

**Experiment title:**

Pressure-induced valence change in Yb metal studied by resonant inelastic x-ray scattering.

**Experiment number:**  
HE1021

<b>Beamline:</b> ID16	<b>Date of experiment:</b> from: 3 <sup>rd</sup> July 2001      to: 13 <sup>th</sup> July 2001	<b>Date of report:</b> 29 <sup>th</sup> August 2001
<b>Shifts:</b> 27	<b>Local contact:</b> Abhay Shukla	<i>Received at ESRF:</i>

**Names and affiliations of applicants (\* indicates experimentalists):**

Claudia Dallera \*  
Politecnico of Milano  
Department of Physics  
Piazza Leonardo da Vinci, 32  
20 133 Milano (Italy)

Frank de Groot  
Sorbonnelaan 14-16  
3584 CA Utrecht  
The Netherlands

**Report:**

The experiment was aimed to study the pressure driven valence change of ytterbium by the technique of Resonant Inelastic X-ray Scattering (RIXS).

Yb metal is divalent at ambient pressure and is known from  $L_3$  x-ray absorption<sup>i</sup> to be predominantly trivalent above 300 kbar. This information was determined by monitoring the change in position and shape of the  $L_3$  whiteline: the ytterbium absorption profile was decomposed into a divalent component and a replica component due to trivalent configuration.

RIXS allows direct access to the different configurations of mixed-valent systems by tuning the excitation energy to a specific point of the excitation curve. Moreover the final state of the inelastic emission process is characterized by a shallower core-hole with respect to the final state of the absorption process. RIXS at the  $L_3$  edges of rare earth elements and their compounds allows to separate the weak quadrupolar ( $E2$ ,  $2p \rightarrow 4f$ ) excitation channel from the dominant dipolar ( $E1$ ,  $2p \rightarrow 5d$ ) excitation channel thanks to the large energy separation of the respective final state multiplets<sup>ii</sup>. The case of Yb is particularly favourable as the divalent ground state corresponds to a completely filled  $4f$  shell and therefore any spectral feature due to a  $4f^{n+1}$  final state indicates the presence of a trivalent component. Therefore the proposed experiment was aimed at the determination of the pressure-dependent valency of Yb metal via the appearance and the intensity increase of the  $4f^{14}3d^9$  final state multiplet in the RIXS experiment at the Yb  $L_3$  edge, thus providing a direct probe of the valence modification as a function of pressure.

The experiment has been performed on a high purity Yb metal foil loaded in a diamond anvil cell (utilizing a beryllium gasket). Ytterbium  $2p_{3/2}$  core level was resonantly excited at and before the edge. The radiation emitted due to  $4d \rightarrow 2p$  decay was analyzed by a silicon (551) spherical crystal mounted in the Rowland geometry. As a reference for the divalent and trivalent state, we measured spectra at ambient pressure from Yb metal and from the pure Yb<sup>3+</sup> compound Yb<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub>.

The emission spectra were first recorded in the Partial Fluorescence Yield spectrum (PFY) mode, i.e. by recording the integrated  $4d \rightarrow 2p$  emission as a function of the incident photon energy.

A selection of PFY spectra is presented in Figure 1 and can be summarized as follows: (i) upon application of pressure, the ytterbium valence change is revealed by the progressive shift of the energy-position of the  $2p^6 4d^9 5d^{n+1}$  final state. The peak position stabilizes above 200 kbar. However (ii) the feature due to the  $2p^6 4d^9 5d^n 4f^{n+1}$  final state is not seen (at variance with the reference case of the ionic trivalent  $\text{Yb}_3\text{Fe}_5\text{O}_{12}$  compound). In fact the onset of the main dipolar line does not shift as in the trivalent ionic case and therefore any quadrupolar feature remains invisible. The comparison with spectra taken on intermediate-valent compounds  $\text{YbInCu}_4$  and  $\text{YbAgCu}_4$  ( $n_f$  around 13.2) suggests that also at the highest pressure the  $f$  electron count for metallic ytterbium differs from 13 (in disagreement with the conclusions of ref. i). We note that the highest applicable pressure was 280 kbar, but that PFY spectra taken at 200 and 280 kbar are identical.

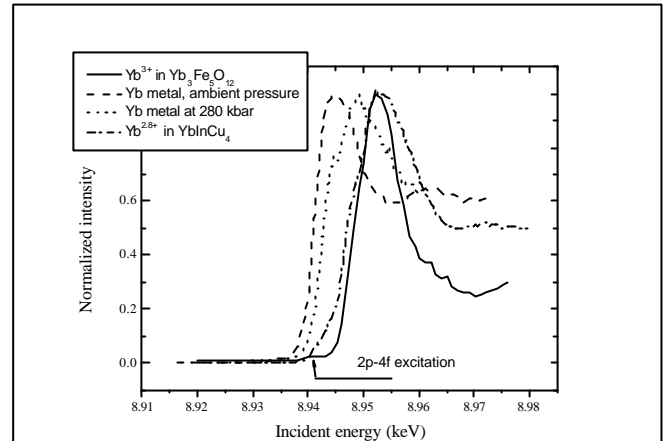


Figure 1. Partial Fluorescence Yield spectra of trivalent ytterbium in a garnet compound, of metallic Yb at ambient and high pressure, and of mixed-valent ytterbium in  $\text{YbInCu}_4$ .

Figure 2 displays  $4d-2p$  de-excitation spectra as a function of the emitted photon energy. The incident photon energy was set to the  $2p-4f$  resonance (indicated by the arrow on Figure 1). The garnet spectrum shows a feature at lower transferred energy, corresponding to the  $4d^9 4f^{14}$  final state of the trivalent Yb ion. The similar spectra of metallic ytterbium do not show any feature which might be attributed to a quadrupolar excitation, regardless of the applied pressure.

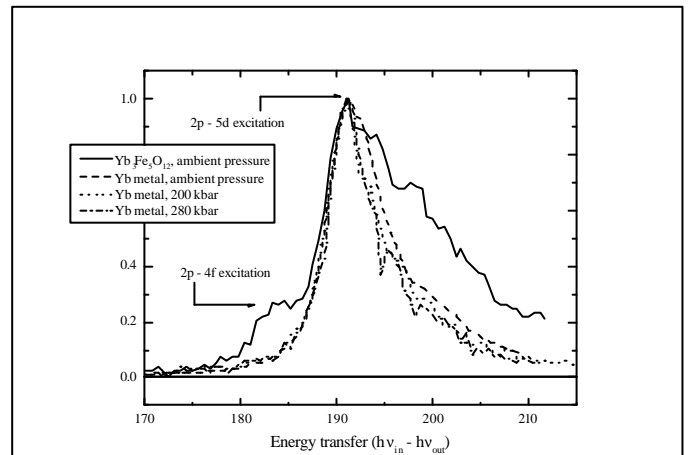


Figure 2.  $4d-2p$  RIXS spectra excited by photons with energy tuned to the  $2p-4f$  excitation energy (shown by the arrow on Figure 1). The signature of the  $4f^{n+1}$  final state is visible only in the ionic garnet compound

The measured spectra call for a better understanding of the mechanism underlying the observed valence change. It has been proposed<sup>iii</sup> that there are two types of  $f$  electrons: localized core-like  $f$  electrons that determine the valence, and delocalized band-like  $f$  electrons that are formed through hybridization with the  $spd$  bands and which participate in the bonding. Pressure can induce the transition of a localized  $f$  electron to the delocalized situation. The valence change will not correspond to the presence of a free  $f$  state, as opposed to the situation of the ionic trivalent case having  $4f^{13}$  occupation. This issue deserves further investigation with the study of more complex systems where also partner atoms are present.

<sup>i</sup> G. Wortmann, K. Syassen, K.H. Frank, J. Feldhaus, G. Kaindl, in *Valence Instabilities* (North-Holland Publishing Company, 1982), p. 159.

<sup>ii</sup> C. Dallera, M.K. Krisch, A. Rogalev, C. Gauthier, J. Goulon, F. Sette, and A. Sole, *Phys. Rev. B* **62**, 7093 (2000).

<sup>iii</sup> P. Strange, A. Svane, W.M. Temmermann, Z. Szotek, H. Winter, *Nature* **399**, 756 (1999)