Linear Magnetoelectric Phase in Ultrathin MnPS$_3$ Probed by Optical Second Harmonic Generation

Hao Chu,1,2 Chang Jae Roh,3 Joshua O. Island,4 Chen Li,1,2 Sungmin Lee,5,6 Jingjing Chen,7 Je-Geun Park,5,6 Andrea F. Young,4 Jong Seok Lee,3 and David Hsieh1,2,*

1Department of Physics, California Institute of Technology, Pasadena, California 91125, USA
2Institute for Quantum Information and Matter, California Institute of Technology, Pasadena, California 91125, USA
3Department of Physics and Photon Science, Gwangju Institute of Science and Technology, Gwangju 61005, Republic of Korea
4Department of Physics, University of California, Santa Barbara, California 93106, USA
5Center for Correlated Electron Systems, Institute for Basic Science (IBS), Seoul 08826, Republic of Korea
6Department of Physics and Astronomy, Seoul National University (SNU), Seoul 08826, Republic of Korea
7School of Physics, Nankai University, Tianjin 300071, China

(Received 22 May 2019; published 16 January 2020)

The recent discoveries of long-range magnetic ordering in exfoliated CrI$_3$ down to a single bilayer, its magnetic order persists down to at least 5.3 nm thickness. However, so far there are no reports of an ultrathin material that directly inherits linear ME properties from its bulk precursor.

Thin film materials that exhibit the magnetoelectric (ME) effect—a coupling between magnetic (electric) polarization and external electric (magnetic) fields—have potentially broad applications in spintronics, sensing, and energy harvesting technologies [1,2]. Although ME effects in single-phase bulk crystals have been continuously pursued since their discovery in Cr$_2$O$_3$ in 1960 [3,4], advances in thin film deposition techniques over the past two decades have opened new pathways to stabilize and to control high quality materials with large ME coupling strengths via epitaxial strain and heterostructure engineering, allowing the possibility of integration into functional nanoscale devices. At present, searching for both single-phase and composite thin film materials with stronger ME coupling, and developing methods to scale them down to the ultrathin few-unit-cell limit, remain active areas of research.

The recent discoveries of long-range magnetic ordering in exfoliated van der Waals (vdW) semiconductors [5–8] potentially offer a new route to realizing ME materials in the ultrathin limit. The simplest type of ME effect, which involves a linear coupling between the external field and induced polarization, is allowed in materials that lack both spatial-inversion and time-reversal symmetries. As most of the naturally occurring vdW crystals are structurally centrosymmetric, a convenient strategy is to rely on the magnetic ordering itself to break inversion symmetry. This suggests that one should focus on antiferromagnetic (AF) rather than ferromagnetic (FM) materials because the latter generally do not break the inversion symmetry of the underlying lattice. It was recently reported that upon exfoliating CrI$_3$ down to a single bilayer, its magnetic order transforms from being FM to AF, breaking inversion symmetry and turning on a linear ME coupling in the process [5,9–11]. However, so far there are no reports of an ultrathin material that directly inherits linear ME properties from its bulk precursor.

The transition metal thiophosphates MPS$_3$ ($M=\text{Mn, Fe, Ni}$) present an interesting family of AF vdW materials for such a study [12–15]. While the AF orders in FePS$_3$ and NiPS$_3$ preserve inversion symmetry [16,17], neutron diffraction studies have shown that the AF order in bulk MnPS$_3$ breaks inversion symmetry and allows a linear ME effect [18]. However, it is not clear if the linear ME-type AF order persists down to the ultrathin limit. Because such order does not exhibit any net magnetization, a magnetooptical Kerr rotation experiment is not applicable. Although Raman spectroscopy has detected phonon anomalies in ultrathin MnPS$_3$, that are potentially associated with AF ordering [19], and spin transport measurements have shown evidence of persistent magnons in few layer MnPS$_3$ devices [20], a technique that directly probes the AF structure in nanoscopic exfoliated samples is still urgently anticipated.

Leveraging the sensitivity of optical second harmonic generation (SHG) to AF order [21], we demonstrate here...
A 5× (50×) microscope objective was used to focus light onto the bulk (exfoliated) samples at normal incidence with a spot size of approximately 30 μm (2 μm), and the intensity of the reflected SHG beam was measured using a photomultiplier tube. The pulse energy of the incoming beam was kept below 50 pJ. The SHG-RA patterns were acquired by rotating the linear polarization of the incoming and outgoing beams (parametrized by the angle ϕ), which were maintained parallel to each other in the ab plane [Fig. 1(c)]. Bulk MPS₃ single crystals were grown by a self-flux method described elsewhere [24].

Despite having a centrosymmetric crystallographic point group, we observe weak but finite SHG-RA signals from all three bulk crystals even above $T_{AF}$ [Fig. 2(a)]. This may arise from surface ED SHG or higher-rank bulk SHG processes such as electric-quadrupole (EQ) SHG [22], both of which are generally allowed in centrosymmetric materials and were found to fit the data equally well [Fig. 2(a)] [25]. For simplicity, we therefore only consider the bulk EQ term in our later fitting. The loss of sixfold rotational symmetry that arises from the stacking offset between adjacent honeycomb layers is apparent in the data, although the degree of departure from sixfold symmetry varies across samples as well as across spots within a single sample. We speculate that this may be due to spatial variations in the strength of interlayer coupling and/or variations in the concentration of 120° twins or stacking faults [29].

Below $T_{AF}$ we observe no changes in the SHG intensity from both FePS₃ and NiPS₃, but an increase in the SHG intensity from MnPS₃ as anticipated. As shown in Fig. 2(b), the low temperature SHG-RA patterns from MnPS₃ can be well fit using the coherent sum of a nonmagnetic EQ contribution and an AF order induced time-noninvariant ED contribution described by the equation [25]

$$P_{i}^{2ω} = \chi_{ijkl}^{EQ}E_{j}^{ω}E_{l}^{ω} + \chi_{ijk}^{ED}(T)E_{j}^{ω}E_{k}^{ω},$$

where $P_{i}^{2ω}$ is the induced electric polarization at the SHG frequency, $E_{i}^{ω}$ is the magnitude of the incident electric field, $\chi_{ijkl}^{EQ}$ is the temperature independent EQ susceptibility from a 2/m crystallographic point group, and $\chi_{ijk}^{ED}(T)$ is a temperature dependent ED susceptibility from the 2'/m magnetic point group describing the Néel phase [18]. As shown in Fig. 2(c), the SHG intensity from MnPS₃ shows an order parameterlike increase below $T_{AF}$. Since $\chi_{ijk}^{ED}(T)$ is directly proportional to the inversion broken Néel order parameter, we can extract the critical exponent of the order parameter (β) by fitting the temperature dependent SHG intensity to the phenomenological function $I^{2ω} \propto [a + b(T_{AF} - T)β]^2$, where a is fixed by the intensity of the EQ contribution above $T_{AF}$ and both b and β are free parameters. Best fits to the region 60 K ≤ $T$ ≤ $T_{AF}$ yield $β = 0.37(8)$ [Fig. 2(c)], which is close to the

---

**FIG. 1.** Crystal and magnetic structure of MPS₃. MPS₃ lattice viewed along the (a) c and (b) b axis. Adjacent ab planes are displaced by a/3 along the a̅ direction. (c) AF structures of MPS₃. Arrows denote spin orientation. Star denotes an inversion center of the AF structure. The inset shows the in-plane orientation of the incident electric field.
The numerical calculation of $\sim 0.369$ for the 3D Heisenberg model [30].

To investigate whether the long-range Néel order in MnPS$_3$ survives in the ultrathin limit, we exfoliated bulk crystals onto an amorphous SiO$_2$ substrate in a nitrogen purged glove box. The choice of pure SiO$_2$ over SiO$_2$=Si as a substrate was made to reduce laser induced heating arising from optical absorption by Si at 800 and 400 nm. In contrast, SiO$_2$ is transparent to both 800 and 400 nm light. Because of the poor thermal conductivity of SiO$_2$ and the relatively high laser power needed for our SHG-RA measurements on MnPS$_3$ compared to other optical techniques for studying vdW magnets such as magneto-optical Kerr microscopy or Raman spectroscopy, we face more stringent sample cooling demands [25]. To increase cooling efficiency, we deposited gold rings around the MnPS$_3$ flakes, which are thermally anchored to the cryostat sample holder by gold electrodes. Figure 3(a) shows an optical image of a typical device. Using atomic force microscopy, we identified ultrathin MnPS$_3$ nanoflakes with 5.3 and 12.5 nm step sizes above the substrate [Fig. 3(b)]. Based on previously published atomic force microscopy data on MnPS$_3$ [24], these correspond to 7 and 16 single layers of MnPS$_3$, respectively. Figure 3(c) shows typical SHG-RA patterns obtained from these flakes at a temperature of 10 K, compared with both thicker (75 nm) flakes and the bare substrate. We find that the overall SHG intensity approximately scales with the sample thickness, consistent with a bulk dominated SHG signal. The SiO$_2$ substrate contributes an isotropic background and is thus easily distinguished from the MnPS$_3$ signal.

As shown in Fig. 2(c), the ED SHG signal from MnPS$_3$ below $T_{AF}$ is of comparable magnitude to the high temperature EQ signal and is thus relatively weak overall. This is likely related to our incident 1.5 eV photon energy being well below the band gap ($\sim$3 eV) of MnPS$_3$. Consequently, when we attempted to protect the MnPS$_3$ flakes by...
encapsulation with a hexagonal boron nitride (hBN) thin flake, we found that the SHG signal was dominated by the hBN. Therefore we had to work with exposed MnPS$_3$ flakes, which are more prone to degradation. At cryogenic temperatures, we found that the SHG intensity from the few-layer regions starts to decrease over a timescale of several hours. This is likely due to surface adsorption of gas molecules and/or chemical reaction processes activated by laser exposure, as is observed in CrI$_3$ nanoflakes [31]. Therefore we were only able to acquire a limited number of SHG-RA scans at low temperatures before the onset of sample degradation. Nevertheless, our data clearly show an order parameter-like increase in the SHG intensity from the MnPS$_3$ nanoflakes below a temperature close to the bulk $T_{AF}$ value (Fig. 4), which again saturates at only several times the high temperature value. This indicates that the linear ME-type Néel ordering observed in bulk crystals persists at least down to 7 layer thick samples. Measurements collected from 3 layer samples also show a markedly higher SHG intensity at 10 K compared to 100 K [25], but their faster degradation prevented a full temperature dependence measurement from being taken.

Given that the low temperature SHG signal from MnPS$_3$ involves the interference between a time-nonvariant ED response and a time-invariant EQ response, the existence of two different 180° AF domains related by time reversal should produce different SHG intensities, analogous to the ultrathin 5.3 nm flakes exhibit an unusual symmetry. In particular, the ac mirror plane (reflection about the horizontal line in the SHG-RA patterns) that is preserved by the ultrathin vdW materials like CrI$_3$ [5] and Cr$_2$Ge$_2$Te$_6$ [6].

We note that the low temperature SHG-RA patterns from the ultrathin 5.3 nm flakes exhibit an unusual symmetry. In particular, the ac mirror plane (reflection about the horizontal line in the SHG-RA patterns) that is preserved by the ultrathin vdW materials like CrI$_3$ [5] and Cr$_2$Ge$_2$Te$_6$ [6].

This mirror symmetry breaking only becomes apparent as the material thickness is reduced and as the temperature is lowered below $T_{AF}$ [Fig. 4(c)]. We believe that this is related to a substrate induced strain because for ultrathin MnPS$_3$ flakes that are exfoliated onto SiO$_2$/Si substrates, which are much smoother than pure SiO$_2$ substrates, there is no clear evidence of ac mirror breaking in the low temperature SHG-RA patterns [25]. Model Hamiltonian calculations [33] show that a spiral spin texture that breaks ac mirror symmetry is favored over the collinear Néel order only if the second nearest-neighbor Dzyaloshinskii-Moriya interaction $D_2$ is comparable to the nearest-neighbor exchange $J_1$ in MnPS$_3$, which is around 1.5 meV according to inelastic neutron diffraction experiments [34]. However, spin Hall based measurements of $D_2$ in MnPS$_3$ put its value at merely 0.3 meV [35]. Since it is unlikely that $D_2$ is several times larger in ultrathin flakes compared to bulk crystals, especially given that Raman spectroscopy studies show no drastic changes in $T_{AF}$ or the phonon spectrum as a function of thickness [19], we rule out a noncollinear spin texture as the cause for ac mirror breaking. Instead, it is possible that the substrate induced strain tilts the easy axis, causing the Néel ordered moments to rigidly cant out of the ac plane. Further structural and magnetic characterization of thin MnPS$_3$ flakes will be necessary to confirm this hypothesis.

In conclusion, we have demonstrated SHG-RA to be a direct and effective probe of inversion breaking AF order.
parameters in exfoliated vdW materials. A linear ME-type Néel order that features in bulk crystals of MnPS$_3$ was found to survive down to the few layer limit. Future quantitative measurements of the ME coupling strength in ultrathin MnPS$_3$ samples will help to assess its potential for applications in nanoscale spintronics and optoelectronics devices.

Work at Caltech and UCSB was supported by ARO MURI Grant No. W911NF-16-1-0361. Work at GIST was supported by National Research Foundation of Korea (NRF) grants funded by the Korea government (MSIP) (No. 2018R1A2B2005331). Work at IBS CCES was supported by Institute for Basic Science (IBS) in Korea (IBS-R009-G1). D. H. and J. S. L. also acknowledge support from a GIST-Caltech collaborative grant. J. O. I. acknowledges the support of the Netherlands Organization for Scientific Research (NWO) through the Rubicon grant, Project No. 680-50-1525/2474.

*Corresponding author. dhsieh@caltech.edu


