Annales de la Fondation Louis de Broglie, Vol. 14, no. 4, 1989

Rare earth electronic configurations and 3d ⇌ 4f transitions

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ABSTRACT. The experimental results suggesting the 4f character of the additional electron of La in comparison to Ba are first recalled. In this work this additional electron is supposed to be in a 4f state, in place of a 5d one as generally supposed. Then we recall the study of the La_2O_3 structure which leads to the hypothesis of cations with ionicity two plus, oxygen ions with ionicity one minus and a cation-anion bond which maintains the oxydation number (o.n.) III for the lanthanum and II for the oxygen. In this hypothesis the ionicity is a different notion from the valency or the o.n.

Then the study of the 3d⇌4f transitions is tackled . The doublet structure of the M_4 and M_5 spectra of lanthanum is interpreted as the result of the division of the 4f shell into two subshells as in Dirac's model. According to this model, the samarium has the first subshell filled and the second one empty. This configuration and those of the following rare earths lead us to expect that the absorption lines corresponding to the first 4f subshell are missing. The comparison of the X-ray absorption spectra to the X-ray emission spectra (taken from publications) of Sm, Sm_2O_3, SmB_6, SmS and SmSe to those of the other rare earths confirms this point. Finally the study of the electron energy loss spectra of Gd and La confirms the characteristic spectral properties of the first full 4f subshell for Gd and the doublet structure of the La spectra.

RESUME. Les résultats expérimentaux suggérant le caractère 4f de l'électron additionnel de La par rapport à Ba sont d'abord rappelés. Dans cette étude, cet électron additionnel est supposé occuper un état 4f à la place d'un état 5d habituellement supposé. L'étude de la structure La_2O_3*, qui conduit à l'hypothèse de cations d'ionicité deux plus, d'ions oxygène d'ionicité un moins et d'une liaison cation-anion qui maintient le nombre d'oxydation (n.o.) III pour le lanthane et II* *pour l'oxygène est ensuite rappelée. Dans cette hypothèse, l'ionicité est une notion différente de la valence ou n.o.*

L'étude des transitions 3d$\rightleftharpoons$4f est ensuite abordée. La structure doublet des spectres M_4 et M_5 du lanthane est interprété comme le résultat de la division de la courbe 4f un deux sous-couches comme dans le modèle de Dirac. Dans ce modèle, le samarium à la première sous-couche pleine et la seconde vide. Cette configuration et celle des terres rares suivantes conduisent à supposer que les raies d'absorption correspondantes à la première sous-couche sont absentes. La comparaison des spectres d'absorption de rayons X à ceux d'émission de rayons X (pris dans la littérature) de Sm, Sm_2O_3, SmB_6, SmS et SmSe à ceux des autres terres rares confirme ce point. Finalement, l'étude des spectres de pertes d'énergie d'électrons de Gd et La confirme les propriétés spectrales caractéristiques de la première sous-couche pleine pour Gd et de la structure doublet des spectres pour La.

I - INTRODUCTION

Our comprehension of the quantum distribution of the electrons in an atom is closely linked to the experimental results of the spectroscopy. In this connection the periodic table has played a very important role. We know that the number of elements in a row is equal to the number of quantum states of different shells of a hydrogen-like atom. Before the hypothesis of the spin there was one puzzling question. The observed number of stationary states for an electron in an atom was twice the number given by the theory. As a result, when Uhlenbeck and Goudsmit proposed the hypothesis of the spin to explain the alkaline or relativistic doublet series, the number of quantum states corresponding to the two kinds of spin into the same shell s,p, d and f were supposed equal. At the same time, the spin and orbital motion were thought to be more or less independant, allowing different kinds of coupling between several electrons of the same shell. Such a conception supposes that the corresponding angular momentum are constants of the motion. But compared to Dirac's model this concept of the spin leads to two difficulties: 1)the numbers of quantum states corresponding to the two kinds of spins into the same shell are different, 2) only the total angular momentum is a constant of the motion.

The dissociated conception of the spin and orbital motions of the electron has led to several models for the calculation of the magnetic moments. In view of the discrepancy between the notion of spin and

Dirac's model, we have recently proposed with Lochak [1] the same calculation of the magnetic moment of an atom based on Dirac's model for heavy rare earth metals, iron, cobalt, nickel and chromium compounds. This work shows that the electronic configuration of the 3d shell for the elements going from Sc to Zn and that of the 4f shell for the rare earths must be described according to Dirac's model. There is an essential consequence for the spectroscopy. The shells 3d and 4f, for the elements corresponding to their filling, are divided into two subshells $3d_{3/2}$, $3d_{5/2}$ and $4f_{5/2}$ $4f_{7/2}$, and they are filled up successively. In X-ray spectroscopy, this division is well-known for the electrons of the deep shells. But in a solid, the interactions between electrons of those elements and those of the neighbouring atoms have not yet allowed us to discover this division.

The purpose of this work is to show this division for the 4f states of the rare earths through the spectroscopy of the transitions 3d $\rightleftharpoons$ 4f of the rare earth elements. In view of this, it is interesting to recall that the reflection of this division appears in some physical and chemical properties. The rare earths are known to exhibit very similar chemical properties. They all have the oxidation number (o.n.) III and often just that. But in spite of this homogeneity, it is possible to distinguish two groups: the ceric or light rare earths going from La to Sm and the yttric or heavy rare earths going from Eu to Yb [2]. In addition people have known for a long time that the magnetic susceptibility of these two groups each has a maximum [3,4]. This gives six elements for the ceric group and eight for the yttric group that is the corresponding number of the quantum states of the $4f_{5/2}$ and $4f_{7/2}$ subshells.This correspondance suggests the hypothesis that we have already used in the calculation of the magnetic moments: the first 4f electron appears with the lanthanum. As a result, all the rare earth elements in their metal have one additional 4f electron in comparison to the three positive charge ion model. This hypothesis which as often been considered will be first discussed in section 2, and a posteriori supported by the discussion on the 3d $\rightleftharpoons$ 4f transitions. In discussing the crystal structure of La_20_3, we have shown that lanthanum in this oxide does not lose three electrons but just the two outer most 6s giving the La_{III}^{2+} ion with the ionicity 2^+ and the oxidation number III [5,6]. Simultaneously there is a O_{II}^{1-} ion an important point actually well established in the works on the valency in the new superconductors $La_{2-x}(Sr,Ba)_xCuO_4$ and $YBa_2Cu_3O_7$. This property also stands for the other rare earths and is useful in understanding the similarity between the spectra of Sm with different o.n. according to the compound. We shall recall this point in section 3.

Let us then focus our attention on the spectroscopy. Whatever the compound or the alloy, samarium always has six 4f electrons, that is the six quantum states of the first subshell $4f_{5/2}$ are occupied. On the other hand the eight quantum states of the second subshell are empty. This is a very particular configuration. *Any absorption of an electron on* $4f_{5/2}$ *is no longer possible.* In the spectra of samarium and the following rare earth elements we can except some missing absorption lines in comparison to that of the others. This fact has often been observed and underlined but is not understood. Classically there is no 4f subshell but just one kind of 4f electrons and such differences cannot be easily understood. It is the central point of this work. It will be studied in section 4 together with the doublets observed in the spectra of lanthanum and which correspond to the two 4f subshells. Finally in section 5 some concluding remarks will be given.

2 - ON THE PLACE OF La AND Lu IN THE PERIODIC TABLE

It is first useful to discuss the nature of the additional electron of La in comparison to Ba. Generally people suppose that this electron is in a 5d quantum state with possibly a partial 4f character. Our hypothesis is that this electron is purely in a 4f quantum state. Below we point out some aspects which can help to adopt this hypothesis. But whatever the interest of such arguments, this hypothesis presents great interest because it opens the way to the interpretation of phenomena as those discussed here, with the $3d \rightleftharpoons 4f$ spectra of rare earths and as before with the calculation of the magnetic moments of the heavy rare earths [6].

Let us now recall that numerous authors have indicated a 4f character for lanthanum. As early as 1932, Russel and Meggers found that the atomic spectrum of La differs from that of Sc, Y and Lu [7]. As pointed out by them "the atom building process which accounts for the rare earth elements is actually anticiped in the electron configuration of lanthanum atom". In 1965 Hamilton proposed to replace the position of lanthanum in the periodic table with lutetium [8]. He gave some reasons for why La should be a rare earth. One of these is the low melting point of La in comparison to that of Sc, Y and Lu. He also stressed that La becomes superconducting at 4.9°K, but superconductivity was not observed for Sc, Y and Lu. Mathias et al. in 1967 also called the low melting point of La in comparison to other elements, an anomaly [9]. They felt that the basic cause of the anomaly is the 4f character of the valence electron. Gschneidner in 1971 working in a similar way, mentioned the 4f nature of the bonding in lanthanide elements [10]. In 1974, Wittig claimed that lanthanum ought to be a 4f band metal [11]. In the discussion he also pointed out the low melting point of La in comparison to that of Sc, Y and Lu. (See also Probst and Wittig 1977 [12]). Very recently in the 1985 IUPAC general assembly Holden underlined several difficulties in the present status of the lanthanides and actinides [13]. These authors also give a number of references of other works on the same topic.

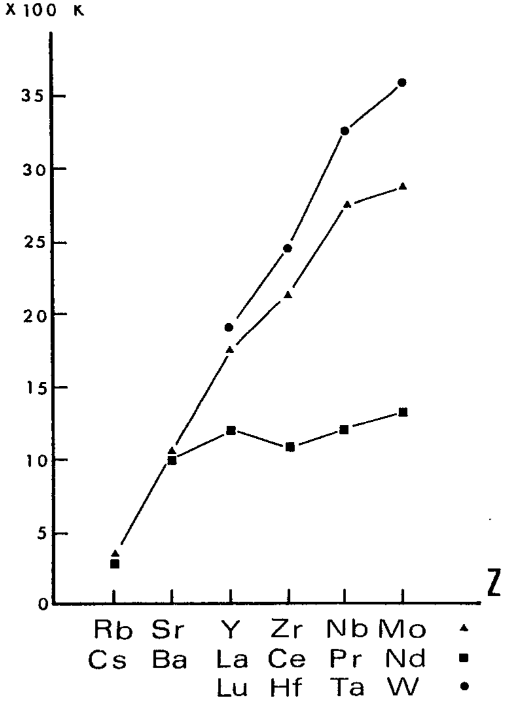

Figure 1. Melting points of lanthanum and some other elements. In the same parallel line on the abscissa the order of the elements is that of their atomic number Z. According to the discussion Y, La and Lu have been put on the same column. On the same line the melting points are characterized by the same symbol, triangles for the line of Y, squares for that of La and dots for that of Lu.

Let us consider the representative curve of the melting points for the elements going from Rb to Mo, from Cs to Nd and from Lu to W as shown in figure 1. We observe two different kinds of variation. The melting points of the 4d elements with respect to Rb and Sr increase more than those of the rare earth elements. For the 5d, the behaviour is close to that of the 4d, but with a higher melting point. If we suppose that for La, the electron in addition to those of Ba is in a 4f state, then we have a possible origin for the low melting point of La compared to Y. A more complete explanation would need to discuss the respective roles played by the deep valence electron in the melting point according to its d or f character. Such a discussion is beyond the scope of this paper.

Now, let us consider lutetium. Its melting point is close to that of yttrium. We are sure that for this element there are fourteen 4f electrons and one 5d electron. If one admits a 5d electron for lanthanum, it would follows that there are two elements which occupy the same place in the periodic table. This is very different to the driving concept which led Mendeleev to the discovery of the periodic table. So we can keep it in mind as a strong indication of the 4f state of the additional electron of La in comparison to Ba.

Here it is interesting to remark that historically such a situation comes mostly from the great difficulty in the separation of the rare earths and from the rarity of lutetium in comparison to the relative abundance of lanthanum. Thus lanthanum oxide was isolated towards 1840 by Mossander while lutetium was isolated in 1907 by Urbain [14,15]. As a result lanthanum took the place in the column of scandium and yttrium before the discovery of lutetium. The fact that lutetium must take the place below scandium and and yttrium has already been recognized and clearly explained by Landau and Lifchitz [16], but unfortunately they give the same outer most electronic configuration $5ds^2$ to lantanum. Finally, Julg also gives the correct place to Lu and furthermore he supposes that the filling of the 4f shell starts with lanthanum [17].

With this hypothesis of one 4f electron in place of 5d for the lanthanum we have to consider for all the other lanthanides one additional electron in comparison to the hypothesis of ion Ln^{3+} (table 1). *To understand this hypothesis of one additional 4f electron in the ground state of the Ln, one also has to suppose that this electron does not have the same deep character as the others.* This electron must be thought as quite delocalized or at least not so localized as the others. This distinction is necessary to understand the bonding property of this electron

Table 1 : The different 4f quantum states according to the two subshells: $4f_{5/2}$, $4f_{7/2}$. The number m defines the wave function ψ. The total observable angular momentum u in the $\hbar$ units and the corresponding magnetic moment $\mu_e = gu$, in Bohr magnetons. The Ln elements with their corresponding number ν of 4f electrons. The place of the Ln elements is such that the additional electron is supposed to occupy the quantum state of the column. Oudet and Lochak 1987. Ref. [1].

$4f_{5/2}$: $\kappa = 3$, $g = 6/7$						
m	3	2	1	0	-1	-2
u	$5/2$	$3/2$	$1/2$	$-1/2$	$-3/2$	$-5/2$
μ	2.14	1.29	0.43	-0.43	-1.29	-2.14
Ln	La	Ce	Pr	Nd	Pm	Sm
ν	1	2	3	4	5	6

$4f_{7/2}$: $\kappa = -4$, $g = 3/7$								
m	4	3	2	1	0	-1	-2	-3
u	$7/2$	$5/2$	$3/2$	$1/2$	$-1/2$	$-3/2$	$-5/2$	$-7/2$
μ	4.00	2.86	1.71	0.57	-0.57	-1.71	-2.86	-4.00
Ln	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
ν	7	8	9	10	11	12	13	14

which gives o.n. III to all the Ln. Such a distinction is also necessary to understand the metallic properties of several compounds like the LnX with X for S, Se and Te. Thus, by this distinction of two kinds of 4f electrons, we suppose that the properties which have been attributed to a 5d electron, in fact belong to one 4f electron. Let us recall that such a distinction has already been proposed in a similar approach by Gschneidner [10]. He calls the more delocalilzed 4f electrons "4f bonding electrons" or "4f band electron" and the more localized 4f electrons "atomic".

But in spite of this distinction the 4f bonding electron occupied one quantum state of the 4f shell. As a consequence for the study of the magnetic moment when this state is occupied, the other electrons, that is the atomic like, have to find other quantum states. This fact leads us to reconsider the interpretations of the magnetic moments as we have already mentioned in the introduction [1]. The case of the Curie constant have been discussed earlier [18].

In numerous 3d $\rightleftharpoons$ 4f spectra there is a strong similarity between those obtained with compounds where the rare earth has the o.n. two or three. In view of this we have to recall that the rare earths always keep their 4f electron even with an oxydation number higher than two.

3 - THE La_2O_3 STRUCTURE

We have to recall the way in which a distinction between the notions of valency (or oxydation number) and ionicity was presented. The sesquioxide of lanthanum La_2O_3 crystallizes with an hexagonal symmetry [19]. With a good approximation, it can be described as an hexagonal close packing of lanthanum cations. In this packing, for two lanthanum ions there are two oxygen ions in a tetrahedral site and another one in an octahedral site, figure 2. “The interest of this structure, arises out of the two sites of oxygen and of the difference of the properties according to the site”; it raises the question : Where can this difference come from [5,6]? To answer this question, let us consider the third electron responsible for the o.n. III. It is a deep-electron. Then we can suppose that just the two 6s electrons from the La atom can be lost at the time of the chemical combination. To make this hypothesis we do not need to know the precise nature of this electron. In view of the charge neutrality from this assumption we have the following exchange :

$$2\mathrm{La} \rightarrow 4\mathrm{e} + 2\mathrm{La}^{2+}$$
$$4\mathrm{e} + 3\mathrm{O} \rightarrow \mathrm{O}^{2-} + 2\mathrm{O}^{1-}$$

$$\text{that is}\quad \mathrm{La_2O_3} \rightarrow \mathrm{O}^{2-} + 2\mathrm{O}^{1-} + 2\mathrm{La}^{2+}$$

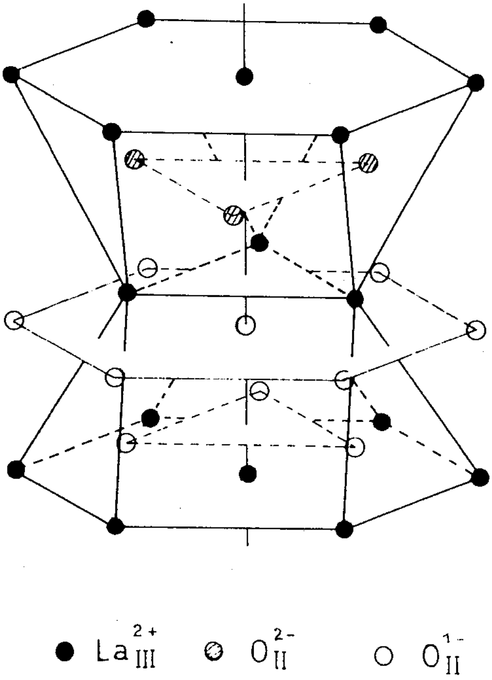

Figure 2. The La$_2$O$_3$ structure.

Thus in a first step, we can understand the existence of the two sites for the oxygen. The octahedral site corresponds to O^{2-} and the tetrahedral sites to the two O^{1-}. But in addition, the lanthanum with the charge 2^+ and the oxygen with the charge 1^- are involved in the La$_2$O$_3$ combination. They respectively have o.n. III and II. To take this fact into account we shall suppose that between these two ions there exists a bond of a covalent type obtained with the third valence electron of lanthanum which gives it its o.n. III. This electron stays on its atom of origin but brings its contribution to the lack of one electron upon the O^{1-} ions. This difference of bonding between the two kinds of oxygen is put in view by associated properties some of which we shall recall. It is this difference that we specify by the ionicity on one side and by the covalent bond on the other. To recall the existence of this supplementary bond in respect to the two ionic bonds, we can adopt the following writing La^{2+}_{III} and O^{1-}_{II}. The Roman numeral being more than one unit to the absolute value of the ionicity reminds us of the existence of a non-ionic bond. To underline this bond, we are led to the following : $La^{2+}_{III} \rightarrow O^{1-}_{II}$ the arrow symbolizing the dissymetry of the role of lanthanum and of oxygen. Thus we have a description of the La_2O_3 structure with two typical ionic bonds pictured by the exchanges of electrons between lanthanum and oxygen, and one covalent bond where the electron responsible for the bond belongs to the lanthanum. In comparison to the theory of the valence [20] where bonds are described as a mixing of ionic and covalent characters, there are some differences but there are also similarities that we want to specify a little more.

As for the exchanges of electrons between lanthanum and oxygen they have the same significance as those which are supposed between sodium and chlorine to describe the NaCl structure. Let us now consider the covalent bond between La^{2+}_{III} and O^{1-}_{II}. We suppose that the third valence electron of lanthanum responsible for this bond remains on its atom. By this hypothesis we mean that, whatever the interactions and in particular the attractions to which this electron is submitted from the neighboring oxygen ions, it keeps a quantum property of the lanthanum atom, allowing us to say that it belongs to this atom. The discussion about the place of lanthanum in the periodic table allows us to suppose that this property is characteristic of the 4f states. The calculation of the magnetic moment of the rare earths metals [1] allows us to specify that this property is the total angular momentum of the 4f states. Now keeping this characteristic quantum property in mind, we must consider that this electron is more or less attracted by one or several O^{1-}_{II} ions. There is a polarisation which can be used as a definition of the strength of the bond. According to its weight, this polarisation can give the appearance of a more or less ionic character to the covalent bond. There is a possibility for research in the description of the chemical bonds that we do not explore more in this work, since the essential point for the following is that the third valence electron of the lanthanum remains on its atom and occupies a 4f quantum state.

Let us now recall some experimental results which show the existence of this bond. The difference between the two kinds of oxygen ions is found in the possibility to easily replace the oxygen O^{2-} ion from the octahedral site by the ions S^{2-}, Se^{2-}, Te^{2-}, So_4^{2-} and so on, whereas the oxygen ions of the tetrahedral site are much more stable [21,22]. This property establishes the stability of the $(LaO)^{1+}$ group and as a result the strong covalent character of the bond between lanthanum and oxygen from the tetrahedral site. In a different way the importance of the group $(LnO)^+$ or $(Ln_2O_2)^{2+}$ in numerous crystal structures, has already been underlined [23]. In spectroscopy in the energy range of the visible, the oxyde Ln_2O_3 or the oxysulfides Ln_2O_2S are known to exhibit a strong red shift, a phenomenon interpreted as a result of a strong covalent character [24,25].

We will see in the following that there is no real important difference between the spectra of 3d $\rightleftharpoons$ 4f transitions of Sm_2O_3 and SmS or SmSe. This result supports the hypothesis of Sm^{2+}_{III} ions having the same electronic configuration as Sm^{2+}.

We want to point out that with the discovery of high-Tc superconductors by Bednorz and Muller [26] numerous investigations have brought new support for the hypothesis of oxygen O^{1-}_{II}. The $La_{2-x}M_xCuO_4$ compounds with M=Ba or Sr and $YBa_2Cu_3O_7$have been intensely studied with the following techniques : ultraviolet or X-ray photoelectron spectra, UPS or XPS, near edge X-ray absorption spectra and so on [27,33]. The most demonstrative result is perhaps the following. The oxygen O(1s) edge has a spike at threshold indicating unoccupied O(2p) states in the $YBa_2Cu_3O_7$compound [29]. These results clearly establish for copper that a cation can keep at least one electron of valence. A long discussion on the problems of valence in the high-T_c superconductors is given elsewhere [34].

4 - SPECTROSCOPIC STUDIES

Let us now tackle the study of the transition $3d^{10}4f^n \rightleftharpoons 3d^94f^{n+1}$ exhibited by the rare earths metals or their compounds. In such an experiment, a 3d electron is ejected by a high energy electron or X-ray photon to the 4f empty levels. This is the excitation process that gives rise to the absorption spectra. In the emission spectra, the inverse process of the excitation, the X-ray lines correspond to transition $3d^94f^{n+1} \rightarrow 3d^{10}4f^n$. If the intensity of the X-ray photon is studied as a function of the energy, we have an X-ray absorption spectra (XAS) or an X-ray emission spectra (XES). In some cases it is useful to study the X-ray emission when the hole in the 3d shell has been produced by X-ray absorption: this is the fluorescence-excitation method. In the experiment called electron energy loss spectra EELS, it is the loss of energy of a single energy beam of electrons. These experiments give the electron absorption spectra. We shall discuss these three kinds of spectra.

The advantage of the study of these transitions in the case of the rare earths is that the energy levels corresponding to the two subshells $3d_{3/2}$ (levels M_4) and $3d_{5/2}$ (levels M_5) are well separated. As a result the structures of these two spectra corresponding to the 4f shell are easily recognized.

4-1 Experimental results on lanthanum

Let us then consider the spectra obtained with lanthanum metal or La_2O_3 oxide. Each main emission line is found in coincidence with each absorption line so they are called resonance lines R [35,36], (figures 3, 4, 5 and table 2). In these two works, in addition to the R lines, the authors have observed some structures located with an energy below the R lines. Let us call them Re lines as in the paper of Motais, Belin, Bonnelle [36]. In M_4 or M_5 the Re and R lines appear as a doublet.

Working with near-threshold-energy incident electrons Liefeld, Burr and Chamberlain [37,38] have shown very interesting properties of the Re lines which they call resonant bremsstrahlung lines RBL, (figure 6). When the excitation energy E_p is increased one step at a time by one electron volt from 833.3eV to 840.3, this structure in the M_5 region exhibits a strong intensity enhancement for $E_p = 837.3$ eV. For this value the M_5 Re line is found at 832 ± 1 eV. Simultaneously the intensity of photon energy of the characteristic lines: M_α also called M_5R , close to 835 eV; M_5O_3 that is the transition $3d^5_{5/2}5p^4_{3/2} \rightarrow 3d^6_{5/2}5p^3_{3/2}$ close to 821 eV and M_5N_3 that is the transition $3d^5_{5/2}4p^4_{3/2} \rightarrow 3d^6_{5/2}4p^3_{3/2}$ close to 628eV, also exhibit a strong enhancement [28]. The simultaneous resonance of these different lines clearly establishes that the phenomena involve the resonant formation of holes on the 3d shell.

Another important property of the Re lines, their RBL lines, is the fact that the position of the maximum moves with the energy of the incident electrons when their energies are lower than 837.5 eV. The position of the peak of this structure is alway about 5.5 eV less than the energy of the incident electron figure 6. The authors also show that for about 5.5 eV from the high-energy limit of a continuous spectrum for incident electrons of 66O eV, a linelike spike appears, figure 7. Similar results are also observed for continuous isochromat at 528 eV, figure 8.

These last results are interesting because they suggest that the M_5Re line can have in part the same origin [37,42]. People know that the linelike spike from continuous isochromat or continuous spectrum

Table 2 - Energy in eV of the Re and R lines making a doublet in the M_5 region of the 3d$\rightleftharpoons$4f spectra of the lanthanum metal and oxide. The energies are given by the authors or evaluated from their spectra.

Compounds	Methods	Re	R
La	XES		835 [a]
	XAS		835 [a]
	XES	832[b]	835 [b]
	XAS	830.6[c]	834.0 [c]
La_2O_3	XES	832[d]	834.9 [d]
La_2O_3	XAS		834.9 [d]
La	EELS	831.3[e]	834.9 [e]
La	EELS	831.7[f]	834.5 [f]
La_2O_3	EELS	831.7[f]	834.5 [f]

[a] ref. 35, [b] ref. 37 and 38, [c] ref. 39, [d] ref. 36,
[e] ref. 40, [f] ref. 41.

are the scanning of the density of states close to the Fermi level [37,42] thus this structure : the ReM_5 lines have to be attributed to empty 4f states.

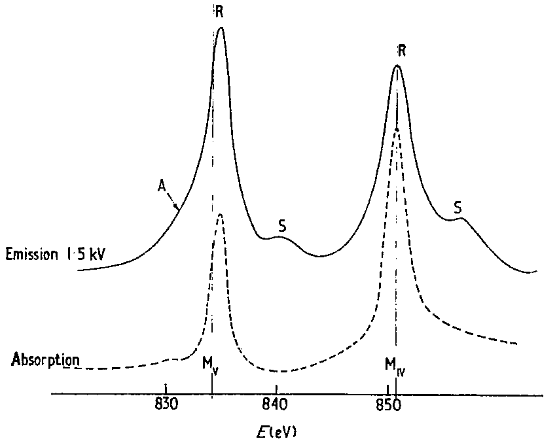

Figure 3. Lanthanum M_4 and M_5 emission and absorption spectra Mariot and Karnatak 1974. Ref. 35.

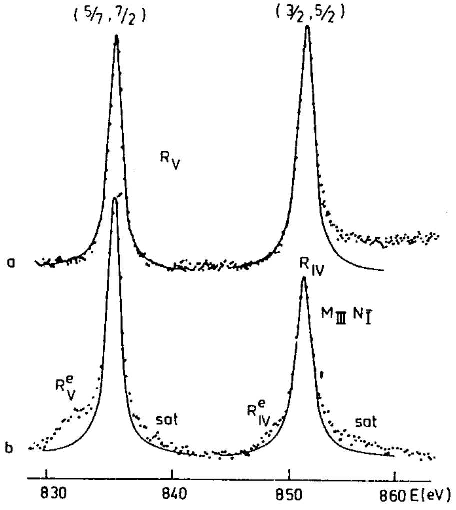

Figure 4. La 3d in La_2O_3, (a) photoabsorption ; (b) emission at 1.2 keV. Dots denote data, solid line denotes Lorentzian curve. Motais, Belin and Bonnelle, 1984. Ref. 36.

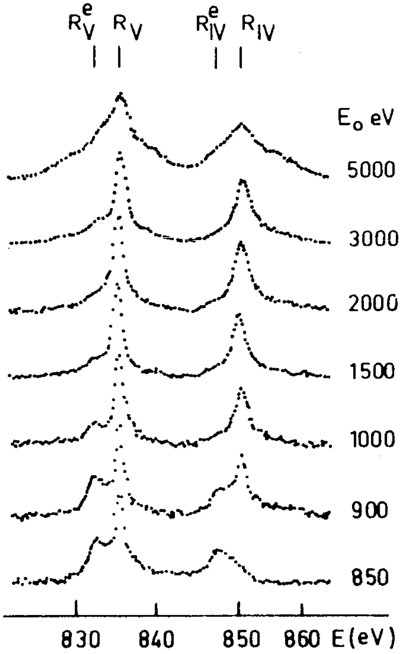

Figure 5. La 3d emissions in La_2O_3 observed for various incident electron energies E_0. Motais, Belin and Bonnelle, 1984. Ref. 36.

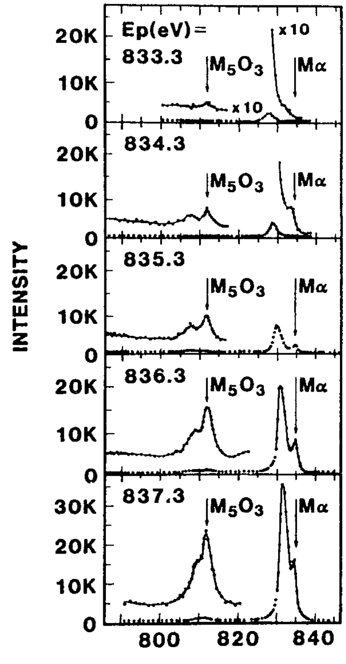

Figure 6. X-ray spectra of La recorded with electron excitation energies spaced at 1 eV intervals. These show the M_α and M_5O_3 characteristic lines near threshold (×10 curves), the intensity enhancements in these lines near the threshold at 833.3 eV, and the resonance at $E_p = 837.3$ eV in the resonant bremsstrahlung line, which is the most intense line in the 837.3 eV spectrum. The dwell time for recording each data point was 100 s. Chamberlain, Burr and Liefeld, 1984. Ref. 38

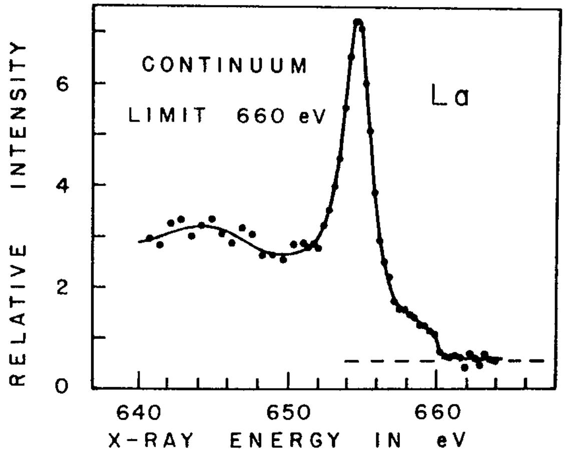

Figure 7. A continuous spectrum from lanthanum for incident electrons of 660 eV ; Liefeld, Burr and Chamberlain, 1974. Ref. 37.

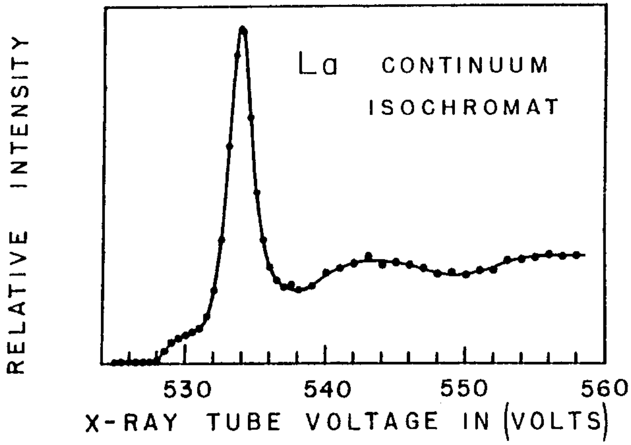

Figure 8. A continuous spectrum isochromat from lanthanum at 528 eV ; Liefeld, Burr and Chamberlain, 1974. Ref. 37.

4-2 The two 4f subshells in Sm, Gd and La spectra

To explain their results on lanthanum, Liefeld, Burr and Chamberlain make the assumption that a 3d electron and the incident electron are temporarily trapped in a 4f state giving the electronic configurations $3d^9 4f^2$. Since, then, these results and this explanation have often been discussed and other explanations have been proposed [40,44]. In our opinion the most important new result is that the structure at 832 eV has also been found in EELS [40,41,45], (table 2) and recognized to have the same origin as the structure of Chamberlain and al. [37,38]. But this last assumption will be better established after the discussion of the case of Sm and Gd. In fact the solution to this problem is like a puzzle and needs the different hypotheses discussed here or used in the calculation of the atomic magnetic moments. These hypotheses are the following :

1) The first 4f electron appears with the lanthanum
2) Lanthanum in a compound where it has the oxidation number (o.n.) three, keeps its 4f electron. As a result the ion has the ionicity 2^+ which is not the valency or the o.n. It can be written La^{2+}_{III}. The same is true for the other rare earths giving Ln^{2+}_{III}.
3) The electronic configuration of the rare earths must be described according to the quantum states of Dirac's model. The important point here is the division of the 4f shell into two subshells : the $4f_{5/2}$ with six quantum states and the $4f_{7/2}$ with eight quantum states. In addition, these two subshells are filled successively, the first being filled is the $4f_{5/2}$ subshell.

Our hypothesis is that the doublet structures of the M_5 *or* M_4 *spectra of lanthanum in its metal or* La_2O_3 *oxide is the reflection of the two subshells* $4f_{5/2}$ *and* $4f_{7/2}$*, and that the R lines correspond to the* $4f_{7/2}$ *subshell and the Re lines to the* $4f_{5/2}$ *subshell.*

The first 4f electron appears with La and belongs to the $4f_{5/2}$ subshell, (table 1). The sixth 4f electron appears with Sm and for this element the electronic configuration is $4f^6_{5/2}\ 4f^0_{7/2}$. The $4f_{5/2}$ subshell is filled up. *As a result for this element and the following, we cannot expect any absorption on this subshell. So the spectra of the rare earths having the* $4f_{5/2}$ *subshell filled up must exhibit some important differences from the others having a* $4f_{5/2}$ *subshell not completely filled.* Indeed for the light rare earths except samarium, the main emission line in both the M_4 and M_5 region is a resonant line, they correspond to a strong absorption line as in the case of lanthanum, (figures 3 and 4). (Ce:Karnatak [46], Pr and Nd, Motais [47]). But with samarium and the heavy rare earths in the M_4 region, the main emission line is not a resonant line: there is no corresponding absorption line. The results for samarium were first published in 1982 by Aita et al. [48] and very recently in 1986 from the same laboratory a new work [49], using the fluorescence-excitation method, has completed the first (figure 9 to 12). The authors of the first paper underline this fact but remark that the reason for this observation is not clear. The energy positions are given in table 3. We also report the case of the gadolinium [50,51,52], where the main line M_β of the emission spectra in the M_4 region is also clearly apart from the absorption lines, figure 13. For the other rare earths the results are given : in [46,52] for Eu, Gd and Dy, in [46] for Yb in [53] for Tb, Ho, Er and Tm.

The presence of a strong resonance line in the M_5 region for all the rare earths and its absence in the M_4 region for the heavy rare earths have been often noticed [46,47,53,54], but never explained. Classically there is no 4f subshell, so people can expect similar resonant lines in both M_4 and M_5 spectra contrary to the experimental results.

Samarium

In their work Aita et al. tried to establish some differences between the spectra of Sm (figure 9) and SmB_6. They did not find any significant difference and to enter deeply in this aspect they also studied Sm_2O_3 (figure 10), SmS and SmSe (figure 11) and no more differences were found. According to the hypothesis (2) that the deep 4f electron contributing to the oxydation number three stays on its atom, there is no difficulty in understanding this first aspect. Samarium and rare earths in general, in any chemical combination always have the same number of 4f electrons.

The second problem is to determine the origin of the structure that they call F and F'. In this view in the second work [49], they use the fluorescence excitation method. In this method the electron in the target material must absorb the whole quantum of energy of the incident photons. So the contribution of photons with the energy of the resonent line in incident continuous radiation is very small relative to the rest of the continuous radiation spectrum. As a result in this method the resonent emission pratically disappears (see figure 9). In fact with photon excitation, the emission spectra just show characteristic lines, that is the transition between occupied state and inner holes. According to the energy of the F peak 1075 eV and that of the F' peak 1102 eV and according to the spin orbit splitting of the 3d shell which is of the order of 27eV (from Bearden and Burr [55] this splitting is 25.8 eV ; from $\alpha_1 L_3 M_4$ and $\alpha_2 L_3 M_5$ it is of 27.7eV [56]), these two lines must be attributed to 4f→3d transitions. Similar results and interpretations will be recalled with gadolinium.

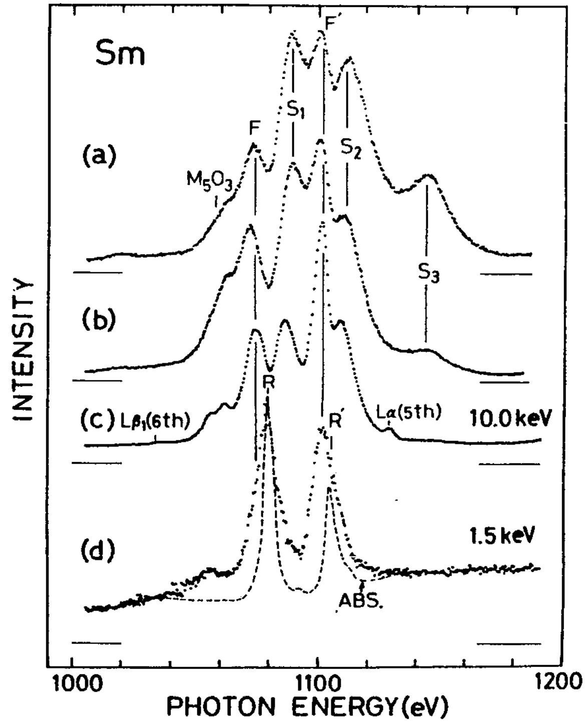

Figure 9. Sm $M_{4,5}$ emission spectra of Sm metal. The spectra (a) and (b) are the fluorescent spectra obtained by the irradiation of the primary X rays through a thin film of Sm metal and by the direct irradiation of the primary X-ray, respectively. The spectra (c) and (d) are the electron-excited spectra obtained with the electron-beam energies of 10.0 and 1.5 keV, respectively. The absorption spectrum measured previously (Ref. 48) is also shown by a dashed line. Aita, Ichikawa, Okusawa, Tsutsumi, 1986. Ref. 49.

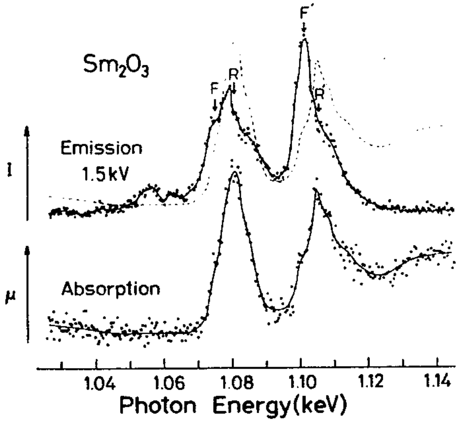

Figure 10. Sm $M_{4,5}$ emission and absorption spectra obtained for powder specimens of Sm_2O_3. The emission spectrum was observed with an electron-beam potential of 1.5 kV. Broken line also show the absorption spectrum. Aita, Watanabe, Fujimoto, Tsutsumi, 1982. Ref. 48.

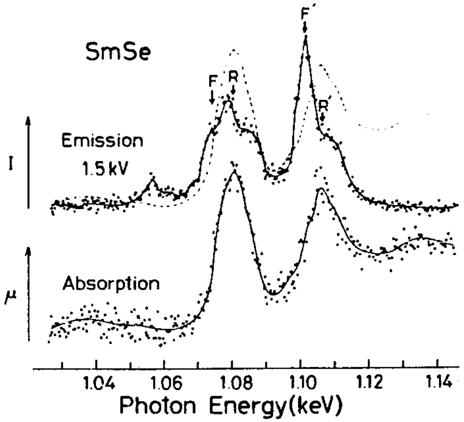

Figure 11. Sm $M_{4,5}$ emission and absorption spectra obtained for powder specimens of SmSe. The emission spectrum was observed with an electron-beam potential of 1.5 kV. Broken lines also show the absorption spectrum. Aita, Watanabe, Fujimoto, Tsutsumi, 1982. Ref. 48.

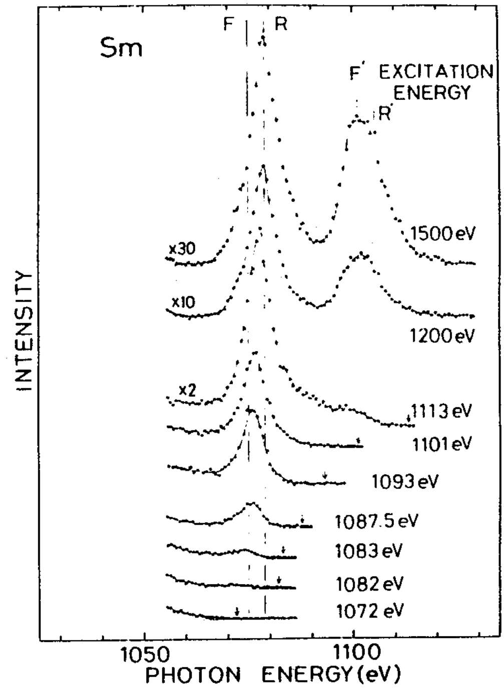

Figure 12. Sm $M_{4,5}$ emission spectra of Sm metal obtained with various electron-beam energies. Aita, Ichikawa, Okusawa, Tsutsumi, 1986. Ref. 49.

Table 3. Energies in eV of the Re and R lines of the $3d \rightleftharpoons 4f$ spectra of samarium metal, references 48,49.

	M_5		M_4	
	F $\simeq$Re	R	F'$\simeq$ Re	R'
XES	1075	1079	1102	
XAS		1079		1105

We explain the F $\simeq$ Re_5 and F' $\simeq$ Re_4 lines of the emission spectra by the following transitions :

$$3d^5_{5/2}4f^6_{5/2} \rightarrow 3d^6_{5/2}4f^5_{5/2} \qquad \text{F}$$

$$3d^3_{3/2}4f^6_{5/2} \rightarrow 3d^4_{3/2}4f^5_{5/2} \qquad \text{F'}$$

As a result of the electronic configuration of Sm $4f^6_{5/2}\ 4f^0_{7/2}$, there is no corresponding absorption line. We explain the R and R' lines by the following transitions :

$$3d^5_{5/2}4f^1_{7/2} \rightarrow 3d^6_{5/2}4f^0_{7/2} \qquad \text{R}$$
$$3d^3_{3/2}4f^1_{7/2} \rightarrow 3d^4_{3/2}4f^0_{7/2} \qquad \text{R'}$$

and the reverse transitions explain the absorption R and R' lines. In their paper of 1986, Aita et al.[49] also study the samarium metal with near-threshold energy incident electrons (figure 12) and obtain different results from those of Chamberlain et al. on lanthanum metal (figure 6). They do not observe the doublet structure in the M_5 region, and there is no similar intensity enhancement. This observation can be easily explained from the configuration $4f^6_{5/2}\ 4f^0_{7/2}$ and the above interpretation of the F and R lines.

1) There is no absorption corresponding to the F line as a result of the full $4f_{5/2}$ subshell.
2) To observe an F emission there must be a hole on the 3d shell. This need and excitation on the $4f_{7/2}$ subshell and incident electrons with energy higher than the corresponding threshold that is 1082 eV.
3) As soon as we have such incident electrons, F and R lines appear simultaneously and we observe just one wide line as one can see on figure 12.

Gadolinium

With the electronic configuration $4f^6_{5/2}\ 4f^2_{7/2}$ for the 4f shell the spectra of the gadolinium (figure 13) are explained in the same way. The case of the gadolinium is very interesting because in addition to the X-ray emission and absorption spectra, we also know the fluorescence spectra [57] of Gd_2O_3, (figure 14) which gives similar results to that obtained with samarium and also the electron energy loss spectra EELS [41] figure 15. The energies are given in table 4. As we have already noticed, EELS give the electron absorption spectra , whereas those called absorption spectra as in figures 3, 4 and 13 for example are obtained by X-ray absorption. As a result we can easily verify from the comparison of the figures 13 and 15 that there is no EELS peak corresponding to the M_β and the M_α lines of the X-ray emission spectra. This last point is very interesting because it first supports that M_α and M_β are lines from

Table 4. Energies in eV of the Re and R lines of the 3d $\rightleftharpoons$ 4f spectra of gadolinium. The energies are given by the authors or evaluated from their spectra.

		M_5		M_4	
Compounds	Methods	Re $\simeq M_\alpha$	R	Re $\simeq M_\beta$	R
Gd	EELS		1182 ; 1184		1212.8 ; 1214.9
Gd	XAS		1183.8		1212.9 ; 1214.6
Gd	XES	1178.8	1184.1	1210	
Gd_2O_3	XAS		1183.7		1212.9 ; 1214.7
Gd_2O_3	XES	1178.8	1184.1	1208.8	
Gd_2O_3	Fluorescence	1178		1209	

for : XAS and XES ref. 47, EELS ref. 41, fluorescence ref. 57.

the filled subshell $4f^6_{5/2}$ and moreover it brings additional support to the interpretation of the lanthanum spectra.

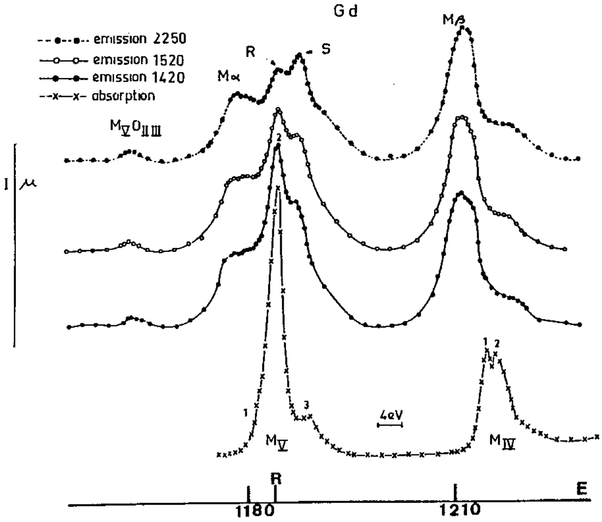

Figure 13. $M_{4,5}$. Emission and absorption spectra from Gd metal. Relative intensity I and absorption μ in arbitrary unit the energy in electron Volt eV. Bonnelle and Karnatak, ref. [50, 52].

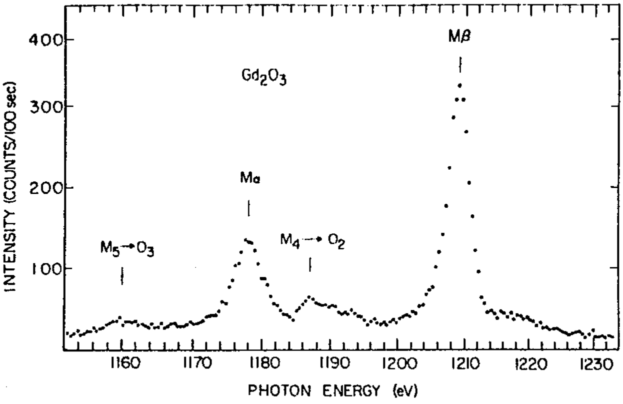

Figure 14. $M_{4,5}$ emission spectrum from Gd_2O_3 obtained in fluorescence. La Villa , 1974. Ref. 57.

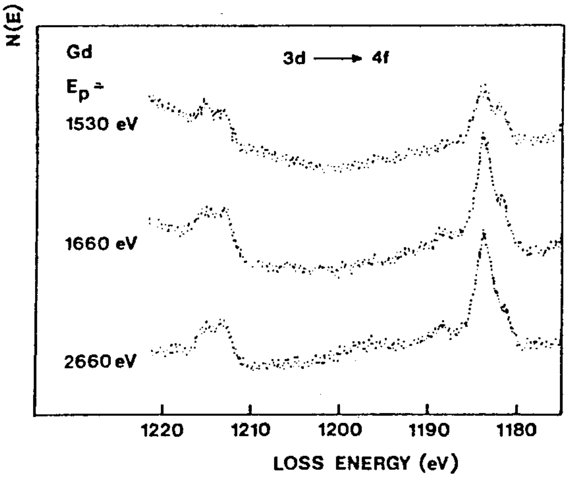

Figure 15. Electron-energy-loss spectra of 3d→4f excitations in Gd for various primary energies. Matthew, Strasser and Netzer, 1983. Ref. 41.

Lanthanum

We have to complete the interpretation of the lanthanum spectra. For this it is interesting to recall that the doublet structure of the M_4 and M_5 spectra is also observed by electron energy loss [30, 31], (figures 16 and 17). The energies of the two peaks are very close to those observed by X-ray emission (table 2). Furthermore there is a redistribution of the relative intensities of these peaks with the changing of the primary energy, and this redistribution goes in the same way as that observed by X-ray emission. This can be seen to comparison for example of figure 5 obtained with La_2O_3 [36], with figures 16 and 17.

According to the case of gadolinium, we can assume that the EELS peak on the low energy side of spectra M_4 and M_5 corresponds to the transition:

$$3d^4_{3/2}4f^1_{5/2} \rightarrow 3d^3_{3/2}4f^2_{5/2} \qquad \text{Re } M_4$$

$$3d^6_{5/2}4f^1_{5/2} \rightarrow 3d^5_{5/2}4f^2_{5/2} \qquad \text{Re } M_5$$

and the reverse transitions explain the Re lines of the X-ray emission spectra, at least in part. Additional points will be discussed in the following section 4,3.

The R lines in the X-ray emission spectra which correspond to the peak of the high energy side of the EELS are explained by the following transitions :

$$3d^3_{3/2}4f^1_{7/2} \rightarrow 3d^4_{3/2}4f^0_{7/2} \qquad \text{R } M_4$$

$$3d^5_{5/2}4f^1_{7/2} \rightarrow 3d^6_{5/2}4f^0_{7/2} \qquad \text{R } M_5$$

The reverse transition explains the corresponding XAS or EELS lines.

4-3 Further discussion

One important difficulty to understand the Re lines is that their maxima shift with the energy E_p of the incident electrons when it is lower than 837.5 eV ([37,38] and figure 6). Nevertheless when E is higher than 837.5 eV this structure keeps a stable position. This fact clearly indicates a common property with the R lines. In our opinion, the fact that the position of the maximum shifts for low excitation energies must be attributed to the presence in the ground state of one electron on the $4f_{5/2}$ subshell. On the contrary, the stable position of the R lines is a result of the empty $4f_{7/2}$ subshell. This is a different explanation from that of Chamberlain, Burr and Liefeld who propose an “emission from the two electron state $3d^9$ $4f^2$ temporarily bound to the 3d vacancy”. Without other possibilities such an explanation was interesting even if the probabilities of such a configuration can seem very small. The interpretation based on the two 4f subshells allows in a more natural approach a better understanding first of these Re lines but also of several other experimental results: the doublet structure of EELS spectra of La and Ba and the absence of some absorption lines that we have discussed in this work like in the case of Sm and Gd, but also the calculation of the magnetic moment of the rare earth metals.

Finally let us consider other results. Motais, Belin and Bonnelle [36], in their work on La_2O_3 and LaF_3 also used the hypothesis of Liefeld et al. to explain the Re line. But there is a counter experience which makes this interpretation difficult to keep. With such an explanation in similar conditions one can expect to observe the Re lines with compounds like BaO or CsCl. The 3d $\rightleftharpoons$ 4f transition has been studied in BaO by Karnatak and Motais [47, 58], (figure 18); in CsCl by Motais, Belin and Bonnelle [59]; but according to their result the R lines are well observed but not the Re lines.

One would like to object that according to the interpretation based on the two subshells we must also observe the Re line with BaO and CsCl. We think that it is not so evident. If the doublet structures is the reflection of the two 4f subshells, the separation decreases with the atomic number. The work of Kansi and Wendin [40] gives the energy loss spectra for: Ba, figure 19, La and Ce, figure 16. The respective M_5 doublet separation from these spectra are 1.6eV, 3.1eV and 3.8eV.

Furthermore in the classical understanding we have the following Cs^{1+}, Ba^{2+} and La^{3+} ions. In our interpretation we have Cs^{1+}, Ba^{2+} but La^{2+}_{III}, and we can expect that the presence of one 4f electron on $4f_{5/2}$ modified the spectra of La, La_2O_3 and LaF_3 in comparison to the case of CsCl or BaO. So we attribute the difference between the spectra of La, LaF_3 or La_2O_3 and BaO or CsCl to the presence of one 4f electron on lanthanum, as we have already proposed [60] and to the small separation of the doublets in the case of Ba and Cs. Now if we consider the EELS figure 19, for Ba the doublet structure is well observed. The Re line that is the peak on the low energy side of M_5, the transition $3d^6_{5/2}4f^0_{5/2} \rightarrow 3d^5_{5/2}4f^1_{5/2}$, is present. It would be very interesting to make experiments with Ba0 or Ba similar to that of Chamberlain, Burr and Liefeld [37, 38]. They must bring new results on this very interesting question.

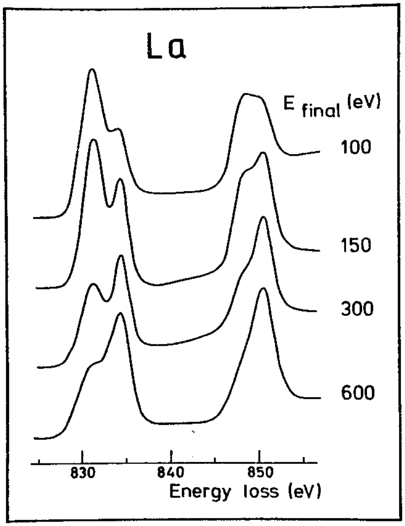

Figure 16. Electron-energy-loss spectra of lanthanum. Kanski and Wendin, 1981. Ref. 45.

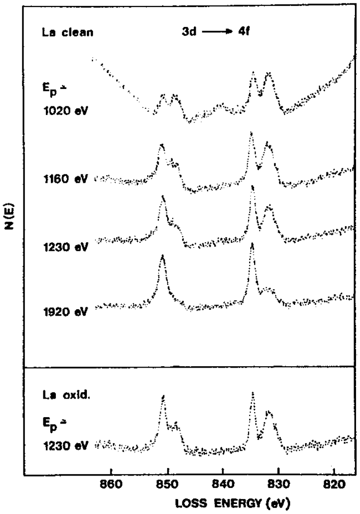

Figure 17. 4d→4f electron-energy-loss spectra of La as a function of primary E_P. A spectrum of oxidized La is also included for comparison (bottom curve). Matthew, Strasser and Netzer, 1983. Ref. 41.

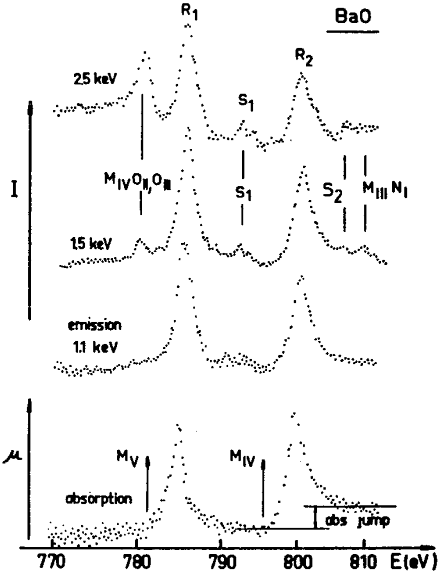

Figure 18. 3d X-ray emission absorption spectra of BaO. Karnatak and Motais 1978. Ref. 58.

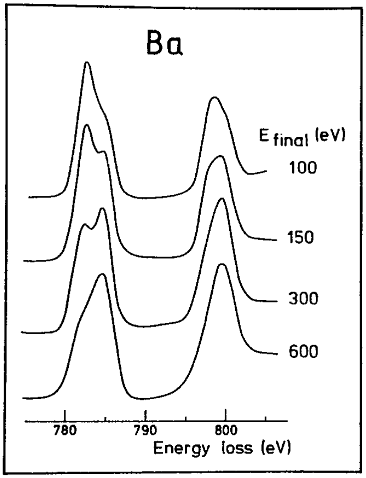

Figure 19. Electron-energy-loss spectra of barium covering the region of 3d level excitations. Kanski and Wendin, 1981. Ref. 45.

5 - CONCLUSION

Starting with the comparison of some properties of lanthanum with those of its neighbouring elements in the periodic table we have proposed, as have several other people, the hypothesis of one 4f electron for the lanthanum. With the study of Dirac's model we are able to interpret the 3d $\rightleftharpoons$ 4f spectra of the rare earth element and to confirm first, the division of the 4f shell into two subshells and secondly, the presence of one additional 4f electron for all the rare earths including lanthanum. These results with those on magnetism open the way to new research. One important aspect to study, in our opinion, is the nature of the metallic bond giving the notion of a band. According to the intensity of the metallic bond several properties can be modified and a better understanding of this point will certainly clarify the notion of valency. There are certainly many interesting things to find in this manner and we hope to be able to do so in the near future.

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(Manuscrit reçu le 10 février 1989)