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RECENT STRUCTURAL RESULTS WITH AMORPHOUS ALLOYS USING NEUTRON DIFFRACTION

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Résumé - Les facteurs de structure partielle, les distances atomiques, les nombres de coordination partielle et les paramètres d'ordre à courte distance ont été déterminés pour les alliages amorphes Dy$_{80}$Ni$_{20}$ et Ni$_{80}$P$_{20}$. Les corrélations D - D ont été également déterminées dans un alliage amorphe Dy$_{69}$Ni$_{31}$ deutéré à 10 % at. Enfin, des mesures de diffusion aux petits angles utilisant le contraste variable de Ni dans am - Ni$_{80}$P$_{20}$ ont mis en évidence l'existence de deux phase de compositions différentes.

Abstract - Partial structure factors and partial pair correlation functions as well as atomic distances, partial coordination numbers and short range order parameters are presented for the amorphous alloys Dy$_{80}$Ni$_{20}$ and Ni$_{80}$P$_{20}$. Comparing to partial functions obtained earlier with Ni$_{81}$B$_{19}$ and Y$_{67}$Ni$_{33}$ we report on striking similarities between the partial pair correlation functions between those pairs which belong to one and the same of the following groups:

Group 1: Ni-P(from Ni$_{80}$P$_{20}$); Ni-B(Ni$_{81}$B$_{19}$); Ni-Dy(Dy$_{69}$Ni$_{31}$); Ni-Y(Y$_{67}$Ni$_{33}$)
Group 2: P-P(Ni$_{80}$P$_{20}$); B-B(Ni$_{81}$B$_{19}$); Ni-Ni(Dy$_{69}$Ni$_{31}$); Ni-Ni(Y$_{67}$Ni$_{33}$)
Group 3: Ni-Ni(Ni$_{80}$P$_{20}$); Ni-Ni(Ni$_{81}$B$_{19}$); Dy-Dy(Dy$_{69}$Ni$_{31}$); Y-Y(Y$_{67}$Ni$_{33}$)

With a-Dy$_{69}$Ni$_{31}$ containing 10a/o D we show that it will be possible to determine D-D correlations by neutron diffraction with an alloy made from zero-scattering Dy and from zero-scattering Ni.

With a-Ni$_{80}$P$_{20}$ we report for the first time on the evaluation of partial structure factors in the small Q-Region which show that a-Ni$_{80}$P$_{20}$ consists of two phases namely a matrix a certain c$_{Ni}$/c$_{P}$-ratio and regions with diameters of 15Å and a different c$_{Ni}$/c$_{P}$-ratio.

I - INTRODUCTION

The present paper is concerned with structural work performed recently within this laboratory by neutron diffraction using the method of isotopic substitution. Thus partial structure factors and partial correlation functions were obtained with the following amorphous alloys:

i) Dy$_{69}$Ni$_{31}$(+10a/o D) high Q-Region
ii) Ni$_{80}$P$_{20}$ high Q-Region
iii) Ni$_{80}$P$_{20}$ small Q-Region

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The total structure factor according to Faber Ziman for a ternary system containing the three atomic species 1, 2, and 3 can be written as

\[
S_{F.Z.}(Q) = \frac{c_1^2 b_1^2}{<b>^2} S_{11}(Q) + \frac{c_2^2 b_2^2}{<b>^2} S_{22}(Q) + \frac{c_3^2 b_3^2}{<b>^2} S_{33}(Q) + \frac{2c_1c_2b_1b_2}{<b>^2} S_{12} + \frac{2c_1c_3b_1b_3}{<b>^2} S_{13} + \frac{2c_2c_3b_2b_3}{<b>^2} S_{23} \tag{1}
\]

with

\[
<b> = c_1 b_1 + c_2 b_2 + c_3 b_3. \tag{2}
\]

From (1) it follows that the contribution \(S_{33}(Q)\) from deuterium (element 3) within the amorphous alloy formed by the elements 1 and 2 can be measured directly by one scattering experiment if

\[
b_1 = b_2 = 0. \tag{3}
\]

Equations (1) and (3) then yield

\[
S_{F.Z.}(Q) = S_{33}(Q). \tag{4}
\]

Four melt spun amorphous alloys were put into V-containing and at room temperature diffraction experiments were performed with the instrument D4B at the high flux reactor of ILL, Grenoble, using neutrons with a wavelength of 0.7 Å. At the same time the background scattering, the crucible scattering, and the Cd-rod scattering were measured.

The isotopic composition of the four specimens was as follows:

i) \(\text{natNi}}_{31}\text{natDy}_{69}\); nat = natural isotopic abundance,

ii) \(\text{natNi}}_{31}\text{0Dy}_{69}\); \(0_{\text{Dy}}\) = zero coherent scattering mixture of \(\text{natDy}\) and \(162_{\text{Dy}}\),

iii) \(\text{0Ni}}_{31}\text{natDy}_{69}\); \(0_{\text{Ni}}\) = zero coherent scattering mixture of \(60_{\text{Ni}}\) and \(62_{\text{Ni}}\),

iv) \(\text{0Ni}}_{31}\text{0Dy}_{69} + 10\text{a/o D};\) the deuterium was loaded under high pressure.

According to eqn. (1), specimen ii) should yield \(S_{\text{NiDy}}\), specimen iii) should yield \(S_{\text{DyDy}}\), and these two partials together with specimen i) should yield \(S_{\text{NiDy}}\).

Fig. 1 shows the partial Faber Ziman structure factors of the amorphous alloy \(\text{Dy}_{69}\text{Ni}_{31}\). These can be compared to those obtained with \(\text{Y}_{67}\text{Ni}_{33}\) by [2] and show pronounced similarity.

Apparently the Y atoms can be substituted by Dy without remarkable change in the structural arrangements.
The curve $S_{DD}$ shows the result of a scattering experiment obtained with $^{0}_{Dy}$Ni$_{31}$ + $^{10a/o}$D, i.e. an alloy which consisted of zero scattering Dy and zero scattering Ni and which was charged with 10a/o deuterium. It is interesting to note that the D-D distance within a D$_2$ molecule should show structural features near 10Å.

Fig. 2 shows the radial distribution functions calculated from the $S_{ij}$ in Fig. 1. The very small first peak in $C_{NiNi}^{NiDy}$ shows that contact of Ni-Ni atoms doesn't exist very often. The rather large difference 0.56 of the electro-negativities of Ni and Dy apparently leads to preference of Ni-Dy contacts. This is expressed in a rather strong first $G_{NiNi}$ maximum. In so far, there exists a striking similarity to Ni$_{33}$Y$_{67}$, too. From the RDF's the partial coordination numbers $Z_{NiNi}=3.2$, $Z_{DyDy}=14.7$, and $Z_{NiDy}=11.0$ were obtained yielding a relative Cargill-Spaepen short range order parameter $\eta_{NiDy}^{rel}=1.3%$. Thus the chemical short range order is about 25% of that obtained in [2] for Ni$_{33}$Y$_{67}$.

Table 1. Partial coordination numbers and short range order parameters.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$\eta_{AB \ rel} [%]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$<em>{31}$Dy$</em>{69}$</td>
<td></td>
</tr>
<tr>
<td>$Z_{NiNi}=3.2$</td>
<td></td>
</tr>
<tr>
<td>$Z_{DyDy}=14.7$</td>
<td></td>
</tr>
<tr>
<td>$Z_{NiDy}=11.0$</td>
<td></td>
</tr>
<tr>
<td>$Z_{DyNi}=5.0$</td>
<td></td>
</tr>
<tr>
<td>Ni$<em>{31}$Dy$</em>{69}$</td>
<td>1.3</td>
</tr>
<tr>
<td>Cu$<em>{33}$Y$</em>{67}$</td>
<td>1.8</td>
</tr>
<tr>
<td>Ni$<em>{33}$Y$</em>{67}$</td>
<td>5.4</td>
</tr>
<tr>
<td>Ni$<em>{81}$B$</em>{19}$</td>
<td>100</td>
</tr>
<tr>
<td>Ni$<em>{80}$P$</em>{20}$</td>
<td>100</td>
</tr>
<tr>
<td>Co$<em>{81}$P$</em>{19}$</td>
<td>100</td>
</tr>
</tbody>
</table>

Further details concerning neutron scattering experiments with amorphous Dy$_{69}$Ni$_{31}$ or Dy$_{70}$Ni$_{30}$ are given in [3,4].
The experimental procedure was the same as with Dy$_{69}$Ni$_{31}$. The isotopic composition of the three specimens was:

i) nat$_{80}$Ni$_{20}$

ii) $^{62}$Ni$_{80}$P$_{20}$

iii) $^{0}$Ni$_{80}$P$_{20}$

According to eqn. (1), specimen iii) should yield $S_{PP}$ and together with the results of specimen i) and ii) one obtains $S_{NiNi}$ and $S_{NiP}$.

The Bhatia-Thornton partial structure factors $S_{NN}(Q)$, $S_{CC}(Q)$, and $S_{NC}(Q)$ are plotted in Fig. 3 and their Fourier transforms in Fig. 4.

![Fig. 3 - Amorphous Ni$_{80}$P$_{20}$: Partial Bhatia-Thornton structure factors $S_{NN}(Q)$, $S_{CC}(Q)$, and $S_{NC}(Q)$.

![Fig. 4 - Amorphous Ni$_{80}$P$_{20}$: Partial density- and concentration-correlation functions $G_{NN}(R)$, $G_{CC}(R)$, and $G_{NC}(R)$.

The series of alternating positive and negative peaks of $G_{NN}(R)$ clearly shows how the atomic structure in the Ni$_{80}$P$_{20}$ glass is governed by chemical ordering effects. The short-range parameter, according to Warren and Cowley, may be calculated from:

$$\alpha = \int_{R_1}^{R_2} RG_{CC}(R)dR/\int_{R_1}^{R_2} (RG_{NN}(R)+4\pi R^2\rho dR)\int$$

where the integration limits $R_1 = 2.0$ Å and $R_2 = 2.88$ Å bound the first coordination shell defined by the principal peak of $G_{NN}(R)$ which covers the $R$ range of the first negative Ni-P- and the first positive Ni-Ni-peak of $G_{NN}(R)$. As a result we obtain $\alpha = -0.20$. The maximum possible value of $|\alpha|$ is given by the ratio of the concentrations $\alpha_{max} = c_P/c_Ni = 0.25$.

Table 2 shows a compilation of structural data obtained with the Faber-Ziman partials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Atomic pair</th>
<th>$R_{ij}$ (Å)</th>
<th>$z_{ij}$</th>
<th>$\delta_{ij}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous Ni$<em>{80}$P$</em>{20}$</td>
<td>Ni-Ni</td>
<td>2.56</td>
<td>9.4</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>P-Ni</td>
<td>2.28</td>
<td>9.3</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>Ni-P</td>
<td>2.28</td>
<td>2.3</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>P-P</td>
<td>3.73</td>
<td>5.3</td>
<td>0.53</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.30</td>
<td>3.3</td>
<td>0.55</td>
</tr>
</tbody>
</table>
The short range order parameter according to the definition given by Cargill III and Spaepen can be calculated from the partial $z_{ij}$ in Table 1 and we obtain $r_{Ni-P} = +0.13$ which is within the accuracy of partial $z_{ij}$ the maximum possible value, thus proving the complete chemical ordering in the Ni$_{80}$P$_{20}$ glass.

Fig. 5 shows a compilation of $G_{EE}(R)$ correlation functions, where $E$ means the smaller atom in the metallic glasses Ni$_{80}$P$_{20}$ /5/, Ni$_{81}$B$_{19}$, Ni$_{64}$B$_{36}$ /6/, Y$_{67}$Ni$_{33}$ /2/, Dy$_{69}$Ni$_{31}$, and Ti$_{60}$Ni$_{40}$ /7/, respectively. Hereby $R/R_m$ is normalized to the position $R_m$ of the largest peak in $G_{EE}(R)$. Keeping in mind that these examples are chosen from quite different groups of metallic glasses we observe exciting similarities: the peak at $R/R_m = 1$ is the main maximum of a double peak structure, and the preceding peak at $R/R_m = 0.5...0.65$ which reflects direct E-E contact is quite small or even not present at all. This suggests that the unlikelihood for close contact between the smaller component is, more or less pronounced, a general feature in the short range ordering which goes through all the different types of metallic glasses.

Fig. 5 - Partial pair correlation function $G_{BB}$ of the Ni-P-, Ni-B-, Y-Ni-, Dy-Ni-, and Ti-Ni-systems, where $B$ is the smaller atomic species.

IV - AMORPHOUS Ni$_{80}$P$_{20}$ ; SMALL Q-REGION ; /8/

Fig. 6 shows for the first time partial Bhatia Thornton structure factors in the small Q-region.
According to these curves the medium range structure consists of:

1) Small regions (15 Å diameter) which differ from the surrounding matrix only by the concentration (because \( S_{CC} \) rises with smaller \( Q \)) but not by the density, because \( S_{NN} \) remains constant.

2) Large regions (~1000 Å diameter) which differ from the surrounding matrix by the concentration and by the density.

In /8/ we presented a method, which allowed the determination of the concentration of the regions of kind i) and the ratio of Nickel to Phosphorus within these regions as well as within the matrix.

Introducing the following concentrations in atomic fractions:

- \( c_R \) = Concentration of regions within the specimen
- \( c_M = 1-c_R \) = Concentration of the matrix
- \( c_{NiR} = \) Concentration of Ni-atoms within the regions
- \( c_{Ni} = \) Concentration of Ni-atoms within the specimen
- \( c_P = 1-c_{Ni} \)

The evaluation finally leads to eqn. (6):

\[
2\pi^2 c_R (1-c_R)(c_{NiR} - c_R c_{Ni})^2 = c_{Ni} c_P \cdot 5.14 \cdot 10^{-3} \tag{6}
\]

This is the analytical form for the plot \( c_{NiR}/c_R \) shown in Fig. 7.

It should be noted that it is not possible to determine from diffraction experiments that point on this curve which represents the specimen under consideration. If we assume the regions to have the same \( c_{NiR}/c_P \) ratio as the first crystallization product \( Ni_3P \), i.e. \( c_{NiR}/c_P = 3 \), then we obtain as a result:

Atomic concentration of regions within the specimen \( c_R = 43.8 \) a/o.
Concentration ratio within the regions \( c_{NiR}/c_P = 3 \).
Concentration ratio within the matrix \( c_{NiM}/c_{PM} = 5.2 \).
This means a disproportion of the original ratio $c_{Ni}/c_p = 4$. Anyhow we should learn from this experiment that this amorphous alloy is not uniform, but heterogeneous.

It should be noted that the term "regions" as used in this paper do not mean well defined particles which then would be separated by a sharp interface from the matrix. Furthermore there are no features in the scattering functions which indicate any distance correlation between the "regions". These "regions" rather should be described as uncorrelated fluctuations in the amorphous structure where the system probably adjusts the short range order locally to that prevailing in the first crystallisation product, i.e. $Ni_3P$ in the case of $a-Ni_{80}P_{20}$.

Acknowledgement

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