

# DESY SUMMER STUDENT PROJECT



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## **Study of thermal expansion of Fe-based metallic glass by pair distribution function**

*Area of research:*

Photon Physics, Material Science

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## Short description of the research project

Presented project dealt with comparison of exact and approximative calculation of the pair distribution function and total structural factor using of the PDFgetX3 software [1]. Also the analysis of XRD data of the  $\text{Fe}_{76}\text{Mo}_8\text{Cu}_1\text{B}_{15}$  alloy was done and its Curie temperature was determined from the volume thermal expansion curve.



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## 1 Introduction

$\text{Fe}_{76}\text{Mo}_8\text{Cu}_1\text{B}_{15}$  is material which belongs to the NANOPERM-type nanocrystalline alloys. This kind of alloy is usually prepared by melt spinning technique which is followed by proper crystallization of amorphous precursor. Such annealing yields a microstructure with considerable amount of the residual amorphous phase in which are randomly dispersed nanometer (10-30 nm) sized crystals of Fe-bcc phase. Due to their specific microstructure, nanocrystalline materials exhibit excellent soft magnetic properties, such as low coercivity, high permeability and relatively high magnetic saturation [2].

Amorphous materials can be characterized by short range order. The atomic pair distribution function (PDF) is powerful tool to determinate local atomic structure of highly disordered materials such as metallic glasses and nanocrystalline alloys. The PDF can give us information about the interatomic bond length, coordination number and degree of atomic disorder. Thus we can quantitatively describe local atomic environment of materials with high degree of structural disorder [3].

## 2 Goals of the research project

The main goal of this project is to study thermal expansion behavior of the  $\text{Fe}_{76}\text{Mo}_8\text{Cu}_1\text{B}_{15}$  amorphous alloy using PDF method. Particular goals can be divided in to two main parts:

- Comparison of two different approaches for calculation of PDF. The first approach is based on the exact calculation whereas the second one is based on the PDFgetX3 software.
- Quantitative comparison of thermal expansion data of  $\text{Fe}_{76}\text{Mo}_8\text{Cu}_1\text{B}_{15}$  amorphous alloy obtained by the exact and approximative PDF calculations.

### 3 PDF (pair distribution function)

The Fourier transformation of the scattered intensity is known as atomic pair distribution function (PDF). The PDF basically gives us the information about the changes in atomic density with respect to the mean atomic density as a function of the radial distance  $r$ . Such a analysis method can be applied for both crystalline or amorphous systems. From PDF we can determine some important material properties such as coordination number, interatomic distance, mean atomic density etc. [3].

Reduced pair distribution function is defined as

$$G(r) = 4\pi r[\rho(r) - \rho_0] = \frac{2}{\pi} \int_0^{\infty} q[S(q) - 1] \sin(qr) dq, \quad (1)$$

where  $\rho_0$  is the mean atomic density,  $\rho(r)$  is the local atomic density,  $r$  is the radial distance,  $q$  is the wave-vector and  $S(q)$  is the total structure factor. Reduced pair distribution function can be also given by expression

$$G(r) = 4\pi r\rho_0[g(r) - 1], \quad (2)$$

where  $g(r)$  is normalized pair distribution function so that, as  $r \rightarrow \infty$ ,  $g(r) \rightarrow 1$ . From the expression (2) we can tell that the reduced pair distribution function  $G(r)$  oscillates around zero in the limit of large radial distance  $r$ . In the limit of  $r \rightarrow 0$  we can write for the reduced pair distribution function following expression

$$G(r) = -4\pi r\rho_0. \quad (3)$$

From expression (3) we can determine the mean atomic density  $\rho_0$ . On the other hand, positions of various peaks give us information about the distance of various neighbors from the central atom [3]. Other important parameter which is average coordination number can be calculated from the radial distribution function (RDF) which is defined as

$$RDF(r) = 4\pi r^2\rho_0 + rG(r). \quad (4)$$

Then the average coordination number can be calculated as

$$N = \int_{r_1}^{r_2} RDF(r) dr. \quad (5)$$

In the expression (1) for the calculation of the reduced pair distribution function we can find the total structure factor  $S(q)$ , which describes intensity distribution and it is continuous function of the wave-vector  $q$ . The total structure factor can be calculated according to Faber-Ziman formalism [4] as

$$S(q) = 1 + \frac{I_{eu}^{coh}(q) - \langle f^2 \rangle}{\langle f \rangle^2}, \quad (6)$$

where  $I_{eu}^{coh}$  is coherent scattering,  $\langle f^2 \rangle = \sum_{i=1}^N c_i f_i^2(q)$  and  $\langle f \rangle^2 = [\sum_{i=1}^N c_i f_i(q)]^2$  in which  $c_i$  are the atomic concentrations of the atomic species of type  $i$  and  $f_i(q)$  is the tabulated atomic scattering factor of the  $i$ -th atom [4]. To obtain coherent scattering  $I_{eu}^{coh}$  from measured data, following corrections have to be applied:

1. parasitic (air, sample container) scattering correction,
2. multiple scattering correction,
3. polarization correction,
4. absorption correction,
5. normalization,
6. inelastic (Compton) scattering correction,
7. Laue diffuse correction.

## 4 Experimental part

### 4.1 Samples and methods

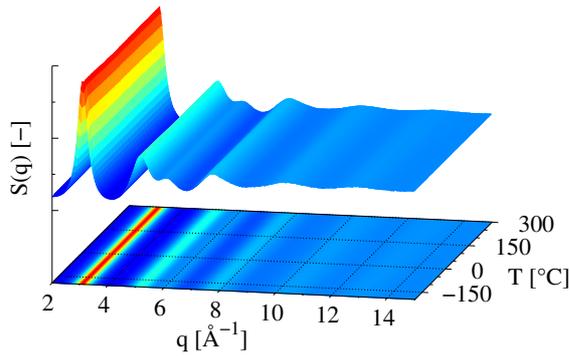
The sample with nominal chemical composition  $\text{Fe}_{76}\text{Mo}_8\text{Cu}_1\text{B}_{15}$  (at %) was prepared in the form of thin ribbon (thickness 20  $\mu\text{m}$ , width 2 mm) by single roller melt spinning technique. About five pieces were stacked together in order to enhance scattering intensity of X-ray diffraction experiment (XRD).

X-ray diffraction experiment was done at the beamline BW5 of the positron storage ring DORIS III (Hamburg, Germany). The energy of photon beam was set to 100 keV, ( $\lambda = 0.123984 \text{ \AA}$ ). XRD experiments were done in the temperature range from  $-195^\circ\text{C}$  to  $300^\circ\text{C}$  with the heating rate of  $20^\circ\text{C}/\text{min}$ . Samples were put into quartz capillary (wall thickness 20  $\mu\text{m}$ ) with a diameter of 1.2 mm and placed inside a Linkam THMS 600 hot stage. X-ray diffraction patterns were continuously recorded in transmission mode using a two-dimensional detector (Perkin Elmer 1621,  $2048 \times 2048$  pixels, pixel size  $200 \times 200 \text{ mm}^2$ ). The temporal resolution between two consecutive diffraction patterns was 12 seconds.

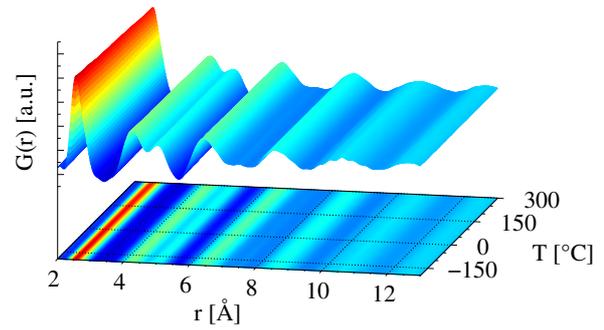
### 4.2 Results and discussion

#### 4.2.1 Thermal expansion

The PDF and the total structural factor were obtained from raw measured data with help of the PDFgetX3 software [1]. The PDF and the total structural factor show almost no temperature dependence. This fact can be seen in Figures 1 and 2.



**Figure 1:** Series of  $S(q)$  as a function of  $T$ .



**Figure 2:** Series of PDFs as a function of  $T$ .

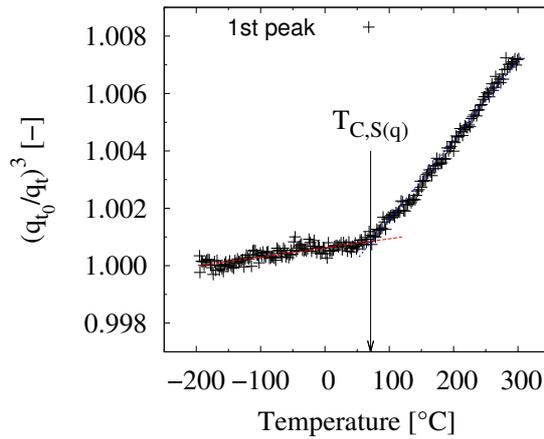
According to [5] relative change in the center of mass of the first diffuse peak can reveal important properties about volume changes and following equation is useful for such analysis:

$$\left[ \frac{q_i(T_0)}{q_i(T)} \right]^3 = \frac{V(T)}{V(T_0)} = 1 + \alpha^q(T - T_0), \quad (7)$$

where  $q_i(T)$  is the center of the mass of  $i$ -th peak at the temperature  $T$  from the reciprocal space,  $V(T)/V(T_0)$  is the reduced mean atomic volume at temperature  $T$  and  $\alpha$  is the volume thermal expansion coefficient. Similar analysis can be done for data in real space:

$$\left[ \frac{r_i(T)}{r_i(T_0)} \right]^3 = \frac{V(T)}{V(T_0)} = 1 + \alpha^l(T - T_0), \quad (8)$$

where  $r_i(T)$  is the center of the mass of the  $i$ -th peak from the real space at the temperature  $T$ . The first two peaks from each reciprocal and real space were fitted by two Gaussian functions and the center of mass for each single peak was determined. Higher coordinations shells of the PDF was also used for analysis. Centers of mass were calculated numerically. The third power of relative change of the peak's center of mass (from PDF and  $S(q)$  function) shows temperature dependence what can be seen in Figures 7 and 9. From these temperature dependences can be seen thermal expansion of the alloy and its transition from ferromagnetic to paramagnetic state. Also the Curie temperature ( $T_C$ ) can be determined from this data analysis which can be seen in the Figure 3. It is worth to note that the change in the slope takes place at the Curie temperature at which transition from ferromagnetic to paramagnetic state occurs. Similar analysis was applied for every single peak appearing on the PDF. Calculated values for the Curie temperature can be found in the Table 1. The Curie temperature was calculated from change in position of the first two peaks in the  $S(q)$  and from the first seven peaks visible on the PDF.



**Figure 3:** Temperature dependence of the third power of the relative change of the first peak position from reciprocal space.

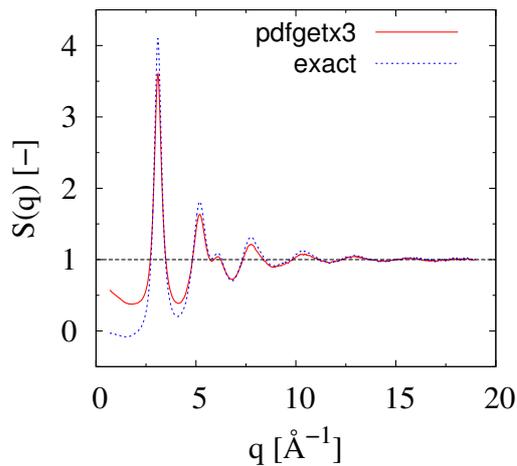
Peak number	$T_{C,PDF}$ [°C]	$T_{C,S(q)}$ [°C]
1	86	71
2	87	84
3	71	-
4	69	-
5	85	-
6	70	-
7	77	-
mean	78	77
$\sigma$	8	9

**Table 1:** Curie temperature calculated from PDF and  $S(q)$ .

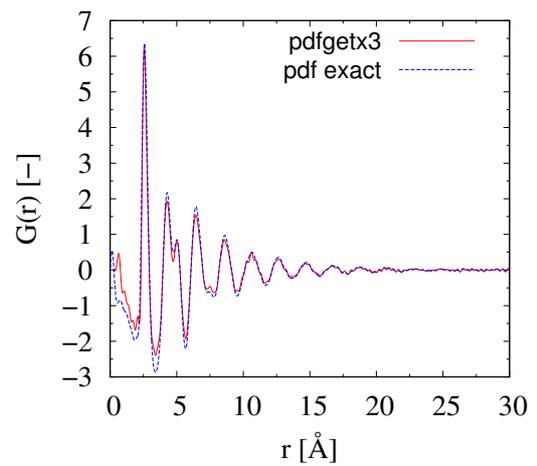
#### 4.2.2 Comparison of the exact and approximative calculation of PDF

The PDF method was used for data analysis and as it was mentioned before this method is very useful tool for analysis of amorphous material. The PDF was calculated in two different ways with the same  $q_{max} = 19 \text{ \AA}^{-1}$ . In the first step the PDFs and the total structure factor  $S(q)$  were calculated by the exact method and after that the PDFgetX3 software was used. All calculations were done from the same data set.

The PDFgetX3 is highly automated software which implements an ad-hoc data reduction algorithm which is able to generate PDFs in very short time. This software program requires little user input and it is very useful for evaluation of many data sets. The PDFgetX3 is written in the Python programming language and it was tested on Windows, Linux and Mac operating systems. Only few parameters have to be specified for the calculation of PDF. It is necessary to specify the wavelength and the approximative composition of the sample. One of the advantages of this software is interactive



**Figure 4:** Comparison of  $S(q)$  of the  $\text{Fe}_{76}\text{Mo}_8\text{Cu}_1\text{B}_{15}$  alloy at the temperature of  $-194.9^\circ\text{C}$  calculated by the exact and approximative method with help of the PDFgetX3, respectively.



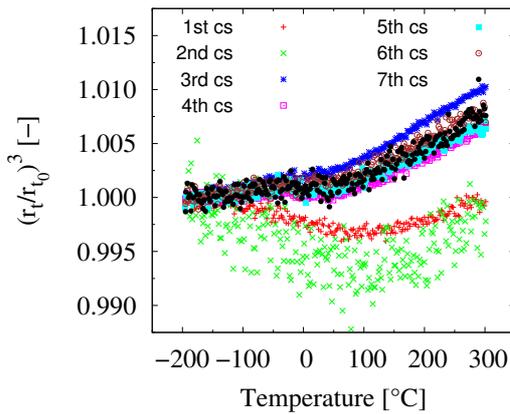
**Figure 5:** Comparison of PDF of the  $\text{Fe}_{76}\text{Mo}_8\text{Cu}_1\text{B}_{15}$  alloy at the temperature of  $-194.9^\circ\text{C}$  calculated by the exact and approximative method with help of the PDFgetX3 software, respectively.

mode which offers various tuning parameters. In this mode it is possible to change these parameters and PDFs are updated in real time in a plot window [1].

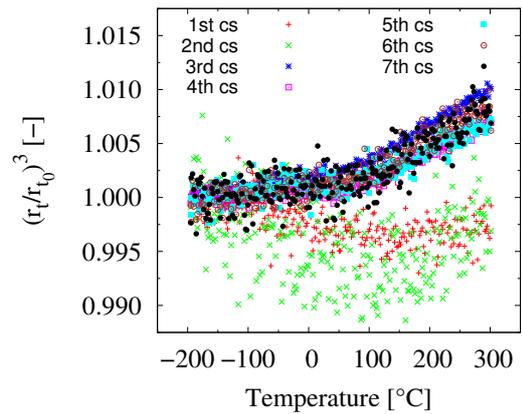
According to [1] the PDFs obtained from the PDFgetX3 are found to be similar to the PDFs calculated by exact method for such samples as nickel ( $\text{Ni}$ ), barium titanate ( $\text{BaTiO}_3$ ) or  $\gamma$ -alumina ( $\text{Al}_2\text{O}_3$ ).

Comparison of PDFs and total structural factors of data set obtained from the  $\text{Fe}_{76}\text{Mo}_8\text{Cu}_1\text{B}_{15}$  sample revealed some differences between the exact and approximative method. In the figure 4 can be seen the comparison of the total structural factors calculated by the exact and approximative methods. There is the difference between these two functions which was confirmed by calculation of the relative change. As can be seen in Figure 5 there are changes mainly in the low  $r$  part of the PDF, from which the mean atomic density  $\rho_0$  is calculated. On the other hand, peaks positions are found to be very similar and they vary only slightly. It also can be seen that areas of single peaks vary so the information about the average coordination number can be distorted.

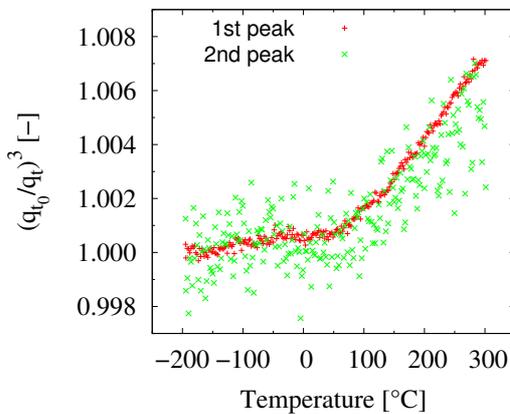
Relative change of the center of mass of single peaks of the total structural factor is shown in the figures 8 and 9. From these figures it can be seen that the difference between the relative center of mass of specific peaks of PDF is notable mainly for the first and the second peak (coordination shell). There is not such a noticeable difference between the relative center of mass of specific peaks in the reciprocal space.



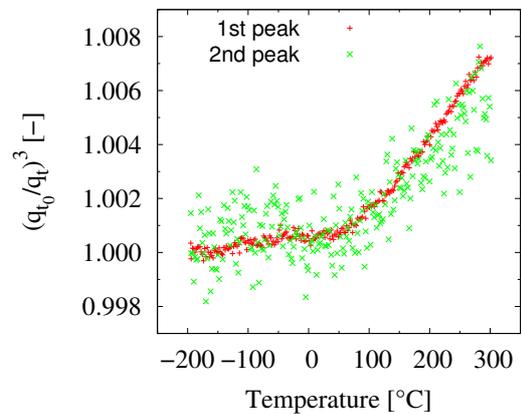
**Figure 6:** Relative change of the center of mass of PDF calculated by the exact method.



**Figure 7:** Relative change of the center of mass of PDF calculated by the approximative method.



**Figure 8:** Relative change of the center of mass of total structural factor calculated by the exact method.



**Figure 9:** Relative change of the center of mass of total structural factor calculated by the approximative method.

## 5 Conclusions

$\text{Fe}_{76}\text{Mo}_8\text{Cu}_1\text{B}_{15}$  samples in the form of thin ribbons were measured at temperatures from  $-195\text{ }^\circ\text{C}$  to  $300\text{ }^\circ\text{C}$  with heating rate  $20\text{ }^\circ\text{C}/\text{min}$ . PDFs and  $S(q)$  functions were calculated by both, the exact and approximative method from the same data set. As for the approximative method the PDFgetX3 software programme was used. Results show that there are some differences between the exact and approximative method, mainly in the low  $r$  part and peaks areas thus it is impossible to precisely determine the mean atomic density  $\rho_0$  and coordination number  $N$ . However PDFgetX3 seems to be very helpful tool for big data sets evaluation because its promptness and interactive mode. This temperature measurement also shows that it is possible to track ferromagnetic-to-paramagnetic transition by in-situ XRD and coefficient of the volume thermal expansion  $\alpha$  changes its slope at the Curie point. Therefore Curie temperature could be calculated

from temperature dependence of the third power of peak positions from each real and reciprocal space. Both mean values (calculated from PDF and  $S(q)$ ) of Curie temperature are similar.

### Acknowledgement

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