Temperature and pressure induced transitions in the mixed valence vanadate NaV$_6$O$_{11}$

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Mixed valence vanadates AV$_6$O$_{11}$ (A=Na, K, Sr, Pb, or Ba) crystallize in structures closely related to magnetoplumbite at ambient conditions [1-5]. They have arisen much interest due to their magnetic and electrical properties (see references in [5]). Their structure is characterized by V(1)O$_6$ octahedra which share common edges and form a Kagomé net normal to [001] (see Figure, top). These layers are connected in the direction of $c$ via dimers of face sharing V(2)O$_6$ octahedra and trigonal V(3)O$_5$ bipyramids. The A atoms are incorporated into cavities of the vanadium oxide framework. The maximum symmetry for all members of the family is P6$_3$/mmc (Z=2).

We are especially interested in temperature and pressure induced structural changes and charge ordering within the individual representatives of this family of compounds. In NaV$_6$O$_{11}$ the observed changes seem to be entirely explainable based on volume effects, which is not the case for other compounds e.g. BaV$_6$O$_{11}$ [6]. This difference could be related to a more flexible valence distribution in BaV$_6$O$_{11}$, when compared to NaV$_6$O$_{11}$.

In the highest symmetrical phase, NaV$_6$O$_{11}$ is a Curie-Weiss paramagnetic metal [7]. At 243 K, it undergoes a second order phase transition, in which the symmetry reduces from P6$_3$/mmc to P6$_3$mc [8]. In the acentric phase, the V(1)O$_6$ octahedra form trimers with a regular triangular shape (see Figure, middle). A $^{51}$V-NMR study revealed that the V(1) atom shows a spin gap character with a spin-singlet ground state, while the V(2) and V(3) atoms maintain their local magnetic moment [4,9]. We could demonstrate that the transition P6$_3$/mmc to P6$_3$mc can be induced also by the application of hydrostatic pressure [10].

NaV$_6$O$_{11}$ is the only representative of the family, which undergoes a second structural transition: at 80 K a first order phase transition P6$_3$mc (Z=2) to Cmc2$_1$ (Z=4) takes place. Up to now, this transition has only been characterized based on powder diffraction data. In the lowest symmetry phase the V(1)O$_6$ trimers distort into isosceles triangles [8,11,12]. In addition, below $T_c=64.2$ K, NaV$_6$O$_{11}$ exhibits a uniaxial magnetic anisotropy with the easy axis of magnetization parallel to [001] [7]. Up to now, the magnetic structure has not been determined experimentally.

The detailed knowledge of the orthorhombic structure of NaV$_6$O$_{11}$ could provide important clues for the understanding of the charge ordering and phase transitions, observed in this family of mixed valence compounds. We therefore decided to study the low temperature phase in more detail using synchrotron single-crystal diffraction. We measured the diffraction intensities of NaV$_6$O$_{11}$ at beamline D3 of the Hasylab using a He-cryostat (Helijet, Oxford Diffraction) at a wavelength of 0.45 Å with a point detector. The symmetry reduction from P6$_3$mc to Cmc2$_1$ suggests the formation of three twin individuals and we could indeed see a splitting of our reflections into three partly overlapping peaks. Naturally,
the pseudomerohedral twinning affects the data quality, yet we could refine the low temperature structure with very high precision using a twin model in which the three individuals are related via a 3-fold axis in the $c$-direction. A detailed analysis of the low temperature phase is currently under way.

![Kagomé net perpendicular to [001] at 290, 100 and 30 K. The V(1)-V(1) distances are indicated. The V(1), V(2) and V(3) atoms are shown as white, yellow, and black spheres, respectively.](image)

References