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PDFFIT, a program for full profile structural refinement of the atomic pair distribution function

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Abstract

The program *PDFFIT* is designed for the full profile structural refinement of the atomic pair distribution function (PDF). In contrast to conventional structure refinement based on Bragg intensities, the PDF probes the *local* structure of the studied material. The program presented here allows the refinement of atomic positions, anisotropic thermal parameters and site occupancies as well as lattice parameters and experimental factors. By selecting individual atom types one can calculate partial and differential PDFs in addition to the total PDF. Furthermore one can refine multiple data sets and/or multiple structural phases. The program is controlled by a command language which includes a Fortran style interpreter supporting loops and conditional statements. This command language is also used to define the relation between refinement parameters and structural or experimental information, allowing virtually any constraint to be implemented in the model. *PDFFIT* is written in Fortran-77, and the source code and documentation are available *via* the World Wide Web.

1. Introduction

The determination of crystal structures is an important part of chemistry, physics and, of course, crystallography. Conventional structure determination is based on the analysis of the intensities and positions of Bragg reflections which only allows the determination of the long-range *average* structure of the crystal. For powder diffraction data this is now routinely performed using the Rietveld (Rietveld, 1969) method. It should be kept in mind that the analysis of Bragg scattering assumes a perfect long-range periodicity of the crystal. However, many materials are quite disordered and, even more important, the key to a deeper understanding of their properties is the study of deviations from the *average* structure or the study of the *local* atomic arrangements (Billinge, 1996). Deviations from the average structure result in the occurrence of diffuse scattering which contains information about two-body interactions (Welberry & Butler, 1995; Frey, 1995). One method to reveal the local structure of crystals is the analysis of the PDF. This method is long known in the field of studies of short-range order in liquids and glasses but has recently been applied to crystalline materials (Egami, 1998; Toby & Egami, 1992; Billinge & Egami, 1993). The PDF is obtained from the powder diffraction data *via* a sine Fourier transform of the normalized scattering intensity $S(Q)$:

$$G(r) = 4\pi r[\rho(r) - \rho_0] = (2/\pi)\int_0^\infty Q[S(Q) - 1]\sin(Qr)\mathrm{d}Q, \qquad (1)$$

where $\rho(r)$ is the microscopic pair density, ρ_0 is the average number density and Q is the magnitude of the scattering vector. For elastic scattering $Q = 4\pi\sin(\theta)/\lambda$ with 2θ being the scattering angle and λ the wavelength of the radiation used. Details of the determination of an experimental PDF can be found *e.g.* in Egami (1998) and Warren (1990) and are not discussed here.

The study of a measured PDF ranges from a simple peak-width analysis revealing information about correlated motion (Jeong *et al.*, 1998) to the full profile refinement of the PDF based on a structural model either using the reverse Monte Carlo technique (Toby & Egami, 1992; Nield *et al.*, 1994) or least-squares regression (Billinge, 1998) as implemented in the program *PDFFIT* described in this paper. Next we will discuss some key features of the program followed by an example refinement of a PDF from nickel.

2. Features

The basic concept, command language and some file formats of *PDFFIT* are taken from the diffuse scattering and defect structure simulation program *DISCUS* (Proffen & Neder, 1997). As we will see in this section, both programs complement each other. The *PDFFIT* program is accompanied by a detailed manual. The program has an on-line help function that allows access to command descriptions while working with the program.

2.1. *Calculating a PDF*

Since the PDF contains Bragg and diffuse scattering, the information about *local* arrangements is preserved. The PDF can be understood as a bond-length distribution between all pairs of atoms i and j within the crystal (up to a maximum distance); however, each contribution has a weight corresponding to the scattering power of the two atoms involved. The PDF can be calculated from a structural model using the relation

$$G_c(r) = (1/r)\sum_i\sum_j\left[(b_ib_j/\langle b\rangle^2)\delta(r - r_{ij})\right] - 4\pi r\rho_0, \qquad (2)$$

where the sum goes over all pairs of atoms i and j within the model crystal separated by r_{ij}. The scattering power of atom i is b_i and $\langle b\rangle$ is the average scattering power of the sample. In the case of neutron scattering b_i is simply the scattering length, in the case of X-rays it is the atomic form factor evaluated at a user-defined value of Q. The default value is $Q = 0$ in which case b_i is simply the number of electrons of atom i. The program *PDFFIT* also allows the user to select which atom types shall be included in the sums over i and j in (2) which allows one to calculate or refine the total PDF as well as partial or differential PDFs.

Generally, there are two different ways to account for displacements (either thermal or static) from the average position. First one can use a large enough model containing the desired displacements and perform an ensemble average. This is the method used by the program *DISCUS* where thermal displacements can be introduced by displacing atoms in the model according to a given (isotropic) Debye–Waller factor. Alternatively, one can convolute each delta-function in (2) with a Gaussian accounting for the displacements. The width σ'_{ij} of the Gaussian is given by the anisotropic thermal factors $U_{lm} = \langle u_l u_m \rangle$ of atoms *i* and *j*. Furthermore, the actual width σ_{ij} shows the *r*-dependence given below (Jeong *et al.*, 1998):

$$\sigma_{ij} = \sigma'_{ij}(p) - (\delta/r_{ij}^2) \qquad (3)$$

with r_{ij} being the separation distance of the atoms *i* and *j*. The program *PDFFIT* offers the user the additional feature to reduce the width of PDF peaks below a given value of $r_{\rm cut}$ by some factor φ. Both values, δ and φ, can be refined. For more details, refer to the users guide that is provided with the program.

As we have seen in the *Introduction*, the experimental PDF is obtained by a Fourier transform of the reduced structure factor. However, the accessible range in Q is limited by a maximum measurable value $Q_{\rm max}$. This can be described by a multiplication of the structure factor up to infinity with a step function cutting off at $Q = Q_{\rm max}$, resulting in the convolution of the PDF with the Fourier transform of the step function, $S(r)$. *PDFFIT* models the finite Q-range by convoluting the model PDF $G_c(r)$ with

$$S(r) = \sin(Q_{\rm max} r)/r. \qquad (4)$$

The termination ripples of the calculated PDF, $G_c(r)$ of nickel for two different values of $Q_{\rm max}$ can be seen in Fig. 1. With the availability of modern synchrotron and neutron sources it is possible to collect powder diffraction data up to high values in Q; however, in many cases a sufficient PDF can be obtained using a conventional X-ray tube. One last correction applied to the calculated PDF, $G_c(r)$, accounts for the limited resolution of the experiment in Q-space. This leads to a decrease of the PDF peak as a function of r according to the relation $\exp(-\sigma_Q^2 r^2/2)$. A detailed discussion of the accuracy of PDF analysis is given by Toby & Egami (1992).

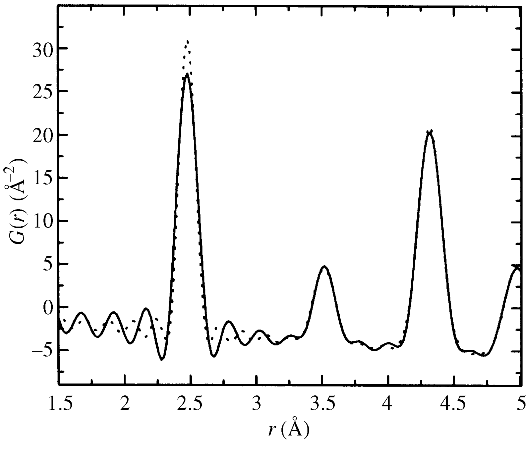

Fig. 1. Calculated PDFs for nickel at different values of $Q_{\rm max}$. The solid line corresponds to $Q_{\rm max} = 25$ Å^{-1} and the dotted line to $Q_{\rm max} = 35$ Å^{-1}.

2.2. *Command language*

The program *PDFFIT* is controlled by a command language which includes the use of variables and a Fortran-style interpreter. The interpreter provides variables linked to structural and PDF-related information (*e.g.* size of the crystal, coordinates or atom type of a certain site, value of the calculated PDF at a specific point,...) and free variables, loops, logical constructions, basic arithmetic and build-in functions. Loops can be programmed using the command `do`. The program supports Fortran-like `if-elseif-endif` control constructions which use the same kind of logical expressions as in Fortran programs. Loops and if constructions can be nested up to a level defined by a parameter which can be adjusted when the program is compiled.

The arithmetic expressions understood by *PDFFIT* include the operators `+,-,*,/` and `**` (power) as well as brackets. All trigonometric functions (`sin, cos, tan`) as well as their inverse functions (`asin, acos, atan`) are present. Arithmetic functions include square root (`sqrt`), absolute value (`abs`), exponential (`exp`) and logarithm (`ln`). Furthermore, conversion functions between real and integer variables are included and random generators for uniformly and Gaussian distributed values. Additionally, crystallographic functions are implemented to calculate bond angles, length and angles of vectors in direct and reciprocal space as well as scalar and vector products in real and reciprocal space.

Another powerful capability of *PDFFIT* is the use of macros. A macro is simply a set of commands stored in a file. Macros can be nested, *i.e.* macro files can be called within macros. It is also possible to pass variables to the macro which allows one to create a macro library for individual standard procedures. All input and output file names can be numbered automatically. This capability allows a cycle of different refinements to be performed, while using a counter to distinguish the output results.

2.3. *Refinement parameter coding*

When using *PDFFIT* we have to distinguish between refinement variables; we simply call p_i (or `p[i]`), and parameters corresponding to the model structure or experimental factors. The parameters that can, in principle, be refined using *PDFFIT* are listed in Table 1 using the actual parameter name recognized by the program. Each experimental or structural parameter that needs to be refined must be assigned to one or more refinement variables *via* the command `par`. For each variable p_i that appears in the definition we have to also specify the derivative of the corresponding structural or experimental parameter with respect to p_i. This is necessary since *PDFFIT* uses analytical derivatives in the least-squares routine, which we found to give more stable refinements. The index *i* of the refinement variables can be freely chosen by the user.

Let us consider the following simple case: The lattice parameters a, b, c of a cubic crystal shall be refined using a single variable. The definitions we need to enter are listed in Fig. 2. The first three lines for the refinement parameter p_1 are associated with the lattice constants *a*, *b* and *c*. The derivatives in this case are rather simple, $\partial a/\partial p_1 = 1$. It is important to remember that one needs to assign a suitable starting value to p_1 as we have done in the last line of Fig. 2.

Although this procedure of refinement-parameter definitions might seem complicated, it allows the user to construct virtually any constraint, *e.g.* the refinement of the tilt angle of a

Table 1. *PDFFIT refineable parameters*

Structural	For each phase p
`lat[1..6]`	Lattice parameters a, b, c, α, β, γ
`delt[p]`	Dynamic correlation factor δ
`srat[p]`	Peak width ratio φ for $r < r_{\rm cut}$
`csca[p]`	Scale factor f_p
Per atom	For each atom n in phase p
`x[n]`	x-position (fractional coordinates)
`y[n]`	y-position
`z[n]`	z-position
`o[n]`	Occupancy
`u[1..6,n]`	Anisotropic thermal parameter U_{ij}
Experimental	For each data set s
`dsca[s]`	Overall scale factor f_s
`qsig[s]`	Resolution factor σ_Q

rigid octahedron. Since the program is designed to determine the *local* structure of a material, there are no predefined constraints imposed by the symmetry of the space group of the average structure. However, the user can easily define the appropriate constraints to force the refined structure to retain the given symmetry. This means that every atom in a chosen unit cell, or supercell, must be explicitly entered and not just the contents of the asymmetric unit. However, these positions can be easily generated from the contents of the asymmetric unit and the space group using the *DISCUS* program (Proffen & Neder, 1997). Further examples of parameter coding can be found in the manual of *PDFFIT*.

2.4. *Bond-length calculation*

One common task after a refinement has been carried out is to analyze the resulting bond lengths and bond angles within the structure. The program *PDFFIT* offers two commands to calculate these geometrical values including a resulting standard deviation propagated from the uncertainties of the refined lattice parameters and atomic positions. Furthermore, all bond lengths between user-defined atom types that lie within a given range can be listed. This allows one to determine which atom pairs contribute to a PDF peak found in a given region of r.

2.5. *File formats*

The file format for PDF data used by *PDFFIT* is a simple text file with r, $G(r)$ and standard deviations $\sigma(r)$ and $\sigma[G(r)]$ on each line. The standard deviation of $G(r)$ is used to calculate the weighting factor for the refinement process. The value $\sigma(r)$ is added for compatibility reasons and ignored by *PDFFIT*. The experimental data used as input as well as the calculated PDF and the difference between observed and calculated PDF produced by the program conform to that format. This type of file can be read by most graphic programs as well as by the data plotting program *KUPLOT* (Proffen & Neder, 1997).

The structure files are text files as well and use keywords to specify information in the header section before a list of atom names, positions and temperature factors is given. The file format is related to the format used by the program *DISCUS*. However, certain information such as anisotropic temperature factors, occupancies and standard deviations for all values are unique to *PDFFIT*. As a result, *PDFFIT* can read and write its own file format as well as the *DISCUS* structure file format. This allows one to use *DISCUS e.g.* to create symmetrically equivalent atoms for a given space group as well as analyzing a resulting structure, or export it for plotting purposes (see Proffen & Neder, 1997).

```
par lat[1]=p[1],1.0
par lat[2]=p[1],1.0
par lat[3]=p[1],1.0
#
p[1]=lat[1]
```

Fig. 2. Parameter coding example.

3. Example

In order to illustrate how *PDFFIT* is actually used, we will discuss the refinement of the PDF of nickel. The data used here were collected at room temperature using the diffractometer at beamline X7A at NSLS, Brookhaven National Laboratory. The data are terminated at $Q_{\rm max} = 22$ Å^{-1}. The sequence of commands used to carry out the refinement is listed in Fig. 3. Note that the line numbers are only added for easy reference and are not actually part of the input. The data are shown as filled circles in Fig. 4.

The command `reset` in line 1 resets *PDFFIT* to have a defined initial state. Next a structural model (line 2) and the experimental PDF (line 3) are read. The parameters of the command `read data` are the radiation type (here X-ray), $Q_{\rm max}$ and the resolution factor σ_Q associated with the data file. Next we define the relationships between refinement and structural/experimental parameters. The lattice parameters a, b, c are refined using the parameter `p[1]` (lines 5–7) as discussed before. In lines 9–13 the temperature factors U_{lm} of the atoms are associated with a single refinement parameter `p[2]`. Note

```
 1 reset
 2 read stru,ni.stru
 3 read data,x,22.0,0.0,ni.data
 4 #
 5 par lat[1]=p[1],1.0
 6 par lat[2]=p[1],1.0
 7 par lat[3]=p[1],1.0
 8 #
 9 do i[1]=1,n[1]
10   par u[1,i[1]]=p[2],1.0
11   par u[2,i[1]]=p[2],1.0
12   par u[3,i[1]]=p[2],1.0
13 enddo
14 #
15 par csca[1]=p[10],1.0
16 par qsig[1]=p[11],1.0
17 par delt[1]=p[12],1.0
18 #
19 p[1]=lat[1]
20 p[2]=u[1,1]
21 #
22 p[10]=1.50
23 p[11]=0.03
24 p[12]=0.10
25 #
26 range 1,0.5,13.0
27 run
28 #
29 save pdf,1,ni_ref.calc
30 save dif,1,ni_ref.dif
31 save stru,1,ni_ref.stru
32 save res,ni_ref.out
```

Fig. 3. Example input file for the refinement of PDF data from nickel.

that we have four Ni sites in our model and, rather than typing the definitions for each atom separately, we are using a loop. The variable `n[1]` contains the number of sites. In our example we only refine an isotropic temperature factor, so we use the same parameter for U_{11}, U_{22} and U_{33} stored in `u[1,n]`, `u[2,n]` and `u[3,n]`. Next we associate individual refinement parameters with the scale factor f_p (line 15), the resolution factor σ_Q (line 16) and the dynamic correlation factor δ (line 17). Note that there is no need for a consecutive numbering of the parameters. Finally, we need to initialize the refinement parameters `p[i]` with suitable starting values; this is performed in lines 19–24. Last we define the *r*-range we want to use for the refinement (line 26), here from 0.5 to 13.0 Å. Finally, the refinement is started using the command `run` (line 27). After the refinement has (hopefully) converged, we have to save the resulting PDF, the difference between observed and calculated PDF, the resulting structure and fit result (lines 28–32). A view graph of the results created using the program *KUPLOT* can be seen in Fig. 4.

This quite simple refinement was used to demonstrate the basic usage of *PDFFIT*. Additional examples can be found in the documentation accompanying the program. A recent application of *PDFFIT* is a study of the local Jahn–Teller distortion in $LaMnO_3$ (Proffen *et al.*, 1999).

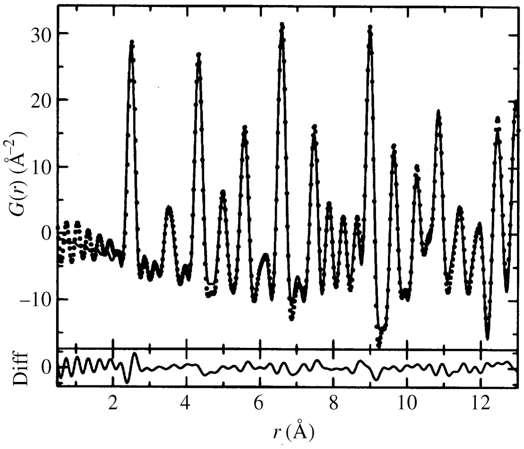

Fig. 4. Result of the PDF refinement of nickel. The solid line is the calculated PDF, the filled circles are the data. A difference curve is plotted below the data.

4. Language, documentation and availability

The program *PDFFIT* is mainly written in standard Fortran 77 and was successfully tested on various UNIX environments. The program can also be compiled under VMS. All system specific routines are stored in a separate file (sys_'operatingsystem'.f). *PDFFIT* can easily be ported to other platforms given a Fortran-77 and C compiler. The necessary amount of memory and disk space depends mainly on the size of the intended structures to be refined. All array dimensions are defined *via* PARAMETER commands in separate include files in order to allow an easy modification for individual needs. The *PDFFIT* distribution contains the complete source code including Makefiles for various platforms, a detailed manual (PostScript) and various example macro files. Additional information about the programs and the most recent distributions can be found on the WWW at *http://www.pa.msu.edu/cmp/billinge-group/discus/pdffit.html*. The programs *DISCUS* and *KUPLOT* mentioned in this paper can be obtained from the same source listed above. Those who have difficulties accessing the WWW pages above can obtain a copy of the distribution or executables directly from the authors.

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