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# Pressure-induced Valence Anomaly in TmTe Probed by Resonant Inelastic X-ray Scattering

*Using resonant inelastic X-ray scattering and the Anderson impurity model, we have probed the Tm valence and 4f-5d hybridization in the high-pressure intermediate-valent TmTe compound. In addition to the general tendency of the f electrons towards delocalization, we find a plateau in both the Tm valence and hybridization pressure dependences between 4.3 and 6.5 GPa which is interpreted in terms of a multi-channel screening process known as n-channel Kondo (NCK) model. Our study raises the interesting possibility that an NCK effect realized in a compressed mixed-valent f system could impede the concomitant electron delocalization.*

## Beamline

SP12XU Inelastic X-ray Scattering

## Authors

### I. Jarrige

Synchrotron Radiation Research Unit,  
Japan Atomic Energy Agency, Sayo, Japan

### J.-P. Rueff

Synchrotron SOLEIL, Gif-sur-Yvette, France

### Y. Q. Cai

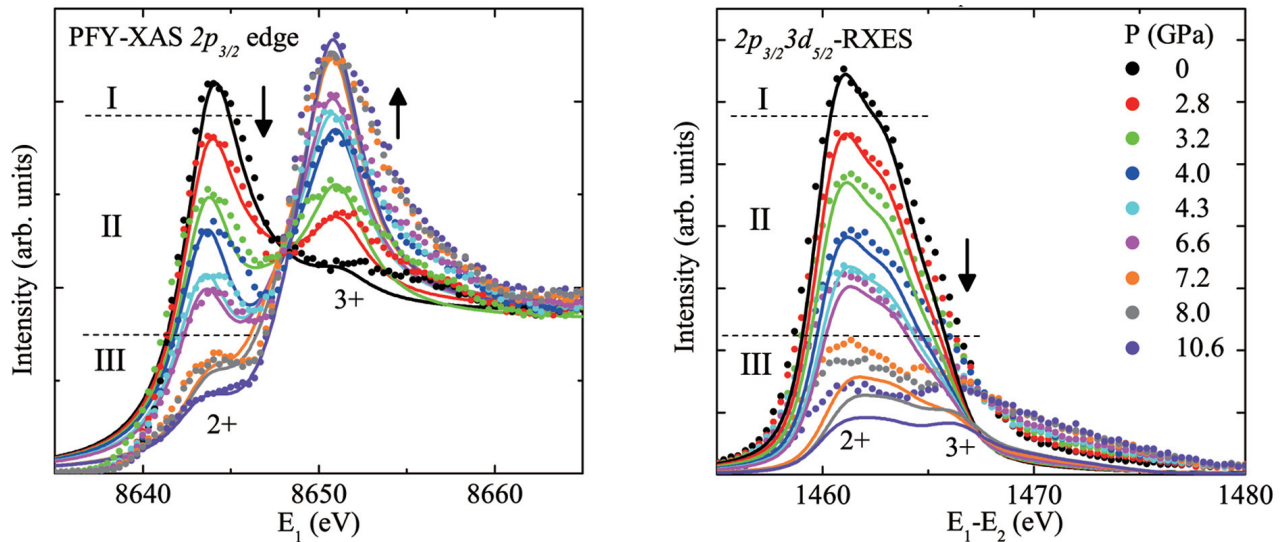
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The Kondo effect is arguably one of the most studied many body problems in solid state physics. Exotic, non-Fermi liquid physics is expected when more than one screening channel of conduction electrons is present, such as in the case of intermediate-valent 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. This calls for a clearcut characterization of the electron response under pressure in this compound which is still lacking. We present here a study of the pressure-induced valence transition in TmTe using two techniques derived from resonant inelastic X-ray scattering (RIXS), X-ray absorption spectroscopy in the partial fluorescence yield (PFY-XAS) and resonant X-ray emission spectroscopy (RXES). The data are analyzed in the light of the Anderson impurity model (AIM).

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<sup>2+</sup> resonance (incident energy of 8644 eV), in the top and bottom panel, respectively. The intensity ratio between the two main structures at 8644 and 8651 eV in the PFY-XAS



**Fig. 1:** (top) PFY-XAS spectra measured for TmTe at the Tm  $L_3$  edge for various pressures up to 10.6 GPa (dots); (bottom) 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.

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 AIM are reported in Fig. 1 as well. The agreement with the experimental spectra is remarkable at low pressures, while less satisfactory above the cubic-tetragonal structural transition at 7 GPa. The discrepancy is attributed to the crystal field and hybridization anisotropy whose strength grows with increasing pressure whereas they are not included in the calculations.

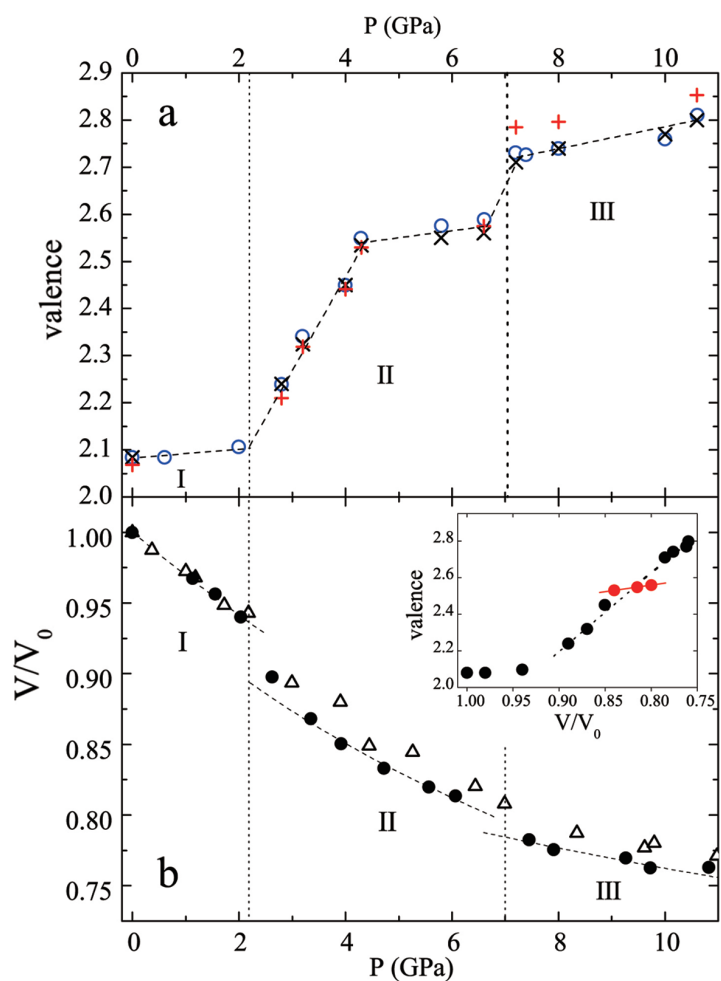
Figure 2(a) shows the pressure dependence of the Tm valence  $\nu$  extracted through fitting the PFY-XAS and RXES spectra and from the theoretical calculations. The agreement between the different techniques is excellent, which gives further confidence to our analysis. Tm remains mostly divalent over the 0–2 GPa range (region I in Fig. 2). 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 (region II in Fig. 2) which similarly extends from 2 to 4 GPa. 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  $\nu$  with respect to volume. The anomaly persists up to the structural transition near 7 GPa where the valence suddenly increases from 2.58 to 2.72. At 10.6 GPa, the Tm valence ( $\sim 2.8$ ) has not reached full trivalent state yet.

The  $f$ - $d$  hybridization  $H$  and the energy difference between the Tm divalent and trivalent configurations  $E_{Tm^{2+}} - E_{Tm^{3+}}$  are derived from the AIM calculations and shown in Fig. 3, along with the known magnetic and electronic ground states and structural properties of TmTe. From Fig. 3 and 2, we can now understand the successive transitions as follows. In the low pressure region, the constant

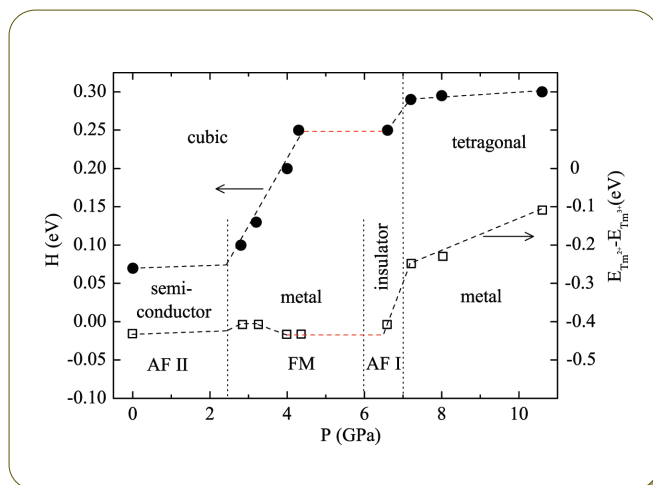
valence and negligible hybridization point to a correlated semiconductor. Above 2.1 GPa, hybridization significantly strengthens while TmTe becomes metallic. The concomitant decay of the magnetic moment suggests a progressive Kondo screening by the conduction electrons as  $P$  increases. Above 4.3 GPa,  $H$  becomes invariant over further compression while  $E_{\text{Tm}2+} - E_{\text{Tm}3+}$  retrieves its low pressure ( $P < 2$  GPa) value. This could indicate a reinforcement of the  $d$ -electron localized character coinciding with the discontinuity in the volume dependence of  $\nu$  and  $H$ . Continuous  $4f$  delocalization is then restored above the structural transition at  $\sim 7$  GPa.

The plateau behavior in the intermediate pressure range above 4 GPa 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  $\nu = 2.4$ . 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 plateaulike regime in the pressure dependence of  $\nu$  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. That the Tm  $4f$  magnetic moment survives throughout the 0–6 GPa range and increases in the AF I phase could further indicate an “overscreened” NCK effect where the



**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 X-ray diffraction in this study (full circles) and from S. Heathman *et al.*, *J. Alloys Comp.* 230, 89 (1995) (triangles). 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, with the red dots and line highlighting the discontinuous points.

local moment would be only partially screened. Finally, our interpretation is in good agreement with the pressure dependence of  $T_{max}$  previously derived from resistivity data



**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, the red zone highlighting the plateaulike behavior.

obtained on TmTe.  $T_{max}$  is characteristic of the transition between the Kondo impurity and Kondo lattice regime and was found to peak at  $\sim 30$  K around 3 GPa.

In conclusion, thanks to the sensitivity of RIXS to the  $f$ -electron properties, we have characterized the changes of Tm valence in the Kondo compound TmTe as a function of pressure with unprecedented details. Besides the overall tendency from localization to itinerancy, we observe valence discontinuities that can be related to the competition between Kondo mechanisms, likely involving multichannel effects, and hybridization growth under pressure. Our results suggest that anomalies of the  $f$ -electron response to compression could be a general signature of the realization of an NCK state in mixed-valent  $f$  systems. Other candidate materials for an NCK effect under pressure could be investigated, such as U compounds. Finally, we hope this work will encourage theoretical advances in the understanding of the NCK systems.◆

### Experimental Station

Inelastic X-ray scattering spectrometer end station

### Publication

I. Jarrige, J. -P. Rueff, S. R. Shieh, M. Taguchi, Y. Ohishi, T. Matsumura, C. -P. Wang, H. Ishii, N. Hiraoka, and Y. Q. Cai, Phys. Rev. Lett. **101**, 127401 (2008).

### Contact E-mail

jarrige@spring8.or.jp