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Spin photogalvanic effect in two-dimensional collinear antiferromagnets

Rui-Chun Xiao^{1,2,3,6}, Ding-Fu Shao^{1b,6}, Yu-Hang Li^{5,6} and Hua Jiang^{1b,2,3}✉

Recent discovered two-dimensional (2D) antiferromagnetic (AFM) van der Waals quantum materials have attracted increasing interest due to the emergent exotic physical phenomena. The spintronic properties utilizing the intrinsic AFM state in 2D antiferromagnets, however, have been rarely found. Here we show that the spin photogalvanic effect (SPGE), which has been predicted in three-dimensional (3D) antiferromagnets, can intrinsically emerge in 2D antiferromagnets for promising spintronic applications. Based on the symmetry analysis of possible AFM orders in the honeycomb lattice, we conclude suitable 2D AFM candidate materials for realizing the SPGE. We choose two experimentally synthesized 2D collinear AFM materials, monolayer MnPS₃, and bilayer CrCl₃, as representative materials to perform first-principles calculations, and find that they support sizable SPGE. The SPGE in collinear 2D AFM materials can be utilized to generate pure spin current in a contactless and ultra-fast way.

npj Quantum Materials (2021)6:35; <https://doi.org/10.1038/s41535-021-00334-5>

INTRODUCTION

Spintronics¹, which exploits the spin degree of freedom of electrons in condensed matters for information storage and processing, has generated persistent interest in both physics and engineering. Conventional spintronics devices are usually constructed by three-dimensional (3D) magnetic materials, and their application in nanoscale spintronics is hence strongly limited by the sizable thickness. The recently discovered two-dimensional (2D) van der Waals magnets naturally circumvent this limitation, thus bring an opportunity for next-generation nanoscale spintronic devices. In particular, 2D collinear antiferromagnetic (AFM) materials are especially interesting [such as bilayer CrX₃ (X = Cl, Br, I)^{2–4}, even-layer MnBi₂Te₄^{5,6}, monolayer MnPS₃^{7,8}]. Except for the advantage of low dimensionality, 2D collinear AFM materials also exhibit ultra-fast dynamic response, robustness against external magnetic perturbations, and have no stray field^{9–11}. However, despite remarkable progress in exploring exotic phenomena in 2D collinear AFM materials^{2–6,12}, the spintronic properties, such as magnetoresistance effect in CrI₃^{4,12} and CrCl₃^{13,14} due to the AFM-ferromagnetic transitions, and quantum anomalous effect Hall of MnBi₂Te₄⁶ induced by a finite magnetization, so far have been restricted to introduce ferromagnetic (FM) orders by strong magnetic fields. These require substantial electric currents and thus suffer from large energy dissipation. A spintronic property that utilizes the intrinsic AFM state will be more desirable for device application of the 2D collinear AFM materials.

One promising mechanism to use these 2D collinear AFM materials directly is the spin photogalvanic effect (SPGE)^{15–23}, which generates spin current by photoexcitation in a contactless and ultra-fast way. In AFM materials, two sublattices with opposite spin polarizations are usually connected by certain symmetry. It was proposed that if the spin–orbit coupling (SOC) effect is negligible, the photogalvanic currents in two magnetic sublattices carry different kinds of spins and propagate in opposite directions,

inducing a pure spin current in total²³. The spin current here has a long spin diffusion length because spin is a conserved quantity.

In this paper, we predict that 2D collinear AFM materials can be utilized to fabricate the nano spintronic devices via the SPGE. We focus on the 2D collinear antiferromagnets with time-reversal-combined-inversion ($\tilde{T}\tilde{I}$) symmetry and weak SOC such as Néel-type monolayer MnPS₃ and A-type bilayer CrCl₃, and demonstrate, based on first-principles calculations, that these materials support sizable SPGE.

RESULTS

Model and candidate materials

A collinear AFM material is composed of two FM sublattices with opposite magnetizations. These two sublattices are usually connected by a symmetry operation, leading to a zero net magnetization. One of the most common symmetry operations to compensate for the magnetization are the $\tilde{T}\tilde{I}$ symmetry, as shown in Fig. 1a. In such an AFM material, even though both the time-reversal ($\tilde{T}$) symmetry and the space inversion ($\tilde{I}$) symmetry are broken, the combined $\tilde{T}\tilde{I}$ symmetry is still preserved and connects the magnetic sublattices with opposite magnetizations. This symmetry enforces the energy bands of two sublattices to be degenerate. In the absence of the SOC effect, the spin is a good quantum number, i.e., a conserved quantity. It allows us to investigate the SPGE of the $\tilde{T}\tilde{I}$ preserved AFM materials in two sublattices with spin-up and spin-down magnetizations separately using the model proposed by Young et al.²³.

We first describe the photogalvanic effect (PGE) in one spin sublattice. When an electron is pumped from a valence band to a conduction band by a linearly polarized light, it generates a shift of wave packet in real space. This “shift vector” can be described by^{24–27}

$$R_{nm}^a(\mathbf{k}) = \frac{\partial \phi_{nm}(\mathbf{k})}{\partial k^a} + r_{nn}^a(\mathbf{k}) - r_{mm}^a(\mathbf{k}), \quad (1)$$

¹Institute of Physical Science and Information Technology, Anhui University, Hefei, China. ²School of Physical Science and Technology, Soochow University, Suzhou, China. ³Institute for Advanced Study, Soochow University, Suzhou, China. ⁴Department of Physics and Astronomy & Nebraska Center for Materials and Nanoscience, University of Nebraska, Lincoln, NE, USA. ⁵Department of Electrical and Computer Engineering, University of California, Riverside, CA, USA. ⁶These authors contributed equally: Rui-Chun Xiao, Ding-Fu Shao, Yu-Hang Li. ✉email: jianghuaphy@suda.edu.cn

Fig. 1 Principle of SPGE. **a** Schematics of an AFM material with $\hat{T}$ symmetry (top) and corresponding symmetry enforced band structure (bottom). **b, c** Spin-polarized sublattices and related singlet band structures, respectively. A light generates a PGE current in each sublattice (top), and the corresponding optical transition occurs in the spin subband (bottom). The situation for the sublattice with spin-up and spin-down magnetizations are shown in **(b)**, and **(c)**, respectively. **d** A spintronic device based on the SPGE with a 2D collinear AFM material.

where a is the Cartesian index, ϕ_{nm} is the phase factor of the interband Berry connection and r_{nm}^a is the intraband Berry connection matrix along a direction. The PGE tensor element σ_{abc} is determined by^{23,24}

$$\sigma_{abc}(\omega) = -\frac{ie^3}{2\hbar^2} \int [d\mathbf{k}] \sum_{n,m} f_{nm}(\mathbf{k}) R_{nm}^a(\mathbf{k}) r_{nm}^b(\mathbf{k}) r_{nm}^c(\mathbf{k}) \delta[\omega_{nm}(\mathbf{k}) - \omega], \quad (2)$$

where $f_{nm}(\mathbf{k}) = f_n(\mathbf{k}) - f_m(\mathbf{k})$ is the difference of occupation factors, $\hbar\omega_{nm}(\mathbf{k}) = \epsilon_m(\mathbf{k}) - \epsilon_n(\mathbf{k})$ is the difference of band energies, and ω is the frequency of light. The δ function originates from the quantum lifetime of electrons (see Supplementary Note 5). Finally, the induced charge PGE current density $\mathbf{J}$ is

$$\mathbf{J}_a = \sigma_{abc}(\omega) E_b(\omega) E_c(-\omega), \quad (3)$$

where $a, b, c \in \{x, y, z\}$, and E_a is the electric field of the linearly polarized light along the a direction. The shift vector is odd under $\hat{T}$ symmetry, i.e. $R_{nm}^a(\mathbf{k}) = -R_{nm}^a(-\mathbf{k})$. Therefore, the integration in Eq. (2) is enforced to be zero in a centrosymmetric material, leading to the vanishing of PGE.

For the spin sublattices shown in Fig. 1b, c, the broken $\hat{T}$ symmetry allows the PGE in each spin sublattice individually. Since the magnetic moments in each sublattice are in FM order, the PGE charge current is spin-polarized with the tensor $\sigma^\uparrow(\sigma^\downarrow)$ for the sublattice with spin-up (spin-down) magnetization. The $\hat{T}$ symmetry converts a spin-up electron to a spin-down one, and the $\hat{T}$ symmetry guarantees the shift vectors to be opposite, i.e., $R_{nm}^{a,\uparrow}(\mathbf{k}) = -R_{nm}^{a,\downarrow}(\mathbf{k})$ (see Fig. 1b, c). On the other hand, the optical transition possibilities ($\propto r_{nm}^b(\mathbf{k}) r_{mn}^c(\mathbf{k})$) of two spin states in the same $\mathbf{k}$ points are equal. As a consequence, in a $\hat{T}$ preserved AFM material, the spin polarizations and directions of the PGE current in different sublattices are enforced to be opposite, i.e. $\sigma^\uparrow = -\sigma^\downarrow$. This results in a vanishing charge current, but a finite pure spin current,

Fig. 2 Schematics of four AFM orders in 2D honeycomb lattice. **a** Zigzag-type, **b** stripy-type, **c** Néel-type, and **d** A-type. The inset in **(d)** shows the side view of the A-type AFM order.

determined by $\sigma^S = \sigma^\uparrow - \sigma^\downarrow$, which leads to the SPGE in an AFM material with weak SOC effect. The model used here includes only the interband optical transition and is suitable for all the AFM semiconductors. For itinerant AFM materials, there should be a nonlinear Drude effect (intraband transition) arising from the Berry curvature dipole^{28,29}. Since all the discovered 2D van der Waals antiferromagnets so far are semiconductors, the intraband optical transition of them in the SPGE is nonexistent and ignored in our work.

Therefore, we can construct a spintronic device based on the SPGE as shown in Fig. 1d: A laser light beam irradiates to a 2D collinear AFM material with $\hat{T}$ symmetry, and generates a pure spin current $\mathbf{J}^S$ without any charge currents $\mathbf{J}^C$, which can inject the spin current to the attached terminal in a contactless and ultra-fast way. The spin current generated by this mechanism is expected to have a longer spin diffusion length compared to that generated by the mechanisms associated with SOC effect^{15–22}. This is due to the spin conservation and the absence of momentum-dependent SOC field, which do not lead to the spin decoherence through the Dyakonov–Perel mechanism³⁰ during the scattering. The spin current may have interesting interactions with the local magnetic moments³¹, which is worth further study.

There is a rich collection of layered magnetic materials^{32–34}. However, not all these magnetic orders support the required symmetry. To determine the suitable AFM order for the SPGE, we use a honeycomb lattice model that most 2D collinear AFM materials adopt. Figure 2 shows four common magnetic orders. The related materials are summarized in Supplementary Table 1. The zigzag-type and stripy-type AFM orders such as MPS_3 ($M = \text{Fe, Co, Ni}$)^{35–39} and MSiSe_3 ($M = \text{V, Fe, Ni}$)⁴⁰ are shown in Fig. 2a, b, respectively. The $\hat{T}$ symmetry of each sublattice can be clearly seen for these AFM orders, preventing the PGE in each sublattice and the SPGE of the AFM lattices. Figure 2c shows the Néel-type AFM order, where the adjacent magnetic moments are coupled with each other antiparallely. This AFM order has been found in monolayer MnPSe_3 ^{7,8,41–43} and MnPSe_3 ⁴⁴ in experiments. In this AFM order, the $\hat{T}$ symmetry of each sublattice is broken, and two sublattices are connected by the $\hat{T}$ symmetry. This type of AFM order satisfies the symmetry for the SPGE. Different from the above AFM orders existing in the monolayer 2D materials, there is an A-type AFM order that can only emerge in multilayer 2D magnets (Fig. 2d), such as CrX_3 ($X = \text{Cl, Br, I}$)^{2–4} and MnBi_2Te_4 ^{5,6}. In these materials, the magnetic atoms are arranged in the FM order within the intralayer, and in the AFM order between adjacent layers. Although $\hat{T}$ symmetry is preserved for monolayer,

Fig. 3 Calculation results of monolayer MnPS₃. **a** Top view (left) and side view (right) of monolayer MnPS₃. The rhombus denotes the unit cell. **b** Calculated densities with the isosurface of 0.047 e/Å³ for spin-up (top) and spin-down (bottom) states. **c** Calculated band structure of monolayer MnPS₃. **d** PGE coefficients for the spin-up state. **e** $\mathbf{k}$ -solved PGE coefficient of $\sigma_{yy}^\uparrow$ (in a.u.) at $\omega = 3.36$ eV.

it is enforced to be broken in bilayer due to the interlayer stacking, which makes the A-type AFM materials preserve $\hat{T}$ symmetry and compatible for the realization of the SPGE. Based on the above analyses, we can choose suitable 2D magnetic materials. As specific examples, we take Néel-type monolayer MnPS₃ and A-type bilayer CrCl₃ as two representative materials. The two experimentally synthesized 2D collinear AFM materials both have negligible SOC effects and suitable bandgaps for the SPGE.

First-principles calculation results

Transition-metal trichalcogenide MnPS₃ is an AFM material with a Néel temperature (T_N) of 78 K in bulk^{45,46}. It has a layered structure, where the Mn atoms form a honeycomb lattice in each layer. A dumbbell-shaped P₂S₆ unit is located at the center of each Mn hexagon (Fig. 3a). The magnetic moments of the nearest-neighbor Mn atoms are antiparallel to each other, forming a Néel-type AFM order. It has been successfully exfoliated down to single-layer recently^{7,8,41–43}, and the Néel-type AFM order can be maintained. The magnetic sublattices in monolayer MnPS₃ have the noncentrosymmetric structure with D_3 point group, which contains a C_3 rotation symmetry along the z -axis, and a C_2 rotation axis around the y direction, as shown in Fig. 3a. The $\hat{T}$ symmetry that connects two sublattices is clearly reflected in the calculated spin density (Fig. 3b). It turns out that the calculated spin densities of the nonmagnetic P and S atoms are identical for two spin states. Nevertheless, the spin densities of the Mn atoms are distributed

asymmetrically for the opposite spin states, which leads to the broken $\hat{T}$ symmetries in two spin states. The densities of the opposite spin sublattices can be transformed into each other by the application of the $\hat{T}$ symmetry. Figure 3c shows the calculated band structure of monolayer MnPS₃, which is consistent with previous works^{40,47,48}. A direct bandgap of 2.50 eV is found at the K points⁴⁷. The bands contributed by spin-up and spin-down electrons are degenerate, and also show negligible SOC effect (see Supplementary Fig. 1). These characteristics support the SPGE in monolayer MnPS₃.

There is only one independent tensor element ($\sigma_{yy}^{(1)} = -\sigma_{yx}^{(1)} = -\sigma_{xy}^{(1)}$) of the PGE coefficients in each sublattice due to the D_3 symmetry (see Supplementary Note 2). The calculated PGE coefficients (Fig. 3d) are consistent with the symmetry. The PGE coefficients are zero at low photon energy, and become nonzero when the photon energy is larger than the bandgap. The value of the PGE coefficient can be as high as $\sim 10 \mu\text{A/V}^2$ at 3.36 eV, which is comparable to the reported charge PGE in monolayer SnTe^{49–52} and bilayer WTe₂²⁹, and 3D conventional ferroelectrics (such as BiTiO₃²⁷ and PbTiO₃²⁶). We notice that the topological Weyl semimetals^{53–55}, such as TaAs, have very large PGE coefficients due to the existence of Weyl cones⁵⁶. Similarly, we speculate AFM topological semimetals possess large SPGE if symmetry is satisfied, which deserves further study.

In order to figure out the major contribution of this large PGE coefficient, we project the $\mathbf{k}$ -solved PGE coefficients of $\sigma_{yy}^\uparrow$ at 3.36 eV

Fig. 4 Calculation results of bilayer CrCl₃. **a** Crystal structure of bilayer CrCl₃. The left panel shows the structure of a single layer, and the right panel shows the bilayer stacking (only the Cr atoms are shown). **b** Calculated densities (side views, the isosurface of 0.09 e/Å³) for spin-up (top) and spin-down (bottom) states of bilayer CrCl₃. **c** Calculated band structure. **d** PGE coefficients of the spin-up sublattice of bilayer CrCl₃.

to Fig. 3e. It can be found that the hot spots (regions where the absolute values of the $\mathbf{k}$ -solved PGE coefficients are large) appear at the $\mathbf{k}$ points in Γ M direction and close to the M point. This may originate from the photo transition from the second valence band to the first conduction band near the M point, as indicated in Fig. 3c where the valence band shows flat character. In addition, the $\hat{T}$ symmetry ensures the PGE coefficients for the spin-down state are opposite to those for the spin-up state. As a result, the total SPGE coefficient $\sigma^S = \sigma^{\uparrow} - \sigma^{\downarrow}$ is expected to be sizable and can be easily detected under visible light energy through the magneto-optic Kerr effect or the inverse spin Hall effect. In addition, the SPGE is not limited to the monolayer, because the multilayer MnPS₃ also hosts the required symmetry (see Supplementary Note 4).

To proceed, we consider the SPGE in bilayer CrCl₃. Bulk CrCl₃ is an AFM semiconductor with $T_N = 15.5$ K⁵⁷. It has been successfully exploited to the atomic limit recently, and A-type AFM order is maintained down to bilayer^{13,14,58}. In each monolayer, the Cr atoms form a honeycomb structure, and six Cl atoms in octahedral coordination surround each Cr atom. An interlayer shifting appears when stacking the monolayers (Fig. 4a). The magnetic moments of the Cr atoms are ferromagnetically coupled in the same layer while antiferromagnetically coupled between the adjacent layers, forming an A-type AFM order. Although the monolayer CrCl₃ is centrosymmetric, the bilayer stacking breaks the $\hat{I}$ symmetry. This broken $\hat{I}$ symmetry is clearly shown in the

calculated densities for two different spin states, as shown in Fig. 4b.

Figure 4c shows the calculated band structure of bilayer CrCl₃. A bandgap of 2.61 eV is obtained. The Kramers degeneracy of the band structure results from the $\hat{T}$ symmetry. The sizable PGE coefficients of each spin state are calculated and shown in Fig. 4d. There are two independent tensor elements ($\sigma_{xxx}^{\uparrow} = -\sigma_{xyy}^{\uparrow(l)} = -\sigma_{yyx}^{\uparrow(l)}$ and $-\sigma_{yxx}^{\uparrow(l)} = \sigma_{yyy}^{\uparrow(l)} = -\sigma_{xxy}^{\uparrow(l)}$) of the PGE coefficients due to the C_3 symmetry. We find that the SPGE coefficients are overall smaller than those in monolayer MnPS₃, because that the broken $\hat{I}$ symmetry originates from the adjacent layer. However, there is a large peak around 4 eV for $\sigma_{yyy}^{\uparrow(l)}$ ($\sigma_{yxx}^{\uparrow(l)}$, $\sigma_{xxy}^{\uparrow(l)}$). The PGE coefficients of spin-down states are opposite to those of spin-up ones due to the $\hat{T}$ symmetry, leading to the SPGE in bilayer CrCl₃. A similar SPGE is also expected in even-layer CrCl₃. Whereas, for CrCl₃ with odd layers, the $\hat{I}$ symmetry is restored, which prevents the SPGE. This indicates an interesting odd-even layer character of the SPGE in the few-layer CrCl₃.

DISCUSSION

According to the above calculations, the SPGE enables monolayer MnPS₃ and bilayer CrCl₃ to be promising candidates for nano spintronics devices, which can inject the pure spin current in a contactless and ultra-fast way. Furthermore, there are many other

2D collinear AFM materials that share similar lattice structures and satisfy the required symmetry of SPGE, such as Néel-type MnPS_3 , A-type NiX_2 , FeX_2 ($\text{X} = \text{Cl}, \text{Br}$), CrBr_3 , etc. Nevertheless, the materials with strong SOC effects, such as the widely investigated A-type CrI_3 and MnBi_2Te_4 , are not good candidates for the realization of the SPGE, though the symmetry requirements are satisfied. Bilayer A-type CrI_3 and MnBi_2Te_4 have similar magnetic structures with bilayer CrCl_3 , but the spin conservation is heavily violated. However, the photoexcitation can still induce charge PGE in these materials, which have already been studied recently^{59–61}. The SPGE proposed here takes advantage of the intrinsic character of the AFM state and holds great potentials to realize long-distance spin transport. Furthermore, the spin polarization of the spin current is parallel to the Néel vector, which offers the possibility to control the spin polarization of the generated spin current by manipulating the Néel vectors of these 2D antiferromagnets. Finally, we note that the switching Néel vector is equivalent to exchange the positions of the two sublattices, leading to the reverse of SPGE coefficients (see Supplementary Figs 4 and 5). Therefore, SPGE also offers an efficient method to detect the Néel vector.

In summary, we theoretically demonstrate the SPGE in 2D collinear AFM materials, which utilizes the intrinsic AFM states to generate pure spin currents. Based on the symmetry analysis of possible AFM orders in the honeycomb lattice, we conclude the suitable 2D collinear AFM candidate materials for realizing the SPGE. Using first-principles calculations, we propose that Néel-type monolayer MnPS_3 and A-type bilayer CrCl_3 , two experimental synthesized 2D collinear AFM materials, satisfying the symmetry requirement and hosting detectable SPGE for promising spintronic applications. We hope our work can stimulate further experimental explorations and broaden the research scope of the 2D AFM spintronics.

METHODS

First-principles calculations

The first-principles calculations based on density functional theory (DFT) are performed by using the VASP package. General gradient approximation according to the Perdew–Burke–Ernzerhof functional is used. The energy cutoff of the plane wave basis is set to 400 eV. The Brillouin zones are sampled with a $12 \times 12 \times 1$ mesh of $\mathbf{k}$ -points. In order to simulate the monolayers, 20 Å vacuum layers are introduced. The vdW force with DFT-D2 correction is considered. Hubbard's U terms of 3 eV and 5 eV are added for Cr and Mn atoms to account for strong electronic correlations. Wannier function method has advantages over the DFT method in calculating the photogalvanic coefficient due to the high-efficiency in the dense $\mathbf{k}$ -mesh calculations and the unnecessary of a large number of unoccupied bands²⁵. Therefore, the DFT Bloch wave functions are iteratively transformed into maximally localized Wannier functions by the Wannier90 code^{62,63}. Mn- d and Se/P- p (Cr- d and Cl- p) orbitals are used to construct the Wannier functions for MnPS_3 (CrCl_3). The effective tight-binding Hamiltonian is obtained to construct the band structures.

SPGE coefficient calculations

The PGE coefficients are calculated for spin-up and spin-down bands separately, and numerically evaluated by response theory as suggested in refs^{24,25,51}. Convergence test of $\mathbf{k}$ -mesh is performed, and $500 \times 500 \times 1$ $\mathbf{k}$ -mesh is sufficient to calculate the PGE coefficients. The 3D-like PGE coefficients are obtained assuming an active single-layer with a thickness of L_{active} ¹³

$$\sigma_{3D} = \frac{L_{\text{slab}}}{L_{\text{active}}} \sigma_{\text{slab}}, \quad (4)$$

where σ_{slab} is the calculated PGE coefficient, and L_{slab} ($L_{\text{active}} < L_{\text{slab}}$) is slab thickness.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

Received: 17 September 2020; Accepted: 9 March 2021;

Published online: 06 April 2021

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ACKNOWLEDGEMENTS

We thank Dr. Shu-Hui Zhang, Yang Gao, Wen Yang, and Ran Cheng for helpful discussions. This work is supported by the National Basic Research Program of China under No. 2019YFA0308403, National Nature Science Foundation of China under Grants No. 11947212, No. 11822407, and No. 11534001.

AUTHOR CONTRIBUTIONS

H.J. planned and integrated the research. R.C.X., D.F.S., and Y.H.L. performed the symmetry analysis, and checked the model. R.C.X. wrote the code and performed the first-principles calculations. The manuscript was written through the contributions of all authors. All authors have approved the final version of the manuscript. R.C.X., D.F.S., and Y.H.L. contribute equally to this work.

COMPETING INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

Supplementary information The online version contains supplementary material available at <https://doi.org/10.1038/s41535-021-00334-5>.

Correspondence and requests for materials should be addressed to H.J.

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