# Pressure-induced Mixed-valence Behavior in Sm*X* (*X*=S, Se, Te) in the Light of Resonant X-ray Emission Spectroscopy

**Ignace Jarrige (賈英山)[1], Hitoshi Yamaoka[2], Jean-Pascal Rueff[3], Takeshi Matsumura[4], Keiichiro Imura[5], Hiroyuki S. Suzuki[6], Jung-Fu Lin[7], Nozomu Hiraoka (平岡望)[8], Hirofumi Ishii (石井啟文)[8], and Ku-Ding Tsuei (崔古鼎)[8]**

[1]**Synchroton Radiation Research Center, JAEA, Sayo-cho, Japan**
[2]**SPring-8/RIKEN, Hyogo, Japan**
[3]**Synchrotron SOLEIL, Saint-Aubin, France**
[4]**Hiroshima University, Higashi-Hiroshima, Japan**
[5]**Nagoya University, Nagoya, Japan**
[6]**National Institute for Materials Science, Tsukuba, Japan**
[7]**University of Texas at Austin, Austin, USA**
[8]**National Synchrotron Radiation Research Center, Hsinchu, Taiwan**

Among the samarium monochalcogenide series Sm*X* (*X*=S,Se,Te), SmS has received the most attention due to its first-order isostructural insulator-to-metal transition (IMT) occurring at 0.65 GPa at room temperature. In contrast, SmSe and SmTe have long been known to undergo a continuous IMT above respectively 3 and 6 GPa. We have measured the pressure dependence of the Sm valence in the three monochalcogenides using x-ray absorption spectroscopy in the partial fluorescence yield mode (PFY-XAS) at the Sm-$L_3$ edge and Sm-*2p3d* resonant x-ray emission spectroscopy (RXES). The experiment was performed at the BL12XU beamline at SPring-8 with a total energy resolution of 0.9 eV, provided by combination of a Si(111) double-crystal monochromator and a 1-m bent Si(422) analyzer for the incident and scattered beams, respectively.

The pressure dependence of the Sm valence, inferred from a fit of the PFY-XAS spectra [1], is shown for the three compounds in Fig. 1. The results confirm that, the larger the radius of the chalcogenide ion (S<Se<Te), the more pressure it requires to trigger the IMT, and the more gradually the transition occurs. One can imagine that these differences stem from the different bandwidths of the chalcogenide *p* states: The larger the bandwith, the more progressive the increase of the valence through hybridization with the Sm *d* states. Interestingly, there seems to be no clearcut distinction between first (SmS) and second (SmSe, SmTe) order for the IMT as was long thought, but rather a progressive softening of the transition as the chalcogenide ionic radius increases. A plateaulike softening of the valence increase is observed for SmS between 1.5 and 6 GPa. According to ref. [2], the zone-boundary phonons of the longitudinal acoustic [111] branch are almost invariant with increasing pressure within the same range, which interestingly suggests a coupling between the charge and lattice anomalies. A measurement of the phonons in SmSe under pressure is in preparation to confirm this phenomenon. The PFY-XAS spectra, compared for the three compounds in Fig. 2, reveal a shoulder on the low-energy side of the 2+ peak. This feature could correspond to a charge transfer from the chalcogenide ion in the intermediate state, as was recently observed in Pr@C82 [3]. Calculations are underway to verify this hypothesis.

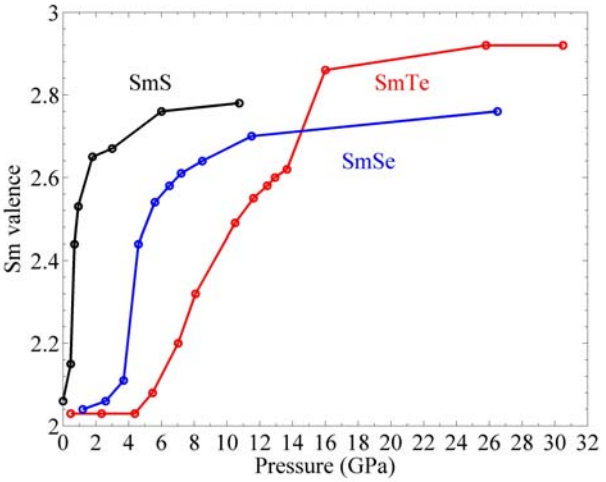


**Fig. 1:** Pressure dependence of the Sm valence in SmS, SmSe, and SmTe, inferred from the PFY-XAS spectra.

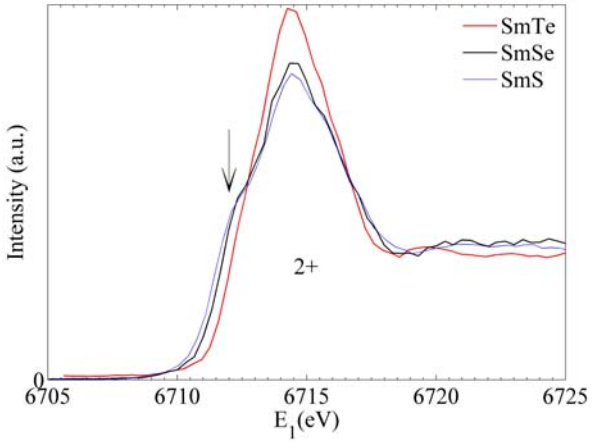


**Fig. 2:** Sm-$L_3$ PFY-XAS spectra measured on SmS, SmSe, and SmTe. The arrow indicates the low-energy shoulder.

References

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