PAIR DISTRIBUTION FUNCTION ANALYSIS OF AMMONIUM NITRATE - COMPARISON OF PDF- AND RIETVELD-ANALYSIS

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Abstract

Energetic materials are often nanocrystalline, amorphous, liquid or gel structured. Therefore, it is difficult to obtain structural information from these materials by conventional structure analysis using X-ray diffraction. This contribution shows the possibility to achieve structural information with the aid of the pair distribution function (PDF) compared to the Rietveld-Analysis.

The energetic material ammonium nitrate was chosen as an example for the test of PDF structure analysis of energetic materials. The diffraction data were used for calculating the PDFs and the results are evaluated in order to improve measurement conditions for energetic materials.

It is shown that it is possible to calculate reasonable PDFs of energetic materials from laboratory measurements.

Introduction

The interest of materials scientists and chemists in complex materials which are amorphous or have structures on the nanometer length-scale is increased in the last years. Examples in the field of energetic materials investigated at Fraunhofer ICT are widespread and include ingredients of plastic bonded explosives as well as of rocked or gun propellants; among them nanoporous and nanostructured materials, binders, ionic liquids, gel propellants and liquid explosives.

It is difficult to study structures at the nanoscale quantitatively using diffraction methods, because the diffraction gives no sharp Bragg peaks but only broad diffuse peaks in the scattering (halos) [1]. Total scattering, in which both Bragg and diffuse components of the scattering are analyzed together, is growing in popularity for the study of this kind of problems [2,3]. One approach analyzes the data in

real space using a Fourier transformation of measured patterns into the atomic pair distribution function (PDF) [4].

The pair distribution function method was originally developed to study the structure of materials characterized by a short-range order restricted to the first few coordination spheres, such as liquids and glasses [e.g. 5]. Such a PDF shows broad halos representing the short-range order and becomes constant at larger distances due to a uniform distribution. The technique is now increasingly applied for investigations of disorder in crystalline materials and for studies of nanomaterials [2]. A PDF from crystalline material is much more structured and also gives information on a medium-range of inter-atomic distances. It is complementary to the traditional crystallographic analysis, which assumes a periodic material and considers only intensities from Bragg reflections. The PDF method does not require periodic order in the sample. The data of the whole measured diffraction pattern, including Bragg and diffuse components, is used to extract the total scattering structure function, *S(Q)*, which contains coherent scattering intensities from the material. This process is described in detail elsewhere [4,6-9].

The energetic material ammonium nitrate (NH_4NO_3) was chosen as example for energetic materials. Ammonium nitrate (AN) is used as fertilizer and also as energetic oxidizer in solid propellants, explosives and gas generator systems. Drawbacks are low performance, low burning rates and phase transitions that influence the material properties. Fig. 1 shows the crystal structure of ammonium nitrate phase IV [10], which is stable at room temperature. Phase IV crystallizes in the orthorhombic space group Pnmm with the lattice constants a = 5.745, b = 5.438 and c = 4.942 Å. The density is 1.736 g/cm^3 and the number of formula units Z is 2.

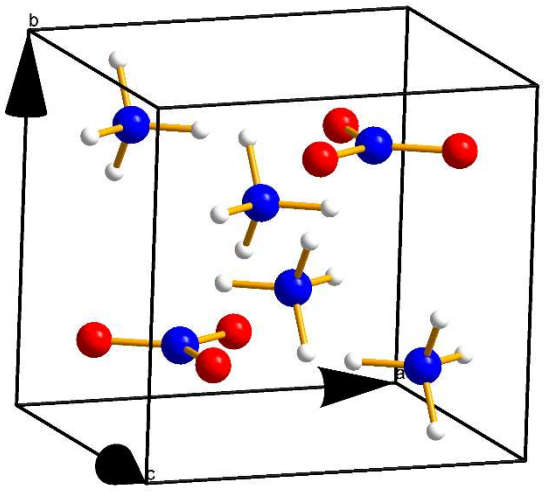

Fig. 1: Crystal structure of ammonium nitrate phase IV.

Background and requirements

A good review about the history of the PDF can be found in [11]. The PDF analysis is a principally well understood method. B.E. Warren already described 1969 in the classical textbook on X-ray diffraction [12] a probability of finding any two atoms at given inter-atomic distances r. The principle of the PDF is shown in Fig. 2. Interatomic 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. Already in the book of Klug and Alexander [13] a method is described similar to the PDF method.

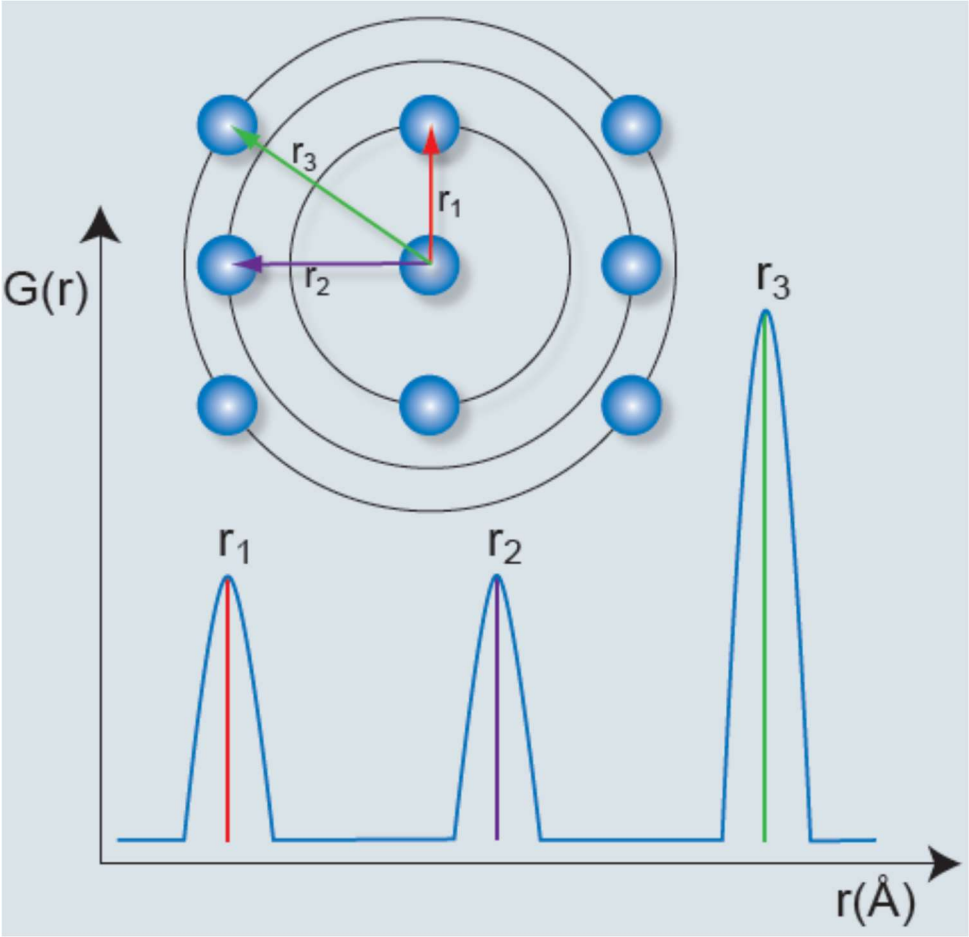

Fig. 2: Principle of the PDF [20].

The quality of the experimental PDF is mainly influenced by several factors: Fourier termination errors, high resolution and counting statistics of the X-ray measurement as well as the data collection temperature.

Sample portfolio and experimental

An ammonium nitrate sample was chosen as energetic reference material and for comparison with former measurements on a diffractometer at Bruker AXS as benchmark. Corundum powder was chosen

for an estimation of the geometrical peak profile of the measuring system and for calibration of a size/strain analysis. Measurements were performed on an X-ray diffractometer D8 from Bruker AXS, equipped with a special optic with silver tube, Göbel mirror for focusing radiation, rotating capillary holder, 2.5° Soller slit, and silicon strip detector (LynxEye) with 3.7 ° detector opening. Further details of the system are reported elsewhere [14].

The samples were prepared in thin-walled borosilicate glass capillaries from Hilgenberg with 2 mm outside radius and a wall thickness of only about 10 µm. As the coherent scattering and thus the signal-to-noise ratio decrease with increasing measuring angle, high angle regions should be measured with long count time for the PDF analysis. Therefore, measurements were divided in four 2θ sections 3.5–20, 20–50, 50–110, and 110–140 °2θ, and the sections were measured with the same step width of 0.016 °2θ, but with increasing count times of 2, 4, 8, and 16 s per step, respectively. The scan times sum up to about 20 h per series. Beside the ammonium nitrate and the corundum, empty capillaries were measured under same conditions[1], and each measurement was repeated five times. Dividing the long measuring time into repeated measurements can balance long term fluctuations, e. g. of the tube performance or climate changes, which otherwise could impact the PDF analysis of measurements over days. For the evaluation, the partial patterns of the five series were accumulated 2θ-section-wise and the sections were merged to a final pattern of the hole 2θ-range from 3.5 to 140 °2θ. To avoid discontinuities of the curve, which would arise in plots of absolute counts per step with varied scan time per step, the diffraction data was transformed to counts per second (cps) before merging the 2θ-sections. For some reasons, the tube parameters varied between the sections 1 and 2, and 3 and 4, which caused intensity steps between the sections. The effect was corrected by scaling the sections 1 and 4 with individual intensity factors.

Evaluation

The theoretical PDF was calculated with aid of the crystal structure of ammonium nitrate [10] and according to the maximal Q value. Q is the magnitude of the scattering vector. For elastic scattering $Q = 4\pi(\sin\theta/\lambda)$. The maximum value of Q is limited by the instrument setting for the highest diffraction angle (typically up to 160 °2θ) and the wavelength of the X-ray source. For an assumed largest angle of 160 °2θ the maximum Q value for Cu-radiation is 8 Å^{-1}. The use of Mo-radiation more than doubles this value to 17.4 Å^{-1} and Ag-radiation enlarges the accessible Q-range up to 24 Å^{-1}.

The experimental atomic pair distribution functions G(r) have been obtained from the corrected diffraction data by Fourier transformation of the total structure function S(Q) using PDFgetX3 [15]; S(Q) is the measured intensity corrected for background, Compton and multiple scattering, absorption,

[1] The corundum and respective empty capillary were measured with 0.02 2θ step width and 3.7° detector opening.

geometric and other effects. The resulting PDF is defined by $G(r) = 4\pi r\,(\rho(r) - \rho_0)$, in which $\rho(r)$ is the local atom number density, and ρ_0 is the mean atom number density.

Termination errors are minimized by measuring to larges extension using Ag-radiation, which enlarges the accessible Q-range to 24 $Å^{-1}$. Consequently, the lowest termination effects can be expected for Ag-radiation when laboratory equipment is used. Q values of 30 $Å^{-1}$ or even higher can be obtained, when synchrotron or neutron radiation is used.

However, the benefit of an extended Q-range using Ag-radiation is gained on a significant intensity loss. The flux of X-rays from an Ag-tube is low compared to Mo, and the detector efficiency is lower for Ag-radiation as well. Furthermore, the decrease of the X-ray scattering power of the atoms with increasing Q frequently contributes no additional information from very high Q data.

The penetration depth of X-rays into the sample is larger for higher energies (smaller wavelengths). In reflection geometry this causes a loss of resolution due to the related peak broadening. Therefore, the use of transmission geometry together with either capillary or flat-sample stages is useful for PDF experiments.

The measurement time needed to collect data of sufficient counting statistics to high-Q values is long. For a very basic instrumental set-up for PDF investigations using Ag-radiation, capillary sample, and scintillation counter the measurement time easily exceeds one day per scan. Such long measurement time clearly calls for a modern linear detector that drastically reduces the counting time. Essential is also the temperature of the measurement. Better structured PDFs are obtained for lower temperatures.

The interpretation of the experimental PDF may be similar to the Rietveld method. A structural model of the atomic arrangement will be used to calculate a PDF. Best agreement with the experimental PDF is obtained by optimizing the model parameters using e.g. PDFfit2 [16], a program for the full profile structural least squares refinement of the atomic pair distribution function.

Results

Rietveld-analysis

Rietveld-analysis of the patterns were performed with the program TOPAS from Bruker AXS [17], using the crystal structure data reported for corundum [18] and ammonium nitrate [10]. Fig. 3 shows the measured patterns (blue), the fitted curves (red), the differences (grey) and reflection positions (blue markers) of corundum (top) and ammonium nitrate (bottom). The fits resulted in error value (r_{WP}) of 6.0 for corundum and 8.2 for ammonium nitrate. For the calibration pseudo-Voigt profiles and tube tails were freely varied for corundum to yield best-fit peak profiles, without peak broadening through size/strain-parameters. In the subsequent analysis of ammonium nitrate the size/strain parameters were refined, but with fixed pseudo-Voigt and tube tail parameter (Tab. 1). The thus calibrated Rietveld-

analysis revealed an integral peak breadth-based volume weighted mean column lengths of crystal domains (size, L_{VolLIB}) of 45 nm and mean microstrain (ε_0) of 0,0007 of the ammonium nitrate sample. So far, the evaluation yielded reasonable values with error values below 10, a moderate mean crystallite size, but low micro strain. The values shall be used in further investigations to compare different qualities of ammonium nitrate, particularly in context of results of a PDF analysis.

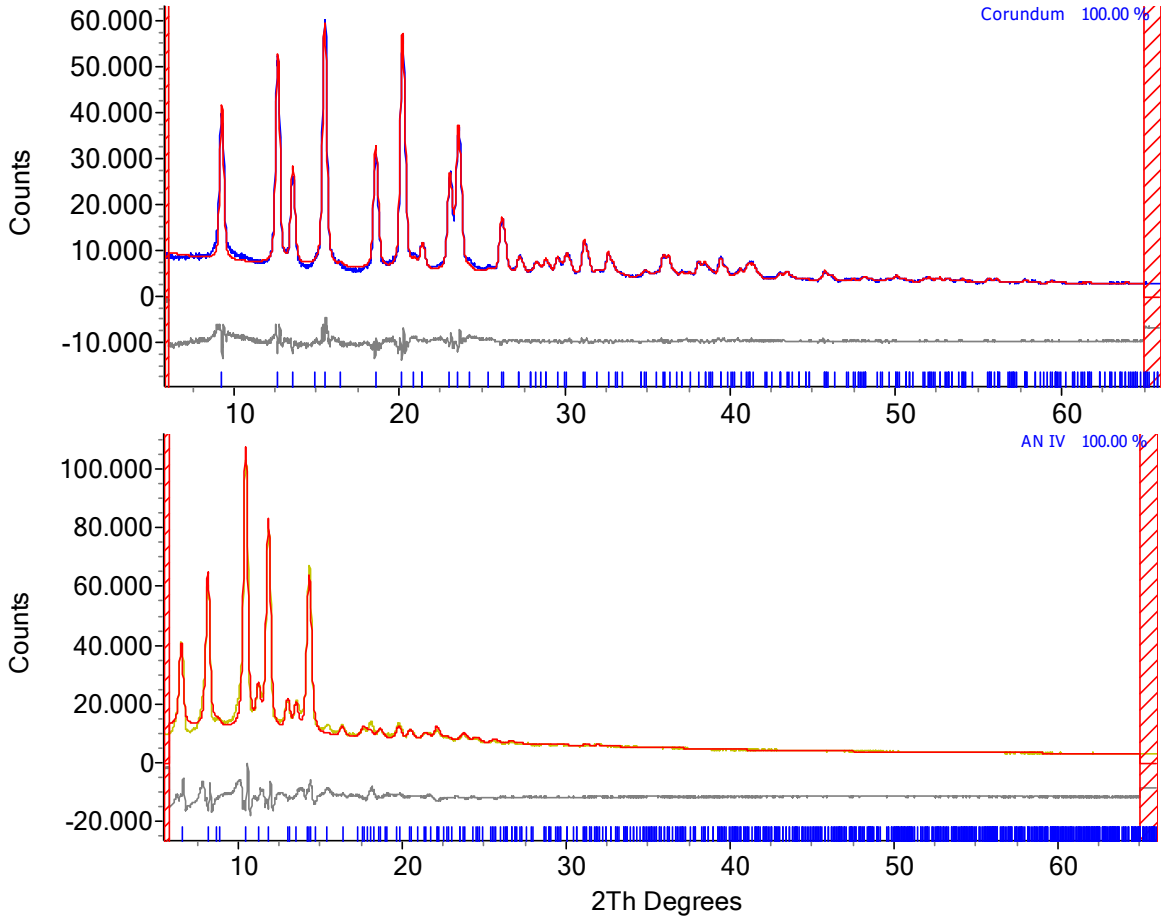

Fig. 3: Sections of Rietveld-plots of corundum (top) and ammonium nitrate (bottom) measured with silver radiation and PDF optics. Measured patterns (blue/light brown), fitted patterns (red), differences (grey), and positions of reflections (blue markers).

Tab. 1: Pseudo-Voigt and tube tail parameters used for the calibration of the size-strain analysis.

PV_MOD		Tube Tails	
Ha	0.0427	Source Width (mm)	0.5
Hb Tan(Th)	0.2056	Z1 (mm)	-0.562
Hc / Cos(Th)	0.0577	Z2 (mm)	0.614
Lor-a	0.5137	Fraction	0.,5
Lor-b Tan(Th)	1.3215		
Lor-c / Cos(Th)	0.4040		

PDF-Analysis

The capillary measurement with Ag-radiation (red) and a background measurement of the empty capillary (blue) is shown in Fig. 4.

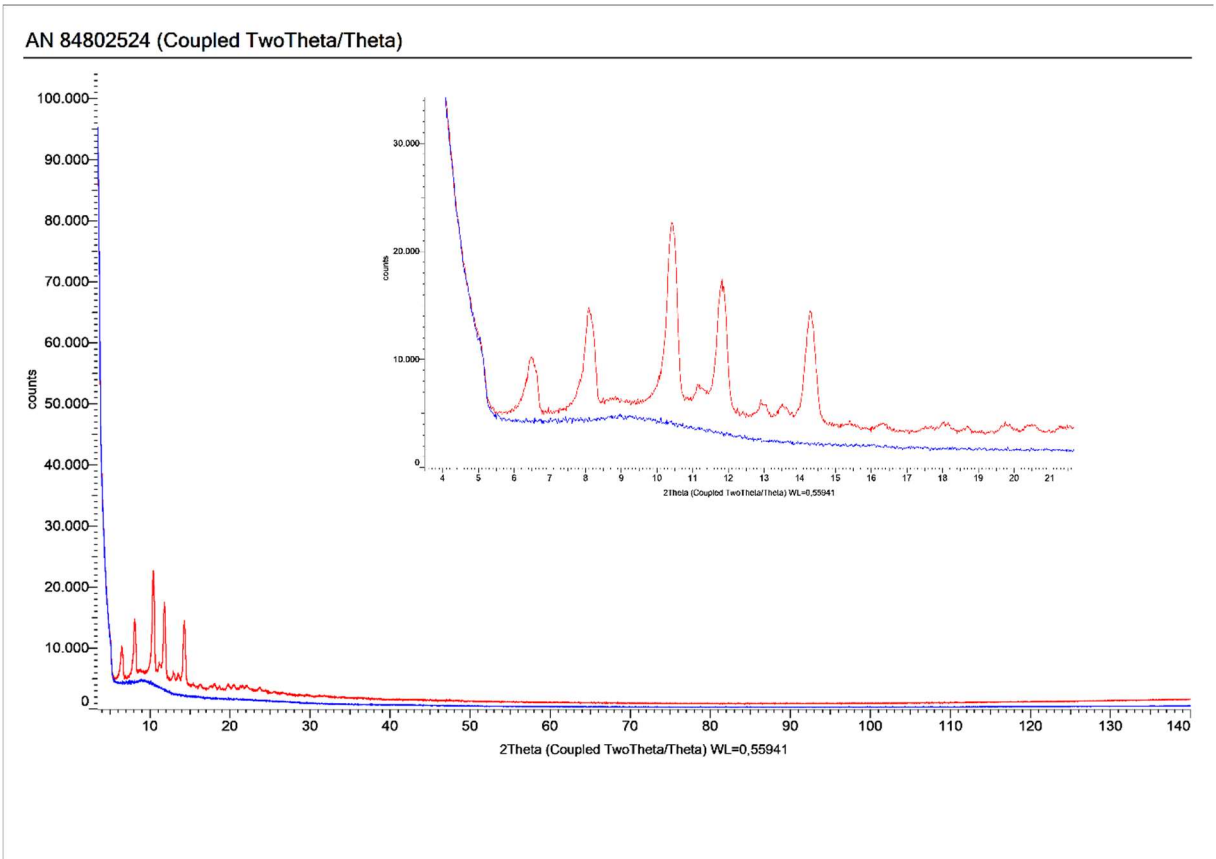

Fig. 4: XRD-pattern of ammonium nitrate (red) with Ag-radiation (red) and a background measurement of the empty capillary (blue).

For calculating the experimentally PDF by Fourier transformation the share of the capillary must be subtracted. The resulting PDF is shown in Fig 5.

With the aid of the crystal structure of ammonium nitrate the PDF, shown in Fig. 6, was calculated.

The PDF-analysis was done by adjustment of the calculated PDF to the experimentally PDF. The analysis resulted in an error value (r_{WP}) of 0.999 for ammonium nitrate. Details about the PDF-Analysis of AN can be found elsewhere [19].

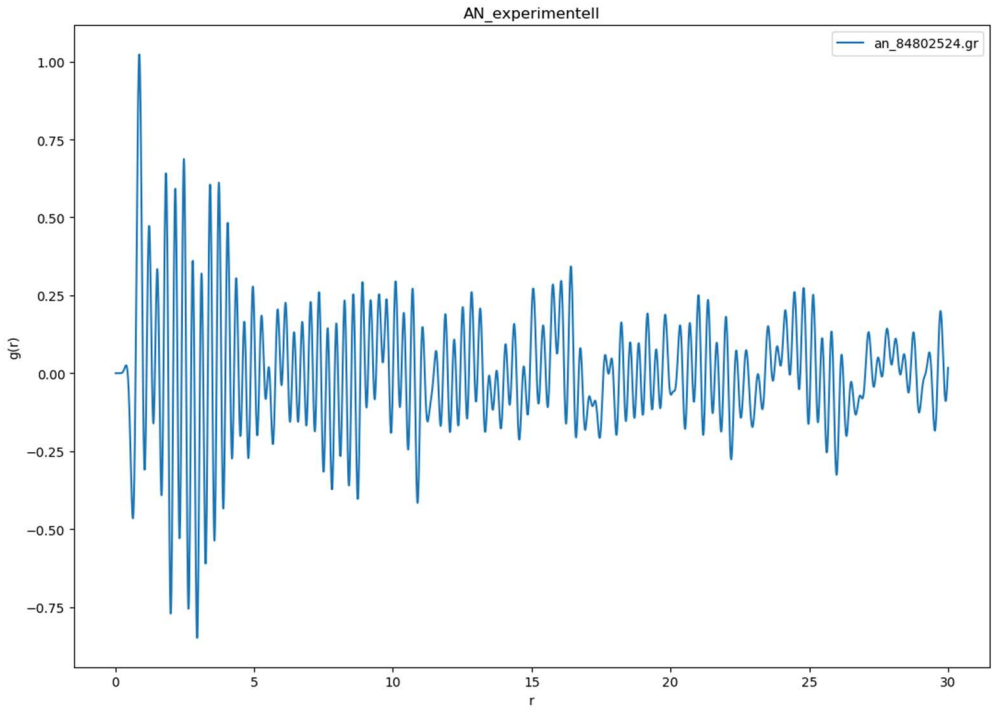

Fig. 5: Experimentally PDF.

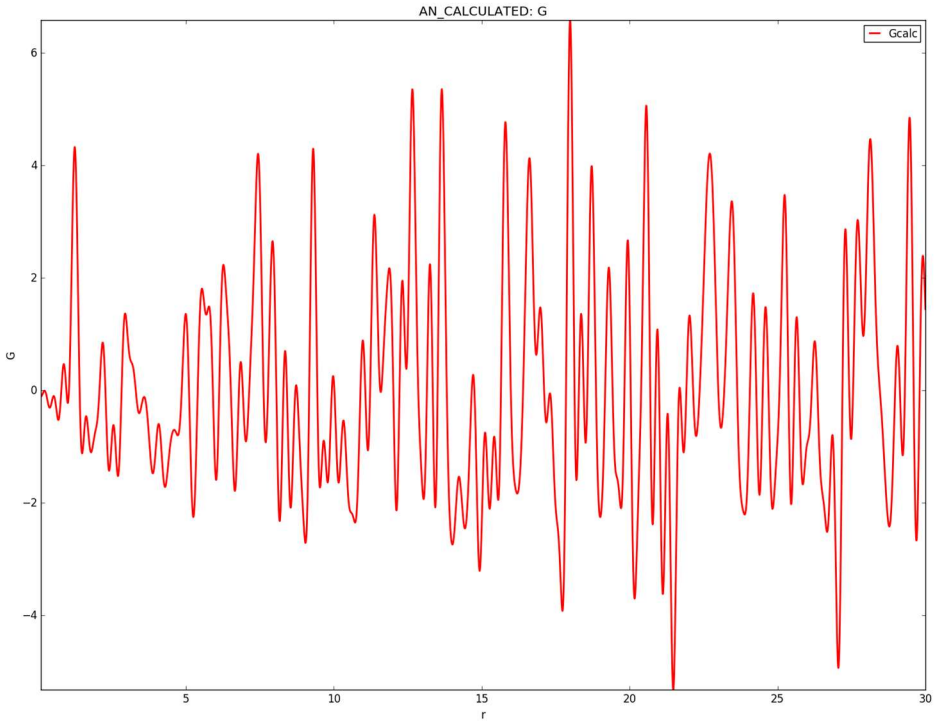

Fig. 6: Calculated PDF.

Summary and conclusion

The comparison of the lattice constants, calculate by Rietveld- and PDF-Analysis shows reasonable values, when compared to the literature data (Tab. 2).

Tab. 2: Refined lattice parameters of ammonium nitrate obtained from Rietveld- and PDF-Analysis.

Lattice constants	Structure [10]	Rietveld-Analysis	PDF-Analysis
a [Å]	5.745	5.721	5.746
b [Å]	5.438	5.432	5.436
c [Å]	4.942	4.922	4.941

Therefore, it was concluded that the calculated maxima (Fig. 5) represent the structure of the energetic material, not Fourier termination effects. The PDF calculated with Ag data is finely structured. Overall, the investigations yielded reasonable PDFs of ammonium nitrate using X-ray laboratory equipment.

Hereby, the X-ray measurement, from which the experimental PDF is then generated with the aid of Fourier synthesis, is of crucial importance. In order to generate a meaningful PDF, high demands must be placed on the X-ray measurement. Even the smallest errors in the measurement influence the resulting PDF to such an extent that an analysis of this PDF becomes difficult or even impossible. For example, a variation in tube voltage can have a negative impact on the quality of the experimental PDF. Considering all the necessary factors that can influence the PDF, it is quite possible to obtain comparable results from PDF analysis and Rietveld refinement. Moreover, PDF analysis is a good tool to obtain structural information from low crystallinity explosives, where Rietveld-analysis is hardly possible.

Abbreviations

AN	Ammonium nitrate
cps	counts per second
ε_0	mean microstrain
G(r)	Experimental atomic pair distribution functions
ICT	Fraunhofer ICT, Pfinztal, Germany
L_{volIB}	integral peak breadth-based volume weighted mean column lengths of crystal domains
PDF	pair distribution function
PV-MOD	modified pseudo-Voigt profile
Q	Magnitude of the scattering vector

r_{WP}	weighted pattern error
S(Q)	Total structure function
XRD	X-ray diffraction

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