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LOCAL STRUCTURE OF AN AMORPHOUS  $\text{Cu}_{24}\text{Zr}_{76}$  BY EXAFS : FROM THE AS-PREPARED ALLOY TO THE FIRST STEPS OF CRYSTALLIZATION EXISTENCE OF FRUSTATION ?

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**Résumé** - Nous rapportons une étude EXAFS de l'alliage  $\text{Cu}_{24}\text{Zr}_{76}$  depuis l'état amorphe jusqu'à l'état cristallisé, où apparaît la phase  $\omega$ -Zr.

**Abstract** - We report an EXAFS study of the  $\text{Cu}_{24}\text{Zr}_{76}$  alloy from the amorphous state to the crystallized state, when the  $\omega$ -Zr phase appears.

### 1 - Introduction

In recent years, a lot of experimental and theoretical work has been done on amorphous alloys in order to understand their physical and mechanical properties. A Cu-Zr amorphous alloy is one example of typical metal-metal amorphous system. Previous EXAFS studies have been carried out on  $\text{Cu}_x\text{-Zr}_{1-x}$  for  $x = 0.60, 0.46, 0.33$  /1, 2/. From this work, a picture of the local order in these very disordered materials can be drawn and also a subshell modelling to interpret it. Moreover, it has become evident that the neighbourhood of a Cu atom is concentration independent in this range of composition ( $0.60 \leq x \leq 0.33$ ).

The present EXAFS study above the Cu and Zr K absorption edges extends to include a zirconium richer composition,  $\text{Cu}_{24}\text{Zr}_{76}$ . For this composition, we report also EXAFS measurements of the amorphous - to - crystalline transition. In  $\text{Cu}_{24}\text{Zr}_{76}$ , the ordering associated with crystallization does not occur homogeneously but begins with heterogeneous nucleation. Two stages in the annealing process are of particular interest. The first step, or structural relaxation, consists of a heat treatment at 200°C. Then, strong modifications occur for several macroscopic properties such as thermal conductivity, specific heat /3/. However, the sample is still fully amorphous. For the second step, at 240-250°C, standard X-ray diffraction shows the presence of a fraction of  $\omega$ -Zr phase surimposed on the pattern of the amorphous matrix. This metastable phase is systematically obtained as the first crystallization stage for these high Zr concentrations /4/. Full crystallization in the form  $\alpha$  Zr + Cu Zr<sub>2</sub> is achieved at 500°C.

For the as-prepared and relaxed samples, the details of the study are given elsewhere /5/ and will be only briefly sketched here.

### 2 - Experimental

Amorphous  $\text{Cu}_{24}\text{Zr}_{76}$  samples have been prepared as thin films by DC magnetron sputtering and the amorphous nature of the samples was ensured by X-ray scanning. Thermal treatments were done first at 200°C in argon for 1h then in ultra high vacuum at 240°C for 24 h.

EXAFS data have been collected above the Cu and Zr K absorption edges at LURE using the DCI ring. The experiments were carried out at 77K so that disorder effects due to thermal Debye Waller factor could be ignored. Then the spectra have been analyzed using standard procedure /5/. Fourier transforms (FT) of the  $k^3\chi(k)$  EXAFS spectra have been achieved using one k-window for all the Cu EXAFS spectra and another one for the Zr EXAFS spectra.

### 3 - Results

FT are compared in Figure 1 for the as-prepared and annealed samples. On the Cu edge, the FT show a single peak at about 2.25 Å (uncorrected for the phase shifts). This first peak represents the first shell of Cu and Zr atoms around a Cu atom. It does not change much with heat treatments, even when the  $\omega$ -Zr phase appears (c).

On the Zr edge, the FT display two peaks for the as-prepared sample (a) and for the sample annealed at 200°C (b). As has been shown previously /2, 5/ the first peak corresponds to the contribution of Cu atoms whereas the second peak corresponds to the contribution of Zr atoms. A third peak appears after heating at 240°C (c). Therefore, the first-shell structure around a Zr atom changes drastically with annealing treatments.

The next stage in the analysis is to back-Fourier transform the first shell of atoms in order to fit the inverse FT using the EXAFS formula. First a narrow R-window was used (such as one covering only one peak) in an effort to find the type of the back scattering atom and a rough estimation of the structural parameters. But, as the peaks are not well resolved, it is not possible to extract, with accuracy, the separate contributions of the two atomic constituents of the amorphous alloy to the Zr EXAFS, despite their greatly different radii. For this reason, a wide window was then applied to the transform in performing the band-pass filter and fits were made to the resulting back transform.

Figures 2a and 2b display the quality of the fits obtained for the sample heated at 240°C. The refined structural parameters yielded from the fits are listed in table 1. N is the number of neighbour atoms at the distance R from the central atom and the disorder parameter  $\sigma$  represents the fluctuation of the distances due to the structural disorder.

### 4 - Discussion

#### a) As-prepared sample

As seen in table 1, the environment of a Cu atom consists of two subshells of Cu atoms at 2.50 Å and 3.10 Å and a single shell of Zr atoms at 2.70-2.74 Å. This neighbourhood is very similar to those found for Cu-rich amorphous alloys /1, 2/ and has some resemblance to the crystalline  $\text{Cu}_{10}\text{Zr}_7$ . On the opposite, the short Cu-Cu distance (2.50 Å) does not exist in crystalline  $\text{CuZr}_2$  where therefore, there are no Cu-Cu next nearest neighbours.  $\text{CuZr}_2$  is our reference phase, since the  $\text{Cu}_x\text{Zr}_{1-x}$  system does not crystallize into a single phase in the concentration range  $0.66 < 1-x < 1$  (pure zirconium), but into a mixture of  $\text{CuZr}_2$  and Zr.

Around a Zr atom, there is one subshell of Cu atoms at 2.70-2.74 Å and two subshells of Zr atoms at 3.12 Å and 3.45 Å. This type of Zr subshells exist in the  $\text{CuZr}$  crystal and was found also for the corresponding amorphous alloy,  $\text{Cu}_{33}\text{Zr}_{67}^{2/21}$ .

It is noteworthy that these results are in good agreement with X-ray diffraction analysis /5/. Indeed, the two types of experiments are complementary. EXAFS is more sensitive to sharp features in the radial distribution function, i.e. to the Cu-Cu pairs and to Zr-Cu ones, the shortest interatomic distances being related to the smallest  $\sigma$  disorder parameter (table 1). On the opposite, X-ray scattering appreciates better the broad features of the radial distribution, thereby the Zr-Zr pairs. This is because X-ray scattering has lower spatial resolution, the wave number entering the product  $q r$  in scattering and  $2kr$  in EXAFS so that the transfert momentum is respectively  $q$  and  $2k$ . Since  $q_{\text{max}}$  is typically  $15 \text{ \AA}^{-1}$  for X-ray, this is equivalent to  $k_{\text{max}} = 7.5 \text{ \AA}^{-1}$ . As our EXAFS spectra extend to  $k_{\text{max}} = 12-13 \text{ \AA}^{-1}$ , EXAFS has significantly higher spatial resolution.

central atom	as-prepared			annealed at 200°C			annealed at 240°C		
	N	R(Å)	$\sigma$ (Å)	N	R(Å)	$\sigma$ (Å)	N	R(Å)	$\sigma$ (Å)
Cu	3.3	Cu 2.50	.116	3.5	Cu 2.52	.116	3.3	Cu 2.52	.116
	5	Zr 2.74	.122	6±1	Zr 2.76	.120	4	Zr 2.74	.122
	1.5	Cu 3.10	.116	1.5-2	Cu 3.10	.116	2	Cu 3.15	.116
Zr	1.5-2	Cu 2.70	.122	2	Cu 2.69	.127	1.5-2	Cu 2.70	.125
	5	Zr 3.12	.137	5.5	Zr 3.13	.132	5.5	Zr 3.28	.124
	1.5-2	Zr 3.45		2	Zr 3.45		2	Zr 3.50	.132
					3	Zr 3.90			

TABLE 1 : Structural parameters for  $\text{Cu}_{24}\text{Zr}_{76}$   
 (Atomic diameter : Cu-Cu = 2.56 Å, Cu-Zr = 2.88 Å,  
 Zr-Zr = 3.20 Å)

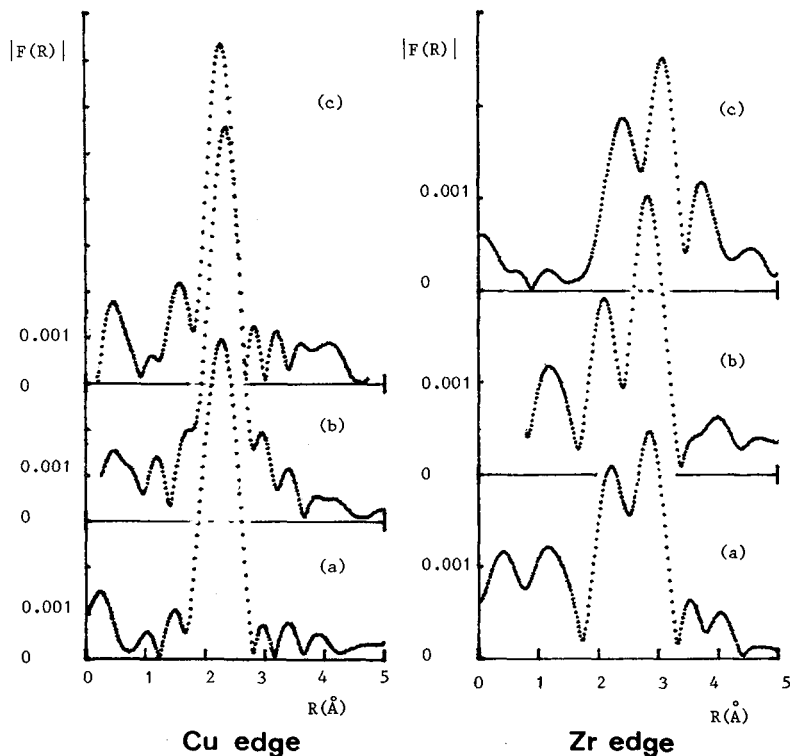


Fig. 1 : Fourier transforms of the Cu K-edge EXAFS of (a) as-prepared  $\text{Cu}_{24}\text{Zr}_{76}$ , (b) relaxed  $\text{Cu}_{24}\text{Zr}_{76}$ , (c)  $\text{Cu}_{24}\text{Zr}_{76}$  annealed at 240°C.

Turning back to the first shell structure, it is interesting to remark that the first of the two distances found for the Cu-Cu pairs and for the Zr-Zr pairs corresponds to the first neighbour distance in the pure metal (2.56 Å for copper and 3.20 Å for zirconium at room temperature). This could be a more general feature in metallic amorphous alloys since this was found also by EXAFS for other concentrations of the  $\text{Cu}_x\text{Zr}_{1-x}$  system /2/ as well as for other systems such as  $\text{Ni}_{66}\text{Y}_{33}$  /1/ or  $\text{Mg}_{70}\text{Zn}_{30}$  /6/. Such a result has also been obtained recently by Mizoguchi et al. /7/ using neutron diffraction in  $\text{Ni}_{36}\text{Zr}_{64}$ . For this alloy, the first Ni-Ni peak points at 2.45 Å and exhibits a shoulder on its high R side. Therefore the Ni-Ni contribution clearly appears doubly composed in two subshells, the first distance corresponding to the first neighbour distance in pure metal.

#### b) Annealed samples

After the annealing treatment at 200°C the local structure of the relaxed sample does not change much. A slight increase of the total number of Zr-Zr pairs, from about 6.75 to 7.5, is however noticeable (Table 1).

On the opposite, the heat treatment at 240°C, which ensures the crystallization of the  $\omega$ -Zr phase, drastically modifies the local structure around a Zr atom. Above the Zr edge, the new  $3^{\text{rd}}$  peak in the FT is identified as being due to Zr-Zr contributions at 3.90 Å. Moreover, the first Zr-Zr subshell is also strongly altered : the Zr-Zr distance is shifted by  $\Delta R = 0.15$  Å and the disorder parameter is reduced from  $\Delta\sigma = -.008$  Å. Indeed, all these results indicate an ordering of the environment of the Zr atoms at higher distances.

On the contrary, for the Cu neighbourhood, the structural parameters are almost unchanged. Nevertheless, a slight decrease of the  $N_{\text{Cu-Zr}}$  coordination number can be pointed out.

Therefore highlights of the atomic rearrangement which takes place during the first steps of crystallization, when the  $\omega$ -Zr phase has crystallized, are :

(1) The neighbourhood of a Cu atom becomes poorer in Zr atoms, while clustering of the Zr atoms appears. This tendency for segregation already exists in the relaxed sample.

(2) The local architecture around the Zr atom builds up in higher coordination subshells.

(3) The organization of the Cu-Cu pairs does not change. This is surely the most surprising point since there are no Cu-Cu pairs in close contact in  $\text{CuZr}_2$ . If we represent the double Cu-Cu subshells by a double-well potential, a supplementary amount of energy is necessary for the Cu atom to become mobile and to jump from the first minimum of configurational energy (2.52 Å) to the second one (3.15 Å). This second distance corresponds to the true Cu-Cu first distance in  $\text{CuZr}_2$ . If the second minimum has a lower energy than the first one, some kind of frustration could occur involving strong constraints in the alloy which induce the formation of the  $\omega$ -Zr phase. In fact, the zirconium undergoes under high pressure a phase transition from  $\alpha$  to  $\omega$  /8/, the lowest pressure at which the  $\omega$  phase was observed to form from the  $\alpha$  phase is 39 kbar at room temperature and around 20 kbar at 200°C.

These results could be correlated with recent calculations of Ashby et Gyorffy (to be published). These authors have studied the "freeze in" of concentrations fluctuations, in metallic glasses, induced by some kind of frustration due to the simultaneous presence of both ordering and clustering tendencies.

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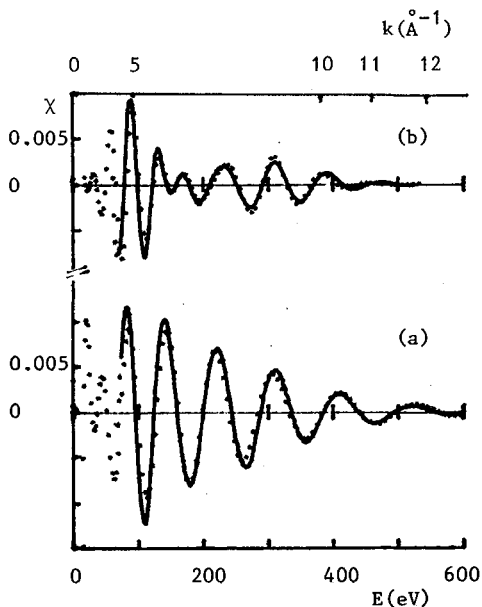


Fig. 2 : Filtered EXAFS spectra (dots) and its simulation (full curve) for  $\text{Cu}_{24}\text{Zr}_{76}$  heated at  $240^\circ\text{C}$  (a) above the Cu edge, (b) above the Zr edge.