


Experiment title:

OBSERVATION OF ORBITAL ORDERING
WITH X-RAY SCATTERING

**Experiment
number:
HE-311**

Beamline:
ID20

Date of Experiment:

from: 17-Jun.-98 to: 23-Jun.-98

Date of Report:

25/08/98

Shifts:
18

Local contact(s):

L. Paolasini ESRF Grenoble

Received at ESRF :
25 AOUT 1998

Names and affiliations of applicants (*indicates experimentalists):

C. Vettier	ESRF Grenoble
F. Yakhou	ESRF Grenoble
D. Mannix	ESRF Grenoble
W. Neubeck	ESRF Grenoble
A. Stunault	ESRF Grenoble
F. De Bergevin	ESRF Grenoble
M. Altarelli	ESRF Grenoble

For this preliminary experiment we have chosen to measure a 2.8% Cr-doped ($V_{1-x}Cr_x$) $_2O_3$ ($x=0.028$) single crystal. It was grown using skull melter by the Chemistry Department of Purdue University (Indiana, USA). The nominal stoichiometry was tested measuring the DC susceptibility at Laboratoire L. Neel (Grenoble). The effect of Cr-substitution at V site is to increase the Mott metal-insulator transition (PM→AFI) at T_N - 180K, whereas the underdoped V sample has a reduced T_N -150K. The understanding of physical properties of these compounds at different dilution is a fundamental question addressed by our project.

V_2O_3 crystallises in the α -corundum structure (space group No. 165, $R\bar{3}c$) and can be described by the hexagonal space group with the lattice parameters $a_H=b_H=5.004$ Å, $c_H=13.932$ Å for 2.8% Cr-doped. At T_N , the samples become antiferromagnetic with an ordered moment on the V-site of $1.2 \mu_B$ and a propagation vector of type $(1/2, 1/2, 0)_H$. The distorted structure can be described by a monoclinic lattice ($I2/a$) with $a_m=7.277$ Å, $b_m=4.997$ Å, $c_m=5.540$ Å and $\beta=96.74^\circ$ [2-5]. The cutting operations as well as the surface preparation have been performed at SPSMS/DRFMC/MDN at CEN Grenoble. The final surface etching was made at Chemical Laboratory of ESRF using a dilution of *Aqua Regia*. The crystal of dimension $1.0 \times 0.5 \times 0.05$ mm³, with the planar surface orientation choose is the $\langle 110 \rangle_H$, was glued with wax on a sample holder and put inside a close cycle refrigerator. The experiment was carried out tuning the incident photon energy around the K-edge of Vanadium (at $E=5476$ eV, $\lambda=2.264$ Å). The preliminary room temperature measurements were undertaken in order to understand the lattice structure, the quality of the surface and the absorption of the crystal. The fluorescence measured with a grazing take-off angle of 3° (Fig. 1, upper panel) shows the transitions allowed at the absorption K-edge of Vanadium. The first derivative allows us to assign the correct energies at the different states involving the dipole and quadrupole transitions. As already pointed out [6], the pre-edge $1s \rightarrow 3d$ transitions, forbidden to zeroth order, become allowed because of the presence of a small admixture of 4p-antibonding states due to the lack of inversion centre in the V-O coordinations [7]. In the AFI region the monoclinic distortion gives rise to a splitting of charge Bragg peaks in three domains, but because the thickness of the crystal used (~ 50 μm), only one domain was formed. This result have permitted us to select only one magnetic domain, with a propagation vector $[0, 1, 0]_m^*$. The lower two panels of Fig. 1 shows the energy-scans taken at 100K of two magnetic reflections $(221)_m^*$ and $(131)_m^*$ with the polarisation analysis configured ($\sigma-\pi$ and $\sigma-\sigma$ channels). The sharp peak at $E=5465$ eV corresponds to the transition associated to the $1s \rightarrow 3d$ antibonding states with $t_{2g}(\pi)$ symmetry, in addition to a complex multiplet structure centred at $E=5476$ eV, observable only in the $\sigma-\pi$ channel (central panel, absent in the lower panel), and covering the energy region where the $1s \rightarrow 4p$ transitions are allowed. The temperature dependence of the integrated intensities of the magnetic peak $(221)_m^*$, at these two energies is show in the lower panel of Fig.2. Obviously, the magnetic signal disappears at $T_N=180K$, as determined by the DC susceptibility. Below $T^* \sim 150K$ a bump appears which is more intense in the quadrupole transition

associated to the $3d-t_{2g}(\pi)$ states. At this temperature the lattice constant, determined by the longitudinal scans around the $(231)^*$, charge peak (central panel of Fig2), show an anomalous behaviour in a continuous manner, in contrast with what is observed in pure V_2O_5 . Note that 150K corresponds to the metal-insulator magnetic transition in the pure compound. The last part of the experiment was dedicated to the search of the peaks of the orbital ordering. In fact, as suggested by many authors [8-9] and following the calculations and suggestions of theoretical group at ESRF [10], the orbital order in V_2O_5 is expected to break the translation symmetries giving rise to a propagation vector located at different positions in reciprocal lattice with respect to the antiferromagnetic one. The two different orbital structures proposed correspond to propagation vectors $(1/3,1,-1/3)^*_m$ and $(2/3,1,1/3)^*_m$ (these reciprocal vectors are expressed in our monoclinic domain, and are equivalent to the hexagonal reflections $(1,-1/2,1)^*_H$ and $(2/3,1,1/3)^*_H$, respectively). Despite the lack of orbital order peaks at the positions proposed, these results are important and motivate the continuation of this project. The main question arising concerns the possibility to have a different behaviour in the 2.8% Cr-doped V_2O_5 single crystal with respect the pure compounds. In fact, from our results it is tempting to ascribe the $T^*=150K$ to the orbital ordering temperature. In this case leading to a two different and separate order parameters where the magnetism drive the orbital order. This fact can explain why the Cr-doped samples have a modified structural transition with respect to the pure. This assumption is confirmed by inelastic neutron scattering [11] where just below the T_N a big increase of inelastic signal is present in samples with different dilution. The bump exist also in the recent magnetoresistance measurements and it is suppressed by the pressure [12].

References

- [1] - K.I. Kugel' and D.I.Khomskii, Sov. Phys. Usp **25**, 231 (1982); Sov. Phys. JETP **37**.
 [2-5] - P.D. Dernier and M. Marezio, Phys. Rev. B **2**, 3771 (1970); J. Phys. Chem. Solids **31**, 2569 (1970); D.B. McWhan and J.P. Remeika, Phys. Rev. B **2**, 3734 (1970); A. Jayaraman, D.B. McWhan, J.P. Remeika and P.D. Dernier, Phys. Rev. B **3**, 3751 (1970); A. Menth and J.P. Remeika, Phys. Rev. B **2**, 3756 (1970).
 [6] - A. Bianconi and C.R. Natoli, Solid State Communications **27**, 1177 (1978);
 [7] - J. Wong, F.W. Lytle, R.P. Messmer and D.H. Maylotte, Phys. Rev. B **30**, 5596 (1984).
 [8-9] - C. Castellani, C.R. Natoli and J. Ranninger, Phys. Rev. B **18**, 4945-4966, 4967-5000 and 5001-5013 (1978); T.M. Rice, in Springer Series in Solid-State Sciences, Vol. 119: "Spectroscopy of Mott Insulators and Correlated Metals", Eds. A. Fujimori and Y. Tokura, Springer Verlag Berlin Heidelberg (1995).
 [10] - M. Fabrizio, M. Altarelli and M. Benfatto, Phys. Rev. Letters **80**, 3400 (1998).
 [11] - Wei Bao, C. Broholm, G. Aeppli, P. Dai, J.M. Honig and P. Metcalf, Phys. Rev. Letters **78**, 507 (1997); Phys. Rev. B **54**, R3726 (1996); to be published in Phys. Rev. B (30 April 1998, #cond-mat/9804320);
 [12] - S. Mederle-Hoffmeister, S. Klimm, M. Klemm and S. Horn, Proceeding of SCES, Paris (1998)

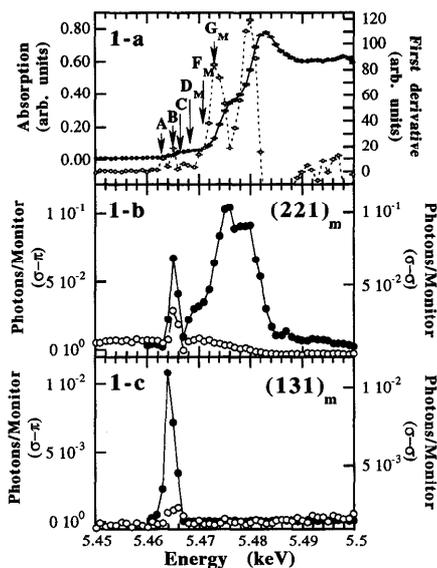


Fig.1 Energy scans of Cr-doped sample. The panel 1-a shows the K-photoabsorption spectrum (filled points) taken at room temperature. The capital letters mark the different transitions determined from the maxima of the absorption first derivative (wide points): the peak B corresponds to the transitions to $3d$ anti-bonding states with symmetries $t_{2g}(\pi)$ [see Ref. 6]. The two panels b-c show the E-scans of antiferromagnetic Bragg peaks $[221]_m$ and $[131]_m$ taken at $T=100K$ in $\sigma-\sigma$ (wide points) and $\sigma-\pi$ (black points) polarisation analysis

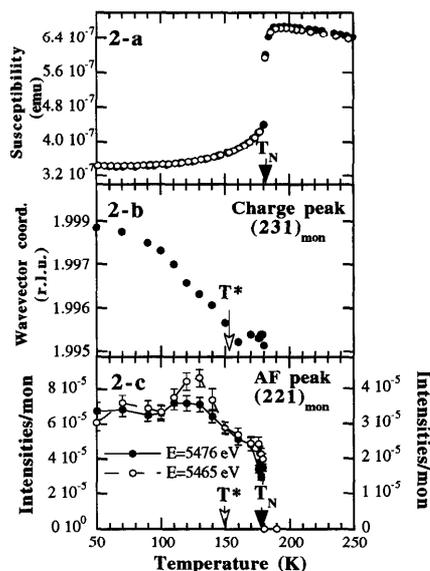


Fig.2 a) DC susceptibility showing the Néel magnetic transition $T_N=180K$ (doped sample). The filled (wide) point is the heating (cooling) measurements.
 b) Temperature evolution of the centre position of charge peak $[231]_m$ taken by a scan along the longitudinal direction $\langle H,H,0 \rangle_m$. $T^*=150K$ is the lattice distortion temperature from rhomboidal to monoclinic structure
 c) Temperature dependence of the integrated intensities of the antiferromagnetic Bragg peak $[221]_m$ at the dipole and at the quadrupole resonant energies of the Vanadium K-edge. The bump appearing at T^* is enhanced at the quadrupole energy.