MAGNETISM OF Py-INTERCALATED MnPS3
K. Okuda, S. Noguchi, K. Kurosawa, S. Saito

To cite this version:

HAL Id: jpa-00228924
https://hal.archives-ouvertes.fr/jpa-00228924
Submitted on 1 Jan 1988

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
MAGNETISM OF Py-INTERCALATED MnPS₃

K. Okuda, S. Noguchi, K. Kurosawa and S. Saito

Department of Electronics, University of Osaka Prefecture, Sakai, Osaka 591, Japan

Abstract. – The effect of pyridine intercalation on the magnetic properties of 2D-antiferromagnet MnPS₃ with \( T_N = 78 \) K was investigated by ESR, magnetic susceptibility and magnetization measurements. The magnetic two-dimensionality was increased by about 40 times by the Py-intercalation and the compound MnPS₃(Py)\(_{4/3}\) shows a magnetic ordering with a weak ferromagnetic moment below 40 K.

Intercalation has been an interesting subject in both solid state physics and technical application to develop new materials. In the present work, the effect of pyridine (Py) intercalation on the magnetic properties of two-dimensional antiferromagnet MnPS₃ with \( T_N = 78 \) K [1] was investigated by ESR, magnetic susceptibility, and magnetization measurements in a temperature range from 4.2 to 300 K.

MnPS₃ has a layered structure of CdCl₂ type in which one third of cations have been substituted by \( \text{P}_2 \) pairs, so Mn\(^{2+} \) ions construct a honeycomb lattice in the \( ab \)-plane and they are separated by Van der Waals' gap between two hexagonal layers of sulfur ions [2]. The pyridine molecules are intercalated into this gap.

Single crystals of MnPS₃ were grown by vapor growth method [1]. The intercalation of pyridine was carried out by heating the single crystals of MnPS₃ in distilled pyridine at 60 °C for one week. The X-ray diffraction measurements showed that the interlayer distance of Mn\(^{2+} \) ions is 12.32 Å, which is about twice as large as that of the pure MnPS₃ 6.49 Å. From the thermogravimetric analysis the composition of the intercalation compound was determined to be MnPS₃(Py)\(_{4/3}\).

ESR measurements were done by a standard reflection type of spectrometer operated at 9.4 GHz with 100 kHz field modulation in a temperature range from 4.2 to 300 K. The angular dependence of the line width in the ac-plane at room temperature is show in figure 1 for the both samples, MnPS₃ and MnPS₃(Py)\(_{4/3}\), where \( \Delta H_{pp} (\theta) \) is defined by the maximum slope of the absorption curve. It shows W-shaped angular dependence which is characteristic of the low dimensional magnet. The line width of Py-intercalated MnPS₃ is about 1.5 times larger than that of the pure MnPS₃, suggesting a weak interlayer coupling of Mn\(^{2+} \) spins. No angular dependence was observed in the \( ab \)-plane.

The W-shaped angular dependence of the line width was analyzed by assuming 2D-spin diffusion effect [3] in the spin correlation function \( \Phi (\tau) \) as shown in the insert of figure 1, where \( \tau_0 \) and \( \tau' \) are the times determined by the intra- and interlayer exchange couplings \( J \) and \( J' \), respectively. The calculated line width is shown by a solid line in figure 1. The fitting parameters \( \tau_0 \) and \( \tau' \) are \( \tau_0 = 3.8 \times 10^{-13} \) sec, \( \tau' = 3.4 \times 10^{-11} \) sec for MnPS₃(Py)\(_{4/3}\) and \( \tau_0 = 3.3 \times 10^{-13} \) sec, \( \tau' = 7.7 \times 10^{-13} \) sec for MnPS₃. From the times, the ratio \( |J'/J| \) is estimated to be 0.01 for MnPS₃(Py)\(_{4/3}\) and 0.4 for MnPS₃, respectively. A clear enhancement of the magnetic two-dimensionality is found in the intercalation compound MnPS₃(Py)\(_{4/3}\). Figure 2 shows the temperature dependence of ESR line width of MnPS₃(Py)\(_{4/3}\) together with that of MnPS₃ which shows a critical divergence at \( T_N = 78 \) K with decreasing temperatures [1]. The width of MnPS₃(Py)\(_{4/3}\) shows a large peak at 40 K for the field direction perpendicular to the \( ab \)-plane, suggesting the magnetic ordering at \( T = 40 \) K. For the direction parallel to the \( ab \)-plane, however, a gradual increase with a weak peak at 40 K is found with decreasing temperature below 50 K.
The magnetic susceptibility was measured by the Faraday method. The results for the field direction parallel to the ab-plane are shown in figure 3 together with that of MnPS$_3$ as a reference [1]. High temperature susceptibility above 65 K follows the Curie-Weiss law $\chi = C/(T - \Theta)$ with the Curie constant $C = 4.7 \pm 0.1$ emu/mol and the paramagnetic Curie temperature $\Theta = -120$ K, which is smaller than that of MnPS$_3$ $\Theta = -230$ K. Low temperature susceptibility below 65 K is quite different form that of the unintercalated MnPS$_3$ as shown in figure 3. Below 65 K the susceptibility turns to ferromagnetic temperature dependence with the Curie temperature $T_m \simeq 40$ K, which coincides with the peak temperature of ESR line width shown in figure 2.

The magnetization was measured at 4.2 K for the direction perpendicular to the ab-plane under a pulsed magnetic field up to 300 kOe in High Magnetic Field Laboratory of Osaka University. The magnetization process of MnPS$_3$ (Py)$_{4/3}$ shows a great change from that of the pure MnPS$_3$, which has a typical spin-flop transition at $H_c = 36.6$ kOe followed a linear increase with the field, as shown in figure 4. For the intercalation compound MnPS$_3$ (Py)$_{4/3}$, the magnetization below 10 kOe leads to a weak ferromagnetic moment of $\sim 0.075 \mu_B$/Mn as seen in the insert of figure 4 and it shows a step-wise increase around 10 kOe with the field. Above 150 kOe the magnetization shws a linear increase with the field. From the linear extrapolation the critical field $H'_c$ for the saturation of moment assuming $5 \mu_B$/Mn is estimated to be $H'_c = 1.44$ MOe. In the same way the $H'_c$ of MnPS$_3$ is estimated to be $H'_c = 2.19$ MOe.

In conclusion the magnetic two-dimensionality is increased by the intercalation and the compound MnPS$_3$ (Py)$_{4/3}$ shows a magnetic ordering with a weak ferromagnetic moment below 40 K. A modification of the spin structure from a simple collinear antiferromagnetic order of MnPS$_3$ [4] to a ferrmagnetic or spin-canted antiferromagnetic structure might be proposed for MnPS$_3$ (Py)$_{4/3}$, though the main exchange interaction [1] in the ab-plane are almost unchanged.