Spinodal Decomposition in Ni-Nb-Y Metallic Glasses Analyzed by Quantitative Anomalous Small-Angle X-ray Scattering

G.Goerigk\textsuperscript{1} and N.Mattern\textsuperscript{2}

\textsuperscript{1}Institut für Festkörperforschung, Forschungszentrum Jülich, Postfach 1913, D-52425 Jülich, Federal Republic of Germany, \textsuperscript{2}Leibniz-Institute IFW Dresden, Institute for Complex Materials, P.O. Box 270116, D-01171 Dresden, Federal Republic of Germany

G.Goerigk@fz-juelich.de

Abstract. Phase separated Ni-Nb-Y metallic glasses were prepared by means of rapid quenching from the melt. Quantitative Anomalous Small-Angle X-ray Scattering experiments were performed at the K-absorption edges of Nickel, Niobium and Yttrium. The paper outlines, that the separation of the pure-resonant scattering contribution is obtained by employing the Gaussian algorithm on a vector equation. Moreover the quantitative analysis of the Resonant Invariant at the K-absorption edges of Niobium and Yttrium provided the chemical concentrations of Yttrium and Niobium in the random density fluctuations, which are attributed to spinodal decomposition. The results are compared to a partially crystallized sample annealed at 773 K over 30 minutes.

1. Introduction

In the last 3 decades the Synchrotron Radiation (SR) provided the small-angle X-ray scattering technique with major improvements. Among other improvements SR provides a photon flux, which is many orders higher compared to classical X-ray sources giving access to systems with only weak SAXS contributions like highly diluted chemical solutions or solid state systems like glasses or amorphous alloys, which are to a high degree homogeneous. Additionally the continuous energy spectrum of SR allows energy tunability in the vicinity of the K- and L\textsubscript{III}-absorption edges of most of the elements. This technique - known as Anomalous Small-Angle X-ray Scattering (\textit{ASAXS}) – is based on the anomalous variations of the atomic scattering factors near the absorption edges and allows the element-specific structural and quantitative characterization of the sample under investigation. After the exploratory studies of the 1980s \cite{1-3} \textit{ASAXS} became in the last decade a precise quantitative technique (\textit{q-ASAXS}), which combines the structural analysis with the quantitative analysis of chemical concentrations (i.e. fluctuations) of the different atomic species of a multi-component system by addressing the elements via the X-ray absorption edges \cite{4-10}.

The ternary Ni-Nb-Y system exhibits an extended miscibility gap in the liquid \cite{11}. By means of rapid quenching technique the decomposed melt can be frozen in to a phase separated metallic glasses \cite{12}. The critical temperature of liquid-liquid decomposition depends on the composition. For Ni content < 60 at\% a hierarchical heterogeneous microstructure is obtained with size distribution from

© 2010 IOP Publishing Ltd
10 nm up to 500 nm which can be analyzed by transmission electron microscopy (TEM). Such microstructures represent a coarsened state of spinodal decomposition, growth of the melts, and secondary decomposition within the liquids. For such phase separated Ni-Nb-Y glasses SAXS curves with fractal q-dependence have been observed [13]. For alloys with Ni > 60 at% early stages of phase separation can be obtained due to reduced critical temperature having fluctuation in nm dimensions with almost no contrast in TEM images. By means of ASAXS quantitative parameters of the fluctuation can be determined.

In this presentation, the application of the Gauss algorithm to the vector equation established by ASAXS measurements at three X-ray energies is demonstrated with the aim to separate the pure-resonant scattering contribution. Moreover the question shall be addressed, how to determine the amount of Yttrium respective Niobium atoms localized in the periodic fluctuations of Ni-Nb-Y metallic glasses undergoing spinodal decomposition with respect to the total amount of Y- respective Nb-atoms in the alloy, by quantitative analysis of what was introduced as the Resonant Invariant in a former publication [7].

2. ASAXS measurements

The remarkable possibilities of the ASAXS technique are based on the energy dependence of the atomic scattering factors giving selective access to the specific SAXS contributions of nanophases, which are built up by different chemical constituents in composites like for instance metallic glasses. In general the atomic scattering factors are complex quantities and energy dependent:

\[ f_Z(E) = f_{0Z} + f'_Z(E) + if''_Z(E) \]  

where \( Z \) represents the atomic number. In this presentation we will deal with the atomic scattering factors of Ni, Y and Nb: \( f_Z = f_{Ni}(E), f_{Y}(E), f_{Nb}(E) \). When performing a SAXS experiment at energies in the vicinity of the absorption edge of one of the elements, three different scattering contributions can be distinguished as a consequence of Eq.(1)[1]:

\[ I(q, E) = \Delta f^2_A A(q) + 2\Delta f_A \text{Re} A(q)[\Delta f_{0Z} + f'_Z(E)] \text{Re} B(q) + [\Delta f_{0Z} + f'_Z(E)]^2 + f''_Z(E)^2 \|B(q)\|^2 \]  

\( A(q) \) represents the scattering amplitude of the non-resonant scattering atoms and \( B(q) \) represents the scattering amplitude of the resonant scattering atoms in the energy range of the absorption edge. The quantity \( \Delta f^2_A = f_{0Z} - \rho_m V_Z \) is the electron density difference between the atom with the volume \( V_Z \) and the surrounding matrix of the alloy with the electron density \( \rho_m \). \( q \) is the magnitude of the scattering vector \( = (4\pi/\lambda) \sin \Theta \), where \( 2\Theta \) is the scattering angle and \( \lambda \) the X-ray wavelength. For instance in the case of the Ni-Nb-Y alloys \( \Delta f_{0Y} + f'_Y(E) \text{Re} B(q) \) represents the scattering amplitude (real part) of the inhomogeneously distributed Y-atoms in the alloy, when performing SAXS measurements in the energy range of the K-absorption edge of Yttrium, while \( \Delta f_A \text{Re} A(q) \) represents the scattering amplitude (real part) of the non-resonant scattering atoms i.e. Ni and Nb, with the contrast, \( \Delta f_A \), of the non-resonant scattering atoms with respect to the entire matrix.

When measuring the scattering curves at three energies in the vicinity of the absorption edge of the atoms with atomic number \( Z \) the following vector equation can be established:

\[ M_{ij}(E_i) \otimes A_j(q) = I_j(q, E_i) \]  

(3a)
The vector on the right side represents the scattering curves measured at the three different energies $E_1, E_2, E_3$ while the vector on the left side represents the squared, respectively multiplied, scattering amplitudes. The matrix, $M_{ij}(E_i)$, contains the atomic scattering factors, which are energy dependent in case of the resonant scattering atoms. Combining the matrix with the vector on the right side of the equal sign yields the so-called extended matrix:

$$
\begin{align}
\Delta f_A^2 & 2\Delta f_A[\Delta f_{0,Z} + f'_Z(E_i)]
\end{align}
$$

When applying the Gaussian algorithm (elimination procedure) to the extended matrix the so-called triangle matrix is obtained,

$$
\begin{pmatrix}
a_{11} & a_{12} & a_{13} & b_1 \\
0 & a_{22} & a_{23} & b_2 \\
0 & 0 & a_{33} & b_3
\end{pmatrix}
$$

where the $a_{i,j}, b_j$ are written in the matrix of Eq.(6):

$$
\begin{align}
G & F(E_1) & H(E_i) \\
0 & F(E_2) - F(E_1) & H(E_1) - H(E_i)
\end{align}
$$

with

$$
G = \Delta f_A^2
$$

$$
F(E_i) = 2\Delta f_A[\Delta f_{0,Z} + f'_Z(E_i)]
$$

$$
H(E_i) = (\Delta f_{0,Z} + f'(E_i))^2 + f''(E_i)^2
$$

When introducing the formula of Eq.(7) into the matrix of Eqs.(5-6) the squared Fourier transform (FT) of the form factor, $|B(q)|^2$, of the spatial distribution of the atoms with atomic number $Z$ can be calculated:

$$
|B(q)|^2 = \left[ \frac{I(q,E_1) - I(q,E_2)}{f'_Z(E_1) - f'_Z(E_2)} \right] \left[ \frac{I(q,E_1) - I(q,E_3)}{f'_Z(E_1) - f'_Z(E_3)} \right] \frac{1}{F(E_1,E_2,E_3)}
$$

$$
F(E_1, E_2, E_3) = f'_Z(E_2) - f'_Z(E_3) + \frac{f''_Z(E_1) - f''_Z(E_2)}{f'_Z(E_1) - f'_Z(E_2)} - \frac{f''_Z(E_1) - f''_Z(E_3)}{f'_Z(E_1) - f'_Z(E_3)}
$$

For this elimination procedure the matrix element $M'_{11}$ of the starting matrix - the so-called Pivotelement – must not be zero. After the first step the new 2x2 submatrix, $M'_{ij}$ with the new Pivotelement $M'_{22} = F(E_2) - F(E_1)$ is obtained. Again the new Pivotelement must be not zero or in
other words the difference \( M_{12}' = f'(E_2) - f'(E_1) \) obtained from Eq.(7) must be large enough to gain significant accuracy from the employed algorithm.

Due to Eq. (8) ASAXS provides a technique to access directly the scattering of the Z-atoms i.e. Ni or Y or Nb depending at which X-ray absorption edge the ASAXS measurements are performed. The structural information of the distribution of the Z-atoms (Ni or Y or Nb) in the alloy can be obtained from the analysis of \( |B(q)|^2 \), which we will call form factor for reason of convenience. More generally spoken, Eq. (8) provides a method, which gives access to the pure-resonant scattering contribution of the selected constituent of an alloy by measuring the small-angle scattering at only three suitable energies [5-10].

In addition to the structural information, which can be obtained from \( |B(q)|^2 \), important quantitative information related to the amount of inhomogeneously distributed Z-atoms can be deduced from the integral \( Q_Z \):

\[
Q_Z(E) = |\mathcal{F}_Z(E)|^2 \int_Q |B(q)|^2 d^3q
\]  

(9)

In analogy to the so-called invariant [14], we will call \( Q_Z(E) \) the Resonant Invariant of the inhomogeneously distributed resonant scattering Z-atoms. The invariant, \( Q_Z(E) \), as defined in Eq. (9), is related to the number density of inhomogeneously distributed Z-atoms, \( v_Z \), as was outlined in detail in a previous publication [7,10]:

\[
Q_Z(E) = |\mathcal{F}_Z(E)|^2 \int_Q |B(q)|^2 d^3q = (2\pi)^3 r_0^2 |\mathcal{F}_Z(E)|^2 v_Z \left( \frac{1}{V_Z} - v_Z \right)
\]  

(10a)

\[
\frac{dQ_Z(E)}{dq} = |\mathcal{F}_Z(E)|^2 4\pi |B(q)|^2 q^2
\]  

(10b)

where \( V_Z = 4\pi/3R_Z^3 \) is the volume of the Z-atoms with atom radius \( R_Z \) and \( r_0 \) is the classical electron radius. Eq. (10b) represents the first derivative of the resonant invariant with respect to \( q \). Finally from the quadratic Eq. (10a) two values for the number density of the Z-atoms can be calculated:

\[
\frac{V_Z - v_Z^2}{V_Z} = \frac{V_Z \cdot Q_Z(E)}{(2\pi)^3 r_0^2 |\mathcal{F}_Z(E)|^2} = \frac{1}{\int_Q |B(q)|^2 d^3q}
\]  

(11a)

\[
\frac{V_Z - v_Z^2}{V_Z} = \frac{1}{V_Z} \pm \sqrt{\frac{1}{4V_Z^2} - \frac{1}{(2\pi)^3 r_0^2 \int_Q |B(q)|^2 d^3q}}
\]  

(11b)

In this presentation only one of the two solutions is significant i.e. the negative sign. It should be mentioned that the number density calculated from Eq.(11b) includes the Z-atoms, which are homogeneously distributed in the alloy. These Z-atoms provide an isotropic scattering contribution at small \( q \)-values similar to the isotropic scattering of the alloys matrix atoms but with a different amount. As will be discussed in more detail below, the amount of the isotropic scattering contribution originating from these remaining Z-atoms in the matrix can be neglected.

3. Experimental

Pre-alloyed ingots were prepared by arc-melting elemental Ni, Nb and Y with purities of 99.9% or higher in a Ti-gettered argon atmosphere. To ensure homogeneity, the samples were remelted several
times. From these pre-alloys, thin ribbons (3 mm in width and 30 μm in thickness) with nominal compositions Ni$_{68}$Nb$_{16}$Y$_{16}$ were prepared by single-roller melt spinning under argon atmosphere. The casting temperature was 1923 K. The chemical compositions were determined by the titration technique. The resulting values were Ni$_{67.9}$Nb$_{17.3}$Y$_{14.8}$ for the as-prepared ribbons. These composition exhibit only slight deviations from the nominal value of up to ~1 at.%. For convenience, the nominal compositions are used in the following sections. Additionally, a partly crystallized sample, c-Ni$_{68}$Nb$_{16}$Y$_{16}$, was produced by heating part of the ribbons in a differential scanning calorimeter (DSC 7, Perkin Elmer) just above the temperature of the first exothermic crystallization event at 773 K over 30 min.

Anomalous small angle X-ray scattering (ASAXS) was measured with the JUSIFA beam line [15,16] at the DORIS storage ring at HASYLAB/DESY Hamburg. ASAXS sequences were performed for both samples Ni$_{68}$Nb$_{16}$Y$_{16}$ and c-Ni$_{68}$Nb$_{16}$Y$_{16}$ with three X-ray energies in the vicinity of the K-absorption edges of Nickel at 8333 eV and with four X-ray energies at the K-absorption edges of Yttrium at 17038.4 eV and Niobium at 18985.6 eV. The tables in Fig.1a-c provide the related anomalous dispersion corrections of Nickel, Yttrium and Niobium at the energies used in the experiment based on the calculations of Cromer and Liberman [17,18]. These were used to permit the separation of the Ni-, Y- and Nb-related pure-resonant scattering described in detail by Eqs. (1)-(8). The scattering intensity is calibrated into macroscopic scattering cross sections in units of cross section per unit volume [cm$^2$/cm$^3$]=[cm$^{-1}$]. Transmission measurements were performed with a precision of better 10$^{-3}$ (Δt/t=2.8x10$^{-4}$) using a special (windowless) photodiode (Hamamatsu S2387-1010N).

![Figure 1: Anomalous dispersion corrections of Nickel, Niobium and Yttrium obtained by Cromer-Liberman calculations [17,18]. The dots represent the X-ray energies, where the ASAXS measurements were performed. The minimum distance of 5 eV to the K-absorption edges was kept, to omit as far as possible the Resonant Raman Scattering, which is for all components of the alloys significant, due to the high chemical concentrations.](image-url)
measurements a beam time of 1h and for the related reference measurements a beam time of 20 min was accumulated at each energy and distance. This strategy was used in numerous publications emerging from the JUSIFA beam line in the last decade (see examples [5-8]) and compromises between the goal of accumulating sufficient scattering intensity (reducing the statistical error bars of the scattering curves) and reducing the influence of the significant beam instabilities of DORIS (2nd generation) as much as possible.

4. Results and Discussion
The SAXS curves, $d\sigma/d\Omega(q)$, of the two samples - Ni$_{68}$Nb$_{16}$Y$_{16}$, and c-Ni$_{68}$Nb$_{16}$Y$_{16}$ - measured at the energy $E=8029$ eV, 304 eV below the Ni-K edge are shown in Figure 2. The increasing intensity below $q < 0.2$ nm$^{-1}$ probably originates from surface scattering also present in the Ni-Nb-Y data. Additionally, the presence of a maximum in the curves gives clear evidence for the existence of correlated fluctuations in electron density for the Ni-Nb-Y alloys. Variation of the energy at the Y- and Nb- K-edges changes the cross section of the SAXS curves in opposite directions indicating that the inhomogeneities are related to clusters enriched in Y or in Nb in agreement with atom probe tomography results [19]. The occurrence of the maximum in the SAXS curves is due to the high density of electron density fluctuations with a dominant correlation length. Using the relationship correlation length $\zeta$ and peak maximum in reciprocal distances $\zeta = \frac{2\pi}{q_{\text{max}}}$ one obtains $\zeta=12.2$ nm.

![Figure 2: Total scattering curves of the alloy Ni$_{68}$Nb$_{16}$Y$_{16}$ with different heat-treatment: as-quenched (red circles) and heat-treated above the first crystallization point at 773 K but below the second crystallization point (blue squares). Above the first crystallization point the asymptotic behaviour of the scattering curves changes from $q^{-2}$ to $q^{-4}$ indicating smooth interfaces probably between the small crystallites and a surrounding amorphous phase.](image-url)

The influence of partial crystallization on the SAXS curves is shown by the comparison of the scattering curves of the alloy Ni$_{68}$Nb$_{16}$Y$_{16}$ far below the K-absorption edge at about 8 keV. (Ni$_{68}$Nb$_{16}$Y$_{16}$ as quenched, c-Ni$_{68}$Nb$_{16}$Y$_{16}$: heat treated at 773 K i.e. beyond the 1st crystallization event). The heat treated sample consists of a nanocrystalline Ni$_2$Y phase and a remaining amorphous Ni-Nb phase. The mean crystallite size is about 5 nm as can be seen from the TEM image in Figure 3b. The lattice parameter of the Ni$_2$Y phase indicates that to some extend Nb is still solved. No inhomogeneous structures could be resolved from the TEM image of the as-cast sample (Figure 3a). In the SAXS curves a dramatic change takes place for the sample, which was heat treated beyond the 1st crystallization temperature. Though the correlation maximum remains unchanged on the q-axis, it is shifted on the y-axis by nearly an order of magnitude probably due to a higher electron density contrast caused by a larger concentration gradient. Additionally the asymptotic behaviour changes from $q^{-2}$ to $q^{-4}$ indicating the formation of small crystallites with smooth interfaces to the surrounding amorphous phase.
phase. Obviously the fluctuation length of the as-quenched state determines the size of the nanocrystals. The phase separation of the glass is also the reason for different crystallization steps of the two phases (the amorphous Ni-Nb phase crystallizes into NbNi$_3$ at higher a temperature of about 900K). The ASAXS sequences of the alloys at three selected X-ray energies in the vicinity of the K-absorption edge of Ni show systematic but very small declination of the cross section in the range between 0.2 and 2 nm$^{-1}$ indicating small differences of Ni-amount in the concentration fluctuations, which constitute the correlation maxima of the alloy. A closer analysis of the resonant invariant obtained from the ASAXS sequences near the Ni-K-edge could not provide reliable numbers for a Ni-gradient (concentration), indicating that the difference of the Ni-concentration in the fluctuations is too small i.e. below the resolution of this experiment. Anyway, because the Nickel component serves as the matrix, the important quantitative parameters of decomposition are related to the concentration fluctuations of Yttrium and Niobium and thus can be only obtained from quantitative ASAXS ($q$-ASAXS) measurements at the K-absorption edges of Yttrium and Niobium.

Detailed quantitative information was obtained from the measurements at the K-absorption edges of Yttrium and Niobium. Figure 4a-b summarizes the results obtained from the Yttrium K-edge (17038 eV) for the two samples Ni$_{68}$Nb$_{16}$Y$_{16}$ and c-Ni$_{68}$Nb$_{16}$Y$_{16}$. The black squares in Figure 4...
represent the total scattering of the as-quenched sample (a) and the heat-treated sample (b). The correlation maximum appears for both samples at about 0.6 nm\(^{-1}\) as known already from the ASAXS measurements at the Ni-K-edge. The total scattering curves are superimposed by a strong isotropic scattering contribution, which originates mainly from the fluorescence of the Ni-component (68at\%). By calculating the separated scattering curves, \(I(q, E_1) - I(q, E_3)\), this isotropic fluorescence contribution is removed revealing a \(q^4\) behaviour in the asymptotic part of the separated scattering curve (blue triangles) of the heat-treated (crystallized) sample, which is already known from the measurements at the Ni-K-edge. As can be seen from the error bars of the separated scattering curve of the as-quenched sample (blue triangles) the asymptotic behaviour above 1 nm\(^{-1}\) is not clear i.e. beyond the resolution and needs a closer consideration by analyzing the pure-resonant scattering contribution with larger q-bins (see below). The solid lines in Figure 4a and 4b represent the \(q^2\) and \(q^4\) behaviour respectively.

![Figure 4: Total scattering curves (squares), separated scattering curves (triangles) and the form factors of the pure-resonant scattering contribution (circles) of the Y-related concentration fluctuations. Figures 6a-b represent the different heat-treatment: as-quenched (a) and partially crystallized (b). Above the first crystallization point the asymptotic behaviour of the scattering curves changes from \(q^2\) to \(q^4\) indicating smooth interfaces probably between the small crystallites and a surrounding amorphous phase. The solid line passing through the red circles of the pure-resonant scattering in Figure 6a represents a model function (see text).](image)

From Eq. 8, the pure-resonant scattering (or more precisely the form factor of the pure-resonant scattering) was calculated for both samples. Because the error bars of the pure-resonant scattering become rather large at higher q-values, especially for the as-quenched sample, the number of q-bins was reduced in comparison to the mixed-resonant and the total scattering curves, with the aim to obtain smaller error bars at q-values larger 0.5 nm\(^{-1}\). The procedure was as follows: the cross-section of the pure-resonant form factor was averaged over neighbouring q-bins. The result gives the cross-section at the centre of the averaged q-interval. The error of the averaged cross-section is the averaged squared error calculated from the errors of the single q-bins. Though the error bars are still large at higher q-values, the pure-resonant scattering for both samples was clearly resolved. Especially at
higher q-values of about 1 nm\(^{-1}\) the pure-resonant scattering contribution of the crystallized sample is nearly an order of magnitude higher compared to the as-quenched sample, indicating a larger amount of Yttrium atoms localized in the crystalline phase. Ni\(_2\)Y has more Y than the average alloy, even when some Nb is solved.

Figure 5: The first derivative of the Resonant Invariant (Eq. 10b) of Ni\(_{68}\)Nb\(_{16}\)Y\(_{16}\) as-quenched (a) and partially crystallized (b) obtained from ASAXS sequences at the Y-K-edge (17038 eV). The integrals (grey area) represent the Resonant Invariant (Eq. 10a) from which the Y-concentrations can be calculated. The right inset represents the upper limit of 16at% homogeneously distributed Y, contributing to the Resonant Invariant. The left inset explains the contribution, which is missing due to the q-resolution. For reason of convenience the division by 4\(\pi\) is not written at the vertical axis.

The latter was analyzed more precisely by employing the Resonant Invariant of Eq. 10. Figure 5 shows the first derivative of the Resonant Invariant (Eq. 10b) of the as-quenched sample (a) and the crystallized sample (b). The grey areas represent the integrals, Q\(_Z\) (i.e. the Resonant Invariant), which are introduced into Eq. 11 for the calculation of the amount of Yttrium atoms, \(Y_v\), which enter the concentration fluctuations of the as-quenched sample and the crystallites of the heat-treated sample respectively. From Eq. 11 an amount of 2.13(28) \(\times 10^{21}\) cm\(^{-3}\) Yttrium (excess) atoms, which enter the crystallites, was calculated corresponding to about 19% of the Y-atoms in the alloy.

A completely different result was obtained from the analysis of the Resonant Invariant of the as-quenched sample. As can be seen already from a simple comparison of the integrals of both samples in Figure 5, the amount of Yttrium atoms, which enter the concentration fluctuations of the as-quenched sample, must be much more smaller. From Eq. 11 a concentration of 0.39(20) \(\times 10^{21}\) cm\(^{-3}\) Yttrium atoms was deduced, which corresponds to an amount of only 4% Yttrium atoms.

Though this result is significant, it is near the resolution limits of the experiment as can be seen from the error bars in Figure 5a. For a more quantitative discussion of the result, the limited integration area has to be extended onto the whole regime \(0 \leq q < \infty\). Because no comprehensive description of the scattering curves of a ternary alloy undergoing spinodal decomposition is at hand, a model function with a \(q^2\)-behaviour (Ornstein-Zernike originally for binary systems, Eq. 12) was
employed. The model function serves only as a guide for the eye with the aim to estimate the amount of the ‘missing’ scattering contributions at higher and lower q-values i.e. beyond the resolution of the experiment.

\[ i(q) = \frac{\text{const}}{c + q^2} \]  \hspace{1cm} (12)

At \( q=0 \) the model function reaches a finite value defined by thermodynamic parameters of the alloy (Eq.12) and the first derivative of the Resonant Invariant approaches 0 with \( q \to 0 \). The amount of missing contribution to the Resonant Invariant can be neglected as can be seen from the left inset in Figure 5a, which shows a magnified part of the Resonant Invariant in the low q-range. The missing part below the resolution at q-values smaller \( q_{\text{min}} \) is the area between the grey histogram and the solid line of the model function.

The right inset in Figure 5a represents the contribution of homogeneously distributed Y-atoms with a concentration of 16at\% to the Resonant Invariant. Although this corresponds to the maximum possible amount – a considerable portion of the Y-atoms are localized in the fluctuations – the contribution is many orders of magnitude smaller than the contribution detected from the Y-atoms in the concentration fluctuations and thus can be also neglected.

Considering the scattering contributions beyond the q-resolution at higher q-values the result must be interpreted as a lower limit as is demonstrated by of the model function (Figure 5a). At higher q-values a cut-off of the scattering function is expected, because otherwise the integral of Eq. 11 would become infinite and the invariant would not exist. As can be seen from Figure 5a the cut-off of the pure-resonant form factor cannot be resolved due to the large error bars and if the cut-off is located at q-values beyond 2 nm\(^{-1}\), the concentration of Yttrium atoms must be higher. In the case of the crystallized sample the scattering curve at larger q-values is deep in the Porod regime and no significant contribution can appear in the integral at higher q-values.

Table I: Structural and quantitative parameters of the two alloys (one of them with different heat-treatment). Column \( \zeta \) is the correlation length. \( \bar{\kappa}(Y) \), \( \bar{\kappa}(Nb) \) give the amount of Yttrium respective Niobium atoms localized in the concentration fluctuations calculated from the Resonant Invariant at the related K-absorption edges. The two columns \( c_Y \) and \( c_{Nb} \) contain the amount in percent of the complete amount of Yttrium or Niobium atoms respectively. The latter concentrations were obtained from the averaged atomic volume, which was calculated from the average atomic weight (68.999 g/mol) and the average density (8.147 g/cm\(^3\)) of the alloy. Additionally the corresponding volume fractions, \( \Phi_Y \) and \( \Phi_{Nb} \), have been calculated (see text).

| Sample         | \( \zeta \) \[nm\] | \( \bar{\kappa}(Y) \) \[10^2[\text{cm}^3]\] | \( c_Y \) [%] | \( \bar{\kappa}(Nb) \) \[10^2[\text{cm}^3]\] | \( c_{Nb} \) [%] | \( \Phi_Y \) [%] | \( \Phi_{Nb} \) [%] |
|----------------|---------------------|----------------------|-----------------|----------------------|-----------------|-----------------|-----------------|
| Ni\(_{68}\)Nb\(_{16}\)Y\(_{16}\) | 12.2               | 0.39(2)              | 4               | 0.6                  | 1.3(3)          | 12              | 1.9             |
| c-Ni\(_{68}\)Nb\(_{16}\)Y\(_{16}\) | 12.2               | 2.1(3)               | 19              | 3.0                  | 1.8(3)          | 16              | 2.5             |

The same arguments hold for the interpretation of the results obtained from the \textit{ASAXS} measurements at the Nb-K-edge. Again the asymptotic behaviour of the pure-resonant scattering turns from \( q^2 \) to \( q^4 \), when applying a heat-treatment beyond the 1\(^{st}\) crystallization temperature. The amount of Niobium atoms in the fluctuations of the as-quenched sample calculated from the Resonant Invariant turns out to be higher (with respect to Yttrium) corresponding to about 12\% of the complete
Niobium amount in the alloy (Table 1). Surprisingly the amount of Niobium atoms is only slightly higher for the partially crystallized sample i.e. 16% of the complete Nb-amount, indicating that the spatial distribution of Niobium in the alloy does not change much, when the partial crystallization (Ni$_2$Y-phase) takes place. This may be attributed to the fact, that the Niobium component crystallizes beyond the 2$^{nd}$ crystallization temperature (beyond 900 K), which we have not yet reached.

![Figure 6: Normalized electron density of the as-quenched sample (a) and the partially crystallized alloy (b).](image)

The step functions represent the volume fractions of the two phases, Y-rich and Nb-rich respectively. The dashed lines show the normalized electron density of homogeneously distributed atoms in the two alloys.

From the concentrations of Y and Nb deduced from the Resonant Invariant in the as-quenched and the partially crystallized state respectively the related volume fractions, $\Phi_Y$ and $\Phi_{Nb}$, can be estimated using the averaged atom volumes of the alloy for $V_Y$ and $V_{Nb}$. In a further step the normalized electron densities have been calculated. The results are summarized in Figure 6. In Figure 6a the normalized electron density of the as-quenched sample is depicted within one correlation period. The dashed line represents the average electron density resulting from homogeneously distributed atoms in the alloy, which cover nearly 97% of the entire volume. The step function shows the different volume fractions of inhomogeneously distributed Yttrium, 0.6%, and Niobium, 1.9%, respectively. The integral of the step function over one correlation period amounts to 1. The inset shows a magnification of the step function with the oscillating function giving a more realistic sketch of a continuously changing concentration over the correlation length.

Again the dashed line in Figure 6b represents the average electron density resulting from homogeneously distributed atoms in the partially crystallized alloy. Because the amount of inhomogeneously distributed Y and Nb increased to 3% and 2.5% respectively (black step function) the value of the volume fraction covered by homogeneously distributed material is reduced to about 93%. The area between the two vertical lines, the step function and the dashed line depicts the volume fraction of the additional amount of Yttrium (excess) atoms in the crystallized phase with respect to the surrounding matrix, while the intersection of the vertical lines with the x-axis represent the volume fraction of the spatial extension of the crystallites, i.e. 55%.

In both Figures the contrast between the Y-rich and the Nb-rich phases is negative explaining the declination of the scattering cross section, when approaching the K-absorption edge of Niobium, while the scattering cross section becomes larger, when approaching the K-absorption edge of Yttrium.

5. Conclusions
In the last years Anomalous Small-Angle X-ray Scattering became a precise quantitative method ($q$-ASAXS) for element specific structural analysis on the mesoscopic length scale. Due to the precision of the techniques small-angle scattering contributions of Ni$_{68}$Nb$_{16}$Y$_{16}$ alloys in the resolution regime $10^{-3} < \Delta I/I < 10^{-2}$ were reliably separated from a superimposed, orders of magnitude larger inelastic background caused by fluorescence and Resonant Raman Scattering. The separated pure-resonant scattering contributions were obtained by employing the Gauss algorithm to a vector equation, which represents the ASAXS measurements at different X-ray energies.

The pure-resonant scattering contributions of inhomogeneously distributed Nickel, Niobium and Yttrium atoms in Ni$_{68}$Nb$_{16}$Y$_{16}$ alloys with different heat-treatment have been separated from the total scattering SAXS curves. The separated scattering curves obtained from the as-quenched sample, show the typical behaviour of concentration fluctuations (Ornstein-Zernike) with a correlation maximum corresponding to a correlation length of 12.2 nm. From the Resonant Invariant an amount of 4% and 12% of the Yttrium atoms and Niobium atoms respectively was found to be localized in the fluctuations corresponding to volume fractions of 0.6 and 1.9% respectively. This compares to about 19% (3% volume fraction) of enriched Yttrium atoms localized in the crystalline phase of the sample, which was heat-treated beyond the 1st crystallization temperature. Surprisingly the amount of enriched Niobium atoms does not change much due to the latter heat-treatment (from 12% to 16%) indicating that the crystallization temperature for the Niobium phases is not yet reached. A model calculation suggests a large volume fraction of 55% covered by small crystallites beyond the 1st crystallization temperature surrounded by an amorphous shell enriched with Nb with a volume fraction of 45%.

The example demonstrates the capability to determine quantitatively the extent of spinodal decomposition in metallic glasses by Anomalous Small-Angle X-ray Scattering.

References

[1] Stuhrmann H B 1985 Adv. Polym. Sci. 67, 123
[2] Simon J P, Lyon O and de Fontaine D J 1985 Appl. Cryst. 18, 230
[3] Stuhrmann H B, Goerigk G and Munk B 1991 In: Ebashi S, Koch M, Rubenstein E, editors. Handbook on Synchrotron Radiation Vol. 4. Amsterdam: Elsevier; 555.
[4] Goerigk G and Williamson D L 2001 J. Non-Cryst. Solids 281, 181
[5] Goerigk G, Schweins R, Huber K and Ballauff M 2004 Europhys. Lett. 66(3), 331
[6] Goerigk G and Williamson D L 2006 J. Appl. Phys. 99, 084309
[7] Goerigk G, Huber K and Schweins R 2007 J. Chem. Phys. 127, 154908
[8] Bota A, Varga Z and Goerigk G 2007 J. Phys. Chem. B 111, 1911
[9] Bota A, Varga Z and Goerigk G 2008 J. Phys. Chem. C 112, 4427
[10] Goerigk G and Mattern N 2009 Acta Mater. 57, 3652
[11] Mattern N, Zinkevich M, Löser W, Behr G and Acker J 2008 J. Phase Equil. Diff. 29, 141
[12] Mattern N, Kühn U, Gebert A, Gemming T, Zinkevich M, Wendrock H and Schultz L 2005 Scripta Materialia 53, 271
[13] Mattern N, Gemming T, Goerigk G and Eckert J 2007 Scripta Mater. 57, 29
[14] Glatter O and Kratky O. 1982 Small-Angle X-ray Scattering, Academic Press, London
[15] Haubold H G, Gruenlager K, Wagener M, Jungbluth H, Heer H, Pfeil A, Rongen H, Brandenburg G, Moeller R, Matzerath J, Hillel P and Halling H 1989 Rev. Sci. Instrum. 60, 1943
[16] Goerigk G 2006 'Electronic and Computer Upgrade at ASAXS Beamline JUSIFA', HASYLAB Annual Report p. 77
[17] Cromer D T and Liberman D 1970 J. Chem. Phys. 53, 1891
[18] Cromer D T and Liberman D 1981 Acta Cryst. A37, 267
[19] Mattern N, Goerigk G, Vainio U, Miller M K, Gemming T and Eckert J 2009 Acta Mater. 57(3), 903