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REAL SPACE METHOD OF POWDER DIFFRACTION FOR NON-PERIODIC AND NEARLY PERIODIC MATERIALS

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ABSTRACT

The use of high-energy neutrons from pulsed or hot sources allows the method of atomic pair distribution analysis to be applied to the structural determination of crystalline as well as amorphous solids. This method complements the standard crystallographic methods in studying non-periodic aspects of solids with or without long range order.

INTRODUCTION

The method of atomic pair distribution function (PDF) analysis has traditionally been used almost exclusively in studying the structure of liquid and amorphous materials for which the standard crystallographic methods are powerless [1,2]. In principle, however, this method is applicable to any powdered materials including crystalline solids. If the solid is perfectly crystalline, there is no advantage in using this approach, while if the solid contains a high density of defects or a high degree of disorder, the PDF method is an attractive alternative to the standard methods. What prevented the wide use of this technique for ordered materials so far was the termination errors which were often introduced in the course of Fourier-transformation and reduced the accuracy of the PDF [2]. This situation was greatly improved by the advent of pulsed and hot neutron sources and synchrotron radiation, which provide neutrons and x-rays with higher energies than have been normally available. In this paper we briefly describe the method, review recent results obtained by this method, and discuss future promises held by this method which we propose to call the "real space method for powder diffraction".

THE PDF ANALYSIS

The instantaneous atomic pair distribution function, $\rho(r)$, is determined by the Fourier transformation of the total structure factor $S(Q)$,

$$\rho(r) = \rho_0 + \frac{1}{2\pi^2 r} \int [S(Q) - 1] \sin(Qr) Q dQ \quad (1)$$

where ρ_0 is the average atomic number density, Q is the scattering vector [1,2], and

$$S(Q) = \int S(Q, \omega) d\omega \quad , \quad (2)$$

where $S(Q, \omega)$ is the dynamic structure factor, ω is the energy transfer by scattering, and the integration covers only the energy range for phonons [3]. For x-ray scattering Q is almost independent of ω for phonons, so that the measured scattering intensity corrected for absorption, Compton scattering, multiple scattering and the atomic scattering factor $\langle f(Q) \rangle^2$, directly gives $S(Q)$. For neutron scattering without an energy analyzer the measured intensity is not exactly equal to $S(Q)$ because of the ω dependence of Q , but after the Placzek correction [4] $S(Q)$ is obtained in approximation.

The range of integration in equation (1) is from 0 to ∞ , however, in practice $S(Q)$ can be determined only up to a limiting Q value, Q_{\max} , which

depends upon the energy of the incident photons or neutrons, and the integration is terminated there. With a room temperature thermal neutron source Q_{\max} cannot exceed 12 1/Å, which is hardly sufficient in evaluating the integration accurately. On the other hand a large portion of neutrons emitted from a pulsed source are epithermal, and have higher energies. Accordingly $S(Q)$ can be determined up to 30 ~ 40 1/Å, and $S(Q)$ and $\rho(r)$ can be obtained with a high accuracy as shown in Figs. 1 and 2 for f.c.c. aluminium. The data shown in Figs. 1 and 2 [5] were obtained at the SEPD station of the Intense Pulsed Neutron Source (IPNS) of Argonne National Laboratory. Since $\rho(r)$ describes an instantaneous nuclear correlation, the peaks have a non-zero width even at $T = 0$ K due to the zero-point oscillation. The peak width which fits the best to the data, 0.086 Å, is very close to the one expected from the Debye model, $\sqrt{2\langle u^2 \rangle} = 0.083$ Å [6].

In general, if the PDF peaks are Gaussian with the standard deviation of σ_r , then the structure factor is given by the Debye-Waller form

$$S(Q) = [S_0(Q) - 1]\exp(-2BQ^2) + 1 \quad , \quad (3)$$

where $B = \sigma_r^2/2$ and $S_0(Q)$ is the structure factor for a system with a PDF composed of δ -function-like peaks. Thus a rule of thumb for the range of Q is

$$Q_{\max} \sigma_r \geq 3 \quad . \quad (4)$$

This ensures that the integrand of (1) is of the order of the 3σ value of the Gaussian distribution (~ 0.01). For metallic glasses, for instance, σ_r is about 0.15 Å or so, thus Q_{\max} should be at least 20 ~ 25 1/Å, while for crystalline solids it has to be larger, typically 30 ~ 40 1/Å. For complex solids such as quasicrystals, $Q[S(Q) - 1]$ decreases rapidly with Q , and Q_{\max} does not have to be greater than 20 1/Å.

On the other hand experimental limitations in the resolution in Q do not present a significant problem in the PDF analysis. If the resolution function is Gaussian with the standard deviation of σ_Q , it results in a slow decay of the PDF with a Gaussian envelope,

$$\rho(r) = \rho_0 + [\rho_s(r) - \rho_0]\exp(-r^2/2\lambda^2) \quad , \quad (5)$$

where $\rho_s(r)$ is the PDF determined with a perfect resolution, and $\lambda (= 1/\sigma_Q)$ is the resolution distance. For a medium range resolution such as 0.01 1/Å (HWHM), the resolution distance is over 100 Å, so that unless the PDF is calculated up to very large distances the Q resolution is unimportant.

In fact for carrying out a successful PDF analysis it is better to reduce the experimental Q resolution and increase the neutron or photon count in order to reduce the statistical noise, which is the most important source of inaccuracy since the range of Q accessible with pulsed neutrons is sufficiently large and renders the termination error less significant. From equation (1) it can be shown that the statistical noise is given by

$$\Delta\rho(r) = \frac{1}{2\pi^2 r} \left[\int \frac{\sin(Qr)}{I_c(Q)} Q dQ \right]^{1/2} \\ - \frac{1}{2\sqrt{2}\pi^2 r} \left[\int \frac{Q^2 dQ}{I_c(Q)} \right]^{1/2} \quad , \quad (5)$$

where $I_c(Q) = N(Q)/\Delta Q$ is the scattered neutron intensity, with $N(Q)$ being the actual neutron count and ΔQ the spacing of the Q values at which the data were taken [7]. Thus $\Delta\rho(r)$ decreases inversely with r , as seen in Fig.

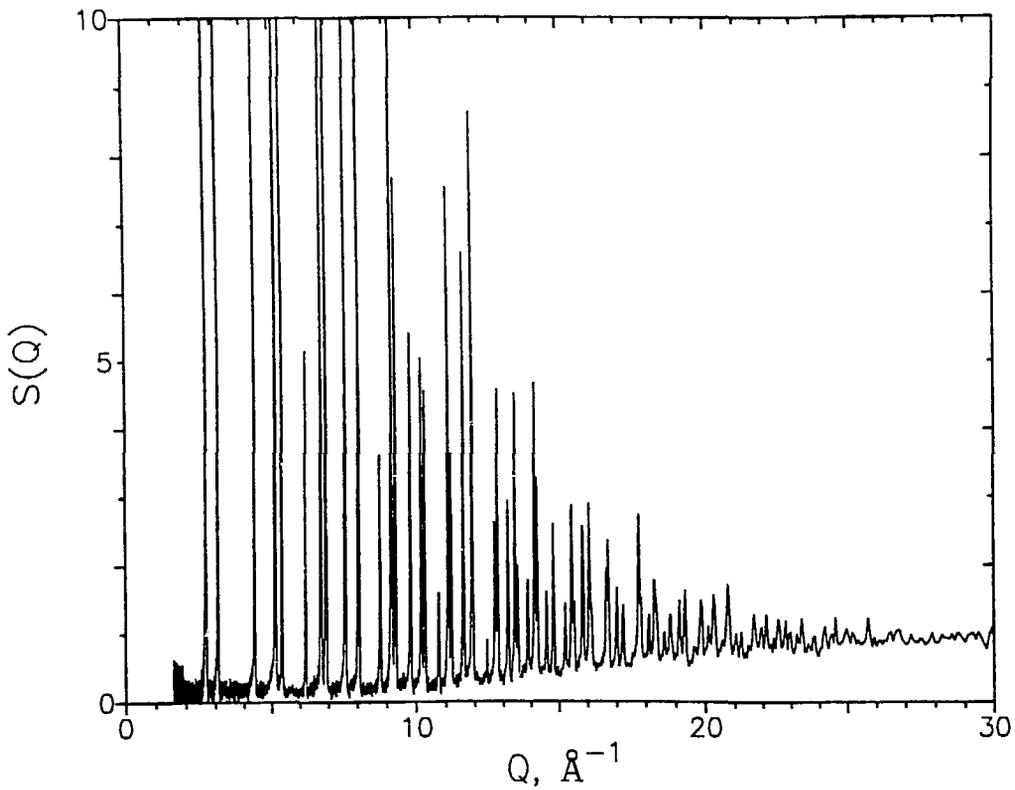


Fig. 1. Total structure factor of f.c.c. aluminium at $T = 10$ K determined by the pulsed neutron scattering at the IPNS. The value of $S(Q)$ at the peaks below $Q = 10$ \AA^{-1} is out of scale. It exceeds 100 in this resolution ($\Delta Q \sim 0.04$ \AA^{-1}) at some peaks.

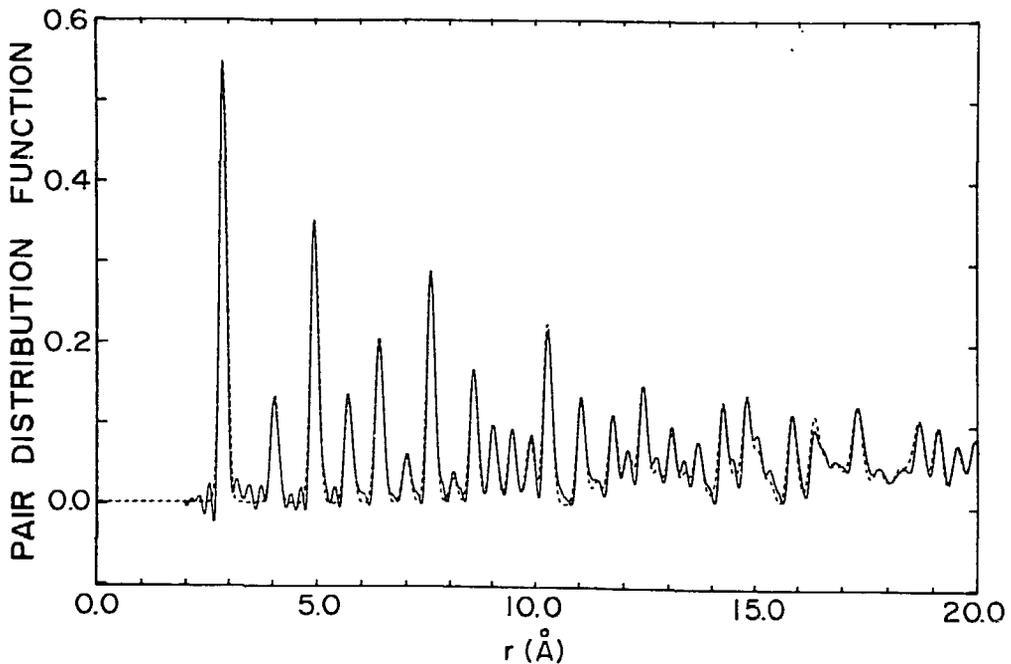


Fig. 2. The atomic pair distribution function of f.c.c. aluminium obtained by the Fourier transformation of $S(Q)$ shown in Fig. 1 [5]. The dashed line is the calculated PDF with Gaussian broadening to represent the zero-point lattice vibration.

2. In collecting the diffraction data, consideration should be given to minimize equation (5), by spending more time at high Q ranges than low Q ranges.

If we use a triple-axis spectrometer we can determine the elastic scattering intensity, $S(Q,0)$, within the energy resolution of the analyzer. The Fourier transform of $S(Q,0)$ is the average density-density correlation function which is slightly different from the instantaneous PDF in that the dynamic correlations are missing. This method was first applied to the study of SiO_2 glass [8], and was recently used for the study of superconducting $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ using the hot neutron source of ILL. The data from this experiment are being analyzed.

RECENT EXAMPLES: SUPERCONDUCTING $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$

The structure of superconducting oxides has been extensively studied by various methods, and their average crystallographic structure is now well known. However, these structures often contain anomalously large temperature factors which describe the amplitude of thermal lattice vibration [9,10]. Such large temperature factors usually imply displacive disorder on a local level which is not adequately modeled in the standard crystallographic analysis. We applied the PDF analysis on the pulsed neutron powder diffraction data of superconducting oxides obtained at the IPNS, and were able to determine the local atomic correlations undetected by crystallographic methods. Here we briefly describe some of the recent results obtained for $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ ($T_c = 110$ K).

Displacive Order of Tl and O

The amplitude of thermal vibration of oxygen in the Tl-O plane determined by single crystal x-ray scattering as well as powder neutron scattering [9,10] is as large as 0.4 Å, while it is expected to be of the order of 0.1 Å. By analyzing the pulsed neutron PDF we found that both Tl and O atoms in the Tl-O plane are deviated from the crystallographic high-symmetry sites, forming displacive short range order [11]. The distance between the Tl and O sites in the crystallographic (tetragonal) structure is 2.73 Å, while the sum of the ionic radii of Tl and O is 2.28 Å [12]. The displacements cause half of the Tl-O pairs move closer to a distance of about 2.3 Å while the rest of them move further apart, thus as a whole minimizing energy.

Anomalous Temperature Dependence

A careful study of the temperature dependence of the pulsed neutron PDF produced evidence of structural anomaly in the vicinity of the superconducting transition temperature. It was found that the PDF shows a qualitative change across the transition, and as shown in Fig. 3 [13] the PDF amplitude, $\Delta\rho$, defined as the average height of the PDF peaks at 3.4 and 3.85 Å measured from the valley at 3.6 Å, deviates from the normal temperature dependence shown by a solid curve. This curve was calculated based upon the phonon density of state of this compound determined by an inelastic neutron scattering measurement carried out at the ILL using a triple-axis-spectrometer IN-1. The result shown in Fig. 3 was produced using primarily the data from the detector bank placed at the scattering angle (2θ) 150° , while a more recent result using also the 90° detector bank shows an even more pronounced anomaly, suggesting that the nature of this anomaly may be dynamic, since the Placzek correction is more reliable at lower angles. The origin of this anomaly is still being investigated, but a strong possibility is that this is due to the displacement of oxygen atoms in the Cu-O plane. Note that no anomaly has been observed in crystallographic parameters such

as the lattice constants and the atomic position parameters determined by the Rietveld method [10,14]. This example illustrates the unique capability of the PDF method to detect local atomic displacements which can go unnoticed by standard crystallographic methods. Further investigation of this anomaly might shed some light on the origin of the superconducting phenomena in cuprates.

ADVANTAGES OF PDF METHOD IN STUDYING NEARLY PERIODIC MATERIALS

Since the PDF is nothing but a direct Fourier-transform of the structure factor, $\rho(r)$ and $S(Q)$ contain the same information. Thus superficially there appears little to be gained by using the PDF method. However, in practice this difference in the representation can have important consequences in the strategy of structural analysis of crystalline or nearly crystalline materials. For instance, lattice symmetry and lattice constants are directly determined by the Bragg peak position of $S(Q)$, while atomic positions are only indirectly determined by examining the diffraction peak intensities. On the other hand $\rho(r)$ is all but useless in determining the lattice symmetry while it provides direct information regarding the atomic separations. Therefore in determining the atomic positions within the unit cell the PDF method offers significant advantages. In fact it is equivalent to the Patterson analysis for single crystals, except that it is averaged over all orientations and all the non-Bragg, diffuse intensities are included. Thus these two approaches are complementary, and should be used in tandem in the structural study of complex systems.

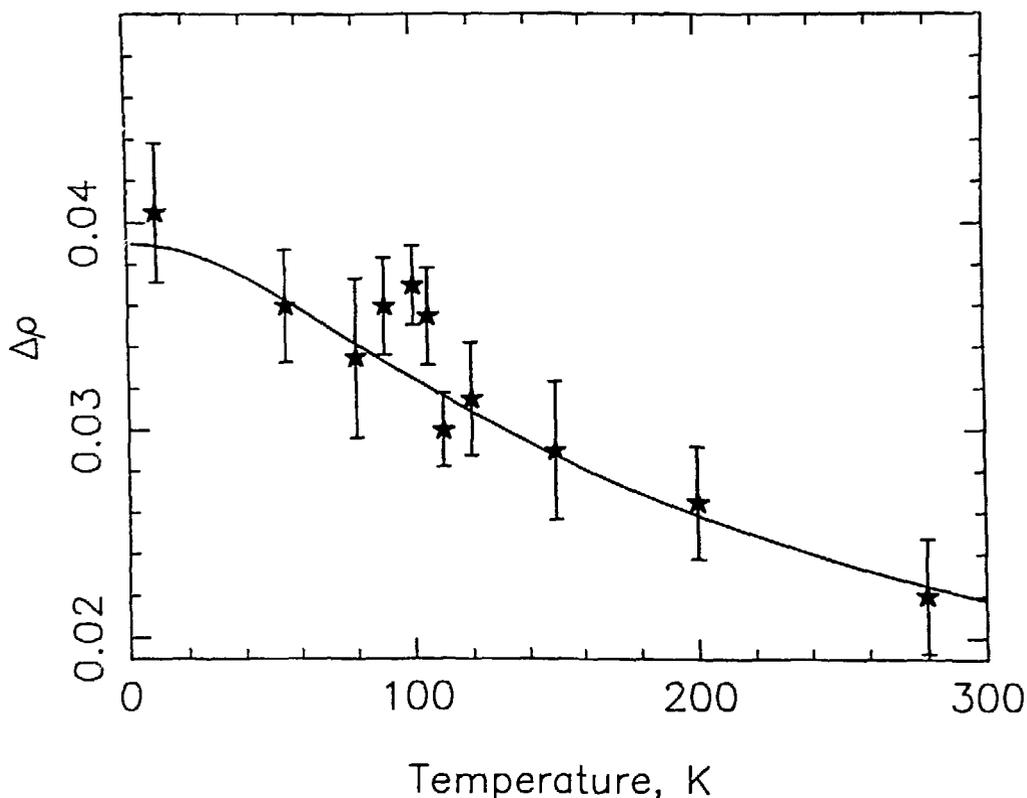


Fig. 3. Temperature dependence of the PDF amplitude defined as the average of the PDF peak heights at 3.4 Å and at 3.85 Å, measured from the valley in-between at 3.6 Å. The vertical bars indicate the statistical error evaluated by eq. (5), and the solid line is the normal temperature dependence calculated from the phonon density of states determined by inelastic neutron scattering [13].

When analyzing the powder pattern of a complex crystalline solid with a large unit cell, one might start off with the Rietveld analysis and then use the PDF method to refine the atomic positions. Comparison of the experimental PDF with the calculated PDF based upon the Rietveld parameters will clearly demonstrate discrepancies, if there are some, between the atomic distances in the model and those in the actual structure. While such discrepancies are usually noted by chemical intuition, this method offers a more direct and reliable means of confirming and improving the structural model. The model can be refined, for instance, by the Monte-Carlo process to minimize the difference between the measured and calculated PDF's [11].

If the sample contains a high density of defects or intrinsic displacive disorder, the PDF method shows its unique strength, as demonstrated in the examples shown above. In particular the ability to model the short range order independent of the medium and long range order, makes this method exceptionally useful. If one were to determine the structure with displacive short range order in the Q space, two kinds of information regarding the nature of the atomic displacement and the spatial extent of correlation are intermixed in $S(Q)$, while in the PDF we can primarily focus on the local displacement alone by terminating $\rho(r)$ at some distance and modelling only the short range correlations. One may then go back to $S(Q)$ to determine the spatial extent of the correlation.

We thus identified two areas where the PDF method is particularly useful in determining the atomic structure of crystalline or nearly crystalline solids. We suggest that this "real space" approach may be included in some crystallographic analysis package such as the Rietveld software, so that the user can move to the real space method when the structure is either very complex or the temperature factor is too large and some displacive disorder is suspected.

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