Area Detector Optimization for Quantitative Analysis of High Resolution Pair Distribution Function Data

by

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ABSTRACT

Area Detector Optimization for Quantitative Analysis of High Resolution Pair Distribution Function Data

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A quantitative high resolution pair distribution function (HR-PDF) analysis is developed for use with large area detectors for synchrotron X-ray scattering measurements. Area detectors enable fast acquisition of scattering data and analysis of samples undergoing phase transitions or multiple sample comparisons. Optimization of the HR-PDF method using an area detector for quantitative analysis allows measurements of lattice constant, thermal expansion, and coordination number. A bulk gold powder sample is used as a standard for optimizing the analysis method. To demonstrate the versatility of the method, gold nanoparticles, bulk platinum, and platinum nanoparticles are measured and analysed. To increase reciprocal space coverage, the area detector is placed at an angle with the X-ray beam. The production of a 1D scattering pattern from the data collected by the tilted area detector is discussed in detail. The accuracy and precision required to conduct quantitative analysis is discussed.
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# Contents

1 Introduction .......................... 1

2 Methods ............................... 4
   2.1 X-ray Beam ................................................................. 4
   2.2 Detector ................................................................. 4
   2.3 Samples ................................................................. 5
   2.4 Scattering Pattern ..................................................... 6
   2.5 Structure Function ..................................................... 15
   2.6 Radial Distribution Function ........................................ 18
   2.7 Shell Area Function .................................................... 19

3 Results and Discussion .............. 23
   3.1 Radial Distribution Functions ........................................ 23
   3.2 Theoretical Radial Distribution Function .......................... 37
   3.3 Previous Experimental Results ....................................... 39
   3.4 Importance of Detector Orientation .................................. 42
   3.5 Orientation Parameter Search ........................................ 53
   3.6 Factors Affecting Quantitative Analysis ............................. 57
   3.7 An Approach to Compton Scattering Removal ....................... 62
   3.8 Future Work ............................................................. 64

4 Conclusion ............................. 66

References ................................ 67
List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Parameter Search Bulk Gold Solution ‘Maximizing Scattering Peak’</td>
<td>55</td>
</tr>
<tr>
<td>3.2</td>
<td>Parameter Search Bulk Platinum Solution ‘Maximizing Scattering Peak’</td>
<td>55</td>
</tr>
</tbody>
</table>
List of Figures

2.1 Area Detector Orientations ........................................................................................................ 7
2.2 Geometric Section for Detector Orientation .............................................................................. 9
2.3 Bulk Gold 10K 2D Diffraction Image ......................................................................................... 11
2.4 Detector Mosaic Dark Current Image ........................................................................................ 13
2.5 Bulk Gold 10K 1D Scattering Function ....................................................................................... 14
2.6 Atomic Scattering Factor ............................................................................................................ 16
2.7 Compton Scattering Function ................................................................................................... 16
2.8 Bulk Gold 10K Interference Function ......................................................................................... 18
2.9 Nanoparticle Shell Boundary Figure ........................................................................................ 21
2.10 Nanoparticle Shell Area Profiles ............................................................................................ 22
3.1 Bulk Gold 10K Radial Distribution Function ............................................................................ 24
3.2 Bulk Platinum 10K Radial Distribution Function ...................................................................... 25
3.3 7nm Gold Nanoparticle 10K Radial Distribution Function ....................................................... 26
3.4 2nm Gold Nanoparticle 10K Radial Distribution Function ....................................................... 27
3.5 7nm Platinum Nanoparticle 10K Radial Distribution Function ............................................... 28
3.6 2.7nm Platinum Nanoparticle 10K Radial Distribution Function ........................................... 29
3.7 2nm Platinum Nanoparticle 10K Radial Distribution Function ............................................... 30
3.8 Bulk Gold Thermal Expansion ................................................................................................ 31
3.9 Bulk Platinum Thermal Expansion .......................................................................................... 32
3.10 7nm Gold Nanoparticle Thermal Expansion ......................................................................... 33
3.11 2nm Gold Nanoparticle Thermal Expansion .......................................................................... 34
3.12 7nm Platinum Nanoparticle Thermal Expansion .................................................................... 34
3.13 2nm Platinum Nanoparticle Thermal Expansion .................................................................... 35
3.14 Coordination Numbers for Bulk and Nanoparticle Gold Samples ......................................... 36
3.15 Coordination Numbers for Bulk and Nanoparticle Platinum Samples .................................. 37
3.16 Theoretical Comparison of Bulk Gold 10K Radial Distribution Function ......................... 39
<table>
<thead>
<tr>
<th>Section Code</th>
<th>Section Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.17</td>
<td>Pritchard 2010 Bulk Gold 10K Radial Distribution Function</td>
<td>40</td>
</tr>
<tr>
<td>3.18</td>
<td>Two Theta Corrected Pritchard 2010 Bulk Gold 10K</td>
<td>41</td>
</tr>
<tr>
<td>3.19</td>
<td>Comparison with Pritchard 2010 Bulk Gold 10K</td>
<td>42</td>
</tr>
<tr>
<td>3.20</td>
<td>Detector Translations along <em>Tilt Axis</em></td>
<td>45</td>
</tr>
<tr>
<td>3.21</td>
<td>Detector Translations Normal to <em>Tilt Axis</em></td>
<td>47</td>
</tr>
<tr>
<td>3.22</td>
<td>Detector to Sample Translations</td>
<td>49</td>
</tr>
<tr>
<td>3.23</td>
<td>Detector Rotations of <em>Tilt Axis</em></td>
<td>50</td>
</tr>
<tr>
<td>3.24</td>
<td>Detector Rotations about <em>Tilt Axis</em></td>
<td>52</td>
</tr>
<tr>
<td>3.25</td>
<td>Parameter Search Radial Distribution Function</td>
<td>54</td>
</tr>
<tr>
<td>3.26</td>
<td>Parameter Search Bulk Gold Thermal Expansion</td>
<td>56</td>
</tr>
<tr>
<td>3.27</td>
<td>Parameter Search Bulk Platinum Thermal Expansion</td>
<td>56</td>
</tr>
<tr>
<td>3.28</td>
<td><em>Air Scattering</em> Effects on Coordination Number</td>
<td>58</td>
</tr>
<tr>
<td>3.29</td>
<td><em>Baseline Signal</em> Effects on Coordination Number</td>
<td>58</td>
</tr>
<tr>
<td>3.30</td>
<td>Compton Scattering Effects on Coordination Number</td>
<td>59</td>
</tr>
<tr>
<td>3.31</td>
<td>Sample to Detector Distance Effects on Coordination Number</td>
<td>60</td>
</tr>
<tr>
<td>3.32</td>
<td>Sample to Detector Distance Effects on Lattice Constant</td>
<td>60</td>
</tr>
<tr>
<td>3.33</td>
<td><em>Tilt Angle</em> Effects on Coordination Number</td>
<td>61</td>
</tr>
<tr>
<td>3.34</td>
<td><em>Tilt Angle</em> Effects on Lattice Constant</td>
<td>61</td>
</tr>
<tr>
<td>3.35</td>
<td>Polarization Fit Bulk Gold 10K Scattering Function Additive Errors</td>
<td>63</td>
</tr>
<tr>
<td>3.36</td>
<td>Polarization Fit Bulk Gold 10K Radial Distribution Function Comparison</td>
<td>64</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

In conventional powder X-ray diffraction, high resolution corresponds to the ability to measure narrow angular widths of sharp diffraction peaks. This method has had great success for characterization and confirmation of polycrystalline sample structures with relatively large (0.5µm to 1µm) perfect crystalline grain sizes (Partin and Okeeffe, 1995). Grains of this size are necessary for producing the sharp diffraction peaks that Reitveld refinement software relies on. If a sample has a significant degree of disorder, small crystalline grain sizes, or is amorphous, the required sharp diffraction peaks are not produced and the conventional powder diffraction method fails to be useful. The High Resolution Pair Distribution Function (HR-PDF) method is an alternative to conventional powder X-ray diffraction. High resolution for the HR-PDF method refers to increased spatial resolution. The HR-PDF method permits the study of disorder in polycrystalline samples, the structure of nanoparticles, and the structure of amorphous materials.

Conventional powder diffraction relies on diffraction interference to produce sharp diffraction patterns. Refinement software is able to index powder patterns and enable quantitative analysis to determine accurate lattice constants, unit cell dimensions, atomic positions, and even chemical disorder. To measure the necessary range of angles, or reciprocal space, experimenters use an in-house X-ray generator producing 8keV to 17keV characteristic X-rays from copper and molybdenum anodes (Giacovazzo et al 2002) and measure scattering angles up to 120 degrees. HR-PDF method sidesteps these limitations by interpreting the entire scattering pattern. Rather than resolving Bragg peaks to extract information, the HR-PDF method is based on performing a Fourier transform of the scattering pattern. Spatial resolution is proportional to the range of reciprocal space meas-
ured, requiring the method to use much higher energies (from 30keV to 120keV) and measuring to relatively large scattering angles. Synchrotron radiation is used in place of in-house X-ray generators to achieve the necessary energies. Synchrotron radiation has the added benefit of increasing X-ray flux by a factor of $10^3$-$10^4$, reducing the necessary collection times (Giacovazzo et al 2002).

The HR-PDF method has had great success over the years when using both neutron and X-ray scattering. The characterization of samples and interpretation of results have been both qualitative, a discussion of the structural features, and quantitative, for example determination of lattice constants, coordination numbers and densities (Bardeau et al, 1999). There are two generally accepted experimental geometries for conducting HR-PDF measurements. The original method uses point detectors for collection of the scattering data, while the more recent method uses area detectors. The area detector allows for the production of many HR-PDFs in a short time, enabling qualitative interpretation of HR-PDFs for samples passing through phase transitions or the comparison of multiple samples. The entire X-ray diffraction pattern can be collected in seconds with an area detector, while collection time with point detectors is on the order of hours. The point detector method is necessary when performing a quantitative analysis. Using the point detector produces clean quantitative data, but requires additional time to acquire statistically sufficient levels of data across the required scattering pattern. Point detectors are able to resolve X-ray energies, allowing for filtration of Compton scattering and fluorescence background from the elastic scattering. When working with area detectors, an estimated Compton scattering signal and an estimated fluorescence must be subtracted from the pattern or additional measurements are conducted to determine the two background contributions.

The principle goal of this thesis is to improve the methods of interpreting area detector data to perform quantitative analyses of polycrystalline structures. A series of X-ray diffraction measurements were conducted at the Cornell High Energy Synchrotron Source (CHESS). A tilted area detector configuration was used to increase the reciprocal space
coverage of the detector. A computer program was written to process the diffraction patterns produced by the detector and perform the necessary calculations to produce HR-RDFs. Sources of error in the data collection are identified, and methods for their removal are presented. Finally the accuracy and precision of positioning the area detector is discussed.
Chapter 2

Methods

2.1 X-ray Beam
The experimental measurements were performed at the Cornell High Energy Synchrotron Source (CHESS) based around the Cornell Electron Storage Ring (CESR) in Ithaca, New York. With a circumference of 768 meters, CESR is an electron-positron collider capable of operating at energies between 3.5-12GeV. For the duration of the diffraction experiment CESR was operating with an electron current of ~194mA at 5.3GeV. The A-2 beam line, used for the experiment, is designed to accommodate diverse X-ray techniques including high energy X-ray diffraction with X-ray energies ranging from 7keV to 60keV. The A-2 beamline is sourced by a 3m long 49 pole permanent magnet wiggler, approximately 35.5m from the center of the experimental hutch. The beam is monochromated to 60keV using two mechanically roughened, flat Si(111) crystals. The beam was trimmed vertically to 0.5mm to increase vertical diffraction resolution and horizontally to 1mm to increase X-ray flux for the diffraction experiment. The beam was then passed through a long collimator to reduce air scattering upstream from the sample.

2.2 Detector
The X-ray diffraction patterns were collected using a 40 x 40cm fixed GE area detector. The detector generates 2048 x 2048 pixel images of the X-Ray scattering pattern. Consequently, each pixel covers an area of 195 x 195µm. The detector was mounted to a fixed aluminum frame at a 45 degree angle, downstream and above the sample. The detector was rotated 45 degrees about its normal to use the longer diagonal length for collecting the vertical scattering of the samples. The detector was positioned to have the X-ray beam strike the bottom corner of the detector. A plumb bob was used to position the
top corner of the detector directly above the sample. A lead beam stop was designed to protect the detector from the incident X-ray beam, but allow X-rays to bleed through, marking the beam's position on the detector. The beam stop was placed between the detector and the sample in a position fixed with respect to the detector.

2.3 Samples

During our time at CHESS, we performed X-ray diffraction experiments on gold and platinum, using both bulk and nanoparticle, powder samples. The samples were mounted on a copper holder, using Kapton, which allowed the X-ray beam to pass through undisturbed. The copper holder was mounted to a closed cycle helium cryostat and positioned at a 45 degree angle to be approximately parallel with the face of the area detector. The cryostat was mounted to a Huber four-circle diffractometer for centering the sample holder with the X-ray beam. The cryostat was used to vary the temperature of our samples between 10K and 300K. The temperature was controlled using heating coils in the cryostat and monitored with two sets of thermocouples. When the temperature on the set of thermocouples stabilized, diffraction patterns were captured. The time for temperature stabilization was determined to be one minute for every Kelvin. A rough vacuum was maintained for temperatures above the boiling point of nitrogen (~77K), below this temperature cryopumping begins decreasing the vacuum further. Diffraction patterns for bulk samples were taken for five temperatures from 10-300K. Diffraction patterns for nanoparticles samples were taken for nineteen temperatures ranging from 10-300K. The changes in temperature cause translations of the sample position due to thermal expansion and was compensated with translations with the diffractometer. A set of exposures, with a total time of 10 minutes, were captured for each temperature. To limit detector saturation, each individual exposure varied from 1 to 33 seconds. A macro was written for the Spec control software which alters the temperature set point, pauses to stabilize the system temperature, and captures the 10 minute set of exposures. The macro begins at a 10K temperature set point and raises the temperature periodically, pausing at 60K to allow the user to switch to a rough vacuum.
2.4 Scattering Pattern

To extract a sample’s scattering pattern from the images, the position of the detector must be defined with respect to the sample and the X-ray beam. We introduce two sets of Cartesian axes, the first which we call the experimental frame is defined by the sample position, incident beam and the horizontal plane defined by the synchrotron orbit. The synchrotron orbit is defined as the circular path taken by the accelerating electrons with the synchrotron. The second set of axes, called the detector frame, is based on the detector position and its orientation with respect to the first experimental frame (Figure 2.1). The intersection of the X-ray beam with the detector is used as the origin for both Cartesian axes. With respect to this origin, the experimental frame is oriented with its positive y-axis vertically upward, positive z-axis anti-parallel to the incident X-ray beam direction and x-axis horizontal, producing a right handed coordinate system. The X-ray detector outputs a two dimensional array of pixels with coordinates $x'$ and $y'$ corresponding to the detector’s horizontal and vertical dimensions. The detector pitch angle is defined by a rotation about a tilt axis defined by the intersection of the experimental frame x-y plane and the detector frame $x'$-$y'$ plane. Five parameters are needed to define the position of the detector: $x'$ and $y'$ translations along the detector's plane to define the origin; $l$, the distance of the sample from the origin; $\phi_o$, the angle defining the tilt axis with respect to the detector's $x'$-axis; and $\tau$, the pitch angle.
Figure 2.1: a) Area detector oriented perpendicular to the incident X-ray beam, with the beam striking the center of the detector. b) The detector has been translated up along the y-axis with the incident X-ray beam striking its bottom edge and tilted 45 degrees upstream. c) In contrast to ‘b’, the detector has been rotated 45 degrees and translated up along the y-axis with the incident X-ray beam striking the bottom corner of the detector. d) Combines ‘b’ and ‘c’ to produce the experimental configuration where the detector has been rotated 45 degrees, tilted 45 degrees upward and translated to have the incident X-ray beam strike the bottom corner of the detector.
To determine the five parameters, a bulk gold powder standard was measured at room temperature. Three Debye-Scherrer rings are used to create a set of triangles along different azimuthal angles, $\varphi'$ (Figure 2.2). The angle $\varphi'$ defined as the angle from the $x'$ axis, about the detector origin, in the detector’s plane. Twenty-five sets of triangles were chosen to maximize sample points and minimize the inaccuracy of the Debye-Scherrer ring positions. The angles $\alpha, \beta$ and $\gamma$ are known from the two-theta scattering angles of the bulk gold sample using 60keV X-rays. Distance $a$, shown in Figure 2.2, is presumed to be unknown, but distances $b$ and $c$ are calculated from the position of the points on the Debye-Scherrer rings. The angle $\delta$, and the lengths $a$ and $l$ are calculated using the following equations:

$$\delta = \tan^{-1} \left[ \frac{\sin(\beta+\gamma)}{b \sin(\varphi') \cos(\beta+\gamma)} \right] - \alpha$$  \hspace{1cm} (2.1)$$

$$a = b \frac{\sin(\alpha) \sin(\delta+\alpha+\beta)}{\sin(\delta) \sin(\beta)}$$  \hspace{1cm} (2.2)$$

$$l = a \frac{\sin(\delta+\alpha)}{\sin(\alpha)}$$  \hspace{1cm} (2.3)$$

The length $l$, the sample to detector origin distance, was found to be 375±2mm. The length $a$ was used to determine the position of the origin on the detector plane, which was located at 6.8±0.3mm in the $x'$ direction and 7.2±0.2mm in the $y'$ direction. The angle $\delta$ as a function of $\varphi'$ is related to the pitch angle, and the tilt axis using the following equation:

$$\delta(\varphi') = \cos^{-1}[\sin(\tau) \cos(\varphi' - \varphi_o)]$$  \hspace{1cm} (2.4)$$

The angles $\tau$ and $\varphi_o$ were determined to be 45.1±0.1° and 45.5±0.1°, using the Levenberg-Marquardt non-linear least square fitting algorithm (Marquardt 1963).
Figure 2.2: Geometric representation of a section of three Debye-Scherrer rings. Length *a* is the distance of the first Debye-Scherrer ring from the detector origin. The lengths *b* and *c* are the distance between the Debye-Scherrer rings, and *l* is the sample to detector origin distance. The three two-theta scattering angles are *α*, *α+β* and *α+β+γ*. The angle *δ* (Equation 2.4) represents angle between the X-ray beam and the detector plane in the frame of this section.
With the detector position characterized we relate individual detector pixels to momentum transfer $Q$ where $Q = 4\pi/\lambda \sin(2\theta/2)$ (Warren 2003) using the following equation to determine $2\theta$:

$$2\theta = \sin^{-1}\left[\frac{l \sin(\delta(\varphi))}{\sqrt{a^2 + l^2 - 2al \cos(\delta(\varphi))}}\right]$$

(2.5)

The images produced by the detector are then averaged along curves of constant $Q$ to produce one-dimensional scattering functions for each sample using the following equation:

$$I(Q_i) = \frac{\sum_{\text{pixel}(Q)} I_{\text{pixel}}(Q)}{N}, \quad Q_i - \frac{\Delta Q}{2} \leq Q < Q_i + \frac{\Delta Q}{2}$$

(2.6)

As can be seen in the scattering pattern of Figure 2.3, the left and right corners have shadows. These were due to portions of the diffractometer and cryostat blocking the scattered X-rays. We chose to limit the interpretation of the pattern to the pie shaped region defined in blue which corresponds to the vertical scattering and avoided the shadowed areas. The vertical polarization of the X-rays produced by the synchrotron, absorption effects, and the rectangular beam shape cause the scattering function peaks to broaden and reduce in amplitude, as the pie shape width is increased. Decreasing the width of the pie shaped slice reduces the available data. The width of the pie shaped slice balance maximizing the scattering function peak amplitudes, and minimize peak broadening, with maximizing available data. In this case, a 20 degree pie shaped slice was used for calculating the scattering function.
Figure 2.3: Diffraction pattern collected for a bulk gold powder sample at 10K. The spectrum scales from black to white, which represents 1 to 32,000 counts respectively, on a logarithmic scale. The blue lines represent the pie shaped region integrated for producing a 1D scattering pattern and the yellow dashed lines represent the integration curves.
Several corrections are applied to the images prior to integration. It was found that every captured detector exposure exhibited a floor signal of approximately 1,700 counts, which was a flat background that must be removed. A non-uniform mosaic dark current pattern was evident and must be removed from each exposure (Figure 2.4). Finally, a separate measurement of air scattering is removed from the diffraction pattern of a sample. The floor signal and the mosaic dark current seemed to be related to a readout noise and were constant for exposure times less than 17 seconds. After 17 seconds a doubling of the floor signal and the mosaic dark current was observed. Every 17 seconds the detector reaches an exposure time limit and must acquire a new exposure. For exposures longer than 17 seconds, the detector adds multiple 17 second time limited exposures together to produce one output file. We measured samples which exhibit very strong scattering, as in the case of our gold powder standard, requiring only 1 second exposures. Other samples exhibited low levels of scattering requiring 33 second exposures. Our air scattering, mosaic dark current and Kapton sample holder measurements were conducted with 33 second exposures. Subtraction of the mosaic dark current and the floor signal scaled with the number of 17 second time limited exposures acquired for each measurement. Subtraction of air scattering and Kapton sample holder measurements are scaled to each measurement by normalizing the exposure time and the X-ray flux of the incident beam. The relative X-ray flux of the incident beam was measured using an ionization chamber positioned upstream from the sample position.
Figure 2.4: Mosaic pattern produced by detector with no X-rays present. The spectrum scales from black to white, which represents 15 to 630 counts respectively, on a logarithmic scale.

All pixels of the area detector are of equal dimension, but are not all at the same distance from the sample, nor are the angles between the surface normal of the pixel and the scattered X-rays the same for each pixel. The resultant solid angle coverage of differs from pixel to pixel. The solid angle coverage of each pixel is normalized to the central detector pixel using the following equation:
\[ \Omega = \frac{I \cos(\tau)}{(\sqrt{a^2 + l^2 - 2ly \sin(\tau)})^3} \]  

With all of the corrections applied we are able to calculate a 1D scattering function for our samples (Figure 2.5). The 1D scattering is a combination of elastic scattering, \( I(Q) \), and Compton scattering. The elastic scattering is the component of the pattern important for producing pair distribution functions.

![Scattering Function](image)

Figure 2.5: Scattering function for a bulk gold powder sample at 10K produced by a proper integration from a 2D image. Mosaic dark current, air scattering and the flat baseline backgrounds have been subtracted.
2.5 Structure Function

A structure function, $S(Q)$, is calculated from the 1D scattering function by first subtracting the Compton scattering, $C_s(Q)$, and then dividing by the square of the atomic scattering function, $f(Q)$ using the following equation, where $a$ and $c$ are scaling factors:

$$S(Q) = \frac{f(Q) - cC_s(Q)}{af(Q)^2}$$

Analytic functions presented by Baro et al. (1994) are used for the atomic scattering factor and Compton scattering functions (Figures 2.6 and 2.7) defined by the following equations:

$$f(x) = Z\frac{1 + a_1 x^2 + a_2 x^3 + a_3 x^4}{(1 + a_4 x^2 + a_5 x^4)^2}$$

(2.9)

$$C_s(x) = Z\left(1 - \frac{1 + b_1 x^2 + b_2 x^3 + b_3 x^4}{(1 + b_4 x^2 + b_5 x^4)^2}\right)$$

(2.10)

$$x = \frac{Q10^{-8} \text{ cm}}{4\pi h}$$

(2.11)
Figure 2.6: Atomic scattering factor for gold using an analytical function presented by Baro et al. (1994).

Figure 2.7: Compton scattering for gold using an analytical function presented by Baro et al. (1994).
The analytical functions are fit to the 1D scattering function to determine the multiplicative factors $a$ and $c$ using the Levenberg-Marquardt algorithm (Marquardt 1963). The resulting structure function typically presents a significant long wavelength oscillation about 1. This oscillation is an artifact due to a combination of many factors including subtraction of the Compton scattering function, division of the atomic scattering function, air-scattering subtraction, and sample volume effects. To correct for this oscillation, the structure function is smoothed using a Gaussian smooth, with a variance, $\sigma$, of $1.1\text{Å}^{-1}$, defined by the following equation, where $Q_i$ ranges the entire structure function:

$$S_{\text{smooth}}(Q_n) = \frac{\sum_i S(Q_n) e^{-\frac{(Q_n-Q_i)^2}{2\sigma^2}}}{\sum_i e^{-\frac{(Q_n-Q_i)^2}{2\sigma^2}}}$$

(2.12)

Smoothing the structure function removes all sharp diffraction features and leaves the long wavelength baseline error curve. Dividing the structure function by the baseline error curve, a corrected interference function is produced from the structure factor (Figure 2.8) using the following equation:

$$i(Q) = Q \left( \frac{S(Q)}{S_{\text{smooth}}(Q)} - 1 \right)$$

(2.13)
2.6 Radial Distribution Function

A reduced pair distribution function is produced through Fourier transform of the structure function using the following function (Warren 2002):

$$G(r) = \frac{2}{\pi} \int_0^\infty i(Q) \sin(Qr)dQ$$  \hspace{1cm} (2.14)

The Fourier transform integral was calculated using the trapezoid method of integration defined by the following equation:

$$\int_{x_1}^{x_n} f(x)dx \approx \sum_{i=0}^{n-1} (x_{i+1} - x_i) \left[ \frac{f(x_{i+1}) + f(x_i)}{2} \right]$$  \hspace{1cm} (2.15)

Higher order integration techniques were unnecessary due to the pixel resolution available with the detector. To reduce ringing effects due to truncation of the Fourier integral, a
cosine dampening function is applied to the interference function using the following equation:

\[ damp(Q) = \cos^n \left( \frac{\pi Q}{2q_{\text{max}}} \right) \quad (2.16) \]

The dampening function causes the spatial resolution of the reduced pair distribution function to decrease, broadening the width of every peak in the function. By varying the exponent \( n \) of the dampening function, a balance between reducing truncation error and peak broadening can be found. The radial distribution function is calculated from the reduced pair distribution function for each of the materials using the following equation (Kruh 1967):

\[ RDF(r) = 4\pi r^2 \rho + rG(r) \quad (2.17) \]

### 2.7 Shell Area Function

The radial distribution function describes the average number of atoms which occur in a shell of radius \( r \) about some arbitrary central atom. In part, the radial distribution function contains a shell area function. Under the assumption of a uniform density of a material, the shell area for a bulk sample is given as \( 4\pi r^2 \). The contribution from the pair distribution function removes the uniformity of the shell area and shapes the atomic peaks within the structure. The finite size of nanoparticles requires a different shell area function. To determine the shell area function of spherical nanoparticles with radius \( R \), the shell areas are averaged about every point within the nanoparticle. Using the symmetry of a sphere, only the points along the radius are required to determine the average. At the center of the sphere, the shell area begins as \( 4\pi r^2 \), similar to the bulk sample, but drops sharply to zero at the surface of the sphere. With the surface area centered away from the center of the sphere, the shell area again goes as \( 4\pi r^2 \), but at a critical point only a portion of the shell passes beyond the edge of the nanoparticle sphere. A critical angle is used to describe the portion of the shell which was beyond the bound of the nanoparticle sphere.
(Figure 2.9) and defined by the following equation:

$$\theta_c = \cos^{-1}\left(\frac{x^2 + r^2 - R^2}{2rx}\right)$$  \hspace{1cm} (2.18)

By integrating, a surface area with some radius $r$, bound by the surface of the nanoparticle sphere and centered anywhere along the sphere's radius is described by the following equations:

$$r^2 \int_0^{2\pi} d\phi \int_0^{\theta_c} \sin(\theta) d\theta = 2\pi r^2[1 - \cos(\theta_c)]$$  \hspace{1cm} (2.19)

$$A(r,x) = \left\{ \begin{array}{ll}
4\pi r^2, & x < R - r \\
2\pi r^2 \left[ 1 + \frac{R^2 - r^2 - x^2}{2rx} \right], & R - r < x < R \\
0, & x > R \\
2\pi r^2 \left[ 1 + \frac{R^2 - r^2 - x^2}{2rx} \right], & r - R < x < R \\
0, & x > R \\
\end{array} \right\}, \hspace{0.5cm} r < R$$  \hspace{1cm} (2.20)

All of the surface areas are then averaged along the nanoparticle sphere's radius, using an integral method, producing a shell area function with dependence on the nanoparticle's radius described by the following equation:

$$\frac{1}{R} \int_0^R A(r,x) dx = \left\{ \begin{array}{ll}
\pi r \left[ 4r \left( R - \frac{r}{2} \right) + (R^2 - r^2) \ln\left(\frac{R}{|R-r|}\right) + \frac{r^2 - 2rR^2}{2} \right], & r < 2R \\
0, & r \neq R \\
\end{array} \right\} \hspace{0.5cm}, \hspace{0.5cm} r < 2R$$  \hspace{1cm} (2.21)

The size and peak area position of the shell area functions change drastically between 2nm, 4nm, and 7nm nanoparticles (Figure 2.10).
Figure 2.9: Demonstrates the bounds of the nanoparticle sphere. The large circle represents a nanoparticle with radius $R$ and the smaller circle represents a shell centered a distance of $x$ from the center of the nanoparticle and a radius $r$. The shaded region demonstrates the section of the shell which remains within the bounds of the nanoparticle. The edge of this boundary is described by a critical angle $\theta$. 
Figure 2.10: Shell area profiles derived for a bulk material and nanoparticles with diameters of 2nm, 4nm, and 7nm.
Chapter 3

Results and Discussion

3.1 Radial Distribution Functions

Radial distribution functions were determined for bulk gold and platinum powder samples at 10K (Figures 3.1 and 3.2). To determine lattice constants for the samples, the position of the first set of peaks in the radial distribution functions are determined using Gaussian fits. The set of peaks are fit to Gaussian functions allowing position, height and width to vary. The positions of the peaks were compared to an expected face centered cubic structure to determine the lattice constant. An average, weighted by the ratio of expected atom distance to lattice constant, is used to determine the lattice constant. Lattice constants for the bulk gold and platinum samples at 10K were determined to be 4.0693±0.0003Å and 3.9141±0.0005Å, respectively. Expected lattice constants of 4.0649Å for bulk gold at 10K and 3.9151Å for bulk platinum at 10k are determined using expected room temperature values (Gray 1972) and Gruneisen-Debye theory for linear expansion (Nix and MacNair 1941 and 1942). The Gruneisen-Debye theory for linear expansion is discussed in more detail in the thermal expansion portion of this section. The errors quoted for the lattice constants represent the error in the fit procedure for determining the lattice constant. Additional errors in calculating the radial distribution function must be considered including errors in X-ray energy, detector orientation and the scattering function.
Figure 3.1: Radial distribution function for a bulk gold powder sample at 10K.
Figure 3.2: Radial distribution function for a bulk platinum powder sample at 10K.

The radial distribution functions for bulk gold and platinum exhibited artifacts amongst the structure, similar to Sinc functions centered about the peaks. The artifacts are appearing due to Fourier transform truncation errors and additive errors in the scattering function. The use of the cosine dampening function causes wide broadening of the peaks in attempts to remove the artifacts.

Applying the shell area function, radial distribution functions were calculated for gold and platinum nanoparticle powder samples at 10K. The 7nm gold nanoparticle exhibited similar additive errors as the bulk gold sample at 10K with broadened peaks (Figure 3.3). To produce the radial distribution function for the 2nm gold nanoparticle, the scattering function was truncated at 25Å⁻¹ to remove unnecessary noise where no elastic scattering was observed (Figure 3.4). The lattice constants for the 7nm and 2nm gold nanoparticles
were calculated to be 4.0654±0.0008Å and 4.058±0.006Å, respectively. The large increase in error is the result of fitting the nanoparticles to a face centered cubic lattice when the expected structure is a combination of octahedral and dodecahedral structures (Leisti 2009). Lattice constants fitted from the radial distribution functions for the 7nm, 2.7nm, and 2nm platinum nanoparticles were 3.9226±0.0005Å, 3.9180±0.0006Å and 3.930±0.003Å respectively (Figures 3.5-3.7).

![Figure 3.3: Radial distribution function for 7nm gold nanoparticle powder sample at 10K.](image-url)
Figure 3.4: Radial distribution function for 2nm gold nanoparticle powder sample at 10K.
Figure 3.5: Radial distribution function for 7nm platinum nanoparticle powder sample at 10K.
Figure 3.6: Radial distribution function for 2.7nm platinum nanoparticle powder sample at 10K.
Figure 3.7: Radial distribution function for 2nm platinum nanoparticle powder sample at 10K.

The lattice constants of the bulk samples are shown as a function of temperature ranging from 10-300K (Figures 3.8 and 3.9). The expansion trend is compared to Gruneisen-Debye linear expansion theory (Nix and MacNair 1941 and 1942). The linear expansion is determined using the following equation.

$$\alpha = \frac{C_v}{3Q_0(1-k\frac{E}{Q_0})^2}$$

(3.1)

The molar specific heat, $C_v$, and the energy of the lattice vibrations, $E$, are calculated using the following equations (Gray 1972).

$$C_v = 3R \left[ 12 \left( \frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{y^3dy}{e^y-1} - 3 \frac{\theta_D}{e^{\theta_D/T} - 1} \right]$$

(3.2)
\[ E = \int_0^T C_v dT \]  

(3.3)

The Debye temperature, \( \theta_D \), and the constants \( k \) and \( Q_\theta \) are given by Nix and MacNair (1941 and 1942) for gold and platinum. The constant \( R \) is the molar gas constant. The lattice constants at 10K for gold and platinum were used to iteratively solve for the lattice constants at higher temperatures using Gruneisen-Debye linear expansion.

\[ \text{Figure 3.8: Lattice constants for a bulk gold powder sample and temperatures ranging from 10K to 300K.} \]
The bulk gold sample exhibits a similar trend to Gruneisen-Debye theory, but with a systematically lower thermal expansion. An unrealistic expansion trend was shown for the bulk platinum sample, beginning with a compression effect as temperature before expanding after 100K. The nanoparticle samples exhibit a general expansion trend from 10-300K with small fluctuations between expansion and compression as temperature rises (Figures 3.10-3.13). A final constant for the nanoparticles was calculated with the samples exposed to air, shown in red in the figures. The discrepancy in the lattice constant for the exposed sample, when compared to the samples under vacuum, shows that the temperatures of the samples were not well known. Small changes in the position of the detector, with respect to the sample, and fluctuations in the sample temperature can account for the errors in the lattice constants.
Figure 3.10: Lattice constants for a 7nm gold nanoparticle powder sample and temperatures ranging from 10K to 300K. The data point in red shows the lattice constant calculated with the sample exposed to air during exposures.
Figure 3.11: Lattice constants for a 2nm gold nanoparticle powder sample and temperatures ranging from 10K to 300K. The data point in red shows the lattice constant calculated with the sample exposed to air during exposures.

Figure 3.12: Lattice constants for a 7nm platinum nanoparticle powder sample and temperatures ranging from 10K to 300K. The data point in red shows the lattice constant calculated with the sample exposed to air during exposures.
The coordination numbers for the gold and platinum samples are determined by integrating a section of the radial distribution function centered about the nearest neighbour peak (Figures 3.14 and 3.15). The coordination number for a bulk gold sample at 10K was determined to be $11.5\pm0.4$, and for 7nm and 2nm gold nanoparticles at 10K to be $9.2\pm0.3$ and $6.84\pm0.02$, respectively. The coordination number for a bulk platinum sample at 10K was determined to be $11.906\pm0.008$, and for 7nm, 2.7nm, and 2nm platinum nanoparticles at 10K to be $11.703\pm0.008$, $10.338\pm0.009$, and $8.98\pm0.03$, respectively. Both gold and platinum bulk crystals have FCC structures and are expected to have a nearest neighbour coordination number of twelve atoms. The finite nature of nanoparticles will result in a decrease in coordination number from surface boundary effects. Incorrect removal of Compton scattering and other additive errors in the scattering function will adversely affect the nearest neighbour coordination number.

Figure 3.13: Lattice constants for a 2nm platinum nanoparticle powder sample and temperatures ranging from 10K to 300K. The data point in red shows the lattice constant calculated with the sample exposed to air during exposures.
Figure 3.14: Integration of the radial distribution function for a bulk gold and nanoparticle powder samples centered about the first nearest neighbour.
Figure 3.15: Integration of the radial distribution function for a bulk platinum and platinum nanoparticle powder samples centered about the first nearest neighbour.

3.2 Theoretical Radial Distribution Function

A theoretical comparison of a FCC structure with the bulk gold powder sample can demonstrate the quality of the experimentally produced radial distribution function. To create a theoretical radial distribution function, pseudo-Voigt functions are placed at the expected atomic positions (Young and Wiles, 1982). Pseudo-Voigt functions are a combination of Gaussian and Lorentz functions as described in the following equation:

\[
pV(x) = \eta \left[ e^{-\frac{(x-\mu)^2}{2\sigma^2}} \right] + (\eta - 1) \left[ \frac{1}{2\pi r} \frac{1}{(x-x_0)^2 + \left(\frac{r}{2}\right)^2} \right]
\]  

\[ \text{(3.4)} \]

The ratio of Gaussian to Lorentz contribution to the pseudo-Voigt functions is fixed. The
area under each pseudo-Voigt function is fixed to the number of atoms expected at each atomic position. The height of the pseudo-Voigt function located at the nearest neighbour position is set to match the height of the peak in the experimental data, allowing the full width at half max width to adjust for the expected area beneath the peak. For the peaks beyond the nearest neighbour, a linear change in the full width at half max of the pseudo-Voigt function adjusts for peak broadening as the radial distance increases. The computer program allows adjustment of the nearest neighbour peak height, the lattice constant, the Gaussian to Lorentz ratio of the pseudo-Voigt function, and the slope of the pseudo-Voigt width change. Plotting the bulk gold powder sample, a face centered cubic structure, with this pseudo-Voigt line shape theory shows appreciable agreement with increasing divergence as the radial distance increases (Figure 3.16). Errors in removing background scattering, Compton scattering, and dark current in the detector are apparent when comparing the resultant radial distribution function with theory. Without proper removal of background, determining fine structure from artifacts is improbable and hampers attempts to characterize unknown structures.
3.3 Previous Experimental Results

The radial distribution function for the bulk gold powder sample used in this experiment was also determined, at temperature of 10K, in a previous experiment outlined by Pritchard, 2010. Pritchard’s scattering pattern was collected using an array of five solid state germanium detectors at a fixed distance from the sample. Before considering the differences between the radial distribution functions, a correction was applied to the interference function determined by Pritchard. An asymmetry was apparent in the peaks of Pritchard’s radial distribution function (Figure 3.17). Applying a linear offset of 0.63° to the two theta angles used for the position of the solid state detector resulted in the peaks in the radial distribution function obtaining a symmetric line shape (Figure 3.18). In determining the radial distribution function, from the scattering function obtained by the
solid state detectors, a cosine dampening was applied to the interference function. To compare the current radial distribution functions, a cosine dampening was applied to the current interference function with some power, $n$, to have the nearest neighbour peak heights match between both methods. The two radial distribution functions could then be compared qualitatively (Figure 3.19). There was a lattice constant change between the two radial distribution functions which could be the result of incorrect detector orientation parameters in the current experiment, incorrect temperature measurement, or incorrect X-ray energy determination in either experiment. Artifacts due to additive errors are noticeably larger in the current experimental determination.

![Figure 3.17: Radial distribution function of a bulk gold powder sample at 10K determined by Pritchard through use of an array of solid state detectors. An asymmetric line shape was apparent with a tapered left shoulder and a sharp right shoulder.](image-url)
Figure 3.18: Radial distribution function of a bulk gold powder sample at 10K from previous experimental data (Pritchard 2010) with a two theta offset of 0.063 applied for this thesis. The two theta offset removed the asymmetry in the peak line shapes.
Figure 3.19: Comparison of the current bulk gold radial distribution function to the previous experimental data (Pritchard 2010). An offset in the lattice constant between both radial distribution functions was clear.

3.4 Importance of Detector Orientation

Determining the correct position and orientation of the detector, with respect to the location of the sample, is important when producing a radial distribution function from the observed diffraction pattern. Inaccuracies in describing the correct location of the detector will result in non-linear offsets to the Q value associated to every pixel. Using visual inspection of the radial distribution function to characterize the effects of purposely misaligning the detector can determine the accuracy of the predicted alignment.

The rates of change in two theta, with respect to each of the orientation parameters, are used to determine the accuracy required for each parameter described by the following equations:
\[
\frac{d\theta}{dl} = \frac{a \sin(\delta(\varphi'))}{\sqrt{a^2 + l^2 - 2al \cos(\delta(\varphi'))}}
\]

(3.5)

\[
\frac{d\theta}{d\tau} = -\frac{l \cos(\delta(\varphi_o)) - \frac{a^2 \sin(\delta(\varphi'))^2}{a^2 + l^2 - 2al \cos(\delta(\varphi'))} \cos(\tau) \cos(\varphi' - \varphi_o)}{\left[a - l \cos(\delta(\varphi_o))\right] \sqrt{1 - \cos(\varphi' - \varphi_o)^2}}
\]

(3.6)

\[
\frac{d\theta}{d\varphi_o} = -\frac{l \cos(\delta(\varphi_o)) - \frac{a^2 \sin(\delta(\varphi'))^2}{a^2 + l^2 - 2al \cos(\delta(\varphi'))} \sin(\tau) \sin(\varphi' - \varphi_o)}{\left[a - l \cos(\delta(\varphi'))\right] \sqrt{1 - \cos(\varphi' - \varphi_o)^2}}
\]

(3.7)

\[
\frac{d\theta}{dx_o} = -\frac{l \sin(\delta(\varphi'))[x - x_o]}{\sqrt{(x - x_o)^2 + (y - y_o)^2}} + \frac{d\theta}{d\varphi_o} \frac{y - y_o}{(x - x_o)^2 + (y - y_o)^2}
\]

(3.8)

\[
\frac{d\theta}{dy_o} = -\frac{l \sin(\delta(\varphi'))[y - y_o]}{\sqrt{(x - x_o)^2 + (y - y_o)^2}} - \frac{d\theta}{d\varphi_o} \frac{1}{\left[1 + \left(\frac{y - y_o}{x - x_o}\right)^2\right] \sqrt{(x - x_o)^2 + (y - y_o)^2}}
\]

(3.9)

With respect to each parameter, the maximum rate of change across the detector is determined and compared to the average two theta width associated to the pixels of the detector, determining maximum allowable errors in each parameter described in the following equations:

\[
\tilde{\theta}_w = \sqrt{\frac{\sum_{x=1}^{N_x} \sum_{y=1}^{N_y} \left(\frac{d\theta}{dx_o}\right)^2 + \left(\frac{d\theta}{dy_o}\right)^2}{N_x N_y}}
\]

(3.10)

\[
\sigma_{l_{\text{max}}} = \frac{\tilde{\theta}_w}{\frac{d\theta}{dl}}
\]

(3.11)

The maximum allowable errors in each parameter limit the two theta error for each pixel to within the resolution limit of the detector configuration, as defined by the average two theta width of the pixels.
With the detector positioned with \( l = 375\text{mm}, \tau = 45.1^\circ, \varphi_o = 45.5^\circ, x_o = 6.8\text{mm} \) and \( y_o = 7.2\text{mm} \), we determine the maximum allowable errors to be \( \sigma_{\_l}^{\text{max}} = \pm 0.22\text{mm}, \sigma_{\_\tau}^{\text{max}} = \pm 0.03^\circ, \sigma_{\_\varphi}^{\text{omax}} = \pm 0.06^\circ, \sigma_{\_x}^{\text{omax}} = \pm 0.029\text{mm}, \) and \( \sigma_{\_y}^{\text{omax}} = \pm 0.029\text{mm} \) with a pixel resolution limit, \( 2\overline{\theta_w} \), of 0.04°. For comparison, a detector oriented perpendicular to the incident X-ray beam with the same detector to sample distance has maximum allowable errors of \( \sigma_{\_l}^{\text{max}} = \pm 0.28\text{mm}, \sigma_{\_\tau}^{\text{max}} = \pm 0.02^\circ, \sigma_{\_\varphi}^{\text{omax}} = \pm 0.14\text{mm}, \) and \( \sigma_{\_y}^{\text{omax}} = \pm 0.14\text{mm} \) and a resolution limit of 0.02°. With the detector perpendicular to the beam, errors in \( \varphi_o \) are only relevant for the polarization of the X-ray beam. An increase in the accuracy of \( \tau \) is required when orienting the detector perpendicular to the X-ray beam; however, a decrease in accuracy of \( l \), and a significant decrease in \( x_o \) and \( y_o \), are allowed to contain \( 2\theta \) errors within the resolution limit. When fitting the tilted detector orientation using the Debye-Scherrer rings of bulk gold standard, the errors in each parameter were calculated to be \( \sigma_{\_l} = 2\text{mm}, \sigma_{\_\tau} = 0.1^\circ, \sigma_{\_\varphi} = 0.1^\circ, \sigma_{\_x} = 0.3\text{mm} \) and \( \sigma_{\_y} = 0.2\text{mm} \). The calculated errors for each parameter are beyond the maximum allowable errors. The resultant effects of errors occurring beyond the maximum allowable errors must be considered.

Translations along two perpendicular axes, within the detector’s plane, were applied to the predicted detector location. One translation was applied along the tilt axis of the detectors. Due to the symmetry about the normal to the tilt axis, only translations in one direction will be discussed. By applying translations \( \leq 0.4\text{mm} \) along the tilt axis, no changes in the radial distribution function were observed (Figure 3.20). At translations \( \geq 1\text{mm} \), the peak heights were visibly decreased. At translations \( \geq 2\text{mm} \), greater reduction of the radial distribution function peak heights occurred at larger radial distance.
Figure 3.20: Radial distribution function comparison of applying detector translations along the tilt axis.
The second translation, requiring translation in both directions, was applied along the normal of the tilt axis within the plane. With translations along an axis normal to the tilt axis and centred at the origin, consistent changes in the line shape of the radial distribution function peaks were observed. A translation, which caused the incident X-ray to intersect the detector plane lower than predicted introduced a steep left shoulder, with a tapered right shoulder, and caused an expansion effect on the lattice (Figure 3.21). At translations of ≤0.4mm a gradual change was observed in the peaks' line shape and lattice expansion. At translations >0.4mm the effects of the new line shape distorted the radial distribution function to the point of altering the structure. Translations in the opposing direction, causing the incident X-ray to intersect the detector plane higher than predicted, developed an opposing change in the peak line shape. The peak resulted in a steep right shoulder, a tapered left shoulder, and a compression effect on the lattice. Similarly to that of the previous translation, translations of ≥-0.4mm had shown gradual transitions into the new line shape and lattice compression. At translations of <-0.4mm, the line shape distorted the radial distribution function to the point of altering the structure.
Figure 3.21: Radial distribution function comparison of applying detector translations normal to the tilt axis
The effects of incorrectly measuring the distance from the sample to the detector origin were also examined. If the detector is closer, or further than, expected the Q value of any pixel will be calculated to be smaller or larger, respectively. Due to the detector being tilted and not being perpendicular to the X-ray beam, any constant Q value ring changes in shape and relative position, when changing the sample to detector distance. From this, the effects of inaccuracies in this distance will be different from translations of the detector on its own plane. Translations causing the detector to be closer than predicted resulted in an expansion effect on the radial distribution function (Figure 3.22). With translations between 0 and 0.5mm, a gradual expansion was observed, while >2.5mm there were observable changes to the peak structure. At translations >5mm, the peaks exhibited broadening and alterations of their line shape. Translations, in the opposing direction, of ≥0.5mm exhibited a gradual compressive effect on the radial distribution function. At translations between 0 and 0.5mm, alterations in the peak structure appeared in the radial distribution function. Broadening of the radial distribution function peaks coupled with changes in peak line shape led to deterioration of the peak structure.
Figure 3.22: Radial distribution function comparison of changes in applying detector to sample distance
The effects of applying an incorrect tilt in the determination of the detector's orientation were examined. Inaccuracies in applying the tilt can occur with an incorrect tilt angle or by applying the tilt about the wrong tilt axis. As errors in the axis used for tilting the detector were symmetric about the correct tilt axis, only positive changes in the angle representing the tilt axis were considered. Alterations of $\leq 1^\circ$, the radial distribution function showed only small observable differences when compared with the radial distribution function with the unaltered tilt axis. With alterations of $>1^\circ$ a compressive effect was observed. Alterations $\geq 2^\circ$, a loss of structure and introduction of artifacts was observed (Figure 3.23).

![Figure 3.23: Radial distribution function comparison of applying rotations in the tilt axis](image)

Figure 3.23: Radial distribution function comparison of applying rotations in the tilt axis
Both positive and negative errors in the tilt angle were examined. Tilting the detector about the rotation axis stretched the Debye-Scherrer rings along the normal to the rotation axis, with greater effects at higher two theta scattering angles. With rotations of $\leq 0.05^\circ$, changes in the line shape of the peaks were observed, a sharp left shoulder with a tapered right shoulder and an expansive effect of the radial distribution function. At a rotation of $>0.25^\circ$, the resultant radial distribution function showed observable changes in the peak structure. Rotations $>0.5^\circ$ resulted in the deterioration of the radial distribution function structure. Applying rotations in the opposite direction resulted in opposing changes within the radial distribution function. Increasing changes in line shape, a steep right shoulder with a tapered left shoulder, and compressive effects were observed in rotations of $\geq 0.05^\circ$. Alterations in the peak structure were observed with rotations $<-0.25^\circ$, resulting in deterioration of the radial distribution function at rotations $<-0.5^\circ$. (Figure 3.24)
Figure 3.24: Radial distribution function comparison of rotations in detector tilt
3.5 Orientation Parameter Search

A parameter search was performed to improve upon the fitted parameters for the detector orientation. The time required to perform a parameter search of the five necessary parameters increases on the order of the size of the parameter space searched to the power of five. A successful parameter search can determine the position of the detector with no prior information about the scattering sample. For the parameter search to be successful some criteria must be determined. Initially parameter space was searched to determine a pair distribution function with the highest chaotic order, under the assumption that the ideal constructive and destruction interference caused by the interference function would result in the single most divergent pair distribution function. The chaotic order was determined using the root mean square of the pair distribution function. The solution for the method was divergent due to artificial expansion of the pair distribution function. A second divergent method was attempted by maximizing the root mean square of the scattering function, but artificial stretching of the scattering function resulted in an increasing root mean square value.

A convergent solution for the parameter search was found by minimizing the agreement of the radial distribution function peak positions for a bulk gold powder sample with the expected face centered cubic structure, allowing the lattice constant to change freely. However the solution produced a radial distribution function with asymmetric peak shapes. Using face centered cubic peak position alone is insufficient for determining the orientation parameters of the detector. A second convergent solution was found using the criteria of maximizing the peak heights in the scattering function. By maximizing the peak heights, the peaks in the calculated radial distribution function continue to show asymmetric peak shapes (Figure 3.25). For a bulk gold powder sample at 10K, the search produced parameters within two standard deviations of the fitted orientation parameters. The determined parameters are presented in Tables 3.1 and 3.2 with the results from the parameter search for the bulk gold and platinum powder sample at various temperatures. The parameters determined vary between each sample and at every temperature, which
illustrates that an assumption of an invariant detector position with respect to the sample is unreasonable. Plotting the lattice constants for both samples, we can see significant differences from the expansion observed from the fitted orientation (Figures 3.26 and 3.27). Unrealistic fluctuations are still present in the expansion of the bulk platinum sample which suggests that maximizing the scattering peak heights was insufficient for orienting the detector. A convergent solution which properly determines the detector orientation parameters could be reached by considering multiple criteria simultaneously.

Figure 3.25: Radial distribution function for a bulk gold powder sample at 10K using a detector orientation determined through a parameter search maximizing scattering peak heights.
Table 3.1: Parameter search solutions determined for the bulk gold powder sample

<table>
<thead>
<tr>
<th>Temperature</th>
<th>x' (mm)</th>
<th>y' (mm)</th>
<th>l (mm)</th>
<th>τ (°)</th>
<th>φ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10K</td>
<td>7.098</td>
<td>7.352</td>
<td>374.636</td>
<td>44.835</td>
<td>45.520</td>
</tr>
<tr>
<td>50K</td>
<td>7.104</td>
<td>7.314</td>
<td>374.683</td>
<td>44.857</td>
<td>45.560</td>
</tr>
<tr>
<td>100K</td>
<td>7.099</td>
<td>7.310</td>
<td>374.682</td>
<td>44.826</td>
<td>45.589</td>
</tr>
<tr>
<td>200K</td>
<td>7.088</td>
<td>7.360</td>
<td>374.648</td>
<td>44.874</td>
<td>45.499</td>
</tr>
<tr>
<td>300K</td>
<td>7.086</td>
<td>7.361</td>
<td>374.652</td>
<td>44.888</td>
<td>45.476</td>
</tr>
</tbody>
</table>

Table 3.2: Parameter search solutions determined for the bulk platinum powder sample

<table>
<thead>
<tr>
<th>Temperature</th>
<th>x' (mm)</th>
<th>y' (mm)</th>
<th>l (mm)</th>
<th>τ (°)</th>
<th>φ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10K</td>
<td>7.115</td>
<td>7.303</td>
<td>374.680</td>
<td>44.850</td>
<td>45.600</td>
</tr>
<tr>
<td>50K</td>
<td>7.137</td>
<td>7.271</td>
<td>374.693</td>
<td>44.970</td>
<td>45.850</td>
</tr>
<tr>
<td>100K</td>
<td>7.105</td>
<td>7.309</td>
<td>374.832</td>
<td>44.978</td>
<td>45.799</td>
</tr>
<tr>
<td>200K</td>
<td>7.099</td>
<td>7.329</td>
<td>374.860</td>
<td>44.913</td>
<td>45.836</td>
</tr>
<tr>
<td>300K</td>
<td>7.129</td>
<td>7.300</td>
<td>374.833</td>
<td>44.913</td>
<td>45.846</td>
</tr>
</tbody>
</table>
Figure 3.26: Thermal expansion for the lattice constant of the bulk gold powder sample using the orientation parameter search solution.

Figure 3.27: Thermal expansion for the lattice constant of the bulk platinum powder sample using the orientation parameter search solution.
3.6 Factors Affecting Quantitative Analysis

With the method used for smoothing the structure function, additive errors have an adverse effect on the radial distribution function and the coordination number. Artificial Sinc functions centered about each peak in the radial distribution function occur due to incorrect removal of the additive errors and truncation of the scattering pattern. Possible sources of additive errors include, but are not limited to, air scattering, the baseline signal, the mosaic dark current, background scattering, and Compton scattering. To illustrate the effects additive errors have on the coordination number of a bulk gold powder sample at 10K, applying changes in the subtraction of air scattering, baseline signal, and Compton scattering were considered. For changes in the subtraction of air scattering and baseline signal, one variable was allowed to fluctuate and the other was held constant while leaving Compton subtraction to fluctuate (Figures 3.28 and 3.29). For changes in the amount of Compton scattering subtraction, the air scattering and linear baseline offset subtractions were held constant (Figure 3.30). Varying all three parameters caused changes to the coordination number of the bulk gold powder sample. As the coordination number increased towards the expected face centered cubic nearest neighbour coordination number of twelve the error in the coordination number increased, indicating additional errors are prevailing in the scattering pattern. To properly subtract a baseline signal, careful measurement of the detector's dark images over the same exposure time must be taken for each diffraction pattern. Careful measurement of air scattering is required while considering all possible equipment interferences, for example absorption effects of the cryostat enclosing the samples. Compton scattering must be measured carefully to ensure correct subtraction. Finally to remove random scattering events in the background of the experiment, lead shielding should be used wherever possible.
Figure 3.28: Effects of varying air scattering removal on the coordination number of a bulk gold powder sample at 10K.

Figure 3.29: Effects of varying baseline signal on the coordination number of a bulk gold powder sample at 10K.
Figure 3.30: Effects of varying Compton scattering removal on the coordination number of a bulk gold powder sample at 10K with respect to the scattering function fitted Compton scattering.

Correcting additive errors in air scattering, baseline signal and Compton scattering are insufficient to obtain an expected coordination number of 12 atoms. The orientation of the detector can affect coordination number.

Changes in detector to sample distance and tilt angle cause adverse effects in the radial distribution function, as discussed in section 3.4. The lattice constant and coordination number can be affected by small deviations in these parameters. For every 1mm change in sample to detector distance there is a 0.5% change in coordination number (Figure 3.31) and a 0.3% change in lattice constant (Figure 3.32). In contrast, for every 0.1° change in tilt angle there is a 0.2% change in coordination number (Figure 3.33) and a 0.01% change in lattice constant. Correcting errors in the orientation of the detector can produce expected coordination numbers; however, the corrections can have severe effects on the radial distribution function as discussed in section 3.4.
Figure 3.31: Effect of sample to detector distance on coordination number.

Figure 3.32: Effect of sample to detector distance on lattice constant.
Figure 3.33: Effect of tilt angle on coordination number.

Figure 3.34: Effect of tilt angle on lattice.
3.7 An Approach to Compton Scattering Removal

A novel method for Compton scattering removal involves using the polarization of the X-rays with the axial scattering captured by the area detector. The axial scattering is affected by the polarization of the incident X-rays while the Compton scattering remains uniform. A fit of the polarization of the scattered X-ray intensity plus a linear offset along constant two theta curves can provide information on the Compton scattering plus any linear additive error. Non-linear errors or multiplicative errors along the constant two theta curve will cause errors in calculating the elastic scattering. Applying this fitting technique to the bulk gold powder sample resulted in an additive correction which included diffraction structure and lacked complete Compton scattering removal (Figure 3.35). The resultant radial distribution function exhibited broadened peaks, but reduced artificial features compared to the previously calculated radial distribution function (Figure 3.36). The rectangular nature of the beam used in the experiment caused broadening of the diffraction peaks when moving axially from vertical scattering to horizontal scattering. A symmetric X-ray beam is required to make using this method for Compton and additive error removal feasible.
Figure 3.35: Additive error to the scattering pattern of a bulk gold powder sample at 10K determined through axial fitting of polarization and linear offset. Some of the necessary diffraction pattern still remained due to non-linear errors, for example axial peak broadening from a rectangular X-ray beam.
Figure 3.36: Comparison of the radial distribution functions from the experimental method with the polarization fitting method. The polarization fitting method exhibits a slight peak broadening with a noticeable reduction in noise about the peaks.

3.8 Future Work

By tilting the detector we have allowed increased coverage of momentum space during the same acquisition time. The increased coverage is important for bulk samples which have valuable diffraction patterns at larger $Q$ values. The accuracy of the orientation of the detector is important for quantitatively analysis of the radial distribution function. Use of lower X-ray energies provides an increase of X-ray flux resulting in an increased peak to noise ratio. With the detector tilted, one could work with 35keV X-rays in order to obtain 25Å$^{-1}$ of momentum space coverage.
With the tilted detector placed downstream and above the sample, a second area detector could be placed upstream and below the sample to further increase momentum space coverage. Positioning the second detector to cover 80° to 170° two theta scattering angle avoids interfering with the incident X-ray beam. With this second detector, 25Å⁻¹ of momentum space would be covered with 25keV X-rays and 43Å⁻¹ of coverage would be obtained with 43keV X-rays. With possible X-ray flux and energy restrictions, these increases of coverage will be useful for X-ray diffraction research scientists.
Chapter 4

Conclusion

For producing qualitative HR-RDFs, careful calibration for the experimental configuration is required. This manuscript shows that large inaccuracies of any parameter for orienting the tilted detector causes detrimental alterations to the produced radial distribution function, it can be simple to remedy errors through direct observation of artificial Debye-Scherrer rings applied to the detector image. Smaller inaccuracies present a more challenging problem. With inaccuracies of detector tilt, sample to detector distance, and detector translations along the normal of the rotation axis causing expansion effects and similar line shape changes, determining acceptable parameter values was difficult. Even with using an accepted lattice constant to determine a solution, expansion effects of two parameters can cancel one another out, producing multiple solutions. Incorrect removal of additive errors in the collection of the scattering pattern can cause severe effects to radial distribution functions. Careful characterization of the area detectors dark current, measurement of air scattering, and determination of Compton scattering contribution is necessary for producing HR-PDFs. With diligent work there is significant promise for the use of area detectors for the HR-PDF method.
References


