# Combination of EXAFS and Differential Anomalous X-ray Scattering for Studying $Ni_2Zr$ Amorphous Alloy

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In this paper we report a first application of the new idea of combining EXAFS and differential anomalous scattering techniques to obtain partial distribution functions for a binary amorphous sample. This method has been successfully employed in extracting Ni–Ni and Ni–Zr pair distribution functions for $Ni_2Zr$ prepared by mechanical alloying. A comparison with results from previous studies is also reported.

*Key words:* Metallic glasses, Synchrotron radiation, Partial pair distribution functions.

## I. Introduction

The technological and scientific interest for amorphous metallic alloys has recently showed a considerable growth [1]. They often are named advanced materials for their high performance properties as needed by today technology.

In order to promote a wider application of this kind of materials a deep knowledge of the structure-properties is required. This, on the other hand, involves development of advanced techniques able to provide fine structural information.

To completely characterize the short range structure of a metallic glass the partial distribution functions (PDFs) must be obtained from suitable experiments. For the simplest case of a binary system, some examples can be found where PDFs are calculated by Fourier transforming the partial structure factors (PSFs) obtained from experiments in which changes in the scattering power of atomic species arise [2–8]. At least three independent experiments are needed.

Neutron diffraction studies on three samples with different isotopic composition offers a good chance to obtain the three PSFs [2–4]. In this case sufficiently high changes in the scattering powers allow to obtain a well conditioned system of linear equations. This system does not suffer dramatically of experimental errors in input data and can be solved with usual procedures. However, some problems may arise in preparing different samples with suitable isotopes.

Another possibility is now available thanks to the tunability and high intensity of synchrotron radiation which allows the performance of high quality diffraction measurements in a wide range of energies, so they can be used to determine PSFs [5–8] via the anomalous X-ray scattering method (AXS). This technique is based on the energy dependence of the scattering factors near an absorption edge due to anomalous dispersion phenomena. In this case, because of the smallness of the changes in the scattering power, an ill-conditioned system of linear equations must be usually solved. The introduction of differential structure factors (DSFs) often allows to reduce the conditioning of such systems [9]. A differential structure factor is calculated by taking the difference between two sets of data collected at two energies just below an absorption edge of an atomic species *i*. In this case all correlations not involving *i* atoms are cancelled out since only the scattering factor of the *i* atoms changes significantly. The resulting DSF contains contributions relative to only two partial structure factors.

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This technique, referred as differential anomalous scattering (DAS), provides local information about the environment of an atomic species similar to that provided by Extended X-ray Absorption Fine Structure (EXAFS) technique. Really, these two techniques are complementary because they cover different ranges of the reciprocal space [10].

In this paper we elucidate a new interesting possibility which consists in combining DAS and EXAFS techniques [11] in order to obtain the partial distribution functions by solving a system of integral equations. We then apply this method in the case of $Ni_2Zr$ amorphous alloy, using both model and experimental data. A comparison with results from previous investigations is also given.

## II. General Formalism

For a binary amorphous system the total structure factor, $a(s, E)$, obtainable from X-ray scattering data, can be expressed, in the Faber-Ziman formalism, as a weighted sum of three PSFs $a_{ij}$ [12, 13]:

$$a(s, E) = w_{11}(s, E)\, a_{11}(s) + 2 w_{12}(s, E)\, a_{12}(s) + w_{22}(s, E)\, a_{22}(s)\,, \quad (1)$$

$$w_{ij}(s, E) = c_i\, c_j\, f_i\, f_j^* / \langle f \rangle^2\,, \quad (2)$$

$$\langle f \rangle^2 = |c_1 f_1 + c_2 f_2|^2\,, \quad (3)$$

$$f_i(s, E) = f_i^0(s) + f_i'(s, E) + i f_i''(s, E)\,, \quad (4)$$

where $s$ is the scattering vector, $E$ the photon energy and $c_i$ and $f_i$ are the concentration and the atomic scattering factor of species $i$, respectively. $f_i^0$ is the Fourier transform of the electron density, $f_i'$ and $f_i''$ are the real and imaginary part of the anomalous dispersion correction.

Naming E1, E2 and E3, E4 the two energies near the absorption $k$-edge of atom 1 and 2, respectively, we can write

$$\mathrm{DSF}_1(s, \mathrm{E1}, \mathrm{E2}) = \Delta w_{11}(s, \mathrm{E1}, \mathrm{E2})\, a_{11}(s) + 2 \Delta w_{12}(s, \mathrm{E1}, \mathrm{E2})\, a_{12}(s)\,, \quad (5)$$

$$\mathrm{DSF}_2(s, \mathrm{E3}, \mathrm{E4}) = 2 \Delta w_{12}(s, \mathrm{E3}, \mathrm{E4})\, a_{12}(s) + \Delta w_{22}(s, \mathrm{E3}, \mathrm{E4})\, a_{22}(s)\,, \quad (6)$$

$$\Delta w_{ij}(s, \mathrm{E}\alpha, \mathrm{E}\beta) = \frac{w_{ij}(s, \mathrm{E}\alpha) \langle f(\mathrm{E}\alpha) \rangle^2 - w_{ij}(s, \mathrm{E}\beta) \langle f(\mathrm{E}\beta) \rangle^2}{\langle f(\mathrm{E}\alpha) \rangle^2 - \langle f(\mathrm{E}\beta) \rangle^2}\,. \quad (7)$$

Now, let us focus the attention on EXAFS experiments.

When two absorption measurements are performed at the K-edge of the atomic species 1 and 2, respectively, each EXAFS signal can be expressed in terms of two contributions coming from different backscattering atoms surrounding the atom $i$, that is

$$\chi_1(k) = c_1\, \chi_{11}(k) + c_2\, \chi_{12}(k)\,, \quad (8)$$

$$\chi_2(k) = c_1\, \chi_{21}(k) + c_2\, \chi_{22}(k)\,, \quad (9)$$

$k$ being the photoelectron wave vector.

Both $\mathrm{DSF}_i(s)$ and $\chi_i(k)$ contain the same information about the chemical environment around the atomic species $i$. In fact the partial functions $a_{ij}(s)$ and $\chi_{ij}(k)$ are related to the partial distribution functions $g_{ij}(r)$ by the following integral equations:

$$a_{ij}(s) = 1 + \frac{4\pi \varrho_0}{s} \int_0^\infty r(g_{ij}(r) - 1) \sin(sr)\, \mathrm{d}r\,, \quad (10)$$

$$\chi_{ij}(k) = 4\pi \varrho_0 \frac{f_j(k, \pi)}{k} \int_0^\infty g_{ij}(r)\, e^{-2r/\lambda(k)} \sin[2kr + \psi_{ij}(k)]\, \mathrm{d}r\,, \quad (11)$$

where $\varrho_0$ is the average atomic density and $f_j(k, \pi)$ the backscattering amplitude of atoms of type $j$; $\exp(-2r/\lambda(k))$ is a mean free path term taking into account the inelastic losses, and $\psi_{ij}(k)$ is the total phase shift. The wavenumber vector $k$ is related to the scattering vector $s$ by $s = 2k$.

Making use of these relations, it is in principle possible to involve the four equations (5), (6), (8), and (9) to form a system of integral equations whose solutions are the unknown $g_{ij}(r)$.

It must be pointed out that the combination of DAS and EXAFS measurements, taken at the K-edge of only one atomic species, is able to provide two $g_{ij}(r)$ (i.e. $g_{11}$ and $g_{12}$ or $g_{21}$ and $g_{22}$). This possibility can be conveniently applied when the measurements near the edge of one of the atomic species is impossible or is affected by errors.

In this paper, we use this simple approach to obtain Ni–Ni and Ni–Zr PDFs. The possibility to obtain the Zr–Zr PDF has not been considered since, as discussed elsewhere [14], the scattering measurements near the Zr K-edge are affected by some unhomogeneities due to a residual crystalline Zr phase in the sample. A similar procedure was proposed several years ago in studying amorphous $Fe_{1-x}B_x$ alloys ($x = 0.15 \ldots 0.20$), for which the B–B correlation was ignored [15]. In this previous study, however, one TSF from the X-ray diffraction experiment was used instead of DSF.

## III. Mathematical Scheme

A full description of the mathematical scheme can be found in [15]; only the changes to treat DSF rather than TSF are here reported.

For a binary compound the Equations (5) and (8) describing, respectively, the differential structure factor and the EXAFS function calculated at the K-edge of an atomic species 1, can be written in the following form

$$\begin{aligned} U_1 &= A_{11}\, h_{11} + A_{12}\, h_{12}\,, \\ U_2 &= B_{11}\, h_{11} + B_{12}\, h_{12}\,, \end{aligned} \tag{12}$$

where $h_{11} = g_{\mathrm{Ni-Ni}}(r) - 1$, $h_{12} = g_{\mathrm{Ni-Zr}}(r) - 1$; while the integral operators $A_{1j}$ and $B_{1j}$ are defined as

$$A_{1j}\, h_{1j} \equiv \frac{4\pi\,\varrho_0}{s}\,\Delta w_{1j}(s, \mathrm{E1}, \mathrm{E2}) \int\limits_{a_j}^{b_j} r\, h_{1j}(r) \sin(sr)\, \mathrm{d}r\,, \tag{13}$$

$$B_{1j}\, h_{1j} \equiv 4\pi\,\varrho_0\, c_j\, \frac{f_j(k, \pi)}{k} \int\limits_{a_j}^{b_j} h_{1j}(r)\, e^{-2r/\lambda(k)} \cdot \sin(2kr + \psi_{1j}(k))\, \mathrm{d}r\,, \tag{14}$$

$a_j$ and $b_j$ being the finite limits in *r*-space of the $h_{1j}$.

The functions $U_i$ include the experimental values and asymptotes of the elements $\mathrm{A}_{1j}$ and $B_{1j}$, which arise from the fact that the interval of $h_{1j}$ functions is finite:

$$U_1(s) = \mathrm{DSF}_1(s) - 1 + \sum_{j=1}^{2} T_{1j}(s)\,, \tag{15}$$

$$U_2(k) = \chi_1(k) + \sum_{j=1}^{2} T_{2j}(s)\,. \tag{16}$$

The additional terms $T_{1j}(s)$ and $T_{2j}(s)$ take into account the passage to the finite limits in *r*-space:

$$T_{1j}(s) = \frac{4\pi\,\varrho_0}{s}\,\Delta w_{1j}(s, \mathrm{E1}, \mathrm{E2}) \int\limits_{0}^{a_j} r \sin(sr)\, \mathrm{d}r\,, \tag{17}$$

$$T_{2j}(k) = -4\pi\,\varrho_0\, c_j\, \frac{f_j(k, \pi)}{k} \int\limits_{a_j}^{\infty} e^{-2r/\lambda(k)} \cdot \sin(2kr + \psi_{1j}(k))\, \mathrm{d}r\,. \tag{18}$$

The solution of the system (12) belongs to the class of inverse ill-posed problems [16]. The mathematical procedure has been described in details in [15]. In this paper the final expressions for calculation by the regularization method with iterative refinement is presented.

The system (12) can be manipulated so that a system of linear algebraic equations in regularized form is obtained:

$$\begin{bmatrix} U_1 \\ U_2 \end{bmatrix} = \begin{bmatrix} A_{11} & A_{12} \\ B_{11} & B_{12} \end{bmatrix} \begin{bmatrix} h_{11} \\ h_{12} \end{bmatrix}, \tag{19}$$

$$\begin{bmatrix} \xi_1 A_{11}^* U_1 + \xi_2 B_{11}^* U_2 \\ \xi_1 A_{12}^* U_1 + \xi_2 B_{12}^* U_2 \end{bmatrix} = \begin{bmatrix} \xi_1 A_{11}^* A_{11} + \xi_2 B_{11}^* B_{11} + C_1 & \xi_1 A_{11}^* A_{12} + \xi_2 B_{11}^* B_{12} \\ \xi_1 A_{12}^* A_{11} + \xi_2 B_{12}^* B_{11} & \xi_1 A_{12}^* A_{12} + \xi_2 B_{12}^* B_{12} + C_2 \end{bmatrix} \cdot \begin{bmatrix} h_{11} \\ h_{12} \end{bmatrix}. \tag{20}$$

Here, $\xi_1$ and $\xi_2$ are weighting coefficients introduced to balance the importance of the DSF and EXAFS data. The symbol * denotes transposition. The matrix $C_j$ has the general form

$$C_j = \begin{bmatrix} \alpha_j + 2\beta_j & -\beta_j & 0 & \dots & 0 \\ -\beta_j & \alpha_j + 2\beta_j & -\beta_j & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & 0 & \dots & \alpha_j + 2\beta_j \end{bmatrix}, \tag{21}$$

where $\alpha_m$ and $\beta_m$ are the regularization parameters, usually characterized by small positive values.

The matrix of the system (20) is symmetric and positive definite. Now it is nondegenerate due to the presence of the matrices $C_j$. Thus a standard method of calculating a reciprocal matrix can be used (in our case, the square root method [16]).

## IV. Experimental

Details about sample preparation, data collection, experimental apparata and data processing for EXAFS and X-ray scattering are discussed elsewhere [8, 14, 17]. Here only the fundamentals are reported.

$Ni_2Zr$ amorphous alloy was prepared by milling elemental powders in a high energy mill with the steel vessel under an argon atmosphere. The amorphization process was followed by X-ray diffraction spectra measured on portions of powder at different steps of the milling time.

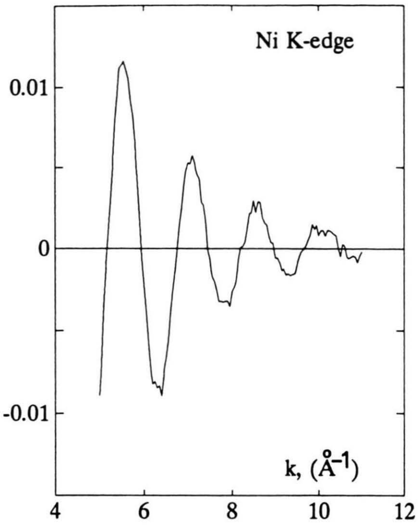

Fig. 1. Experimental EXAFS spectrum, $\chi(k)$, measured above Ni K-edge.

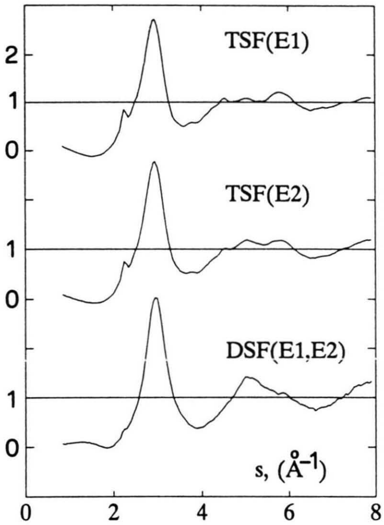

Fig. 2. Experimental total structure factors measured at E1 = 8.200 keV and E2 = 8.329 keV. Differential structure factor (below) relative to Ni K-edge.

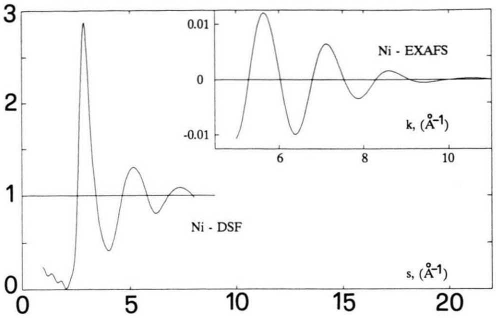

Fig. 3. Input data for the numerical experiment: differential structure factor and EXAFS spectrum, calculated by model functions, relative to Ni K-edge.

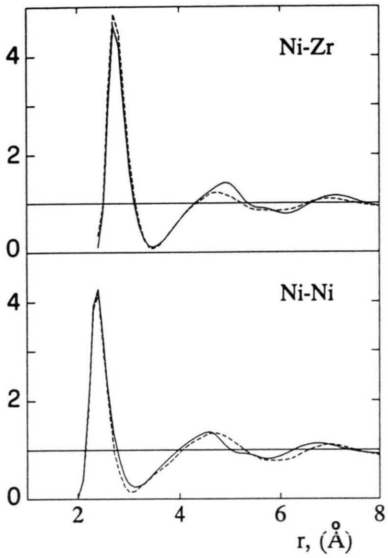

Fig. 4. Results from the numerical experiment: model partial distribution functions $g_{ij}(r)$ (dashed lines) and solutions (full lines) obtained by regularization procedure.

The X-ray scattering and EXAFS experiments were carried out at Lure using DCI synchrotron radiation source. The EXAFS interference function $\chi(k)$ and the differential structure factor, used as input information to obtain the PDFs, are shown in Figs. 1 and 2, respectively. In Fig. 2, the two TSFs involved in calculating the DSF are also shown.

Some features in the TSFs, in particular the small peak at about 2.2 Å$^{-1}$, due to a residual Zr crystalline phase, are cancelled out in DSF. This effect was expected, as the scattering power of Zr is the same at the two energies used to calculate the $\mathrm{DSF}_{\mathrm{Ni}}$. On the contrary, the crystalline contributions are enhanced in $\mathrm{DSF}_{\mathrm{Zr}}$. For this reason only $\mathrm{DSF}_{\mathrm{Ni}}$ was considered in this paper.

## V. Results and Discussion

As a first step, we carried out a model calculation with the aim of testing the regularization procedure when the input functions are available in limited

Table 1. Values of the parameters used in the regularization procedures. $\xi_j$: weighting coefficients to balance DSF and EXAFS input data, respectively; $\alpha_j$ and $\beta_j$: parameters defining the regularization matrices $C_j$; $a_j$ and $b_j$: finite limits (Å) of the investigated $r$ ranges for Ni–Ni and Ni–Zr.

| | | | |
|---|---|---|---|
| $\xi_{DSF} = 1$ | $\xi_{EXAFS} = 250$ | | |
| $\alpha_1 = 0.1$ | $\beta_1 = 0.01$ | $a_1 = 2.0$ | $b_1 = 13.9$ |
| $\alpha_2 = 0.25$ | $\beta_2 = 0.01$ | $a_2 = 2.4$ | $b_2 = 14.3$ |

Table 2. Comparison of peak positions and coordination numbers relative to the first shell of input $g_{ij}(r)$ and of the solutions obtained from the model calculation.

| | $R$ (Å) | $N$ |
|---|---|---|
| Ni–Ni model | 2.42 | 6.6 |
| Ni–Ni solution | 2.42 | 5.8 |
| Ni–Zr model | 2.78 | 4.4 |
| Ni–Zr solution | 2.78 | 4.7 |

Table 3. Comparison of peak positions and coordination numbers relative to the first shell of the PDFs obtained from experimental data.

| | Ni–Ni | | Ni–Zr | |
|---|---|---|---|---|
| | $R$ (Å) | $N$ | $R$ (Å) | $N$ |
| Present work | 2.49 | 6.27 | 2.72 | 5.00 |
| AXS study [8] | 2.58 | 5.98 | 2.72 | 4.83 |

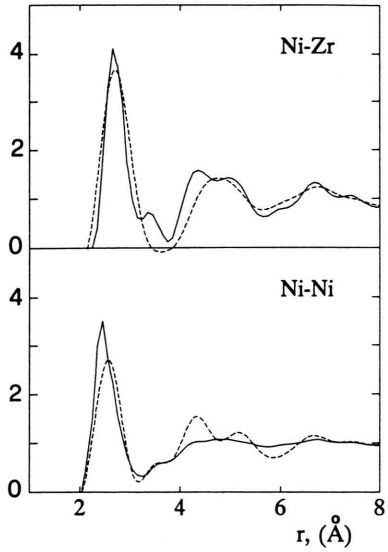

Fig. 5. Results from experimental data: partial distribution functions $g_{ij}(r)$ from AXS study [8] (dashed lines) and solutions (full lines) obtained by regularization procedure.

ranges of the reciprocal space. Obviously, in the case of an error free model the best values for the regularization parameters would be $\alpha = \beta = 0$. However, non-zero values typical of an experimental situation were used in practice.

Model PSFs for the $Ni_2Zr$ amorphous alloy were calculated in the $s$-range [0.05–30 Å$^{-1}$] by solving Percus-Yevick equations [18]. Then the PDFs for Ni–Ni and Ni–Zr were calculated by Fourier transformation. This allows to model $DSF_{Ni}$ and EXAFS data using (5) and (8), respectively. These functions are reported in Figure 3. The range for model calculations was set to $s \in$ [0.95–8 Å$^{-1}$] for $DSF_{Ni}$ and $k \in$ [5–11 Å$^{-1}$] for EXAFS in order to simulate the experimental situation. Anomalous corrections at E1 = 8200 eV and E2 = 8329 eV were determined earlier [8]. Backscattering amplitude and phase shifts for EXAFS were taken from Teo and Lee tables [19]. Some other parameters are collected in Table 1.

The PDFs obtained by the numerical experiment are compared in Fig. 4 with the model ones. Distances and coordination numbers for the Ni–Ni and Ni–Zr first coordination shell are compared in Table 2.

The agreement is quite good, in particular in the region of the nearest distances. Some troubles appear beyond 5 Å, which can be ascribed to an insufficient input information regarding the high $r$ region.

These results support the possibility to perform the same calculation by using our experimental DSF and EXAFS data. The regularization parameters used were those reported in Table 1. The PDFs thus obtained are shown in Fig. 5 and compared with the PDFs obtained by anomalous X-ray scattering on the same sample [14]. The structural parameters of the first shell of coordination are compared in Table 3.

As discussed in [14] the results obtained by the AXS study are to be considered quite good, so they provide a significant reference to evaluate the present results.

For both Ni–Ni and Ni–Zr PDFs the behaviour of the first peak, and its structural parameters, show a sufficient agreement with the AXS results. Nevertheless, going to look at the medium range only a general resemblance between the two results can be found but detailed features are not reproduced. This partial disagreement in the medium range can be assigned to an uncompleted experimental input information. In particular the difficulties to interpret straightforwardly the low $k$ features of the absorption experiment (due to multiple scattering effects) force to leave out this important source of information. Furthermore, when light elements ($Z < 30$) are studied by AXS the resulting DSFs are available in a limited $s$ range ($s_{\max} < 9\ \text{Å}^{-1}$). The combination of these two lacks hampers experimental data to cover entirely the reciprocal space with a significant range of superimposition.

However we believe that this first result is important since it shows that EXAFS and DSF data can be combined to obtain reliable partial distribution functions for disordered material. Important improvements should be possible when the reciprocal space investigated will be extended either interpreting low $k$ EXAFS data in terms of multiple scattering or when heavier atoms are objects of the investigation.

Really, this method must be considered as a further possibility to obtain partial distribution functions in a complementary way with AXS and neutron scattering with isotopic substitutions.

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