ESRF	**Experiment title:** High-energy 3d resonant photoemission in Sm and Eu compounds excited at the L3 edge.	**Experiment number**: HE-1079
Beamline: ID32	**Date of experiment**: from: 27/3/2001 to: 3/4/2001	**Date of report**: 27/2/2002
Shifts: 18	**Local contact(s)**: B. Cowie	*Received at ESRF:*

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Report:

Results of the experiment have appeared in the *ESRF Highlights 2001* issue.
The article 'High-Energy Photoemission Study of the Bulk and Surface of Samarium Compounds' is attached in the following pages.

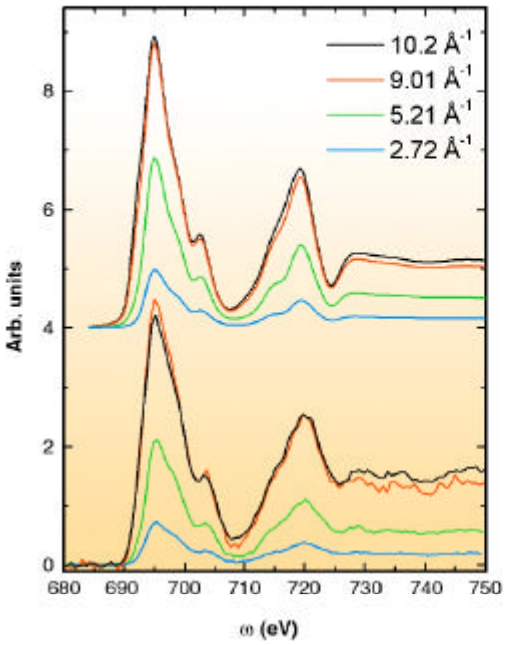

Fig. 1: The experimental (lower) and the theoretical NRIXS (upper) spectra of fluorine K-edge in LiF. The various momentum values used are indicated in the figure.

Figure 1 shows the measured high-resolution NRIXS scattering spectra from LiF measured at beamline **ID16** using an eV-resolution backscattering Rowland-circle spectrometer utilising a spherically bend analyser crystal, together with our *ab initio* calculation. As expected, there is no dramatic momentum transfer dependence in the spectral shape beyond the expected q^2 intensity variation. However, when the edge region is measured with better energy resolution (as shown in **Figure 2**), peculiar intensity dependence for the resolution-limited pre-peak is observed. Our calculation, which takes into account the important electron-hole interaction [2], shows that the observed feature is associated with excitons, typical for a wide-gap insulator like LiF. Furthermore, since our computational scheme is not limited to the dipole approximation, we can associate the pre-peak as an s-type exciton (with an expected q^4 intensity dependence).

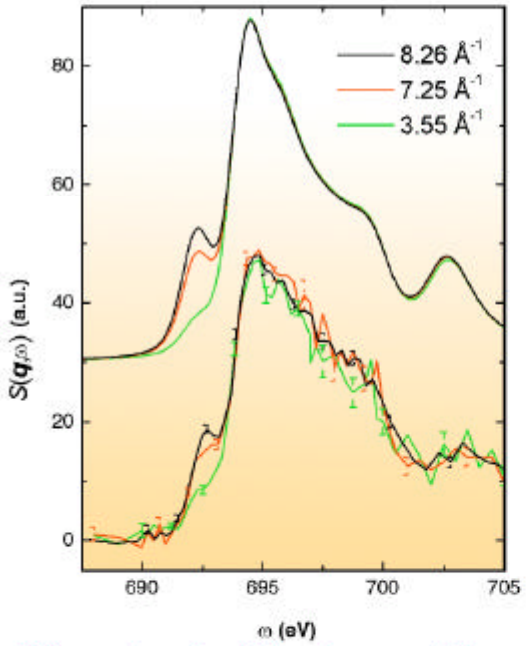

Fig. 2: The pre-edge region of Figure 1 measured with energy resolution of about 1 eV. The spectra above the pre-edge region are normalised to the same peak value to emphasise the different momentum dependence of the s-type exciton feature at about 692.5 eV.

With this work we have shown that high resolution NRIXS experimental data together with an ab initio computational scheme can give detailed information about the electronic structure beyond absorption spectroscopy, giving an opportunity to distinguish the various core excitations with different spatial symmetries.

References

[1] W.A. Caliebe, J.A. Soininen, E.L. Shirley, C.-C. Kao and K. Hämäläinen, *Phys. Rev. Lett.* **84**, 3907 (2000).
[2] J.A. Soininen and E.L. Shirley, *Phys. Rev. B* **64**, 165112 (2001)

Principal Publication and Authors

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High-Energy Photoemission Study of the Bulk and Surface of Samarium Compounds

Photoemission spectroscopy is a powerful tool for investigating the electronic structure of solids. It provides information on a topmost layer whose depth depends on the kinetic energy of the measured electrons. The minimum value of the electron escape depth (few Å) occurs for kinetic energies around 10÷100 eV, while for increasing kinetic energies it gets larger. Hence bulk-sensitive information can be obtained in photoemission experiments only if high-energy electrons are detected. Few experiments [1,2] have been performed so far in the high kinetic-energy range, due to the unavailability of intense photon fluxes (required by the low cross-section values at high energy) and of analysers able to measure large photoelectron energies.

The analyzer limits were extended to their present capabilities in a recent experiment on **ID32**: we performed a photoemission study of Samarium in selected samples that

have different valence in the bulk and at the surface: Sm as a pure metal is divalent at the surface and trivalent in the bulk, in SmSe it is mixed valent, and in $SmPd_3$ it is trivalent. Spectra of 3d core levels measured with high-energy excitation are largely bulk sensitive and allow the valence of the rare-earth component in the volume to be determined. Photon energies from 3 to 6 keV were used in order to investigate the change of the surface vs. bulk sensitivity.

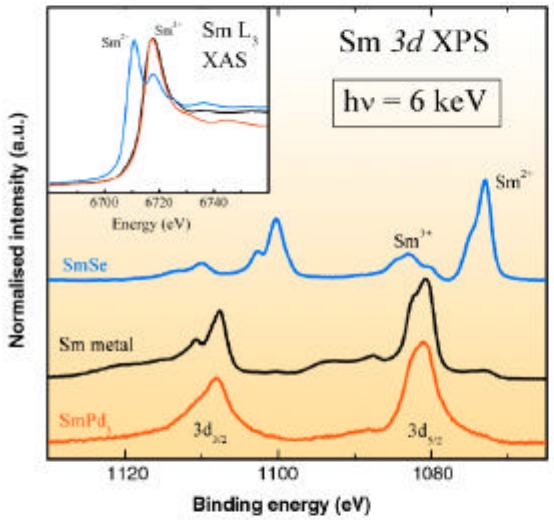

Fig. 1: Photoemission spectra of Samarium 3d levels in three samples with different weight of the divalent and trivalent component in bulk and surface, after background subtraction. The L_3 edge absorption spectra (inset) show less structure due to the larger lifetime broadening.

Figure 1 shows photoemission spectra of the 3d levels of Sm in the different samples, excited at hν = 6 keV. The peaks related to the Sm^{2+} and Sm^{3+} configuration are well separated and reflect the different valence states. It is interesting to compare the photoemission spectra with absorption spectra of the Sm L_3 edge in the same compounds (inset of Figure 1): the two techniques have similar bulk-sensitivity (sampled depth ~ 40 Å) but the larger lifetime broadening of the 2p levels hides the small divalent surface component of metallic samarium in the absorption spectrum. SmSe, at variance with the previous samples, shows a clear Sm^{2+} feature.

The change of the surface vs. bulk contribution to the spectral shape is shown in **Figure 2**. Our photoemission spectra of the Sm 3d core levels are compared with a spectrum excited with a conventional X-ray tube. The spectral weight at lower binding energies originates from the divalent configuration present in the outer layers of samarium. A striking decrease of the surface component intensity is seen in the bulk sensitive spectra excited at 3 and 6 keV. The decrease of the divalent intensity when increasing the photon energy from 3 to 6 keV is slower than expected from the anticipated square root dependence of the escape depth on the photoelectron kinetic energy. This might perhaps indicate the presence of a divalent

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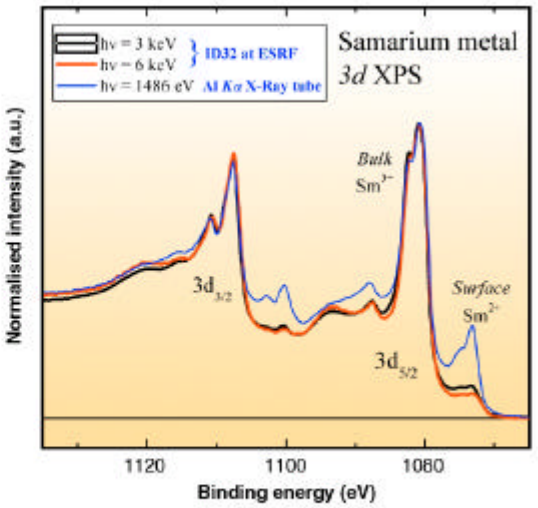

Fig. 2: Photoemission spectra of 3d levels in pure metallic Samarium. Spectra at 3 and 6 keV were measured at ID32 while the spectrum excited at 1486 eV was taken with an X-ray tube. A relevant decrease of the divalent surface component with increasing energy is seen.

component in the bulk, or a trend of the escape depth different from what was derived from earlier data. Both hypotheses are challenging and deserve being studied on further samples and in a wider photon-energy range.

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