

Incommensurate Magnetic Structure and Chemical Modulation in SbVO₄ Catalyst

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SbVO₄ series of compounds could be a promising catalyst for the production of 20% cheaper acrylonitrile by the ammoxidation of propane compared to current method from propylene producing above 8 million ton/year, thus more than 1 Kg per human inhabitant of the planet. Composition, oxidation state and subtle structural features influence the activity and selectivity of the highest performance catalyst.

In the non-stoichiometric series described as Sb_{0.9V_{0.9+x}[]_{0.2-x}O₄ (0 ≤ x ≤ 0.2), cation vacancies ([]) in the basic rutile type-structure balance V³⁺/V⁴⁺ charges while antimony remains as Sb⁵⁺. A reduced phase (richest in V³⁺) has been reported to be Sb_{0.9V_{1.1}O₄, which shows by electron diffraction (ED) superlattice reflections characteristic of a 2-fold rutile superstructure along c. The reciprocal lattice study by ED revealed the following unit cell for the rutile superstructure: $\sqrt{2}a_r \times \sqrt{2}b_r \times 2c_r$ (subindex r refers to the basic rutile unit cell). Its space group, I4₁md, was determined by CBED. A structural model based on alternating Sb and V cations ordering along c in the chains of edge-sharing octahedra was proposed. No cation vacancies have been observed for this reduced phase, while for the compounds synthesized in oxidizing conditions the presence of vacancies has been confirmed. Magnetic susceptibility data indicate possible magnetic ordering in reduced phases rich on V³⁺ which are close to the nuclear superstructure by Sb-V ordering. For the simultaneous crystal and magnetic structure determination we have performed a neutron diffraction study on different samples of the series with composition \sim SbVO₄.}}

Below $T_N \leq 50K$, new Bragg reflections of pure magnetic nature appear due to the 3D-AF interaction of the vanadium spins changing gradually from the paramagnetic disorder to the magnetically ordered state as the temperature decreases. The periodicity of the magnetic structure develops being close to doubling again the two-fold commensurate supercell of rutile type described by the alternate ordering of Sb and V along the rutile c-axis in SbVO₄, giving rise to a final 4-fold rutile superstructure. However, the exact periodicity of the spin arrangement is clearly not commensurate with the nuclear cell but close to that. The refinement of the incommensurate magnetic propagation vector to $k = [0, 0, \pm kz]$ with $kz = 0.266(1)$ r.l.u. is close to the commensurate value $\frac{1}{4}$. It accounts both for the magnetic satellites and it is compatible with the absence of a commensurate nuclear 2-fold supercell but the observed modulated chemical structure with modulation vector $q = 0.532 c^*$.

Keywords: [Incommensurate magnetic structures](#), [short range order](#), [neutron diffraction](#)