XANES investigations on mixed-valence $YbGa_{6+x}$

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The phase $YbGa_{6+x}$ is a representative of the serie RGa_6 which exist for almost all rare earth elements (R) with exception of Lu and Eu. The R:Ga ratio of 1:6 (RGa_6) is realised in the atomic arrangement of the related $PuGa_6$ structure type (space group P4/*nbm*) [1] but in case of the title compound additional interstitial Ga atoms modify the structural motif to form a tetragonal unit cell with *P*4/*mmm* symmetry and lattice parameter a = 4.30481(3) Å, c = 7.65442(5) Å, V = 141.847(3) Å^3. It crystalize in the structure type $CeCu_{0.6}Ga_6$. The $YbGa_{6+x}$ exists up to the peritectic temperature of 555 K. So, single phase samples and single crystals were synthesized by using self-flux method combined with the high temperature centrifugation to filter and purify the intermetallic phase from the excess of liquid Ga. Our ongoing investigations shows that $YbGa_{6+x}$ undergoes a polymorphic phase transformation at approx. 298 K which leads to an orthorhombic distortion characterised by the lattice dimensions of a = 4.31749(3) Å, b = 4.29976(3) Å, c = 7.65184(4) Å, V = 142.050(3) Å^3. The valence state of Yb was investigated by X-ray absorption spectroscopy at the Yb L_{III} edge. The spectra were recorded in transmission arrangement at the EXAFS beamline C of the Hamburg synchrotron radiation laboratory HASYLAB at DESY. Temperature was controlled by the Oxford cryostat equipment at T= 260 K, 297 K and 309 K which represents the upper operational limit of the cryostat. Wavelength selection in the range 8740 – 9400 eV with a minimal step size of 0.25 eV in the near edge region 8910 – 8960 eV of the Yb L_{III} absorption edge (8944 eV) was realized by means of a Si(111) double crystal monochromator. The mass of approx. 10 mg of powdered $YbGa_6$ with partial size < 20 μm was diluted with CB_4 powder and mounted in paraffin wax on kapton foil within an area of 1 cm^2. The step height of 0.4 in the absorption behaviour corresponds to $\Delta\mu \cdot d \approx 1$ ($\Delta\mu$ …difference of the background absorption coefficient at the absorption edge, d …sample thickness). Yb_2O_3 was used as an external reference for the Yb $4f^{13}$ configuration.The Yb L_{III} near edge region of the absorptions spectra of the phase $YbGa_{6+x}$ at 260 K e.g. the low temperature modification is shown in the figure 1. Both peaks at energies E = 8942 eV and 8950 eV represent the contributions of Yb with $4f^{14}$ (Yb^{2+}) and $4f^{13}$ (Yb^{3+}) electron configuration, and clearly evidence the mixed valence situation. The deconvolution of both peaks lead to a mean valence of +2.45. This calculation was realised by using the software XASWin [2]. The absorption spectrum does not show any temperature dependence. This preliminary result indicates that the phase transformation is not accompanied with valence changes of the Yb. The ongoing in-situ x-ray diffraction experiments and magnetic susceptibility measurements are performed to characterize the phase transformation in more detail.

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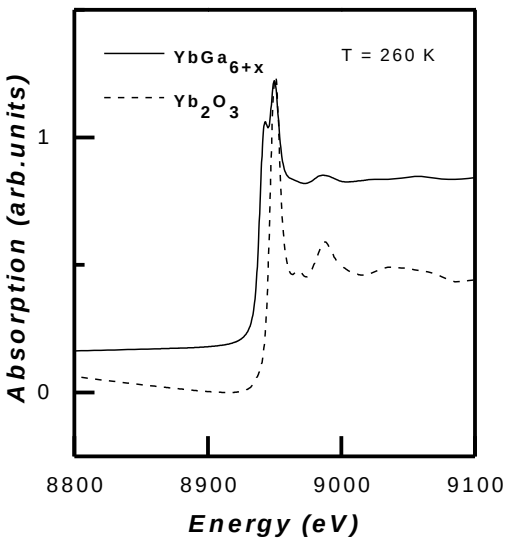

Figure 1: Yb L_{III} XANES at T = 260 K showing the mixed valence Yb configuration of the low temperature modification of $YbGa_{6+x}$.

References

[1] J. Pelleg, G. Kimmel, D. Dayan, J. Less-Comm. Met. 81 (1981) 33-44.

[2] L.G. Akselrud, Yu. Grin, XASWin Program, MPI-CPfS, Dresden, 2004.