ESRF	**Experiment title:** The electronic structure of black and gold SmS from resonant inelastic x-ray scattering (RIXS)	**Experiment number**: HE1593
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Report:

The experiment HE-1593 was aimed at determining the valence of Sm in the black and gold phases of SmS as a function of pressure by using x-ray absorption spectroscopy (XAS) in the partial fluorescence yield (PFY) mode and resonant inelastic x-ray scattering (RIXS). The measurements have been carried out in 16-bunch mode at beamline ID16. A Si(111) monochromator and a 1 m spherical Si(422) analyzer were used to perform PFY-XAS and RIXS scans at the Sm L_{III} edge ($h\nu$ = 6.72 keV), with a total energy resolution ΔE = 1.3 eV. In PFY-XAS scans the intensity of the emitted Sm $L\alpha_1$ fluorescence ($h\nu$ = 5.64 keV) was measured while scanning the energy of the primary beam. RIXS spectra were collected by analyzing the energy of the emitted beam at fixed values of the primary energy. The sample (a single crystal with dimensions of ~100×40×50 μm^3) was placed in a Mao-Bell diamond anvil cell (DAC) and kept at room temperature. Be was used as a material for the gasket and Fluorinert as a pressure transmitting medium. The beam was focused to a size of ~150×150 μm^2. Although the experiment was scheduled in 16-bunch mode (with average intensity reduced by a factor of 2-3 as compared to multibunch mode) PFY-XAS and RIXS scans were possible for 7 different pressures between 1 and 18 GPa.

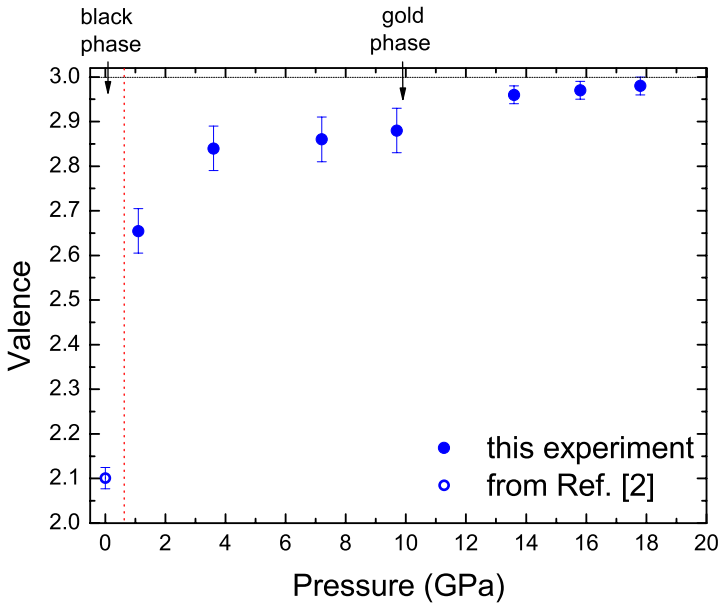

Figure 1 – The valence of Sm in SmS as a function of pressure at room temperature, as obtained from RIXS scans

At ambient pressure SmS is a non-magnetic ($Sm^{\sim 2+}$, $4f^6$: $^7F_0$) semiconductor (black phase). It undergoes a pressure-induced first-order isostructural (NaCl-type) transition at $p_{B\text{-}G}$ = 0.65 GPa (room temperature) towards a metallic phase (gold phase) where the Sm ions are in an intermediate valence state (v ~ 2.65). Low temperature resistivity measurements show that the gold phase of SmS ends up below a crossover temperature T_Δ in an insulating phase, but above a well defined pressure p_Δ = 2 GPa, the ground state is metallic. It was expected that, by further increasing the pressure to a critical value p_C, SmS would be driven into integer trivalency (Sm^{3+}, $4f^5$: $^6H_{5/2}$), where a magnetic ground state is expected. However, until very recently, there was no clear experimental evidence that SmS orders magnetically at higher pressures. This situation changed dramatically when, by using ^{149}Sm NFS and ac-calorimetry measurements, we provided clear proofs that the collapse of the gap in SmS coincides with the appearance of long range magnetic order [1]. The main aim of experiment HE-1593 was therefore to correlate the onset of long range magnetic order at 2 GPa with the valence of Sm at this and higher pressures. Fig. 1 shows the Sm valence as determined from RIXS scans as a function of pressure at room temperature. Two main conclusions can be drawn from these results:

1) at the onset of long range magnetic order (p = 2 GPa) the valence of Sm (at least at room temperature) is considerably lower than 3+ [v = 2.84(5) at p = 3.6 GPa]; this would imply (if the result is confirmed at low temperature) that SmS is at the same time *intermediate valent* and *magnetically ordered*;
2) integer trivalency is not reached even at the highest pressure of this study [v = 2.98(2) at p = 17.8 GPa].

Low temperature measurements (in the magnetically ordered phase) are planned.

[1] A. Barla et al., Phys. Rev. Lett. 92, 066401 (2004)
[2] J. Röhler et al., Valence Instabilities. P. Wachter and H. Boppart Eds., North-Holland 1992, p. 215