



	<b>Experiment title:</b> Bulk-sensitive 3d core-level photoemission study of strongly correlated Pr, Sm and Yb compounds by using high-energy excitations	<b>Experiment number:</b> HE-1422
<b>Beamline:</b> ID32	<b>Date of experiment:</b> from: 28/08/2002 to: 03/09/2002	<b>Date of report:</b> 10/09/2016
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## Report:

Photoemission from 3d core-levels is an element-specific measurement that can probe the 4f electronic states of strongly correlated rare-earth compounds as well as the mean valence of the rare-earth ions, which are responsible for interesting phenomena such as the Kondo effect, heavy fermion behavior, valence-fluctuation, etc. However, the binding energies of 3d core-levels in the rare-earths Pr, Sm, Yb range from 900 to 1600 eV and when conventional soft x-ray sources such as Mg-K $\alpha$  and Al-K $\alpha$  lines ( $h\nu < 1500$  eV) are employed, the Yb 3d core-level cannot be measured and the surface contribution is high for Pr and Sm 3d core-level photoemission spectra due to the low photoelectron kinetic energies. Since the surface electronic states are essentially different from the bulk states in the rare-earth compounds without exception, it is compulsory to use synchrotron radiation in order to obtain truly bulk-sensitive rare-earth photoemission spectra. Therefore, we have performed the experiments at the highest possible photon energies, aiming to a precise determination of both bulk and surface mean valences of the strongly correlated (mixed-valence) rare-earths Pr, Sm, Yb compounds by measuring the photon-energy dependence of the 3d core-level photoemission spectra.

The hard x-ray photoemission spectroscopy (HAXPES) were carried out at ID32 of ESRF by using a PHI hemispherical analyzer. In order to obtain clean surfaces, the samplers were fractured in situ under the base pressure of  $\sim 10^{-8}$  Pa at the measuring temperature of  $\sim 180$  K.

We selected photon energies of 2450, 3950 and 5450 eV in order to systematically examine the surface contributions in the core-level spectra.

The excitation photon energy dependence of the Yb  $3d_{5/2}$  spectra of a valence-fluctuating system  $\text{YbAl}_3$  is displayed in Fig. 1 [1,2]. The line shape in the energy region where the  $\text{Yb}^{3+}$   $3d$  final-state multiplet structure appears does not change between  $h\nu = 2450$  and  $5450$  eV indicating that there is no surface contribution of the  $\text{Yb}^{3+}$  state. When the spectra are normalized by the intensity of the  $\text{Yb}^{3+}$   $3d_{5/2}$  spectral weights, the intensity of the  $\text{Yb}^{2+}$   $3d_{5/2}$  single peak is stronger at  $h\nu = 2450$  eV than  $h\nu = 5450$  eV. This different spectral weight of the  $\text{Yb}^{2+}$  component originates from a different surface contribution depending on the kinetic energy. As shown in the figure, the peak energies of the  $\text{Yb}^{2+}$  contributions are mutually different between the bulk and surface, where the surface core-level shift has been estimated as  $\sim 0.5$  eV. From the analyses of the spectra, the bulk contribution in each spectrum has also been estimated as  $\sim 85\%$  at  $h\nu = 2450$  eV (corresponding to the photoelectron kinetic energy  $E_K \sim 930$  eV) and  $\sim 95\%$  at  $h\nu = 5450$  eV ( $E_K \sim 3930$  eV).

We also carried out HAXPES for heavy fermion Pr compounds [3,4] and  $\text{Sm}_4\text{As}_3$  [5,6]. A significant spectral intensity of the  $3d^9 4f^3$  final state was observed in Pr  $3d$  core-level spectra of  $\text{PrFe}_4\text{P}_{12}$ . The spectra obtained by the configuration-interaction cluster model calculation reproduce the experimental spectra for well-hybridized  $\text{PrFe}_4\text{P}_{12}$  and localized Pr metal. Results of the calculations suggest that the Kondo behavior observed in  $\text{PrFe}_4\text{P}_{12}$  arise from the mixing of the  $4f^2$  ( $\text{Pr}^{3+}$ ) and  $4f^3$  ( $\text{Pr}^{2+}$ ) configurations due to the c-f hybridization. For  $\text{Sm}_4\text{As}_3$ , it has been found that the absence of valence mixing, that is, the valence of Sm ions is definitely trivalent in the bulk and divalent on the surface. Atomic multiplet calculations taking into account the bulk and surface spectral weights well reproduce the experimental Sm  $3d$  core-level spectra, supporting the valence difference between bulk and surface in  $\text{Sm}_4\text{As}_3$ .

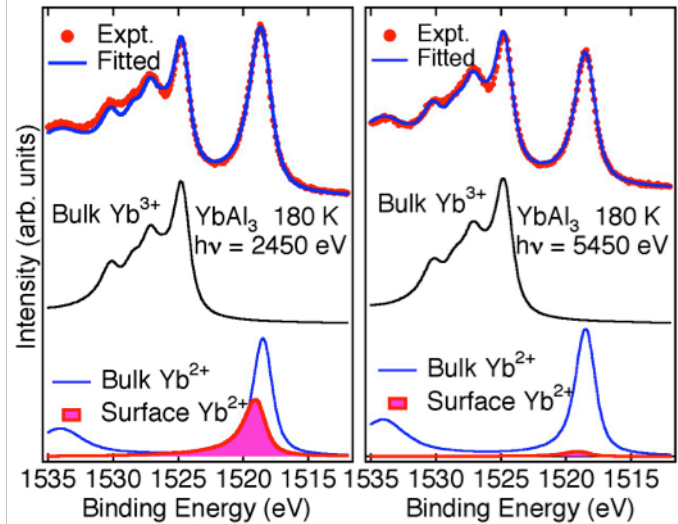


Fig. 1 Yb  $3d_{5/2}$  core-level HAXPES spectra of  $\text{YbAl}_3$  at  $h\nu$ s of 2450 and 5450 eV, and deconvolution into the bulk  $\text{Yb}^{3+}$ , bulk  $\text{Yb}^{2+}$  and surface  $\text{Yb}^{2+}$  contributions.

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