DETERMINING X-RAY DIFFRACTION DATA AT VARYING DEPTHS – A PRELIMINARY THEORETICAL APPROACH

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ABSTRACT

A theoretical method for extracting diffractograms from a range of depths will be described. The method is non-destructive and requires only a series of traditional data collections, where the incident angle is varied. The measured spectra are transformed to give calculated X-ray diffraction data arising from different depths. This is in contrast to conventional approaches where either a specific feature is examined, or the inherent depth averaging of grazing angle X-ray diffraction is tolerated. The resultant calculated spectra may be analysed by any of the current techniques to provide information about any number of different characteristics. In order to obtain X-ray diffraction patterns from specific depths within samples, a Fredholm integral equation of the first kind is solved using regularisation techniques. Using known solutions of the Fredholm integral equation to create pseudo-experimental data, the method was validated by transforming this data and thus recovering the solution used.

INTRODUCTION

Many current methods of structural depth profiling are destructive, where a small amount of material is removed from the surface of the sample between each analysis. This is not suitable or desirable in many cases as additional stresses, for example, may be introduced into the sample with each layer of material removed [1]. Alternatively, non-destructive methods may be used which reduce the probe incident angle, thus reducing the depth of analysis. However, this method only gives information about the characteristics of the sample averaged over the penetration depth at each incident angle. The method introduced here aims to produce data from specific depths by transforming experimental data collected over a range of different incident angles.

Li et al [2] and Wu et al [3] have previously proposed a similar approach to this problem. However, the diffraction data recovered at varying depths was produced on the scale of absorption depth, whereas the method outlined in this study gives the diffraction data on a direct-depth scale. Further, in the work presented by Li et al, a single $2\theta$ value was used for analysis, whereas in the work presented here, we extended this to a range of $2\theta$.

Predecki [4] described a method of transforming profiles of quantities that are functions of the penetration depth into quantity profiles that are functions of the depth below the surface of the sample. Laplace transforms were used to perform this transformation, but a function was also required to be fitted to the observed quantity profile. The method described in our work makes no assumptions regarding the depth distribution of structural features.

In this paper, pseudo-experimental data was used to test and refine our methodologies.
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METHOD

EXPERIMENTAL THEORY

The X-ray diffraction pattern observed for a particular incidence angle, \( \gamma \), (the angle between the sample surface and the incident beam) is a weighted sum of the diffraction data from different depths over which the analysis is performed. Thus, the observed X-ray diffraction intensity observed may be derived as [5]:

\[
I_{\text{obs}}(\theta, \gamma) = A \int_0^D I(\theta, x) \exp \left( - \int_0^{D} \mu(x) dx \left( \frac{1}{\sin \gamma} + \frac{1}{\sin(2\theta - \gamma)} \right) \right) dx
\]

Here, \( I_{\text{obs}}(\theta, \gamma) \) is the observed diffraction data collected from a sample; \( I(\theta, x) \) is the diffraction data from a specific depth, \( x \), within the sample which we wish to determine. \( \mu(x) \) is the linear absorption coefficient of the material at position \( x \) within the sample. The factor \( A \) takes into account the geometry of the system that varies with varying incident angle. The upper limit of the integral equation, \( D \), can be described as being the maximum depth of penetration over which analysis takes place, and is defined in this work as the point at which the beam intensity has fallen to 99% of that of the incident beam.

Equation 1 is of the form of a standard Fredholm integral equation of the first kind, which can be written as [6-8]:

\[
b(\theta, \gamma) = \int_0^d y(\theta, x) K(\theta, \gamma, x) dx
\]

Here, \( b(\theta, \gamma) \) are the scaled experimental data and \( y(\theta, x) \) are the unknown solutions we wish to find. \( K(\theta, \gamma, x) \) is the kernel and characterises the physical process considered. Integral equations of such forms may be observed in many areas of science such as the measurement techniques used in aerosol science [7]. Unfortunately, Fredholm integrals of the first kind are ill-conditioned [9] as any small errors in \( b(\theta, \gamma) \) may cause large errors in \( y(\theta, x) \) [10]. Therefore, the determination of \( y(\theta, x) \) is an ill-posed problem.

SOLUTION METHOD

In order to solve equation 2, the integral is discretised using Simpson’s rule at each \( \theta \) to give:

\[
b(\gamma_i) = \frac{h}{3} \left[ y_1 k_{1,i} + 4(y_2 k_{2,i} + y_4 k_{4,i} + \ldots + y_{n-1} k_{n-1,i}) + 2(y_3 k_{3,i} + y_5 k_{5,i} + \ldots + y_{n-2} k_{n-2,i}) + y_n k_{n,i} \right]
\]

where \( i=1,2,\ldots,m \), and \( j=1,2,\ldots,n; y_j=y(x_j) \), the required solution at \( x=x_j \) and \( k_{ij}=k(x_j, \gamma_i) \). \( m \) is the number of different \( \gamma \)'s at which X-ray spectra are obtained, and \( n \) is the resolution at which the solution is calculated. \( h \) is defined as being \( \frac{x_n - x_1}{n-1} \), where \( x_n=d \) and \( x_1=0 \). This can then be written as a matrix equation \( \mathbf{b} = \mathbf{A} \mathbf{y} \).

In general \( m \neq n \), and hence \( \mathbf{A} \) is not a square matrix. To solve this equation, a least-squares method is used, the aim being to minimise the size of the residual, \( \mathbf{r} \), of the solution, where:

\[
\mathbf{r} = \mathbf{A} \mathbf{y} - \mathbf{b}
\]

The value of \( \mathbf{y} \) at which this is minimised is given by the solution of the normal equation:

\[
\mathbf{A}^T \mathbf{A} \mathbf{y} = \mathbf{A}^T \mathbf{b}
\]
As the Fredholm integral is ill-conditioned, equation 5 is also ill-conditioned. In the present study this ill-conditioning is overcome using a regularisation technique.

**REGULARISATION**

With regularisation techniques, additional assumed properties of the solution are included into the problem. This is achieved by including an extra term into the residual to be minimised. This extra term reduces to zero when the solution obtained exactly satisfies the assumed properties. The residual to be minimised is then taken to be:

\[ r = Ay - b + \alpha F(y) \]  

(6)

\( F \) is a function of the solution \( y \) chosen to regularise the system, and \( \alpha \) is the weighting parameter. Choosing \( \alpha \) to be non-zero ensures the matrix equation is well-conditioned and standard matrix solving methods may then be used.

For first order regularisation, or constrained linear inversion, the regularising function is chosen to minimise a measure of the overall slope of the solution giving:

\[ F(y) = B \gamma \]  

(7)

where \( B = \begin{pmatrix} -1 & 1 & 0 & \ldots & 0 & 0 \\ 0 & -1 & 1 & \ldots & 0 & 0 \\ \vdots & \vdots & \ddots & \ddots & \vdots & 0 \\ 0 & 0 & 0 & \ldots & -1 & 1 \end{pmatrix} \)

The value of \( y \) that minimises equation 6 can then be shown to be given by:

\[ \left( A^T A + \alpha B^T B \right) y = A^T b \]  

(8)

This method may also be extended for use with higher order regularisation, and \( B \) is varied accordingly.

**RESULTS**

**VALIDATION OF NUMERICAL METHOD**

Programs were written to generate pseudo-experimental measured data using equation 1, which was then solved using the above technique to obtain the depth-dependent solution.

Numerical experiments showed a value of \( \alpha \) of 0.3×tr\((A^T A)\)/tr\((B^T B)\) removed the ill-conditioning without over-smoothing the solution.

A number of different systems were simulated, including a thick homogeneous sample, a thin homogeneous film and a sample with varying crystallite size with depth. For each system tested, different combinations of \( m \), the number of observation points, and \( n \), the number of solution points, were used. In each case, the spectra at each incident angle was generated at 100 2\( \theta \) values.

**HOMOGENEOUS SAMPLE**

For the thick homogeneous sample, a single diffraction peak was considered, Figure 1. The assumed form of the diffraction data with depth was then used to produce pseudo-experimental data expected for a homogeneous sample collected at \( m=80 \) evenly spaced incident angles between 0.25° and 20°, and this was then transformed back into the depth-dependent diffraction
data using the algorithm with \( n = 110 \) unknowns. The maximum error and rms error between the expected and calculated solutions were found to be 0.02 (2d.p.) and 0.004 (3d.p.) respectively.

Figure 1. (a) Simulated diffraction data for a homogeneous sample over a range of depths; (b) pseudo-observations of (a); (c) recovered solution after transformation (all spectra offset for clarity)

**THIN FILM**

For the homogeneous thin film, a single peak was considered that was present until an arbitrary depth. This assumed form of the diffraction data was then used to produce pseudo-experimental data collected at 100 evenly spaced incident angles between 0.25° and 20°. Using the algorithm, this was then transformed into the depth-dependent diffraction data with 200 solving points. The maximum error in this case is 28.11 (2d.p.), and the rms error is 3.386 (3d.p.). In this case, higher errors were expected and they arise from the fact that the recovered solution does not have the sharp discontinuity the assumed solution has.
Figure 2. (a) Simulated diffraction data for a thin film over a range of depths; (b) pseudo-observations of (a); (c) recovered solution after transformation (all spectra offset for clarity)

VARYING CRYSTALLITE SIZE

For this system, one peak was again considered, and the diffraction data for a varying crystallite size with depth was assumed to vary in a linear fashion from larger to smaller crystallite size with depth. This form of the diffraction data with depth was then used to generate pseudo-experimental data for 100 evenly spaced incident angles between $0.25^\circ$ and $20^\circ$. This was then transformed into depth-dependent diffraction data using the algorithm with 200 solving points.
CONCLUSIONS

A direct method for determining X-ray diffraction data from various depths has been presented. By using a known form of diffraction data with depth for a range of systems, the method was validated by creating pseudo-experimental data and then recovering the solutions.

The method presented here is novel as data from different depths are determined rather than information about a specific characteristic. In principle, the analytical process could be applied generically to any experimental method where changing the incident angle changes the penetration depth. For example, Particle Induced X-ray Emission (PIXE) may be used to find information about the composition of samples, as this method may be used to determine trace elements present.

This method is currently being applied to experimental data collected with the Synchrotron Radiation Source at the Daresbury Laboratory (station 2.3). It is also being extended to solving for the unknowns in the $2\theta$-direction as well as in the x-direction.

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REFERENCES


