Poster

Reinvestigation of the crystal structure and magnetic properties of $M(VO)_2(PO_4)_2*4H_2O$ and $Ni_{0.5}(VO)_2(PO_4)_2*1.5H_2O$ ($M = Ni^{2+}, Co^{2+}$) compounds

Lovro Šarić[1], Georgia Cametti[1], Ivica Živković[2]

[1]Mineralogical Crystallography, Institute of Geological Sciences, University of Bern , Baltzerstrasse 3, CH-3012 Bern, Switzerland, [2]Laboratory for Quantum Magnetism, Institute of Physics, EPFL, PH D2 435 (Bâtiment PH), Station 3, CH-1015 Lausanne, Switzerland

lovro.saric@unibe.ch

In today's technology, the need for data- and energy storage devices with a high efficiency and capacity, as well as a high writing speed for the former is ever increasing. For such applications, materials with a magnetic nature, i.e. *Ferro*-, *Ferri*- and *Antiferromagnetic,* are indispensable [1]. In such a context, a variety of transition-metal phosphates is receiving a growing interest [2- 3].

Previous studies on transition metal intercalated vanadyl-phosphates have shown that these materials may successfully be obtained through hydrothermal synthesis [4,5]. The structures have been reported to be tetragonal, space group *I4/mmm* for $Co(VO)_2(PO_4)_2*4H_2O$ and $Ni(VO)_2(PO_4)_2*4H_2O$ [4], and orthorhombic, space group *Pnma,* for $Ni_{0.5}(VO)_2(PO_4)_2*1.5H_2O$ [6]. The tetragonal compounds consist of layers of a 4-connected net where corner-sharing VO_5 and PO_4 tetrahedra alternate. Water molecules and transition metal cations sit in-between the $VOPO_4$ layers. Studies of the magnetic susceptibility indicate a bulk ferromagnetic coupling, which is attributed to the existence of the V = O – M – O =V linear trimers and the corresponding nearest neighbour V^{4+} - M^{2+} interactions within them[7]. In contrast, the structure of the orthorhombic compound has a three-dimensional architecture with channels parallel to the *b*-axis and the aquo-ligands located within them. The framework consists of units of one NiO_6 and two VO_6 octahedra. Previous magnetic studies have shown that an antiferromagnetic ordering and interaction seem to take place at low temperatures. Based on the measured value of the Ni magnetic moment per formula unit, the authors concluded that the behaviour is clearly more complex than what may be described by the Curie-Weiss law.

Although different synthesis routes were proposed for both Ni-and Co vanadyl-phosphates, a detailed and standard optimized procedure is lacking in literature, and was therefore the focus of our study. By implementing relevant modifications to the known synthesis routes, we successfully obtained single crystals of the title compounds. The structural investigations indicated a tetragonal symmetry for the layered vanadyl-phosphates and an orthorhombic symmetry of the 3D network Ni-compound. However, a disagreement in terms of the space group, which describes the structure of the tetragonal compounds, exists, with our findings pointing to the space group *I4/m*. In addition, we performed new susceptibility measurements on the obtained compounds. Preliminary results on the layered structure-compounds showed that the interactions are more complex than previously considered, and that the interlayer interactions between V^{4+} atoms bridged by phosphate tetrahedra require more attention. Magnetic susceptibility investigations indicate that the compound description as a bulk ferromagnetic is flawed, and that a low-dimensional magnetic system, which has hitherto been undescribed, is present and requires further characterization. Likewise, the consideration of the different magnetic moments for the distinct crystallographic sites of vanadium in $Ni_{0.5}(VO)_2(PO_4)_2*1.5H_2O$ has not been investigated. This implies a myriad of possible exchange interactions that may occur in a complex, low-symmetry three dimensional framework that need to be considered further.

[1] Spaldin, N. (2010) *Magnetic Materials, Fundamentals and Applications*. Cambridge University Press, p. 274.

[2] Papoutsakis, D., Jackson, J. E., Nocera D. G. (1996). *Inorganic Chemistry*, **35** (4), 800-801.

[3] Guillou, N., Gao Q., Forster P.M., Chang J.S., Noguès M., Park S.E., Férey G., Cheetham A.K. (2001). *Angewandte Chemie*, **40** (15), 2831-2834.

[4] Lii, K. H., H.Y. Kang, Lee W.C., Wang S.L. (1992). *Inorganic Chemistry*, **31**(23), 4743-4748.

[5] Haushalter, R. C., Soghomonian V., Chen Q., Zubieta J. (1993). *Journal of Solid State Chemistry*, **105**(2), 512-519.

[6] Lii, K. H., Mao, L. F. (1992). *Journal of Solid State Chemistry*, **96**(2), 436-441.

[7] Zheng, L.M., Lii, K.H. (1998). *Journal of Solid State Chemistry*, **137**(1), 77-81.