	Experiment title: Resonant Inelastic X-ray Scattering of V and Cr K pre-edge in spinels and garnets	**Experiment number**: HE-2318
Beamline: ID26	**Date of experiment**: from: 31 january 2007 to: 6 february 2007	**Date of repor** 06-03-07
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Names and affiliations of applicants (* indicates experimentalists):

Amélie JUHIN*	IMPMC University Paris VI
Amélie BORDAGE*	IMPMC University Paris VI
Dr. Etienne BALAN*	IRD - IMPMC University Paris VI
Pr. Johan de VILLIERS	University of Pretoria (RSA)
Dr Delphine CABARET	IMPMC University Paris VI
Dr Laurence GALOISY	IMPMC University Paris VI
Prof. Georges CALAS	IMPMC UniversityParis VI

Report:

The goal of the experiments carried out last month (February 2007) was to investigate the K pre-edge features of the RIXS spectrum of trivalent chromium and vanadium in spinel and garnet structures. These measurements will bring original constraints about the electronic structure, and therefore about the mechanisms related to the contrasted coloring properties of chromium in cubic structures. In addition, a detailed analysis of the pre-edge feature of vanadium will improve the determination of the V redox state in natural compounds, such as magmatic titanomagnetite, using RIXS spectroscopy.

During these experiments we have measured the K-edge RIXS spectrum (3p1s decay channel) of Cr and the high-energy resolution X-ray emission spectra of Cr in garnet (pyrope $Mg_3Al_2Si_3O_{12}$) and a series of synthetic spinels ($MgAl_2O_4$) with various Cr contents. We have also measured the angular dependence of the K-edge RIXS spectrum (3p1s decay chanel, analyzer Ge (3,3,3) of Cr in spinel and that of the K-edge RIXS spectrum (2p1s decay chanel, analyzer Ge(3,3,1) of V in garnet (grossular $Ca_3Al_2Si_3O_{12}$). In these cubic compounds the angular dependence of the pre-edge features is related to anisotropic electric quadrupole terms. The measurements were performed on the (110) face of crystals cuts, with the propagation and polarization vectors varying between **k**:(-100), **E**:(010) and **k**:(-1/2,-1/2,

1/√2), **E**:(1/2,1/2,1/√2). The crystal was rotated around the (1,1,0) direction, with the previous configurations corresponding respectively to a rotation angle of 0° and 90°.

A pair of Si (1,1,1) crystals was used to select the energy of the incident beam. In order to limit the absorption of the fluorescence, a bag filled with gazeous He was positioned between the sample holder and the detection area. The RIXS spectra were recorded in the quick scan mode : for each rotation angle, we recorded 2 EXAFS (used for normalization), 2 XANES and 10 Pre-edge spectra. The spectra recorded using the high-energy resolution spectrometer of the ID26 beamline have very low background and very good signal-to-noise ratio, making it possible to measure the small quadrupolar dependence of pre-edge features in cubic crystals. As expected, the maximum variation of pre-edge as a function of the experimental geometry was observed for the two configurations above mentioned (Figure 1). However, we registered the full angular dependence circle with steps of 15°, to get rid of possible experimental artifacts. Three shifts were needed for the Cr-dilute spinel in order to record a nice angular dependence from the Kß fluorescence. The pre-edge features are very different for Cr and V in their respective sites, but we obtained a very clear angular dependence for the two crystals investigated. Comparison with theoretical multiplet calculations of pre-edge spectra is now under progress. This will provide us with important information about the electronic environment of Cr and V in these compounds.

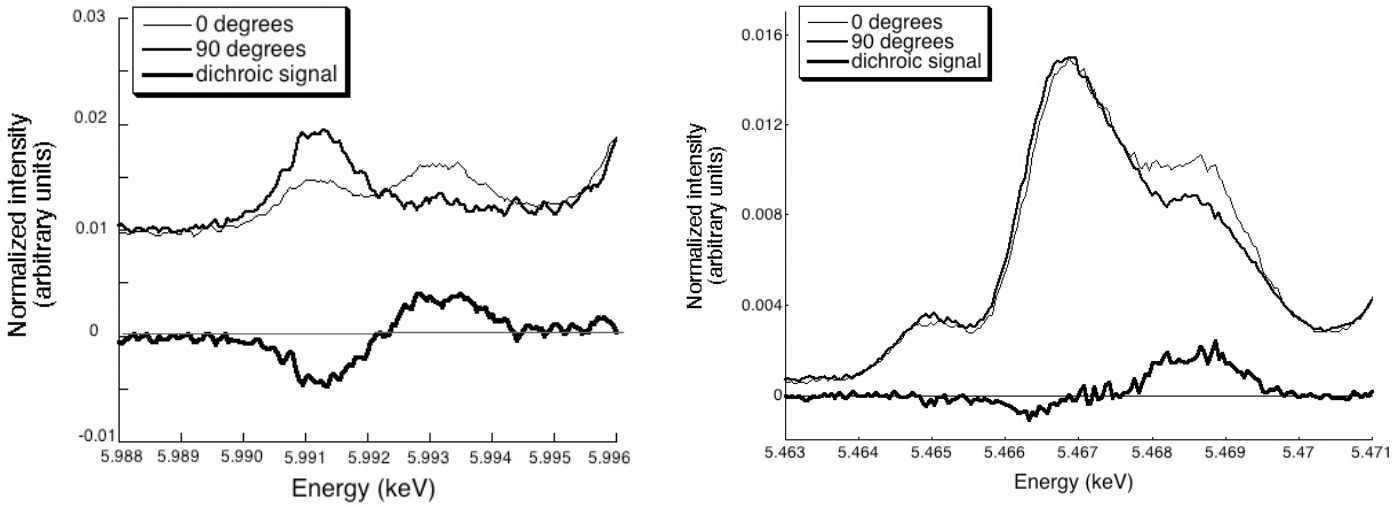

Figure 1 : Angular dependence of the XANES K pre-edge in Cr-bearing spinel (left) and V-bearing garnet (right). The label indicates the angle of the rotation performed around the (1,1,0) direction, from the starting configuration (**k**:(-100), **E**:(010)).

High-energy resolution X-ray emission spectra showing the Kß main and satellite lines of Cr have been recorded on ten powdered samples, with both different structure (corundum, garnet, spinel) and Cr-content. For each, we recorded also the EXAFS, XANES and pre-edge spectra. Two shifts of beamtime were required to complete it. Significant variations of the position and intensity of the satellite lines ($K\beta_{2,5}$) have been observed as a function of Cr concentration in spinel (Figure 2). The emission spectra will enable us to quantify the changes of the iono-covalent nature of the Cr-O bond with the Cr-content and the Cr-site symmetry.

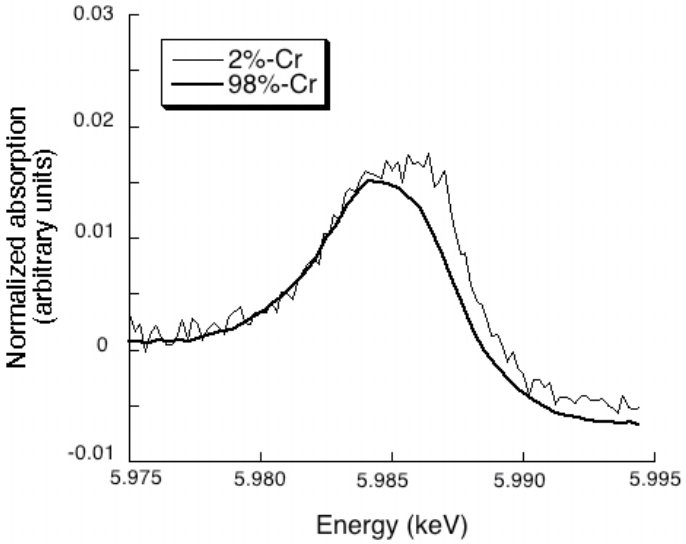

Figure 2 : $K\beta_{2,5}$ satellite lines of Cr in spinels as a function of Cr concentration

From a technical point of view, these experiments were very successful. The first results indicate also that RIXS spectroscopy is fully adapted to investigate the electronic environment of Cr and V in spinel and garnet samples. We particularly appreciated the technical help provided by S. Eeckhout, P. Glatzel and M. Sikora during the experiment.