

Local Structure of the Amorphous Ni₂₅Zr₇₅-Alloy by Using the Isotope-Substitution Neutron Diffraction Method

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Using neutron diffraction as well as the method of isotopic substitution the partial Bhatia-Thornton as well as the partial Faber-Ziman structure factors of amorphous Ni₂₅Zr₇₅ were determined. A compound forming tendency was found. The atomic distances, partial coordination numbers, and the chemical short range order parameter are evaluated.

1. Introduction

Using anomalous X-ray diffraction, in amorphous Ni₂₅Zr₇₅ no Ni–Ni-correlation was found within the first coordination sphere [1]. On the other hand, using Mössbauer spectroscopy, in amorphous Fe₁₀Ni_{90–x}Zr_x the existence of nearest Ni–Ni neighbours was suggested [2]. It was one of the aims of the present work to clear up this discrepancy.

2. Experiments and Results

We prepared four amorphous Ni₂₅Zr₇₅-samples by melt spinning. The Zr was of natural isotopic abundance, whereas four kinds of Nickel were used; namely Ni^{nat} (natural isotopic abundance, coherent scattering length $b^{\text{nat}} = 1.03 \cdot 10^{-12}$ cm), Ni⁶⁰ ($b^{60} = 0.28 \cdot 10^{-12}$ cm), Ni⁰ ($b^0 = 0$), and Ni⁶² ($b^{62} = -0.84 \cdot 10^{-12}$ cm). Neutron diffraction ($\lambda = 0.7$ Å) was done using the instrument D4B (ILL, Grenoble). Thus four total structure factors $S_{\text{tot}}^{\text{FZ}}(Q)$ were obtained according to the definition by Faber and Ziman [3]:

$$S_{\text{tot}}^{\text{FZ}}(Q) = \{I_{\text{coh}}(Q) - [\langle b^2 \rangle - \langle b \rangle^2]\} / \langle b \rangle^2 \quad (1)$$

with

$I_{\text{coh}}(Q)$ = coherent scattering intensity,

$Q = (4\pi/\lambda) \sin \Theta$,

2Θ = scattering angle,

λ = neutron wavelength,

$\langle b \rangle = c_1 b_1 + c_2 b_2$,

$\langle b^2 \rangle = c_1 b_1^2 + c_2 b_2^2$,

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c_i = atomic fraction of component i ,
 b_i = mean coherent scattering length of component i .

The total structure factor is a weighted sum of the Faber-Ziman partial structure factors:

$$S_{\text{tot}}^{\text{FZ}}(Q) = \{c_1^2 b_1^2 S_{11}(Q) + c_2^2 b_2^2 S_{22}(Q) + 2c_1 c_2 b_1 b_2 S_{12}(Q)\} / \langle b \rangle^2$$

$$= W_{11} S_{11} + W_{22} S_{22} + W_{12} S_{12} \quad (2)$$

A measure for the quality of the partial structure factors as calculated from a set of three total structure factors is given by the normalized determinant of the coefficients W_{ij} in (2),

$$\| \det W \| = \frac{|\det W|}{\prod_i \sqrt{\sum_j W_{ij}^2}}, \quad (3)$$

the values of which can lie between 0 and 1, where 1 stands for the best conditioned set of equations.

With four total structure factors, four sets of three total functions can be chosen for the evaluation of the three partial structure factors. The four possible sets are compiled in Table 1 together with the corresponding values of the normalized determinant.

Table 1. Normalized determinant for the four possible different combinations of three total structure factors.

Set of three total structure factors with Ni-isotopes			$\ \det W \ ^2$
Ni ^{nat}	Ni ⁶⁰	Ni ⁰	0.030
Ni ^{nat}	Ni ⁶⁰	Ni ⁶²	0.171
Ni ^{nat}	Ni ⁰	Ni ⁶²	0.182
Ni ⁰	Ni ⁶⁰	Ni ⁶²	0.040

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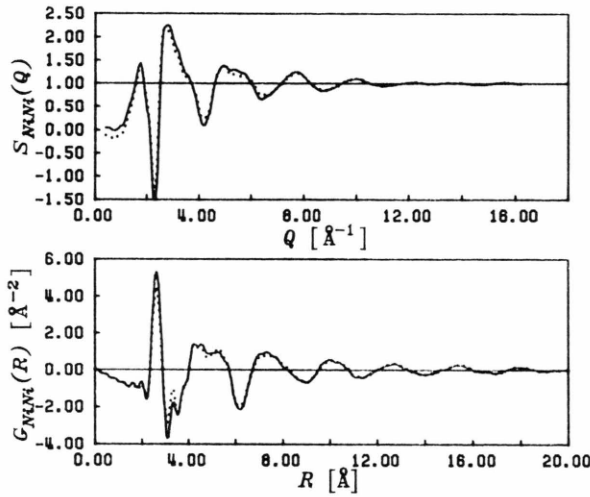


Fig. 1. Amorphous $\text{Ni}_{25}\text{Zr}_{75}$. $S_{\text{NiNi}}(Q)$ (above) and $G_{\text{NiNi}}(R)$ (below), evaluated from $\text{Ni}_{25}^{\text{nat}}\text{Zr}_{75}$, $\text{Ni}_{25}^{62}\text{Zr}_{75}$ together with $\text{Ni}_{25}\text{Zr}_{75}$ (—) or $\text{Ni}_{25}^{60}\text{Zr}_{75}$ (·····), respectively.

From Table 1 one can see that only two sets may yield good results, namely the second and the third. The partial NiNi-structure factors and -pair correlation functions as evaluated from these two sets are shown in Figure 1.

The shapes of the curves as obtained from the two different sets of experimental data look very similar. Therefore we evaluated the final partial structure factors as the mean value of the two sets. The partial structure factors as obtained finally according to Faber-Ziman are shown in Figure 2. An alternative definition of three partial structure factors was given by Bhatia and Thornton [4]. These were also calculated from the two sets of total structure factors and are shown in Figure 3.

By Fourier transform the $S_{ij}(Q)$ yield the partial pair correlation functions $G_{ij}(R)$ in real space

$$G_{ij} = \frac{2}{\pi} \int_0^\infty Q(S_{ij}-1) \sin(QR) dQ. \quad (4)$$

Figure 4 shows the three Faber-Ziman $G_{ij}(R)$ functions $G_{\text{NiNi}}(R)$, $G_{\text{ZrZr}}(R)$, and $G_{\text{NiZr}}(R)$ in comparison with the Bhatia-Thornton partial function $G_{\text{CC}}(R)$. This function describes the concentration-concentration correlations. The following linear relationship is valid:

$$G_{\text{CC}}(R) = c_{\text{Ni}} c_{\text{Zr}} [G_{\text{NiNi}}(R) + G_{\text{ZrZr}}(R) - 2 G_{\text{NiZr}}(R)]. \quad (5)$$

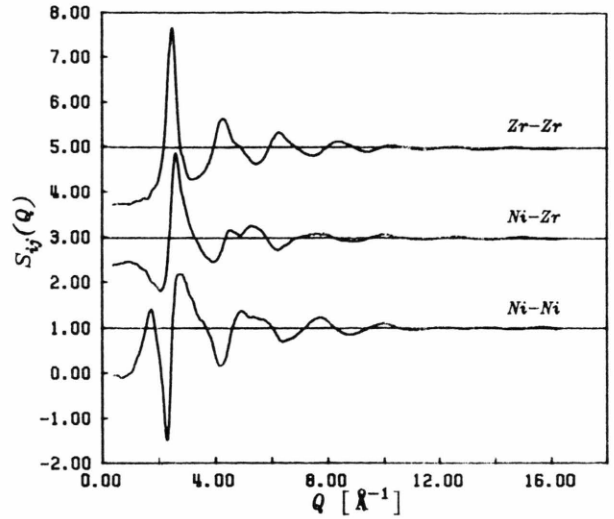


Fig. 2. Amorphous $\text{Ni}_{25}\text{Zr}_{75}$. Partial structure factors according to Faber-Ziman. The curves for Ni-Zr and Zr-Zr are shifted upwards.

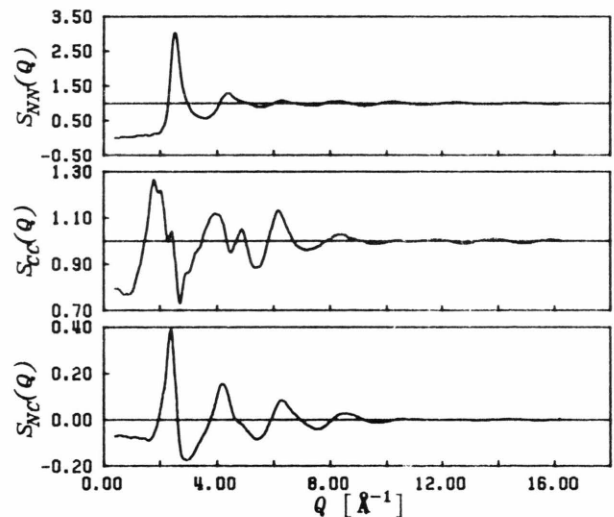
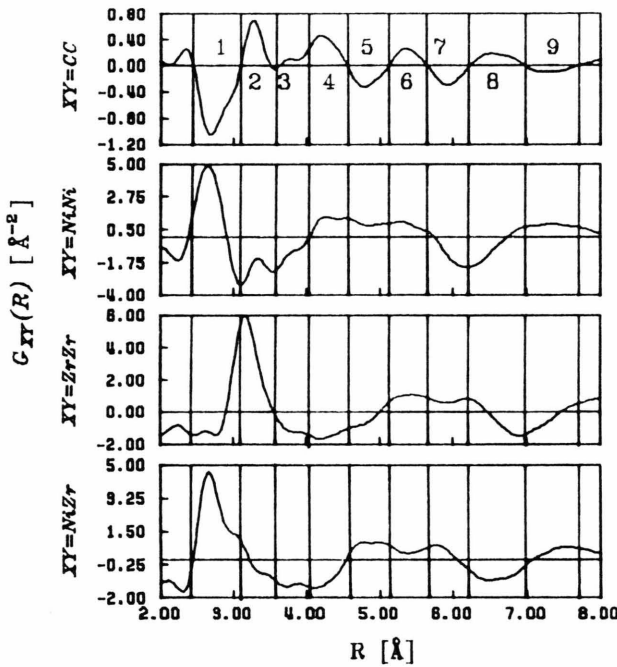


Fig. 3. Amorphous $\text{Ni}_{25}\text{Zr}_{75}$. Partial structure factors according to Bhatia-Thornton.

From (5) one learns that positive $G_{\text{CC}}(R)$ -values mean the predominance of equal pairs, whereas negative $G_{\text{CC}}(R)$ -values mean the predominance of unequal pairs. The classification of an alloy as segregation type or compound forming type is always done according to the predominance in the first coordination sphere.

Fig. 4. Amorphous Ni₂₅Zr₇₅. Correlation functions.

3. Discussion of the Results

3.1. Pair Correlation Functions

The $G_{ij}(R)$ in Fig. 4 are shown only up to $R=8$ Å. However, they were calculated up to 20 Å [5]. Table 2 shows the atomic distances and partial coordination numbers as obtained from the main maximum of the $G_{ij}(R)$ -curves.

The Goldschmidt-diameter for coordination number 12 amounts to 2.49 Å for Ni and to 3.19 Å for Zr [6].

The Zr–Zr distance agrees well with the Goldschmidt-diameter of Zr, whereas the Ni–Ni-distance is larger. The observation that the Ni–Zr distance is distinctly smaller than the mean value of R_{ZrZr} and R_{NiNi} points to the chemical interaction between the Ni- and the Zr-atoms in the amorphous alloy.

In Fig. 4 the $G_{CC}(R)$ -curve is subdivided into nine regions:

- Region 1: (2.45 Å–3.08 Å). According to (3) G_{NiZr} dominates compared with G_{NiNi} .
Region 2: (3.08 Å–3.53 Å). G_{ZrZr} dominates.

The run of $G_{CC}(R)$ in the subsequent regions can easily be explained using (5) and the runs of G_{NiNi} , G_{ZrZr} , and G_{NiZr} .

Table 2. Amorphous Ni₂₅Zr₇₅. Atomic distances and partial coordination numbers.

Atom		Distance R_{ij} [Å]	Number Z_{ij}
Central	Surrounding		
Ni	Ni	2.63	1.8
Ni	Zr	2.66	8.6
Zr	Ni	2.66	2.8
Zr	Zr	3.16	10.9

3.2. Short Range Order Parameter

Since the atomic diameters 2.49 Å and 3.19 Å for Ni and Zr, respectively, are rather different, the short range order parameter η_{NiZr} according to Cargill and Spaepen [7] has to be applied, which is defined as

$$\eta_{NiZr} = \frac{Z_{NiZr}}{Z_{NiZr}^*} - 1 \quad (6)$$

with

$$Z_{NiZr}^* = \frac{c_{Zr} Z_{Ni} Z_{Zr}}{\langle Z \rangle}, \quad (7)$$

$$Z_{Ni} = Z_{NiNi} + Z_{NiZr}, \quad (8)$$

$$Z_{Zr} = Z_{ZrZr} + Z_{ZrNi}, \quad (9)$$

$$\langle Z \rangle = c_{Ni} Z_{Ni} + c_{Zr} Z_{Zr}, \quad (10)$$

η_{NiZr} is positive for compound formation, zero for statistical distribution, and negative for segregation tendency. Its possible values lie between $-1 \leq \eta_{NiZr}$

$$\leq \eta_{NiZr}^{\max} = \frac{c_{Ni} Z_{Ni}}{c_{Zr} Z_{Zr}}.$$

For compound forming tendency we use the normalized parameter

$$\eta_{NiZr}^{\circ} = \frac{\eta_{NiZr}}{\eta_{NiZr}^{\max}}. \quad (11)$$

With the data from Table 2 we obtain $\eta_{NiZr}^{\circ} = 0.14$, which means compound formation in amorphous Ni₂₅Zr₇₅.

We mention, that coordination numbers usually are determined with an error of $\Delta Z \pm 10\%$. This leads to an inaccuracy in η_{NiZr}° which therefore may cover the range $+0.35 \geq \eta_{NiZr}^{\circ} \geq -0.03$. The lower limit follows with $Z_{NiNi} + \Delta Z_{NiNi}$; $Z_{ZrZr} + \Delta Z_{ZrZr}$; $Z_{NiZr} - \Delta Z_{NiZr}$. The upper limit correspondingly with $Z_{NiNi} - \Delta Z_{NiNi}$; $Z_{ZrZr} - \Delta Z_{ZrZr}$; $Z_{NiZr} + \Delta Z_{NiZr}$.

In Table 3 we compare the R_{ij} -, Z_{ij} -, and η_{NiZr}° -data as obtained in the present work with those reported in [1].

Table 3. Amorphous Ni₂₅Zr₇₅. Atomic distances, partial coordination numbers, and normalized short range order parameter.

	Present work	[1]		Present work	[1]
R_{NiNi} [Å]	2.63	—	R_{NiZr} [Å]	2.66	2.83
Z_{NiNi}	1.8	—	Z_{NiZr}	8.6	9.9
R_{ZrZr} [Å]	3.16	3.22	$\eta_{\text{NiZr}}^{\circ}$	0.14	1.00
Z_{ZrZr}	10.9	10.8			

Table 4. Amorphous Ni_xZr_{1-x}-alloys. Short range order parameter.

Ni-concentration (atomic fractions)	Ref.	$\eta_{\text{NiZr}}^{\circ}$	Ni-concentration (atomic fractions)	Ref.	$\eta_{\text{NiZr}}^{\circ}$
0.25	[1]	1.00	0.50	[10]	0.19
0.25	this work	0.14	0.64	[11]	0.07
0.33	[1]	0.06	0.64	[12]	0.13
0.35	[8]	0.23	0.67	[13]	0.09
0.36	[9]	0.06			

In [1] the method of X-ray diffraction using anomalous dispersion was applied. With that method no Ni–Ni correlation could be found which, however, according to the present paper exists, namely 1.8 Ni-atoms around each Ni-atom at a distance of 2.63 Å. $Z_{\text{NiNi}} = 0$ means per definition $\eta_{\text{NiZr}}^{\circ} = 1 \pm 0$. The coordination number Z_{ZrZr} as obtained with both methods is in accordance, the discrepancies for R_{ZrZr} , R_{NiZr} ,

and especially $\eta_{\text{NiZr}}^{\circ}$ are substantial. The existence of a Ni–Ni correlation as proved in the present paper was predicted in [2] by Mössbauer-spectroscopy with amorphous Fe₁₀Ni_{90-x}Zr_x-alloys.

In Table 4 we present a compilation of short range order parameters $\eta_{\text{NiZr}}^{\circ}$ as reported up to date in the literature.

Apparently, the 1.00 value lies outside the range between 0.06 and 0.23 as obtained throughout the system of amorphous Ni–Zr-alloys. Furthermore we state that with the two different and well defined sets of three total structure factors the determination of the three partial functions was possible with rather high accuracy. From these two facts we conclude that Ni–Ni-pairs are really present in the first coordination shell in the Ni₂₅Zr₇₅-alloy. The reason why no direct Ni–Ni correlation has been found in [1] may be due to the ill-conditioned system of linear equations in the case of using anomalous X-ray scattering with the Ni₂₅Zr₇₅-alloy. This caused a very difficult estimation of the partial structure factors. The authors tried to overcome these difficulties by using a least squares minimization method which turned out to be very successful in the case of a-Ni₃₃Zr₆₇ [1] and a-Ni₆₇Zr₃₃ [12], but which seems to have failed in the case Ni₂₅Zr₇₅.

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