ESRF	**Experiment title:** XANES studies on Ytterbium valence states in dicarbide compounds	**Experiment number**: HE 3501
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Shifts: 18	**Local contact(s)**: Pieter Glatzel	*Received at ESRF:*

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Report:

The rare-earth metal carbide with the highest carbon contents has the general formula REC_2 and contains C_2 dumbbells. Isostructural compounds are found for alkaline-earth metals with CaC_2 being the most prominent example. The later is a typical colorless ionic compound with insulating properties. It can be best described as being composed of Ca^{2+} and C_2^{2-} ions. Rare-earth metal carbides of composition REC_2 exhibit a different behavior. Most of them show metallic luster and metallic conductivity. In a simplifying notation they can be described as being composed of RE^{3+} and C_2^{2-} ions: $RE^{3+}(C_2^{2-})(e^-)$. The additional electron is "responsible" for the metallic properties. This very simple picture is confirmed by band structure calculations. In this respect EuC_2 and YbC_2 are most interesting, as Eu and Yb are known to exist in the divalent as well as in the trivalent state. For EuC_2 we found semiconducting properties and Eu being in a divalent state.[1] Former work on YbC_2 resulted in an intermediate valence of approx. 2.8 based on magnetic susceptibility measurements and neutron scattering data.[2,3] But despite the similar valence obtained in these investigations the underlying models are completely different pointing to a homogeneous[3] and a heterogeneous[2] valence, respectively.

To shed some light upon these discrepancies we conducted temperature dependent XANES spectroscopic investigations on YbC_2 at the L_3 edge using the HERFD mode.[4] Comparison with Yb_2O_3 (Fig. 1) with trivalent Yb showed additional features in the XANES spectra of YbC_2, which were assigned to divalent Yb. Using an empirical fitting procedure an Yb valence of approx. 2.8 was obtained for YbC_2 confirming the results in the literature. But in sharp contrast to a homogeneous Yb valence[3] no temperature dependence was observed in the temperature range 15-1123 K (Fig. 2). This temperature-independent behavior of the Yb valence in YbC_2 is confirmed by neutron diffraction experiments.[4] Further experiments (e.g. ^{170}Mössbauer spectroscopy) are under way to understand the physical properties of YbC_2 in more detail.

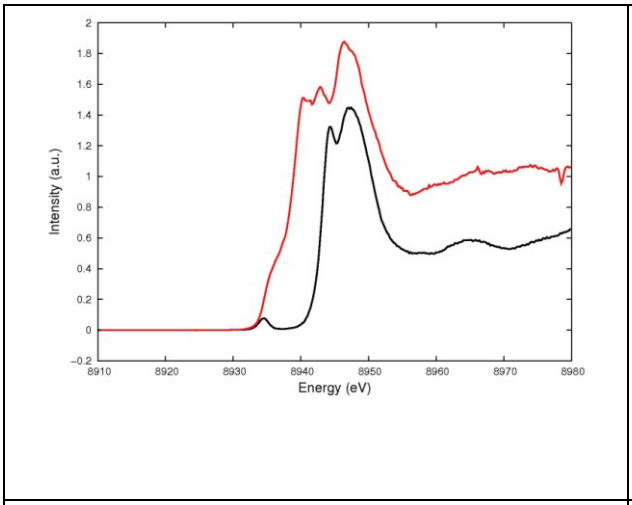

Figure 1. Yb L_3 HERFD-XANES spectra of YbC_2 (red) and Yb_2O_3 (black).

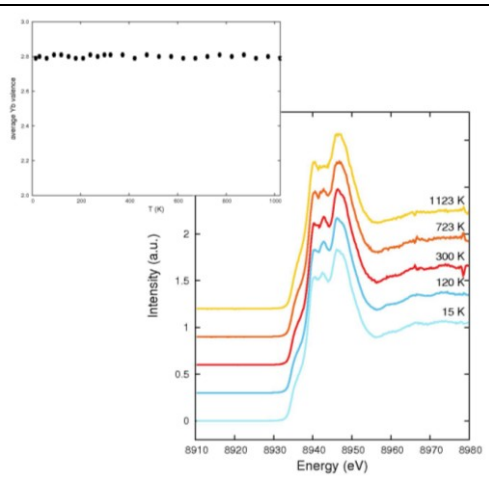

Figure 2. Yb L_3 HERFD-XANES spectra of YbC_2 at selected temperatures (right) and average Yb valence as a function of temperature (left).

The intermediate valence in YbC_2 suggests that it should be possible to manipulate the Yb valence state by external factors. Therefore, we studied the impact of "chemical pressure" on the Yb valence by synthesising solid solutions $Yb_xEA_{1-x}C_2$, composed of YbC_2 and an alkaline earth metal dicarbide EAC_2 (with EA = Ca, Sr, Ba). Using XANES-HERFD spectroscopy at the Yb L_3 edge we found interesting valence effects in $Yb_xCa_{1-x}C_2$ depending upon the composition (Fig. 3) and the temperature (Fig. 4). These valence effects are in nice agreement with the structural properties obtained from synchrotron powder diffraction data.

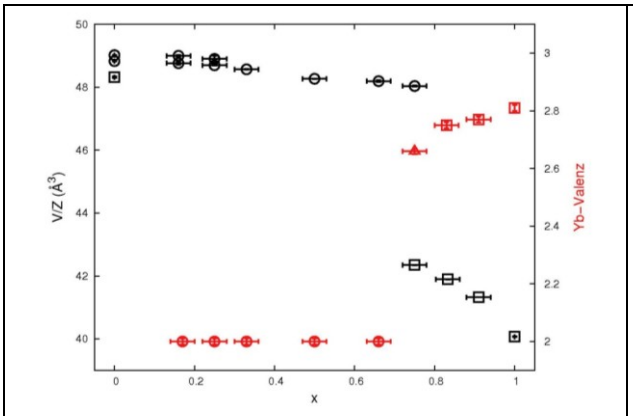

Figure 3. Yb valence (red, XANES-HERFD spectroscopy) and normalized unit cell volume (black, synchrotron powder diffraction data) of $Yb_xCa_{1-x}C_2$ in dependence of x.

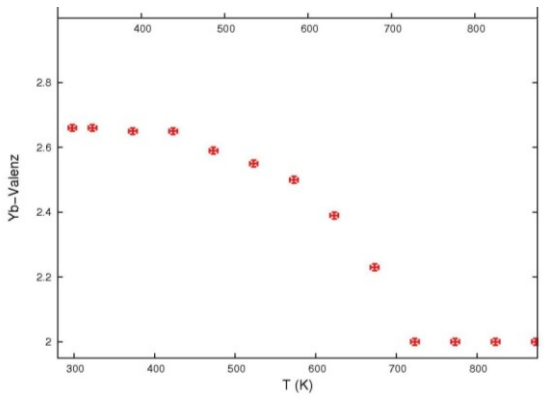

Figure 4. Yb valence (XANES-HERFD spectroscopy) of $Yb_{0.75}Ca_{0.25}C_2$ in dependence of the temperature.

References:

[1] D. Wandner, P. Link, O. Heyer, J. Mydosh, M. A. Ahmida, M. M. Abd-Elmeguid, M. Speldrich, H. Lueken, U. Ruschewitz, *Inorg. Chem.* **2010**, *49*, 312-318.

[2] M. Atoji, *J. Chem. Phys.* **1961**, *35*, 1950-1960.

[3] B. C. Sales, D. K. Wohlleben, *Phys. Rev. Lett.* **1975**, *35*, 1240-1244.

[4] P. Link, P. Glatzel, K. Kvashnina, R. I. Smith, U. Ruschewitz, *Inorg. Chem.*, submitted.