Raman spectroscopy as an indicator of antiferromagnetic to paramagnetic phase transition in transition metal thiophosphates

M. Peter[1], J. Kopaczek[1], M. Rybak[1], Z. Sofer[2], and R. Kudrawiec[1]

[1] *Department of Semiconductor Materials Engineering, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland*

[2] *Department of Inorganic Chemistry, University of Chemistry and Technology, Technická 5,166 28 Prague 6, Czech Republic*

Over the years, while electronic and optical properties of two-dimensional (2D) semiconductors were extensively studied experimentally, magnetic properties have remained neglected. That situation was related to the view that ferromagnetic order could not survive in a 2D regime due to increased thermal fluctuations [1]. However, a few years ago, Lado and Fernández-Rossier experimentally showed for CrI_3 crystal that magnetic order could be stabilized and survive in a low-dimensional regime [2]. Since then, 2D magnets are drawing growing interest, but plenty of phenomena still require extensive studies. Among 2D magnets, transition metal thiophosphates (MPS_3 - where M is transition metal) are a large family of van der Waals crystals exhibiting various types of intrinsic magnetic ordering.

In this work, we focused on correlating changes in Raman modes behavior with phase transition from antiferromagnetic to paramagnetic order for $MnPs_3$, $FePS_3$, $CoPS_3$, and $NiPs_3$. Moreover, we have elucidated how the replacement of transition metal influences the position of a given vibrational mode and its coupling to the antiferromagnetic phase. It can be seen in fig. 1 that around Néel temperature, one of the Raman modes loses its intensity and disappears completely while a new one of different symmetry emerges. The mentioned changes in symmetry were confirmed by angle-resolved Raman spectroscopy measurements fig. 1 (c). Furthermore, our experimental findings were supported by density functional theory that let us identify vibrational modes.

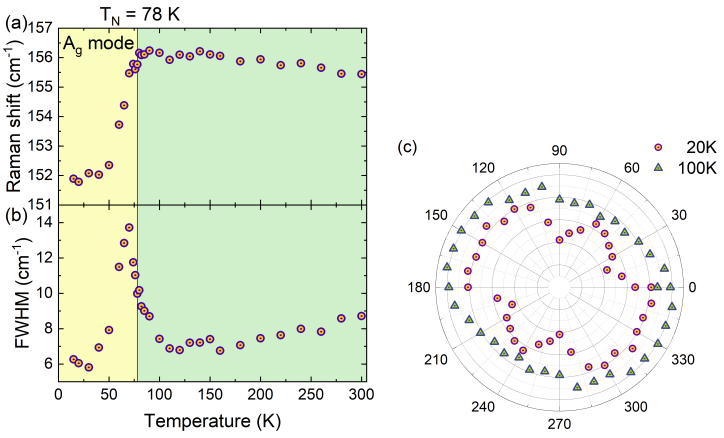

Figure 1: The analysis of A_g Raman mode behaviour with (a,b) temperature and (c) polarization for $MnPS_3$ with a Néel temperature of 78 K.

[1] N. D. Mermin, and H. Wagner, Phys. Rev. Lett. **17**, 1133 (1966)
[2] J. L. Lado, and J. Fernández-Rossier, 2D Mater. **4**, 035002 (2017)