Experimental report

07/09/2022

Proposal: **4-01-1728**

Council: 4/2021

Title: Magnetic dynamics in the high-pressure phase of antiferromagnet MnPS3

Research area: Physics

This proposal is a new proposal

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Samples: MnPS3

Instrument	Requested days	Allocated days	From	To
IN5	4	4	07/09/2021	13/09/2021

Abstract:

The MPX3 materials (M = Fe, Ni, Mn; X = S, Se) are a family of quasi-2D antiferromagnetic insulators, with most sharing a similar monoclinic unit cell and C2/m space group. The metal M2+ ions form a honeycomb lattice in the ab planes, which are weakly coupled by van der Waals forces. These layered magnets are of significant current interest in low-dimensional materials communities.

Our previous studies show that MPX3 materials undergo two structural transitions under pressure, the second of which coincides with metallisation or the emergence of superconductivity. These transitions are also seen to dramatically modify the magnetic structure in these compounds. MnPS3 undergoes the first transition at the lowest pressure in the family and has dynamics well studied previously at ambient pressure.

We propose to advance the existing work by measuring the evolution of magnetic dynamics into the first high pressure phase of MnPS3 for the first time. We will use high-pressure apparatus at low-temperature on IN5 to measure inelastic magnetic scattering above the 2 GPa transition. This work will also help to develop high pressure capabilities for inelastic measurement at the ILL.

Report for experiment 4-01-1728: Magnetic dynamics in the high-pressure phase of antiferromagnet $MnPS_3$

$MnPS_3$ belongs to a family of van der Waals layered compounds. It is magnetic, adopting long-ranged antiferromagnetic order below its Néel temperature of 78 K at ambient pressure [1]. It is also a Mott insulator, but when subjected to a hydrostatic pressure it undergoes a metal-insulator transition at ~28 GPa [2].

The compound undergoes a series of structural phase transitions under pressure. Similar behaviour has been observed and quantified in $FePS_3$, a sister compound [4]. It has a monoclinic structure with the space group $C\frac{2}{m}$ at ambient pressure, with angle $\beta \sim 107°$ [2]. The first structural change occurs at ~2 GPa, involving a shear of the van der Waals planes. The $C\frac{2}{m}$ space group is maintained, but the monoclinic angle reduces to $\beta \sim 90°$. The second structural change involves a transition to a higher symmetry space group, yet to be identified in $MnPS_3$, and occurs concurrently with the metal-insulator transition.

The magnetic properties for $MnPS_3$ should differ between the structural phases. IN5 was used to measure the spin waves from powdered $MnPS_3$ under pressure. The experiment aimed to measure the magnetic dynamics as a function of pressure in the two monoclinic phases, at close to ambient pressure and between 2 and 28 GPa, which were achievable with a Paris-Edinburgh (PE) cell. An incident wavelength of 2 Å was chosen to access the full dynamic range of the spectral weight.

The experiment began with a measurement of the "empty" cell containing only the methanol-ethanol pressure medium in a TiZr gasket to quantify the background from the sample environment and to test the cooling protocol for the PE cell. The "empty cell" was measured for a total of ~12 hours. The cell was then removed and loaded with powdered $MnPS_3$ sample. The cell was pressurised to a nominal value of 1.3 GPa to seal the gasket. The pressure was sufficiently low that the sample maintained its ambient-pressure crystal structure. The cooling protocol was to initially cool the cell to 80 K by immersing in liquid nitrogen. The nitrogen was then blown off and the cell was cooled to 25 K using the dedicated cryorefrigerator. After sufficient statistics were collected, amounting to ~24 hours, the cell was warmed to 300 K and the pressure was increased to a nominal value of 4 GPa, above the first structural transition. The cell was then cooled to 25 K using the established protocol and measurements continued. The scattering at this pressure was weaker as the distance between the anvils of the PE cell becomes smaller with increasing pressure, masking the signal, and data were collected for a total of ~70 hours for sufficient statistics. The pressure in the cell was not measured directly, but was determined from a previously-determined load-vs-pressure curve.

Figure 1 show the spin-wave scattering from powdered $MnPS_3$ at the two pressures and at 25 K. The "empty cell" data were crucial for data reduction, and the data in figure 1 have had the estimated background from the sample cell subtracted. The subtraction is not perfect. In particular, there is increased scattering close to the elastic line at small momentum transfers, some extra intensity at the maximum limit of the energy transfer, and some spurious scattering close to the elastic line between $\sim 3.5 \leq Q \leq 4.5$ Å^{-1}. However, overall the quality of the data is very good and clear, analysable signals can be seen.

Figure 1(a) shows the scattering at 1.5 GPa. The scattering may be compared to the measured spin waves from single crystals at ambient pressure, which show the dynamics of

$MnPS_3$ to be well-described by a Heisenberg Hamiltonian with a small uniaxial single-ion anisotropy [5]. Exchange interactions up to the third in-plane nearest-neighbours must be included to model the dynamic structure factor. The energy band width for the spin waves has the range $\sim 0.5 \leq \Delta E \leq 11.5$ meV, with strong spectral weight at the upper range as the spin waves at the Brillouin zone boundaries have very little dispersion. The data measured at 1.5 GPa correspond well to the expected spin wave scattering, with strong spectral weight at $\Delta E \sim 11.5$ meV and dispersive modes emerging from momentum transfers that correspond to the magnetic Bragg peaks.

Figure 1(b) shows the background-subtracted spin wave scattering measured at 4 GPa. The scattering is qualitatively very similar to that at 1.5 GPa, indicating that $MnPS_3$ has the same magnetic structure above the first pressure-induced structural phase transition. Quantitatively, the upper energy limit of the scattering has increased to $\Delta E \sim 12.5$ meV indicating that the magnetic exchange parameters have changed. Further analysis will determine the extent of the changes.

The selected incident wavelength of 2 Å gave a sufficiently large dynamic range to follow the evolution of the full spectral distribution as a function of pressure. However, the energy resolution of the chosen configuration was insufficient to probe whether the spin wave gap, which is $\Delta E \sim 0.5$ meV at ambient pressure [5], changed as a function of pressure. A future experiment will be required to focus on smaller energy transfers to determine the evolution of the gap.

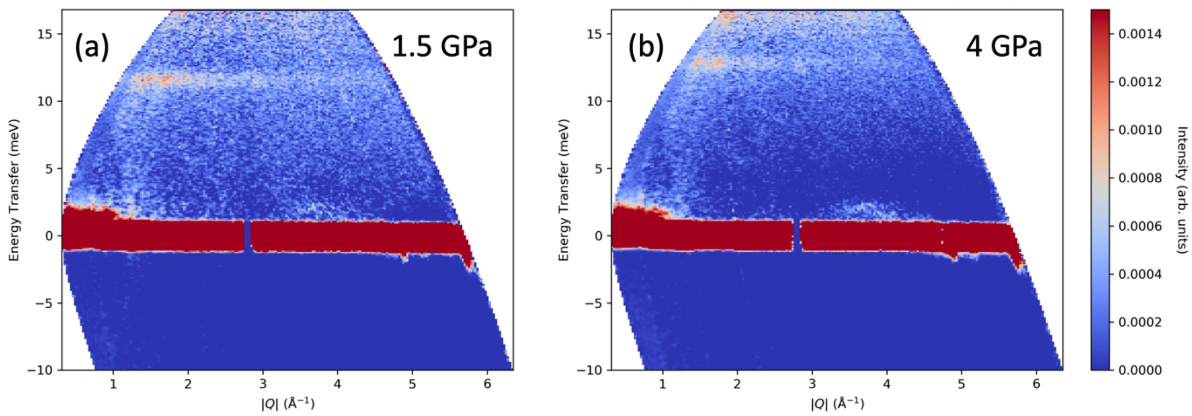

Figure 1: The spin wave scattering from $MnPS_3$ at 25 K measured under pressures of (a) 1.5 GPa and (b) 4 GPa. An estimate for the background from the instrument and sample environment has been subtracted.

References:

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[4] C. R. S. Haines *et al.*, PRL **121** (2018) 266801
[5] A. R. Wildes *et al.*, JPCM **10** (1998) 6417