Pressure-Induced Valence Anomaly in TmTe Probed by Resonant X-Ray Emission Spectroscopy

The Kondo effect is arguably one of the most studied many body problems in solid state physics. Exotic, non-Fermi liquid physics is expected when more than one screening channel of conduction electrons is present, such as in the case of intermediate-valent Tm compounds. This situation is known as the *n*-channel Kondo (NCK) problem. A particularly intriguing case of NCK effect is foreseen in intermediate-valent Tm compounds where the valence fluctuation of the Tm ion occurs between two magnetic states ($J=6$ and $J=7/2$).

Among Tm intermediate-valent compounds, TmTe appears as an outstanding example of the interplay between structural, magnetic and electronic degrees of freedom under pressure. Divalent semiconductor at ambient conditions, TmTe is supposed to reach trivalency at the completion of the volume collapse transition (VCT) around 6 GPa. But in the vicinity of the VCT and before trivalency is reached, TmTe shows singular behaviors which one is tempted to associate with more exotic effects in relation to an NCK effect: The resistivity presents a Kondo-like maximum at low temperature and antiferromagnetic (AF) order suddenly reappears under pressure. We measured the electron response of TmTe under pressure using X-ray absorption spectroscopy in the partial fluorescence yield (PFY-XAS) and resonant X-ray emission spectroscopy (RXES). The measurements were performed at beamline **BL12XU**. The compressibility was measured by X-ray diffraction (XRD) at beamline **BL10XU**. Hydrostatic pressure was achieved by using silicon oil as a pressure transmitting medium.

Figure 1 summarizes the pressure dependence of the Tm L_3 PFY-XAS spectra and of the Tm $2p_{3/2}3d_{5/2}$ RXES spectra collected at the maximum of the Tm^{2+} resonance, in the top and bottom panel, respectively. The intensity ratio between the two main structures at 8644 and 8651 eV in the PFY-XAS spectra, corresponding, respectively, to the transitions to the empty Tm^{2+} and Tm^{3+} $5d$ states, is seen to markedly decrease with pressure, signifying notable changes of the Tm electronic state. This is corroborated by the strong decrease of the RXES signal. The spectra calculated within the Anderson Impurity Model (AIM) are reported in Fig. 1 as well.

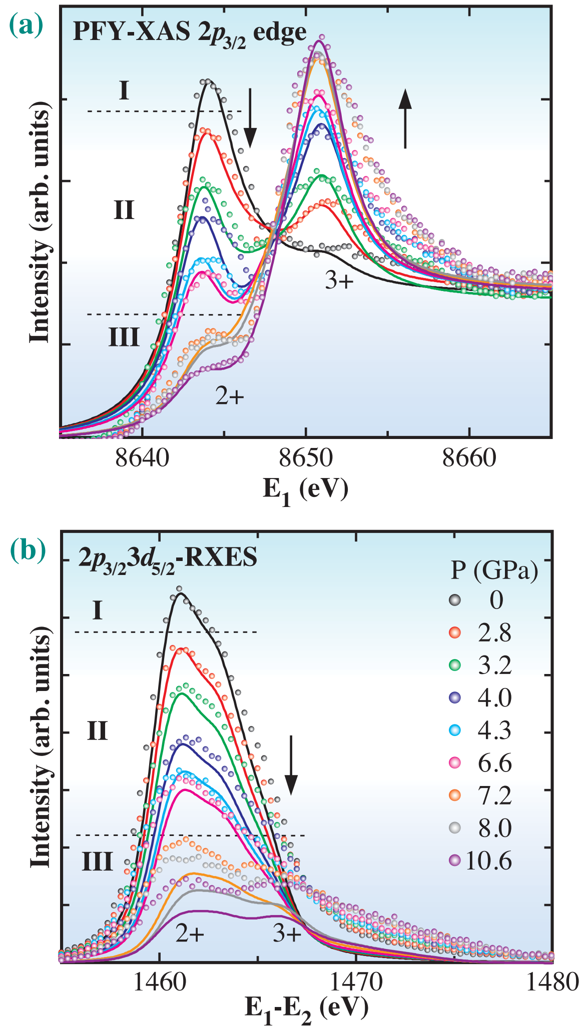

Fig. 1. **(a)** PFY-XAS spectra measured for TmTe at the Tm L_3 edge for various pressures up to 10.6 GPa (dots); **(b)** The $2p_{3/2}3d_{5/2}$ RXES spectra measured with an incident energy of 8644 eV (dots). The solid lines in both panels are the spectra calculated using the AIM.

Figure 2(a) shows the pressure dependence of the Tm valence *v* extracted through fitting the PFY-XAS and RXES spectra and from the theoretical calculations. As soon as the gap closes and TmTe enters the metallic regime, above 2 GPa, the valence abruptly increases to reach 2.55 at 4.3 GPa, coinciding with the isostructural VCT. The valence in the collapsed state, 2.55, is much lower than the near trivalent state reported in previous compressibility measurements under pressure. Above 4.3 GPa, the valence levels off as the volume recovers a normal compressibility behavior. As seen in the inset, the plateau coincides with a discontinuity in the evolution of *v* with respect to volume.

The *f-d* hybridization *H* and the energy difference between the Tm divalent and trivalent configurations E_{Tm2+}-E_{Tm3+} are derived from the AIM calculations and shown in Fig. 3. Above 2.1 GPa, *H* significantly strengthens while TmTe becomes metallic. The concomitant decay of the magnetic moment suggests a progressive Kondo screening by the conduction electrons as P increases. Above 4.3 GPa, H becomes invariant over further compression while E_{Tm2+}-E_{Tm3+} retrieves its low pressure (P<2 GPa) value. This plateau behavior bears the most significant results of our study as it reveals novel Kondo effects. Based on the NCK interpretation of valence fluctuating Tm impurities, the Kondo temperature T_K is supposed to reach a maximum near v=2.4. As it seems, this value matches well the measured TmTe valence in the 4.3–6.5 GPa range. Hence, the NCK effect is expected to be largest in this pressure range. Here we speculate that, when more than one screening channels are involved, the contribution of the Kondo screening to the localization is sufficient to counterbalance the concomitant pressure-induced delocalization through band widening. It follows that the plateau-like regime in the pressure dependence of v and H is likely induced by the growing NCK scattering of the conduction electrons from the local magnetic moments. The peculiarity of the NCK effects on the Tm valence is further stressed by the contrast with the monotonic electron delocalization usually observed in other compressed f-electron systems that is consistent with a single-channel Kondo picture.

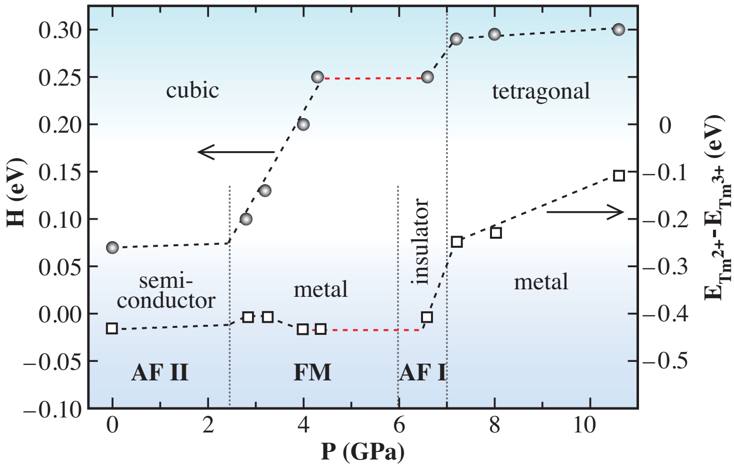

Fig. 3. Pressure dependence of the hybridization (full circles) and the energy difference between the Tm divalent and trivalent configurations (open squares) used in the AIM calculations, along with the structural properties and the electronic and magnetic ground states of TmTe. The dashed line is a guide for the eye.

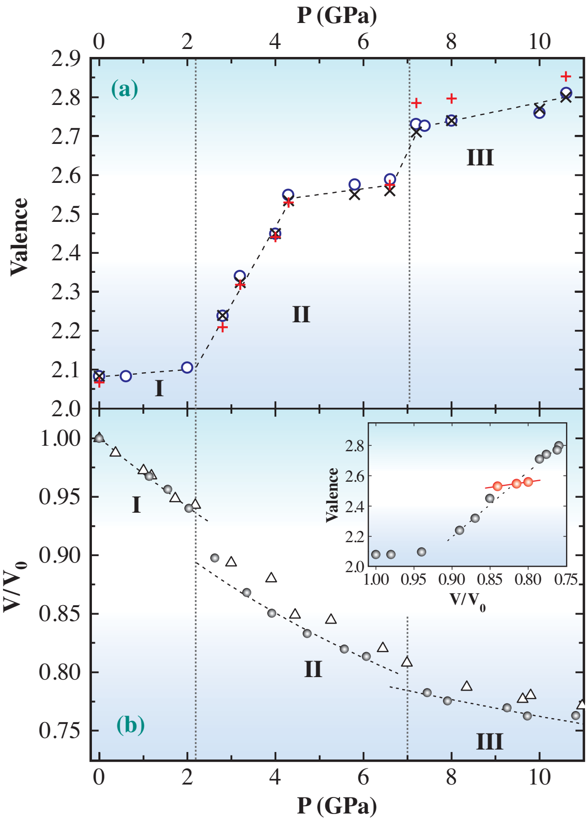

Fig. 2. **(a)** Pressure dependence of the thulium valence in TmTe as determined by PFY-XAS (blue circles), RXES (black crosses), and the calculations (red pluses). The dashed line is a guide for the eye; **(b)** Pressure dependence of the relative volume of TmTe as determined by XRD in this study (full circles). The dashed curves are Birch-Murnaghan equation of states fitted to our data. The relation between the valence from the PFY-XAS data and the volume is shown in the inset.

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References

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