ESRF	**Experiment title:** Anomalous scattering on $BaVS_3$	**Experiment number**: HE-1507
Beamline: ID-20	**Date of experiment**: from: 23-04-2003 to: 28-04-2003	**Date of report**:
Shifts: 18	**Local contact(s)**: Carsten Detlefs	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

*Dr S. Ravy, *Dr P. Foury-Leylekian, *S. Fagot
Laboratoire de physique des solides, CNRS UMR8502, Bât. 510, Université Paris-sud, 91405 Orsay, France
*Dr E. Lorenzo
Laboratoire de Cristallographie, CNRS, B.P.166X, F-38043 Grenoble

Report:

$BaVS_3$ consists of a hexagonal packing of chains of face sharing VS_6 octahedra directed along the c axis. It undergoes three second-order low temperature phase transitions at T_S = 240 K, T_{MI} = 70 K, and T_X = 30 K. At T_S, a zigzag displacement of the V atoms inside the chains of octahedra induces a structural transition to an orthorhombic phase [1]. At T_{MI}, $BaVS_3$ undergoes a metal to insulator transition. Below T_X neutron scattering experiments have provided evidence of an incommensurate magnetic modulation [2].

The quasi-octahedral environment of the V^{4+} induces 3 crystal-field split V(3d) t_{2g} orbitals : a high energy d_{z2} level and two quasi-degenerate d_{xy} ones ($e(t_{2g})$). Ab initio band structure shows that three bands are associated to these levels [3]. One (d_z^2) is strongly dispersive and presents a quasi-1D character and the two others (d_{xy}) are flat and quasi-2D.

At T_{MI}, a structural modulation is stabilized at the $(1\ 0\ ½)_O$ reduced wave vector. This structural transition is announced by a huge 1D regime of fluctuations till 140 K. This is similar to a Peierls transition in which the occurrence of satellite reflections at twice the Fermi wave vector $2k_F$ is accompanied by the opening of a charge gap. Following this interpretation, the experimental value of $2k_F = 0.5\ c^*$ indicates the presence of one electron (half filling) on the 1D d_{z2} band, and another one in the two other bands. The localization of electrons on different types of sites or orbitals would lead to charge or orbital ordering [4].

The aim of this experiment was to check the presence of such orbital or charge ordering of the 3d vanadium states using anomalous scattering at the vanadium K edge.

One single crystal of $BaVS_3$ (~2 mm x 0.2 mm^2) has been pasted on a copper sample holder and mounted into a displex cryostat going down to 20 K. Unfortunately, we had some difficulties with the temperature measurement during the experiment. Indeed, we have systematically measured a temperature shift of –30K for the critical temperature of the T_{MI} transition (which can be attributed neither to a beam heating nor to an irradiation damage).

We have recorded a fluorescence scan as well as energy scans of 5 satellite reflections at T=20K. Some scans are shown in fig. 1. The fluorescence spectrum shows a weak pre-peak at 5.466 keV. The edge energy is 5.472 keV, determined by the maximum of the derivative of the fluorescence curve. Most of the energy scans measured on the satellite reflections show a strong absorption term. Indeed, the vanadium K edge being between Barium L2 and L3 edges, both atoms contribute to the absorption. These strong additional contribution could have masked anomalous effects on the vanadium K edge.

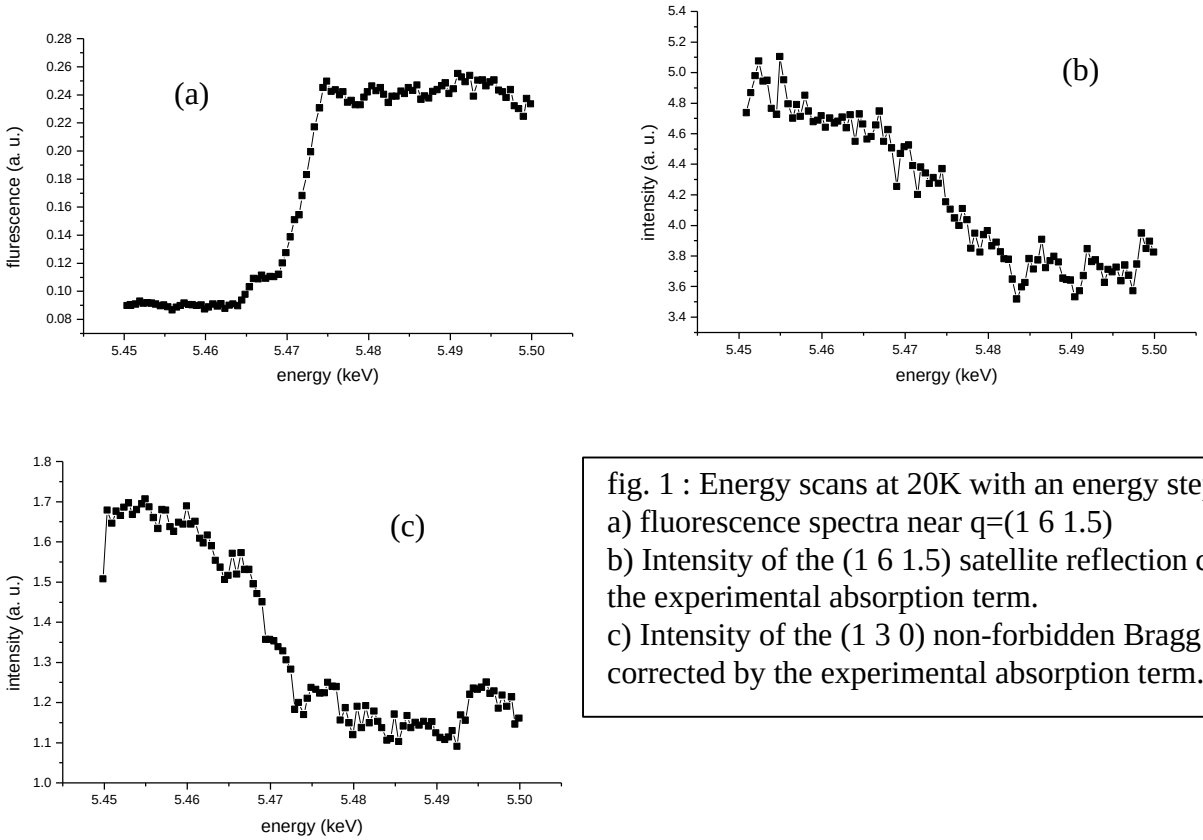

fig. 1 : Energy scans at 20K with an energy step of 0.5eV.
a) fluorescence spectra near q=(1 6 1.5)
b) Intensity of the (1 6 1.5) satellite reflection corrected by the experimental absorption term.
c) Intensity of the (1 3 0) non-forbidden Bragg reflection corrected by the experimental absorption term.

Following the method developed in ref [5], we have studied the possible charge order on the V atoms by measuring satellite reflections supposed to exhibit a derivative effect of the f" anomal scattering factor. None of the satellite reflections measured have shown the expected effect. We must notice that, the modulated structure being unknown, the choice of the adequate satellite reflections determined via the calculation of the structure factor is not reliable.

In order to investigate the orbital structure and the local electronic environment of the V^{4+} atoms in $BaVS_3$, we have measured both the satellite reflections and the Bragg reflections (forbidden and non forbidden) as a function of the polarization. For the satellite and non-forbidden Bragg reflections the energy curves, as expected, behave similarly in the sigma-sigma and sigma-pi channels (the intensity for the sigma-pi polarization is however more than 10^{-2} weaker). On the contrary, for the forbidden Bragg reflection (0 0 -1), the intensity is detectable only for the sigma-pi polarization. As shown fig.2, a huge peak at 5.466 keV is observed. In addition, a fine structure is measured several eV above the edge. As a function of temperature and in particular above T_{MI}, this spectrum is nearly not modified. A simulation of the (0 0 -1) sigma-pi scan has been performed using multiple scattering of the photoelectrons calculated in the FDMNES program developed by Y. Joly. The agreement with the experiment is good since a precise fit scan is still out of reach. Further calculations are in progress in order to extract information on the local electronic environment of the vanadium atoms.

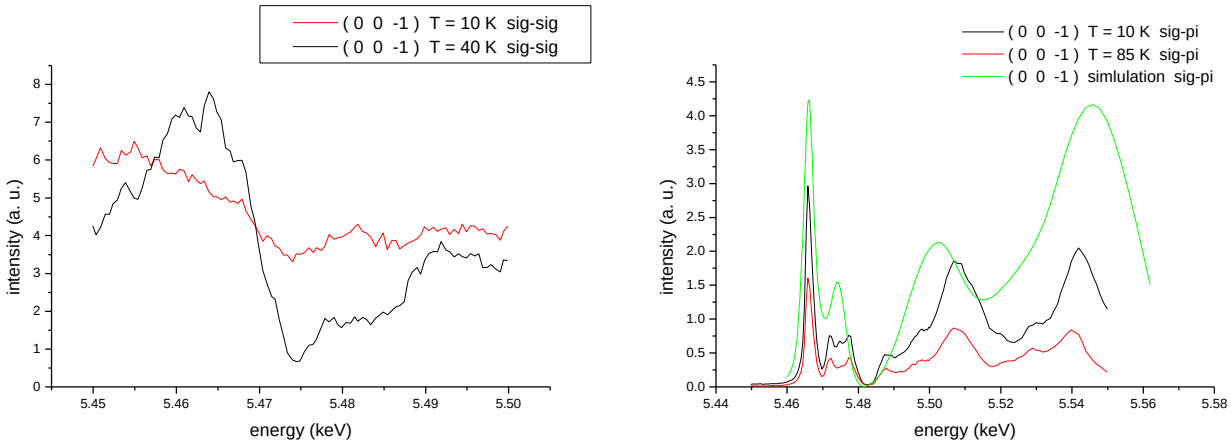

fig.2: Intensity of the (0 0 -1) reflection in polarization σ–σ (a) and σ–π (b) at various temperatures

Finally, we have tried to detect the magnetic reflections related to the T_X transition. We have investigated the same wave vectors than these measured in the neutron scattering study [3] : (0 0.452 0) and (2.452 0 0). The measurements have been performed at 5.466, 5.51 and 5.55 keV. No additional reflection has been detected. The temperature was probably above T_X due to the temperature shift, that's why none was observed.

In conclusion, anomalous scattering at the vanadium K edge shows interesting behavior of forbidden Bragg reflections which needs to be understood with the help of XANES calculations and the low temperature structure. A powder diffraction study, which will be performed on the ID31 ESRF beam line, is in progress to determine the low temperature structure. This result will enable us to choice satellite reflections on which interesting anomalous effects should be observed.

[1] M. Gherida et al, J. Phys. C **19**, 6489 (1986)
[2] H. Nakamura et al, J. Phys. Soc. Jpn. **69**, 2763 (2000)
[3] M. H. Whangbo et al, J. Solid State Chem. **165**, 345 (2002)
[4] S. Fagot et al, Phys. Rev. Lett. **90**, 196401 (2003)
[5] S. Grenier et al, Phys. Rev. B **65**, 180101 (2002)