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X-RAY ABSORPTION NEAR EDGE STRUCTURES OF TmSe SINGLE CRYSTAL.

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ABSTRACT.

L_3 and L_1 X-ray absorption spectra of single crystals of TmSe and Tm metal were measured at the synchrotron radiation facility PULS using the Frascati storage ring Adone. Valence fluctuations in TmSe appear from the analysis of the X-ray Absorption Near Edge Structures (XANES). The XANES of TmSe show two well resolved "giant resonances" at the L_3 threshold due to $2p \rightarrow 5, \bar{6} d^*$ transitions localized on the Tm^{3+} and Tm^{2+} ions.

The joint analysis of the L_1 and L_3 edges gives information on the symmetry of the conduction states at the Fermi level. The validity of the "sudden" or of the "adiabatic" approximation in the photoionization near the absorption edge and the effects of the core hole induced relaxation on the measured mixing valence ratio are discussed.

1. - INTRODUCTION.

The X-ray absorption near edge structure (XANES) are a sensitive probe of local structures^(1,2) and local electronic states⁽³⁾ in molecules⁽⁴⁾ and solids. The XANES of the L_2 and L_3 threshold of rare earth compounds are dominated by a "giant resonance" due to atomic-like $2p \rightarrow 5, \bar{6} d^*$ transition which is so strong that it covers all the other solid state or molecular effects on the XANES. Similar "giant resonances" appear also in atomic spectra^(8,9) near the thresholds of core transitions from p core states. The local character of this spectroscopy could be particularly useful for studying valence fluctuations in rare earth compounds. In the

homogeneous mixed valence state⁽¹⁰⁾ the rare earth ions fluctuate between two valence states and corresponding core level transitions exhibit a large energy shift. We have found that evidence of the homogeneous mixed valence (HMW) of a solid can be easily extracted from XANES but a quantitative estimate of the mixing valence ratio r requires an accurate analysis of fundamental aspects of core level transitions like valence band relaxation and autoionization processes.

TmSe is a typical crystal in the HMW state. The Tm ions in TmSe fluctuate between the trivalent Tm^{3+} , $4f^{12} 5d^1$ configuration and the divalent Tm^{2+} , $4f^{13} 5d^0$ configuration. From bulk measurements^(11, 12) it is considered a dynamic random mixture of 75% Tm^{3+} and 25% Tm^{2+} giving a mixing valence ratio $r = \text{Tm}^{3+}/\text{Tm}^{2+} = 3$. XPS data show the HMW of TmSe⁽¹³⁾. Recently the magnetic properties of TmSe have been the object of an active experimental⁽¹⁴⁻¹⁶⁾ and theoretical⁽¹⁷⁾ interest with the aim of establishing the influence of stoichiometry on valence fluctuations. The rare earth metal Tm has been studied for comparison because it is well known that here Tm is only in a trivalent state.

2. - EXPERIMENTAL.

The experiment was performed at the Frascati synchrotron radiation facility PULS using X-rays emitted by the 1.5 GeV storage ring Adone. The X-rays were monochromatized by a Si(220) channel-cut single crystal at about 17 m from the source. The high stability, high collimation ($\Delta\theta = 5 \times 10^{-5}$ rad) and the high intensity of the X-ray beam give high resolution and signal-to-noise ratio spectra. A PDP/11 computer was used for data acquisition and analysis. To resolve the most important experimental difficulty of this experiment, i. e. the oxidation of the sample, we have used bulk single crystals. The photoabsorption spectra have been measured from transmission measurement $\alpha = \frac{1}{d} \ln \frac{I_0}{I}$ where I_0 and I are the measured incident and transmitted X-ray intensities. The surface contribution in this measurement in comparison with the bulk contribution can be estimated $\sim 10^{-3}$. The thickness of the single crystals were in the range of $\sim 20 \mu$. Several samples with different thickness were used to eliminate thickness effects in the shape of the absorption spectra. We have prepared the samples also using a different approach and we have found the same results. The crystal was filed in He atmosphere and TmSe powder was spread on the Kapton window of a small cell and immediately put in the vacuum of the experimental chamber. Using this procedure the powder samples were never in contact with air and no indication of oxide formation was found. The lattice parameter of the TmSe sample is $5.71 \pm 0.03 \text{ \AA}$ as determined by X-ray diffraction.

3. - RESULTS.

Figs. 1 and 2 show the L_3 and L_1 absorption spectra of TmSe and Tm. Also the derivative spectrum of the L_3 edge is reported. The zero of the energy scale has been taken at the first maximum of the derivative spectrum E_{O1} for TmSe and E_0 for Tm of both L_3 and L_1 spectra. The pre-edge continuum background has been subtracted. The curves have been nor-

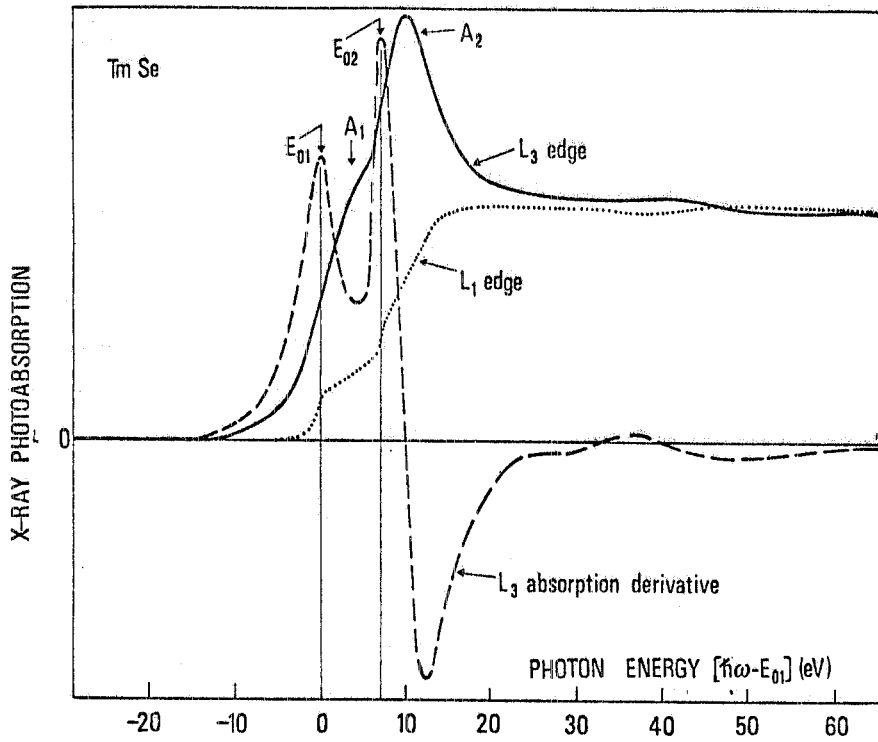


FIG. 1 - L_3 and L_1 X-ray absorption spectra of TmSe. The zero of the energy scale has been taken at the first maximum of the derivative spectrum E_{01} .

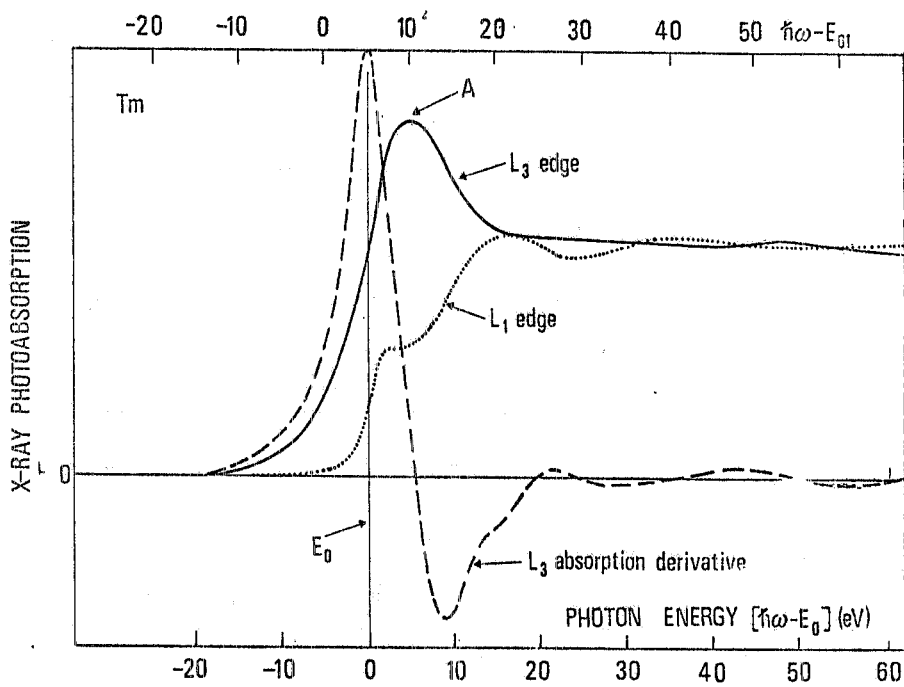


FIG. 2 - L_3 and L_1 X-ray absorption spectra of Tm. The zero of the energy E_0 scale has been taken at the derivative maximum. We report in the upper part of the figure the same energy scale of the TmSe spectrum.

malized in order to have the same intensity at 70 eV above the edge. The L_2 spectra have been measured but are not reported because they are identical to the L_3 spectra except for a lower ($\sim 1/2$) oscillator strength. The comparison of the L_3 and L_1 spectra clearly shows that the "giant resonance" $2p_{3/2} \rightarrow \overline{5, \epsilon} d^*$ in the L_3 spectrum is completely suppressed in the L_1 spectrum because the transition from the $2s$ level is dipole forbidden. Due to matrix element effects the two core spectra of the same compound probe the d -components and the p -components of the final states. This point is confirmed from the weak EXAFS structures at higher energies where the L_3 spectrum shows maxima where the L_1 spectrum have minima and vice-versa. The photo-absorption spectrum of Tm shows a single peak A and a single threshold in L_3 and L_1 spectra respectively. The spectrum of TmSe clearly shows two peaks A_1 and A_2 at the L_3 edge and two thresholds E_{O1} and E_{O2} at the L_1 edge. The energy positions of the peak A_2 and the threshold E_{O2} coincide with the position of the corresponding structures of Tm. Therefore E_{O2} and A_2 are due to transitions localized on the Tm^{3+} ions and E_{O1} , A_1 to transitions on the Tm^{2+} ion. This result is a clear experimental evidence of the presence of the presence of Tm^{2+} ions with lower $2p$ binding energy in TmSe. The energy splitting E_o of the Tm^{2+} and Tm^{3+} core levels is determined by the splitting of the derivative peaks E_{O1} and E_{O2} in the L_3 spectrum and by the splitting of the L_1 edge, $\Delta E_o = 7.0 \pm 0.2$ eV. The L_3 spectrum can be separated into two contributions from Tm^{3+} and Tm^{2+} ions as it is plotted in Fig. 3.

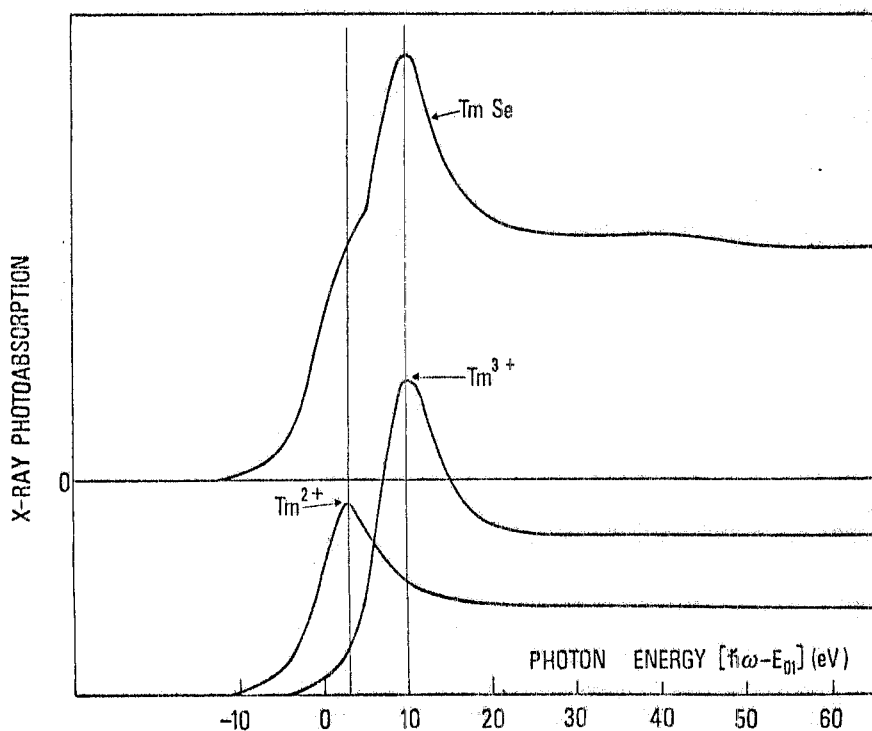


FIG. 3 - Deconvolution of the TmSe spectrum in two components due to Tm^{3+} and Tm^{2+} . From the intensity ratio of the Tm^{3+} and Tm^{2+} curves a mixing valence ratio r can be determined.

A mixing valence ratio $r = \text{Tm}^{3+}/\text{Tm}^{2+} = 1.6$ has been found. This value is smaller than that calculated from lattice constant $r = 3$ but close to that calculated from XPS data⁽²⁵⁾.

4. - DISCUSSION.

a) The energy splitting of the core absorption threshold.

We have found the same energy splitting of the core absorption threshold at the $L_{2,3}$ and at the L_1 edges in the mixed valence TmSe crystal: $\Delta E_0 = 7$ eV.

The measured value of ΔE_0 is close to the reported value of the splitting of the $4f^{13}-4f^{12}$ levels in XPS spectra^(12, 13), and to the value of the interconfiguration energy U_{eff} ⁽¹⁸⁾. This effect is due to the $4f$ radial wavefunction $\psi(r)$ which has $(n-1)$ maxima i. e. only one maximum at about the same distance from the nucleus of the $4p$ levels. Removal of a $4f$ electron will therefore increase the binding energy of core levels by the same amount. The problem is complicated by the effect of the change of the atomic Coulomb field on the outer filled levels $5s$ and $5p$. The radial wavefunctions $\psi^2(r)$ of these levels have several maxima inside the atomic radius and induce a different shift on each core level. Our data indicate that this effect is small within the errors of our and XPS estimate of ΔE , in agreement with the shift of $K_{\alpha_{1,2}}$ ($2p \rightarrow 1s$) and K_{β} ($4p \rightarrow 1s$) X-ray emission lines⁽¹⁹⁾ which in TmSe show only a 0.1 eV energy shift.

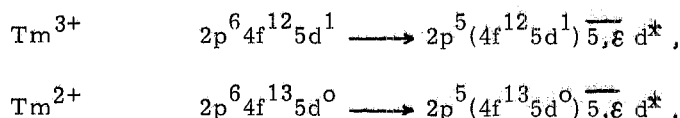
b) Core hole relaxation and the measured mixing valence ratio.

It is well known that cross section effects, valence changes and autoionization can strongly modify the relative intensity of Tm^{2+} and Tm^{3+} signals in photoemission experiments as a function of the exciting photon energy^(12, 20, 21). Such effects can play an important role also in XANES. In fact the intensity and lineshape of the peak A due to the "giant resonance" from the $2p_{3/2}$ core level to $\overline{5,8}d^*$ level⁽⁸⁾ at the Fermi level is determined by valence relaxation and autoionization effects. This resonance is superimposed on a continuum of transitions to delocalized states which can be assumed to have a distribution of the oscillator strength similar to the L_1 spectrum. The $\overline{5,8}d^*$ final state is expected to be a quasi-bound state localized by the centrifugal potential acting on the $l=2$ dipole excited photoelectrons. Such local character of the final state induce a large overlap between initial and final states. This "giant resonance" is similar to the atomic resonance observed in atomic spectra^(8, 9) and the effect of the neighbour atoms can induce an increase in the localization of the final states like in the case of "shape resonances" in molecules⁽⁴⁾. This resonance has a Fano lineshape⁽²²⁾ superimposed on an arctan function due to transition to continuum states. The Fano lineshape is expected for any core transition to localized states which are always superimposed on the continuum transitions from the valence band and from levels with lower binding energy. Relaxation effects following the creation of the $2p$ hole and the decay channel of the excited state can drastically affect the measured shape of the total photoabsorption process⁽⁹⁾.

The fundamental point in the interpretation of core photoionization process is the validity of the "sudden" or the "adiabatic" approximation. In the "adiabatic" approximation the excited

state is completely relaxed and the 4f states are pulled below the Fermi level by the higher Coulomb field due to the 2p core hole which can be approximated using the Z+1 analogy⁽²³⁾. In the "sudden approximation" the energy position of the levels in the initial state remains unchanged in the final state. Clearly the transition from the adiabatic limit to the sudden limit is determined by the competition between the excitation time T_{ex} and the relaxation time τ . When their values are close some intermediate situation occurs. Evidence for such effects has been found in Auger⁽²⁰⁾ and photoemission spectra^(20, 23).

The effect of going from the "sudden" to the "adiabatic approximation"⁽²⁴⁾ is expected to be dramatic in our photoabsorption spectra. In fact if the "sudden approximation" is valid the excitation processes in TmSe will be:



In the adiabatic approximation the creation of a 2p hole will induce a complete transfer of electrons from the 5d to 4f level i. e. a change from $4f^{12} 5d^1$ into $4f^{13} 5d^0$ i. e. a transition from Tm^{3+} to Tm^{2+} valence state and possibly even a change from $4f^{13}$ to $4f^{14}$, i. e. Tm^{2+} to $\text{Tm}^{1+} \approx \text{Yb}^{2+}$. The first step will suppress completely the structures in the photoabsorption spectra due to the Tm^{3+} ion. It has been observed in the Auger spectra of YbAl_3 a complete disappearing of the structure due to the Yb^{3+} valence state. This indicates that the relaxation time τ is smaller than the estimated lifetime of the 4d core hole in YbAl_3 , which is 1.5×10^{-16} sec. The lifetime of the excited state in our L_3 spectra can be determined by the width Γ of the "giant resonance" A at the L_3 edge. We have found $\Gamma = 7.4 \pm 0.2$ eV which is little affected by the instrumental resolution, at 8650 eV, ~ 1.5 eV i. e. about 20% of the measured width. This gives a lifetime $T_{ex} = 6.6 \times 10^{-16} / \Gamma = 0.9 \times 10^{-16}$ sec for the excitation process at the L_3 edge. The same valence mixing ratio can be obtained from the analysis of the L_1 edge as can be observed in Fig. 2. The excitation time T_{ex} at the threshold of 2s core transitions is $\sim 1.15 \times 10^{-16}$ sec as determined by the 2s core lifetime. Therefore the relaxation time τ is larger than T_{ex} and than the shorter measuring time of XPS spectra which give also a similar value⁽²⁵⁾. The explanation of the larger value deduced from crystal lattice require further investigation.

c) Effects of the conduction band density of states at the Fermi level.

Generally the role of the density of states of the conduction band is important in a energy range of few eV at the core photoabsorption threshold. The joint analysis of the L_3 and L_1 thresholds is necessary to obtain some information on the electronic states at the Fermi level. In fact in the photoionization of atomic core levels the selection rules are very active. Therefore the L_1 spectra are determined by delocalized p-like final states while the $L_{2,3}$ spectra are determined by localized d-like final states.

The shape and the width of the $2p_{3/2} \rightarrow \overline{5,8} d^*$ giant resonance is affected also by the d-density of states and the autoionization process. The effect of the density of states can be indicated by the different width and intensity of the giant resonance in TmSe and in Tm. In Tm it is broader and weaker. Such a large effect could be partially due to the fact that in Tm metal the d-states are more delocalized and a large mixing occurs (the bands are wider) moreover due to closer Tm-Tm interaction the d-states are shifted up in energy. In fact the maximum of the resonance in Tm is at 5.2 eV above the first derivative maximum and in TmSe it is at 2.8 eV; 4f count change (i. e. 4f relaxation) of the Tm^{3+} in Tm can however contribute also to this effect. The last point to consider is the autoionization process of the excited state $2p^5 4f^{13} \overline{5,8} d^*$ into $2p^6 4f^{12} +$ ejected f photoelectron which has a large probability in rare earth compounds^(26, 27). However to establish the effect of this last process accurate calculation of the oscillator distribution strength compared with the measured of total photoabsorption cross-section is required.

The L_1 spectrum of Tm in Fig. 2 shows a strong absorption jump at the threshold due to final states of mixed p and d symmetry of the conduction band crossing the Fermi level. This shape of the threshold is typical of a metal and it is similar also in TmSe and TmTe, but the absorption jump at the L_1 threshold of TmSe is relatively much smaller (see Fig. 1). Therefore in TmSe the partial density of states of the p-like components of the conduction band at the Fermi energy is small. The small mixing of the d-like conduction bands is in agreement with the observed sharper $2p \rightarrow \overline{5,8} d^*$ resonance at the L_3 edge.

The L_1 spectrum shows a chemical shift of the core absorption threshold. In Table I the energies of the thresholds (E_{01} and E_{02}) of the Tm compounds are reported. A shift of the

TABLE I - Energy of structures in L_3 and L_1 spectra ± 0.2 eV.

	E_{01}	A_1	E_{02}	A_2 ± 0.2	$E_{01}(L_1)$	$E_{02}(L_1)$
TmSe	8644.2		8651.2	8654	10109.5	10116.5
Tm			8648.8	8654		10114.5
TmTe	8644.2				10109.5	

$E_{02}(L_1)$ threshold of the transitions from the 2s levels in the Tm^{3+} ion of about 2 eV going from Tm to TmSe has been found. The chemical shift can be related both with a larger binding energy of the 2s level in TmSe and with the shifting up to the p-like final states. The effects of the chemical bonding appear at L_1 edge while the energy of the giant atomic-like resonance at the L_3 edge remains the same in TmSe and in Tm.

5. - CONCLUSIONS.

In conclusion we have confirmed that the XANES are a probe of the mixed valence state of materials to be added to the conventional techniques like lattice constant, XPS and UPS, Mössbauer isomer shift and magnetic susceptibility.

A recent paper has shown that joint edge and EXAFS analysis can give evidence of the homogeneous mixed valence state⁽²⁸⁾.

Here we have shown that electronic relaxation effects in XANES are important and can affect the measured mixing valence ratio, and the core hole relaxation time in TmSe is longer than 1.15×10^{-16} sec. The analysis of the L_3 and L_1 edges gives the same valence mixing ratio and core level splitting, despite the quite different nature of excited states at the two edges.

Moreover the joint analysis of the L_3 and L_1 edges can give information on the chemical bonding and symmetry of the conduction band at the Fermi level.

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