MS22-O5 Pressure-induced phase transitions to non-superconducting polymorphs in the Wadsley-type bronzes β-$A_{0.33}V_2O_5$ (A = Li, Na)

Andrzej Grzechnik[1], Yutaka Ueda[2,3], Toru Yamauchi[3], Michael Hanfland[4], Paul Hering[5], Vasily Potapkin[5], Karen Friese[5]

1. Institute of Crystallography, RWTH Aachen University, 52066 Aachen, Germany
2. Toyota Chemical and Physical Research Institute, Nagakute, Aichi 480-1192, Japan
3. Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba 277-8581, Japan
4. European Synchrotron Radiation Facility, BP 220, 38043 Grenoble, France
5. Jülich Centre for Neutron Science, 52425 Jülich, Germany

email: grzechnik@xtal.rwth-aachen.de

β-$A_{0.33}V_2O_5$ bronzes (A = Li, Na, Ag) have a crystal structure (C2/m, Z = 6) [1] built of zigzag double strings of distorted VO_6 octahedra forming layers by joining corners. The adjacent layers are linked by chains of edge-sharing VO_5 tetragonal pyramids resulting in tunnels along the *b* axis. Each tunnel contains one symmetrically independent site that is partially occupied by the A^{1+} cations.

The low-dimensional β-$A_{0.33}V_2O_5$ bronzes exhibit metal-insulator phase transitions with successive charge-spin ordering at atmospheric conditions [2]. They are superconducting below about 8 K under high pressure, possibly due to a phase transition from the charge ordered to the superconducting phase [3]. The superconductivity occurs at about 7 GPa in β-$Na_{0.33}V_2O_5$ and β-$Ag_{0.33}V_2O_5$ and at about 9 GPa in β-$Li_{0.33}V_2O_5$. The exact mechanism of the superconductivity in these bronzes has not been presented so far. One of the most fundamental issues to be resolved is the determination of the underlying crystal structures. Here, we report on the high-pressure behaviour of β-$Li_{0.33}V_2O_5$ and β-$Na_{0.33}V_2O_5$ studied with synchrotron single-crystal diffraction in diamond anvil cells to 13 GPa and 20 GPa, respectively, at room temperature. β-$Li_{0.33}V_2O_5$ undergoes a series of transitions at about 9 and 11 GPa. β-$Na_{0.33}V_2O_5$ transforms to a new polymorph at about 12 GPa. Structure determinations and refinements reveal that the phase transitions in both materials are due to relative displacements of the adjacent octahedral layers. The relative position of the chains of edge-sharing VO_5 polyhedra with respect to the octahedral layers is changed. As a result, the tunnels populated by the A^{1+} cations collapse on compression. There is no evidence for the charge ordering of mixed-valence vanadium. Very strong one-dimensional diffuse scattering is observed in the intermediate high-pressure polymorphs indicating the presence of stacking faults.

Our observations strongly support the hypothesis that the underlying mechanism for superconductivity in the Wadsley-type β-$A_{0.33}V_2O_5$ vanadium bronzes is related to pressure-induced inter- and/or intra-ladder charge transfer or charge fluctuations in the two-leg ladder system present in the polymorphs with superconducting ground states [3].

References

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Keywords: mixed-valence vanadates, crystal structure, high pressure