Antiferromagnetic ordering in van der Waals 2D magnetic material MnPS$_3$ probed by Raman spectroscopy

Kangwon Kim$^1$, Soo Yeon Lim$^1$, Jungcheol Kim$^1$, Jae-Ung Lee$^{1,2}$, Sungmin Lee$^{2,4}$, Pilkwang Kim$^{2,5}$, Kisoo Park$^{2,4}$, Suhan Son$^{4,5}$, Cheol-Hwan Park$^{3,4}$, Je-Geun Park$^{1,4}$ and Hyeonsik Cheong$^1$

$^1$ Department of Physics, Sogang University, Seoul 04107, Republic of Korea
$^2$ Department of Physics, Ajou University, Suwon 16499, Republic of Korea
$^3$ Center for Correlated Electron Systems, Institute for Basic Science, Seoul 08826, Republic of Korea
$^4$ Department of Physics and Astronomy, Seoul National University, Seoul 08826, Republic of Korea
$^5$ Center for Theoretical Physics, Seoul National University, Seoul 08826, Republic of Korea

E-mail: cheolhwan@snu.ac.kr, jgpark10@snu.ac.kr and hcheong@sogang.ac.kr

Keywords: antiferromagnetism, magnetic ordering, isotropic Heisenberg model, MnPS$_3$, manganese phosphorus trisulfide, Raman spectroscopy

Abstract

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 MnPS$_3$, a 2D antiferromagnetic material. In bulk MnPS$_3$, the Raman peak at $\sim 155$ cm$^{-1}$ becomes considerably broadened near the Néel temperature, and upon further cooling it 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 MnPS$_3$, the peak at $\sim 155$ 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 long-range 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

$$H = -J_{XY} \sum_{j,\delta} (S_{j+\delta}^x S_j^x + S_{j+\delta}^y S_j^y) - J_1 \sum_{j,\delta} S_{j+\delta}^z S_j^z,$$

where $J_{XY}$ and $J_1$ are spin-exchange energies on the basal plane and along the $c$-axis, respectively; $S_{\alpha}^\alpha$ is the $\alpha (\alpha = x, y, or z)$ component of total spin; and $j$ and $\delta$ run through all lattice sites and all nearest-neighbors, respectively. All three fundamental models can be realized with the generic Hamiltonian: $J_{XY} = 0$ for the Ising model, $J_1 = 0$ for the XY model and $J_{XY} = J_1$ 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 (T MPS3) 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 (10 mm inner diameter and 150 mm in length) and sealed at a pressure of ~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 mm × 10 mm × 100 µm. 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 µm 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 Microrstat He2) at temperatures of 10 K and 290 K. The laser beam was focused onto the sample by a 40 × 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 µW 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 back-illuminated 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 half-wave 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 MnPS\(_3\) 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 MnPS\(_3\) using a Heisenberg-type spin Hamiltonian with a single-ion easy-axis anisotropy refined from the previous inelastic neutron scattering study on MnPS\(_3\) [26]:

\[
H = \sum_{ij} J_{ij} S_i \cdot S_j + \Delta \sum_i (S_i^z)^2. \quad (2)
\]

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:

\[
D(k, \omega) = \pi \sum_{q,m,n} \delta (\hbar \omega - \hbar \omega_m(q) - \hbar \omega_n(k - q))
\]

where \( \omega_m(q) \) is the energy of the \( m \)th magnon band.

3. Results and discussion

Bulk TMPS\(_3\) crystals have a monoclinic structure with the point group of \( C_{2h} \) (2\( \text{/m} \)) [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 MnPS\(_3\) exhibits Heisenberg-type antiferromagnetic ordering with the Néel temperature of 78 K. Figure 1(b) shows the representative polarized Raman spectra of bulk MnPS\(_3\) at 290 K and 10 K 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, \( P_3, P_4, P_5 \) and \( P_6 \), are mostly due to the molecular-like vibrations from the \( (P_\text{Sb})^4^- \) bipyramid structures, and are similar to the corresponding modes observed in FePS\(_3\) or NiPS\(_3\). On the other hand, the low-frequency peaks, \( P_1 \) and \( P_2 \), are from vibrations involving the TM Mn atoms [29, 31] and reflect different atomic masses and magnetic structures from those of FePS\(_3\) or NiPS\(_3\) (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 \( \pm 5 \text{cm}^{-1} \) in the case of the most prominent mode \( P_6 \) and less than \( 15 \text{cm}^{-1} \) \( P_4 \). 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 FePS\(_3\) or NiPS\(_3\), 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 MnPS\(_3\). For example, the intensity of \( P_1 \) decreases substantially and \( P_2 \) is red-shifted in the spectra taken at 10 K with respect to those measured at room temperature. As we will see below, the shift of \( P_2 \) correlates well with the antiferromagnetic ordering, whereas it is more difficult to establish an immediately recognizable correlation between the intensity of \( P_1 \) and the magnetic ordering because of the low intensity of this peak. The small splitting of \( P_3 \) and \( P_5 \) might indicate a deviation from the three-fold rotational symmetry, which can be attributable to the interlayer interaction. The inset of figure 1(b) shows that the \( P_3 \) splitting changes little between 290 K and 10 K. Figures 1(d) and (e) show that the position of \( P_5 \) 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 \( P_5 \)), which is similar to that observed in the corresponding Raman modes of FePS\(_3\) [13] and NiPS\(_3\) [16]. Due to the shifted stacking of the layers, as shown in figure 1(a), multilayer MnPS\(_3\) has
a monoclinic structure which has in-plane anisotropy. This anisotropy leads to the splitting of $P_3$ and $P_5$, 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 10 K 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 78 K, 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 $P_2$ 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 closed-cycle cryostat due to the temperature gradient inside.

Figure 1. (a) Crystal and magnetic structures of MnPS$_3$. (b) Polarized Raman spectra of bulk MnPS$_3$ at 10 K and 290 K in parallel and cross-polarization configurations. (c) Calculated polarized Raman spectra of bulk MnPS$_3$ in parallel and cross-polarization configurations. (d) and (e) Incident polarization dependence of Raman spectra at (d) 290 K and (e) 10 K.
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 P$_2$ 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 (~89 cm$^{-1}$) [26]. By using the parameters obtained from [26], we calculated the spin-wave dispersion and the two-magnon DOS of MnPS$_3$ (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 P$_2$ (~155 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 P$_2$ 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 red-shift 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, MnPS$_3$ is known to have an intermediate phase above the Néel temperature, which is characterized by short-range spin–spin correlations below 120 K, 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 FePS$_3$ 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 $P_1$ 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 $P_2$ (see supplementary information note S2, figures S12 and S13). We also find that $P_6$ 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 $P_6$ 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 $(P_2S_6)^{2-}$ 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 290 K and 10 K for different numbers of layers in figure 3(c). The spectra from a very thick (~1 µm), bulk-like 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 10 K, $P_2$ shows a noticeable red-shift for all thicknesses, implying that the magnetic ordering is surprisingly sustained down to 2L. For the monolayer, the $P_2$ 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 Ising-type FePS$_3$ [13], whereas in XXZ-type NiPS$_3$ it is only stable down to 2L before being completely suppressed.

Figure 3. (a) Optical contrast and (b) atomic force microscope images of few-layer MnPSe$_3$ on SiO$_2$/Si substrate. (c) Raman spectra of few-layer and bulk MnPSe$_3$ at 290 K and 10 K, measured in the partially parallel-polarized configuration.
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 MnPS₃ 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 MnPS₃, 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.

Acknowledgments

This work was supported by the National Research Foundation (NRF) grants funded by the Korean government (MSIT) (NRF-2019R1A2C3006189 and No. 2017R1A5A1014862, SRC program: vdWMRC center, No. 2016R1A1A1A05919979), by a grant (2013M3A6A5073173) from the Center for Advanced Soft Electronics under the Global Frontier Research Program of IBS and by the Creative-Pioneering Research Program through Seoul National University. Computational resources have been provided by KISTI Supercomputing Center (KSC-2018-C2-0002). The work at IBS CCES was supported by the Institute of Basic Science (IBS) in Korea (Grant No. IBS-R009-G1).

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.

ORCID iDs

Je-Geun Park https://orcid.org/0000-0002-3930-4226
Hyeonsik Cheong https://orcid.org/0000-0002-2347-4044

References

[1] Burch K S, Mandrus D and Park J-G 2018 Magnetism in two-dimensional van der Waals materials Nature 563 47–52
[2] Bethe H 1931 Zur Theorie der Metalle Z. Theor. Met. 71 205–26
[3] Mahan G D 2011 Condensed Matter in a Nutshell (Princeton, NJ: Princeton University Press)
[4] Mermin N D and Wagner H 1966 Absence of ferromagnetism or antiferromagnetism in one- or two-dimensional isotropic Heisenberg models Phys. Rev. Lett. 17 1133–6
[5] Onsager L 1944 Crystal statistics. I. A two-dimensional model with an order–disorder transition Phys. Rev. 65 115–49
[6] Kuo C-T et al 2016 Exfoliation and Raman spectroscopic fingerprint of few-layer NiPS₃ van der Waals crystals Sci. Rep. 6 20904
[7] Long G et al 2017 Isolation and characterization of few-layer manganese thiophosphate ACS Nano 11 11330–6
[8] Joy P A and Vasudevan S 1992 Magnetism in the layered transition–metal thiophosphates MPS₃ (M = Mn, Fe, and Ni) Phys. Rev. B 46 5425–33
[9] Park J-G 2016 Opportunities and challenges of 2D magnetic van der Waals materials: magnetic graphene? J. Phys.: Condens. Matter 28 301001
[10] Gong C et al 2017 Discovery of intrinsic ferromagnetism in two-dimensional van der Waals crystals Nature 546 265–9
[11] Huang B et al 2017 Layer–dependent ferromagnetism in a van der Waals crystal down to the monolayer limit Nature 546 270–3
[12] Tian Y, Gray M J, Ji H, Cava R J and Burch K S 2016 Magnetoelastic coupling in a potential ferromagnetic 2D atomic crystal 2D Mater. 3 025035
[13] Lee J-U, Lee S, Ryoo J-H, Kang S, Kim T Y, Kim P, Park C-H, Park J and Cheong H 2016 Ising-type magnetic ordering in atomically thin FePS₃ Nano Lett. 16 7433–8
[14] Wang X et al 2016 Raman spectroscopy of atomically thin two-dimensional magnetic iron phosphorus trisulfide (FePS₃) crystals 2D Mater. 3 031009
[15] Jin W et al 2018 Raman fingerprint of two terahertz spin wave branches in a two-dimensional honeycomb Ising ferromagnet Nat. Commun. 9 5122
[16] Kim K, Lim SY, Lee J-U, Lee S, Kim T Y, Park K, Jeon G S, Park C-H, Park J-G and Cheong H 2019 Suppression of magnetic ordering in XXZ-type antiferromagnetic monolayer NiPS₃ Nat. Commun. 10 345
[17] Pascale F, Zicovich-Wilson C M, López Gejo F, Civalleri B, Orlando R and Dovessi R 2004 The calculation of the vibrational frequencies of crystalline compounds and its implementation in the crystal code J. Comput. Chem. 25 888–97
Zicovich-Wilson C M, Pascale F, Roetti C, Saunders V R, Orlando R and Dovesi R 2004 Calculation of the vibration frequencies of α-quartz: the effect of Hamiltonian and basis set J. Comput. Chem. 25 1873–81

Perdew J P, Burke K and Ernzerhof M 1996 Generalized gradient approximation made simple Phys. Rev. Lett. 77 3865–8

Perdew J P, Burke K and Ernzerhof M 1996 Generalized gradient approximation made simple Phys. Rev. Lett. 77 3865–8

Pack J D and Monkhorst H J 1977 Special points for Brillouin-zone integrations Phys. Rev. B 16 1748–9

Peintinger M F, Oliveira D V and Bredow T 2013 Consistent Gaussian basis sets of triple-zeta valence with polarization quality for solid-state calculations J. Comput. Chem. 34 451–9

Maschio L, Kirtman B, Rérat M, Orlando R and Dovesi R 2013 Ab initio analytical Raman intensities for periodic systems through a coupled perturbed Hartree–Fock/Kohn–Sham method in an atomic orbital basis. II. Validation and comparison with experiments J. Chem. Phys. 139 164102

Maschio L, Kirtman B, Rérat M, Orlando R and Dovesi R 2013 Ab initio analytical Raman intensities for periodic systems through a coupled perturbed Hartree–Fock/Kohn–Sham method in an atomic orbital basis. I. Theory J. Chem. Phys. 139 164101

Dovesi R et al 2017 CRYSTAL17 User’s Manual (University of Torino)

Dovesi R et al 2018 Quantum-mechanical condensed matter simulations with crystal Wiley Interdiscip. Rev. Comput. Mol. Sci. e1360

Wildes A R, Roesli B, Lebech B and Godtfred K W 1998 Spin waves and the critical behaviour of the magnetization in MnPS₃ J. Phys.: Condens. Matter 10 6417–28

Toth S and Lake B 2015 Linear spin wave theory for single-Q incommensurate magnetic structures J. Phys.: Condens. Matter 27 166002

Berciaud P 1986 Review on structural and chemical properties of transition metal phosphorus trisulfides MPS₃ Solid State Ion. 22 5–30

Bertassoni M, Marra G L, Benedek G, Miglio L, Jouanne M, Julien C, Scagliotti M and Balkanski M 1988 Lattice dynamics of layered MPX₃ (M = Mn,Fe,Ni,Zn; X = S,Se) compounds Phys. Rev. B 38 12089–99

Susner M A, Chysanovichyus M, McGuire M A, Ganesh P and Makyrovych P 2017 Metal thi- and selenophosphates as multifunctional van der Waals layered materials Adv. Mater. 29 1602852

Hashemi A, Komsa H-P, Puska M and Krasheninnikov A V. 2017 Vibrational properties of metal phosphorus trichalcogenides from first-principles calculations J. Phys. Chem. C 121 27207–17

Jiang Y C, Gao J and Wang L 2016 Raman fingerprint for semi-metal WTe₂ evolving from bulk to monolayer Sci. Rep. 6 19624

Du T, Xu B, Wu M, Liu G and Ouyang C 2016 Insight into the vibrational and thermodynamic properties of layered lithium transition-metal oxides LiMO₂ (M = Co, Ni, Mn): a first-principles study J. Phys. Chem. C 120 5876–82

Larbi T, Doll K and Manoubi T 2016 Density functional theory study of ferromagnetically and ferrimagnetically ordered spinel oxide Mn₆O₁₄ A quantum mechanical simulation of their IR and Raman spectra J. Alloys Compd. 688 692–8

Champagne A, Shi L, Ouisse T, Hackens B and Charlier J-C 2018 Electronic and vibrational properties of V₇C₆-based MXenes: from experiments to first-principles modeling Phys. Rev. B 97 115439

Toms D J and O’Sullivan W J 1974 Light scattering from two-magnon modes in K₂NiF₄ Solid State Commun. 14 715–8

Choi K-Y, Lemmens P, Heydhausen D, Güntherodt G, Baumann C, Klingeler R, Reutler P and Büchner B 2008 Anomalous orbital dynamics in LaSeMnO₄ observed by Raman spectroscopy Phys. Rev. B 77 064415

Wildes A R, Kennedy S I and Hicks T J 1994 True two-dimensional magnetic ordering in MnPS₃ J. Phys.: Condens. Matter 6 L335–41

Shin Y-J, Tan Q-H, Liu X-L, Gao Y-F and Zhang J 2019 Probing the Magnetic Ordering of antiferromagnetic Mn₆O₁₄ by Raman spectroscopy J. Phys. Chem. Lett. 10 3087–93