a rather direct \(U\) ruler (Supplementary Information). The complete DFT band structure with marked orbital contributions is plotted in Fig. 3b. Since matrix elements in our experimental geometry (p-polarized light with incident photon beam at 65° relative to the sample normal, Fig. 3b) strongly select s-type, \(p_z\)-type and \(d_{z^2}\)-type states (Supplementary Information), we replot the DFT results with only these contributions in Fig. 3b. This selection provides a very good agreement to the experimental data and, in addition, identifies the two bands with the strongest splittings below \(T_N\) as dominated by Mn \(d_{z^2}\) orbitals (lower energy) and S \(p_z\) orbitals (upper energy), respectively.

Figure 4 shows the \(k_z\) dispersion of the bands along the \(\overline{KK}\) direction as probed by varying \(h\nu\). We used the optimization of the agreement between experimental and DFT data to tentatively determine \(k_z = 0.05\) Å for \(h\nu = 50\) eV. Then, we propagate to higher \(k_z\) by the accordingly deduced inner potential \(V_0 = 18.6\) eV (Supplementary Information). The \(k_z\) dispersion indeed changes with \(k_z\). This includes the size of the band splitting around \(\Gamma\) of the Mn \(d_{z^2}\) band, which increases between \(h\nu = 50\) eV and \(h\nu = 64\) eV (Brillouin zone boundary) as well as an upwards shift of the upper part of the Mn \(3d_{z^2}\) band (see red lines in Fig. 4b–f).

The sample quality prior to and after the ARPES measurements is probed by XPS and AFM. Figure 5a shows an overview XPS scan recorded after ARPES measurements with labeled peaks revealing the presence of O and C contamination. By comparing with the S 2p peak using peak calibration data [78, 79], we determined that the oxygen density is about 8% of the sulfur density only. The relative peak heights are the same in XPS data recorded before the ARPES measurements. This excludes that the O and C contamination originates from ARPES. Since the electron extraction area is significantly less focused for XPS (~ 15 µm), it could be that the C and O peaks
Figure 5. (a) XPS data of 13 layer MnPS₃ area recorded after extensive ARPES measurements on that area, $h\nu = 700$ eV. Peaks are labeled by chemical element and atomic orbital. A comparison of the O 1s and the S 2p peak reveals that the oxygen density is less than 8 % of the sulfur density. (b)-(d) Higher resolution XPS data of the studied 62 layer MnPS₃ area of Fig. 4(b) for the Mn 3p, S 2p and P 2p peak, respectively. Fit lines are displayed in red. They consist of the labeled dashed Lorentzian peaks and the blue Shirley–Proctor–Sherwood background. Peaks labeled blue belong to intact MnPS₃. Peaks labeled black are likely caused by remaining intercalated pure sulfur and phosphorus from the crystal growth. (e,f) A posteriori AFMi image of the area of 62 layer MnPS₃ displayed at two different scales. The area exposed to the photon beam during the ARPES measurements of Fig. 4 is marked. No beam damage is apparent.

are caused by remaining glue on the surface that is partially also observed by AFM. In order to reveal possible oxidation of the Mn, S and P of MnPS₃, we fitted the corresponding peaks (Fig. 5b-d). For the S 2p and P 2p peak, we can exclude oxidation that would appear at larger binding energy ($164 - 170$ eV for S, $> 134$ eV for P) [80, 81]. In contrast, we observe contributions at lower binding energies that we attribute to pure S and P likely intercalated between the layers during the crystal growth. The single Mn peak (Fig. 5b) can be either caused by an S or O induced charge transfer. Hence, we cannot exclude partial oxidation of the Mn. However, even if, this would be the case, it would only affect 8 % of the S bonds (Supplementary Information). Notice that replacement of S by O has been observed in electron microscopy, but there it is induced by the high energy electrons that kick off the S atoms prior to oxidation [82, 83].

The AFMi data of the spot area of the photon beam recorded after ARPES (Fig. 5a-f) exhibit the same flatness of the surfaces as prior to ARPES.

Eventually, we also probed thinner layers (Fig. 6a-d), albeit the DFT+U calculations did not imply strong changes in the band structure (Supplementary Information). Nevertheless, we found that the energy splittings are less pronounced for a thickness of 4 layers (Fig. 6e) and, for the probed monolayer, the band structure changes significantly, appearing much more blurry than for thicker layers (Fig. 6f). This blurring is most likely related to the corrugation of the thinnest MnPS₃ areas on top of the relatively rough Au/SiO₂ substrate (Fig. 6g). The substrate roughness ($\sigma = 0.33$ nm) is indeed fully transferred to the MnPS₃ monolayer ($\sigma = 0.43$ nm, Fig. 6h) and still significant for the four-layer areas ($\sigma = 0.19$ nm, Fig. 6i). In contrast, thick MnPS₃ as probed in Figs. 4 is rather flat (Fig. 6j, $\sigma = 0.14$ nm).

A possible explanation for the blurred ARPES data could be a local variation of the $\Gamma$ point direction along the surface. To check this possibility, we used the spectrum of the thick film and overlapped correspondingly tilted spectra according to the measured angular distribution of the surface normal of the one-layer area (Fig. 6b) (Supplementary Information). However, this effect barely changes the measured band structure. Another possibility is the relatively strong strain in the outer sulfur layers due to the strong bending of the thin films while adhering to the substrate. The measured monolayer roughness implies a strain distribution with standard deviation $\sigma = 2.0$ % (Fig. 6i). The four-layer film is still strained with a distribution of $\sigma = 0.9$ %, if one assumes the absence of mutual slips between the layers (Supplementary Information). DFT+U indeed reveals that isotropic tensile strain of up to 2.5 % shifts the bands downwards by 200–300 meV (Fig. 6j). This explains the blurring of the spectroscopic data at lower thicknesses qualitatively, albeit the calculations can not be directly compared to the experimental data of the monolayer, since they are recorded above $T_N$. The strong influence of strain on the band structure is interesting in itself, but also calls for experiments on smoother substrates.
We have demonstrated the first successful ARPES study on ultrathin magnetic 2D materials using the rather new technology ARUPS. We found a pronounced splitting of a Mn 3d band while cooling below the Néel temperature and also exhibit this for different isotropic tensile strains as marked, resulting in rms roughnesses: (f) Tapping mode AFM images of MnPS film (Supplementary Information). A Gaussian fit (red line) with σ = 2% is added. The large variety of similar MPX materials (M = Ni, Fe, Co, Zn: X = S, Se) as well as corresponding alloys open a vast field for studying magnetic and magnetoelectric structure properties in a critical temperature range. The large variety of thin films (1 layer, 4 layers) we find that the band structure appears blurred also exhibit this for different isotropic tensile strains as marked, resulting in rms roughnesses: (f) Tapping mode AFM images of the Mn substrate G = 3.3. (g) Gaussian fit (red line) with σ = 2% is added.

V. SUMMARY

The large variety of similar MPX materials (M = Ni, Fe, Co, Zn: X = S, Se) as well as corresponding alloys open a vast field for studying magnetic and magnetoelectric structure properties in a critical temperature range. The large variety of thin films (1 layer, 4 layers) we find that the band structure appears blurred also exhibit this for different isotropic tensile strains as marked, resulting in rms roughnesses: (f) Tapping mode AFM images of the Mn substrate G = 3.3. (g) Gaussian fit (red line) with σ = 2% is added.

Figure 6. (a) Same as Fig. 1f. (b) Overlap of multiple spectra as in subfigure a with a Gaussian distribution of sample normals. (c) ARPES curvature intensity along the Γ-M direction for different isotropic tensile strains as marked, resulting in rms roughnesses: (f) Tapping mode AFM images of the Mn substrate G = 3.3. (g) Gaussian fit (red line) with σ = 2% is added. The large variety of thin films (1 layer, 4 layers) we find that the band structure appears blurred also exhibit this for different isotropic tensile strains as marked, resulting in rms roughnesses: (f) Tapping mode AFM images of the Mn substrate G = 3.3. (g) Gaussian fit (red line) with σ = 2% is added.
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