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A NEUTRON DIFFRACTION DETERMINATION OF SHORT RANGE ORDER IN A

 $\text{Ni}_{63.7}\text{Zr}_{36.3}$ GLASS

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Résumé - Une détermination précise des trois facteurs de structure partiels, pour la composition eutectique $\text{Ni}_{63.7}\text{Zr}_{36.3}$, a été faite par diffraction des neutrons sur trois échantillons de composition isotopique différente. L'utilisation d'un "alliage zéro" fournit une détermination directe du facteur de structure partiel de Bhatia-Thornton S_{CC} . L'existence d'un fort ordre chimique à courte distance et d'un effet de taille très net est évidente. La présence de cet ordre chimique se traduit par des facteurs de structure partiels tout à fait incompatibles avec ceux calculés dans un modèle de sphères dures en utilisant l'équation de Percus-Yevick. A cause de l'effet de taille un paramètre d'ordre local du type Warren-Cowley ne peut pas être calculé. L'écart à la répartition statistique autour d'un atome de nickel est comparé aux résultats récemment publiés sur deux autres verres Ni-Zr, de compositions différentes.

Abstract - A precise determination of the three partial structure factors for the eutectic composition $\text{Ni}_{63.7}\text{Zr}_{36.3}$ has been carried out using neutron diffraction on three isotopically substituted glasses. The use of a "zero alloy" yields a direct determination of the Bhatia-Thornton structure factor S_{CC} . Evidence for the existence of strong chemical short-range order and a clear size effect is obtained. Due to this chemical order, the partial structure factors cannot be consistent with the ones calculated for a two components system of hard spheres using the Percus-Yevick equation. Due to the size effect, a short-range order Warren-Cowley parameter cannot be calculated. The deviation from a purely statistical distribution around a nickel is compared to the results recently published for two other Ni-Zr glasses.

Introduction

The stability and the ease of glass formation of amorphous alloys are thought to be related to the existence of chemical short range order. In the amorphous $\text{Zr}_{1-x}\text{Ni}_x$ alloys the composition dependence of the activation energy for crystallization has been taken as reflecting the occurrence of CSRO, which would be a particularly important effect in the composition regions close to $x = 0.38$ and $x = 0.64$ /1/. Hence diffraction studies giving the change in CSRO with concentration are important. Recently, partial structure factors have been determined for $\text{Ni}_{36}\text{Zr}_{64}$ /2/, $\text{Ni}_{35}\text{Zr}_{65}$ /3/ and NiZr /4/. We present here the three partial structure factors (P.S.F.) for the eutectic composition $\text{Ni}_{63.7}\text{Zr}_{36.3}$, determined by neutron diffraction on isotopically substituted samples. A preliminary report of this study has been published elsewhere /5/.

Experiment

For binary amorphous alloys, at least three different experiments are required to obtain the three PSF's. The isotopic compositions we have chosen are $^{nat}\text{Ni}_{63.7}\text{Zr}_{36.3}$, $^{60}\text{Ni}_{63.7}\text{Zr}_{36.3}$ and $^{62}\text{Ni}_{39.2}^{60}\text{Ni}_{24.5}\text{Zr}_{36.3}$. The amorphous ribbons were obtained by planar flow casting /6/ under a helium pressure of 375 Torr. The ribbons are typically 6 mm wide and 35 μ m thick.

The experiments have been carried out on the spectrometer 7C2 on the hot source of ORPHEE (wavelength 0.704 Å) with a 640 cells position sensitive detector /7,8/. Data reduction consisted of correction for transmission, incoherent multiple scattering and inelastic scattering following classical procedures. The scattering lengths used are those compiled by Mughahghah et al. /9/.

The total structure factor $S(q)$ may be defined by the relation

$$S(q) = I_{\text{coh}}(q)/\langle b^2 \rangle$$

which is particularly appropriate for alloy whose $\langle b \rangle$ value might be zero, the so-called "zero alloy".

According to the Faber-Ziman formalism /10/ the total structure factor for a binary AB alloy is a sum of the three weighted partial structure factors $S_{ij}(q)$:

$$S(q) - 1 = \frac{C_A^2 b_A^2}{\langle b^2 \rangle} (S_{AA}(q) - 1) + \frac{C_B^2 b_B^2}{\langle b^2 \rangle} (S_{BB}(q) - 1) + \frac{2C_A C_B b_A b_B}{\langle b^2 \rangle} (S_{AB}(q) - 1)$$

The coefficient $w_{ij} = c_i c_j b_i b_j / \langle b^2 \rangle$ are given in table 1 for the three samples.

TABLE 1

TABLE 2

	w_{NiNi}	w_{ZrZr}	w_{NiZr}	$\langle b \rangle^2 / \langle b^2 \rangle$	$2\Delta b \langle b \rangle / \langle b^2 \rangle$	$\Delta b^2 / \langle b^2 \rangle$
$^{nat}\text{Ni}_{63.7}\text{Zr}_{36.3}$	0.499	0.078	0.396	0.973	-0.6674	0.1169
$^{60}\text{Ni}_{63.7}\text{Zr}_{36.3}$	0.136	0.285	0.394	0.815	1.614	0.8008
$^{62}\text{Ni}_{39.2}^{60}\text{Ni}_{24.5}\text{Zr}_{36.3}$	0.231	0.231	-0.462	0	0	4.329

Very few precise determinations of PSF's of binary metal-metal amorphous alloys have been presented up to date. The three diffraction experiments provide a set of three equations from which the partials can be extracted.

In this work the normalized determinant of the three linear equations to be solved to obtain the PSF's $S_{\text{NiNi}}(q)$, $S_{\text{NiZr}}(q)$ and $S_{\text{ZrZr}}(q)$ is exceptionally high (0,112), allowing a direct determination of the partials from the data without using constraints or inequality relations. A precision of 1% on each total structure factor leads

to a precision of 3.85, 5.45 and 2.33% on the $S_{NiNi}(q)$, $S_{ZrZr}(q)$ and $S_{NiZr}(q)$ partials, respectively.

In the Bhatia-Thornton formalism /11/, PSF's are associated with the correlations between density fluctuations and concentration fluctuations. This formalism is therefore quite useful to study the local order phenomena. $S_{NN}(q)$, $S_{CC}(q)$, $S_{NC}(q)$ describe the topological short-range order, the chemical short-range order and the correlation between number density and concentration, respectively. The different coefficients of $S_{NN}(q)$, $S_{NC}(q)$, $S_{CC}(q)$ are given in table 2 for the three samples. It should be noted that for the sample which is a "zero alloy" ($\langle b \rangle = 0$), $S_{CC}(q)$ can be obtained directly.

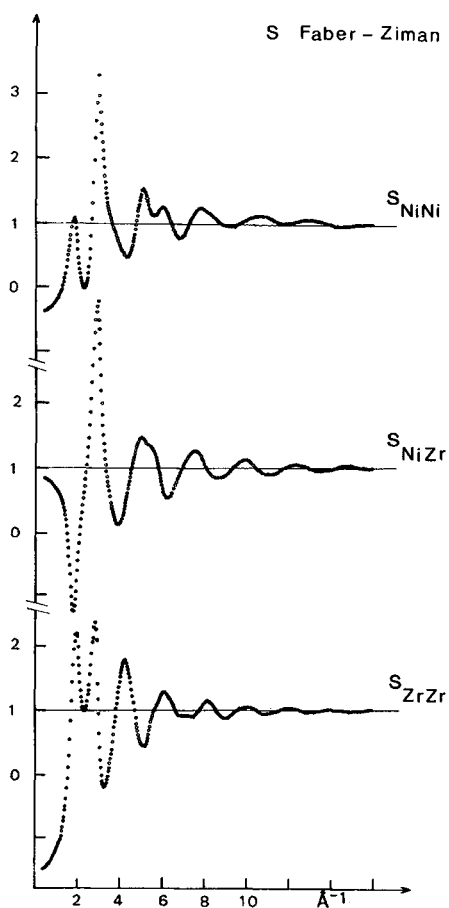


Fig.1. $Ni_{63.7}Zr_{36.3}$ Faber-Ziman partial structure factors

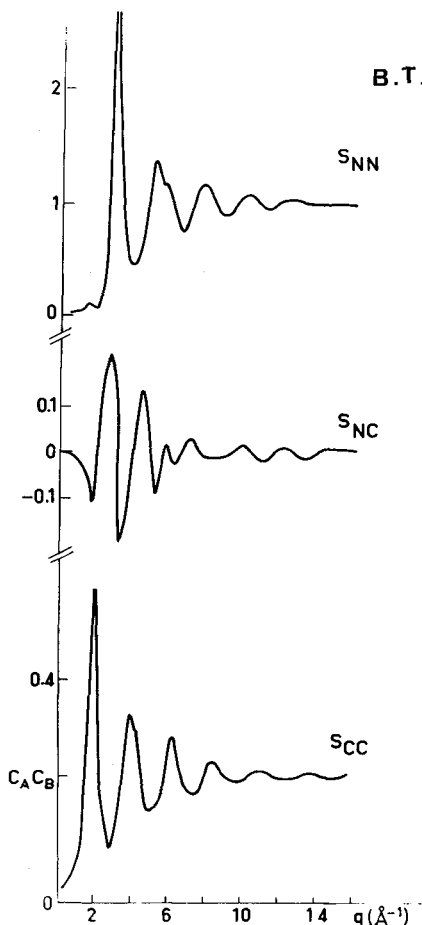


Fig.2. $Ni_{63.7}Zr_{36.3}$ Bhatia-Thornton partial structure factors

Results

The Faber-Ziman and the Bhatia-Thornton P.S.F. are shown in Figures 1 and 2. They give evidence for the existence of a well defined chemical short-range order and an important size effect. Chemical short-range order produces, at small values of q , a sharp and intense peak or dip in the Faber-Ziman partials. A comparison of these with $S_{CC}(q)$, together with the calculations of the relations between the FZ partials and the BT ones show that this sharp feature is really due to the $S_{CC}(q)$ first peak. In analogy with the order phenomena in crystalline alloys, this is a "superstructure peak" corresponding to a new pseudoperiodicity with a longer range.

Negative values of $S_{CC}(0) - C_{ACB}$ indicate a preference for unlike neighbours. The Fourier Transform of $S_{CC}(q)$ still confirms this preference (figure 3). Figure 3 also shows the Fourier Transforms of $S_{NC}(q)$ and $S_{NN}(q)$. An average coordination number of 13.12 atoms was calculated by integrating the first peak of $4\pi r^2 \rho_0 g_{NN}(r)$.

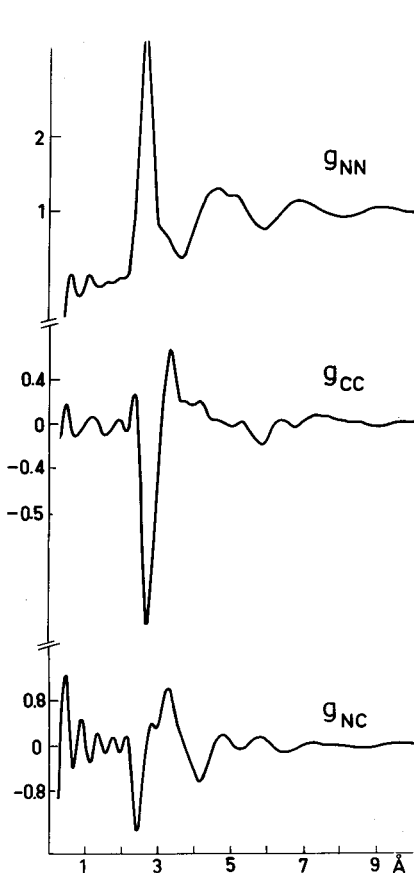


Fig.3. $Ni_{63.7}Zr_{36.3}$ Pair partial correlation functions

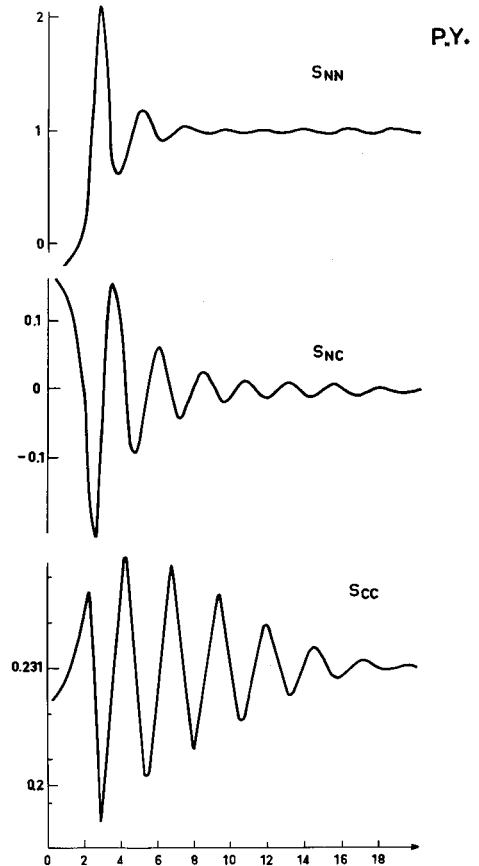


Fig.4. $Ni_{63.7}Zr_{36.3}$ Percus-Yevick hard spheres partial structure factors.

Percus-Yevick Hard Spheres S_{NN} , S_{CC} and $S_{NC}(q)$ curves have been calculated for a misfit ratio of $\sigma_{Ni}/\sigma_{Zr} = 2.07/2.68 = 0.775$ and a packing fraction of 0.43 (Figure 4). They are very different from the experimental curves. In particular, in this alloy the P.Y. $S_{NC}(q)$ curves cannot be used instead of a third experiment to determine the partials as previously proposed by other authors /3,12/.

Table 3 gives the first neighbours distances r_1 and coordination numbers N_1 calculated from the partial radial distribution functions $4 r^2 c_j \rho_0 g_{ij}(r)$. The two sets of values correspond to two experiments carried out on the same samples but separated by a time interval of six months. The reproducibility is very good as long as r_1 or N_1 are concerned.

TABLE 3 - First neighbours distances and partial coordination numbers

	r_1		N_1		Random
	First Experiment	Second Experiment	First Experiment	Second Experiment	
NiNi	2.52	2.51	6.00	5.96	7
NiZr	2.67	2.67	5.00	5.18	4
ZrZr	3.28	3.27	5.84	5.91	
ZrNi	2.67	2.67	8.77	9.1	

Owing to the strong size effect a Warren-Cowley parameter cannot be calculated. However the deviation from a purely statistical distribution is confirmed by the values of the partial coordination numbers. In $Ni_{63.7}Zr_{36.3}$ a nickel atom has on average 5 nearest Zr neighbours instead of 4 for a random distribution. In $NiZr$ /4/ it has 6.7 nearest Zr neighbours instead of 5. In $Ni_{36}Zr_{64}$ /2/ it has 8.56 nearest Zr neighbours instead of 7.59.

Thus the CSRO is of the same nature throughout this composition range. The deviation from a purely random distribution is typically one atom out of the eleven of the first coordination shell for the two compositions corresponding to the deep eutectics ($Ni_{63.7}Zr_{36.3}$ and $Ni_{36}Zr_{64}$), and 1.7 out of 10 for the composition corresponding to the compound $NiZr$. Hence, the correlation suggested by Buschow /1/ between the maxima of the activation energy for crystallization and a stronger CSRO is not established.

References

- /1/ Buschow K.H.J., J. Phys. F : Met Phys. 14 (1984) 593-607.
- /2/ Mizoguchi T., Yoda S., Akutsu N., Yamada S., Nishioka J., Suemasa T. and Watanabe N., Rapidly Quenched Metals, 5th International Conference, Ed. S. Steeb and H. Warlimont, to be published (1985).
- /3/ Lee A., Etherington G. and Wagner C.N.J., J. non Cryst. Solids 61 and 62 (1984) 349-354.
- /4/ Fukunaga T., Hayashi N., Watanabe N., Suzuki K., Rapidly Quenched Metals, 5th International Conference, Ed. S. Steeb and H. Warlimont, to be published (1985).

- /5/ Lefebvre S., Quivy A., Bigot J., Calvayrac Y., and Bellissent R., J. Phys. F : Met. Phys. 15 (1985) L99-L103.
- /6/ Bigot J., in "Les Amorphes Métalliques" (Aussois, 1983) : Ed. de Physique (Paris) (1984) p.33.
- /7/ Ambroise J.P. and Bellissent R., P.S.D. of Thermal Neutrons (1983) (London : Academic).
- /8/ Ambroise J.P.; Bellissent-Funel M.-C. and Bellissent R., Revue Phys. Appl. 19 (1984) 731-4.
- /9/ Mughabgha S.F., Divadeeman M. and Holden N.E., Neutron Cross Sections, vol.1 (1981) (New-York Academic).
- /10/ Faber T.E. and Ziman J.M., Phil. Mag. 11 (1965) 153-73.
- /11/ Bhatia A.B. and Thornton D.E., Phys. Rev. B 2 (1970) 3004 12.
- /12/ Wagner C.N.J., Etherington G., and Lee A., Rapidly Quenched Metals, 5th International Conference, Ed. S. Steeb and H. Warlimont, to be published (1985).