

Magneto-optical anisotropies of two-dimensional antiferromagnetic MPX_3 from first principles

Miłosz Rybak¹, Paulo E. Faria Junior², Tomasz Woźniak³, Paweł Scharoch¹,
Jaroslav Fabian² and Magdalena Birowska^{3,*}

¹*Department of Semiconductor Materials Engineering Faculty of Fundamental Problems of Technology,
Wrocław University of Science and Technology Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland*

²*Institute of Theoretical Physics, University of Regensburg, 93040 Regensburg, Germany*

³*Institute of Theoretical Physics, Faculty of Physics, University of Warsaw, Pasteura 5, 02-093 Warsaw, Poland*



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Here we systematically investigate the impact of the spin direction on the electronic and optical properties of transition metal phosphorus trichalcogenides (MPX_3 , $M = \text{Mn, Ni, Fe}$; $X = \text{S, Se}$) exhibiting various antiferromagnetic arrangements within the 2D limit. Our analysis based on the density functional theory and versatile formalism of Bethe-Salpeter equation reveals larger exciton binding energies for MPS_3 (up to 1.1 eV in air) than $MPSe_3$ (up to 0.8 eV in air), exceeding the values of transition metal dichalcogenides (TMDs). For the $(\text{Mn,Fe})PX_3$, we determine the optically active band-edge transitions, revealing that they are sensitive to in-plane magnetic order, irrespective of the type of chalcogen atom. We predict the anisotropic effective masses and the type of linear polarization as important fingerprints for sensing the type of magnetic AFM arrangements. Furthermore, we identify the spin-orientation-dependent features such as the valley splitting, the effective mass of holes, and the exciton binding energy. In particular, we demonstrate that for MnPX_3 ($X = \text{S, Se}$), a pair of nonequivalent $K+$ and $K-$ points exists yielding the valley splittings that strongly depend on the direction of AFM aligned spins. Notably, for the out-of-plane direction of spins, two distinct peaks are expected to be visible below the absorption onset, whereas one peak should emerge for the in-plane configuration of spins. These spin-dependent features provide an insight into spin flop transitions of 2D materials. Finally, we propose a strategy for how the spin valley polarization can be realized in 2D AFM within a honeycomb lattice.

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I. INTRODUCTION

The subtle interplay between the spin, charge, orbital, and lattice degrees of freedom driven by the electron correlation is one of the key aspects in condensed matter physics behind novel electronic phases of matter and intriguing physical phenomena. In particular, the electronic properties can be modified whenever the spin direction is altered, as spin-orbit coupling (SOC) depends on the spin direction. For instance, spin-valley coupling serves as the fundamental mechanism in optically controlled valley polarization [1], spin-Hall and valley-Hall effects [2]. Contrast to most of the findings in non-magnetic 2D materials [3–5], where pseudospins are involved, 2D magnets exhibit active carrier spins, enabling studies of magnetism in reduced dimensions [6].

Unlike ferromagnets (FMs), the antiferromagnets (AFMs) are commonly found in nature and they are permitted in each magnetic point group, however they are less utilized than FMs [7]. Currently, AFM materials are considered as promising

candidates for future spintronic applications, due to unique properties including insensitivity to external magnetic fields, lack of stray fields, and ultrafast spin dynamics in the terahertz regime [8]. The spontaneously long-range ordered of microscopic magnetic moments, resulting in zero net magnetization, which makes the AFMs insensitive to external magnetic fields. Thus a control of AFM state requires very high magnetic fields and demands unconventional means of detection [7].

Many properties such as optical, electronic, and vibrational, rely on the magnetic ordering [9–11], as well as magnetic moment orientation [12]. In particular, a giant impact of the spin direction on the band structure, have been recently demonstrated for 2D ferromagnetic CrI_3 material [13]. Although, the spin-direction properties are reported for conventional and layered FMs [14,15], the research on 2D AFM materials is very limited and scarce [6,7,16,17].

One of essential feature for manipulating AFM state is the magnetocrystalline anisotropy (MAE) which is evident in spin flip or spin flop transitions. The latter one requires relatively weak MAE and it is reported in literature for AFM compounds exhibiting various electronic states such as topological insulators [18], layered materials [19], and conventional semiconductors [20]. In addition, the experimental techniques including indirect means of magnetic phases such as anisotropic magnetoresistance (AMR), anomalous Hall effect (AHE) or second harmonic generation (SGH)

*Corresponding author: magdalena.birowska@fuw.edu.pl

[7,21,22], are employed to detect the AFM orientation in 2D materials. Interestingly, the magnetic phase transition of controlled anisotropic phenomenon in layered magnets provides crucial understanding of fundamental magnetism in reduced dimensions.

The present work is motivated by the lack of systematic studies regarding the impact of AFM orientation of magnetic moments on the optoelectronic properties of 2D materials. Hence, in this paper we put particular attention to pinpoint the magnetic fingerprints in indirect properties that can engineer the AFM ordering. We conduct a theoretical analysis based on density functional theory (DFT) and effective Bethe-Salpeter equation (BSE) to identify various spin direction features, which can be utilised in spin-processing functionalities. This study focuses on spin angle evolution of the effective masses of carriers, optically active band-edge transitions, exciton binding energies, which remain almost unexplored in the context of van der Waals (vdW) AFM crystals.

Here, we present a systematic study of the impact of spin orientation on the electronic and optical properties of series of the monolayers of MPX_3 , where $M = \text{Mn, Ni, Fe}$ and $X = \text{S, Se}$, assuming collinear arrangement of the magnetic moments. The results are presented as following: first we examine the magnetic ground state, determining easy and hard axes of magnetization at the level of PBE+ U +SOC approach. Next, we consider the electronic features such as band extrema, effective masses, valley splitting, and excitonic properties including the excitonic binding energy. Although, the electronic properties have been widely reported for particular spin arrangement and direction, the impact of the orientation of the collinearly ordered spins on opto-electronic properties MPX_3 are largely missing. Finally, band-edge excitons have been systematically predicted for this class of materials for the first time.

II. COMPUTATIONAL DETAILS

The calculations were performed in the framework of density functional theory (DFT) using the generalized gradient approximation within the PBE flavor [23,24], as implemented in VASP software [25]. The ion-electron interactions were described by the projector augmented wave (PAW) method [26]. Plane-wave basis cutoff and Γ centered Monkhorst-Pack [27] k -point grid were set to 500 eV and $10 \times 6 \times 1$, respectively. A Gaussian smearing of 0.05 eV was employed for the Brillouin zone (BZ) integration. The interlayer vdW forces were treated within the Grimme scheme using D3 correction [28]. A vacuum of the thickness equal to 20 Å was added to mimic the isolated monolayer. Most of the results were obtained using PBE+ U method based on Dudarev's approach [29], with the effective on-site Hubbard U parameter ($U_{\text{eff}} = U - J$, where J is fixed to $J = 1$ eV) assumed for $3d$ orbitals. Note that U_{eff} is hereafter denoted as U . To check its impact on various properties two values of $U = 3$ and 5 eV were employed. The SOC within the noncollinear treatment of magnetism was taken into account on the top of the PBE+ U scheme. The position of the atoms and unit cell were fully optimized within the PBE+ U approach. In order to predict the magnetic easy and hard axis, the spins of the magnetic ions have been rotated from out-of plane to in-plane directions with polar angle step $\Delta\Theta = 15^\circ$.

For every Θ , the atomic positions and the lattice parameters have been fully optimized. The effective masses of carriers at the band edges were examined using finite difference method [30]. The direct interband momentum matrix elements were computed from the wave function derivatives using density functional perturbation theory (DFPT) [31] in order to determine the optically active transitions, as discussed in Ref. [32]. The macroscopic optical dielectric constant frequencies ϵ_∞ were obtained using DFTP in the independent particle approach with (DFT-TD) and without local field effects (IP) [31].

Exciton calculations were performed within the effective BSE formalism [9,33–37] using the effective masses and dielectric constants obtained from the DFT calculations. We solve the effective BSE numerically using the parameters given in Ref. [9]. BSE formalism employed here does not account for exchange terms since its contribution is one order of magnitude smaller than the direct term [38]. Although our approach provides reliable trends for the exciton binding energies, it does not account for possible exchange-driven valley-mixing effects [39].

III. RESULTS

A. Magnetic ground state and magnetic easy axis

First, we examine the impact of the rotation of spins on the energy profile to determine the magnetic ground state and magnetic easy/hard axes for all employed MPX_3 systems. Previous neutron scattering experiments revealed a collinear antiferromagnetic order for MPS_3 [40] and $MPSe_3$ ($M = \text{Mn, Fe}$) [41] layered systems. Hence, we assume a collinear alignment of the spins and angle of rotation Θ [see Fig. 1(a)] varied from the out-of plane to in-plane configuration. The rotation of the spins within the basal plane yields up to two orders of magnitude smaller energy changes compared to out-of plane ones, hence in-plane rotations are not further considered.

The magnetic ground state exhibits antiferromagnetic Neel (AFM-N) and antiferromagnetic zigzag (AFM-z) arrangement of the spins for Mn and $M = \text{Ni, Fe}$, respectively (see Fig. 1), in line with other theoretical reports [9,10,42,43] and neutron scattering experiments [40,41,44]. The MPX_3 materials are reported to be robust antiferromagnets [10] and even high concentration of the substitutional dopants could not alter the magnetic ordering of the host [10,45]. Additionally, changing the angle of spin alignment Θ requires at least one order of magnitude lower energy (tens of meV per magnetic ion) than change of the AFM ordering (at least tens of meV per magnetic ion). The computed energy difference (ΔE) between the out-of plane and in-plane directions can be one order of magnitude greater for Se than S compounds [see Figs. 1(b)–1(d)], which is expected for heavier atoms, exhibiting larger SOC coupling [45]. Surprisingly, FePS_3 exhibits a larger MAE than FePSe_3 [see Fig. 1(e)]. The value of U does affect neither the type of AFM ordering nor the direction of the magnetic easy axis. However, the ΔE depends on the Hubbard U parameters. Namely, the smaller values are generally obtained for larger U , except for FePS_3 monolayer (see Fig. S2 in Ref. [46]). For the employed materials, an increase in the effective U resulted in larger lattice constants by up to 1.5% and larger magnetic moments (see Table S2).

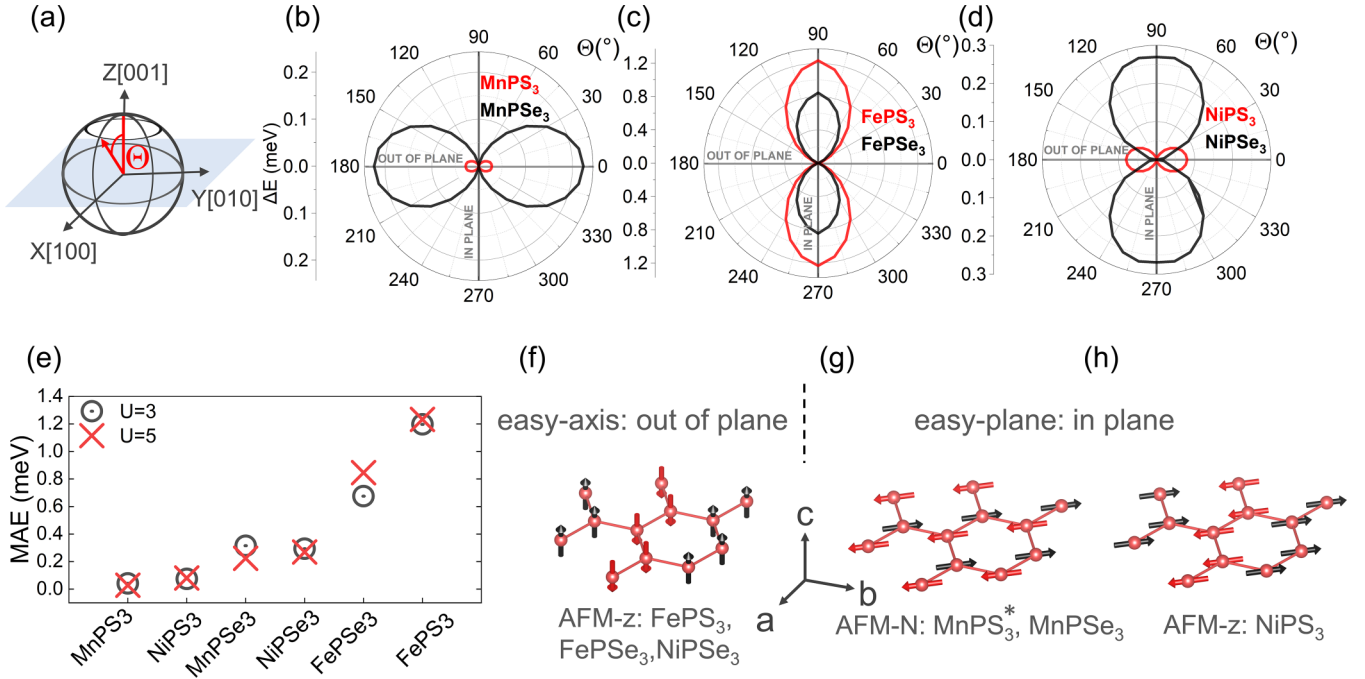


FIG. 1. (a) The rotation angle Θ of collinearly aligned AFM spins directed towards the (001) plane. [(b)–(d)] Polar plots of energy difference ΔE between the particular direction of the spins and the lowest energy configuration for Hubbard $U = 5$ eV. (e) The magnetocrystalline energy (MAE) is defined here, as a difference between the energies of spins parallel to hard (highest energy) and easy axes (lowest energy) of magnetization. [(f)–(h)] Structural arrangement of the spins exhibited by the magnetic ground state for all employed systems. The direction of the spins are parallel to the easy axis/plane of magnetization. The ΔE and the MAE are given in meV per magnetic ion.

Let us now consider the easy axes of magnetization, which are presented in Figs. 1(f) and 1(g) for all employed structures, with the hard axes predicted to be orthogonal to the corresponding easy axis/plane. In particular, for FePX_3 the magnetic easy axis points along the c crystallographic direction as reported in previous studies [40–42,47–49]. Hence, this kind of systems are considered to be Ising-type antiferromagnets, with a strong uniaxial magnetic anisotropy.

For the MnPX_3 compounds, we predict that the easy plane coincides with monolayer plane, unlike the recent experimental report for MnPS_3 , which has demonstrated that the spins are slightly tilted from the c axis [50]. In our approach the SOC is included within the PAW pseudopotential as implemented in the VASP package. Notably, the MAE for MnPS_3 is very small [see Fig. 1(e)], hence, we do not exclude that the direction of magnetic easy axis (easy plane) could change whenever SOC is considered using an all-electron approach. In general, the direction of the ordered spins for MPX_3 compounds result from the interplay between the single-ion anisotropy and magnetic dipolar interactions (MDIs), as already discussed in a recent publication [45]. In addition, the spin-orbit splitting is negligible for MnPS_3 , which manifests itself as the lowest MAE for all employed structures [see Figs. 1(b) and 1(e)]. Thus the MDI, generally regarded to be weak [51], might be decisive in determining the direction of the MnPS_3 spins. Note that the MDIs are not accounted for in our PBE+ U +SOC approach. On the other hand, in the case of the MnPSe_3 , the MDIs could be neglected due to larger lattice parameters and SOC. Hence, the magnetic easy axis of MnPSe_3 coincides with the monolayer plane,

in agreement with other reports in the literature [40,41,52], and confirmed by spin flop transition reported upon the non-magnetic substitution in MnPS_3 thin films [45]. Regarding NiPS_3 , the in-plane position of the magnetic moments are preferable and the magnetic ordering can be described by the XY Heisenberg Hamiltonian [47,48,53,54]. Our results predict the easy plane of magnetization within the monolayer frame, without any deviation in the z direction as reported recently for monolayer [55]. However, we do not exclude that a small anisotropy component along the z direction is plausible, as it was demonstrated by combined studies of neutron scattering measurements and linear spin wave theory for bulk NiPS_3 [44]. Here, we studied rather large changes of Θ angles. The subtle changes of Θ as well as the angles within monolayer plane are out of the scope of this research. Additionally, we also do not rule out the possibility that the inclusion of the MDIs interaction can facilitate the rotation of the spins towards the out of the plane direction. Moreover, for the case of NiPSe_3 , we determined the easy axis of magnetization to be in out-of-plane direction in line with recent report [56]. Similar results regarding the easy axis/plane of magnetization have been reported for the corresponding bulk systems [45].

B. Electronic properties

1. Electronic band gaps

Our results reveal that the structures containing Mn and Fe exhibit direct band gaps located at K high symmetry point [see Fig. 2(a)], in line with previous reports [9,43,57], while the NiPS_3 system is an indirect semiconductor confirmed by

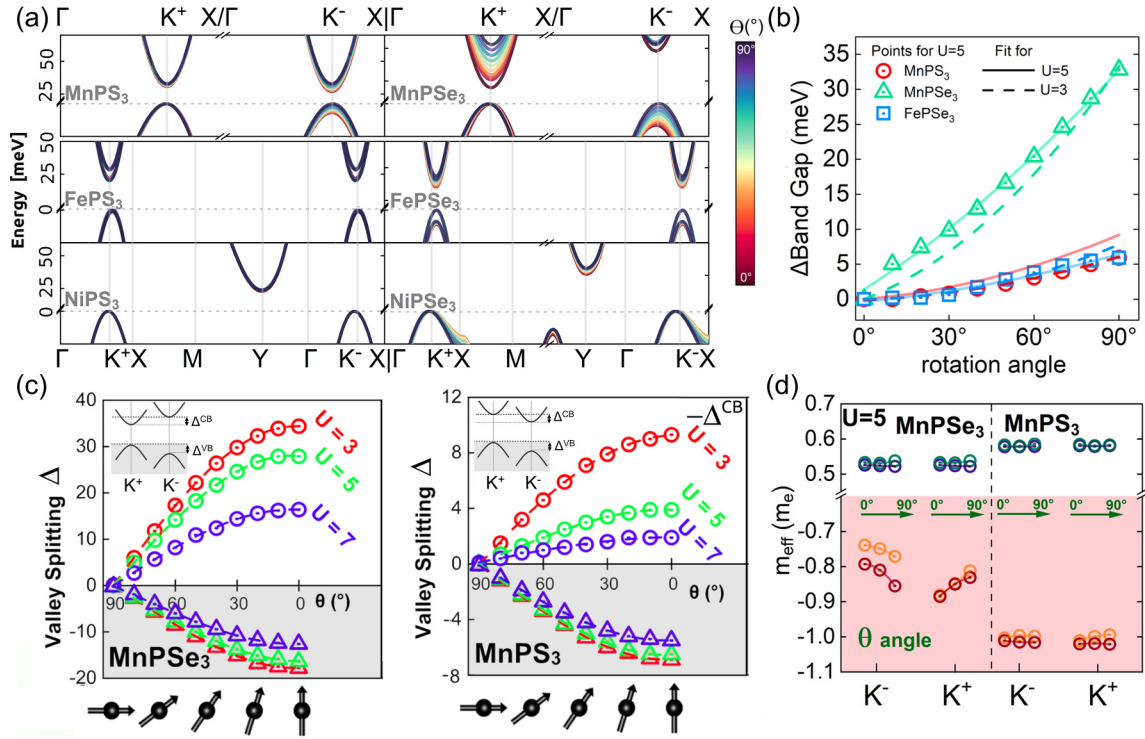


FIG. 2. Spin-orientation electronic properties. (a) Band extrema for all employed monolayers as a function of spin direction (color scale). (b) Enhancement of the electronic band gaps ΔE_{gap} for particular spin directions in respect to out-of-plane spins. (c) Valley splitting Δ^{VB} and Δ^{CB} are defined $\Delta^{\text{VB}} = E_{K^-}^{\text{VB}} - E_{K^+}^{\text{VB}}$ and $\Delta^{\text{CB}} = E_{K^-}^{\text{CB}} - E_{K^+}^{\text{CB}}$, respectively, for Mn and Fe contained monolayers, given in meV. Note, that for the clarity of picture regarding MnPS₃, the $-\Delta^{\text{CB}}$ is plotted. (d) In-plane components of effective mass tensor for electrons (positive masses) and holes (negative masses) of MnPX₃ in respect to spin direction and for two nonequivalent $\pm K$ valleys.

experiments [53]. In particular, for FePS₃ and NiPSe₃ there is a strong contribution of the 3d states to the bands in vicinity of Fermi level. Hence, for these systems, significant changes of the position of the band extrema (VBM and CBM) and their curvatures upon the Hubbard U parameter are visible (see Tables S2 and S4 in Ref. [46] and discussions therein).

Regarding the direct transitions, the main contribution to the VBM comes from p states of S atoms, whereas for CBM significant contributions originate also from 3d states for both transition metals (see Table S3 in Ref. [46]). The main difference between the MnPX₃ (AFM-N) and FePX₃ (AFM-z) is due to the major contribution to the CBM, which is p and 3d states for MnPX₃ and FePX₃, respectively. In particular, in Fe-based systems, d_{yz} and d_{xz} orbital contributions are evident, being negligibly small in Mn-based systems. In addition, a moderate contribution of s states in CBM is observed in all the employed systems.

2. U dependence

For all employed compounds, except MnPX₃, the U parameter significantly affects the curvature of the conduction bands as reported previously [43], and hence the effective masses of holes. Hence, all features are examined assuming two Hubbard U parameters $U = 3$ and 5 eV. In particular, the large value of the effective masses of electrons exhibited for Ni-based systems, indicating a flat character of the conduction bands, which can be further enhanced by adopting larger values of U (see Table S4 in Ref. [46]). By applying

the Hubbard U to 3d states, one can shift the 3d states away from the Fermi level. In particular, for MnPX₃ structures the conduction bands are mainly build from p states, and further shifting 3d states do not affect the band curvature nor the band gap value, whereas for FePX₃ compounds the conduction bands consist mainly of 3d states, hence further enlargement of U strongly impacts electronic features around band edges. Additionally, our results corroborate the previous reports on strong dependence of Hubbard U on fundamental energy band gap (see Table S2) [43].

3. Effective masses

For all of employed monolayers, the heaviest effective mass is obtained for NiPX₃, whereas the lightest one is demonstrated for MnPSe₃ (see Table S4 and Fig. S3 in Ref. [46]). Generally, the lower effective masses are exhibited by the electrons than holes, and for Se contained structures than corresponding S systems (by about 30%), except for NiPX₃ structures where these trends are opposite. Additionally, the anisotropic in-plane components of effective masses ($m_1 \neq m_2$) are exhibited by monolayer with AFM-z ground state, whereas for MnPX₃ monolayers with AFM-N ordering, the in-plane components are isotropic ($m_1 = m_2$). Note that the AFM-z magnetic arrangement breaks the hexagonal symmetry, as it consist of spins ferromagnetically aligned along zigzag chain [see Fig. 1(g)], whereas the AFM-N type of magnetic order is commensurate with the structural symmetry. Hence, the anisotropic effective masses, and thus, anisotropic

TABLE I. Spin-dependent electronic features for direct band-edge transition occurring at $\pm K$ valleys (VBM $\rightarrow$ CBM) in the presence of SOC [PBE+ U (5 eV)+SOC approach]. The valley splitting of the VBM (Δ^{VB}) and CBM (Δ^{CB}) are defined as $\Delta^{\text{VB}} = E_{K-}^{\text{VB}} - E_{K+}^{\text{VB}}$ and $\Delta^{\text{CB}} = E_{K-}^{\text{CB}} - E_{K+}^{\text{CB}}$, respectively. The spin degeneracy of the band edges δ^{VB} and δ^{CB} are calculated as $\delta^{\text{VB}} = |E_{\uparrow}^{\text{VB}} - E_{\downarrow}^{\text{VB}}|$ and $\delta^{\text{CB}} = |E_{\uparrow}^{\text{CB}} - E_{\downarrow}^{\text{CB}}|$, respectively. We refer intensity (Inten.) to the oscillator strength of the band-edge transitions. The optically active transitions coupled to linear polarization of light (x, y, z) are collected in the last column. The intensity is given by $|\frac{\hbar}{m_e} \hat{e} \cdot \vec{p}_{cv}|^2$ in which $\hat{e} = \{\hat{x}, \hat{y}, \hat{z}\}$ is the light polarization (pol.) and $\vec{p}_{cv}$ is the matrix element between CBM and VBM.

MPX ₃ (magn. state)	spin direction (Θ)	$K + /K - (\Delta^{\text{VB}}, \Delta^{\text{CB}})$	Spin deg. ($\delta^{\text{VB}}, \delta^{\text{CB}}$)	Hex. symm.	(pol.) Inten. [(eVÅ) ²]
MnPS ₃ (AFM-N))	0°	✓ (−6.4, −4.4)	X	✓	(z) 0.59
	90°	X (0, 0)	X	✓	(z) 0.62
MnPSe ₃ (AFM-N)	0°	✓ (−17.7, 33.1)	X	✓	(z) 0.13
	90°	X (0, 0)	X	✓	(z) 0.18; (x, y) 0.05
FePS ₃ (AFM-z)	0°	X	✓ (1.8, 9.1)	broken	0.71 (y)
	90°	X	✓ (1.5, 7.4)	broken	0.73 (y)
FePSe ₃ (AFM-z)	0°	X	✓ (7.4, 3.1)	broken	(y) 0.27; (x) 0.04
	90°	X	✓ (9.3, 5)	broken	(y) 0.29; (x) 0.02

transport properties can be regarded as a magnetic marker distinguishing different type of antiferromagnetic ordering within hexagonal lattice. In addition, the inclusion of the SOC does not affect the curvature of examined systems, except for MnPSe₃ where slight changes are shown for $K+$ and $K-$ valleys (see Table S5 in Ref. [46]).

4. Spin-orientation-dependent electronic features in MPX₃ ($M = \text{Mn, Fe}$; $X = \text{S, Se}$)

Now, let us make closer inspection on the band edges of MLs exhibiting direct transitions. The electronic features are collected in Table I. Note that in the absence of the SOC, the band extrema are doubly degenerated for all employed systems. The presence of SOC in the structures containing Mn preserves the spin degeneracy of the band extrema (VBM, CBM), however causing the valley splitting at $+K$ and $-K$, which is expected for the honeycomb lattice with AFM-N arrangements of the spins with SOC included [58]. Namely, the SOC preserves the spin degeneracy but leads to a renormalization of the valleys ($+K$ and $-K$ are not equivalent) for AFM-N magnetic ground state. The size of the valley splitting (Δ) depend on the chalcogen atoms (larger values for Se atoms), Hubbard U , and spin directions (see Fig. 2 and Tables I, S7 in Ref. [46]). In particular, the largest valley splitting is attained for the out-of-plane direction of the spins ($\Delta^{\text{CB}} = 39$ meV for MnPSe₃ and $U = 3$ eV) and lower value of U as presented in Fig. 2(c), whereas no polarity of the valleys are observed for the in-plane direction of the spins. Namely, the rotation of the spins towards out-of-plane directions results in enhancement of the valley splitting. Hence, the band gap of MnPSe₃ can be changed by up to 35 meV as presented in Figs. 2(b) and 2(c), whereas for the rest of the compounds the minor changes are observed [see Fig. 2(b)]. Additionally, the effective masses of holes for MnPSe₃ are sensitive to the direction of the spins as presented in Fig. 2(d). Interestingly, in the case of MnPS₃, the band gap changes its character from direct to indirect when the spins are rotated from an out-of-plane to an in-plane directions.

Regarding the monolayer of FePX₃, the presence of SOC and local inversion symmetry breaking in FeX₆ octahedra

lift the degeneracy of the band extrema (few meV), irrespective to the spin direction (see column 4 in Table I). In particular, larger spin polarization δ is obtained for CBM than VBM ($\delta^{\text{CB}} = 9.1$ meV, $\delta^{\text{VB}} = 1.8$ meV), and for higher values of U for FePS₃. In contrast to the FePS₃, the opposite trends are obtained for FePSe₃ (for the details see Table S7 in Ref. [46]). Hence, the spin splitting of the bands is obtained for hexagonal lattices exhibiting in-plane structural anisotropy, as reported for MnPS₃ (see Fig. 5(d) in Ref. [57]). In this case, the spin polarization occurred, alongside with renormalization of the $+K/ -K$ valleys as expected for AFM-N. In addition, one of the consequences of the local inversion symmetry breaking exploited in Fe monolayers is a lattice distortion reflected in the ratio of the lattice parameters deviated from hexagonal symmetry ($b/a \neq \sqrt{3}$) [57,61].

C. Excitonic properties

1. Dielectric properties

We start our discussion by analyzing the dielectric properties of the employed systems. Generally, the in-plane components of static dielectric constants (ϵ_{xx} , ϵ_{yy}) are isotropic for all studied systems, except for monolayers of (Ni,Fe)PX₃, where they differ by up to 4% (see Tables S8 and S9 in Ref. [46]). Due to the fact that dielectric tensor is well defined for the bulk materials, we calculate the 2D polarizability $\chi_{\parallel}$ (dielectric screening length, for the details see Ref. [46]). Our results reveal that the dielectric screening length increases as the atomic number of the metal also increases $\chi_{\parallel}^{\text{Mn}} > \chi_{\parallel}^{\text{Fe}} > \chi_{\parallel}^{\text{Ni}}$, exhibiting the smallest and highest values equal to 3.25 Å (MnPSe₃, $U = 5$ eV) and 6.13 Å (NiPSe₃, $U = 5$ eV), respectively. In addition, the systems containing Se exhibit $\approx 40\%$ larger screening properties than their corresponding S systems. The screening properties of MPX₃ compounds are generally smaller than for other vdW structures such as MoSe₂ (8.23 Å). Note that for the (Ni,Fe)PX₃ systems, the dielectric screening lengths strongly depend on the Hubbard U . In particular, the larger values of $\chi_{\parallel}$ are attained for the smaller Hubbard U , which correlates with the strong impact of the U on the DOS [see Fig. S2(b)].

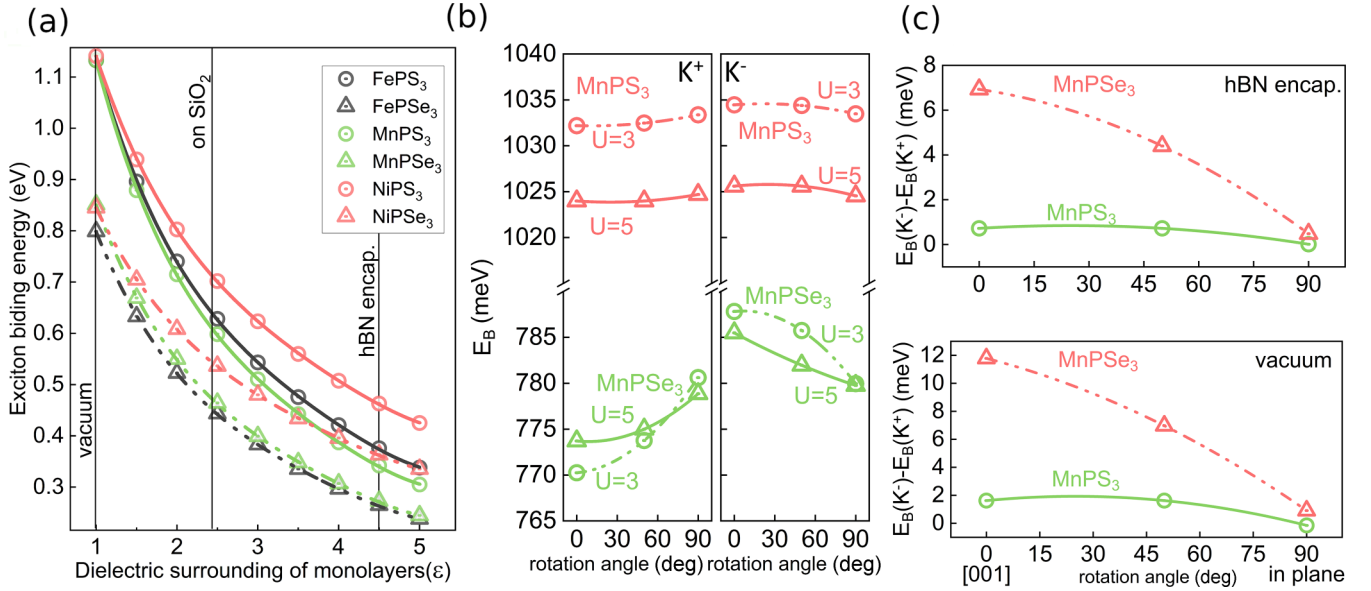


FIG. 3. (a) Large exciton binding energies obtained for all considered monolayers with magnetic ground state with respect to the dielectric screening of the surroundings. The values for air/vacuum, SiO₂ [59] substrate, and hBN encapsulation [60] are denoted by vertical lines. (b) Evolution of the E_B with respect to the spin direction for two values of Hubbard U (3 and 5 eV). (c) The energy difference between the E_B calculated for $-K$ and $+K$ valleys as a function of the spin direction angle Θ (within DFT+ U = 5 eV and DFT-TD approaches), for hBN encapsulated and freestanding layers.

2. Band-edge excitons

Let us now examine the band-edge excitons using the relevant information from DFT (m_{eff} , $\chi_{\parallel}$) combined with the effective BSE [33,34]. We show the exciton binding energies (E_B) in Fig. 3(a) (for the details of calculations see Ref. [9]). All employed structures exhibit large E_B exceeding 1 and 0.8 eV for bare monolayers of MPS₃ and MPSe₃, respectively, outperforming the values in TMDCs [9] (the exact values are collected in Tables S10 and S11 in Ref. [46]). The excitons have been recently experimentally reported for few layers of NiPS₃ [53,62,63] and FePS₃ [57], however, their origin is still under a hot debate. Generally the E_B are larger by about 30% for S-based structures than corresponding Se compounds, mainly due to larger effective masses and smaller dielectric screening for MPS₃. The E_B decreases as the effective dielectric constant of the environment increases, preserving the same trend for all monolayers. This can be explained within the oversimplified exciton picture (hydrogen model) for which E_B is proportional to effective mass and inversely proportional to the square of dielectric screening.

3. Optical transitions and selection rules

Besides the binding energy, it is also relevant to determine the selection rules of the direct band-edge transitions, which are summarized in Table I. All of the transition are optically allowed (nonzero oscillator strength) exhibiting linear polarization of light. In particular, for monolayers with AFM-N phase (MnPX₃) the polarization of light is along z direction, whereas for the AFM-z (FePX₃) pointing along y direction. Interestingly, similar conclusions are observed assuming various AFM metastable phases within the same magnetic material [9]. Therefore the polarization of light is sensitive to magnetic order irrespective of the type of transition metal and

chalcogen atoms. This is in line with recently reported linear polarization of the sharp emission, that aligned perpendicular to the spin orientation [63]. Hence, the polarization of light might be a tool to distinguish the type of AFM ordering. All of these direct band-edge excitons are optically active transitions and couple to z -polarized light. Comparing with the widely studied TMDCs, these transitions in MPX₃ systems have an intensity two orders of magnitude smaller than the bright (A and B) transitions but have comparable intensity to the dark (D) transitions [32,64].

4. Spin-orientation-dependent excitonic features in MnPX₃

Interestingly, the excitonic properties are sensitive to the direction of the spins. Owing to the spin direction dependent effective masses observed in MnPX₃ presented in Fig. 2(d), we discuss below only these type of monolayers. The effect of the spin direction on E_B is on the order of 1–2 meV in MnPS₃ but on the order of 10 meV in MnPSe₃ monolayer, as presented in Fig. 3(b), irrespective of the value used for the Hubbard U parameter. Furthermore, opposite K valleys (at $+K$ and $-K$) show different effective masses and, consequently, different values of E_B , as shown in Fig. 3(c). Hence, the E_B depends on the orientation of the AFM aligned spins. Particularly, due to the sizable valley-dependent curvature of the VBM [see Fig. 2(d)] observed for the MnPSe₃, the E_B of excitons at $\pm K$ valleys differ by up to $E_B^- - E_B^+ = 12$ meV (for MnPSe₃ in vacuum). Additionally, the changes in direction of the spins not only impact the exciton wave functions, but also the spreading of the exciton wave functions, as recently calculated for the antiferromagnetic 2D semiconductor CrSBr [65]. Essentially, both the magnetic order and to a lesser extent the direction of the spins modify the band structure (electronic energies and wave functions), which is the initial ingredient

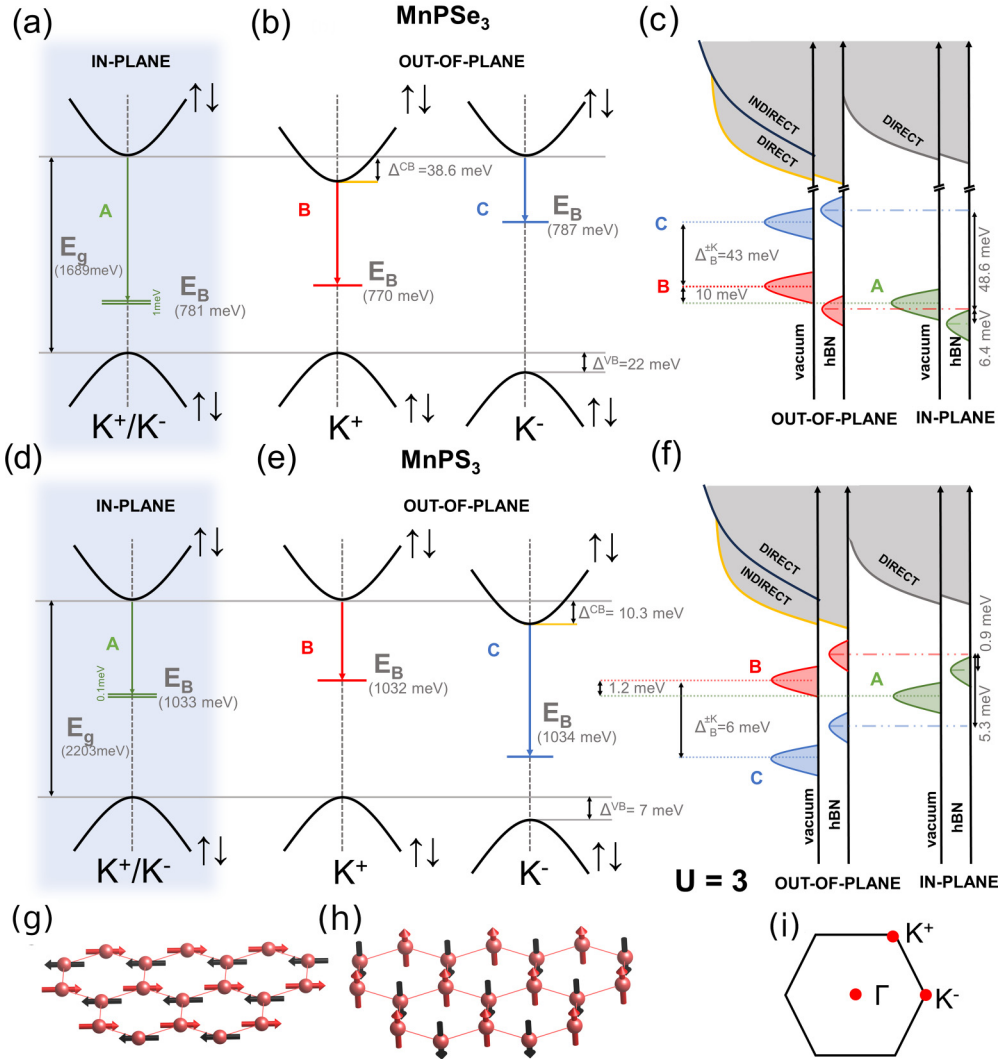


FIG. 4. Schematic diagrams ($U = 3$ eV) of direct transitions for [(a) and (b)] MnPSe₃ and [(c) and (d)] MnPS₃ exhibiting in-plane and out-of-plane directions of the AFM aligned spins, as schematically denoted at the bottom of the picture [(g) and (h)]. Schematic absorption onsets [(c) and (f)] with depicted in coloured exciton peaks A, B, and C. Namely, green (A), red (B), and blue (C), peaks indicate band-edge excitons for in-plane and out-of-plane spin configurations of AFM aligned spins at $+K$ and $-K$ valleys, respectively. Black arrows close to bands indicate spin degenerated bands. The position of the peaks are in order but not in scale. All of the presented direct transition are coupled to “z”-polarized light with the intensities listed in Table I. (i) The first BZ with labeled high symmetry k points.

to obtain the exciton properties. Furthermore, if the binding energies change, the exciton distribution will also change and the more the binding energy changes the larger the changes in the exciton wave function. The exciton wave functions for the different calculated magnetization angles are shown in the SI (see Fig. S4 in Ref. [46]) for MnPSe₃. Since MnPSe₃ has a larger binding energy, the effect on the exciton wave function is more pronounced. Furthermore, from the wave functions of MnPSe₃ in real space, we can estimate an exciton radii on the order of 1–2 nm.

Combining the information of the optical selection rules and exciton binding energies, we present in Fig. 4 the schematic diagram of optically active band-edge transition considering the in-plane and out-of the plane direction of spins. Our calculations reveal that the emissions from the opposite $+K$ and $-K$ valleys are energetically below the onset of absorption spectrum. For the in-plane directions of the spins,

the energy difference between $+K$ and $-K$ is rather small [separated about 1 and 0.1 meV for MnPSe₃ and MnPS₃, respectively, as shown in Figs. 4(a) and 4(d)]. On the other hand, for out-of-plane spins, the exciton emission from $\pm K$ valleys are separated by 42 and 6 meV for MnPSe₃ and MnPS₃, respectively. The separation of the exciton peaks at $\pm K$ valleys (see difference between the position of the B and C peaks in Fig. 4) is calculated as

$$\begin{aligned} \Delta_B &= [E_g(K-) - E_B(K-)] - [E_g(K+) - E_B(K+)] \\ &= \Delta E_B + \Delta^{VB} - \Delta^{CB}, \end{aligned} \quad (1)$$

where $\Delta E_B = E_B(K-) - E_B(K+)$ is the difference between the exciton binding energies at $\mp K$ valleys and $E_g(K\pm)$ the electronic band gap at a given K valley. We predict that one peak should be observed for in-plane oriented spins (green peak in Fig. 4) whereas two peaks emerge for the spins

deflected from the monolayer plane (red and blue peaks in Fig. 4). Therefore the energy Δ_B is a robust magnetic fingerprint of the AFM spin directions. Note that the energy separation of $\pm K$ valleys depends on the dielectric environment, as presented in Fig. 3(c), but should be visible in hBN encapsulated samples, specially in MnPSe_3 since the valley splitting is dominated by the electronic counterparts Δ^{CB} and Δ^{VB} .

IV. CONCLUSIONS

Here, we systematically examine the MPX_3 materials emphasizing the role of spin reorientation, magnetic arrangement and electron correlation effects in various properties. In this regard, the chemical trends in respect to the type of the chalcogen atom as well as transition metal are examined. We have demonstrated that the electronic features such as band gaps, effective masses, dielectric screening and exciton binding energies strongly depends on the type of chalcogen atom. Notably, larger effective masses are attained for S than Se contained monolayers (by about 30%), whereas smaller dielectric screening (up to 40%) are reached for MPS_3 . In general, the larger effective masses and smaller dielectric screening length are obtained for employed materials than for widely examined TMDs, resulting in larger exciton binding energies of direct transitions of MPX_3 than corresponding monolayers of TMDs. Generally, all examined band-edge direct transitions of $(\text{Mn,Fe})\text{PX}_3$ monolayers turned out to be optically active coupled to linear polarized light, with type of polarization sensitive to magnetic arrangement.

Regarding the direct band-edge transitions, the MnPX_3 are of particular importance as could be exploited as promising valley electronics materials. In particular, we have shown that the valley splitting at the $\pm K$ can be effectively controlled by the direction of the magnetic moments. In particular, the sizable valley splitting occurs for the out-of-plane direction of the magnetic moments in monolayer of MnPSe_3 (smaller effect observed for MnPS_3), resulting in valley dependent gaps. Namely, two distinct peaks are expected to be visible below the absorption onset for the out-of-plane AFM aligned spins,

whereas one peak for the in-plane case. Hence, the number of the peaks and the separation of the peaks can be regarded as magnetic fingerprint of the orientation of AFM aligned spins. The change in the separation of the peaks points towards the plausible spin rotation.

On the other hand, the $\pm K$ valleys obtained for MnPX_3 are spin degenerated, which might hinder their spintronic applications. Hence, we have also propose a novel way how the spin valley polarization can be attained. We have suggested that particular deformation of the hexagonal lattice of MnPX_3 could lead to the spin resolved valley splitting. Our results give insight into the valley splitting realization in 2D antiferromagnets. In addition, the anisotropic effective masses and the type of linear polarization can be regarded as magnetic markers probing the type of AFM arrangements. Finally, the spin dependent features have been identified such as valley splitting of VBM and CBM, the effective mass of holes and exciton binding energies. These features can be referred as sensitive parameters that provide insight into spin flop transitions.

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