

Cationic superstructures and incommensurate magnetic structure in SbVO_4 catalyst

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Abstract. Chemical and magnetic structure modulations in antimony vanadium mixed oxide with composition $\text{Sb}_{0.92}\text{V}_{1.08}\text{O}_4$ prepared in reducing conditions are studied using diffraction techniques, mainly nuclear and magnetic neutron scattering, electron and X-ray powder diffraction. Magnetic susceptibility measurements show possible magnetic order of V^{3+} magnetic moments that is confirmed with neutron diffraction at $T_N \sim 50\text{K}$. The average commensurate nuclear cell belongs to the tetragonal rutile structural type with cell constants: $a=4.6066(11)\text{\AA}$ and $c=3.0812(8)\text{\AA}$ at 60K. However the nature of the magnetic structure is incommensurate with propagation vector $\mathbf{k}=[0, 0, \pm 0.266(1)]$ related to short range order phenomena and V-Sb alternating occupancy along the crystallographic c -axis.

1. Introduction

SbVO_4 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 8×10^6 ton/year, i.e. more than 1 Kg per human inhabitant of the planet. In the non-stoichiometric series with ratio Sb:V $\sim 1:1$ described as $\text{Sb}_{0.9}\text{V}_{0.9+x}\text{O}_{4-0.2x}$ ($0 \leq x \leq 0.2$), cation vacancies ($\square$) are introduced in the basic rutile type-structure following the mechanism: $4\text{V}^{3+} \rightarrow 3\text{V}^{4+} + \square$, while antimony remains as Sb^{5+} . Composition, oxidation state and subtle structural features influence the activity and selectivity for the highest performance catalyst.

The reduced phase richest in V^{3+} has been reported to be $\text{Sb}_{0.9}\text{V}_{1.1}\text{O}_4$ [1], which shows by electron diffraction superlattice reflections characteristic of a 2-fold rutile superstructure along c -axis. However the X-ray powder diffraction pattern showed only basic rutile reflections. The careful reciprocal lattice study by electron diffraction has revealed the following unit cell for the rutile superstructure: $a = \sqrt{2}a_r$, $b = \sqrt{2}b_r$, $c = 2c_r$. (subindex r refers to the basic rutile unit cell in $P4_2/mnm$). The superstructure space group, $I4_1md$, was determined by means of convergent beam electron diffraction CBED [1]. 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 [2]. In fact, electron diffraction experiments have shown that vacancies order in the basic rutile structure giving rise to a



modulated structure on the other end member of the series, namely $\text{Sb}_{0.9}\text{V}_{0.9}\text{O}_4$ [3,4]. On the other hand, our magnetic susceptibility data indicate for the first time possible magnetic ordering in reduced phases rich on V^{3+} 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 $\sim\text{SbVO}_4$.

2. Experimental details

The synthesis of the samples in reducing atmosphere has been carried out by mixing stoichiometric amounts of high purity reactants Sb_2O_3 and V_2O_5 in an equimolar ratio (1:1) and heating in a tubular furnace at 800°C under argon flow with copper filter in two runs of 12 hours with a careful grinding between steps. Samples have been characterized by powder X-ray diffraction in a Powder Diffractometer Bruker D8 Advance with $\text{Cu K}\alpha$ radiation.

Electron diffraction experiments were carried out in a JEOL 2000FII transmission electron microscope with a double-tilt holder running at 200kV acceleration voltage.

Bulk magnetic measurements between 1.9K and RT were performed using a SQUID magnetometer MPMS-XL Quantum Design. Isothermal magnetization measurements were collected up to 50 kOe.

Neutron diffraction data between 1.5K and RT were collected on the E6 powder diffractometer at the BENSC nuclear reactor in the Hahn-Meitner-Institut Berlin. The focusing PG-monochromator gave a wavelength $\lambda=2.446(1)\text{\AA}$. Both X-ray and neutron powder diffraction data have been analyzed with the Rietveld method using the program FullProf [5].

3. Results and discussion

3.1. Magnetic measurements

In Figure 1 the magnetic molar susceptibility curve of reduced $\sim\text{SbVO}_4$ is shown. The net maximum at $T=31\text{K}$ could indicate the appearance of three-dimensional antiferromagnetic 3D-AF order within the magnetic V sublattice. The linear fitting of χ^{-1} vs T , that follows the Curie-Weiss law, yields a paramagnetic moment value $\mu_{\text{eff}} \sim 2.8\mu_{\text{B}}$ which agrees well with the theoretical moment calculated for the free ion V^{3+} ($S=1$) following $\mu=2[S(S+1)]^{1/2} = 2.828 \mu_{\text{B}}$. It is fully compatible with the stoichiometry of the sample $\text{Sb}_{0.92}\text{V}_{1.08}\text{O}_4$ found by simultaneous refinement of X-ray and neutron diffraction data for the atomic occupation factors (Sb/V) and XEDS measurements, which in this case amounts to 0.16V^{4+} ($S=1/2$) and 0.92V^{3+} ($S=1$) per formula unit.

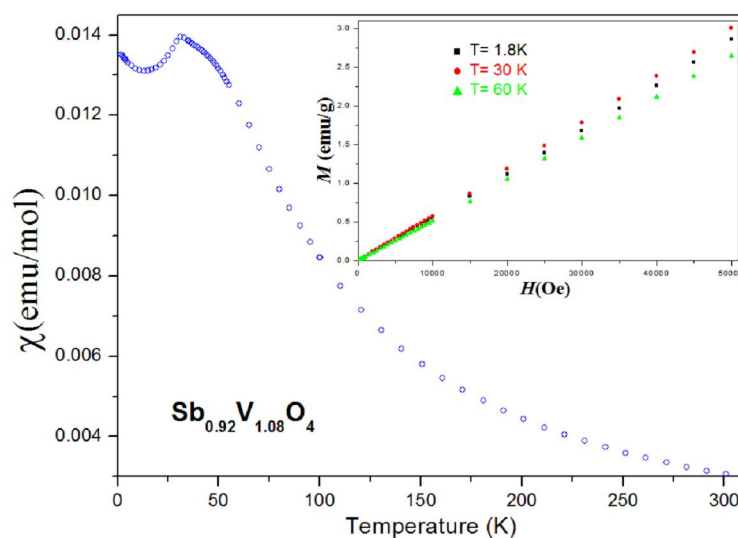


Figure 1. Magnetic susceptibility as function of T measured at an applied field $H=500\text{Oe}$. Inset shows magnetization isotherms at the indicated temperatures.

This bulk properties are in contrast with other $\sim\text{SbVO}_4$ compositions not prepared under inert atmosphere (Ar or N_2 gas flow) where no magnetic order has been observed. The substitution of $\text{V}^{3+}(\text{S}=1)$ by $\text{V}^{4+}(\text{S}=\frac{1}{2})$, while the synthesis conditions become more oxidizing, affects the spin arrangement of $\text{Sb}_{0.9}\text{V}_{0.9+x}\square_{0.2-x}\text{O}_4$ in such a way that the magnetic order seems to be destroyed by the appearance of vacancies and the chemical disorder in the cationic positions [6], as we have observed in samples prepared either in air or under oxygen flow.

We collected magnetization isotherms up to $H=5\text{T}$ at 10 different temperatures above and below that of the susceptibility maximum. The inset of Figure 1 shows some selected ones, a linear increase of M with magnetic field H is observed in all cases. Anomalies below the Néel temperature are not present like metamagnetic transitions induced by the field neither level-off by saturation.

3.2. Electron and X-ray diffraction measurements

For the reduced compounds $\sim\text{SbVO}_4$, X-ray powder diffraction patterns might be refined within the rutile structure with random statistical occupancy for Sb/V in $2a$ Wyckoff positions (Figure 2). However, electron diffraction patterns show additional periodicities either doubling the unit cell of the basic rutile structure along the crystallographic c -axis (Figure 3 left side), or showing intense diffuse lines running between the rutile-type Bragg maxima (Figure 3 right side).

While alternating -Sb-V-Sb-V- ordered cations along the chains of octahedra sharing edges along c might explain a commensurate superstructure order, diffuse lines would be compatible maintaining this ordered sequence intrachain but breaking the order between different chains. Furthermore, it has been found some incommensurability due to the imperfect ordering between vanadium and antimony atoms so statistically the periodicity is below $2\times c$ in real space and $q > 1/2 c^*$ in reciprocal space.

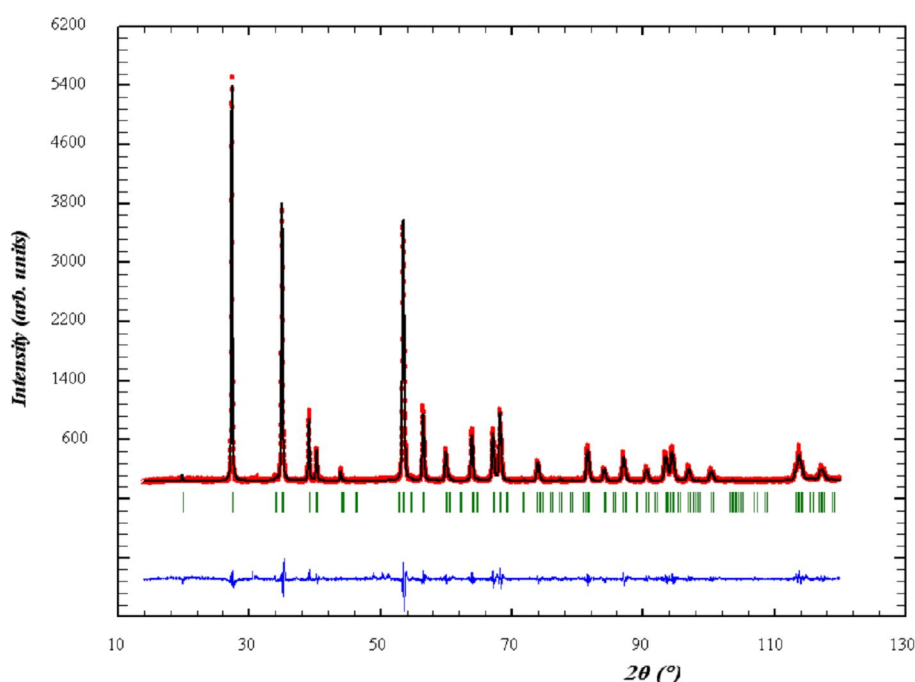


Figure 2. X-ray powder diffraction pattern refined with the Rietveld method for $\text{Sb}_{0.92}\text{V}_{1.08}\text{O}_4$ oxide. Red dots are the experimental data, continuous black line is the calculated profile and blue horizontal line is the difference between them, vertical green ticks mark the allowed Bragg reflections.

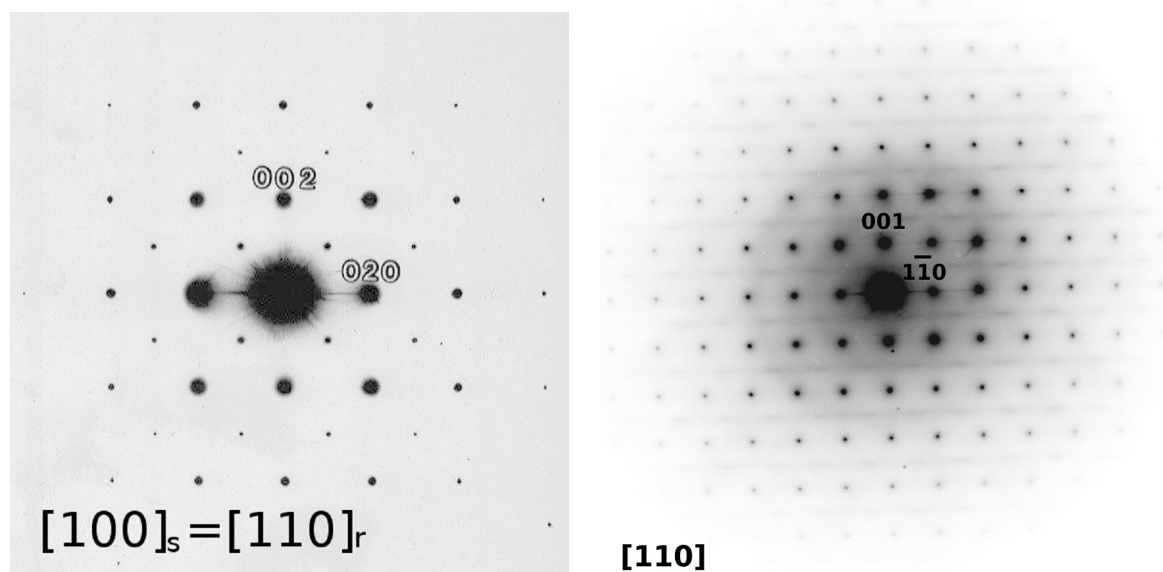


Figure 3. Selected area electron diffraction patterns for reduced compounds $\sim\text{SbVO}_4$. To the left notice superlattice commensurate reflections in SAED oriented along the $[100]$ zone axis of the supercell equivalent to $[110]$ basic rutile direction. To the right lines of diffuse scattering running perpendicular to the c^* -axis are observed for the same orientation in another sample.

3.3. Neutron diffraction measurements

Figure 4 shows the neutron diffraction pattern at 1.5K of the sample with composition $\text{Sb}_{0.92}\text{V}_{1.08}\text{O}_4$ where reflections of magnetic origin develop below $T_N \sim 50\text{K}$ [6].

Above the Néel temperature, and taking into account the absence of extra superlattice reflections coming from atomic order, the Rietveld refinement of the pure nuclear structure at $T=60\text{K}$ in tetragonal $P4_2/mnm$ space group (rutile structure) with position atomic coordinates Sb/V $2a$ (0,0,0) and O $4f$ ($x, x, 0$) $x=0.3035(5)$; lattice parameters: $a_r = 4.6066(11)\text{\AA}$, $c_r = 3.0812(8)\text{\AA}$ fits the experimental intensities (Agreement factor $R_B = 4.2\%$). The refined fractional cation occupancies are: 0.068(1) and 0.057(1) for V/Sb respectively, normalized using the multiplicity of the general Wyckoff position *i.e.* 16k. The result of simultaneous joint Rietveld refinement of high resolution neutron diffraction and X-ray data at room temperature will be published elsewhere.

Below $T_N \leq 50\text{K}$, 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 SbVO_4 , giving rise to a final 4-fold rutile superstructure, see schematic representation in Figure 4 inset.

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 $\mathbf{k} = [0, 0, \pm k_z]$ with $k_z = 0.266(1)$ *r.l.u.* is close to the commensurate value $1/4$. It accounts both for the magnetic satellites and it is compatible with the absence of a commensurate nuclear 2-fold supercell. Thus it fully agrees with half the value in reciprocal lattice units and double periodicity in real space to that of the observed modulated chemical structure considering a modulation vector $\mathbf{q} = 0.532\ c^*$ measured experimentally in the electron diffraction patterns.

Because the intensity of the magnetic reflections is proportional to the square of the perpendicular component of the magnetic structure factor $\mathbf{F}_M$ to the scattering vector $\mathbf{Q}$ one might expect that the antiferromagnetic coupling of V^{3+} magnetic moments favours their alignment close to the ab plane approaching $2S\ \mu_B$ value at saturation but with some degree of frustration due to interchain disorder.

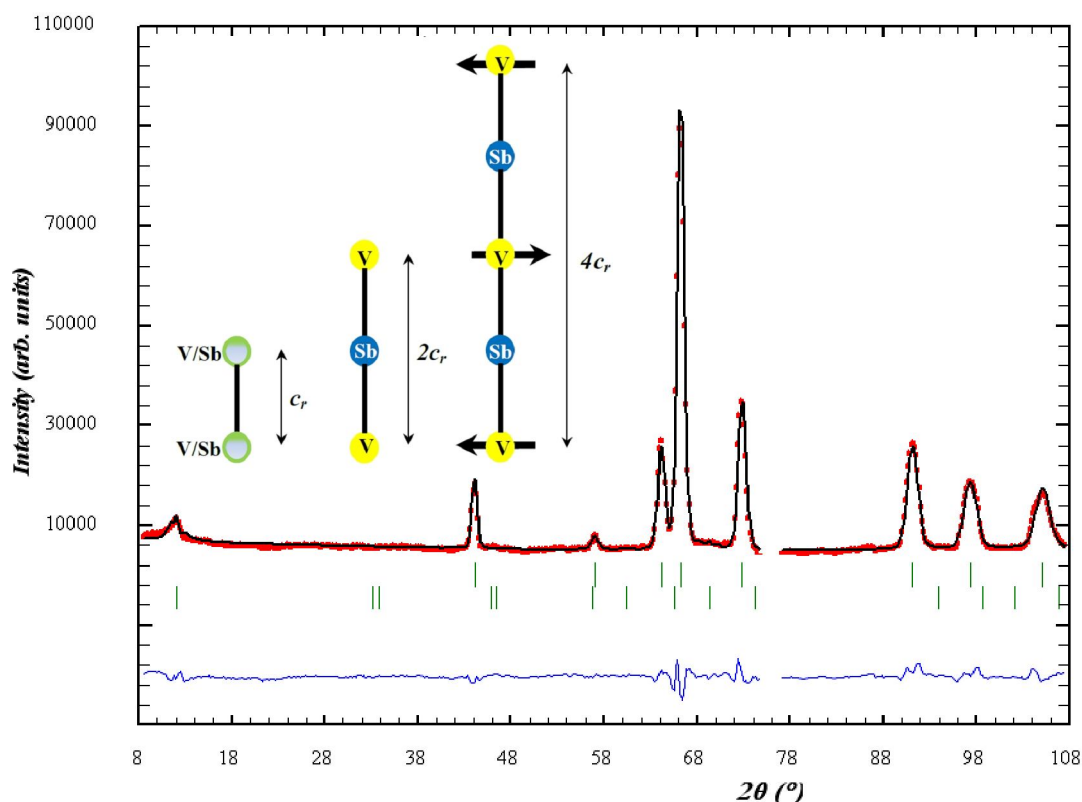


Figure 4. Neutron diffraction pattern of $\text{Sb}_{0.92}\text{V}_{1.08}\text{O}_4$ at $T=1.5\text{K}$ refined with the rutile structural model for the nuclear part while the magnetic scattering has been fitted with a profile matching mode. Bottom row of reflections corresponds to the magnetic structure driven by the incommensurate propagation vector described above in the main text.

Nevertheless, the fact that V coherent scattering length for neutrons b_c is rather small give us an advantage to determine the superstructures and incommensurate modulations due to alternating Sb-V occupation of two crystallographic positions split from the substructure in $I4_1md$ and additional information constrained with X-ray data. Also due to the unique property of the neutrons to interact with ordered magnetic moments, the magnetic scattering coming from the V spins could be linked to its crystallographic position, giving more information than at first glance could be expected by its almost null nuclear scattering. In summary, the combination of diffraction techniques gives a better knowledge of the structure to property relationship in this system of high industrial interest.

Acknowledgments

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