Quantitative structure refinement from the ARCS chopper spectrometer

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Abstract. The new wide angular-range chopper spectrometer ARCS at the Spallation Neutron Source at Oak Ridge National Laboratory has been successfully used in white-beam mode, with no Fermi chopper, to obtain neutron powder diffraction based atomic pair distribution functions (PDFs). Obtained PDF patterns of Si, Ni, and Al2O3 were refined using the PDFfit method and the results compared to data collected at the NPDF diffractometer at Los Alamos National Laboratory. High quality resulting fits are presented, demonstrating that reliable powder diffraction data can be obtained from ARCS when operated in this configuration.

1. Introduction

Time-of-flight (TOF) instruments at spallation sources, such as the NPDF [1] at the Los Alamos Neutron Science Center (LANSCE) or the general materials diffractometer (GEM) [2] at ISIS, are routinely utilized to carry out neutron powder diffraction measurements. It is less common to exploit chopper spectrometers to obtain powder diffraction data suitable for structure refinements, since their primary role is inelastic neutron scattering measurements to obtain information about a system’s dynamics. However, if operated without the monochromating Fermi chopper in the primary beam, a chopper spectrometer resembles the configuration of a TOF powder diffractometer. If there is no appropriate detector coverage at large scattering angles, the $Q$-resolution and $Q$-range, where $Q$ is the magnitude of the scattering vector, may be insufficient for PDF analysis. However, the ARCS spectrometer at SNS has high detector coverage over a wide angular range, scattering angles between 2 and 135 degrees, resulting in an acceptable $Q$-resolution for the higher-angle detectors. The ARCS spectrometer is situated on a relatively short flight-path (13.6 m primary, and 3.0-3.4 m secondary) at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory (ORNL) in Tennessee, currently the brightest spallation neutron source in the world. The Fermi chopper mechanism at ARCS is mounted on a motorized translation table, allowing one to easily switch between two installed Fermi chopper slit packages and an open ‘white-beam’ position. This feature means that it becomes straightforward to analyze structure and dynamics from the same sample without dismounting it from the instrument. Here we present in greater detail the preliminary experiments, which
demonstrate this capability on ARCS, that were reported in an earlier brief communication [3]. Quantitative structural information could be obtained from ARCS by obtaining reliable atomic pair distribution functions (PDFs) from the data [4] and refining models to them using the PDFgui software [5]. Here we describe in greater detail the procedure and the results.

Complete time-focussing of diffraction data from ARCS is not achievable at present due to lack of appropriate software routines. The data presented here were histogrammed to produce the 1D powder diffraction pattern using a generic TOF to \(d\)-space conversion protocol, without applying standard second order corrections. As a consequence, the data have a degraded resolution, and with poorly defined peak shapes. Attempts were made to refine the data by the Rietveld method using Fullprof [6, 7] and GSAS [8, 9] with poor results. Because the data were not fully time-focussed and inherently low resolution, the time was not spent to explore this issue any further and we concentrated on obtaining structure refinements from atomic pair distribution functions (PDFs) obtained from the data [4, 10] since the PDF is not very sensitive to details of the profile function. Successful refinements were performed as described below, demonstrating that this approach can be used even in the absence of software codes that do the full time-focussing, which is a significant challenge from a diffractometer of the complexity of ARCS. The data from Si and Ni samples are benchmarked against data from similar samples collected at the NPDF diffractometer at LANSCE with comparable statistics. NPDF is currently the highest resolution neutron powder diffractometer situated at a spallation source in the US [1] and is also a highly successful PDF instrument [11, 12, 13, 14, 15]. Finally, data for a corundum \(\text{Al}_2\text{O}_3\) sample were collected and the PDF successfully refined, demonstrating the capability for carrying out research-quality diffraction experiments on nontrivial systems at the ARCS instrument.

2. Experimental

In this study we collected neutron TOF data at ARCS at SNS on three different commercially available standard samples: Ni, Si, and \(\text{Al}_2\text{O}_3\). In addition, data from neutron TOF powder diffraction measurements on Ni and Si, carried out using the high-resolution NPDF diffractometer at LANSCE, are presented. All data were collected at room temperature.

For the ARCS experiment, loose powder samples (3.0 grams of Si, 8.3 grams of Ni, and 3.8 grams of \(\text{Al}_2\text{O}_3\)) were sealed in extruded vanadium tubes (1.11 cm in diameter, approximately 5.08 cm in height, and with wall thickness of 0.015 cm). Data for all the samples, as well as for the empty vanadium container (background), were collected for about 30 minutes each. A vanadium rod measurement was also performed to obtain incident spectrum information. The experiments were carried out using a neutron beam produced by 1.25 coulombs of charge impinging on a liquid mercury target surrounded by a decoupled water moderator [16]. In the case of standard NPDF measurements, to obtain the total scattering structure function, \(S(Q)\), raw data are corrected for experimental effects, such as sample absorption and multiple scattering, and normalized by the incident spectrum [4], using the program PDFgetN [17]. The data from ARCS were converted from scattering events as a function of TOF and detector position to histogrammed intensity as a function of \(d\)-spacing with bin sizes 0.0005 Å for 0.0625 ≤ \(d\) ≤ 0.25 Å, 0.001 Å for 0.25 ≤ \(d\) ≤ 1.5 Å, and 0.005 Å for 1.5 ≤ \(d\) ≤ 12.0 Å using Distributed Data Analysis for Neutron Scattering Experiments (DANSE) software. Variable bin sizes were chosen because of the variation in resolution as a function of \(d\)-spacing. To get \(S(Q)\), these data were minimally processed, using custom made programs to correct for the background parasitic scattering and to normalize by the incident spectrum only, without any other standard correction. This works because many of the corrections are the same for the sample and the vanadium standard and cancel during the normalization. We note that even with this coarse data treatment, it is possible to obtain useful structural information of reasonably high quality. A typical total scattering function of data collected at ARCS is shown in Figure 1(a), with the corresponding \(F(Q)\) function from NPDF shown in Figure 1(b). The structure function from ARCS is accurate
Figure 1. Total scattering function $F(Q) = Q[S(Q) - 1]$ of Ni from data collected at (a) ARCS and (b) NPDF, and $\text{Al}_2\text{O}_3$ obtained from ARCS data (c). All data were collected at room temperature for 30 minutes.

The total scattering function of $\text{Al}_2\text{O}_3$ data collected at ARCS is shown in Figure 1 (c).

The PDF, $G(r)$, is obtained from the structure function, $F(Q)$, by a Fourier transformation according to

$$G(r) = 2 \pi \int_{Q_{\text{min}}}^{\infty} Q[S(Q) - 1] \sin Qr \, dQ,$$

where $Q$ is the magnitude of the scattering vector and $Q_{\text{min}}$ is a value of $Q$ beyond the limit of the small angle scattering but below the limit of the lowest wide-angle scattering and $S(Q)$ is the properly corrected and normalized powder diffraction intensity [18]. The PDF gives the probability of finding an atom at a distance $r$ away from another atom. The PDFs presented in this study were produced using various upper limits of integration in the Fourier transform, $Q_{\text{max}}$, as follows: Ni data $Q_{\text{max}} = 25.0 \, \text{Å}^{-1}$, Si data $Q_{\text{max}} = 20.5 \, \text{Å}^{-1}$, and $\text{Al}_2\text{O}_3$ data $Q_{\text{max}} = 35.0 \, \text{Å}^{-1}$. The upper $Q$-limits in these cases are dictated by factors such as signal to noise ratio, as well as by the imperfections at higher momentum transfers resulting from incomplete data processing procedures that were used.

Assessment of the structure information was carried out via refinements of the experimental PDFs, using the program PDFgui [5]. The details of the PDF method are provided elsewhere [4, 10].

3. Results and Discussion
Here we show the quality of PDFs that can be obtained from ARCS and compare them to PDFs from NPDF. Representative experimental PDFs of Si and Ni are shown in Figure 2 (open symbols), obtained using the same value of $Q_{\text{max}}$ for both instruments. Simple visual comparison of the ARCS and the NPDF PDFs demonstrates that the ARCS data is of high quality. Furthermore, all ARCS datasets could be successfully refined. In Figure 2 fully converged structure models (solid lines) are plotted on top of the data. Standard structural models were used for Si ($Fd\overline{3}m$), and Ni ($Fm\overline{3}m$). The corresponding difference curves are shown offset for clarity.
Refinements of Si, Figure 2(a) and (b), give lattice parameters of 5.4515(2) Å and 5.4361(2) Å, and $U_{\text{iso}}$ of 0.0086(6) Å$^2$ and 0.0060(7) Å$^2$ for ARCS and NPDF data respectively, with corresponding goodness of fit, $r_W$, of 0.120 and 0.086. The quantitative results for the other samples are reported elsewhere [3]. In PDF refinements the $Q_{\text{damp}}$ parameter [5], which attenuates the PDF with increasing $r$, is the parameter that is most affected by the instrumental resolution. This parameter, as refined for the Ni standard, is markedly larger for ARCS (0.046(11) Å$^{-1}$) than it is for NPDF data (0.017(4) Å$^{-1}$) [3]. This is illustrated in Figure 3 where two datasets for Si, one from ARCS and the other from NPDF, are plotted on top of each other over a wide range of $r$. The PDF from the ARCS data clearly damps out more quickly with increasing $r$ due to the lower resolution of these ARCS data. To emphasize this, a dashed line is shown that depicts the Gaussian envelope function that is multiplied with the model-PDF to simulate this effect in the calculated PDFs. However, a significant signal persists up to 60 Å, which is beyond the range over which most PDF refinements are carried out. This suggests that powder diffraction data from ARCS are quite appropriate for PDF analysis.

Interestingly, the PDF peak width in the ARCS data also appears to be larger than that for the NPDF data for the same $Q_{\text{max}}$ used. This effect is known to appear when data have a $Q$-dependent peak broadening [19, 20] but appears to be particularly marked in these ARCS data. It is also apparent that there exists a small but systematic offset of about $+0.01$ Å in the lattice parameters obtained from the refinement of ARCS data of both Si and Ni [3], compared to those obtained for NPDF data. This is presumably an artifact that comes about due to the inadequate TOF conversion used in our procedure. In a real experiment this is readily
Figure 3. Comparison of experimental PDF data for Si 640c standard obtained at ARCS (red solid line) and NPDF (gray solid line) at room temperature, processed using the same value of $Q_{max}$. Thick dashed green line depicts the effect of diminishing PDF profile of ARCS data due to limited reciprocal space resolution.

Figure 4. PDFgui fit of the Al$_2$O$_3$ structural model to ARCS data collected at room temperature. The data are shown as open symbols and the calculated curve as a solid line. Offset below is the difference curve.

corrected for using a calibration measurement such as carried out here.

In Figure 4 we show an example of a structural refinement to data from corundum Al$_2$O$_3$, which has more structural parameters than the simple Ni and Si structures. The results [3] are in reasonable quantitative agreement with the literature values [21].

4. Summary
We have refined the first powder diffraction data from the ARCS chopper spectrometer instrument at the Spallation Neutron Source, operating in white-beam mode. The PDF data have been obtained and also refined using PDFgui. The refinements were compared to similar refinements from an established neutron powder diffractometer, NPDF at LANSCE. They yielded high quality fits and quantitatively reliable structural data, although some systematic offsets have been identified. Thus, we verify that high quality powder diffraction data, suitable also for nano-scale structure determination using the PDF, can be obtained from ARCS when used in white-beam mode without the Fermi chopper operating. This may be useful, for example, when it is desired to measure both structure and dynamics of a sample in situ without removing
it from the instrument. The ARCS Fermi chopper is able to be remotely removed from the beam to switch between white-beam diffraction and monochromatic dynamics measurements quickly.

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