



	Experiment title: Crystal structures of β -Na _{0.33} V ₂ O ₅ at low temperatures and high pressures	Experiment number: HC-1068
Beamline: ID09A	Date of experiment: from: 20/11/2013 to: 24/11/2013	Date of report: 28/02/2014
Shifts: 12	Local contact(s): M. Hanfland	<i>Received at ESRF:</i>
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Report: The β -A_{0.33}V₂O₅ bronzes (A = Li, Na, and Ag) exhibit metal-insulator phase transitions with successive charge-spin ordering at atmospheric conditions [1-6]. They are known to become superconducting at pressures above 7 GPa, arguably due to a phase transition from the charge ordered to the superconducting phase. The transitions to the superconducting phases are well studied with magnetic susceptibility and resistivity measurements; however, the exact mechanism of the superconductivity in all these bronzes has been debated ever since the article by Yamauchi et al. [1-5]. One of the fundamental issues which remain still unresolved is the determination of the underlying crystal structures of the superconducting phases. Earlier studies on the P-T phase diagram of Na_{0.33}V₂O₅ have been carried out using synchrotron powder diffraction and Raman measurements [7-10]. The powder diffraction studies at high pressures have clearly shown anomalies and discontinuities in the pressure dependence of the lattice parameters and unit-cell volumes, yet the information content of the powder diffraction diagrams was not high enough to identify the underlying structural reasons for these anomalies.

We now performed single crystal measurements on β -Na_{0.33}V₂O₅ and β -Li_{0.33}V₂O₅ at various P-T conditions using diamond anvil cells at room and low temperatures on the beamline ID09a at the ESRF. Our samples were synthesized by Y. Ueda (University of Tokyo) and were extensively characterized in [1-8,10-11]. For β -Na_{0.33}V₂O₅ we performed a series of measurements at varying temperature-pressure conditions (T: 7-300 K; P: 0-20 GPa) using the membrane diamond anvil cells available at the beamline. The cells were introduced in a He- cryostat, so that it was possible to measure at non-ambient conditions of pressure and temperature simultaneously. Due to the limited time the high pressure experiments on β -Li_{0.33}V₂O₅ were performed only at ambient temperature (P: 0-20 GPa).

We have started analyzing the data obtained at room temperature and we can clearly see pressure-induced phase transitions in both compounds. According to our preliminary results, for the Li-compound there are two phase transitions, one in the pressure range between 8.40 and 9.21 GPa and a second one in the range between 9.70-11.04 GPa. At pressures above 12.86 GPa we are not able to index the data anymore and the crystal seems to be cracked. In the Na-compound we observe a phase transition in the pressure range between 10.60 GPa and 12.21 GPa. The critical pressure of the transition in Na_{0.33}V₂O₅ is in good agreement with earlier results from powder diffraction data.

The reconstructions of reciprocal space for Na_{0.33}V₂O₅ and Li_{0.33}V₂O₅ show that the phase transitions lead to drastic changes in the diffraction patterns. Extensive one-dimensional diffuse scattering is observed for the high pressure phase of Na_{0.33}V₂O₅ and the intermediate phase of Li_{0.33}V₂O₅ (Figure 1). These observations suggest that the phase transition mechanism is related to the shifting of layers which lead to a

state that is strongly affected by stacking disorder. In the course of the second phase transition in the Li-containing compound the diffuse scattering disappears again and the diffraction pattern of the second high pressure polymorph is characterized mainly by sharp Bragg reflections. The determination of the structures of the involved high pressure polymorphs is currently underway.

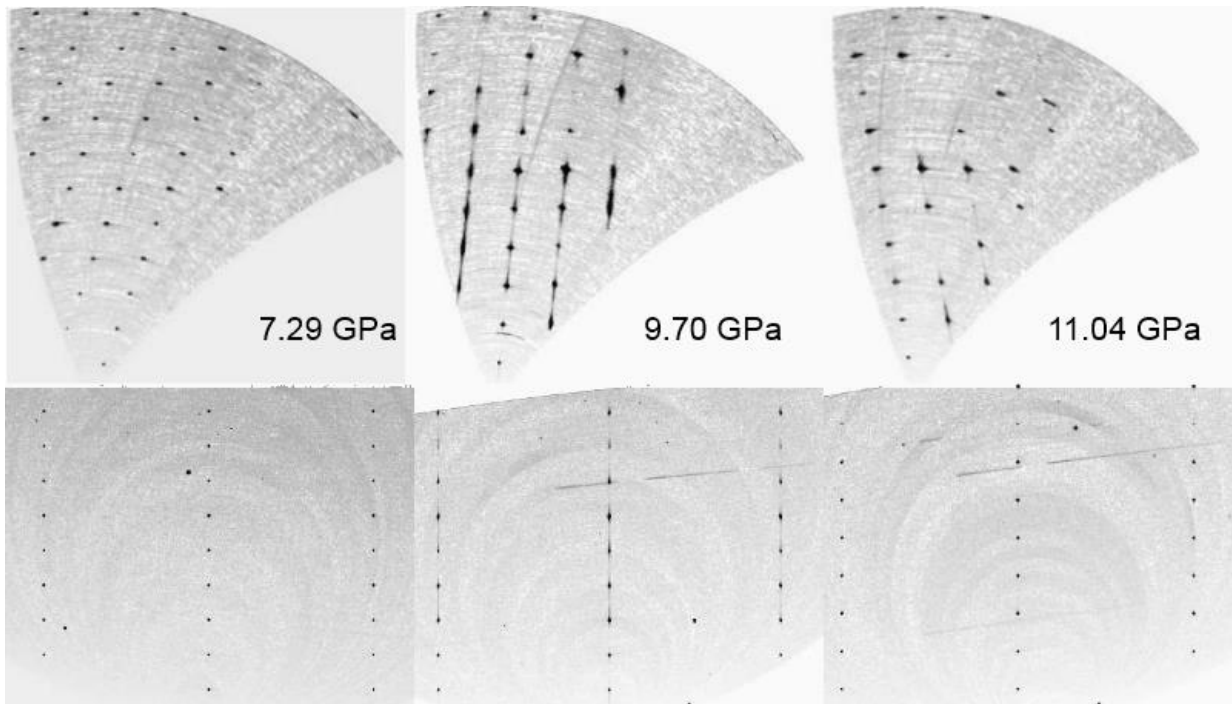


Figure 1: Reciprocal space sections of $\text{Li}_{0.333}\text{V}_2\text{O}_5$ at selected pressures (top: $h0l$; bottom: $0kl$)

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