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M. Maret, A. Pasturel. Study of crystallization of Y-based metallic glasses by differential scanning calorimetry and neutron diffraction. Journal de Physique, 1987, 48 (9), pp.1541-1546. <10.1051/jphys:019870048090154100>. <jpa-00210586>

HAL Id: jpa-00210586

<https://hal.science/jpa-00210586v1>

Submitted on 4 Feb 2008

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HAL Authorization

Classification
 Physics Abstracts
 61.40D — 61.12

Study of crystallization of Y-based metallic glasses by differential scanning calorimetry and neutron diffraction

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(Reçu le 26 février 1987, révisé le 12 mai 1987, accepté le 22 mai 1987)

Résumé. — La cristallisation des verres métalliques $\text{Ni}_{33}\text{Y}_{67}$ et $\text{Cu}_{33}\text{Y}_{67}$ a été étudiée par calorimétrie différentielle à balayage et diffraction de neutrons. La cristallisation se fait en deux étapes qui correspondent pour l'alliage $\text{Ni}_{33}\text{Y}_{67}$ à la cristallisation primaire du composé Y_3Ni suivie de la cristallisation eutectique des composés Y_3Ni et Y_3Ni_2 , et pour l'alliage $\text{Cu}_{33}\text{Y}_{67}$ à la coprécipitation de la phase cubique YCu , d'yttrium hexagonal et d'une phase métastable, suivie à plus haute température de la décomposition de la troisième phase en YCu et Y . En comparant avec des données sur les verres à base de zirconium et en utilisant le modèle de trou de Buschow [1], nous montrons que l'effet de taille important peut expliquer les faibles énergies d'activation de cristallisation des alliages $\text{Ni}_{33}\text{Y}_{67}$ et $\text{Cu}_{33}\text{Y}_{67}$ et que l'existence d'un ordre chimique à courte distance tel que dans l'amorphe $\text{Ni}_{33}\text{Y}_{67}$, ne conduit pas toujours à une stabilité thermique élevée.

Abstract. — The crystallization of the $\text{Ni}_{33}\text{Y}_{67}$ and $\text{Cu}_{33}\text{Y}_{67}$ metallic glasses has been investigated by differential scanning calorimetry and neutron diffraction. The crystallization occurs in two steps which for $\text{Ni}_{33}\text{Y}_{67}$ are the primary crystallization of the Y_3Ni compound and the eutectic crystallization of the Y_3Ni and Y_3Ni_2 compounds, and for $\text{Cu}_{33}\text{Y}_{67}$ the coprecipitation of the cubic YCu phase, the hcp Y phase and a metastable phase and at higher temperatures the decomposition of this third phase into YCu and Y . From a comparison with data on Zr-based glasses and using the hole model of Buschow [1], we show that the important size effect can explain the small activation energies for the crystallization of $\text{Ni}_{33}\text{Y}_{67}$ and $\text{Cu}_{33}\text{Y}_{67}$ and the occurrence of a chemical short-range order, as in $\text{Ni}_{33}\text{Y}_{67}$, does not always imply a higher thermal stability.

1. Introduction.

The knowledge of the thermal stability of metallic glasses by crystallization studies is a prerequisite for most potential applications. The crystallization of various metal-metal glasses has been widely investigated most frequently by differential scanning calorimetry [1-6]. In the kinetic approach of crystallization, Buschow [1, 2] has shown that the crystallization temperature T_x defining the thermal stability is proportional to the formation enthalpy of a hole the size of the smaller atoms in binary amorphous alloys ΔH_h .

$$T_x \propto \Delta H_h. \quad (1)$$

Here we present a study of the crystallization of the $\text{Ni}_{33}\text{Y}_{67}$ and $\text{Cu}_{33}\text{Y}_{67}$ glasses by two complemen-

tary methods appropriate for the investigation of the bulk of amorphous ribbons: differential scanning calorimetry and neutron diffraction.

The crystallization of other Y-based glasses ($\text{Fe}_x\text{Y}_{1-x}$ and $\text{Co}_x\text{Y}_{1-x}$) has been previously studied [1, 7] and the relation (1) stands fairly well. The composition of $\text{Ni}_{33}\text{Y}_{67}$ and $\text{Cu}_{33}\text{Y}_{67}$ is very close to the eutectic composition occurring for 66.5 at. % in NiY and 67 at. % in CuY , but the equilibrium crystalline phases for this composition, Y_3Ni_2 and Y_3Ni for $\text{Ni}_{33}\text{Y}_{67}$ and CuY and hcp Y for $\text{Cu}_{33}\text{Y}_{67}$, are completely different in composition and in structure. A strong chemical short-range order (CSRO) in $\text{Ni}_{33}\text{Y}_{67}$ and in contrast a tendency of random mixing of both constituents in $\text{Cu}_{33}\text{Y}_{67}$ have been found by neutron diffraction using the isotopic substitution method and X-ray diffraction [8, 9].

The influence of CSRO and size effect (characterized by the ratio of the atomic radii of both elements) on the thermal stability in binary amorph-

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ous alloys will be discussed from a comparison with the results obtained in Zr-based amorphous alloys [3, 4].

2. Experimental procedure.

Alloys of $\text{Ni}_{33}\text{Y}_{67}$ and $\text{Cu}_{33}\text{Y}_{67}$ were prepared by induction melting in a water cooled Ag-boat under an argon atmosphere. The starting materials were 99.9 % yttrium, 99.998 % nickel and 99.999 % copper. Amorphous ribbons ($\sim 30 \mu$ thick, 1-2 mm wide) were formed by the melt-spinning technique under a He atmosphere.

The thermal stability of the amorphous ribbons was studied by using a Perkin-Elmer DSC-2 under an Ar atmosphere. The DSC scans were registered with scanning rates from 10 K/min to 160 K/min. Their formation enthalpies ΔH_f were determined by means of a solution calorimeter based on liquid Al described elsewhere [10].

The crystallization processes were followed by *in situ* neutron diffraction measurements on the D1B diffractometer at the Institute Laue Langevin (Grenoble) with a wavelength of 2.52 \AA and a multidetector covering an angular range 2θ of 80° with an angular path of 0.2° . The ribbons maintained in a vanadium container of 8 mm diameter were placed at the centre of the furnace on the D1B diffractometer in a vacuum of 4×10^{-5} torr. The temperature of the sample and the thermic effects released during each transformation were monitored by three thermocouples arranged as described by Tete *et al.* [11]. When increasing the temperature at a rate of 1 K/min, the diffraction patterns were recorded each 5 min, simultaneously for diffraction angles 2θ between 5° and 85° for $\text{Ni}_{33}\text{Y}_{67}$ and between 40° and 120° for $\text{Cu}_{33}\text{Y}_{67}$; the corresponding q -ranges were $0.25 \text{ \AA}^{-1} < q < 3.55 \text{ \AA}^{-1}$ and $1.7 \text{ \AA}^{-1} < q < 4.32 \text{ \AA}^{-1}$.

3. Results.

Typical DSC thermograms of $\text{Ni}_{33}\text{Y}_{67}$ and $\text{Cu}_{33}\text{Y}_{67}$ are shown in figure 1. For both amorphous alloys a two-step crystallization process is observed. However for $\text{Ni}_{33}\text{Y}_{67}$ the first and the second peaks are not completely separated and with low heating rates the first peak becomes hardly visible. For $\text{Cu}_{33}\text{Y}_{67}$ the first exothermic peak is preceded by a weak endothermic effect attributed to the glass transition, the second transformation is less exothermic and is no longer detected with heating rates lower than 40 K/min. In table I, we list the peak temperatures obtained with different scanning rates s : T refers to the minimum of the strong exothermic peak for $\text{Ni}_{33}\text{Y}_{67}$, T_1 and T_2 to the minima of the two peaks for $\text{Cu}_{33}\text{Y}_{67}$ and T_g to the onset of the glass transition of $\text{Cu}_{33}\text{Y}_{67}$. Obviously all these temperatures increase with the heating rate. We observed [12] that an

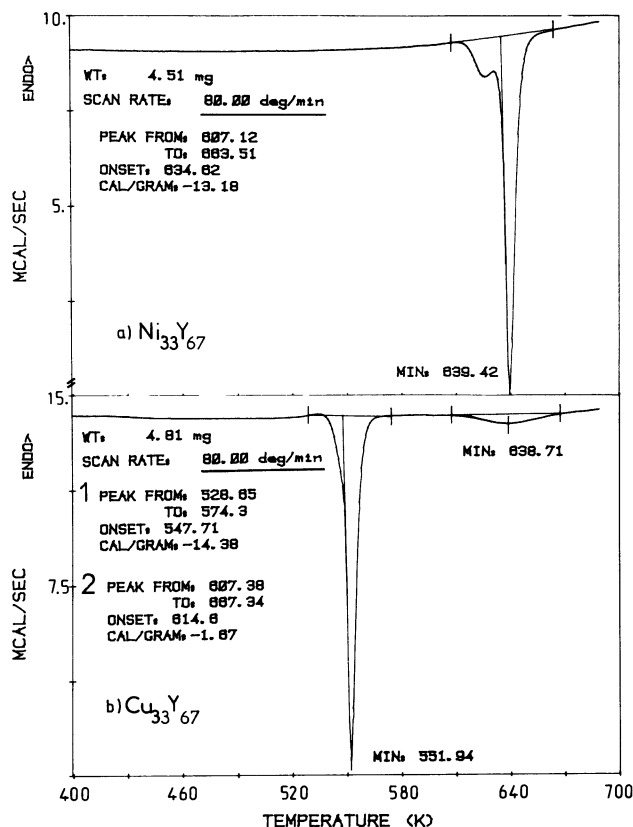


Fig. 1. — DSC thermograms with a heating rate of 80 K/min of a) amorphous $\text{Ni}_{33}\text{Y}_{67}$ and b) $\text{Cu}_{33}\text{Y}_{67}$.

Table I. — Peak temperatures T , T_1 , T_2 for $\text{Ni}_{33}\text{Y}_{67}$ and $\text{Cu}_{33}\text{Y}_{67}$ (see also text) and temperature of glass transition T_g for $\text{Cu}_{33}\text{Y}_{67}$.

$a\text{-Ni}_{33}\text{Y}_{67}$		$a\text{-Cu}_{33}\text{Y}_{67}$		
s (K/min)	T (K)	T_1 (K)	T_2 (K)	T_g (K)
160	656	567	655	530
80	639	552	639	523
40	628	542	623	519
20	617	534		
10	608	527		

amorphous alloy of $\text{Cu}_{33}\text{Y}_{67}$ prepared by sputtering also crystallized in two steps. However, the two transformations occurred at slightly different temperatures with $T_1 = 565 \text{ K}$ and $T_2 = 620 \text{ K}$ ($s = 80 \text{ K/min}$) and the second transformation is twice more exothermic.

The analysis of the neutron diffraction patterns of the $\text{Ni}_{33}\text{Y}_{67}$ alloy from the amorphous state (Fig. 2, curve a) to the fully crystallized one (Fig. 2f) allows us to characterize each exothermic reaction. In curves b and c (Fig. 2) the dark peaks at 2.25 \AA^{-1} and 2.36 \AA^{-1} , which appear above 530 K on the broad peak of the amorphous phase, can be clearly attributed to the Y_3Ni compound with an orthorhombic

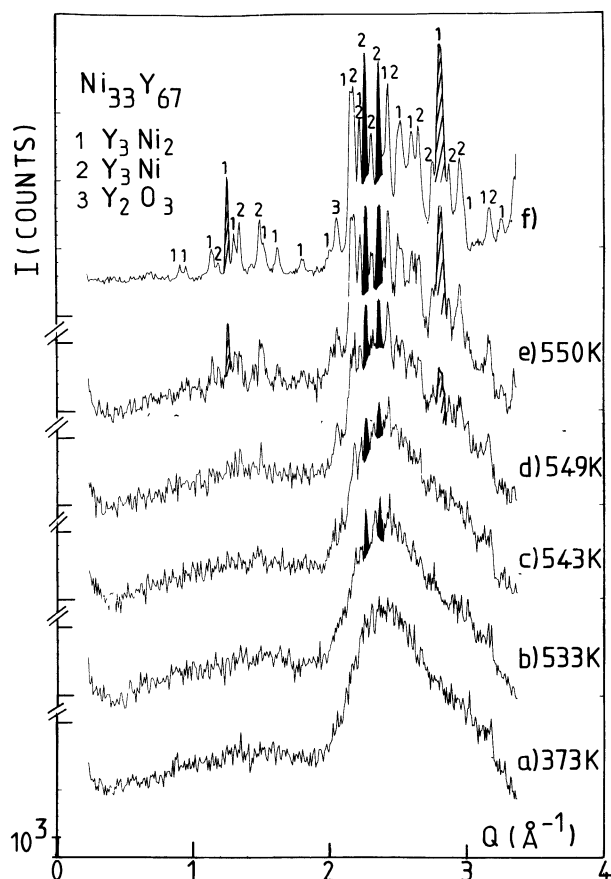


Fig. 2. — Neutron diffraction patterns of the $\text{Ni}_{33}\text{Y}_{67}$ amorphous alloy measured at different temperatures. The dark and hatched Bragg peaks are relevant to the precipitation of the Y_3Ni and Y_3Ni_2 compounds respectively.

bic Fe₃C-type structure [13]. Above 545 K, the hatched peak at 2.81 Å⁻¹ (Figs. 2d-e) is significant of the formation of the Y₃Ni₂ compound with a tetragonal structure [14]. The first small peak on the DSC thermogram (Fig. 1a) is thus related to the primary crystallization of Y₃Ni in the amorphous phase and the second strongly exothermic peak to the eutectic crystallization of Y₃Ni and Y₃Ni₂. The low heating rate used on the D1B diffractometer is consistent with the crystallization temperatures being lower than those listed in table I.

The scattered intensity of $\text{Cu}_{33}\text{Y}_{67}$ measured just after the onset of crystallization at about 485 K is shown in figure 3a. The Bragg peaks result from the coprecipitation of the hcp Y phase, the cubic type-CsCl YCu phase and a third phase. This transformation is associated with the first exothermic effect registered by DSC (Fig. 1b). The dark peaks which correspond to the third phase (Fig. 3a) can be attributed neither to the equilibrium phase Cu_2Y in the phase diagram [15], nor to the metastable phase Cu_5Y structurally close to the equilibrium phase Cu_4Y . Above 500 K the third phase decomposes into the two equilibrium phases Y and YCu, as shown in figure 3b. The curve c (Fig. 3) is the diffraction

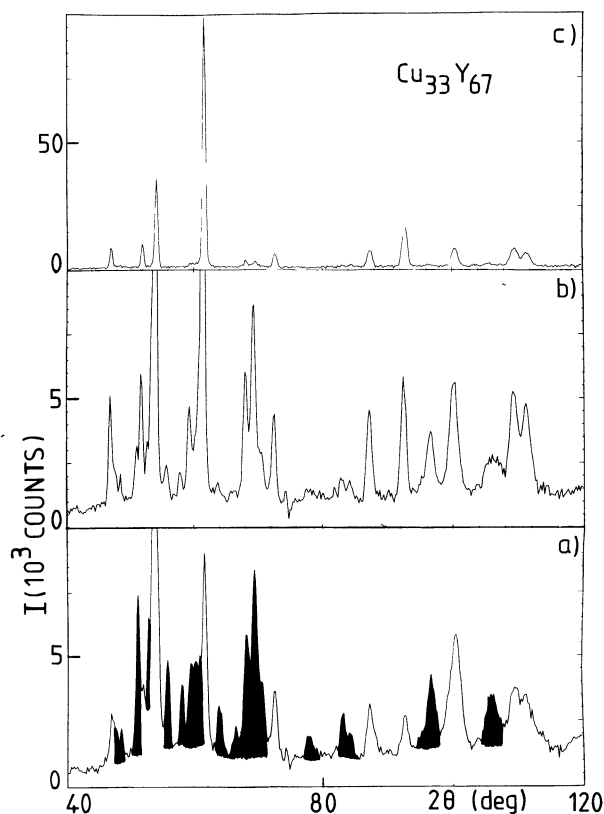


Fig. 3. — Neutron diffraction patterns measured at a) the beginning, b) an intermediate stage and c) the end of the crystallization of the $\text{Cu}_{33}\text{Y}_{67}$ amorphous alloy. (The dark Bragg peaks refer to the metastable phase.)

pattern measured after an increase at 600 K, which, except for the small peaks at 68° and 69.4°, can be indexed as a mixture of Y and YCu. Figure 4 shows a general change of the scattered intensity with temperature. In particular we observe that the more intense peaks of Y and YCu at 54.2° and 61.6° respectively begin to sharpen up after the decomposition of the metastable phase. The second exothermic effect in figure 1b is therefore to be associated with this decomposition.

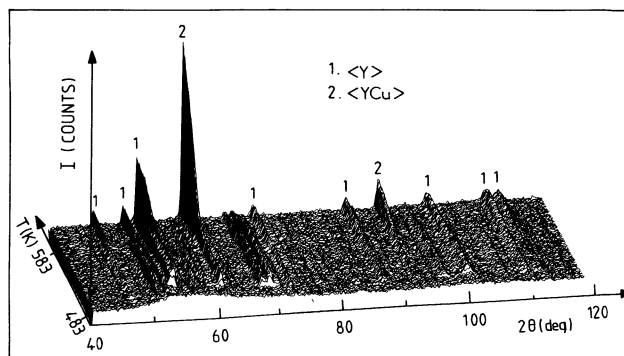


Fig. 4. — Evolution of the neutron diffraction pattern of the $\text{Cu}_{33}\text{Y}_{67}$ alloy from the amorphous state to the crystallized state.

4. Discussion.

The Kissinger plots obtained from DSC at various constant heating rates are shown for $\text{Ni}_{33}\text{Y}_{67}$ and $\text{Cu}_{33}\text{Y}_{67}$ ribbons in figure 5. In table II we give the values of the activation energy for crystallization ΔE (deduced from the slope of these curves) and the crystallization enthalpy, ΔH_{crist} , corresponding to the area under the two peaks for $\text{Ni}_{33}\text{Y}_{67}$ and the area under the first peak for $\text{Cu}_{33}\text{Y}_{67}$. The enthalpy of the second reaction for $\text{Cu}_{33}\text{Y}_{67}$ is of about 0.7 kJ/mole. The results of the $\text{Ni}_{35}\text{Zr}_{65}$ and $\text{Cu}_{38}\text{Zr}_{62}$ glasses whose composition in Zr is close to this one in Y are also reported in table II. We observe that, as indicated by the crystallization temperatures and the activation energies, the Y-based glasses are less stable than the Zr-based glasses.

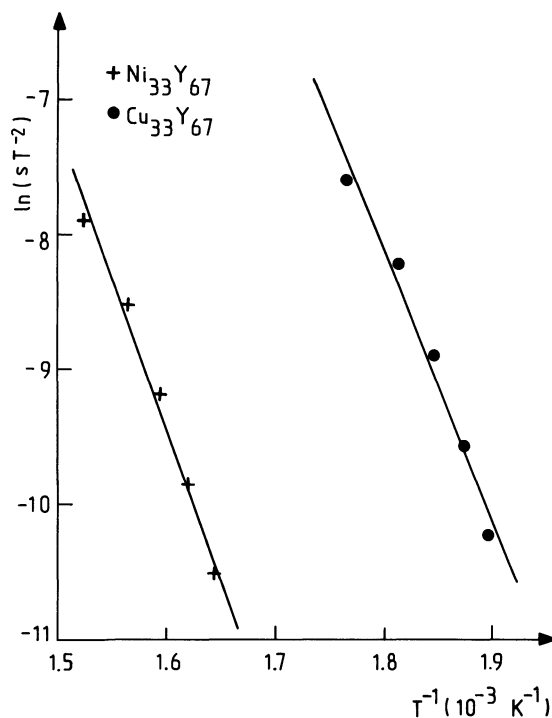


Fig. 5. — Kissinger plots of amorphous $\text{Ni}_{33}\text{Y}_{67}$ and $\text{Cu}_{33}\text{Y}_{67}$ alloys. In the product sT^{-2} , s is the heating rate and T the corresponding peak temperature of crystallization given in table I. (For $\text{Cu}_{33}\text{Y}_{67}$ T is the first peak temperature, called T_1 in Tab. I.)

In the following, we would like to study more particularly the influences of the size effect and the chemical short range order on the properties of crystallization of Y and Zr-based metallic glasses.

— *size effect* :

As mentioned in the introduction, a simple model has been developed by Buschow [6] in which the crystallisation temperature T_x is described in terms of a semi-empirical relationship of the form :

$$T_x \approx 7.5 \Delta H_h, \quad (2)$$

where ΔH_h is the formation enthalpy of a hole of the same size as the smaller atom in the amorphous alloy.

The hole enthalpy can be estimated by using Miedema's results obtained from an analysis of monovacancies in metals and alloys [20].

$$\Delta H_h = x_B \Delta H_{1V}^B + x_A \left(\frac{V_B}{V_A} \right)^{5/6} \Delta H_{1V}^A \quad (3)$$

where ΔH_{1V}^A and ΔH_{1V}^B are the formation enthalpies of a monovacancy in pure A and B respectively and V_A , V_B the molar volumes ; x_A and x_B are the effective compositions.

We have thus estimated ΔH_h for the Y-based glasses ; the values of ΔH_h for the Zr-based glasses previously calculated [6, 8] are also reported in table II.

The ratios of the metallic radii which quantify the size effect are 1.44, 1.41, 1.28 and 1.25 for $\text{Ni}_{33}\text{Y}_{67}$, $\text{Cu}_{33}\text{Y}_{67}$, $\text{Ni}_{35}\text{Zr}_{65}$ and $\text{Cu}_{32}\text{Zr}_{68}$ respectively.

The correlation between T_x and ΔH_h means that the larger size effect in Y-based glasses makes the creation of a hole of the size of the smaller atoms easier and can explain the weaker thermal stability of the $\text{Ni}_{33}\text{Y}_{67}$ and $\text{Cu}_{33}\text{Y}_{67}$ glasses.

The above description of the thermal stability of amorphous alloys is based on a kinetic approach which assumes the temperature of crystallisation and the activation energy ΔE_0 to be proportional for a viscous flow. This is a consequence of the diffusion constant being proportional to the reciprocal of the viscosity ($\eta = \eta_0 \exp \Delta E_0 / S_c T$). Viscous flow and

Table II. — Temperature of crystallization T_x ($s = 80$ K/min), ($T_x = T$ or T_1 , a) for the first peak of crystallization enthalpy, activation energy for crystallization ΔE , crystallization enthalpy ΔH_{crist} , formation enthalpy of the amorphous alloy at 298 K $\Delta H_{f,a}$, ratio $r = \Delta H_{\text{crist}} / \Delta H_{f,a}$, chemical short-range order parameter α_1 (extracted from [9]) and formation enthalpy of a hole ΔH_h . Data are taken for $\text{Ni}_{35}\text{Zr}_{65}$ in [4, 16, 17] and for $\text{Cu}_{32}\text{Zr}_{68}$ in [3, 18].

Glass	T_x (K)	ΔE (KJ/mole)	ΔH_{crist} (KJ/mole)	$\Delta H_{f,a}$ (KJ/mole)	r	α_1	ΔH_h (KJ/mole)
$\text{Ni}_{33}\text{Y}_{67}$	639	184	— 4.13	— 28	0.15	— 0.14	69
$\text{Cu}_{33}\text{Y}_{67}$	552	164	— 4.73	— 10.8	0.44	— 0.01	60
$\text{Ni}_{35}\text{Zr}_{65}$	720 (a)	478	— 6.62	— 29.7	0.22	— 0.06	95
$\text{Cu}_{32}\text{Zr}_{68}$	723	385	— 5.74	— 11.6	0.49	~ 0.0	95

subsequent crystallization become possible when a critical value ($\eta_{cr} \approx 10^{13}$ P) is reached, leading to the relation :

$$T_x \approx \frac{\Delta E_0}{S_c} \quad (4)$$

S_c is the configuration entropy and is assumed to be independent of the temperature.

However our experimental results of table II, like other results reported in the literature, show that the experimental T_x values are not proportional to the experimental activation energies ΔE . Without any doubt it is an unsatisfactory aspect associated with the model description. In order to improve it, some attempts have been made taking the chemical short range order into account.

— CSRO :

As remarked by Chen [9], S_c may no longer be regarded as temperature-independent when CSRO does occur. In this case, the experimental value of the activation energy ΔE is related to ΔE_0 by :

$$\Delta E = \Delta E_0 \left(1 + \frac{d \ln S_c}{dT} \right) \quad (5)$$

Thus from Buschow [6, 17] large values of ΔE are a consequence of the dependence of $\ln S_c$ with T which may be expected in amorphous alloys exhibiting CSRO, while this short range order does practically not affect the crystallization temperature (see Ref. [6] for more details).

However our experimental results do not display such a trend : on the one hand, while ΔE values are rather similar to ΔH_h , there is a strong difference in CSRO between $Ni_{33}Y_{67}$ and $Cu_{32}Y_{67}$ amorphous alloys, as shown by the values of α_1 reported in table II (we recall that a negative value of α_1 indicates a high degree of chemical ordering). On the other hand, the difference in CSRO between $Ni_{35}Zr_{65}$ and $Cu_{32}Zr_{68}$ glasses is smaller while the difference between the ΔE values is larger, ΔH_h keeping the same value for both alloys like T_x values. Thus, the account of incorporating CSRO does not seem to be sufficient to explain the failure of the relationship between T_x and the experimental values of ΔE .

To study the influence of a relatively high degree of CSRO on the crystallization of amorphous alloys, the crystallization enthalpy appears to be a more relevant quantity. ΔH_{crist} is currently regarded as the driving force for the amorphous to crystalline transition although this quantity has hardly any influence

on the thermal stability. In fact, as shown by Ansara *et al.* [3], due to the small difference of the specific heats between the amorphous and the crystallized alloys, the crystallization enthalpy can be written in terms of the formation enthalpies of the amorphous and crystallized alloys at T_0 as :

$$\Delta H_{crist} = \Delta H_{f,c}^{T_0} - \Delta H_{f,a}^{T_0} \quad (6)$$

Amorphous alloys are characterized by formation enthalpies which take less negative values than those of crystalline alloys of similar composition. The most obvious mechanism which could stabilize an amorphous alloy is the occurrence of CSRO, since in this case the enthalpy value found for the amorphous alloy tends to be close to the value expected for the crystalline material [21].

Thus the quantity $r = \Delta H_{crist} / \Delta H_{f,a}$ does decrease when CSRO increases. In table II, we report the formation enthalpies of the studied glasses as well as the r values. We effectively find such a trend between the r values and the CSRO parameters α_1 . However, as also seen in table II, a strongly negative formation enthalpy $\Delta H_{f,a}$ is not necessarily related to a good thermal stability.

To conclude from the comparison of the Zr-based and Y-based glasses, we have shown that the occurrence of CSRO does not necessarily lead to a good thermal stability. The hole model proposed by Buschow has been applied successfully for the crystallization temperatures T_x . However, the experimental values of the activation energy for crystallisation, ΔE , determined from rate-dependent measurements, are not proportional to the experimental T_x and cannot be regarded as a measure of the thermal stability. Moreover, from our experimental results, it appears that ΔE is not a relevant quantity to the occurrence of CSRO. We also emphasize that, in the kinetic approach, the stability of the crystalline compounds is not taken into consideration, and the weaker stability of $Cu_{33}Y_{67}$ compared to that of $Ni_{33}Y_{67}$ may come from the precipitation of a metastable phase during the first step of the crystallisation process.

Acknowledgments.

The authors wish to thank Ph. Mangin (ILL, Grenoble) for his experimental assistance on the D1B diffractometer, M. Atzmon (Caltech, Pasadena) for the melt-spinning of the glasses and C. Colinet (LTPCM, St-Martin d'Hères) for her help in measuring the formation enthalpies.

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