Validation of Rapid Acquisition Pair Distribution Function (RA-PDF) Technique

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Introduction

The image plate (IP) detector system offers a powerful choice for recording powder diffraction patterns. An IP detector coupled with high-energy synchrotron radiation has been recently successfully used for atomic pair distribution function (PDF) analysis [1], with high probed momentum transfer Q_{max}, from several crystalline materials [2]. Medium-high real-space resolution PDF data analysis from crystalline materials has been performed using image-plate data and shows promising results. Comparable or even better statistics than from conventional X-ray measurements can be achieved with significantly shorter counting times. This new combination of a real-space probe and fast counting time, named RA-PDF, opens up a broad field for future applications to a wide variety of materials of both scientifc and technological interest [2,3]. For example, PDF methods could be used to study structural changes *in-situ* [4], and the time development of chemical reactions and biological systems over time scales of minutes may be studied. On the other hand, this type of data can be subject to a rather high background which can represent a big challenge to proper data corrections when used for atomic PDF studies [1].

To address this important issue in detail we carried out a series of measurements to assess the quality of the data obtained using the RA-PDF method. In this experiment, a series of materials with differing structural complexities and with a wide range of scattering powers were used to test the validity of the quantitative data analysis using data obtained by the RA-PDF approach.

Methods and Materials

The X-ray experiment was performed at the 6-ID-D beam line at the Advanced Photon Source (APS) at Argonne National Laboratory. A series of finely powdered samples were loaded into hollow flat metal plate sample containers with thickness of 1.0 mm, and then sealed between thin Kapton films. Measurements were carried out in flat-plate transmission geometry. Data acquisition employed the RA-PDF technique, with an X-ray energy of 98.0 keV (λ = 0.126530 Å). A Mar345 image-plate camera, a round disk with a usable diameter of 345 mm, was mounted orthogonal to the beam centered on the IP. Silicon standard sample was used to calibrate the sample-to-detector distance and the tilt of the IP relative to the beam path, using the software Fit2D [5]. The sample to detector distance was 178.4 mm. The count is always adjusted ensure that there are no saturated pixels in the detector. All raw 2D data , like the one shown in Fig.1, were integrated and converted to intensity versus 2θ format using the Fit2D program package, where 2θ is the angle between the incident and scattered X-rays. Standard corrections for multiple scattering, polarization, absorption, Compton scattering and Laue diffuse scattering were applied to the integrated data to obtain the reduced total structure function *F(Q)*. Direct Fourier transformation gives the pair distribution function *G(r)*. Data correction and processing utilized the PDFgetX program package [6].

Data for simple elements (C, Mg, Al, Si, Ni, Cu, Zn, Ag, Cd and Pb) were collected at room temperature, and for ternary alloy $ZnSe_{0.5}Te_{0.5}$ at 15 K in displex closed cycle refrigerator environment. The PDF data were further modeled using average structure models and the results were compared to the literature values or directly compared to the data collected by other established and well trusted methods. The average structure models were refined using the profile-fitting least-squares regression program PDFFIT [7].

Results

All the PDFs from simple element samples show high reproducibility and are of exceptional quality. This is evident, for example, in the Ni data presented in Fig. 2. The top panel shows the reduced total structure function, *F(Q)*, obtained by integrating and correcting the 2D data shown in Fig.1.

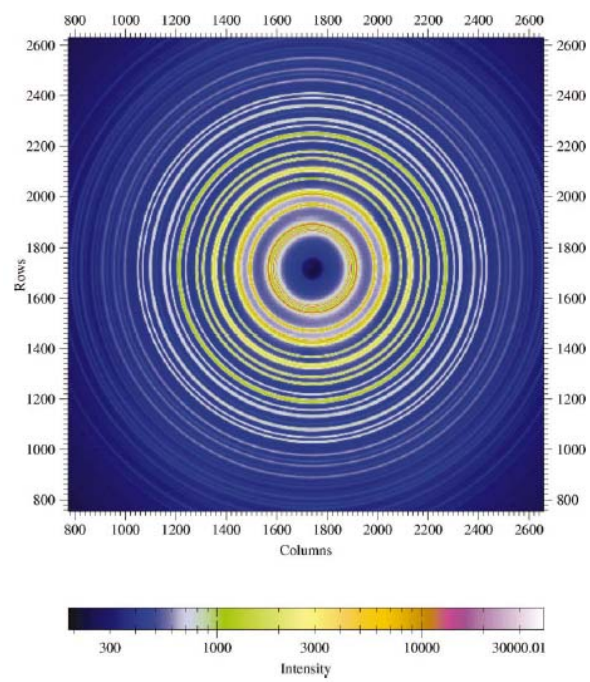

Fig.1. Two-dimensional contour plot from the Mar345 image-plate detector. The data are from Ni powder measured at room temperature. The concentric circles are where Debye- Scherrer cones intersect the area detector

The PDF of Ni (Fig. 2(b)) obtained using Q_{max}=30.0 Å^{-1}, has minimal systematic errors (unphysical features) which appear in the data as small ripples before the first PDF peak at r =2.4 Å

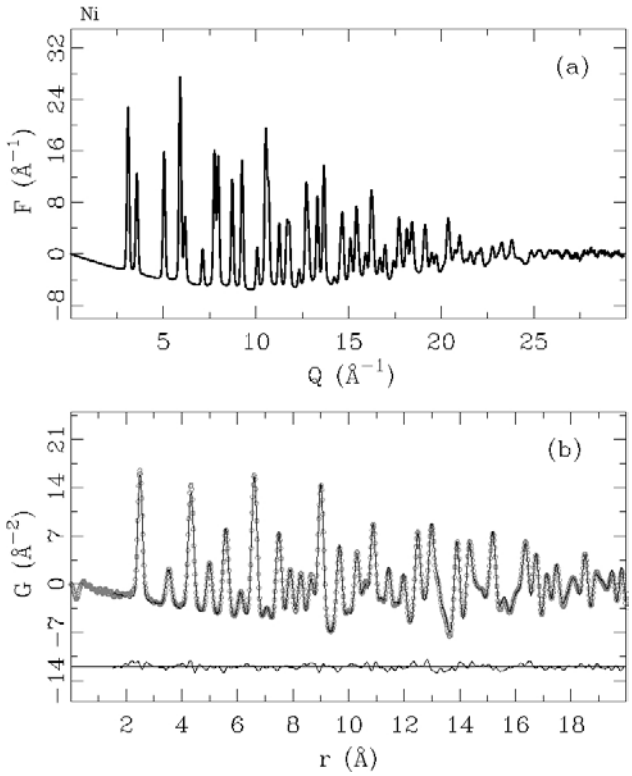

Fig.2. (a) The experimental reduced structure function F(Q)=Q(S(Q)-1) of Ni powder data collected at room temperature from the X-ray RA-PDF measurement. (b) Corresponding experimental PDF (open symbols) with a PDF of the structural model (solid line). The difference curve is shown underneath and is offset for clarity.

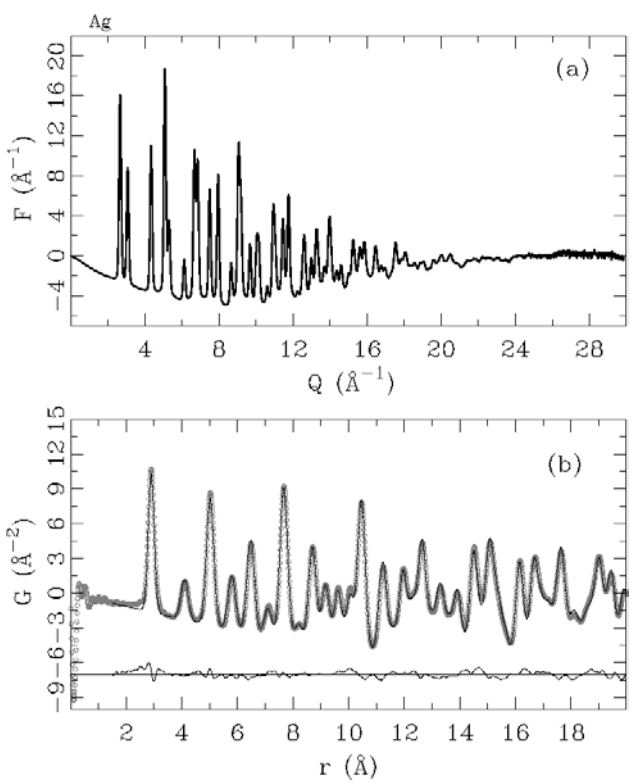

Fig.3. (a) The experimental reduced structure function F(Q)=Q(S(Q)-1) of Ag powder data collected at room temperature from the X-ray RA-PDF measurement. (b) Corresponding experimental PDF (open symbols) with a PDF of the structural model (solid line). The difference curve is shown underneath and is offset for clarity.

distance. The PDF of the modeled average structure, space group *Fm-3m*, shown as solid line in Fig. 2(b), was readily refined and gave excellent agreement (R_{wp} =0.086) with the data, as evident from the difference curve.

A selected set of the reduced total scattering functions, corresponding experimental PDFs and model PDFs are shown in Figs. 3 – 5.

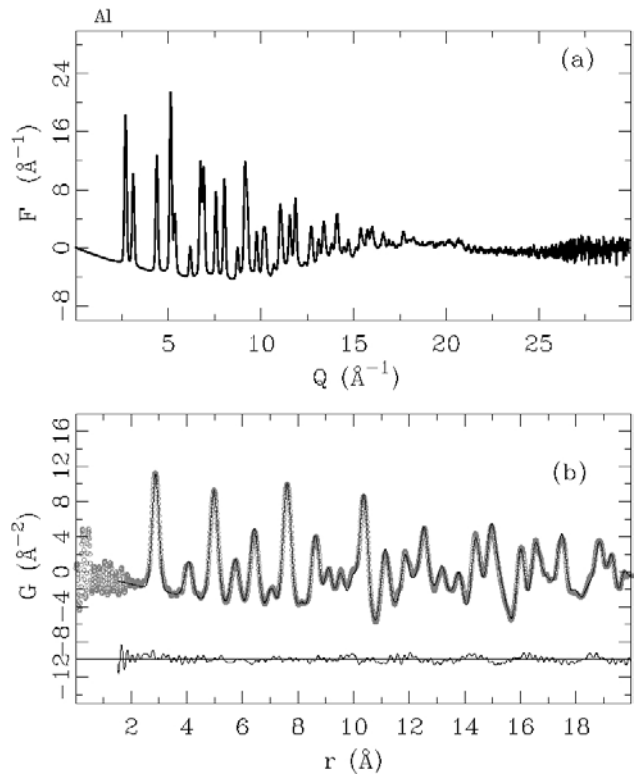

Fig.4. (a) The experimental reduced structure function F(Q)=Q(S(Q)-1) of Al powder data collected at room temperature from the X-ray RA-PDF measurement. (b) Corresponding experimental PDF (open symbols) with a PDF of the structural model (solid line). The difference curve is shown underneath and is offset for clarity.

One of the important issues to be addressed in this experiment is concerning the low temperature experimental setup within the RA-PDF methodology. We wanted to establish whether the level of the background signal arising from the low temperature environment setting is sufficiently weak such that it does not obscure the subtle structural information in the experimental data. In Fig. 6 we show a comparison of a raw signal of $ZnSe_{0.5}Te_{0.5}$ sample (light solid line) and a signal corresponding to a beryllium heat shield background (dark solid line). It is easily noticeable that the signal from beryllium heat shield and shroud (dark solid line), which represent one of the major contributors to the background in this case, is negligibly small compared to that from $ZnSe_{0.5}Te_{0.5}$ sample (light solid line). Distinct Be Bragg peaks are found in the background intensity, as shown in the inset of Fig.6.

The PDF of $ZnSe_{0.5}Te_{0.5}$ obtained using the RA-PDF method is shown in Fig. 7 (lower solid line), compared to the neutron time-of-flight data (upper curve). Q_{max} =33 Å^{-1} was used to obtain PDFs for both cases.

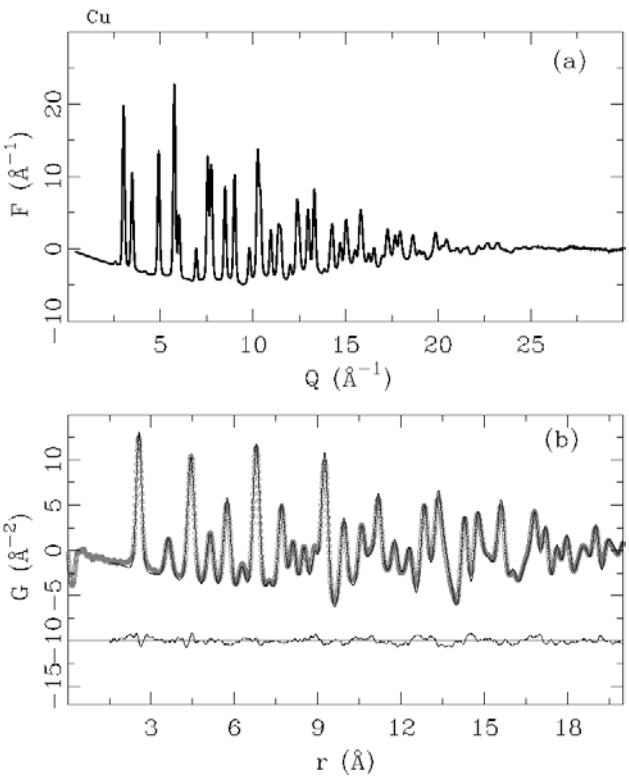

Fig.5. (a) The experimental reduced structure function F(Q)=Q(S(Q)-1) of Cu powder data collected at room temperature from the X-ray RA-PDF measurement. (b) Corresponding experimental PDF (open symbols) with a PDF of the structural model (solid line). The difference curve is shown underneath and is offset for clarity.

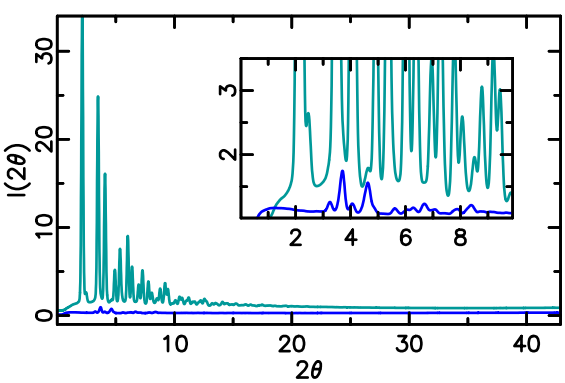

Fig.6. Comparison of normalized raw signal of $ZnSe_{0.5}Te_{0.5}$ sample (light solid line) to the normalized raw signal of the beryllium heat shields background (dark solid line). Inset: distinct Be Bragg peaks are found in the background intensity.

The existence of two distinct nearest-neighbor distances in this ternary alloy is inferable from the RA-PDF data from clearly appearing shoulder of the first peak at 2.45 Å. The neutron PDF of $ZnSe_{0.5}Te_{0.5}$ was obtained at 15 K from data collected at high-resolution NPDF diffractometer at the Lujan Center at Los Alamos National Laboratory. Two PDFs are comparable (up to the different scattering properties due to differing probes) indicating that the RA-PDF method provides high quality low temperature PDF which is not affected by the background signal from the low temperature environment setting.

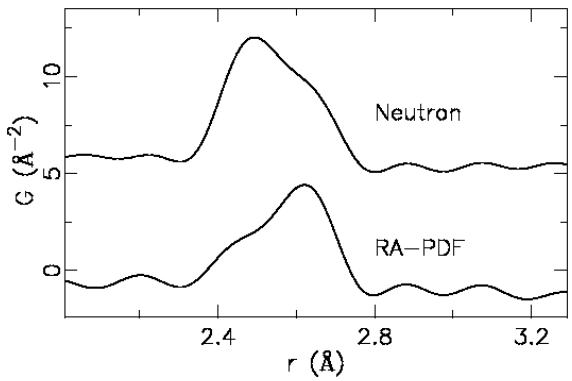

Fig.7. Comparison over the selected r-region of the experimental reduced PDFs, G(r), of $ZnSe_{0.5}Te_{0.5}$ sample measured at 15 K, obtained using time-of-flight neutron scattering based PDF (upper curve) and synchrotron X-ray based RA-PDF (lower curve). Both PDFs were generated using the same Q_{max} of 33 Å^{-1}.

Discussion

As demonstrated, the RA-PDF technique can be confidently and successfully used in structural studies at both room and low temperature. The method provides high quality low temperature PDFs which is not affected by the background signal from the low temperature environment setting. The diffraction patterns show good counting statistics, with measurement times ranging from one to tens of seconds. The PDFs obtained are of high quality. Structures can be refined from these PDFs, and the results of the structural models are consistent with the published literature. Data sets from similar samples are highly reproducible.

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