ESRF	**Experiment title:** Low-temperature structural study of low-dimensional quantum magnets $LiVOAsO_4$ and $Na_{1.5}VOPO_4F_{0.5}$	**Experiment number**: HE3385
Beamline:	**Date of experiment**: from: 13.07.2010 to: 15.07.2010	**Date of report**: 01.03.2011
Shifts: 9	**Local contact(s)**: Andrew Fitch	*Received at ESRF:*

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Report:

The experiment was aimed at the precise structure determination for quantum magnets $Na_{1.5}VOPO_4F_{0.5}$ and $LiVOAsO_4$. Both structures have been reported in the literature, but the accuracy of the atomic positions is insufficient for an adequate description of the magnetic behavior. Moreover, the complex low-temperature evolution of $Na_{1.5}VOPO_4F_{0.5}$ (structural phase transitions and phase separation) were completely overlooked.

$Na_{1.5}VOPO_4F_{0.5}$ has tetragonal crystal structure with layers formed by corner-sharing VO_5F octahedra and PO_4 tetrahedra. Sodium cations are partially disordered and located between the layers. According to [1], the structure is body-centered tetragonal with $a_{sub} \sim 6.38$ Å and $c \sim 10.62$ Å. However, we were able to observe superstructure reflections even in the laboratory XRD data at room temperature. Synchrotron measurements at ID31 were done in the temperature range 150–560 K, and revealed further remarkable features: i) a sequence of phase transitions related to the ordering of Na atoms; ii) low-temperature phase separation.

The body-centered tetragonal structure (α-polymorph, *I*4/*mmm*, $a = 6.39563(1)$ Å, $c = 10.65908(2)$ Å at 560 K) was observed above 500 K only. It matches the atomic positions reported in [1]. Below 500 K, we found the primitive tetragonal unit cell showing the superstructure in the *ab* plane (β-polymorph, $P4_2/mnm$, $a = 9.03051(2)$ Å, $c = 10.62002(3)$ Å at 298 K). This superstructure results from the partial ordering of Na atoms that occupy one filled position and one half-filled position instead of the two partially filled positions in the α-polymorph. The volume of the subcell changes continuously across the α–β transition (see Fig. 1), thereby the transition is of the order-disorder type.

Below 250 K, a more complex superstructure in the *ab* plane sets in. The transition is accompanied by a discontinous change in the subcell volume and a sponaneous separation of a single-phase sample into two distinct phases having same cell volume but different c/a_{sub} ratio (see Fig. 1). Combining synchrotron data with low-temperature electron diffraction, we found that one of the phases exhibits complete long-range order of Na atoms (γ-polymorph, $P4_2/mbc$, $a = 12.76716(2)$ Å, $c = 10.57370(4)$ Å at 150 K). The arrangement of Na atoms in the second phase is short-range-ordered, thereby XRD shows subcell reflections only (γ'-polymorph, *I*4/*mmm*, $a = 6.37996(4)$ Å, $c = 10.5910(1)$ Å).

The refined structure of γ-$Na_{1.5}VOPO_4F_{0.5}$ enabled us to establish the microscopic magnetic model of this compound. The ordering of Na atoms splits the simple square lattice of magnetic V^{+4} cations into plaquettes (Fig. 2). This leads to a novel magnetic model of the tetramerized square lattice. Such a model has been proposed theoretically, but never accessed experimentally. To explore the low-temperature magnetic behavior and get additional insight into the intriguing phase separation, we performed electron spin resonance and nuclear spin resonance measurements. Since neither of the techinques revealed the coexistence of two phases, we conclude that both γ- and γ'-polymorphs contain V^{+4} and have same composition (within available resolution) in agreement with XRD refinements. The results are published in *Phys. Rev. B*, **84**, 014429 (2011).

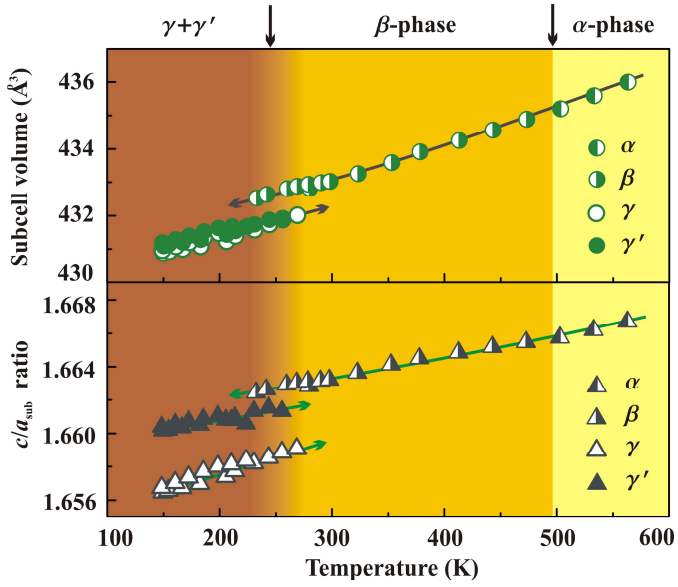

Figure 1. Temperature dependence of lattice parameters for $Na_{1.5}VOPO_4F_{0.5}$. Lines are guide-for-the-eyes, arrows denote the data obtained on heating/cooling.

$LiVOAsO_4$ has an orthorhombic crystal structure with chains of corner-sharing VO_6 octahedra. The chains are joined into a framework by AsO_4 tetrahedra. Basic features of the crystal structure have been reported in [2]. However, the sample contained unidentified impurities that reduced the accuracy of the refinement. We were able to prepare a single-phase sample and to study the structure in the 4.2–300 K temperature range. Our results do not show any structural transformations. The temperature dependence of lattice parameters is smooth. Below 80 K, the structure is basically unchanged. This result has two implications: i) our structure refinement improves the accuracy of atomic positions, which is important for the reliable modeling of the magnetic behavior; ii) the lack of structural changes rules out a spin-Peierls (structural dimerization) scenario that could be expected for a spin-1/2 chain compound with a gap in the magnetic excitation spectrum. Additionally, we show that the vanadium position is fully occupied, thereby no magnetic defects are expected. To verify the occupancy of the Li position, we recently performed a neutron diffraction experiment. The results are presently analyzed and will be used for a combined structure refinement from x-ray and neutron data. The structural information on $LiVOAsO_4$ supports our intepretation of the magnetic behavior and will be published in Physical Review B.

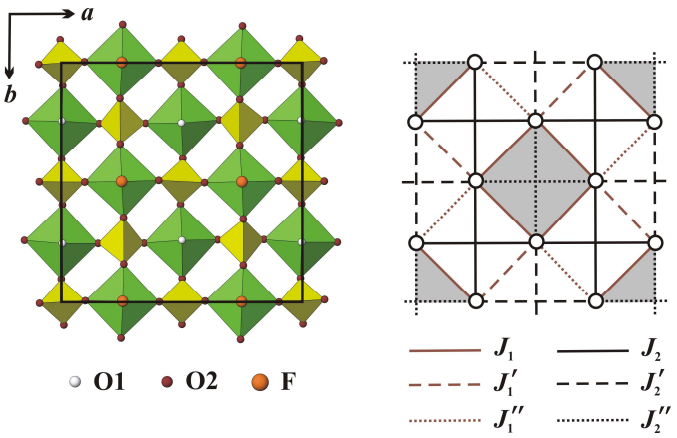

Figure 2. Refined low-temperature structure of γ-$Na_{1.5}VOPO_4F_{0.5}$ and the respective spin model of the tetramerized square lattice.

Additionally, we studied the low-temperature crystal structure of $AgVOAsO_4$, which is a close analog of $LiVOAsO_4$. Structure refinements at 20 K and at room temperature identified similar atomic arrangement. Accurate crystallographic information based on the high-quality synchrotron data improved our understanding of the peculiar magnetic behavior, involving possible Bose-Einstein condensation of magnons in high magnetic fields. A comprehensive study of $AgVOAsO_4$, including the ID31 data, is published in *Phys. Rev. B*, **83**, 144412 (2011).

[1] W. Massa *et al.* Solid State Sci. 4, 495 (2002).

[2] J. Gaubicher *et al.* J. Solid State Chem. 150, 250 (2000).