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Antiferromagnetic ordering in van der Waals 2D magnetic material MnPS₃ probed by Raman spectroscopy

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Abstract

5

Magnetic ordering in the two-dimensional (2D) limit has been one of the most important issues in condensed matter physics for the past few decades. The recent discovery of new magnetic van der Waals materials heralds a much-needed easy route for the studies of 2D magnetism: the thickness dependence of the magnetic ordering has been examined using Ising- and *XXZ*-type magnetic van der Waals materials. Here, we investigated the magnetic ordering of MnPS₃, a 2D antiferromagnetic material of the Heisenberg-type, by Raman spectroscopy from bulk all the way down to the bilayer. The phonon modes that involve the vibrations of Mn ions exhibit characteristic changes as the temperature gets lowered through the Néel temperature. In bulk MnPS₃, the Raman peak at ~155 cm⁻¹ becomes considerably broadened near the Néel temperature, and upon further cooling is subsequently red-shifted. The measured peak positions and polarization dependences of the Raman spectra are in excellent agreement with our first-principles calculations. In few-layer MnPS₃, the peak at ~155 cm⁻¹ exhibits the characteristic red-shift at low temperatures down to the bilayer, indicating that the magnetic ordering is surprisingly stable at such a thin limit. Our work sheds light on the hitherto unexplored magnetic ordering in the Heisenberg-type antiferromagnetic systems in the atomic-layer limit.

1. Introduction

Two-dimensional (2D) van der Waals magnetic materials are attracting intense interest, not only for their technological importance but also because they can address the fundamental question of magnetism in low-dimensional systems [1]. Typically, strong fluctuations can easily destroy magnetic ordering in low-dimensional systems. For example, no magnetic ordering is possible in one dimension [2]. The 2D systems are much more interesting because the longrange order depends on both the symmetry of the order parameter and the type of spin–spin interactions, which compete with intrinsic fluctuations of either quantum and/or thermal nature. The XXZ Hamiltonian for such systems can be written as [3]

$$H = -J_{XY} \sum_{j\delta} \left(S_j^x S_{j+\delta}^x + S_j^y S_{j+\delta}^y \right) - J_I \sum_{j\delta} S_j^z S_{j+\delta}^z,$$
(1)

where J_{XY} and J_I are spin-exchange energies on the basal plane and along the *c*-axis, respectively; S_j^{α} is the $\alpha(\alpha = x, y, \text{ or } z)$ component of total spin; and *j* and δ run through all lattice sites and all nearestneighbors, respectively. All three fundamental models can be realized with the generic Hamiltonian: $J_{XY} = 0$ for the Ising model, $J_I = 0$ for the XY model and $J_{XY} = J_I$ for the Heisenberg model. According to the Mermin–Wagner theorem [4], no magnetic ordering is possible at any nonzero temperature in 1D or 2D isotropic Heisenberg models. On the other hand, 2D Ising systems can have magnetic ordering at finite temperatures according to Onsager [5].

Transition-metal phosphorus trisulfides (TMPS₃) belong to a class of 2D van der Waals magnetic materials that can be exfoliated to atomically thin layers [6, 7]. For transition-metal (TM) elements such as Fe, Ni and Mn, the materials share the same crystal structures but the magnetic phase at low temperatures varies depending on the magnetic elements: Ising (Fe), XXZ (Ni) and Heisenberg (Mn) antiferromagnets, respectively [8]. It therefore offers a unique opportunity to investigate the magnetic ordering behavior in the 2D limit for different types of exchange interactions.

Unfortunately, conventional tools such as neutron scattering are not suitable for atomically thin layers of these compounds due to a very small sample volume [1, 9]. Moreover, because antiferromagnetic phases do not have net magnetization, direct measurement of antiferromagnetic ordering using a tool such as the magneto-optical Kerr effect (MOKE), which is otherwise useful in the case of atomically thin ferromagnetic materials, is not possible either [10, 11]. Raman spectroscopy, on the other hand, has proven to be a powerful tool to investigate magnetic ordering in atomically thin 2D magnetic materials [12–16]. A simple reason is that some of the phonon modes can be coupled with magnetic ordering to exhibit characteristic changes across the critical temperature, or other Raman features due to magnetic structures, such as magnons, can be correlated with magnetic ordering. Due to the lack of more direct measurement techniques such as MOKE for antiferromagnetic materials, Raman spectroscopy has therefore become the most important tool for probing antiferromagnetic ordering in the 2D limit. For example, Raman spectroscopy has been recently utilized to demonstrate that antiferromagnetic ordering is indeed sustained down to the 2D limit of monolayer FePS₃ [13, 14]. In XXZ-type NiPS₃, many Raman spectroscopic features indicate that the magnetic ordering occurs down to the bilayer (2L) with a slight decrease in the Néel temperature as the thickness is decreased, but is strongly suppressed in the monolayer [16]. Here, we report on Raman spectroscopic analysis of the Heisenberg-type antiferromagnet MnPS₃ using Raman spectroscopy. We discovered a unique feature of the Raman spectrum that correlates well with the antiferromagnetic ordering. We further show that such magnetic ordering is surprisingly observed down to bilayer MnPS₃.

2. Method

2.1. Crystal growth and characterization

Single crystals of MnPS₃ were grown by a self-flux chemical vapor transport method in a quartz tube ampoule evacuated to high vacuum. Manganese powder (99.95%, Alfa Aesar), red phosphorous (99.99%, Sigma-Aldrich) and sulfur flakes (99.99%,



Sigma-Aldrich) were mixed in the stoichiometric ratio with 5 wt% of extra sulfur within an Ar atmosphere (<1 ppm of moisture and oxygen). The mixture was loaded in a quartz tube ampoule (10mm inner diameter and 150mm in length) and sealed at a pressure of $\sim 10^{-2}$ Torr. The sealed tube was placed in a two-zone furnace and heated to 780 °C (containing powder mixture)/720 °C for 7 d. The quartz tube was cooled to room temperature over 2 d. Single crystals are found as green and transparent plates with a typical size of $10 \,\mathrm{mm} \times 10 \,\mathrm{mm} \times 100 \,\mu\mathrm{m}$. After additional 1 day annealing under Ar atmosphere to remove extra sulfur, we verify the sample stoichiometry with energy dispersive x-ray spectroscopy (EDX). The measurements of the magnetic properties were performed using a SQUID magnetometer (Quantum Design, MPMS3), as shown in figure 2(e).

2.2. Raman measurements

The temperature-dependent Raman spectra of a bulk MnPS3 crystal was measured in a macro-Raman system using a closed-cycle He cryostat. The 488 nm (2.54 eV) line of an Ar⁺ laser was used as the excitation source for all the measurements, except for the excitation energy-dependent Raman measurements (figure S10 (stacks.iop.org/TDM/6/041001/mmedia)), and the temperature-dependent Raman measurements with the 2.41 eV excitation energy (figure S13). The excitation laser was focused by a spherical lens (f = 75 mm) to a spot of size ~50 μ m with a power of 1 mW. To measure the polarized Raman spectra of bulk and few-layer MnPS₃ at low and room temperatures, a micro-Raman system with backscattering geometry was used with the samples prepared on Si substrates with a layer of 90 nm SiO₂ by mechanical exfoliation. The atomically thin samples are relatively stable in air but can be degraded when the samples are exposed in ambient conditions for more than a week. After exfoliation, the samples were kept in a vacuum desiccator to prevent possible degradation. All the micro-Raman measurements were performed in vacuum using an optical cryostat (Oxford Micorostat He2) at temperatures of 10 K and 290 K. The laser beam was focused onto the sample by a $40 \times \text{microscope}$ objective lens (0.6 N.A.), and the scattered light was collected and collimated by the same objective. The laser power was kept below 100 μ W to avoid local heating. The scattered signal was dispersed by a Jobin-Yvon Horiba iHR550 spectrometer (2400 grooves mm⁻¹) and detected with a liquid-nitrogen-cooled backilluminated charge-coupled-device (CCD) detector. An achromatic half-wave plate was used to rotate the polarization of the linearly polarized laser beam to the desired direction. The analyzer angle was set such that photons with polarization parallel to the incident polarization pass through. Another achromatic halfwave plate was placed in front of the spectrometer to keep the polarization direction of the signal entering the spectrometer constant with respect to the groove

direction of the grating. The crystal axes of the samples were determined by comparing x-ray diffraction measurements with polarized Raman measurements. In particular, the polarization dependences of P_3 and P_5 were used to find the *a* and *b* axes in the plane (see supplementary information figure S1). For few-layer samples, the background signal from the substrate was subtracted from the Raman spectra. For measurements where the polarization dependence is not critical, we removed the analyzer to maximize the signal. Nevertheless, because the excitation laser is linearly polarized and the spectrometer efficiency has a polarization dependence, the polarization condition can be described as 'partially parallel-polarized'.

2.3. Calculation details

We calculated the vibrational modes of MnPS₃ by diagonalizing the Hessian matrix obtained from analytic derivatives of the total energy (obtained from first principles using density functional theory) with respect to ionic displacements [17, 18]. The exchange-correlation energy was calculated using the Perdew–Burke–Ernzerhof functional [19] with 12.5% of Hartree-Fock exchange energy. The Brillouin zone was sampled with $8 \times 8 \times 6$ Monkhost–Pack K-point mesh [20], and the polarized triple-zeta (pob-TZVP) basis set [21] was employed with all-electron core potentials. We optimized both the lattice parameters and the nuclear coordinates. Raman intensities were calculated using the coupled-perturbed Hartree-Fock/Kohn-Sham (CPHF) approach [22, 23]. All our calculations were performed using the CRYSTAL 17 package [24, 25].

Spin wave calculation We calculated the one-magnon spectra of MnPS₃ using a Heisenberg-type spin Hamiltonian with a single-ion easy-axis anisotropy refined from the previous inelastic neutron scattering study on MnPS₃ [26]:

$$H = \sum_{i,j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j + \Delta \sum_i (S_i^z)^2.$$
(2)

The isotropic exchange interactions, J_{ij} , up to the 3rd in-plane nearest neighbor are labelled $J_1 - J_3$. The spin Hamiltonian was diagonalized using the SpinW package [27] for the antiferromagnetic ground state. After obtaining one-magnon energies at randomly chosen 10^6 sample **q** points throughout the full Brillouin zone, we calculated the two-magnon density of states (DOS) satisfying the following sum rule:

$$D(\mathbf{k},\omega) = \pi \sum_{q,m,n} \delta \left(\hbar \omega - \hbar \omega_m(\mathbf{q}) - \hbar \omega_n(\mathbf{k} - \mathbf{q}) \right)$$
(3)

where $\omega_m(\mathbf{q})$ is the energy of the *m*th magnon band.

3. Results and discussion

Bulk TMPS₃ crystals have a monoclinic structure with the point group of C_{2h} (2/m) [28–30]. As shown in figure 1(a), the TM atoms form a honeycomb lattice

and are surrounded by six S atoms [28-30]. These S atoms themselves are connected to two P atoms above and below the TM plane, like a dumbbell. Bulk MnPS₃ exhibits Heisenberg-type antiferromagnetic ordering with the Néel temperature of 78K. Figure 1(b) shows the representative polarized Raman spectra of bulk MnPS3 at 290K and 10K measured in parallel- and cross-polarization configurations. The room-temperature spectrum is similar to the previously reported (unpolarized) Raman spectrum [29]. The high frequency modes, P₃, P₄, P₅ and P₆, are mostly due to the molecular-like vibrations from the $(P_2S_6)^{4-}$ bipyramid structures, and are similar to the corresponding modes observed in FePS3 or NiPS₃. On the other hand, the low-frequency peaks, P₁ and P₂, are from vibrations involving the TM Mn atoms [29, 31] and reflect different atomic masses and magnetic structures from those of FePS₃ or NiPS₃ (see supplementary information figure S3). The calculated results of the corresponding vibrational modes for $MnPS_3$ can be found in figure 1(c) and the supplementary information (table S1, figures S4 and S5). The discrepancy in the frequencies of the Raman spectra obtained from calculation and experiment is as small as $\sim 5 \text{ cm}^{-1}$ in the case of the most prominent mode (P_6) and less than 15 cm^{-1} (P₄). This discrepancy is small compared to the standard state-of-the-art first-principle calculations on similar TM compounds [13, 32-35]. Moreover, theory and experiment show remarkable agreement in the Raman intensities and their light-polarization dependences. Based on this agreement, we can assign the corresponding lattice vibrational mode to each peak in the measured Raman spectra. Unlike FePS₃ or NiPS₃, where the Raman spectra change dramatically as the temperature is lowered through the Néel temperature, the changes in the Raman spectra are rather subtle for MnPS₃. For example, the intensity of P1 decreases substantially and P2 is red-shifted in the spectra taken at 10K with respect to those measured at room temperature. As we will see below, the shift of P₂ correlates well with the antiferromagnetic ordering, whereas it is more difficult to establish an immediately recognizable correlation between the intensity of P1 and the magnetic ordering because of the low intensity of this peak. The small splitting of P3 and P5 might indicate a deviation from the threefold rotational symmetry, which can be attributable to the interlayer interaction. The inset of figure 1(b)shows that the P₃ splitting changes little between 290 K and 10 K. Figures 1(d) and (e) show that the position of P₅ varies slightly with the incident polarization, indicating that this peak is a superposition of two peaks with orthogonal polarization dependences (see supplementary information figure S6 for the full polarization dependence of P₅), which is similar to that observed in the corresponding Raman modes of FePS₃ [13] and NiPS₃ [16]. Due to the shifted stacking of the layers, as shown in figure 1(a), multilayer MnPS₃ has

а



100

150

200

250



a monoclinic structure which has in-plane anisotropy. This anisotropy leads to the splitting of P₃ and P₅, which are isotropic E_{g} modes in a monolayer. The Raman tensor analyses for the modes are included in the supplementary information (note S1 and figures S1 and S2).

The correlation between the Raman spectrum and the antiferromagnetic phase transition is further investigated by measuring the Raman spectrum of a bulk crystal as a function of temperature as the sample is cooled down through the Néel temperature. Figure 2(a) shows the Raman spectra in the vicinity of P_2 measured as a function of temperature in 10K steps (see supplementary information figure S7 for temperature dependence of the full spectrum). As the temperature is lowered from room temperature, this peak slightly blue-shifts due to the usual volume contraction effect, and it becomes somewhat sharper owing to the suppression of anharmonic effects at lower temperatures. As the temperature is further lowered through the Néel temperature at 78K, several additional changes are observable: the peak becomes significantly broader and the peak height is decreased. For

temperatures below the Néel temperature, the peak becomes even sharper and, at the same time, is shifted toward lower frequencies. Since the other peaks on higher frequencies (P_3 to P_6) do not show any abrupt changes in this temperature range (see supplementary information figure S8), these changes are not likely to be caused by a structural phase transition. These changes are summarized in figures 2(b)-(d) and are compared with the susceptibility data in figure 2(e). It is immediately clear that there is a very good correlation between our data: the changes in the Raman spectrum, i.e. the shift of the peak frequency (figure 2(b)) and the increase in the full width at half maximum (FWHM) (figure 2(c)), and the antiferromagnetic ordering measured from the magnetic susceptibility. This is reasonable because the P₂ mode has a significant weight from the Mn vibrations (see supplementary information figure S4). There is an offset of ~10 K between the Raman and susceptibility data: probably because the actual temperature at the measurement spot in the Raman experiments is slightly higher than at the thermometer in our cold-finger-type closedcycle cryostat due to the temperature gradient inside

450

350

400

300



Figure 2. (a) The temperature dependence of P_2 for bulk MnPS₃, measured in the partially parallel-polarized configuration. The temperature dependence of (b) the peak position, (c) FWHM of P_2 and (d) the spectral weight of the spectra in the 140–180 cm⁻¹ range. (e) The magnetic susceptibility of bulk MnPS₃. The inset is the first derivative of the magnetic susceptibility. Red and blue dashed lines indicate the Néel temperature and the temperature at which the susceptibility is maximum, respectively.

the cryostat and local heating by the laser. Figure 2(d) shows the spectral weight in the 140–180 cm⁻¹ range, which increases more or less monotonically as the temperature is decreased, with some variations near the Néel temperature. The lack of any dramatic change in the spectral weight as the temperature is varied through the Néel temperature indicates that no new scattering channel opens as a result of the magnetic transition.

A full understanding of the intriguing behavior of P2 across the Néel temperature requires further analysis. One may speculate that it is due to a coupling with the two-magnon scattering that becomes significant below the Néel temperature. The position of this feature approximately coincides with the two-magnon frequency: inelastic neutron scattering measurements found the zone-boundary magnon energy of ~11 meV $(\sim 89 \,\mathrm{cm}^{-1})$ [26]. By using the parameters obtained from [26], we calculated the spin-wave dispersion and the two-magnon DOS of MnPS₃ (see supplementary information figure S9). The calculated two-magnon DOS have a strong peak near 180 cm^{-1} . Indeed, in the Raman spectra measured with different excitation energies, there is a somewhat broad peak at ~178 cm⁻¹ (see supplementary information figure S10). However, the intensity of this feature at the frequency of P₂ $(\sim 155 \,\mathrm{cm}^{-1})$ is very weak, which implies that the coupling with this broad feature, presumably due to the two-magnon scattering, is not the major cause of the dramatic changes in the position and line shape of P₂ near the Néel temperature. Furthermore, the smooth, monotonic temperature dependence of the spectral weight of P_2 (figure 2(d)) around the Néel temperature also indicates that interaction with two-magnon scattering is less likely to be the main cause of the redshift because the contribution of two-magnon scattering opens an additional Raman channel that usually results in an abrupt increase in the spectral weight of the Raman spectrum through the Néel temperature [36, 37]. On the other hand, MnPS₃ is known to have an intermediate phase above the Néel temperature, which is characterized by short-range spin-spin correlations below 120K, where the susceptibility has a maximum [8, 38]. Figure 2(c) shows that the linewidth increases sharply below ~120 K and displays a maximum at or near the Néel temperature. The peak frequency, on the other hand, starts to red-shift below ~80 K. In general, a phase transition is accompanied by large fluctuations near the critical temperature. Such fluctuations should disrupt the coherence of the lattice vibration modes, shortening the phonon lifetime. The observed temperature dependence of the linewidth can be explained as a combination of the overall monotonic decrease due to suppression of anharmonic effects at low temperatures and the sharp increase of the linewidth due to fluctuations near the phase transition. A similar trend of increasing was observed in the linewidth of the corresponding Raman mode of FePS₃ near the Néel temperature, although less dramatically (see supplementary information figure S11). This broadening of the Raman peak and its subsequent red-shift as the temperature



is lowered below the Néel temperature is attributed to spin-phonon coupling, namely, the change in the phonon energy due to magnetic ordering.

We should also note that the line shape of P_2 becomes significantly asymmetric near the Néel temperature, reminiscent of a Fano resonance. However, since the two-magnon continuum has little overlap with this phonon energy, it is not likely that the asymmetry is a result of a Fano-like resonance with the magnon band. We suspect that the asymmetry is related to the disruption of the phonon coherence near the phase transition due to the large fluctuations. Another change in the Raman spectrum is the apparent disappearance of P₁ at low temperature, as shown in the inset of figure 1(b). This peak is better resolved in the spectra measured with the 2.41 eV excitation energy and seems to have similar temperature dependences of the position and FWHM as P2 (see supplementary information note S2, figures S12 and S13). We also find that P₆ becomes slightly asymmetric at low temperatures (figure 3(c)). The other peaks (P_3 to P_6) do not show any abrupt changes in the line shape or the intensity near the Néel temperature, except that the FWHM of P6 increases at low temperatures due to the asymmetry of the peak (see supplementary information figure S8(k)). Since this mode is due to a breathing-like vibration of the $(P_2S_6)^{4-}$ bipyramid structures (A_g) , a magnetic-ordering-induced splitting is not possible. At the same time, polarized Raman scattering measurements show that the asymmetric line shape does not vary with polarization (see supplementary information figure S14). The origin of this asymmetric line shape at low temperature needs further investigation.

To investigate the dependence of the magnetic ordering on the number of layers, we measured the Raman spectra of several exfoliated samples at both room temperature and 10 K. Figures 3(a) and (b) show the optical and atomic force microscope images of the sample measured. Bilayer, trilayer (3L), five-layer (5L) and thick 14 nm regions are readily identified in the figures. We also compare the Raman spectra taken at 290K and 10K for different numbers of layers in figure 3(c). The spectra from a very thick (~1 μ m), bulklike exfoliated sample are also plotted for comparison. Because of the very small intensity of P_2 , it is rather difficult to pinpoint the phase transition temperature precisely, unlike in the case of the bulk sample. However, the comparison shows convincingly enough that whereas other peaks blue-shift in going from 290 K to 10K, P2 shows a noticeable red-shift for all thicknesses, implying that the magnetic ordering is surprisingly sustained down to 2L. For the monolayer, the P₂ signal could not be resolved due to extremely weak intensity (see supplementary information note S3 and figure S15). For comparison, the magnetic ordering is found down to the monolayer limit for Isingtype FePS₃ [13], whereas in XXZ-type NiPS₃ it is only stable down to 2L before being completely suppressed

in the monolayer [16]. In Heisenberg-type MnPS₃, the magnetic ordering is supposedly more susceptible to fluctuations due to its isotropic nature, and is thus expected to be more fragile in the 2D limit than in *XXZ*-type NiPS₃. Our experimental results indicate that the Heisenberg-type antiferromagnet MnPS₃ can still host magnetic ordering down to two layers.

4. Conclusions

We investigated the thickness dependence of the magnetic phase transition in Heisenberg-type 2D antiferromagnetic material $MnPS_3$ by Raman spectroscopy. The phonon modes that involve the vibrations of the Mn ions exhibit characteristic changes as the temperature is lowered through the Néel temperature. In bulk $MnPS_3$, the Raman peak at ~155 cm⁻¹ becomes considerably broader near the Néel temperature and is red-shifted below the Néel temperature. Another weak peak at ~117 cm⁻¹ also shows similar changes in the line shape near the Néel temperature, although the changes are less dramatic. Using these changes in the phonon modes induced by the magnetic ordering, we found that the magnetic ordering is surprisingly stable down to the bilayer MnPS₃.

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Author contributions

J-GP and HC conceived the experiments. SL and SS grew and characterized bulk MnPS₃ crystals. KK, SYL, JK and J-UL carried out Raman measurements. PK carried out first-principles calculations on the lattice vibrations and Raman spectra. KP calculated the spin waves. All the authors discussed the data and wrote the manuscript together.

Note added in proof

After submission of this work, we became aware of a similar study by another group [39].

Additional information

Supplementary information is available in the online version of the paper.

Competing financial interests

The authors declare no competing financial interests.

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