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Intermediate valence behaviour under pressure: how precisely can we probe it by means of resonant inelastic x-ray emission?

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Abstract

Rare earths and their compounds show many interesting physical phenomena caused by the complex electronic structure related to *f* electrons. External pressure can affect the hybridization between 5*d* band electrons and the more atomic-like 4*f* ones, giving rise to intermediate valence behaviour. Resonant x-ray emission spectroscopy (RXES) has been shown to be a very effective tool for probing the mixed valence ground state under pressure. A RXES experiment detects the x-ray emission that follows decay into a resonantly created core hole. Being a photon-in–photon-out spectroscopic technique, it is not hindered by the presence of the pressure cell. In the case of rare earths we chose to detect the 3*d*–2*p* x-ray emission following a 2*p*–5*d* resonant excitation process. The divalent and trivalent components of the ground state are separately enhanced because they resonate at different incident photon energies. Very good precision in the determination of even small changes of valence is reached. We will present experimental results on ytterbium compounds (YbAl₂ and YbS), as well as recent data on the valence state of SmS in the gold phase, that have allowed us to unveil the progressive valence change towards the completion of trivalency.

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The spectral changes and the way to extract the valence from measured spectra will be discussed.

1. Introduction

Chemical bonds are defined as an interaction between atoms associated with a collectivization of the valence electronic orbitals [1]. The sharing of the electrons affects all main physical and chemical properties of the system, which form an experimental criterion for chemical bonds. In this set, electronic spectra give the most sensitive diagnostics of the electronic structure. The traditional classification of chemical bonds is based on the idea of atomic valence. The usual definition of valence from chemistry [2], useful in the ionic limit, must be generalized for materials with partially localized d or f electrons. In transition metal compounds, the hybridization of the d electrons with the ligand orbitals leads to non-integer occupancies—and therefore valencies—at the cation sites, and determines most physical properties [3]. Intermediate valence compounds, like many lanthanide materials, are even further removed from the conventional picture of valence as a well-defined oxidation state. The 4f wavefunctions are localized at the ion sites and their direct overlap is negligible. The small binding energies would favour itinerancy, but large on-site Coulomb interactions oppose hopping and multiple occupancy. The interplay between opposite tendencies to localization and delocalization leads, e.g. in cerium and ytterbium compounds, to a great variety of physical properties, including Kondo and heavy fermion behaviour, unconventional superconductivity, and various kinds of electronic instabilities [4, 5].

Intermediate valence behaviour and valence changes are driven by chemical substitution, temperature and externally applied pressure. High pressure experiments are most challenging: thermodynamic and transport measurements under pressure, although extremely demanding from the technical point of view, have now formed the traditional ‘toolbox’ of high pressure studies. Spectroscopy measurements have been less widely explored due to the strong intensity losses through the pressure cell. The only viable spectroscopies under pressure are photon-in–photon-out ones. Of particular interest are resonant core level photon-only spectroscopies such as x-ray absorption (XAS) and resonant x-ray emission spectroscopy (RXES). XAS and RXES spectra provide bulk sensitivity and chemical and configuration selectivity and allow determination of the typical energies of charge fluctuations, of Coulomb interactions (e.g. in narrow 4f or 3d bands) or of magnetic and crystal field excitations. Core level spectroscopies are well suited to studies of covalence in solids, and reveal unique information on the relevant configurations, the hybridization strength and the amount of mixing. Thanks to the now available synchrotron radiation fluxes it is possible to explore a reasonable number of parameters during a normal synchrotron beam time period in a photon-in–photon-out experiment under pressure.

In this paper we discuss the performances of RXES experiments in the hard x-ray energy range as a tool for investigating pressure-induced valence changes, at the L_3 edge of ytterbium compounds (YbAl_2 and YbS) and of the samarium monochalcogenide SmS . We will discuss how precisely valence values can be extracted from the measured spectra, and the advantages of RXES experiments with respect to the more conventional XAS technique, widely used in the past to determine valence and valence changes.

The paper is organized as follows. In section 2 we give an introduction to the RXES process (the reader experienced in the technique can safely skip that section). After a short note on the experimental set-up (section 3) we devote sections 4 and 5 to results.

2. Resonant x-ray emission in mixed valence compounds

The difference between RXES and a normal fluorescence x-ray emission process lies in the excitation mode. In a fluorescence experiment the emission spectrum does not depend on the excitation energy which is much larger than the core electron binding energy. In the RXES process the core electron is resonantly excited at the absorption threshold. In these conditions the absorption and emission steps form a coherent second-order process, and the emission spectrum depends strongly on the incident photon energy. More information is available from a *bi-dimensional* experiment where RXES spectra are measured at different incident photon energies than in a simple absorption experiment. The evolution of the spectral shape as a function of the excitation energy provides powerful hints useful for identifying a specific component of the spectrum.

Thanks to the localized nature of the probed core wavefunctions and to optical selection rules, RXES is element specific. Resonant excitation makes RXES a sensitive probe of valence and hybridization. The energy which can be transferred to the solid is specific to the excited chemical species. Hence a RXES spectrum contains, at different values of the transferred energy, spectral signatures of each particular electronic configuration involved in the process. Moreover, the final state of RXES is characterized by a less excited configuration than excitation spectroscopies such as XAS, and hence by a longer lifetime.

A unique advantage of RXES with respect to other spectroscopies lies in its bulk sensitivity. In RXES experiments probing resonant excitation of the 2p electrons of ytterbium ($h\nu_{\text{IN}} \sim 8.9$ keV) followed by the decay of 3d levels ($h\nu_{\text{OUT}} \sim 7.4$ keV), the sampled depth is determined by the lower energy photons and reaches a few microns. Bulk sensitivity makes RXES applicable to the study of samples in high pressure cells, when the emitted radiation has to go through the thick diamond anvils.

We introduce the RXES process referring to the case of $L\alpha_1$ RXES in IV ytterbium compounds. The ground state of the Yb ion in an IV compound is a hybrid state: $|\Psi_G\rangle = \alpha|4f^{13}\rangle + \beta|4f^{14}\rangle$ (see the total energy scheme of figure 1). Resonant excitation at the L_3 edge involves the excitation of a $2p_{3/2}$ core electron primarily into unoccupied Yb 5d-derived states. In the intermediate state the two continua $2p^5 4f^{14} \epsilon d$ and $2p^5 4f^{13} \epsilon d$ are split by $\sim 7\text{--}8$ eV due to the strong Coulomb interaction energy between the 2p core hole and the ‘spectator’ 4f hole (ϵd indicates an electron added to the empty d states). This energy separation has largely been explored in XAS experiments for probing mixed valence systems [6], although with the limitation of the intrinsic lifetime broadening associated with the Yb $2p_{3/2}$ hole. In the de-excitation phase the 2p hole is filled by a 3d core electron. The emitted photons can be measured using two detection schemes: (i) collecting radiation of energy $h\nu_{\text{OUT}}$ equal to the fluorescence energy $h\nu_0$ (i.e. the peak emission energy for excitation well above threshold) as a function of $h\nu_{\text{IN}}$; or (ii) scanning $h\nu_{\text{OUT}}$ at fixed $h\nu_{\text{IN}}$. The first mode is called the partial fluorescence yield (PFY) [7]. Lifetime broadening is less severe in the final state detected in the PFY mode than in the corresponding absorption process. Although a PFY spectrum is not strictly equivalent to a XAS spectrum with a reduced broadening [8], it is of great interest, because it reveals fine details that are lost in the broad XAS line shape (see an example in [9]).

The intensity of the overall RXES transition is given by the Kramers–Heisenberg formula:

$$I(\nu_{\text{IN}}, \nu_{\text{OUT}}) = \sum_j \left| \sum_i \frac{\langle j|T^\dagger|i\rangle \langle i|T|\Psi_G\rangle}{E_0 + h\nu_{\text{IN}} - E_i - i\Gamma_{2p}} \right|^2 \frac{\gamma/\pi}{(E_j + h\nu_{\text{OUT}} - E_0 - h\nu_{\text{IN}})^2 + (\gamma)^2}.$$

The sum is over intermediate states $|i\rangle$ with a 2p core hole and energies E_i , and final states $|j\rangle$ with energies E_j . E_0 is the ground state energy and T is the optical transition operator. The squared modulus of the sum over the intermediate states indicates interference

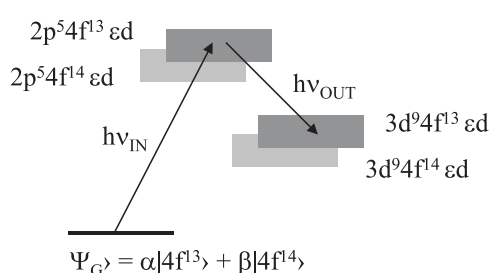


Figure 1. The schematic total energy scheme for the $L\alpha_1$ RXES process in an intermediate valence Yb compound. A PFY experiment integrates photons from the *fluorescent* 3d–2p radiative decay channel. The RXES experiment performs the energy analysis of the same decay channel.

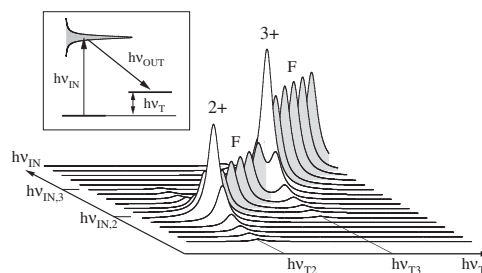


Figure 2. An artist's view of an Yb $L\alpha_1$ RXES experiment on an intermediate valence Yb system. Resonant Raman signals for both the 2+ and 3+ configurations are visible at constant transferred energy $h\nu_T = h\nu_{IN} - h\nu_{OUT}$. The signal F is the $L\alpha_1$ fluorescence which is emitted at a constant outgoing photon energy and therefore involves an energy transfer that increases with increasing incident energy. Inset: a simplified total energy scheme. (This figure is in [16].)

between processes leading to the same final state. Energy conservation is ensured by the two denominators, within the energy widths Γ_{2p} and γ of the intermediate and final states. For each intermediate state $|i\rangle$ with a 2p core hole, absorption is maximum at $h\nu_{IN} = h\nu_i = (E_i - E_0)$. Within a range $\Delta(h\nu_{IN}) \sim \Gamma_{2p}$ of $h\nu_i$ the energy of the emitted photon tracks the incident energy: $\Delta h\nu_{OUT} = \Delta h\nu_{IN}$. This is the so-called *Raman regime*.

Figure 2 illustrates the expected outcome of a RXES measurement on an IV Yb compound. Emission spectra measured at various values of $h\nu_{IN}$ across the L_3 edge are plotted as a function of the *transferred energy* $h\nu_T = h\nu_{IN} - h\nu_{OUT}$. In the Raman regime $h\nu_T$ is constant. As $h\nu_{IN}$ approaches the threshold $h\nu_{IN,2}$ for the L_3 absorption involving the Yb^{2+} configuration, a feature appears in the emitted spectrum at transferred energy $h\nu_{T2}$. The emitted signal is resonantly enhanced, and the maximum intensity occurs in correspondence with the 2+ feature in the XAS spectrum. The Yb^{2+} Raman signal decreases rapidly beyond $h\nu_{IN,2}$, while a new spectral component (F) appears, representing the $L\alpha_1$ fluorescence emitted at a constant energy $h\nu_{OUT} = h\nu_0$. The corresponding transferred energy tracks with the incident photon energy. The 3+ component is resonantly enhanced at the 3+ threshold energy. A new fluorescent emission appears past $h\nu_{IN,3}$. The integrated fluorescent intensity closely reproduces the XAS profile.

3. Experimental note

All experiments discussed in this paper were performed at beamline ID16 of the European Synchrotron Radiation Facility (Grenoble, France). The incoming photon beam is monochromatized by a Si(111) monochromator. The emitted radiation is energy analysed by a 1 m radius spherical Si analyser cut along the proper reflection ((620) for Yb and (422) for Sm). The radiation is then collected by a Peltier-cooled Si diode. The two types of spectrum discussed, i.e. PFY and RXES, were measured for each of the examples that will be discussed here. All measurements were performed at room temperature, with the sample loaded in a diamond anvil cell along with ruby chips, using high strength Be as the gasketing material. The pressure transmitting medium depended on the sample. Pressure values were measured *in situ* by the conventional ruby fluorescence technique. The experiments were done in radial

geometry, i.e. with both the incident and scattered radiation passing through the Be gasket, in order to avoid the strong absorption by the diamonds. The beam was focused to a size of $\sim 150 \times 150 \mu\text{m}^2$ ($H \times V$) at the sample position. The overall energy resolution was 1.9 eV for the Yb $L\alpha_1$ experiment and 1.5 eV for Sm $L\alpha_1$. Contributions from the Si(111) monochromator and from the Si analyser of the spectrometer were respectively 1.2 eV (around $h\nu_{\text{IN}} = 8.944$ keV) and 1.5 eV (around $h\nu_{\text{OUT}} = 7.415$ keV) for Yb, and 0.9 eV (around $h\nu_{\text{IN}} = 6716$) and 1.2 eV (around $h\nu_{\text{OUT}} = 5.636$ keV) for Sm.

4. Valence changes in ytterbium compounds

In Yb-based materials, the Yb valence is directly related to the number of 4f holes n_h by $v = 2 + n_h$. Metallic Yb is divalent ($n_h = 0$) at ambient pressure, but for compounds n_h spans a broad range between 0 and 1. Intermediate valence values reflect hybridization of the energetically close Yb^{2+} ($4f^{14}$) and Yb^{3+} ($4f^{13}$) configurations. Valence also varies with pressure and temperature. Temperature provokes thermal population of states with different f occupation numbers and, through thermal expansion, influences the energy separation of electronic levels. The pressure dependence is the result of a balance between the gain in cohesive energy for the 3+ configuration, confirmed by the smaller atomic volume, and the energy price of promoting a 4f electron into the conduction band [10]. The changes in 4f occupation influence the structural, transport, thermodynamic and magnetic properties and can be investigated by various spectroscopies—optical, nuclear, electronic—which probe directly or indirectly the 4f population. RXES provides very precise and direct information on the electronic configuration, as discussed in the next section.

4.1. YbAl_2

As a first example we present the case of YbAl_2 . Its physical properties exhibit many interesting peculiarities: the quasi-elastic neutron response suggests strong valence fluctuations and a correspondingly large Kondo temperature $T_K \sim 2000$ K [11], typical signatures of non-integer valence. The temperature dependence of the magnetic susceptibility (a broad maximum around 800 K, and saturation below 200 K [12]) and the anomalous thermal expansion were interpreted in terms of a valence change from $v \sim 2$ at 90 K to $v \sim 2.5$ at 800 K [13]. A comparison of the lattice constant of YbAl_2 with those of other divalent and trivalent rare earth Al_2 compounds yields $v \sim 2.4$ at room temperature [14]. The dependence of valence on applied pressure was studied by means of compressibility measurements, that suggest a complete transition to Yb^{3+} above ~ 90 kbar [15]. A pioneering Yb L_3 XAS experiment [6] indicated a continuous increase from $v \sim 2.3$ at ambient pressure to $v \sim 2.6$ at 30 kbar.

We studied the pressure-induced valence change of Yb in YbAl_2 by PFY and RXES analysis at the L_3 edge. Having access to a much wider pressure range than investigated in previous experiments, we observed the complete valence change of ytterbium and found an increase of the Yb valence in YbAl_2 from 2.25 ± 0.05 at ambient pressure to 2.9 ± 0.05 at 385 kbar.

A polycrystalline YbAl_2 sample reduced to powder was loaded into the diamond anvil cell, without a pressure transmitting medium since the powder filled the empty space between the diamonds. The main results are summarized in figure 3. Panel (A) presents PFY spectra of the integrated fluorescent $L\alpha_1$ emission excited at the L_3 edge, from ambient pressure up to 385 kbar. The typical double-peaked spectral shape of a mixed valence rare earth system is observed: the peak at lower incident energy corresponds to transitions involving mainly Yb^{2+} and, ~ 8 eV above, Yb^{3+} gives rise to the second broad peak. A quantitative estimate of

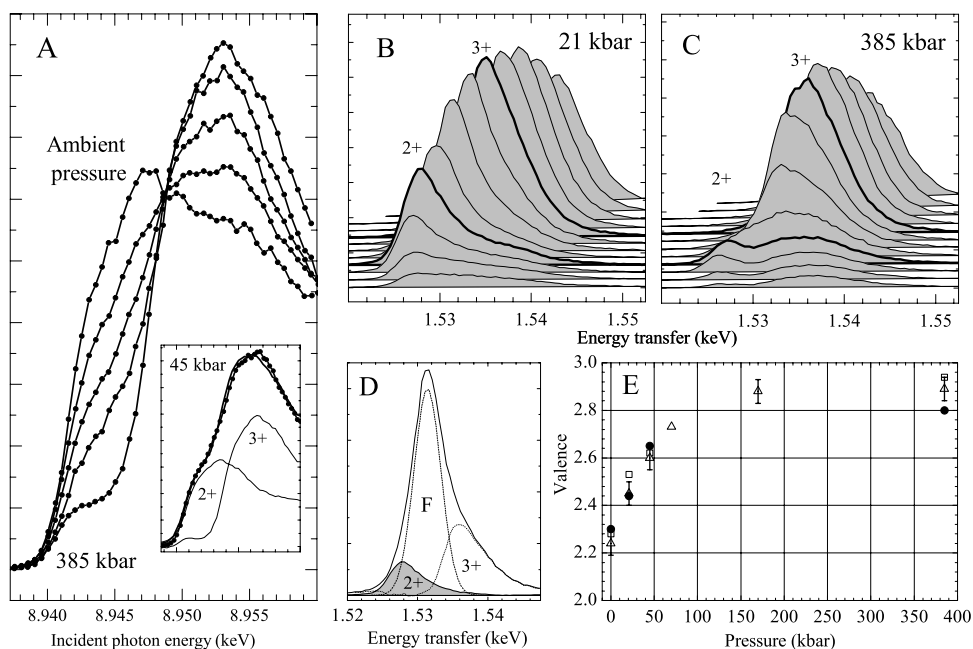


Figure 3. $YbAl_2$ under pressure. (A) PFY $L\alpha_1$ spectra at 0, 21, 45, 70 and 385 kbar (the fit at 45 kbar is shown in the inset). ((B), (C)) $L\alpha_1$ RXES spectra at 21 and 385 kbar (thick curves indicate spectra excited at the resonance of the 2+ and 3+ components). (D) Decomposition of the RXES spectrum at 21 kbar ($h\nu_{IN} = 8.946$ keV, above 2+ resonance). (E) Valence values extracted from PFY spectra (triangles), series of RXES spectra (squares) and RXES spectra excited far below L_3 edge (dots).

the valence is obtained by fitting the spectra with two components. Due to the broad spectral shape of metallic $YbAl_2$, the PFY spectra could be fitted with two replica components, obtained through self-consistent iterations starting from the nearly divalent spectrum at ambient pressure (the typical fit quality is shown in the inset). Series of RXES spectra measured at incident energies across the L_3 edge (in 2 eV steps starting at $h\nu_{IN} = 8.936$ keV, at increasing $h\nu_{IN}$ from front to back) are shown in panels (B) and (C) for 21 and 385 kbar. They exhibit the evolution explained in the introduction to the RXES process: two components at fixed energy transfer resonate at $h\nu_{IN}$ values ~ 8 eV apart. Significant spectral intensity derives from non-resonating fluorescence events that set in past the resonances. The details of the fitting procedure required to extract the intensity of the 2+ and 3+ components at their respective resonances are given in [16]. We report the decomposition of a spectrum at 21 kbar in panel (D). As a third analysis tool we evaluate the valence trend from the relative peak intensities in the RXES spectra excited well below threshold (spectra on the front of panels (B) and (C)). These spectra are free from the fluorescence component and, being excited at $h\nu_{IN}$ far from the resonance of the divalent component, show a more relevant 3+ contribution. The extracted valence values are reported in panel (E). The small spread of the data points suggests high precision and reliability of our estimates.

4.2. YbS

YbS belongs to the family of rare earth monochalcogenides, characterized by a pressure-induced semiconductor–metal transition [17]. The transition begins when pressure reduces

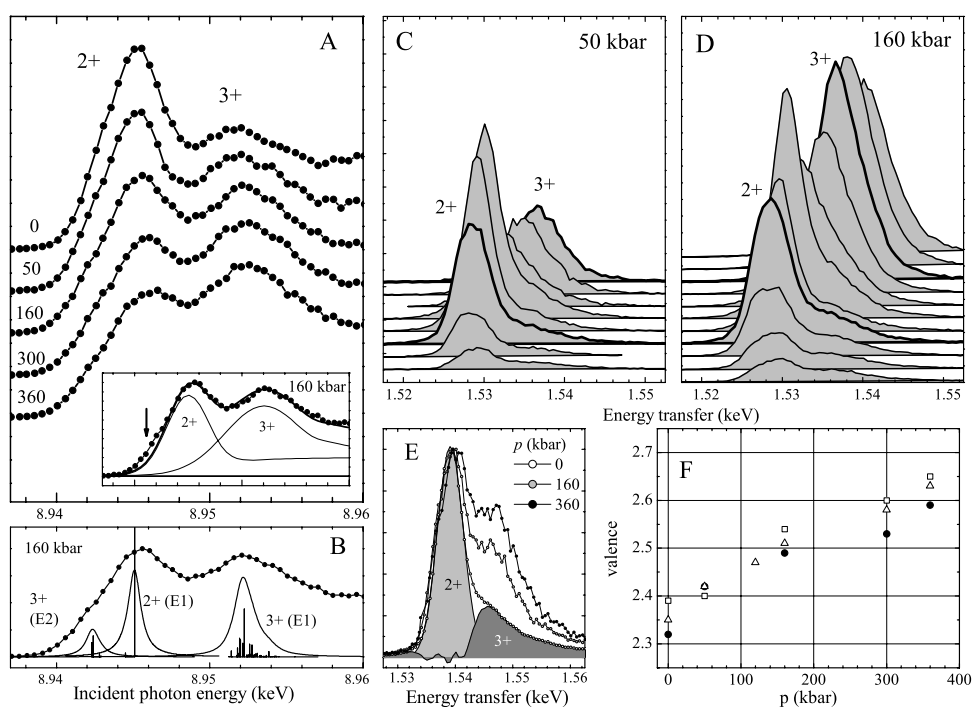


Figure 4. YbS under pressure. (A) PFY $L\alpha_1$ spectra at 0, 50, 160, 300 and 360 kbar (the fit at 160 kbar is shown in the inset). (B) Atomic multiplet calculations of dipolar (E1) and quadrupolar (E2) transitions involving Yb^{2+} and Yb^{3+} . ((C), (D)) $L\alpha_1$ RXES spectra at 50 and 160 kbar (thick curves indicate spectra excited at the resonance of the 2+ and 3+ components). (E) Decomposition of RXES spectra excited far below threshold ($h\nu_{IN} = 8.936$ keV). (F) Valence values extracted from PFY spectra (triangles), series of RXES spectra (squares) and RXES spectra excited far below the L_3 edge (dots).

the energy separation between the localized 4f states and the 5d conduction band, and 4f electrons start to spill into the 5d bands [18]. The transition, like the associated valence change, requires several hundreds of kilobars, due to the high stability of the divalent $4f^{14}$ configuration. The variation of the 4f occupation is reflected in the pressure dependence of the lattice constant and in the anomalies shown by the compressibility curves [19, 20]. From the scaling of the lattice parameter a valence $v = 2.4$ at 250 kbar can be obtained, but a large uncertainty (± 0.15) remains, because reference volume values are not well established at high pressures. Optical properties bear the signature of the semiconductor–metal transition: the optical 4f–5d gap is closed at ~ 200 kbar, where a change of colour is seen, from black to golden yellow. Precise knowledge of the 4f occupation was lacking, because the results of the still pioneering XAS experiment at the Yb L_3 edge of YbS under pressure [21] are affected by the unavoidable uncertainties connected with the $2p_{3/2}$ lifetime broadening.

Following the lines of the results presented in the previous paragraph for YbAl_2 , we have performed a study of the valence change of YbS under pressure [22]. A single crystal of YbS was crushed into powder and loaded in the diamond anvil cell. $L\alpha_1$ PFY and RXES spectra measured at the L_3 edge are shown in figure 4. The data analysis procedure differs from the one performed on YbAl_2 in that it had to take into account the much sharper spectral features of YbS, a more ionic compound whose 5d band is ~ 6 eV wide (to be compared with YbAl_2 , with a 5d band extending over almost 15 eV [23]). It was therefore impossible to fit the measured

PFY spectra with replica components as was done for YbAl_2 . Two different line shapes, each of them the sum of a Gaussian and an error function, were used. Best results were obtained by assigning a different Gaussian width for the divalent ($\text{FWHM} = 4 \text{ eV}$) and trivalent components ($\text{FWHM} = 7 \text{ eV}$), while the width of the error function was kept at a constant value of 1.5 eV , corresponding to the lifetime broadening of the $3d \rightarrow 2p$ decay channel. The choice of the line shape was purely phenomenological. PFY spectra at different pressure values were fitted by adjusting only the relative weight of the two line shapes. This fit does not account for a small pre-edge feature that we attribute to $2p \rightarrow 4f$ quadrupolar transitions. As a simplified but illuminating investigation of the origin of the different spectral widths, we calculated the XAS final state multiplets for both Yb configurations, using Cowan's code [24]. The ground state configurations are $2p^6 4f^{14} 5d^0$ (Yb^{2+}) and $2p^6 4f^{13} 5d^1$ (Yb^{3+}). The usual rescaling of the Slater integrals to 80% of their Hartree–Fock value was applied to account for intra-atomic screening effects. Dipolar (E1) transitions were calculated for both configurations, and the quadrupolar (E2) transition for Yb^{3+} . The multiplets were convoluted with a Lorentzian line shape with $\text{FWHM} = 1.5 \text{ eV}$ and all calculated curves were rescaled by arbitrary factors to ease visual comparison with the experimental spectrum (panel (B) of figure 4). The atomic calculation cannot reproduce the measured spectral shape but indicates that the energy width of the Yb^{3+} PFY peak is due to the larger spread of the $3+$ final state multiplet, and provides a rationale for the different widths of the PFY line shapes. The full series of RXES spectra excited across the L_3 edge ($h\nu_{\text{IN}}$ in 2 eV steps starting at 8.936 keV) are reported in panels (C) and (D), where the thick curves indicate the resonances of the $2+$ and $3+$ components. The strong variation of the trivalent weight in the spectra excited below the absorption edge ($h\nu_{\text{IN}} = 8.936 \text{ keV}$) is seen in panel (E). Valence estimates from all analysis procedures are summarized in panel (F). The valence variation that we measure (~ 0.3) fully agrees with the theoretical prediction of [25], although with a clear offset: we find a valence value at ambient pressure larger than the calculated value and larger than that found in [21]¹¹.

5. The valence transition of SmS under pressure

The last example is the recent study of the valence transition of SmS under pressure. Sm monochalcogenides present in their semiconducting state a much smaller $4f^6$ – $5d_{t_2g}$ energy gap than the corresponding Eu or Yb monochalcogenides. The history and study of the Sm monochalcogenides as IV materials started when the pressure-induced semiconductor–metal transition was observed [26], with a colour change from black to gold, and it was suggested that the metallic state would be an intermediate valence one. The isostructural (NaCl) transition of SmS occurs at 6.5 kbar . The transition mechanism is based on the pressure reduction of the lattice constant: the $5d_{t_2g}$ – $5d_{e_g}$ crystal field splitting increases until the $5d$ band overlaps with the $4f^6$ state and the energy gap is closed, with the result that $4f$ electrons spill into the $5d$ band leaving a $4f^5$ state behind. The $4f^5$ ionic radius is $\sim 15\%$ less than that of the $4f^6$ state; the lattice shrinks with a further increase of the $5d$ crystal field splitting, which results in an avalanche effect and a first-order valence transition. Since, having smaller lattice constants, SmS is less compressible, it was believed that the valence transition could not go all the way to trivalency but would stop where the gain in electronic energy was compensated by an increase in lattice energy. At pressures just above the phase transition the quoted values of the Sm valence are spread from 2.6 to 2.8 depending on the technique adopted [18]. With further increasing pressure the hybridization gap is gradually closed and the temperature dependence

¹¹ Given the bulk sensitivity of the technique, the effect of a possible surface contamination from trivalent Yb_2O_3 should be negligible, especially in the measurements at ambient pressure which were performed on an intact single-crystal sample.

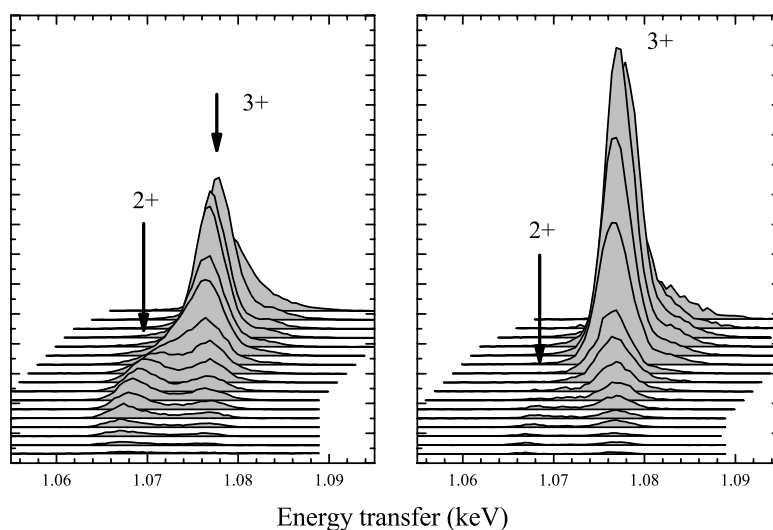


Figure 5. SmS RXES series across the L_3 edge, at 30 (left panel) and 180 kbar (right panel). The arrows point to features from divalent and trivalent Sm components.

of the resistivity turns to metallic behaviour at low temperatures (lower than ~ 40 K) above 19.5 kbar. It was expected that at even larger pressure values, SmS would be driven to integer trivalency, where a magnetic ground state is expected. However, until very recently, there was no clear experimental evidence of magnetic ordering of SmS at higher pressures. The abnormally large pressure derivative of the bulk modulus near 22 kbar led to the suggestion that trivalent behaviour was only reached at pressure of the order of 100 kbar [27], at variance with band structure calculation predictions which were always of a magnetic ground state for the gold phase [28]. The L_3 absorption [29] spectroscopic investigation of the pressure dependence of samarium valence at room temperature showed a non-linear increase above the transition pressure, reaching a value of $\nu \sim 2.9$ at 72 kbar with an inflection point near 22 kbar.

Answers were given recently to the combined question of the pressure-induced completion of trivalency and crossover towards a magnetic state. Clear evidence that the collapse of the gap at ~ 20 kbar coincides with the appearance of magnetic ordering was provided for the first time by ^{149}Sm high pressure nuclear forward scattering (NFS) of synchrotron radiation [30] at low temperature (3 K). The NFS data show that at ~ 20 kbar a first-order phase transition occurs from the non-magnetic mixed valence state to a magnetically ordered state stable up to at least 190 kbar. This result seemed to support the idea that at 20 kbar the Sm ions are already trivalent. The RXES experiment on SmS under pressure was therefore performed to determine with confidence the Sm valence and correlate its evolution with the onset of long range magnetic order. RXES spectra were measured at room temperature. Pressure was transmitted to the sample (a single crystal with dimensions of $\sim 100 \times 40 \times 50 \mu\text{m}^3$) by Fluorinert. The main result can be seen at a glance from figure 5 where the full sets of RXES spectra excited (in 1 eV steps) across the Sm L_3 absorption edge are shown, at 30 and 180 kbar, the highest pressure reached. Whereas a sizable contribution from Sm^{2+} is present at 30 kbar, at 180 kbar the electronic configuration is almost purely trivalent. Along the lines of the data analysis performed on ytterbium compounds, we were able to follow the valence evolution and conclude that at the onset of long range magnetic order ($p = 20$ kbar) the valence of Sm is considerably lower than 3 ($\nu \sim 2.84$ at $p = 30$ kbar). Integer trivalency is not reached even at the highest pressure of this study ($\nu \sim 2.98$ at $p = 180$ kbar). If the result is confirmed at

low temperature, this would imply that SmS is at the same time of intermediate valence type and magnetically ordered.

6. Conclusions

The chemical selectivity and bulk sensitivity of resonant x-ray emission make it a very valuable tool for the study of electronic properties of strongly correlated materials. Now that the available photon fluxes have relaxed the intensity limitations, a wide range of experimental conditions can be explored. The precise data obtained from RXES are precious complements to the results given by other techniques, and set new challenges to existing theories.

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