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PuGa alloys: an X-ray absorption study

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Abstract

A structural study on several PuGa alloys in the δ-phase (fcc structure) by EXAFS is reported. Low temperature measurements (80 K) allowed us to obtain information up to the third coordination shell for which multiple scattering had to be taken into account. The local collapse around Ga atoms is confirmed. The short-range order around Ga atoms is close to an fcc arrangement whatever the Ga content, whereas the strong disorder around Pu atoms increases with Ga content. © 1998 Elsevier Science S.A.

Keywords: PuGa alloys; EXAFS; X-Ray absorption

1. Introduction

Plutonium metal can take six different phases between ambient temperature and its melting point (640°C). Among these, the δ-phase (fcc structure), stable from 320 to 485°C, can be maintained at room temperature by alloying with a so-called ''deltagen'' element such as Ga, Al, Ce, Am... The stabilizing mechanisms induced by such additions are however still not well understood. X-Ray absorption fine structure spectroscopy (EXAFS) was then investigated in order to study the local environment around Ga and Pu: interatomic distances, neighboring atoms numbers and disorder. First results, published by Cox et al. on PuGa 3.3 at%, showed a contraction around Ga atoms [1]. EXAFS measurements performed later at 300 K on different PuGa alloys led to the same result [2]. Here, measurements were recorded at 80 K, in order to get information about the higher coordination shells, and to follow their evolution with Ga content.

2. Experimental details

PuGa alloys were elaborated with a Ga content ranging from 1.89 to 10.43 at%. Arc-furnace cast massive samples were laminated (thickness of about 10 μm), and the metallic structure of the strips was restored by a thermal treatment (20 h at 450°C); the oxides present at the surface were removed by electropolishing. X-Ray patterns were recorded in order to verify that the δ-phase existed as a single phase, and to determine the unit cell parameter.

EXAFS measurements were performed at the LURE (France) radiation synchrotron facility (DCI storage ring running at 1.85 GeV with a current of 300 mA). Spectra were recorded at the Pu LIII-edge (18 057 eV) and at the Ga K-edge (10 367 eV) in the transmission mode. The refinement was achieved using the FEFF6 code [3], which was previously validated on a reference sample with a known structure: the definite compound Pu_3Ga [4].

3. Results

For the spectra recorded at 300 K, the information was limited to the first coordination shell around Ga and Pu [2]. Reducing the thermal damping by working at low temperature (80 K) allowed us to obtain information about the higher coordination shells (second and third shells) at both the Ga and Pu edges.

For highly symmetrical structures, the possibility of multiple scattering becomes important; if not taken into account, this phenomenon can lead to erroneous interatomic distances, *R*, and neighboring numbers, *N*. The amplitude of the multiple scattering was evaluated with the FEFF6 code (structure of Pu-δ for the Pu LIII-edge, and a hypothetical cubic structure based on Ga exclusively surrounded by Pu atoms for Ga K-edge), and this showed that this phenomenon had to be taken into account to refine the third peak (R3) of the radial distribution function (Fig. 1).

In this paper, results from the refinements of the first

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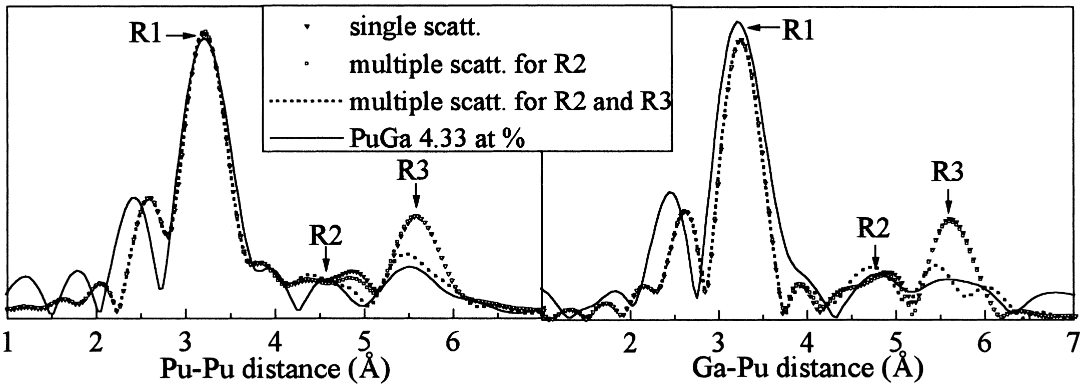

Fig. 1. Influence of the multiple scattering at the Pu LIII-edge (left) and the Ga K-edge (right). The Debye–Waller temperature used in the calculation was set to 132 K according to Lawson et al. [5].

(R1) and the second (R2) coordination shells are presented, assuming single scattering.

R1 distances refined at both the Ga and Pu edges, at 80 K, were similar to those previously obtained at 300 K and the lattice collapse around Ga atoms was confirmed (Fig. 2). Furthermore, the cell parameter *a* deduced from X-ray diffraction (XRD) allowed us to calculate the corresponding first neighbor distances. The interatomic distances refined from EXAFS at the Ga K-edge were noted $R1_{Ga}$(EXAFS) and $R2_{Ga}$(EXAFS), and the relative contraction in Ga–Pu distances was then expressed as:

$$\frac{\Delta R1}{R1} = \frac{R1_{Ga}(EXAFS) - R1(XRD)}{R1(XRD)},$$

$\Delta R1/R1$ was more representative than $R1_{Ga}$(EXAFS) since the cell parameter *a* changed with Ga content. Fig. 2 shows a decrease in the relative contraction around Ga atoms with Ga content; this can be explained by an increasing correlation between $GaPu_{12}$ clusters as Ga content increases. Furthermore, the relative contraction for R1 and R2 are rather similar, which reveals that the short-range order around Ga atoms is close to an fcc structure whatever the Ga content studied here.

As previously discussed [2], the local lattice contraction around Ga atoms leads to bond length variations around Pu atoms, which depend on its proximity to the Ga atoms. The calculation of R1 and R2 was performed for PuGa 6.25 at% Ga (Ga atoms accommodated in a bcc arrangement with a lattice constant twice that of the original fcc lattice, R1(DRX) = 3.24 Å); the crystallographic structure consisted of two nonequivalent Pu atoms, noted Pu(1) and Pu(2), that corresponded to 80 and 20% of the Pu atoms, respectively. The contraction around Ga atoms was estimated from EXAFS results on PuGa 7 at%; the calculation then gave the following distances around Pu atoms (all distances are expressed in Å):

First shell: 1 Ga + 2 Pu (3.18), 2 Pu (3.24) and 7 Pu (3.30) around Pu(1); 4 Pu (3.30) and 8 Pu (3.24) around

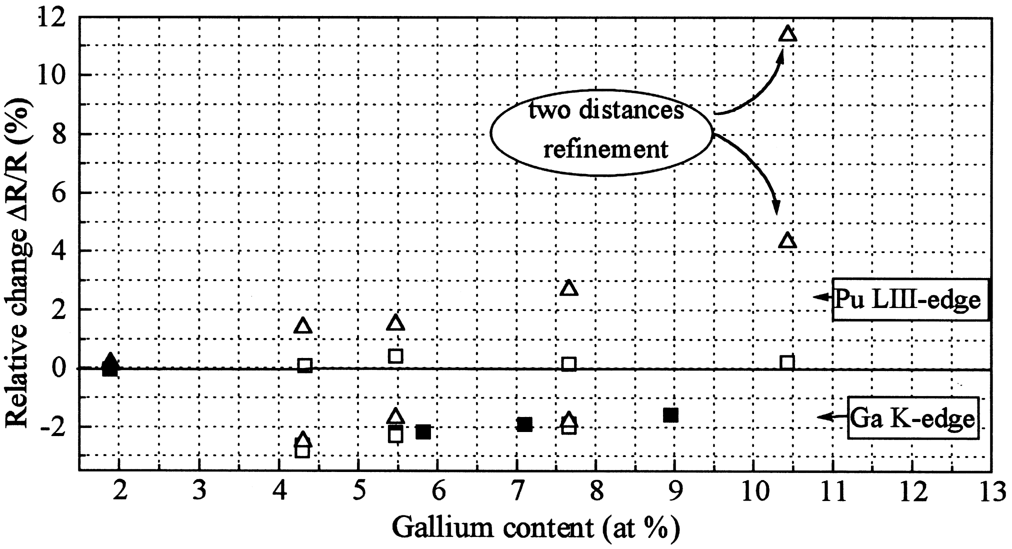

Fig. 2. Relative changes in distances around Ga and Pu atoms, for R1 (■,□) and R2 (▲,△). Measurements at 80 and 300 K are indicated as open symbols (□,△) and solid symbols (■,▲), respectively.

Pu(2), leading to a mean distance $R1_{mean}=3.26$ Å, and $\Delta R1/R1=+0.6\%$.

Second shell: 6 Pu (4.67) around Pu(1); 2 Ga+4 Pu (4.58) around Pu(2), leading to a mean distance $R2_{mean}=4.65$ Å, and $\Delta R2/R2=+1.5\%$.

Ga substitution then appeared to be accompanied by a mean expansion in distances around Pu atoms; this was effectively observed for the different PuGa alloys, for which the higher the Ga content, the higher the expansion (Fig. 2). Moreover, the relative expansion strongly increases from R1 to R2, revealing the strong disorder created by Ga substitution in PuGa alloys; this becomes obvious for the PuGa 10.43 at% for which two distances had to be considered in order to achieve a satisfactory fit of the second coordination shell.

The relative expansion around Pu atoms deduced from the work of Cox et al. [1] was in agreement with our results ($\Delta R1/R1=+0.9\%$ for 3.3 Ga at%) whereas the contraction observed by these authors around Ga atoms decreased from R1 to R2 ($\Delta R1/R1=-3.7\%$ and $\Delta R2/R2=-0.9\%$).

4. Conclusion

EXAFS measurements recorded at 80 K on several PuGa alloys allowed us to follow the changes in the first and second coordination shells versus Ga content. The collapse around Ga atoms was confirmed, revealing the hybridization between Ga $4p^{3/2}$ and Pu $5f^{5/2}$ bands [6]. Moreover, increasing correlations between $GaPu_{12}$ clusters led to a decrease in the relative contraction around Ga atoms, as Ga content increased. For all the alloys studied, the environment around Ga atoms was close to an fcc arrangement, whereas the disorder around Pu atoms increased with Ga content. The study of the evolution in the XANES spectra versus Ga content, at both the Ga K-edge and Pu (L,M)-edges is planned to get more precious information concerning the changes in the electronic configurations of Pu and Ga atoms versus Ga content.

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