Pressure Dependence of the Magnetic Properties of MnPS$_3$

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Abstract. The pressure dependence of the magnetic properties of two-dimensional transition metal phosphorus trichalcogenides MnPS$_3$ has been investigated. In this compound, the lattice constant $c$ which includes the van der Waals gap is reported to decrease rather rapidly with pressure, compared with the lattice constants $a$ and $b$. The magnitude of the interlayer exchange interaction can be increased by reducing the van der Waals gap with applying a pressure. While the effective magnetic moment is almost independent of the pressure and close to spin only value of Mn$^{2+}$ ion, the Néel temperature $T_N$ and the spin flop magnetic field $H_F$ show the pressure dependence. The increase rate of $T_N$ and the decrease rate of $H_F$ are 13 K/GPa and 4.0 $\times$ 10$^3$ Oe/GPa, respectively. These results are well explained by the increase of the dimensionality and the decrease of the anisotropy.

1. Introduction

Two-dimensional layered magnetic compounds have been extensively studied because of their curious behaviors. Transition metal trichalcogenides MPX$_3$ (M = transition metal ions, X = chalcogenide ions) are a cation ion ordered CdCl$_2$-type two-dimensional layered magnetic

![Figure 1. Schematic array of Mn ions in MnPS$_3$. The arrows indicate the direction of magnetic moment of the ordered state.](image)
compound[1]. They belong to a monoclinic crystal system and their space group is $C2/m$. The M ion has a localized magnetic moment and forms a honeycomb lattice. The array of M ions in MPX$_3$ is schematically shown in Fig. 1. Super exchange interaction between M ions is mediated by sulfur ions. The magnetic structure varies with the combination of M and X. MnPS$_3$ is antiferromagnet with a Néel temperature $T_N$ of 78 K. The magnetic structure of MnPS$_3$ consists of Mn ions coupled antiferromagnetically to their three nearest neighbors in the layer, and interlayer coupling of spins is also antiferromagnetic. The direction of the magnetic moment in the ordered state is perpendicular to the $ab$ plane (along the $c^*$ direction) [2]. Previously, Zhang et al. intercalated organic molecules in the inter-layer distance of MnPS$_3$ and measured the change of magnetic properties [3]. However, as Mn ions are partially lost in the intercalation process, the effect of the change of the inter-layer distance is not strictly estimated. Masubuchi et al. reported the pressure dependence of the lattice parameters and concluded that the pressure coefficients of $a$, $b$ and $c$ were $8.1 \times 10^{-3}$ Å/GPa, $-5.4 \times 10^{-2}$ Å/GPa and $-9.8 \times 10^{-2}$ Å/GPa, respectively [4]. The effect of the pressure on $c$ is larger than that on $a$ and $b$. As the inter-layer distance is reduced by the pressure, it is expected that the magnetic interaction between the layers increases with a pressure and that the three dimensionality is increased.

Then, we have firstly measured the magnetization of MnPS$_3$ at ambient and applied pressure. In this study, we report the change of magnetization by the pressure.

2. Experimental

Single crystalline MnPS$_3$ samples were synthesized by the chemical vapor transport method using iodine as the transport agent. Stoichiometric amounts of Mn, P and S powders were thoroughly mixed for 30 minutes in an Ar atmosphere. The mixed powders and the iodine powders were sealed in a quartz tube at about $2.0 \times 10^{-3}$ Torr. The chemical vapor transport reaction was carried out for 120 h in a two-zone electric furnace. The temperature of charge zone and the growth zone are 1003 and 903 K, respectively. The distance between the charge and growth zone was about 10 cm. Single crystals about $3.0 \times 3.0$ mm were obtained.

X-ray powder diffraction (XRD) measurement was carried out using RIGAKU RINT 1100 with a Cu-K$\alpha_1$ line. The obtained sample was found to be of single phase because no impurity phase was observed. Compositional analysis was carried out using HORIBA EMAX-5700. The composition ratio of the single crystals corresponded to that of starting materials within 5 percent of errors. The magnetization measurements at ambient and applied pressures were carried out between 5 and 300 K using Quantum Design MPMS system. The pressure was calibrated with the superconducting transition temperature of lead. Daphne oil 7373 was used as a transmitting fluid.

![Figure 2. Temperature dependence of magnetization $M$ at ambient pressure and 0.47 GPa with a magnetic field of 10 kOe applied parallel to $c^*$ axis.](image)
3. Results and Discussion
The temperature dependences of the magnetization $M$ at ambient pressure and 0.47 GPa with a magnetic field of 10 kOe applied parallel to $c^*$ axis are shown in Fig. 2. A Néel temperature is usually defined by the temperature at which the temperature derivative of the magnetization has a maximum in a two-dimensional magnetic system [5]. The Néel temperature increases from 78 K to 86 K with a pressure. However, the broad peak around 120 K observed at ambient pressure, which is typical for the two-dimensional magnetic materials is remained at 0.47 GPa. The temperature dependence of the inverse magnetic susceptibility at ambient pressure and 0.47 GPa is shown in Fig. 3. The inverse magnetic susceptibility obeys the Curie-Weiss law above 200 K. The effective magnetic moment $\mu_{\text{eff}}$ of ambient pressure and 0.47 GPa are 5.51 $\mu_B$ and 5.29 $\mu_B$, respectively. Those are close to spin only value of Mn$^{2+}$ ion. The Weiss temperatures $\Theta_p$’s estimated by the extrapolation to the temperature axis are -251 K at ambient pressure and -235 K at 0.47 GPa, respectively. This may suggest the increase of the ferromagnetic interaction. However, it is not considered to have a sufficient meaning because the temperature range used for the extrapolation is narrow. The magnetic field dependence of the magnetization $M$ at ambient pressure and 0.47 GPa at 10 K with an applied magnetic field parallel to $c^*$ axis is shown in Fig. 4. The drastic change of the magnetization around $3.8 \times 10^4$ Oe is known to be due to the spin flopping as the direction of magnetic moment of Mn ions in ordered state is parallel to the applied magnetic field. The spin flop magnetic field $H_F$ at 10 K decrease from

![Figure 3](image3.png)

**Figure 3.** Temperature dependence of the inverse magnetic susceptibility at ambient pressure and 0.47 GPa with a magnetic field of 10 kOe applied parallel to $c^*$ axis.

![Figure 4](image4.png)

**Figure 4.** Magnetic field dependence of $M$ at ambient pressure and 0.47 GPa at 10 K with an applied magnetic field parallel to $c^*$ axis.
3.8 × 10^4 Oe to 3.6 × 10^4 Oe with a pressure. Figure 5 shows the pressure dependence of $T_N$ and $H_F$. The solid lines are determined by the least-square method. The increase rate of $T_N$ and the decrease rate of $H_F$ are 13 K/GPa and 4.0 × 10^3 Oe/GPa, respectively. Assuming the Néel temperature is proportional to the geometric average of the inter and intra layer exchange interaction constants, the increase of $T_N$ is considered to be due to the increase of inter layer interaction caused by the decrease of inter layer distance. By the simple model, $H_F$ is known to be proportional to the square root of anisotropic constant. The decrease of $H_F$ indicates that the anisotropic constant is decreased with a pressure.

The broad peak which is characteristic to the low dimensional compounds is still remained in the temperature dependence of the magnetization and the change of $H_F$ is not large below 1 GPa. In order to observe the change of the dimensionality, the experiment under the more intense magnetic field is necessary and now in progress.

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