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# VALENCE RELAXATION IN THE 2p CORE PHOTOIONIZATION OF MIXED VALENCE TmSe CRYSTAL

A. Bianconi, S. Modesti
Istituto di Fisica dell'Università di Roma

M. Campagna, K. Fischer
Institut für Festkörperforschung der KFA, Jülich (Germany)

S. Stizza
Istituto di Fisica dell'Università di Camerino.

ABSTRACT.

The $L_3$ X-ray absorption spectrum of TmSe has been measured using synchrotron radiation emitted by the storage ring Adone. Evidence of homogeneous mixed-valence of TmSe and of the core hole induced relaxation has been found.

One foundamental point in core level photoionization is the effect of relaxation induced by the core hole. These effects are expected to be important in core level spectroscopy of all rare earths especially of stable chalcogenides and of compounds in the homogeneous mixed valence state[1]. A recent paper[2] has shown that the valence change induced by the creation of a hole in a core level has large effects on the Auger spectrum of $YbAl_3$. We have studied the core transitions from the $2p_{3/2}$ core level of TmSe to study the effect of core relaxation in the total photoionization cross-section.

It is well known that TmSe is in a homogeneous mixed valence state where the Tm ions fluctuate between a $4f^{13}5d^0$ and $4f^{12}5d^1$

configuration[3]. From bulk measurements for stoichiometric samples the mixing-valence-ratio $r = Tm^{3+}/Tm^{2+} \sim 3$ has been determined[4].

Following the photoionization of the $2p_{3/2}$ core level in the "adiabatic limit" a fully relaxed valence band is expected. The effect of the core hole on the valence 4f 5d states can be estimated by using the (Z + 1) analogy, i. e. the valence orbitals will be the same as the following Z + 1 atom having a Z + 1 positive charge localized in the nucleus. For stable $Tm^{3+}$ configuration ($4f^{12}$) the $4f^{13}$ level will drop below the Fermi level after switching on the core hole. The Tm atom starts in $4f^{12}5d^{1}$ configuration of the $Tm^{3+}$ ion and in the fully relaxed state it changes to the $4f^{13}$ configuration of the $Tm^{2+}$ ion. Therefore it will no longer be possible to clearly distinguish the two valence states of the initial homogeneous mixed valence state in core level photoionization measurements. In fact the $M_{4,5}VV$ Auger spectrum of $YbAl_3$ does not show any effects due to valence fluctuations[2]. The fully relaxed state is reached if the characteristic response time of the valence electrons is shorter than the lifetime of the excited state (the measuring time).

In the "sudden" regime the characteristic time of the measurement is so short that the valence electron have no time to relax. In XPS measurements of core levels where a fast photoelectron is excited the "sudden" approximation is expected to be a good approximation although evidence for partial relaxation in rare earth metals and Ce compounds especially has been found[5, 6].

The experiments have been performed at the synchrotron radiation facility PULS using the X-rays emitted by the storage ring Adone. The X-rays were monochromatized by a Si(220) single channel-cut crystal at 17 m from the source. The resolution was about 1.5 eV at the $L_3$ threshold of Tm at 8650 eV. The samples were single crystals of TmSe in thickness $d = 20\ \mu$.

The $L_2$ spectrum has been measured and we have found that except for one factor it was the same as the $L_3$ spectrum. The incident photon flux $I_o$ and the transmitted flux I were measured and the photoabsorption coefficient $\alpha = 1/d \ln I_o/I$ is plotted in Fig. 1 as a function of the photon energy. The zero of the energy scale has been taken at the first maximum of the absorption derivative.

The $L_3$ spectrum of rare earths is dominated by a "giant resonance" near the threshold due to transitions to d states near the Fermi level[7]. This resonance is partially due to the high density of d-states but the large oscillator strength should be explained by the local character of the final states confined in the core region by the high centrifugal potential acting on the d-electrons. Such large atomic resonance covers all the other molecular or solid state effects which determine the X-ray Absorption Near Edge Structures.

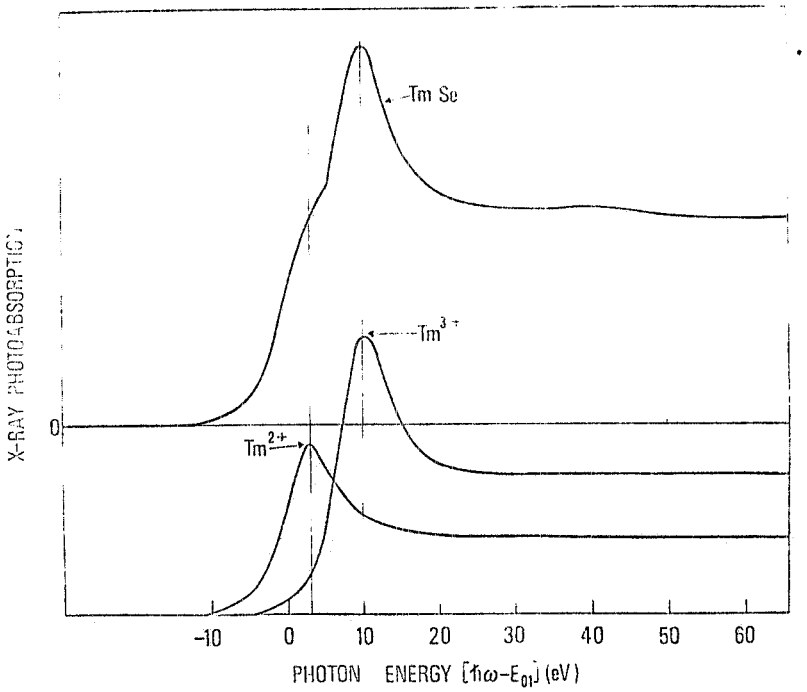


FIG. 1 - The $L_3$ X-ray photoabsorption spectrum of single crystal TmSe. In the lower part the individual contributions of the $Tm^{3+}$ and $Tm^{2+}$ ions are plotted. The pre-edge continuum background has been subtracted.

The Fano line-shape[8] well describes this transition to a quasi bound state superimposed on a continuum. The spectrum can be fitted by an asymmetric Lorentzian and an arctan.

The curve in Fig. 1 has been deconvoluted in two curves due respectively to $Tm^{3+}$ and $Tm^{2+}$ ions. The intensity ratio between the spectrum due to $Tm^{3+}$ and $Tm^{2+}$ is $r = 1.6$ to be compared with the expected mixing valence ratio 3. The lifetime of the excited state is estimated from the full width of the "giant resonance" ($\Gamma = 7.4 \pm 0.2$ eV) to be $T = 0.9 \times 10^{-16}$ sec.

The evidence of transitions due to $Tm^{3+}$ ions indicates that we are not in a fully "adiabatic" regime also if valence band relaxation is present as it is shown by the weak intensity of the $Tm^{3+}$ component. Such an intermediate regime between the "sudden" and the "adiabatic" regime is expected if the characteriastic time of the photoexcitation is close to the response time of valence electrons. Therefore we have an extimate for the relaxation time in TmSe $\tau \gtrsim$ $\gtrsim 0.9 \times 10^{-16}$ sec.

The lineshape of the resonances is determined by the autoionization channels of the excited states like the $2p^5(4f^{13}5d^0)\,\varepsilon d^* \longrightarrow$ $\longrightarrow 2p^6(4f^{12}5d^0)$ + photoelectron which is the same final state in continuum photoexcitation of a 4f electron in the d-conduction band.

In conclusion the data show an intermediate relaxation regime in the core level photoionization of TmSe.

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