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X-RAY ABSORPTION SPECTROSCOPY (L₃ EDGES, XANES, EXAFS) ON 4f MIXED-VALENT COMPOUNDS

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Résumé. - L'utilisation de la spectroscopie d'absorption X à l'étude des composés à valence intermédiaire est résumée. Cette technique expérimentale, qui permet la détermination absolue du taux d'occupation 4f, est souvent critiquée, étant donné l'existence possible de processus multielectroniques qui peuvent fausser les résultats. Aussi, dans cet article, une attention toute particulière sera portée à ce problème ainsi qu'à son influence à la fois dans le cas des composés de terres rares légères (La, Ce), et lourdes (Sm, Eu, Tm, Yb). D'autres mécanismes, pouvant être confondus avec les processus multielectroniques, seront envisagés. Finalement, l'utilisation de l'EXAFS et du XANES pour la détermination des relaxations atomiques dans les composés à valence intermédiaire sera envisagée.

Abstract. - The use of X-ray absorption spectroscopy (XAS) in the study of mixed-valence (MV) compounds is reviewed. This technique which allows an absolute determination of the 4f occupancy is often criticized because of the possible existence of multielectron process in the final state which may falsify the results. Therefore a special attention will be paid in this paper to this problem and on its possible influence both in the case of light rare-earth (RE) (La, Ce) and heavy RE (Sm, Eu, Tm, Yb) compounds. Particularly, several other mechanisms, which may be confused with final state effects, are discussed. Finally the use of EXAFS and XANES for the determination of atomic relaxations in MV compounds is investigated.

1. Introduction.

The possibility that the 4f orbitals in RE compounds may hybridize with the conduction electrons has opened, since a decade, a wide and interesting field of research both in Solid State Physics and in the Chemistry of Solids. Some fascinating results have been obtained for the so-called mixed-valent (MV) materials and recently for the heavy-fermions compounds (1, 2, 3). In both cases the particular properties of the ground state are the consequence of the presence at the Fermi level (or very close from it) of degenerate 4f levels which are, more or less, hybridized with the conduction electrons (4). I shall restrict myself in this paper to discuss the case of MV compounds.

Due to the hybridization the 4f electrons form a "band" and thus, may fluctuate between localized and extended states according to: 4 fn-1 5d 6s)MH⁺. The characteristic time for this 4f charge fluctuation (τf) depends directly on the hybridization. (τf = Δ = τfCEF ρo) (5). For MV compounds, Δ is typically 0.1 + 1 eV and thus τf is 10⁻¹³ - 10⁻¹⁴ sec. These quantum-mechanical fluctuations yield a non-integral 4f occupation number (n4f) which may be in a simple way related to the mean valence V. (The valence of a RE ion is, by definition, the number of (5d, 6s) electrons, i.e. n). Because the X-ray absorption process takes place on a very short time scale (10⁻¹⁸ < τf) both the 4fn (5d 6s)MH⁻⁴ and 4fn-1 (5d 6s)MH⁻⁴ configurations are directly observed in the absorption spectrum of a MV compound (6).
If the hybridization drops to zero \((V_{K_F} = 0)\) thus \(\gamma_f\) tends to infinity. In this last situation the MV state, if it occurs, is static and often labelled as inhomogeneous. However, as all the intermediate situation may occur, the distinction between homogeneous (dynamic) and/or inhomogeneous (static) MV states may be, in some cases, quite artificial.

The problem of MV compounds resumes to the "old" and difficult situation, currently encountered in Solid State Physics, where the hybridization \((\Delta)\) is of the same order as the intraatomic Coulomb interaction \((U_{eff} and/or U_{df})\). The analogy with highly correlated systems is striking (e.g. Mott-Hubbard insulators \((7)\)).

For the 4f compounds the problem is not straightforward because the degeneracy of the 4f orbitals and the spin-orbit coupling (including relativistic corrections) must be taken into account.

The aim of this paper is to discuss, from an experimental point of view, how high energy spectroscopies may give valuable information on the fundamental parameters of the MV problem (particularly \(n_f (V)\) and the hybridization). The paper is divided into two main parts. In the first one (sections 2 and 3) the direct use of L3 spectroscopy in the determination of \(V (n_f)\) will be presented, paying a special attention to the problem of multielectron process which are often invoked to minimize the quantitative use of high energy spectroscopy \((8, 9, 10)\). A comparison with other experimental techniques will be given.

In the second part (section 4), the information that may be obtained from the XANES \((20 \rightarrow 100\) eV above the L3 edge) and the EXAFS \((100 \rightarrow 1000\) eV) experiments will be presented. I shall focus on the problem of atomic relaxations (i.e. how the lattice responds to a change in the 4f occupancy) which are sensitive to the hybridization parameter.

### 2. L3 edges spectroscopy on mixed-valent materials: comparison with other experimental techniques.

In the last decade L3 absorption spectroscopy has widely been applied in the field of MV compounds. Particularly the valence transitions induced by pressure \((\text{Cerium metal}(11), \text{Sn S}(12))\) temperature \((\text{Eu Pd}_2 \text{Si}_2(13), \text{Eu Cu}_2 \text{Si}_2(14))\) or by alloying effects \((15, 16)\) have been investigated.

The basic idea for the use of L3 edge spectroscopy in MV materials is simple. If we suppose that at a given time two types of 4f configurations \((\text{say 4f}^{m+1} (5d 6s)^m \text{and 4f}^{m-1} (5d 6s)^{m+1})\) coexist in a compound and if their lifetimes are longer than \(10^{-16}\) sec, then, because the screening of the nucleus charge is more efficient for a 4f electron than for a 5d, the L3 absorption edges (and more generally all core-level excitations) will be made of two well-separated contributions \((7-10\) eV) corresponding to the two 4f configurations \((17)\). In principle we need just to weight the intensities of the two contributions to get the mean valence: \(\bar{V} = 2 + \langle I \rangle (4f^{m-1})/\langle I \rangle (4f^{m}) + I (4f^{m+1})\). The main advantage of this high energy spectroscopy is the possibility to get an absolute determination of \(\bar{V}\). For all the other experimental techniques which may be used to deduce \(\bar{V}\) (Mössbauer effect, susceptibility or lattice parameter measurements) references for the integral valent states are needed.

In table I the values of \(\bar{V}\), obtained from several experimental techniques, on various MV (or Integral Valant) systems are reported.

<table>
<thead>
<tr>
<th>(\bar{V})</th>
<th>L3</th>
<th>XPS</th>
<th>Latt. con</th>
<th>Suscept.</th>
<th>Mössbauer</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha-\text{Ce})</td>
<td>3.1 (11)</td>
<td>&lt;3.04</td>
<td>3.5</td>
<td>non mag.</td>
<td>-</td>
</tr>
<tr>
<td>Ce Ni5</td>
<td>3.3 (17)</td>
<td>3.12 (18)</td>
<td>4.0</td>
<td>non mag.</td>
<td>-</td>
</tr>
<tr>
<td>Sn S (HF)</td>
<td>2.57 (12)</td>
<td>-</td>
<td>2.77 (19)</td>
<td>-</td>
<td>2.61 (20)</td>
</tr>
<tr>
<td>Sn B6</td>
<td>2.65 (21)</td>
<td>2.65 (22)</td>
<td>2.77 (23)</td>
<td>-</td>
<td>2.65 (24)</td>
</tr>
<tr>
<td>Eu Pd3</td>
<td>3. (25)</td>
<td>2.5 (26)</td>
<td>3. (27)</td>
<td>3 (27)</td>
<td>3. (27)</td>
</tr>
<tr>
<td>Eu Pd2 Si2</td>
<td>2.3 (13)</td>
<td>-</td>
<td>2.3 (28)</td>
<td>non mag.</td>
<td>2.2 (13)</td>
</tr>
<tr>
<td>Eu Pd2 P2</td>
<td>2.2 (8)</td>
<td>2.2 (9)</td>
<td>2.4 (29)</td>
<td>2 (8)</td>
<td>2. (8)</td>
</tr>
</tbody>
</table>

Table I
As a matter of fact there is some dispersion between the $V$ values. Some of them may be explained in a simple way. In XPS the occurrence of surface effects complicates seriously the problem (30). (However such surface effects are absent in the cerium compounds (17).) For the lattice constant the relationship between volume and valence is non linear (31), etc. However in some other cases the results are definitively unreconcilable. For instance in all the cerium MV compounds the $V$ values obtained from the $L_3$ (or XPS) differ completely from those deduced from lattice constant and/or magnetic susceptibility measurements. This point has been verified in numerous cerium systems (6). Even in the case of heavy RE compounds there are some puzzling situations. For instance Eu Pd$_2$ P$_2$ is undoubtedly purely divalent in its ground state whereas it appears to be mixed-valent ($V = 2.2$) from the high energy spectroscopies results.

At evidence such discrepancies must be explained if we want to be confident in the results obtained from high energy spectroscopy. In order to underline the possible sources of errors let us first describe the mechanism of a $L_3$ absorption process and the usual approximations which are made for the data analysis.

A $L_3$ absorption process is a $2\,p_{3/2} + 5\,\epsilon\,d^* (or\,2\,p_{3/2} + 6\,\epsilon\,s^*)$ transition. Because of the dipolar selection rules ($1 = \pm 1$) only empty states with $d$ or $s$ symmetries can be reached in the final state. ($\epsilon$ means that there may be some admixture with other symmetries in the $5d$ or $6s$ initial state and the $*$ is simply here to underline the fact that we are in a final state with one more electron in the $5d$ (or $6s$) states and a core hole on the $2p$ level). As the transition probability matrix elements for a $2p_{3/2} + 6s$ transition are two order of magnitude weaker than those for a $2p_{3/2} + 5d$ transition they can be neglected in the physical description of a $L_3$ absorption process. In principle if we want to describe correctly an experiment it is necessary to calculate the transition probability matrix elements $P (E) = \left| \langle \psi^* \mid \exp (i\,R_{ij}^2) \mid \psi \rangle \right|^2$ where $\mid \psi^* \rangle$ is the wave function of the final state (i.e. in the presence of the core hole) and their energy dependence. This is an impossible challenge and thus several simplifications must be made.

- a) The most important (and probably the more delicate) is to suppose that a one-electron picture can be used. In the final state all the orbitals which are not directly involved in the absorption process are passive. It means that they are insensitive to the creation of the core hole. For $4f$ metals recent calculations have shown that this single electron picture works strikingly well (32). However in the case of MV materials the situation is a little bit more complicated.
- b) Often an oversimplified model is used. It supposes that the same $L_3$ profile may be used for the $2\,p_{3/2}$ ($4f^{15+}$) + $5\,\epsilon\,d^*$ and the $2\,p_{3/2}$ ($4f^{15-1}$) + $5\,\epsilon\,d^*$ transitions. This approximation is not correct because i) there is no reason to suppose that the $P (E)$ are identical and ii) the shape of the $5d$ density of empty states may be rather different. The procedure becomes particularly hazardous if one tries to reproduce the $L_3$ edge of a given RE atom using that obtained for another RE even if the local environments are quite identical.

The problem of multielectron process (i.e. the breakdown of the one-electron picture) will be discussed in section 3. Let us now consider in details what kind of errors may result from the second point we mentioned just above (b).

In the one-electron approximation a $L_3$ edge may be fairly well reproduced (14) by i) the convolution of a Lorentzian (assuming the core hole lifetime) with a $5\;d^*$ density of empty states weighted by $P (E)$, ii) adding an arctang curve to take into account the transition towards the continuum, iii) a final convolution with a Gaussian reproducing the experimental broadening. It is thus possible to deduce experimentally the product $N (E) = P (E) \cdot (5\;\epsilon\;d^*)$ by several deconvolutions process (33).

The corehole lifetimes for all the RE elements are well known and the experimental resolution may be precisely deduced by taking the rocking curve of the monochromator used for the experiment. Such a procedure needs low noise data and it supposes that all other experimental difficulties (thickness and homogeneity of the samples, absence of holes, etc.) have been overcome. All these parameters affect drastically the shape of the white line.
The results obtained for several Eu/Pd and Eu Pd$_2$ Si$_2$ compounds are shown on figure 1. The shapes of N(E) are significantly different for Eu$^{2+}$ (4f$^7$) and Eu$^{3+}$ (4f$^6$); moreover they are highly dependent from the chemical environment. It is interesting to notice that, in the case of Eu Pd$_3$(fig. 1 a) the shape we found for N(E) well agrees with the BIS experiments (53). Whether, for Eu$^{2+}$/Pd, the particular shape of N(E) may be due to a modification of the density of states or to the occurrence of a shake-up effect (see section 3) is still an open question.

Fig. 1: N(E) for several Europium compounds (see text) (a means amorphous compounds). The vertical bars in fig. 1 a for Eu Pd$_3$ indicate the positions and intensity of the 5d density of states as deduced from BIS experiments (53).

Any fitting procedure which will use identical or unappropriate values for N(E) yields, to a more or less extent, incorrect results. It is possible to estimate the error one can make. Let us suppose that, instead of the correct N(E) for Eu Pd$_3$, we use the dashed symmetric shape shown on fig. 1 a. The new fit is shown on figure 2. In order to bring some intensity in the 5 → 10 eV region, one may try to introduce a small component (7%) above the Eu$^{3+}$ edge. This is exactly the energy position expected for Eu$^{4+}$. Such a configuration has never been observed in any Eu compound.

The final conclusion of such an experiment will be that Eu Pd$_3$ is mixed-valent with V = 3.07 (!!). Thus even in the one-electron picture, without involving any experimental falsification it is possible to get wrong results.

Let us mention here an additionnal complication which may come from the XANES structures. In some cases (34) the multiple scattering of the photoelectron may give an extra contribution near the edge structure (10 eV) contributing to the error we can make on V. Before to invoke any multielectron process it is thus important to check the following points: a) Are we sure that the sample is homogeneous, exempt of any contamination (oxidation, etc.)? b) Are we confident in the N(E) used for the fitting procedure? c) Can we ascertain that there is no XANES contribution in the energy range where the 4f$^{7-1}$ is expected?

If the answers to these questions are all positive then multielectron process may be suspected.
3. The problem of multielectron process in $L_3$ spectroscopy.

Since the pioneering work of KOTANI and TOYOZAWA (35) which have studied how the electrons react to the sudden creation of a core hole, it has been a lot of theoretical and experimental jobs on this subject particularly in the case of 4f materials (36, 37). As this point will be extensively discussed at this conference it is not necessary to enter the details of the subtle mechanisms which are at the origin of the multielectron process. Let us just underline the main features:

- Due to the attractive potential of the core hole a 4f level, unoccupied in the initial state, is lowered below the Fermi level in the final state. Depending on the hybridization this 4f state will be either occupied or unoccupied in the final state. This is the shake-down process encountered in metallic materials.
- In the case of insulating compounds, because there are no conduction electrons, such shake-down process becomes improbable and in such a case a shake-up process takes place. This may be also the case even in metallic compounds if, for instance, the shake-down process is energetically unfavourable.

For the 4f materials a shake-down means that there is one more 4f electron in the final state and the shake-up one electron less. At evidence we will have some problem in the determination of $V$. For the purpose of this paper it is interesting to answer briefly the following questions:

1) Is it possible to predict the occurrence of such multielectron process?
2) Are they important for $L_3$ spectroscopy?

Shake-down satellites have been clearly observed in the XPS core level spectra of numerous La and Ce compounds (18, 38). For instance the intensity of this satellite is 40% in La Pd$_3$ and 20% in Ce Pd$_3$. Light RE elements like La or Ce are good candidates for multielectron process because the 4f wave function is extended in real space and thus the hybridization with the conduction electrons is enhanced. As shown by the recent theoretical calculations of GUNNARSSON and SCHÖNHAMMER (36, 37) the XPS spectra (and also the BEIS and $M_V$ edges) are well reproduced if the hybridization is properly taken into account both in the initial and final states. It means that the $V (n_f)$ values obtained from high energy spectroscopy are roughly correct. In these cases lattice constant or magnetic measurements are unable to yield the correct value of $n_f$. The concept of valence breaks down in this high hybridization limit. For heavy RE elements (Sm, Eu, Tb, Yb), because the hybridization becomes smaller (the 4f orbitals are more localized), such multi-electron processes are less probable. It explains why the agreement between high energy spectroscopy and other experimental techniques is better (see table 1).

Except the puzzling case of Eu Pd$_2$ P$_2$, and more generally that of divalent Eu, where atomic calculations (39) have shown that the shake-down processes are impossible, there is no direct experimental evidence of shake-up process in metallic compounds.

Up to now we discuss essentially the way by which the electrons will react to the sudden creation of a core hole. In fact if this situation is exactly encountered in XPS (or in EXAFS), it differs a lot for an absorption process. There are at least two fundamental differences:

i) the photoelectron has an almost zero kinetic energy; thus we are in an adiabatic limit where the electrons will have time enough to relax in order to screen the core hole,

ii) the photoelectron stays on the atom and plays a role in the screening of the 2p core hole. For these reasons multielectrons satellites are weaker in XAS than in XPS and it is always difficult to show their existence (40). This is well illustrated on fig. 3 where the XPS (3d) and XAS ($L_3$) of La in La Pd$_3$ have been reported. The $L_3$ data are deconvoluted from the core hole lifetime (3, 4 eV) in order to enable the comparison with XPS. The intensity of the 4f shake-down is considerably reduced in XAS. Similar conclusions have been obtained for numerous La and Ce compounds (41, 42). It explains simply why the $n_f$ ($V$) deduced from the $L_3$ well agrees with the values calculated in the Gunnarsson and Schönhammer's model. We do not really understand in this context why for Eu Pd$_2$P$_2$ the same "shake-up" intensity is observed both in XAS and XPS.
Fig. 3 : Lg of La\textsubscript{3} in La Pd\textsubscript{3} (The results have been deconvoluted from the core hole lifetime.) The vertical bars give the intensity observed in XPS for the La\textsubscript{3} d\textsubscript{sp2} core level.

4. XANES and EXAFS experiments on mixed-valent compounds.

Only a few EXAFS experiments have been performed on MV materials \cite{43, 44, 45, 25} and there are no XANES results (except a recent paper we published on this subject \cite{46}). This is well explained by the difficulty to analyse the EXAFS results in that particular cases \cite{47} and the lack of XANES theory for \textit{4f} materials. However the information we can get from such experiments are important. A MV compound may be written as [\textit{RE \textit{4f}^{n}}\textsubscript{x} (\textit{RE \textit{4f}^{n-1}}\textsubscript{1-x}) \textit{X}] where \textit{X} is any chemical element involved in the formation of the MV material. The situation resembles that encountered, for instance, in [Ga\textsubscript{1-x} In\textsubscript{x}]\textit{As} where EXAFS experiments have shown the existence of atomic relaxation \cite{48} : The Ga-As and In-As distances are quite similar to those of pure Ga As and In As compounds and thus differ from those obtained from X-ray diffraction where the average lattice constant follows Vegard's law. It is quite obvious that such a situation may be encountered in MV compounds, at least in the static limit (small hybridization). The difficulty in the MV case is that it is impossible to perform independent EXAFS experiments above the L\textsubscript{3} edges of a \textit{RE} either in the \textit{4f}\textsuperscript{n} or \textit{4f}\textsuperscript{n-1} configurations. (They are separated by a few eV).

Before to process any EXAFS data on MV materials one must solve the "Energy Threshold Puzzle" \cite{49} : is it necessary to consider one or two threshold energies for the data processing ? In the static case there is no doubt that two thresholds must be taken into account \cite{25} ; in the dynamic one the conclusion is not so evident. However our recent studies \cite{46, 47} support the two-threshold model in all MV situations. A justification may be found simply by comparing the EXAFS and XPS processes : in XPS the photoelectron leaves definitively the solid whereas in EXAFS it is backscattered by the surrounding atoms. In an XPS experiment performed on a MV material the (measured) kinetic energies of the photoelectrons (i. e. \textit{k}) are different for the \textit{4f}\textsuperscript{n} and \textit{4f}\textsuperscript{n-1} photoemission process. (The difference is roughly the energy splitting between the two structures in the L\textsubscript{3} edges). Then two different kinetic energies (i. e. two different thresholds) must be considered in the EXAFS process. At evidence the EXAFS results are highly dependent from this hypothesis.

In the static case (inhomogeneous) the atomic relaxation, that we defined by \textit{\delta R} = d (\textit{RE \textit{4f}^{n}} - X) - d (\textit{RE \textit{4f}^{n-1}} - X) where \textit{d} are the interatomic distances is large (up to 0.15 Å for a first neighbour shell) whereas in the dynamic (homogeneous) case it drops on the 0.06 Å range \cite{25, 47}. (i. e. in the sensitivity limit of EXAFS experiments). The atomic relaxation is the result of a competition between the elastic energy and the hybridization energy \cite{50}. The reduction of the atomic relaxation in the homogeneous case is due to the importance of the hybridization energy and, in principle, EXAFS experiments should be able to test the hybridization via these atomic relaxations ; however, due to the difficulty in the data processing, it is unlikely to use them except in a few simple situations (simple cristallographical structures, binary systems, etc.)

One may ask the question if XANES experiments (20 \text{ to } 100 \text{ eV}) are not able to yield more directly the importance of the atomic relaxation. At first sight XANES seems to be more difficult (and indeed it is) than EXAFS. However several simple arguments may be used for a preliminar approach of the problem.
1) It is well known that the XANES structures of a given compound may be reproduced by those obtained for another one (in the same cristallographical structure) rescaling the energy by a factor \((d_1/d_2)^2\) where \(d_1\) and \(d_2\) are the interatomic distances of compounds 1 and 2 [51].

2) This procedure is strikingly correct, even for 4f materials [32] and has been successfully applied to the Ce\(\gamma\alpha\) transition [52].

The XANES spectra \(X(E)\) of MV materials, in this simple model, may be written as:

\[
X(E) = x [X'_{4f}^{\text{ref}}(E)] + (1 - x) [X'_{4f}^{\text{ref}}(E)]
\tag{1}
\]

where

- \(X'_{4f}^{\text{ref}}\) is obtained from the XANES spectrum of the integral valent (4f\(^1\)) compound rescaling the energy by the factor \((d_{4f}^{\text{ref}}/d_{4f}^{\text{int}})^2\)
- \(X'_{4f}^{\text{ref}}\) is obtained from the XANES spectrum of the integral valent (4f\(^{n-1}\)) compound rescaling the energy by the factor \((d_{4f}^{\text{ref}}/d_{4f}^{\text{int}})^2\)

In order to take into account the energy splitting, this contribution is shifted by 7 eV to higher energy.

- \(x\) is the intensity of the 4f\(^n\) component in the edge.

In principle the strength of the atomic relaxation may be deduced from such experiments. I refer the lector to the papers we present at this conference (BEAUREPAIRE et al. and MALTERRE et al.) in which this simple formalism has been applied to several homogeneous and inhomogeneous MV cases. The results we obtained are in good agreement with those given by EXAFS measurements.

5. Conclusion.-

X-ray Absorption Spectroscopy is a powerful tool for the study of Mixed-Valent compounds and it yields valuable information about the ground state properties. The effect of multielectron process is almost non important for L\(_3\) spectroscopy; however such mechanisms cannot be completely ruled out in some particular cases. We need more experimental studies on the subject before any definite conclusion. Nevertheless it appears that Solid State effects may be confused with multielectron process and a great care must be given to the fitting procedure of an absorption edge if we want to be able to separate these different contributions. EXAFS and XANES experiments should be more systematically performed on MV materials because they can give interesting information on the strength of the hybridization parameter. Up to now it was commonly accepted that it was impossible to deduce the nature of a MV state from L\(_3\) spectroscopy (either static or dynamic). It is possible to get this piece of information directly from the XANES spectra which are always recorded with the L\(_3\) edges.

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