Unified understanding of the valence transition in the rare-earth monochalcogenides under pressure


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(Received 26 September 2012; published 6 March 2013)

Valence instability is a key ingredient of the unusual properties of f-electron materials, yet a clear understanding is lacking as it involves a complex interplay between f-electrons and conduction states. Here we propose a unified picture of pressure-induced valence transition in Sm and Yb monochalcogenides, considered as a model system for mixed valent f-electron materials. Using high-resolution x-ray-absorption spectroscopy, we show that the valence transition is driven by the promotion of a 4f electron specifically into the lowest unoccupied (LU) 5d band. We demonstrate with a promotional model that the nature of the transition at low pressures is intimately related to the density of states of the LU band, while at high pressures it is governed by the hybridization strength.

DOI: 10.1103/PhysRevB.87.115107

PACS number(s): 71.20.Eh, 62.50.—p, 75.20.Hr, 78.70.Ck

Valence fluctuations play an essential role in some of the f-electron systems’ most exciting behaviors, such as quantum criticality and unconventional superconductivity.¹,² But their understanding has proven challenging to capture in a unified theory because they arise from subtle many-body interactions between the f-electrons and the conduction states.³,⁴ Pressure, on the other hand, is an efficient way to act on f-electron interactions and localization and thus can serve as a window onto the f-electron physics. Notably, the pressure-induced valence transition of the lanthanide monochalcogenides is a paradigmatic illustration of f delocalization phenomena and their tremendous diversity. For instance, SmS undergoes a first-order transition to near trivalency coinciding with the onset of magnetic ordering,³ whereas the transition of YbS into an intermediate-valent correlated metal is extremely sluggish.⁶ These diverse behaviors, while establishing a severe test bed for theoretical understanding of f-electron systems, have been overlooked for the past decades. Here, we address them in the light of a direct measurement of the electronic structure of Sm and Yb monochalcogenides (SmS, SmSe, SmTe, YbS, YbSe) under pressure performed using high-resolution x-ray-absorption spectroscopy in the partial fluorescence yield (PFY-XAS) mode. Our data reveal that the valence discontinuity and concomitant closing of the gap under pressure are caused by the specific filling of the lowest unoccupied (LU) 5d band by a 4f electron, offering a unified picture of electron delocalization and intermediate valency. Using a promotional model, we show that both the steepness and the amplitude of the valence transition of the Sm compounds increase with the density of states (DOS) of this LU band. When exceeding a critical DOS, the transition becomes first order for SmS.

The model fails to describe the prolonged transition of the Yb compounds, which suggests that at high pressures the valence transition is impeded by enhanced hybridization. Ultimately, we suggest that our analysis can serve as a prototype for understanding the general mechanism of delocalization in f-electron materials.

The PFY-XAS measurements were carried out at room temperature at the Taiwan beamline BL12XU, SPring-8. Details of the experimental setup have been published elsewhere.⁷ For each compound, a fragment of single crystal ~100 μm in size was loaded into the sample chamber of a Be gasket with silicone oil used as pressure transmitting medium. Pressure was achieved using a diamond-anvil cell. The pressure dependence of the PFY-XAS spectra measured at the L3 edge on the Sm and Yb monochalcogenides is shown in the top panels of Figs. 1(a) and 1(b). The spectra consist of two main peaks corresponding to the dipolar transition 2p → 5d for the divalent and trivalent states, respectively decreasing and increasing under pressure. A closer look at the leading edge of the divalent peak reveals a shoulder located around 2.3 (SmS, YbS), 2.0 (SmSe, YbSe), and 1.6 (SmTe) eV below the peak maximum (open circles in Fig. 1). A fit of the divalent component actually requires the use of three Gaussian functions in order to reproduce the low-energy shoulder, the main peak, and a high-energy shoulder, hereafter referred to as A, B, and C, as shown in the center and bottom panels of Figs. 1(a) and 1(b).

In order to understand the origin of these spectral features, we have calculated the electronic structure of the Sm and Yb monochalcogenides using the density-functional theory within the generalized gradient approximation (GGA). The DOS obtained for the Sm 5d band and the crystal-field split...
The calculated bands are metallic. Structures $t_{2g}$ and $e_g$ subbands are compared with the experimental spectra in Fig. 2(a) for the Sm compounds. We note that the Coulomb interaction is not taken into account and therefore not contributing to the divalent weight, which resulted in an overestimation of $v$ by $\sim 0.1$ for SmS and 0.3 for YbS.$^{5,8}$ All five compounds display a steady increase in $v$ at their insulator-to-metal transition pressure, coinciding with the pressure ranges reported for their volume collapse.$^{10}$ The abrupt increase in $v$ around 15 GPa for SmTe is due to a structural transition. The onset pressure of the collapse gradually increases as a function of both the ligand (S, Se, Te) and more starkly the rare earth (Sm $\ll$ Yb). This reflects the difference in the gap values at ambient pressure, $\varepsilon_{\text{gap}} = 0.20$ eV for SmS, 0.45 eV for SmSe, 0.65 eV for SmTe, 1.4 eV for YbS, and 1.75 eV for YbSe,$^{11-14}$ and the idea that the wider the gap, the larger the pressure to close it.

We now address the large variety of slopes and amplitudes of the transitions, and its intimate connection with the LU band.

$\varepsilon_{\text{gap}}$ and $\varepsilon_{\text{g}}$ subbands are compared with the experimental spectra in Fig. 2(a) for the Sm compounds. We note that the Coulomb interaction is not taken into account and therefore the calculated bands are metallic. Structures $A$ and $C$ are found to be respectively of pure $t_{2g}$ and $e_g$ character, while $B$ is a mix of both. The energy splitting between the three structures and the relative intensity of $A$ and $C$ increase along the series SmTe $<$ SmSe $<$ SmS, which reflects the increase of the crystal field as the lattice constant decreases. We can therefore conclusively rule out the previous assignment of $A$ to the quadrupolar pre-edge.$^{5,8}$ Also, the band structures calculated for YbS in Fig. 2(b) and for the Sm compounds in Ref. 9 show that the low-energy part of $A$, which we call $A'$, corresponds to an isolated $t_{2g}$ band sandwiched between the Fermi level and the rest of the conduction band, making it the LU band.

The pressure dependence of the valence $v$ as derived from the fits of the PFY-XAS spectra is shown for the five monochalcogenides in Fig. 3(a). In previous estimations of $v$, $A$ was incorrectly assigned to a quadrupolarlike feature and therefore not contributing to the divalent weight, which resulted in an overestimation of $v$ by $\sim 0.1$ for SmS and 0.3 for YbS.$^{5,8}$ All five compounds display a steady increase in $v$ at their insulator-to-metal transition pressure, coinciding with the pressure ranges reported for their volume collapse.$^{10}$ The abrupt increase in $v$ around 15 GPa for SmTe is due to a structural transition. The onset pressure of the collapse gradually increases as a function of both the ligand (S, Se, Te) and more starkly the rare earth (Sm $\ll$ Yb). This reflects the difference in the gap values at ambient pressure, $\varepsilon_{\text{gap}} = 0.20$ eV for SmS, 0.45 eV for SmSe, 0.65 eV for SmTe, 1.4 eV for YbS, and 1.75 eV for YbSe,$^{11-14}$ and the idea that the wider the gap, the larger the pressure to close it.

We now address the large variety of slopes and amplitudes of the transitions, and its intimate connection with the LU band.
We start by showing in Fig. 3(b) the enlarged divalent region of three PFY-XAS spectra selected for four compounds, SmS, SmSe, YbS, YbSe, normalized in intensity to the maximum of $B$. These spectra were collected at ambient pressure (AP), just before the collapse (BC), and after the collapse (AC). The BC and AC pressures are respectively indicated by yellow and cyan filled markers in Fig. 3(a). The changes brought on by pressure on the line shape of $A$ are significant. First, judging from the shape of the shaded area between the AP and BC spectra, $A$ stretches towards low energies between AP and BC, and the extent of the stretch increases with the BC pressure $P_{BC}$, i.e., SmS $\prec$ SmSe $\prec$ YbS $\prec$ YbSe. Second, the collapse coincides with a decrease of $A$, implying that $A$ gets filled during the electronic transition. The decrease of shoulder $A$ through the pressure-induced volume collapse is further illustrated in Fig. 4(a), where representative spectra measured at four successive pressures across the collapse are superimposed with the spectrum measured before the collapse for SmS and SmSe. All spectra are normalized in intensity to the maximum of the $B$ feature.

In Fig. 5(b), the pressure dependence of key parameters derived from the fits of the PFY-XAS spectra gives a more precise view of the transition mechanism. For $A$, we use a phenomenological approach to subdivide the lower-energy portion of the peak which does not overlap with $B$, $A'$, and the higher-energy portion which does, $A''$ [cf. Fig. 5(a)], in order to distinguish the filling of the low-energy part of the LU band truly isolated from the rest of the conduction band ($A'$) from that of the higher-energy, hybridized part of the LU band ($A''$). The sum $I_A + I_B + I_C$ is scaled to the total number of $5d$ holes, i.e., between 10 for $v = 2$ and 9 for $v = 3$. The pressure axis is rescaled by $P_{BC}$ indicated by the vertical dashed lines. The error on the intensities and width is estimated to be under $\pm 5\%$, as illustrated in Fig. 4(c) where the effect on the fit of a $\pm 5\%$ error is shown.

Confirming the trend observed in Fig. 3, a close correspondence is observed between the increase of $v$ and the decrease of $A$. More strikingly for Sm, the pressure ranges of the successive decline of $I_A$ and $I_{A''}$ correlate respectively with the valence jump and the start of the slow increase [cf. blue circles and black crosses in Fig. 5(b)]. This demonstrates that the volume collapse transition results from the dumping of $f$ electrons into $A'$, while the transition notably slows down as soon as $f$ electrons are promoted into $A''$, and slows even more when they start to fill the $B$ band beyond AC. For YbS and YbSe the whole transition is considerably slower, as $A'$ is not yet filled up at 30 GPa. The increase in $I_{B+C}$ observed across the transition for all five compounds occurs as a result of $B$ significantly broadening [cf. $W_B$ in Fig. 5(b)], causing portions of $A$ and $C$ to merge with $B$. We attribute the concomitant decrease of $A$ and $C$ illustrated in Fig. 5(a) for SmS to increased merging of $A$ and $C$ with $B$. The amplitude of the valence discontinuity is therefore determined by the remaining intensity of $A$. Also noteworthy is the finding that the monochalcogenide gaps are closed by a combination of both band broadening and shift under pressure, as seen from the $E_A$ and $A_k$ panels.

For a systematic understanding, we have developed a simple model of the promotion of an electron from a $4f$ level of width zero into a square 5$d$ band (corresponding to the LU band) of width $W$ and occupancy $z$, as illustrated in Fig. 5(d). $W$ is taken as 1 eV, which is an approximation of $W_A$ at BC [cf. Fig. 5(b)], and $z$ is taken as $v_{AC} - 2$. We consider that $U_{fd}$, the Coulomb interaction between the $4f$ and the conduction electrons, is effective. For $U_{fd} < \frac{W}{2}$ the valence transition is continuous, and its pressure range, defined by the values of $P_{BC}$ and $P_{AC}$, depends on the value of $U_{fd}$. In this case, the energy of the Fermi level $\varepsilon_F$ is given by (cf. details in the Appendix)

$$\varepsilon_F = \frac{\varepsilon_f - 2U_{fd}\left(\frac{W}{2}\right)\left(E - \frac{W}{2}\right)}{1 - 2U_{fd}\left(\frac{W}{2}\right)},$$

where $\varepsilon_f$ is the energy of the $4f$ level and $E$ is the center of the square 5$d$ band. The valence is then expressed as

$$v = 2 - \frac{z}{W} \left[\varepsilon_f - \varepsilon_f - \frac{W}{2}\right] \left[1 - 2U_{fd}\left(\frac{W}{2}\right)\right].$$

In our calculation of $v$, we put

$$E - \varepsilon_f - \frac{W}{2} = \varepsilon_{gap} - cP,$$

with $c = \varepsilon_{gap}/P_{BC}$.

For $U_{fd} \geq \frac{W}{2}$, at a critical value of the pressure there is a first-order transition and the valence changes discontinuously from 2 to $2 + z$. The critical pressure is determined based on the condition that the total energy of the system under pressure is equivalent to the value at ambient pressure.
The transition for the Sm compounds is best reproduced for the parameters indicated in Fig. 5(c). Remarkably enough, the main features of the valence transition are properly captured for the three Sm compounds, a higher DOS of the LU band ($A'$) resulting in a steeper transition, ultimately first order for SmS, as shown in the top panel of Fig. 5(b). This lends support to the relevance of the promotional model, which has been an open question since the work of Ramirez and Falicov on Ce.\textsuperscript{15} Because our model describes the linear filling of one band, it approximates a constant slope through the transition between BC and AC, and does not account for the filling of $A''$ and $B$ beyond AC. For YbS and YbSe, our model yields unphysical negative values of $U_{f\delta}$. For YbS for instance, using Eqs. (2) and \textsuperscript{13}(3) the experimental values $P_{BC} = 8.7$ GPa, $P_{AC} = 18.0$ GPa, $z = 0.4$, and $\varepsilon_{gap} = 1.4$ eV, together with $W = 1.0$ eV, we obtain $U_{f\delta} = -0.62$ eV. A very plausible explanation is that hybridization effects between the $4f$ electron and the $5d$ band become stronger at the higher transition pressures of the Yb compounds, so that $A'$ no longer retains its isolated character.

This analysis thus delineates two broad scenarios for the electronic transition of the monochalcogenides. In the first, the LU band is isolated from the rest of the conduction band, allowing for a steep transition, whose slope and amplitude are proportional to the DOS of the LU band. Hybridization thrives in the second scenario, which leads to a sluggish transition, for which a Kondo description may be appropriate. We note that because $\frac{1}{z}$ decreases and hybridization increases with increasing pressure, slower transitions may be more often found at higher pressures. This approximation holds for other rare-earth monochalcogenides, the transition being first order for TmSe,\textsuperscript{15} Te,\textsuperscript{15} at 1 GPa,\textsuperscript{16} second order but steep for TmTe at 2 GPa,\textsuperscript{17} and sluggish between 16 and 20 GPa for EuSe.\textsuperscript{18} Our interpretation may also be generalized to other rare-earth monochalcogenides, the transition being first order for $n$ $4f$ electrons per Sm are promoted to the $5d$ band in the system sketched in Fig. 5(d), the value of $n$, and therefore of the Fermi level $\varepsilon_F$, is determined for the stable state by minimizing the total energy change $E_{band} + E_{4f} + E_{int}$ with

\begin{table}[h]
\centering
\begin{tabular}{|l|l|l|l|}
\hline
 & SmS & SmSe & SmTe \\
\hline
$P_{BC}$ (GPa) & 0.6 & 5.0 & 9.5 \\
$P_{AC}$ (GPa) & 0.6 & 0.52 & 1.0 \\
$U_{f\delta}$ (eV) & 0.78 & 0.64 & 0.769 \\
$W/2z$ (eV) & 0.8935 & 0.8936 & 0.8937 \\
\hline
\end{tabular}
\caption{Parameters for the promotional model.}
\end{table}

**APPENDIX**

We first explain how Eq. (1) is derived. If we assume that $n$ $4f$ electrons per Sm are promoted to the $5d$ band in the system sketched in Fig. 5(d), the value of $n$, and therefore of the Fermi level $\varepsilon_F$, is determined for the stable state by minimizing the total energy change $E_{band} + E_{4f} + E_{int}$ with
respect to \( n \) (or \( \varepsilon_F \)):

\[
\frac{d}{d\varepsilon_F} (E_{\text{band}} + E_{4f} + E_{\text{int}}) = 0,
\]

(A1)

where \( E_{\text{band}} \) and \( E_{4f} \) are respectively the kinetic energy changes of the electrons in the 5\( d \) band and of the 4\( f \) electrons per Sm, and \( E_{\text{int}} \) the Coulomb interaction energy between the 5\( d \) band electrons and the 4\( f \) holes per Sm:

\[
E_{\text{band}} = \frac{z}{2W} \left[ \varepsilon_F^2 - \left( E - \frac{W}{2} \right)^2 \right],
\]

(A2)

\[
E_{4f} = \left[ 1 - \frac{z}{W} \left( \varepsilon_F - E + \frac{W}{2} \right) \right] \varepsilon_F,
\]

(A3)

\[
E_{\text{int}} = -U_{fd} \left[ \frac{z}{W} \left( \varepsilon_F - E + \frac{W}{2} \right) \right]^2.
\]

(A4)

with \( W \) and \( z \) being respectively the width and the occupancy in the postcollapse state of the 5\( d \) band, and \( U_{fd} \) the Coulomb interaction between the 4\( f \) and the conduction electrons.

Next, the expression for the valence in Eq. (2) of the paper is obtained by \( v = 2 + n \), with \( \varepsilon_F \) and \( n \) being connected by the following relation:

\[
n = \frac{z}{W} \left[ \varepsilon_F - E + \frac{W}{2} \right],
\]

(A5)

One of the authors (A. Kotani) was partially supported by a Grant-in-Aid for Scientific Research C (Grant No. 90029504) from the Japan Society for the Promotion of Science. J.-F.L. acknowledges support from Energy Frontier Research in Extreme Environments (EFree) and Carnegie/DOE Alliance Center (CDAC).

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