

# DESY SUMMER STUDENT PROJECT



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## **Study of Fe-base nanoparticles by pair distribution function**

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## Short description of the research project

This projects deals with Fe nanoparticles prepared by controled precipitation of copper matrix. Series of X-ray diffraction (XRD) patterns of Fe nanoparticles acquired in-situ during constant rate heating experiment up to 600 °C. All XRD patterns were processed using the pdfgetx3 program [1]. In this way corresponding structure factors  $S(q)$  and reduced pair distribution functions  $G(r)$  were calculated. The main accent was put on determination of the mean grain size from PDF therefore the experimental settings (namely angular resolution) were optimized so that PDF offers resolving power in the high  $r$ -region. The mean value of diameter of nanoparticle is 15.3 nm. This value is in very good agreement with 15 nm, obtained from TEM observations.



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## 1 Introduction

Nanomaterials refer to a family of materials in which a single unit is having size (at least in one dimension) between 1 and 100 nm. Due to large specific surface, particles in nanomaterials exhibit high number of atoms on their surface in comparison with the number of atoms in their inside. As a consequence, nanomaterials usually show strong size-dependence of various physical properties such as optical, magnetic and electrical, which is not a case for bulk materials [2]. Size-dependent properties are observed such as superparamagnetism in magnetic materials.

Currently there are many established methods for preparation of nanoparticles such as arc-discharge, sol-gel, co-precipitation etc. [2]. Nanoparticles described in this report were prepared by precipitation in solid state and isolated by electrochemical dissolution of matrix. This project deals with spherical iron nanoparticles with diameter smaller than 20 nm. Such nanoparticles have specific core-shell structure. The core consists of  $\alpha$ -Fe whereas the shell is passivated by oxygen layer, which is very common for iron nanoparticles. Figure 1 shows sketch of iron nanoparticles with the core-shell structure described in this research project. When decreasing the particles' diameter down to the critical size of cca. 8 nm, they became superparamagnetic [3].

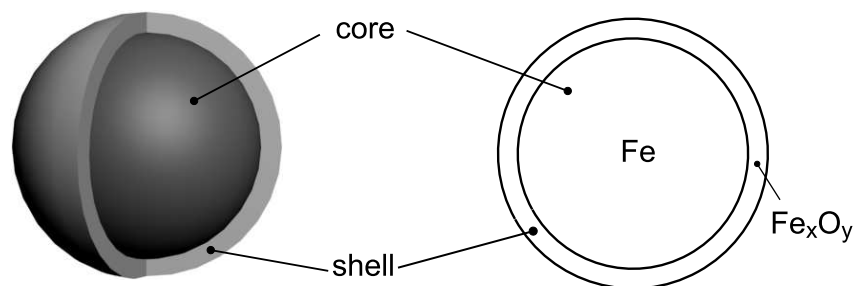


Figure 1: The core-shell structure of Fe-nanoparticle (reproduced from [3]).

## 2 Goals of the research project

The main goal of the project is to study atomic structure of the Fe nanoparticles during constant rate heating in-situ X-ray diffraction experiment. Partial goals of this project can be divided into two groups:

- analyze in-situ X-ray diffraction data in real space using the pdfgetx3 software
- determine grain size of nanoparticles from the pair distribution function

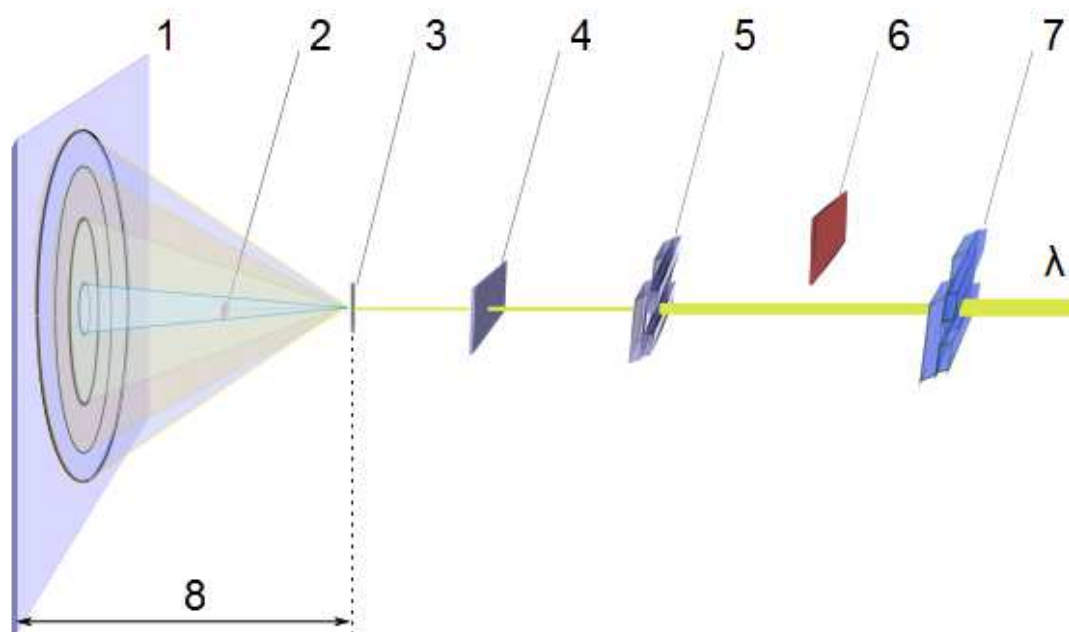
### 3 Experimental part

#### 3.1 Preparation of samples

The nanoparticles were produced by precipitation in solid state of Cu-Fe alloy with 1.25 wt.% Fe. The alloy was solution annealed at 1000 °C for 24 hours then quenched into the water. Supersaturated solid solution was precipitation annealed at 700 °C for 3 hours and subsequently was quenched into the water. Prepared precipitates were isolated from the copper-rich matrix by electrochemical dissolution. Electrolyte consisted of aqueous solution  $NH_4OH + H_2O_2$  with volume ratio 17:3 was used for potentiostatic dissolution of matrix at constant potential -230 mV. Nanoparticles were agglomerated by magnet, separated from electrolyte, several times washed in pure ammonia solution and dried at ambient condition [4, 5].

#### 3.2 High-energy X-ray diffraction at P02.1

Diffraction experiments were carried out at the P02.1 beamline of the accelerator ring PETRA III at DESY (Hamburg, Germany). The sketch of the beamline can be seen in Fig. 2. XRD experiments were done in transmission mode using a monochromatic photon beam having the energy of 59.82 keV ( $\lambda = 0.20727 \text{ \AA}$ ). Diffraction patterns were recorded using a two-dimensional image plate detector Perkin Elmer 1621 (2048



**Figure 2:** Schematic drawing of the high resolution powder diffraction beamline P02.1: 1 – detector, 2 – beam stop, 3 – sample, 4 – pinhole, 5 – secondary slits, 6 – small shutter, 7 – primary slits, 8 – sample-to-detector distance.

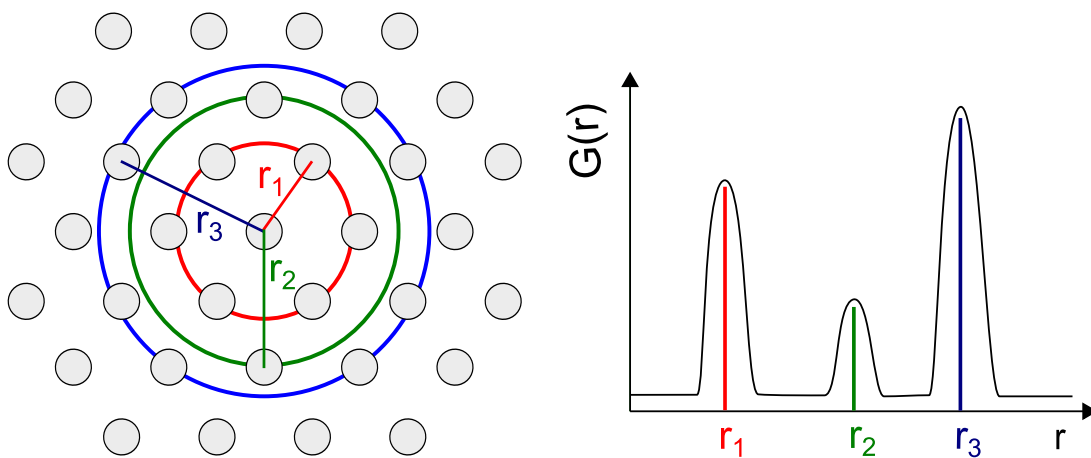
$\times 2048$  pixels, pixel size  $200 \mu\text{m} \times 200 \mu\text{m}$ , 16 bit intensity resolution). The Perkin Elmer 1621 is a fast detector and can acquire up to 15 full frames per second. Radial integration of the diffraction patterns was done using the software package Fit2D [6]. Room temperature X-ray diffraction experiments were realized at two different sample-to-detector distances in order to provide proper angular resolution for reciprocal and real space analysis, respectively. In-situ XRD experiments at elevated temperatures were realized using heating stage Linkam THMS600 available at the beamline P02.1. These studies were performed in the temperature range between 20 and 600 °C with heating rate 10 °C/min. Nanoparticles were put inside quartz glass capillary with the diameter of 1 mm. 2D XRD patterns as a function of temperature were collected every 10 s.

#### 4 Pair distribution function (PDF)

Atomic pair distribution function (PDF) gives the probability of finding an atom at a given distance  $r$  from another atom. In other words it can be understood as a bond length distribution (see Fig.3). According Faber-Ziman formalism [7] the structure function,  $S(q)$ , can be defined in the following form

$$S(q) = \frac{I_{eu}^{coh}(q) - \left\{ \left[ \sum_{i=1}^n c_i f_i^2(q) \right] - \left[ \sum_{i=1}^n c_i f_i(q) \right]^2 \right\}}{\left[ \sum_{i=1}^n c_i f_i(q) \right]^2} \quad (1)$$

where  $q$ ,  $I_{eu}^{coh}(q)$ ,  $c_i$  and  $f_i(q)$  are the magnitude of the scattering vector, coherently scattered intensity expressed in electron units, the atomic concentration and scattering factor of the atomic species of type  $i$ , respectively. The total reduced pair distribution



**Figure 3:** Principle of the PDF. Inter-atomic distances  $r_i$  cause maxima in the PDF  $G(r)$ . The area below the peaks correspond to the number of neighbors, scaled by the scattering power of the respective atoms.

function  $G(r)$  can be obtained using the sine Fourier transformation of the total scattering structure factor  $S(q)$  [8, 9].

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

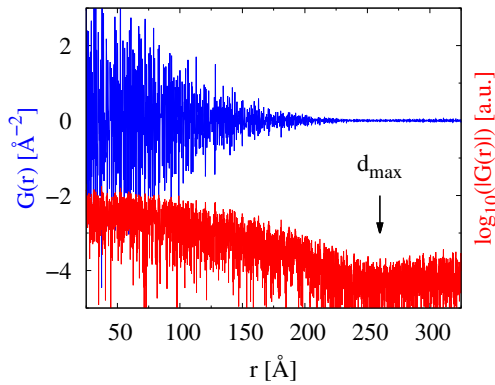
where  $r$  is the radial distance,  $\rho(r)$  and  $\rho(r)_0$  the local and mean atomic density, respectively. The PDF defined by eq. 2 represents variations of atomic density  $\rho(r)$  with respect to the mean atomic density  $\rho_0$ . In other words the PDF is a measure of the probability of finding an atom at a distance  $r$  from another atom and gives information about both average and the local structure of materials. Quantitative information about the local atomic structure can be extracted from the peaks profiles appearing on  $G(r)$ , for example:

- peak position gives information about atomic bond length,
- peak width represents length distribution of atomic bonds,
- peak area corresponds to the average coordination number.

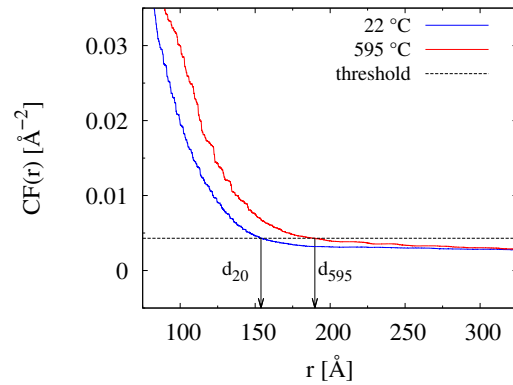
#### 4.1 Particle size determination from the PDF

The extent of oscillations in the PDF is related to the maximum correlation length which can be used to determine the mean grain size  $d$  [10, 11]. It is worth to note that the instrument resolution function (IRF) in  $q$ -space determines the resolution of the PDF, namely in the high- $r$  region [12]. The structure factor  $S(q)$  we determine by the equation 1 is actually the convolution of the intrinsic sample response with the IRF of the beamline setup. According to the convolution theorem it follows that the experimental PDF is given as the product of the Fourier transform of the IRF and the Fourier transform of the intrinsic response of the sample. The simplest approximation is that the IRF is a single Gaussian of constant width  $\sigma_q$ . The result from this model is multiplication of the PDF by a broad Gaussian envelope function in real space with a width of  $1/\sigma_q$  [13].

In order to achieve  $q$ -space resolution of  $\sigma_q = 0.03 \text{ \AA}^{-1}$  we set the sample-to-detector distance to 720 mm. This however limits the  $q_{max}$  to  $11 \text{ \AA}^{-1}$  but improves the structural information in the high- $r$  region of the PDF. Figure 4 shows PDF of the standard powder material  $\text{CeO}_2$ . The inset (red curve) in Fig.4 shows that structural oscillations enter the noise level at the  $r=260 \pm 10 \text{ \AA}$ . This distance actually corresponds to the maximum particle size which can be determined with the PDF method and is strongly limited by the IRF.



**Figure 4:** PDF of the standard powder material  $\text{CeO}_2$ . The inset (red curve) shows that structural oscillations enter the noise level at the  $d_{max} = 260 \pm 10 \text{ \AA}$ .



**Figure 5:** The cumulative functions  $CF(r)$  calculated using equation (3) for Fe-nanoparticles acquired at two different temperatures. The horizontal dashed line represents the noise level and the vertical arrows depict corresponding particle sizes.

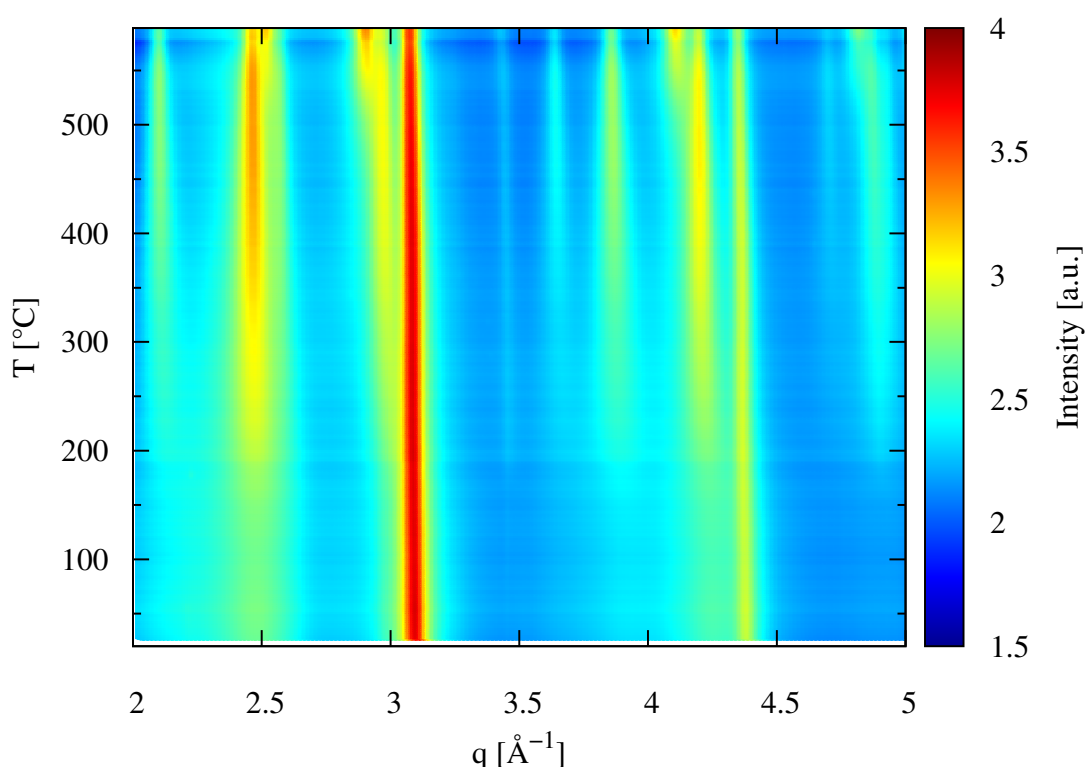
As proposed by Bednarcik and co-workers [10], the grain size can be determined from  $G(r)$  using the cumulative function  $CF(x)$  defined in the following way

$$CF(x) = \sqrt{\frac{1}{r_{max} - x} \int_x^{r_{max}} [G(r)]^2 dr}, \quad (3)$$

where  $r_{max}$  is fixed to  $500 \text{ \AA}$ , which is safely above the  $d_{max}$  given by the IRF. The  $CF(x)$  actually calculates the root mean square value of the  $G(r)$  on interval  $\langle x, r_{max} \rangle$ . The mean grain size  $d$  can be then defined as the distance at which the  $CF(x)$  drops below the noise level (see Figure 5).

## 5 Results and discussion

Figure 6 shows series of XRD patterns of Fe-nanoparticles acquired during constant rate heating experiment up to 600 °C. The strongest peaks belong to the bcc-Fe phase. It can be seen that at the temperature  $T = 200$  °C intensity of initially weak set of peaks (with  $q$  positions 2.1, 3.4, 3.67, 3.86 and 4.9 Å<sup>-1</sup>) starts to increase whereas their widths decrease with increasing temperature. Such behavior can be associated with improving degree of crystallinity of the CuFe<sub>2</sub>O<sub>4</sub> phase which forms nanoparticle shell. Another set of peaks appearing just above 500 °C suggests formation of CuO<sub>2</sub> by decomposition of CuFe<sub>2</sub>O<sub>4</sub> phase.

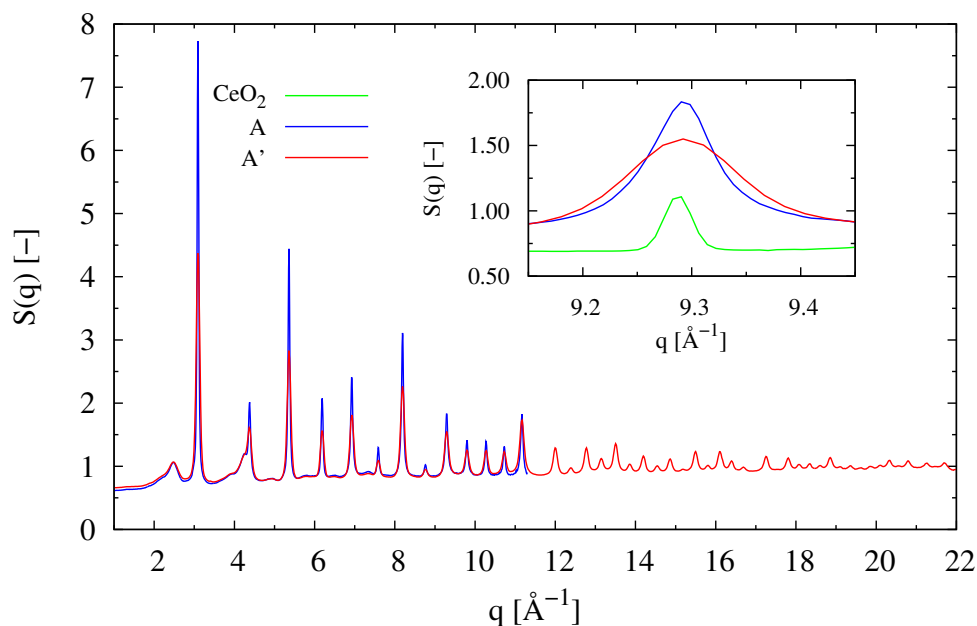


**Figure 6:** Series of XRD patterns of Fe-nanoparticles acquired during constant rate heating experiment up to 600 °C. To make small peaks visible the intensity (denoted by color) is plotted in logarithmic scale.

In the next part all XRD patterns were processed using the pdfgetx3 program [1]. In this way corresponding structure factors  $S(q)$  and reduced pair distribution functions  $G(r)$  were calculated. The background signal stemming from the capillary was automatically subtracted. The Fourier transform was performed between  $q_{min} = 1$  Å<sup>-1</sup> and  $q_{max} = 11$  Å<sup>-1</sup>.

Figure 7 shows the influence of the sample-to-detector distances on structure factors. The measurement done with the shorter distance (220 mm) covers larger  $q$ -range but with the lower angular resolution ( $\sigma_q = 0.08$  Å<sup>-1</sup>). When moving 2D detector to larger

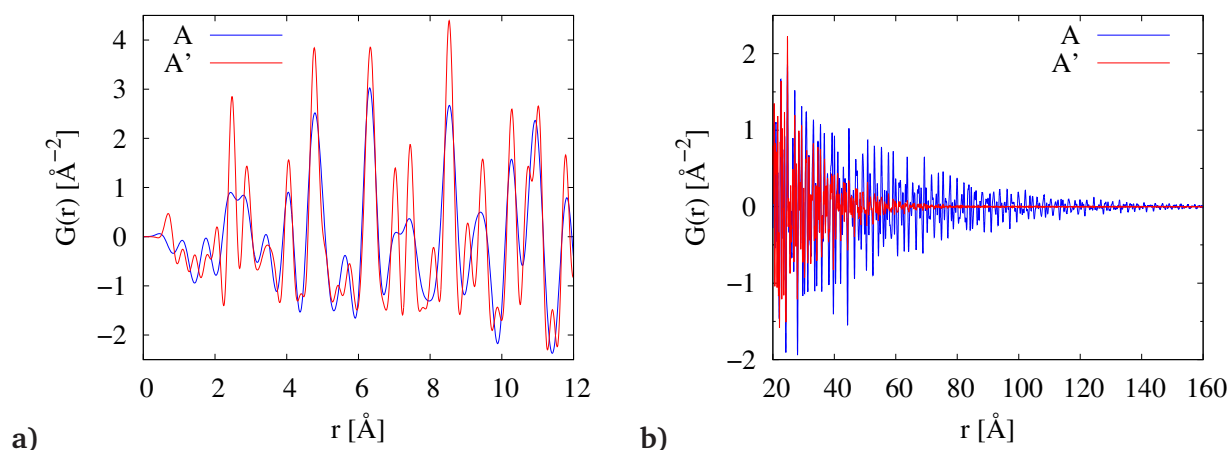




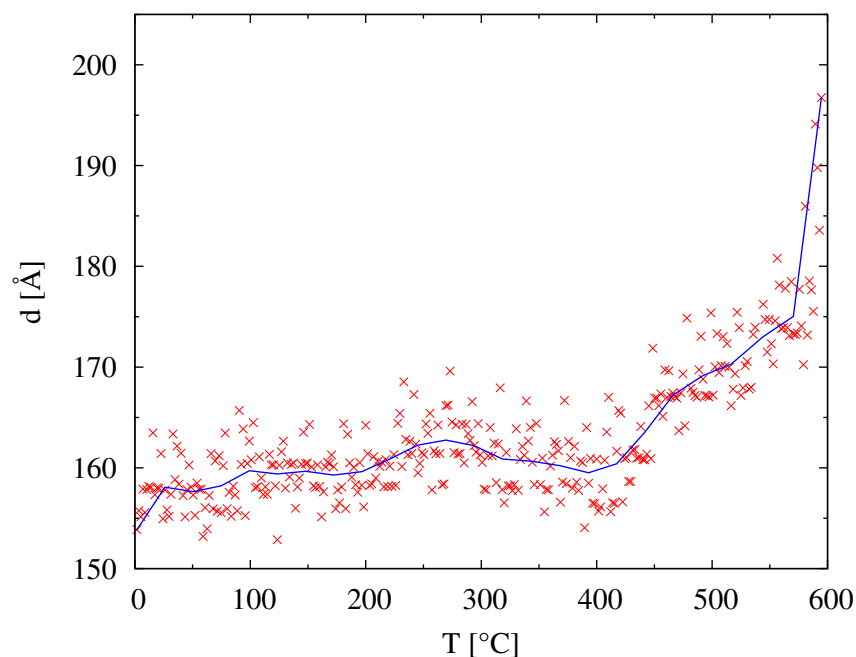
**Figure 7:** X-ray total structure factor for Fe-nanoparticles determined at two different sample-to-detector distances. The  $A$  and  $A'$  denote structure factors obtained at distances 720 and 220 mm, respectively. The inset shows comparison of the (411) Bragg reflection of bcc-Fe acquired at two different distances. Furthermore the (800) Bragg reflection of  $\text{CeO}_2$  acquired at long distance (720 mm) is depicted.

distance (720 mm) we gain the angular resolution ( $\sigma_q = 0.03 \text{ \AA}^{-1}$ ) at the expense of limited  $q_{max} = 11 \text{ \AA}^{-1}$ .

Figure 8 shows comparison of PDFs of Fe-nanoparticles acquired at two different sample-to-detector distances. When increasing the sample-to-detector distance from 220 mm up to 720 mm the  $q_{max}$  is reduced from  $22 \text{ \AA}^{-1}$  down to  $11 \text{ \AA}^{-1}$ . As can be seen from the Fig.8a, having larger  $q_{max}$  is essential for resolving the local atomic structure.



**Figure 8:** Comparing **a)** low  $r$ -regions and **b)** high  $r$ -regions of Fe-nanoparticles PDFs acquired at two different sample-to-detector distances. The  $A$  and  $A'$  refer to the measurements done at 720 and 220 mm, respectively.



**Figure 9:** Temperature dependence of the mean grain size (red 'x' signs) as determined from series of PDFs by means of the cumulative function  $CF(r)$  defined by equation (3). The blue line represents the trend line and is just a guide for the eyes.

However as can be seen from the Fig.8b, the measurement done at the larger sample-to-detector distance has better angular resolution and thus obtained PDF show oscillations up to larger  $r$  values. In this study the main accent was put on determination of the mean grain size from PDF therefore the experimental settings (namely angular resolution) were optimized so that PDF offers resolving power in the high  $r$ -region. Figure 9 shows temperature dependence of the mean grain size (red 'x' signs) as determined from series of PDFs by means of the cumulative function  $CF(r)$  defined by equation (3). The mean value of observed diameter of nanoparticle at room temperature is 15.3 nm. This value is in very good agreement with 15 nm, obtained from previous TEM observations. Mean grain size tends to increase with increasing temperature. These results are still preliminary and subject of further analysis.

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