ESRF	**Experiment title:** X-ray powder diffraction study of the low temperature structures of $BaVS_3$	**Experiment number**: HS 2280
Beamline: ID 31	**Date of experiment**: from: 8 / 10 / 2003 to: 10 / 10 / 2003	**Date of report**:
Shifts: 3	**Local contact(s)**: Dr Michela BRUNELLI	*Received at ESRF:*

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Report:

$BaVS_3$ is a metallic one-dimensional compound formed of V^{4+} chains, exhibiting a succession of phase transitions. $BaVS_3$ crystallizes in a hexagonal $P6_3/mmc$ structure, which consists in VS_6 octahedra sharing faces in the **c** direction, well separated by Ba atoms in the **a**,**b** planes[1]. Below T_S = 250 K, an orthorhombic structure (space group $Cmc2_1$) is first stabilized, adding a zigzag arrangement of the linear V^{4+} chains[2]. At T_{MI} = 70 K, a metal/insulator phase transition is observed in conductivity measurements together with a sharp spike in the paramagnetic susceptibility. Finally, below T_x = 30 K a phase characterized by magnetic neutron reflections at the reduced wave vector (0.226, 0.226, 0) is stabilized. The nature of the T_{MI} and T_x transitions is a matter of controversy.

Recent key experiments have evidenced a structural phase transition at T_{MI}, associated to the doubling of the orthorhombic unit cell in the **c** direction[3]. This electronic and structural phase transition has been interpreted as a Peierls-like transition, leading to the stabilization of a $2k_F$ Charge Density Wave (CDW). Moreover, at T_{MI}, a huge variation of the main Bragg reflection intensity has been observed, indicating a strong modification of the average structure[3]. This shows that the transition is not a conventional Peierls transition and suggests a possible occurrence of a charge or orbital ordering of the V $e(t_{2g})$ electrons. An accurate structure determination is thus of tremendous importance to understand the successive transitions of $BaVS_3$. The aim of the present experiment was thus to solve the structure of the insulator phases below T_{MI} and below T_X using the high resolution powder diffractometer on ID31.

A capillary of $BaVS_3$ powder was set in a helium cryostat. The wave length used was 0.501813 Å in order to avoid absorption phenomena. The diffracted intensity was collected with a 9-channel analyzer. Four diffraction patterns have been registered at four temperatures to compare the spectra and structures : 300 K, 100 K, 40 K and 5 K. The data have been treated with the Rietveld refinement software Fullprof.

Results :

-) Room temperature results confirm the $P6_3/mmc$ structure.

-) At 100 K, the systematic extinctions at h + k odd and (h 0 l) l odd lead to 3 possible space groups : Cmcm, $Cmc2_1$ and C2cm (Ama2 in international tables). They all have been tested. As expected, the more reliable model is $Cmc2_1$ with a chi2 of 13.14 (Cmcm gives a chi2 of 16.27 and C2cm didn't converge). The high chi2 value is due to asymmetry of peak shape (fig 3) not modeled by Fullprof. It is probably due to the presence of a residual hexagonal (or orthorhombic) phase.

-) At 40K and 5K, the X-ray patterns are identical inside the error bars. The structure is slightly monoclinic as shown by a splitting of certain orthorhombic peaks in the pattern (fig. 1). The unique axis is the orthorhombic **a** axis. In spite of a very high statistic over the background, only weak additional superstructure peaks have been observed (fig 2).

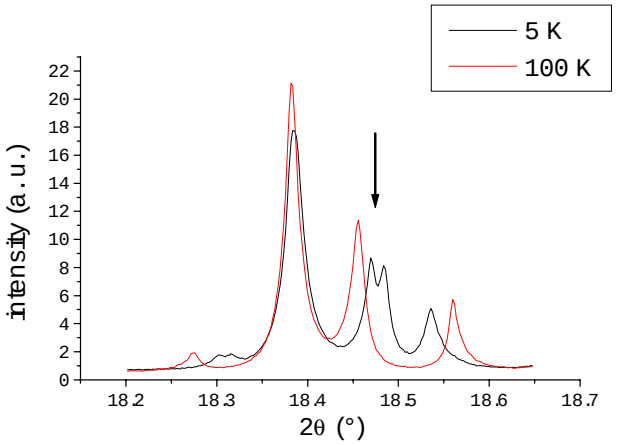

Fig 1 : Monoclinic distortion characterized by the peak splitting indicated by the arrow

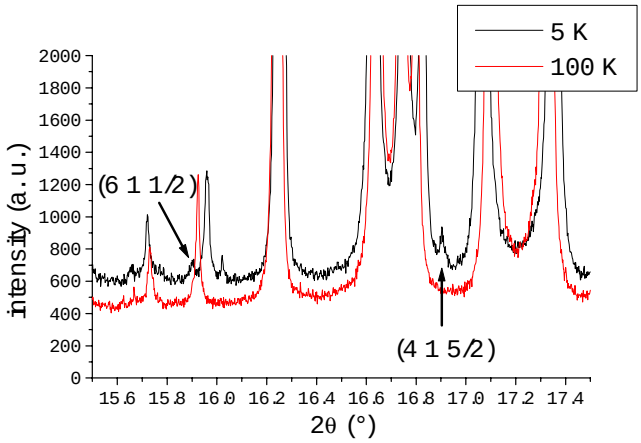

Fig 2 : Two superstructure reflections indicated by arrows

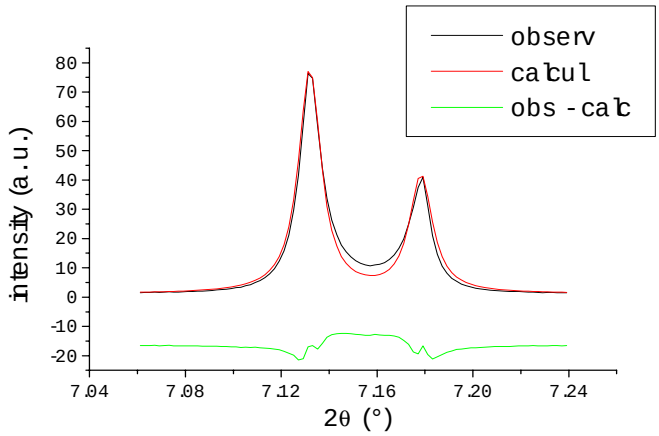

Fig 3 : Typical asymmetry of the peak shape not modeled by Fullprof

The average structure at 40 K (and 5 K) has been refined in the Cm space group, the only subgroup of $Cmc2_1$ compatible with **a** as unique axis. While in the orthorhombic phase, the V-V distance is unique (2.84 Å), in the monoclinic low temperature phases, there are two V-V distances (2.81 Å and 2.89 Å). This dimerisation of the V chain is a key result of the present experiment. However, concerning the superstructure, the weakness of satellite reflections and the asymmetry of peak shape prevent to obtain a reliable refinement.

temperature	room	100 K	40 K	5 K
space group	$P6_3/mmc$	$Cmc2_1$	Cm	Cm
a (Å) b (Å) c (Å) β (°)	6.71382620 (4) 5.61549430 (5)	6.750700 (7) 11.48464 (1) 5.596751 (6)	11.45832 (1) 6.763618 (6) 5.594972 (5) 90.0451 (1)	11.45648 (1) 6.763688 (6) 5.593914 (5) 90.0477 (1)
Rp Rwp Rexp Chi2	14.8 15.4 12.3 1.574	11.5 13.2 3.66 13.02	9.64 10.9 2.71 16.24	10.0 10.9 3.28 11.00

Table 1 : cell parameters and conventionnal Rietveld reliability factors given at each temperature

1. R.A. Gardner et al, Acta. Crystallogr. B **25**, 1101 (1977).
2. M. Ghedira et al, J. Phys. C: Solid State Phys. **19** 6489 (1986)
3. S. Fagot et al, Phys. Rev. Lett. **90**, 196401 (2003)