LOCAL ENVIRONMENT IN AMORPHOUS Ce BASE ALLOYS THROUGH EXAFS MEASUREMENTS
D. Malterre, G. Krill, J. Durand, G. Marchal

To cite this version:
D. Malterre, G. Krill, J. Durand, G. Marchal. LOCAL ENVIRONMENT IN AMORPHOUS Ce BASE ALLOYS THROUGH EXAFS MEASUREMENTS. Journal de Physique Colloques, 1985, 46 (C8), pp.C8-199-C8-203. <10.1051/jphyscol:1985828>. <jpa-00225171>
LOCAL ENVIRONMENT IN AMORPHOUS Ce BASE ALLOYS THROUGH EXAFS MEASUREMENTS

D. Malterre, G. Krill, J. Durand and G. Marchal

Laboratoire de Physique du Solide, (U.A. au C.N.R.S. N° 165), Université de Nancy I, B.P. 239, 54506 Vandoeuvre lès Nancy Cedex, France

Résumé - Des mesures EXAFS sur les seuils L_{III} du cérium et les seuils K des métaux de transition ont été effectuées dans les alliages amorphes Ce Si_{2}, Ce Co_{5} et Ce Ni_{5} qui présentent dans l'état cristallin un comportement valence intermédiaire. Alors que dans l'alliage amorphe Ce Si_{2} l'état trivalent du cérium est stabilisé, la valence intermédiaire est conservée dans les alliages amorphes Ce Co_{5} et Ce Ni_{5}. Les mesures EXAFS montrent que dans Ce Si_{2} amorphe l'environnement local autour des ions cérium est préservé alors qu'aucune oscillation EXAFS n'est observable après le seuil L_{III} du cérium dans le cas de Ce Co_{5} et Ce Ni_{5} amorphes. La question est de savoir si le désordre autour des ions de cérium est dû uniquement à un terme statique ou si le caractère valence intermédiaire joue un rôle dans la très forte réduction du signal EXAFS.

Abstract - EXAFS measurements have been performed on the L_{III} edges of cerium and K edges of transition metals in amorphous Ce Si_{2}, Ce Co_{5} and Ce Ni_{5} which present in their crystalline counterparts a mixed-valent ground state. Whereas in amorphous Ce Si_{2} the trivalent state of cerium is stabilized, the mixed-valent ground state is preserved in Ce Co_{5} and Ce Ni_{5}. EXAFS measurements show that in amorphous Ce Si_{2}, the local environment is roughly preserved around cerium ions and in amorphous Ce Co_{5} and Ce Ni_{5} no EXAFS signature is observed after the L_{III} edge of cerium. The open question is to know if the disorder around the cerium ions is due only to static term or if the mixed-valent character play a role in the damping of the EXAFS signal.

I - INTRODUCTION

In the last few years cerium compounds have been extensively studied because of their particular properties related to the existence of an unstable 4f shell /1, 2/, which yields to mixed-valent ground state properties. One open question in the physics of mixed-valent materials is to know the possible influence of local disorder on the mixed-valent ground state. Indeed if we know that long range is not necessary to produce a mixed-valent ground state /3/ we cannot ascertain if such ground state can survive to a strong local disorder. This is the aim of this paper to discuss this point.

X-ray absorption technic is a powerful tool for such investigation because both instantaneous electronic configuration of the rare earth ions and their local environment may be deduced from the near edge region (XANES) and the extended one (EXAFS).

The Ce_{x} Si_{1-x} and Ce_{x} TM_{1-x} (TM = Co, Ni,...) systems are good candidates for our study because, in the crystalline state, several compounds present this mixed-valent ground state (eg. Ce Si_{2}, Ce Co_{5}, Ce Co_{2}, Ce Ni_{5}). Moreover these systems exist on a wide range of concentration in the amorphous state /4/. We shall mainly focus in this paper on the problem of local environment effects studied through EXAFS experiments. We shall use without discussion the results we previously obtain on the electronic configuration of cerium from L_{III} edge experiments /5/.

II - EXPERIMENTAL

Amorphous samples were obtained by co-evaporation onto liquid nitrogen cooled substrates under UHV conditions. The amorphous state of the sample has been checked by...
electron diffraction. The crystalline compounds studied here are the same as those used for previous XAS studies /6/. The X-ray absorption experiments have been performed using the beam delivered by the DCI storage ring at L. U. R. E. (Orsay, France) operating at 1.72 GeV and 200 mA on the EXAFS II station.

III - EXPERIMENTAL RESULTS

1 - The Ce$_x$ Si$_{1-x}$ alloys

Crystalline Ce Si$_2$ presents the typical properties of Ce- a compounds (i. e. absence of magnetization at low temperature...). From L$_{III}$ experiments a weak mixed character can be deduced $\bar{V} = 3.08 \pm 0.02$/7/. On the contrary, the amorphous counterpart Ce$_{0.33}$Si$_{0.67}$ presents the normal behaviour of a pure trivalent compound. This is well demonstrated with magnetic measurements and L$_{III}$ experiments /5/. On fig. 1 we report the radial distribution function (RDF) obtained by a Fourier analysis of the 77 K EXAFS data after the cerium L$_{III}$ edge both in c-Ce Si$_2$ and a-Ce$_{0.33}$ Si$_{0.67}$. We can notice the attenuation of the first peak in the amorphous alloy as compared to the crystalline one. The higher order peaks associated to higher shell are completely damped in the amorphous state.

![Fig. 1 - Radial distribution function around cerium in a-Ce Si$_2$ and c-Ce Si$_2$ (T = 77 K)](image_url)

<table>
<thead>
<tr>
<th></th>
<th>N atoms</th>
<th>$R$ (Å)</th>
<th>N atoms</th>
<th>$R$ (Å)</th>
<th>$\sigma_{DW}$ (Å)</th>
<th>$\sigma_{DYS}$ (Å)</th>
<th>Nature of the edge</th>
</tr>
</thead>
<tbody>
<tr>
<td>c.CeSi$_2$</td>
<td>4 Si</td>
<td>3.16</td>
<td>8 Si</td>
<td>3.19</td>
<td>0.06</td>
<td>0.06</td>
<td>L$_{III}$ of Cerium</td>
</tr>
<tr>
<td>a.CeSi$_2$</td>
<td>12 Si</td>
<td>3.16</td>
<td>-</td>
<td>-</td>
<td>0.06</td>
<td>0.25</td>
<td>L$_{III}$ of Cerium</td>
</tr>
<tr>
<td>c.CeCo$_5$</td>
<td>6 Co</td>
<td>2.81</td>
<td>12 Co</td>
<td>3.2</td>
<td>0.08</td>
<td>-</td>
<td>L$_{III}$ of Cerium</td>
</tr>
<tr>
<td>c.CeCo$_5$</td>
<td>8 Co</td>
<td>2.44</td>
<td>-</td>
<td>-</td>
<td>0.07</td>
<td>-</td>
<td>K of Cobalt</td>
</tr>
<tr>
<td>a.CeCo$_5$</td>
<td>8 Co</td>
<td>2.44</td>
<td>-</td>
<td>-</td>
<td>0.07</td>
<td>0.06</td>
<td>K of Cobalt</td>
</tr>
</tbody>
</table>

Table I - Summary of EXAFS results
The main peak in the RDF associated to first Si neighbors has been Fourier filtered and backtransformed in k space. These filtered data have been adjusted using the general EXAFS formula. The fits to the data are shown on fig. 2 a and 2 b. The results are summarized in table I.

Fig. 2 - a) Adjustment of the first shell contribution (Ce-Si) in c-CeSi₂
b) idem for a-CeSi₂
(the continuum line is the result of the fit).

From our adjustments it appears that in the case of a-Ce₀.₃₃Si₀.₆₇, it is necessary to introduce a static disorder term q₀ (i.e. the third moment in the RDF) which is quite comparable to that used for other amorphous alloys /11/. In the accuracy limit of our experiments it seems that the local environment of cerium ions in the amorphous alloys is identical to that of crystalline CeSi₂.

2 - The CeₓCo₁₋ₓ and CeₓNi₁₋ₓ alloys

In the cerium low concentration region (x ≤ 0.2) the crystalline compounds (CeCo₅, CeNi₅) present physical properties which have been interpreted for a long time as "direct" evidence for the absence of 4 f character in their electronic configurations (i.e. a "pure" tetravalent 4 f⁰ ground state). Recently XAS experiments have shown on the contrary that the ground state of such compounds in strongly mixed valent (V = 3.3)/6, 8/. This may be interpreted by a strong hybridization between the 4 f and the conduction electrons /9/. For our purpose the interesting point is that there is no difference between the electronic configuration of cerium in the amorphous and the crystalline states /5/. The LIII absorption edges of cerium are identical in c-CeCo₅ and a-Ce₀.₁₇Co₀.₈₃ (c-CeNi₅ and a-Ce₀.₁₇Ni₀.₈₃). Let us now consider the EXAFS results:

i) even at low temperature (down to 4.2 K) it is impossible to extract any EXAFS signature after the LIII edge of cerium in the amorphous state. It means that the static disorder is so huge that the EXAFS oscillations are completely damped. This is true both for a-Ce₀.₁₇Co₀.₈₃ and a-Ce₀.₁₇Ni₀.₈₃. In previous study performed on RE alloys, it has been shown that the static disorder term (q₀) around the RE ions never exceeds 0.3 Å /11/. It seems that in the present case this static disorder is much higher,

ii) after the K edges of cobalt or nickel, the EXAFS oscillations are clearly observed. On fig. 3 we report the RDF obtained for CeCo₅ and a-Ce₀.₁₇Co₀.₈₃; the attenuation in the first peak intensity still exists for the amorphous alloy but it is less important than in the case discussed in section III-1.
It is important to precise that in the Ce Co₅ structure the cobalt atoms are only surrounded by cobalt, i.e. the local environment of cobalt is insensible to the presence of cerium (at least in the first shell). This point is well illustrated on fig. 4 a and 4 b. Both in c- Ce Co₅ and a- Ce₀.₁₇ Co₀.₈₃ good fits to the data are obtained using the crystallographic data. In the case of the amorphous alloys it is however necessary to introduce a small σ₀ value (see table I). Let us precise that similar results are obtained for the a- Ce₀.₁₇ Ni₀.₈₃.

Fig. 4 - a) Adjustment of the first shell contribution (Co-Co) in c- Ce Co₅
b) idem for a- Ce Co₅
(the continuum line is the result of the fit).
These preliminary results confirm once more that the local environment of the ions is quite identical both in the amorphous and the crystalline state. Concerning the problem of mixed-valent properties versus local disorder, the answer is not easy; however several comments can be made.

It seems on first sight that the existence of local disorder cannot be directly related to the existence of a mixed-valent ground state. Indeed the mixed-valent state of CeSi₂ is suppressed in the amorphous state whereas it survives in a-CeNi₅ and a-CeCo₅ when the static disorder appears to be more important as indicated by the EXAFS experiments performed above the cerium L₃ edges.

Nevertheless we must underline that in the CeₓMₓ₋ₓ systems the static disorder around the transition ions is quite small; therefore before any definite conclusion it is necessary to investigate the hypothesis that the disorder around the cerium ions in the amorphous alloys may be due to the mixed-valent character of the cerium ions. Usually, in crystalline homogeneous mixed-valent materials, the atomic relaxation around the RE ions is very small (≲ 0.04 Å) and does not contribute significantly to the disorder factor /10/. However it is well established that atomic relaxations are very sensitive to the elastic properties and thus such conclusion may not be correct for amorphous mixed-valent compounds. We think that EXAFS experiments should be done at higher cerium concentration in these systems when the valence of cerium goes down to the trivalent state, in order to clarify this point.

Acknowledgment - We want to acknowledge the collaboration of M. F. Ravet during this work.

REFERENCES

/1/ Proceedings of the International Conference on Valence Instabilities, Wachter, F., Boppard, H. Editors (Zurich, North Holland, 1982)
/5/ Malterre, D., Krill, G., Ravet, M. F., Durand, J. and Marchal, G., to be published
/7/ Krill, G. and Kappler, J. P., unpublished results