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# **XRAYL: A Powder Diffraction Profile Refinement Program**

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J. M. Stewart and Y. Zhang, University of Maryland;  
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U.S. DEPARTMENT OF COMMERCE  
National Institute of Standards and Technology  
(Formerly National Bureau of Standards)  
Electronic Materials Group  
Ceramics Division  
Gaithersburg, MD 20899

October 1988



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## ABSTRACT

In many applications of X-ray powder diffraction in material studies, when overlap occurs it is necessary to separate the total (or composite) profile into its components. A computer program, XRAYL, has been developed to fit analytical functions to powder diffraction lines. After fitting, the powder diffraction data, given as counts at steps in  $2\theta$ , is represented, diffraction line by diffraction line, by parameters of a profile function. The resulting profile parameters may then be used to generate "idealized" powder diffraction lines, effectively free of statistical noise and contributions from overlapping lines, extending to background intensity on each side. Because of this capability XRAYL may be employed in X-ray powder diffraction profile analysis as a preprocessor program, that is, separating peaks and feeding the "resolved" data to subsequent analysis programs. This NBS-IR contains: (1) profile functions and the non-linear least-squares algorithm utilized in XRAYL; (2) user options and execution of the program; and (3) several examples.





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## I. Introduction

A powder diffraction profile analysis preprocessor program, XRAYL, has been written in FORTRAN 77. The purpose of this program is to separate overlapping x-ray powder diffraction lines with fidelity to their shape.

X-ray powder diffraction is a widely used method to identify and characterize crystalline phases. The diffraction pattern consists of a series of intensity readings measured as a function of  $2\theta$ , the scattering angle. The pattern from a crystalline material consists of a slowly varying background and a number of narrow lines whose positions are defined by the unit cell parameters and crystal symmetry. With a small cell and cubic symmetry, for example, the diffraction lines are well separated and can individually be measured. However, as the symmetry of a material is reduced, more lines are observed, and many lines overlap. Further, for the majority of diffraction systems the  $K\alpha_1, K\alpha_2$  doublet remains, causing additional overlaps in complex patterns. The shape of a diffraction line is a convolution of the instrumental effects, including monochromatization, instrumental alignment, and microstructure of the specimen in terms of crystallite size and residual lattice strain. One of the major goals of program XRAYL is to separate the individual diffraction lines from the overlapping total pattern and to present these separated line profiles for further analysis.

In many applications of X-ray powder diffraction in material studies, when overlap occurs it is necessary to separate the total (or composite) profile into its components. Examples of applications requiring separated lines include measurement of accurate line positions for lattice parameter determination, of line intensity for quantitative phase and texture analysis, and of line profile shape for crystallite size and residual microstrain analysis. The profile fitting technique<sup>1,2</sup> is effective for decomposing overlapping reflections into individual component profiles without prior knowledge about the crystal structure of the material. However, profile fitting can not be applied unless certain specific shapes are assumed for the line shapes. A few analytical functions have been reported<sup>3,4,5</sup> to represent adequately the shape of a real powder diffraction line. Functions frequently implemented include the Gaussian, Lorentzian, Voigt, Pearson VII and "Rational" functions.

Another approach to obtaining microstructure as well as atomic structural information is the Rietveld<sup>6</sup>, or whole pattern, approach to profile fitting method. This method overcomes most of the limitations in obtaining accurate structure information from raw powder diffraction data. It has become widely used when single crystals are unobtainable. Parametric representation of diffraction profiles has been applied with great success in the Rietveld method. Recently, Young and Wiles<sup>7</sup> reviewed the profile shape functions as applied to neutron studies. Their analysis has direct bearing in the work in the area of powder diffraction profile fitting for X-ray data. In the Rietveld method, a complete pattern is usually collected and analyzed. The typical analysis involves fitting a functional representation of the instrumental breadth<sup>8</sup>, a slowly varying background,

atomic positions, atomic thermal motion parameters, and in defect structures a site occupancy<sup>9</sup>. In some cases, Rietveld analysis is used for quantitative analysis<sup>10</sup> of multiphase samples (usually two phase samples). Occasionally, microstructure parameters, such as mean coherent domain size and mean residual microstresses, are also introduced<sup>11</sup>.

Typical examples of the difficulties which both the Rietveld and individual profile fitting methods resolve are: statistical noise in the intensity data, determination of background intensity, separation of complex patterns due to large cell parameters or a low symmetry crystal system, and resolution of overlapping lines due to multiple phases. However, in many materials the microstructure is quite anisotropic and the determination of mean values of microstrain with the Rietveld method provides only limited information. For these cases, the fitting of an individual profile function for selected peaks in the pattern is required. This profile fitting approach, compared to use of raw data, provides several important additional benefits, namely elimination of truncation errors and freedom to choose the data collection range at will<sup>12</sup>.

XRAYL is a computer program for fitting analytical functions to powder diffraction lines. After fitting, the powder diffraction data, given as counts at steps in  $2\theta$ , are represented, diffraction-line-by-diffraction-line, by parameters of a profile function. The resulting profile parameters may then be used to generate "idealized" powder diffraction lines effectively free of statistical noise and contributions from overlapping lines and extending to background intensity on each side. Because of this capability XRAYL may be employed in X-ray powder diffraction profile analysis as a preprocessor program, that is, separating peaks and feeding the "resolved" data to subsequent analysis programs. To date, we have used XRAYL to analyze selected diffraction regions and to write the "resolved" data for use in our crystallite size - residual microstrain package CRYsiz<sup>13</sup>. When broadened and reference profile data sets are to be processed by XRAYL, they should be analyzed in the same run, not two separate runs. Analyzing the two data files within a single run provides the program the ability to prepare the generated data files with the identical  $2\theta$  range and with the profile centered at the same  $2\theta$  (requirements for meaningful Fourier deconvolution). With this capability the reference and broadened profile data files may be collected with different step size and range. XRAYL could be easily modified to write data files for analysis by some other data processing software, for example, by the quantitative analysis package NBS\*QUANT<sup>14</sup>.

This report contains the following information to guide the user in the use of the program XRAYL: (1) introduction to profile functions, (2) the non-linear least-squares algorithm utilized by the program, (3) user options and execution of the program; and (4) several examples.



## II. Background

### A. Parametric Representation of XRD Profiles

In X-ray powder diffraction, the most useful profile functions are those that can be applied over the entire angular range of data collection. The profile parameters of these functions must include angle-dependent breadth and shape parameters. Ideally, the profile parameters should be easily interpreted by the user and should change slowly as a function of the scattering angle. The breadth and shape parameters should accurately account for XRD line asymmetry. The profile breadth is most simply expressed as the full width at half maximum (FWHM). It is theoretically desirable to select profile functions based on the convolution of each component in line broadening<sup>15</sup>. Unfortunately, no parametric representation for the convolution is available. However, representation of an X-ray diffraction peak with a simple mathematical function is convenient even if there is no physical justification for the selection. So far, the widely used mathematical functions for XRD line profiles are Gaussian (G), Lorentzian (L), modified Lorentzian (ML), intermediate Lorentzian (IL), Voigt (V), pseudo-Voigt (P-V), and Pearson VII (P-VII). The Rational polynomial function is another model that has been proposed.

Table 1 lists the functions implemented in XRAYL and the refining parameters in the least-squares refinement. In these functions,  $x = (2\theta - 2\theta_0)$ , the distance between any  $2\theta$  position and the maximum position of the peak,  $2\theta_0$ .  $\gamma_G$  and  $\gamma_L$  are the FWHM of the peak for the Gaussian or Lorentzian forms\*.  $N$ 's are the corresponding normalization factors for the functions. For example, the normalization factor for a Pearson VII function is:  $N_{P-VII} = I \cdot \Gamma(m) / [\sqrt{(\pi m a)} \cdot \Gamma(m-1/2)]$ ; where  $I = \int y(x) dx$  and  $\Gamma(m)$  is the gamma function and  $m$  and  $a$  are the refining parameters.

For the implementation of these functions for profile refinement by XRAYL, several things should be pointed out:

(1) The forms of Lorentzian, Gaussian, and Pearson VII functions implemented in XRAYL are expressed in terms of the FWHM of the peak. A clear benefit of expressing these profile functions in terms of FWHM is that the starting values for the profile parameters may be obtained easily and the refined parameters are readily interpreted by the user.

(2) In XRAYL, the asymmetric nature of powder diffraction profiles is modeled by using "split" functions, that is, by using different profile parameters of the same functional form for each side of the peak. The "split" function, left side and right side, shares the same peak maximum and peak positions. The FWHM used in the scaling for the

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\* An example of the derivation for writing the parametric functions in terms of FWHM is given in the Appendix.

Table 1. Profile Functions Implemented in XRAYL

| <u>Function</u> | <u>Typical Notation(s)</u>  | <u>Notation Implemented</u>   | <u>Refining Parameters</u> |
|-----------------|---|---|----------------------------|
| Lorentzian      | $N/(1+kx^2)$  | $\frac{2S}{\pi\gamma_L} \cdot \left( \frac{1}{1 + 4x^2/\gamma_L^2} \right)$   | k or $\gamma_L$            |
| Gaussian        | $N \cdot \exp(-x^2/k^2)$  | $\frac{\sqrt{(4 \ln 2)} \cdot S}{\sqrt{\pi} \cdot \gamma_G} \exp\left[-4 \ln 2 \cdot \left(\frac{x}{\gamma_G}\right)^2\right]$        | k or $\gamma_G$            |
| Voigt           | $N \cdot \text{Re}(\omega(z))$<br>$\omega(z) = \exp(-z^2) \text{erfc}(-iz)$<br>$z = \alpha + i\beta$<br>$\alpha = 2(\ln 2)^{1/2} \cdot (x/\gamma_G)$<br>$\beta = (\ln 2)^{1/2} \cdot (\gamma_L/\gamma_G)$ | same  | $\alpha, \beta$            |
| Pearson VII     | $N \cdot [1+x^2/(mk^2)]^{-m}$   | $\frac{2 \cdot \Gamma(m) \cdot S}{\sqrt{\pi} \cdot \Gamma(m-0.5) \cdot \gamma_P} \cdot \left(1 + \frac{4x^2}{\gamma_P^2}\right)^{-m}$ | $\gamma_P, m$              |
| Rational        | $N/(1+Ax^2+Bx^4)$   | same  | A, B                       |

split function is taken as the arithmetic mean of the left and right FWHM parameters.

(3) In addition to modeling the diffraction profiles, several other contributions in XRD profiles are also considered. They are a linear background with constant intensity ( $b$ ) and slope ( $m$ ), the scaling factor ( $S$ ), and the intensity ratio of the  $\alpha_1$  and  $\alpha_2$  lines ( $R$ ). As the result, the calculated intensity at every  $2\theta$  position within a limited  $2\theta$  range may be written as:

$$I_{c_{a1}}(2\theta_i) = \sum S \cdot R \cdot Y(2\theta_i - 2\theta_0) + b + m \cdot (i-1) \cdot \Delta(2\theta),$$

where,  $\sum$  denotes the sum over the contributions to intensity from all the overlapped peaks and both  $\alpha_1$  and  $\alpha_2$  lines;  $i$  is the step number from the beginning of the region;  $Y$  is the calculated intensity; and  $\Delta(2\theta)$  is the step size in degrees  $2\theta$ .

(4) The raw data input is normalized such that the strongest intensity within the data region has the value 1.0. On this scale the background intensity typically has a normalized value of 0.05 to 0.2. The profile models, however, are normalized functions that have an integrated area of 1.0. The scaling parameter ( $S$ ) is the product of the height at maximum above background of the normalized data times the reciprocal of the maximum of the model function. A separate scaling parameter is needed for each peak within the region. XRAYL will estimate  $S$  using a symmetric Gaussian model if the starting value of  $S$  in the instruction file is 0.0.

## B. The General Description of Program XRAYL

Program XRAYL is designed to operate on "windows" in  $2\theta$ , that is, on regions in  $2\theta$  space. The program dimensions permit each window to contain up to five powder lines; this number may be changed by increasing the array dimension and recompiling the program.

There are two types of profile parameters. The first are "regional" ones as they are the same for all peaks within the window. The "regional" parameters include the background intensity, slope of the background intensity, and the ratio of  $\alpha_2$  to  $\alpha_1$  peak intensity. The second type of parameter depends upon the functional form selected and whether or not an asymmetric refinement is selected. The maximum number of parameters is six per line:  $2\theta$  of peak maxima, intensity scale, low and high FWHM, and low  $2\theta$  and high  $2\theta$  shape parameters. The selection of profile model and symmetry/asymmetry is under user control. The initial values of the parameters are either estimated by computation within the program or they may be supplied by the user. Every parameter may be either refined or held constant.

The program reads either one or two intensity data files. The first file is called the "reference" file and is used to establish values for an unbroadened diffraction pattern. The second is a file containing data for a sample which shows broadening and is called the "broadened" file. The



reference and broadened file may have been collected with different step size and  $2\theta$  range. XRAYL will write the generated profile reference and broadened data file with identical step size (as specified by the user) and  $2\theta$  range ( $a_3$ , as specified by the user). Neither of the designations is required and one broadened file may be supplied alone if parameter refinement is carried out appropriately. Another input file is used to select the profile model and control of the refinement process. This file is referred to as the "instruction" file.

In the course of the calculations the data input files are read, the intensity data are stored in immediate access memory, and a survey is made of the starting parameters. When starting parameters are not supplied in the instruction file, estimates are made from the input intensity data. Then, based upon the chosen function to be used in the fitting process, a non-linear-Marquardt least-squares fitting is carried out. The fitting subroutines used by XRAYL are those from the International Mathematical and Statistic Library (IMSL).<sup>17</sup> This fitting process usually produces analytical curves which match the input raw data quite well.

However, a number of caveats must be given. First, if the initial values of the parameters are too far from the best values, the fitting may fail. The most sensitive parameters are those of the  $2\theta$  maxima. The initial value for the  $2\theta$  maximum must be very close to the actual maximum position of the peak. This problem is greatest when several peaks overlap strongly within the window. In general, sharp lines of a reference pattern should be used to establish  $2\theta$  values for the broadened lines, and the  $2\theta$  maxima of the broadened lines should not be refined. If problems arise during refinement, close attention should be given to the values of all starting parameters. A symmetric refinement prior to an asymmetric refinement can be useful to estimate good starting parameters in difficult problems. The estimated FWHM must also be given if the peaks are not cleanly separated above the half maximum intensity level. A general statement may be made that any starting parameters that is too far from the refined value may cause non-linear least-squares to fail.

### C. Non-linear Least-squares Refinement

In the least-squares refinement, the function minimized is  $\sum [w_i (I_{o_i} - I_{c_i})^2]$ , where  $I_{o_i}$  and  $I_{c_i}$  are the observed and calculated intensities at  $2\theta_i$ , respectively, and  $w_i$  is a weighting factor. Each intensity may be weighted by the square root of the number of counts. This means that the fitting will be closest on the peaks and less dependent on the background or small peaks within the window. If desired, the weighting can be set to 1.0, and is recommended when the purpose of refinement is to separate a weak peak from a much stronger peak.

The IMSL program ZXSSQ<sup>16</sup> continues to refine the parameters until any one of three convergence criteria is met. The first criterion is that all parameters in two successive cycles agree to  $n$  (a user-given integer number) significant digits. The second one is that the relative difference of the residual sum of squares estimates on two successive iterations is less than or equal to a specified value, SV. The third criterion is that



the norm of the approximate gradient is less than or equal to another specified value, delta. All these criteria are under user control. The maximum number of cycles allowed is 1500.

Once the least-squares fitting has been completed, the profile parameters of the chosen equation are used to generate output intensity data. For each profile written, the output may have any step size  $\Delta 2\theta$  and  $2\theta$  range. Lines, such as  $\alpha_2$  or those due to spurious phases may be omitted from the output file. Components of overlapped regions are individually written to the output files as completely resolved lines. Besides the separation of overlapping lines and the smoothing of the raw data, this operation serves another purpose. First, carefully screened data with constant  $a_3$  values (regions of  $1/d$  space)<sup>17</sup> are generated for use by the subsequent program CRYISZ, which estimates crystallite size and residual strain. The output parameter data file serves two purposes. First, it may be edited by the user and then provided as an instruction file for a subsequent refinement. Second, the parameter file can be used to fit a  $2\theta$ -dependent model to each profile parameter. With the  $2\theta$  dependence modeled, one can generate reference lines at any  $2\theta$  for use with substances where a sample free of strain and size broadening is not available<sup>18</sup>.

The estimates of the errors of the refined profile parameters are obtained from the Jacobian matrix produced by the IMSL program ZXSSQ<sup>17</sup>. As overall evaluation for the fitting, two quantities are calculated. One is called the correlation of fit (COF), which is also based upon the Jacobian matrix. Its definition can be seen from the formula:

$$\text{COF} = \frac{\sum(I_{\text{obs}} - I_{\text{ave}})^2 - \sum(I_{\text{obs}} - I_{\text{cal}})^2}{\sum(I_{\text{obs}} - I_{\text{ave}})^2}$$

where  $I_{\text{obs}}$ ,  $I_{\text{ave}}$ ,  $I_{\text{cal}}$  are the observed, average, and calculated intensities, respectively. For a perfect fit, COF should equal 1, and for a random fit, it should equal 0. The other measure of fit is the conventional R factor, which has been widely used in both single crystal and powder diffraction. The definition of the R factor in XRAYL is:

$$R = \left\{ \frac{\sum(I_{\text{obs}} - I_{\text{cal}})^2}{\sum I_{\text{obs}}^2} \right\}^{1/2}$$

#### Data for Size and Strain Error Estimates

For the purpose of estimating errors in the subsequent data analysis, such as in size and strain analysis, two additional files may be written. One is for profiles generated using the refined parameter values plus  $X \cdot \sigma$  and the other one is for  $X \cdot \sigma$  below, where  $X$  is any number and  $\sigma$  is the standard deviation. The values of  $X$  and the number of profile parameters which will be modified may be specified by the user. These files permit calculation of a numerical estimate of the limit of errors in predicting size and strain parameters by the program CRYISZ.

### III. Program Files and Execution

The user's instructions and one or two raw data files are the input required by XRAYL. The program XRAYL produces up to four "idealized" diffraction data files and one refined profile parameter file. The program writes each of these files to a "logical unit". The corresponding unit numbers are:

|  |      |   |
|--|------|---|
| User instruction file                          | ---- | unit 8;   |
| Input raw data files                           | ---- | unit 20 - obs. reference profiles;<br>unit 21 - obs. broadened profiles;  |
| Output parameter file                          | ---- | unit 9;   |
| Output generated data files                    | ---- | unit 10 - gen. reference profiles;<br>unit 12 - gen. broadened profiles;  |
| Output generated data files for error analysis | ---- | unit 11 - gen. broadened profiles with minus $X*\sigma$ ;<br>unit 13 - gen. broadened profiles with plus $X*\sigma$ |

Following is the detailed description about the contents and the formats of these files.

#### A. User Instruction File.

The user instruction file, unit 8, contains several lines that provide the problem title, wavelength of the radiation used, and convergence criteria for the non-linear refinement. In order to distinguish the records easily, the first field of each record is reserved for the record name. The last line of unit 8 must contain the three characters "END" which indicates the end of the instruction file. All of the input items are in free format, and therefore none of these items can be omitted.

Each of the following records must be included in unit 8. Records 1 and 2 provide the general information for the problem and will be used for all diffraction angle regions.

Record 1: TITLE, an alphanumeric title for the problem.

Field #1: TITLE

Field #2: Alphanumeric title information

Record 2: GENREF, provides the general information for the least-squares refinement for all the diffraction data. It contains the following fields:

Field #1: GENREF

Field #2: wavelength of  $K\alpha_1$  in units of Å; The default value is that for Cu target ( $\lambda(K_{\alpha_1})=1.5405981\text{Å}$ );

Field #3: Relative intensity weight of  $K\alpha_1$ . The default is 1.0;

Field #4: Wavelength of  $K\alpha_2$ . The default is that for Cu target ( $\lambda(K_{\alpha_2})=1.5444342\text{Å}$ );

Field #5: Relative intensity weight of  $K\alpha_2$ . The default is 0.5;

Field #6: Signal for whether  $\alpha_1$  lines alone or  $\alpha_1$  and  $\alpha_2$  components to the profile are to be generated and placed in the output files. If Y (for yes) the  $\alpha_2$  will be included with weight as specified by Field #5. If N (for no) the  $\alpha_2$  component will be omitted from the output files.

Field #7: The first convergence criterion of least-squares fitting. It is an integer used in the significant digit test based on the difference between parameter values of two successive fitting cycles. That is, if any two successive cycles agree, parameter by parameter, to within this number of significant digits, the fitting is considered to have converged. The default value is 5.

Field #8: The second convergence criterion of least-squares fitting. If the difference of the residual sum of squares estimates of any two successive cycles is less than or equal to this number, the fitting is considered converged. The default value is  $1.0 \times 10^{-4}$ .

Field #9: The third convergence criterion of least-squares fitting. If the (Euclidean) NORM of the approximate gradient is less than or equal to this number, the fitting is considered converged. The default value is 0.0.

Field #10: A signal to create additional output files for error analysis. 1/0 for generated/not generated. When the input signal is 0, only one output file will be generated for the broadened data; the refined profile parameters are used in the data generation. This best estimate output data file of generated profiles will be written to unit 12. If the input signal is 1, two additional data files will be generated for the broadened data. One of them is generated using the parameters obtained by subtracting  $n_j \cdot \sigma$  from the refined parameter  $j$ , where  $n$  is a number specified by the user,  $\sigma$  is the least-squares estimated standard deviation, and  $j$  is the  $j$ -th parameter for the region. This file is written to output unit 11. The other file is generated using the parameters obtained by adding  $n_j \cdot \sigma$  to the  $j$ th refined parameter. This file is written to output unit 13. The purpose of this feature is to provide the user the means to estimate the errors in the diffraction data analysis with a subsequent program.

Following the GENREF record, the instruction file provides the information needed for the least-squares refinement, window by window. For each window in  $2\theta$ , there must be a record that specifies the number of reflections in the window and some refinement instructions applicable to all the peaks in the window (WINREF). This record must then be followed by four records per reflection within the window which give specific information and other refinement instructions for each reflection. Note that in these records, all diffraction angle related quantities must be in the units of degrees  $2\theta$ .

The record WINREF provides the universal instructions for the refinement for the window. It contains the following items:

Field #1: WINREF

Field #2: The number of reflections in the window. Maximum number is 5.

Field #3: The refinement function to be employed.

- 1 --- Lorentzian
- 2 --- Gaussian
- 3 --- Voigt
- 4 --- Pearson VII
- 5 --- Rational

Field #4: A signal to indicate if a split function is to be used. 1/0 for split function/symmetric function refinement.

Field #5: A signal for whether one or two input raw data files are to be treated. 0/1 for one/two raw data files.



- Field #6: The number of background points on each side of the  $2\theta$  region. These background points will be used to calculate the starting values for the background intensity and its slope.
- Field #7: A signal for whether background intensity will be excluded or included in the output profile data. 0/1 for exclude/include the background intensity in the output.
- Field #8: The  $a_3$  value, the period or spread in Angstroms, for the output profile data. The value of  $a_3$  sets the  $1/d$  scan range in the output data. If  $a_3$  is outside the range 15 to 100.0 Å, the minimum value of  $a_3$  in the experimental input file will be used.
- Field #9: The step size in degrees  $2\theta$  for the generated output profile data.
- Field #10: A signal for printer plots.
- 0 --- no plots
  - 1 --- plot fitted curves only
  - 2 --- plot generated curves only
  - 3 --- plot input raw data only
  - 4 --- plot everything
- Field #11: A signal for whether background intensity will be refined or held constant. 1/0 indicate refined/held constant. Default is 1.
- Field #12: A signal for whether background intensity slope will be refined or held constant. 1/0 for refined/held constant. The default value is 1.
- Field #13: A signal for whether the intensity ratio of the  $\alpha_1$  and  $\alpha_2$  lines will be refined or held constant. 1/0 for refined/held constant. The default is 0. It is recommended that this parameter be held constant for peaks at low  $2\theta$  containing  $\alpha_1$  and  $\alpha_2$ .
- Field #15: A signal for whether the line position of the diffraction peaks in the "broadened" data file will be held constant in the multi-line refinement. When it is requested to hold them constant, the corresponding refined  $2\theta$  positions of the "reference" peaks will be assigned to them. This feature is useful when rather severe overlap occurs to the "broadened" peaks due to line broadening. Y/N for hold them constant/not hold them constant.

Field #14: A signal for whether the intensity difference in the least squares refinement will be weighted by a counting statistics factor or not. Y/N for weighted/not weighted.

Following the general information for the window, there must be four additional instruction records for each of the reflections in the window. The first line of these four, denoted as LINERF, contains reference line information:

Field #1: LINERF

Field #2: hkl, the indices of the peak, 3I2.

Field #3:  $2\theta$  position of the  $\alpha_1$  peak. Note that the  $2\theta$  value given must be very close to the actual values in the input raw data file. If this condition is not met the least-squares may fail to converge.

Field #4: User provided starting value for the intensity compression scaling factor. When input is 0.0, this factor will be estimated in the program.

Field #5: Estimated FWHM in degrees  $2\theta$  for the reference peak, symmetric case. If Fields 4, 5 and 6 are all 0.0, then the necessary FWHM values will be estimated within the program. Input of 0.0 is recommended if there is only one peak in the window. If multiple peaks are present, reasonable estimates by the user will aid convergence. For the rational polynomial function, Field #4 is the refining parameter A for the symmetric case.

Field #6: Estimated FWHM for the left side, reference peak.  
(or  $A_L^{**}$  for Rational polynomial model)

Field #7: Estimated FWHM for the right side, reference peak.  
(or  $A_H$  for Rational polynomial model)

Field #8: Estimated starting shape parameters of the reference peak, symmetric case. Default value is 1.0. (Pearson VII, Voigt and Rational functions. Equals B, another refining parameter for Rational polynomial).

Field #9: Estimated shape parameter, left side of reference peak.  
(or  $B_L$  for Rational model)

---

\*\*  $A_L$ ,  $A_H$ ,  $B_L$ ,  $B_H$  are the low and high angle side refining parameters for a split Rational function.

Field #10: Estimated shape parameter, right side of reference peak. (or  $B_R$  for Rational model)

Field #11: Signal for whether the current peak is to be included in the output data set or not.

0 --- current peak will be included in the output.

1 --- current peak is treated as impurity peak and will be excluded from the output.

The second line of these four, denoted as LINEBR, contains broadened line information. Only the parameter portions should be different than the values for the reference line. If only a reference data set is to be analyzed, the input of this line is still required. However, in such cases, this line may be simply duplicated from LINERF. The fields of LINEBR are:

Field #1: LINEBR

Field #2:  $hkl$ , the indices of the peak (same as for reference line)

Field #3:  $2\theta$  position of  $\alpha_1$  of the peak. The value will be reset to the refined value for the reference line and not refined.

Field #4: User-provided starting value for the intensity compression scaling factor. When input is 0.0, this factor will be estimated in the program.

Field #5: Estimated FWHM in degree  $2\theta$  (or A of Rational polynomial) for the corresponding broadened peak, symmetric case. If Fields 4, 5 and 6 are all 0.0, the needed values will be estimated within the program.

Field #6: Estimated FWHM (or A) for the left side, broadened peak.

Field #7: Estimated FWHM (or A) for the right side, broadened peak.

Field #8: Estimated starting shape parameter (or B of Rational polynomial), broadened peak. Default value is 1.0. (Pearson VII, Voigt and Rational functions)

Field #9: Estimated starting shape parameter (or B) for the left side of the broadened peak.

Field #10: Estimated starting shape parameter (or B) for the right side of the broadened peak.

Field #11: Same as the Field #10 in LINERF.

The next record, PARCON, is the profile parameter refinement control line for the current reflection. It provides signals indicating whether each of the profile parameters will be refined or held constant. When it is a 1, then the corresponding parameter will be refined. When it is a 0 the parameter will be held constant. The reference and broadened data refinements will be refined identically, except that the  $2\theta$  values for the broadened profiles will be held constant. The sequence of these signals and their default values are as follows:

- Field #1: PARCON
- Field #2: Refine  $2\theta$  position of the current peak. Default is 1.
- Field #3: Refine intensity scale. Default is 1.
- Field #4: Refine FWHM of symmetric mode. Default is 0.
- Field #5: Refine FWHM of the left side of the peak when split function mode. Default is 0.
- Field #6: Refine FWHM of the right side of the peak when split function mode. Default is 0.
- Field #7: Refine shape parameter of symmetric function mode. (Pearson VII, Voigt and Rational functions). Default is 0.
- Field #8: Refine shape parameter of the left side of the peak when split function mode. Default is 0.
- Field #9: Refine shape parameter of the right side of the peak when split function mode. Default is 0.

The last record for a diffraction lines is SETSIG which is paired with the PARCON record. It contains eight numbers, which are the user specified multipliers of sigma for each of the parameter errors. These must be specified when output data files for the error analysis are requested. A value between -3.0 to 3.0 is recommended. These numbers are for the eight profile parameters defined above for record PARCON. The sign of the multiplier affects the profile shape differently for different parameters. For example, using +n for the FWHM parameter will broaden the peak. With the Pearson VII model, the shape parameter should be changed by -n to broaden the peak. Thus the greatest change of a Pearson VII profile is achieved by using +n for the FWHM and -n for the shape parameter.

- Field #1: SETSIG
- Field #2 - #9: "n" multiplier value for each parameter defined under



PARCON. Default values are 0.0. Leave blank if field #10 of GENREF is 0.

The records LINERF, LINEBR, PARCON and SETSIG repeat diffraction peak by diffraction peak for lines within the  $2\theta$  window. Each new region or window begins with a WINREF record. The last line in the instruction file will be a record which contains only three characters, END, in its first three columns.

Table 2 is an example of a short instruction file. This instruction file is for least-squares fitting of the raw data collected for  $\text{Fe}_3\text{O}_4$ . This raw data set contains two diffraction regions or windows. The first region has only one peak, (111), and the second region has two peaks, (311) and (222).

Table 2. Example of Instruction File (unit 8)

```
TITLE Fe3 O4 reference powder, bottle #3456.
GENREF 1.5405981 1.0 1.54433 0.5 Y 4 1.0E-5 1.0E-8 1
WINREF 1 4 1 1 10 0 30.0 0.005 4 1 0 0 N Y
LINERF 1 1 1 18.269 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0
LINEBR 1 1 1 18.269 0.0 0.0 0.0 0.0 0.0 0.0 0.0
PARCON 1 1 0 1 1 0 1 1
SETSIG 0.0 0.0 0.0 3.0 3.0 0.0 -3.0 -3.0
WINREF 2 4 1 1 10 0 30.0 0.005 4 1 0 0 N N
LINERF 3 1 1 35.422 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0
LINEBR 3 1 1 35.422 0.0 0.0 0.0 0.0 0.0 0.0 0.0
PARCON 1 1 0 1 1 0 1 1
SETSIG 0.0 0.0 0.0 3.0 3.0 0.0 -3.0 -3.0
LINERF 2 2 2 37.052 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0
LINEBR 2 2 2 37.052 0.0 0.0 0.0 0.0 0.0 0.0 0.0
PARCON 1 1 0 1 1 0 1 1
SETSIG 0.0 0.0 0.0 3.0 3.0 0.0 -3.0 -3.0
END
```

## B. The Input Raw Intensity Data Files

The raw data files, containing the observed intensity data for the reference and broadened materials, are read from logical units 20 and 21, respectively. In the case of one input raw data file it should be assigned to unit 20.

The format for the raw data files is given below. The file structure begins with a title record for the first region followed by a region definition record and the intensity data for each step across the region. The region information records contain the indices, sample ID, beginning and ending angles, counting time at each data point, and the step size. Every intensity datum occupies an individual line. Record types 1, 2, 3 are repeated for each region in the data file.

RECORD 1 TITLE

Field #1 TITLE (A5)  
Field #2 Sample ID (A12)  
Field #3 hkl indices in parentheses, 3I2.  
Field #4 hhl indices in parentheses, 3I2.

RECORD 2 REGION DEFINITION

Field #1 Number of data points (I5)  
Field #2 Count time in seconds (F10.2)  
Field #3 Starting  $2\theta$  for region (F10.4)  
Field #4 Ending  $2\theta$  for region (F10.4)  
Field #5 Step size in  $2\theta$  (F10.4)

RECORD 3 INTENSITY DATA (repeats for the number of data points)

Field #1 Intensity (F11.2)

TITLE Ba2SM600C ( 0 3 0) ( 0 3 0)  
161 7.90 22.0000 23.6000 .0100  
3438.97  
3444.11  
3420.28  
3451.28  
3439.04  
3420.00  
3428.00  
3513.00  
3453.00  
3579.00  
3508.00  
3427.00  
3397.00  
3414.00  
.  
.  
.  
.

### C. The Output Generated Data Files.

The generated data are written to units 10, 11, 12, and 13, depending on data input and user options. Units 10 and 12 contain the data generated by using the refined profile parameters directly from the least-squares results. Unit 10 contains the generated profiles corresponding to the reference data read from unit 20. Unit 12 contains the generated profiles for the broadened data read from unit 21, if input. In the case of a single input data file, the output will be written to unit 10. The data

written to units 11 and 13 are the modified profile data for use in subsequent error analysis algorithms.

The input raw intensity data file and the generated output file have essentially the same structure given in Section B above. The only difference between the input and the output files is that in the generated output file each region contains only one reflection while in the input raw data each region may contain one or several peaks. Thus the output may have several regions, each with a different "isolated" peak, covering the same  $2\theta$  region.

#### D. The Output File of Refined Profile Parameters

The refined profile parameters are written, peak by peak, into an output file on unit 9. Unit 9 also duplicates the control information for the least-squares process. The format of this file is identical with that of the user instruction file (logical unit 8) defined above. Thus, the output parameter file can be used to establish the starting values of a second refinement. The ability to restart a refinement is particularly useful when the refinement is constrained on the first few cycles (for example, refining only background and  $2\theta$  values). To prepare an instruction file for subsequent refinements unit 9 can be edited with a text editor and used as the instruction file, unit 8, for the next refinement.

#### IV. Execution Examples

In this section, three example analyses are presented as a guide to use of program XRAYL. The first one uses a generated diffraction data set of Gaussian form. This generated profile, reference and broadened, is refined using all five implemented profile functions. The other two examples are the Pearson VII refinement results for experimental data collected for  $\text{LaB}_6$  powder and a gadolinium barium cuprate powder. The former material gives a very good distribution of narrow diffraction peaks without any overlap, evenly spaced in  $2\theta$ . Many of the reflections of the latter material are heavily overlapped. Therefore, the last example will show the peak separation feature of XRAYL.

##### 1. Gaussian Generated Profiles:

In this example, two sets of input "raw" data were generated utilizing a symmetric Gaussian function. One set was the reference data which is assumed to be free of strain and size broadening in its diffraction peaks. The other set was the broadened data which was assumed to have a size of  $100\text{\AA}$  and strain of  $1 \times 10^{-3}$ \*\*\*. These two files were then fed into the program XRAYL to be refined by both symmetric and split profile models of Gaussian, Pearson VII, Voigt, and Rational forms. The purpose of these refinements was to test the program and to assure that the least-squares refinement works appropriately. In these test runs, two parameters, background intensity slope and the  $\alpha_2$  and  $\alpha_1$  intensity ratio, were held constant. Table 3 lists the refinement results for the various symmetric profile models on the simulated Gaussian "broadened" data. Table 4 lists the results for the asymmetric models.

The refinement results show that, in addition to a Gaussian function, a Voigt function, either symmetric or split, also fits the input "Gaussian" profile perfectly. This result is not surprising because the Voigt function is a convolution of Gaussian and Lorentzian functions. The results in Tables 3 and 4 also show that the Pearson VII and the Rational function profiles exactly match the input profile as well. Note that the resultant shape parameters,  $m$ 's in P-VII case, are reasonable in the sense that they reflect the Gaussian nature of the input data (according to theory, for  $m=1$  the P-VII is Lorentzian, and for  $m=\text{large number}$ , the P-VII is Gaussian). All of the refinements have a perfect COF (=1) and a very small R factor except when the Lorentzian function was used.

---

\*\*\* If the crystallite size and strain distributions are assumed to be in Gaussian form, the following relationship among the FWHM of the overall observed peak, size, and strain values exists:  $(\beta \cos \theta / \lambda)^2 = (1/D)^2 + 16\epsilon^2 (\sin \theta / \lambda)^2$ ; where  $\beta$ ,  $D$ ,  $\epsilon$  are the FWHM, size, and strain values, respectively.



Table 3. Symmetric Refinement Results for Simulated Symmetric Gaussian Profile

| FUNC | B                | 2θ(°)            | N                | γ                           | S                         | COF   | R    |
|------|------------------|------------------|------------------|-----------------------------|---------------------------|-------|------|
| Sy-G | .0001<br>±.00001 | 28.538<br>±.000  | .4881<br>±.0000  | .9171<br>±.0000             |                           | 1.0   | .000 |
| Sy-L | -.3554<br>±.0051 | 28.538<br>±.0004 | 1.2761<br>±.0096 | 1.1915<br>±.0049            |                           | .9997 | .014 |
| Sy-V | .0000<br>±.0000  | 28.538<br>±.000  | .4064<br>±.0000  | .9172<br>±.0000             | .0000<br>±.0000           | 1.0   | .000 |
| Sy-P | -.0244<br>±.0012 | 28.538<br>±.000  | .5180<br>±.0014  | .932<br>±.01971             | 12.11<br>±.51             | 1.0   | .002 |
| Sy-R | -.0751<br>±.0012 | 28.538<br>±.000  | 1.0733<br>±.0012 | <u>A</u><br>11.620<br>±.024 | <u>B</u><br>95.62<br>±.89 | 1.0   | .003 |

Table 4. Asymmetric Refinement Results for Simulated Symmetric Gaussian Profile

| FUNC | B                 | 2θ(°)            | N                | γ <sub>L</sub>                          | γ <sub>H</sub>                          | S <sub>L</sub>                        | S <sub>H</sub>                        | COF   | R     |
|------|-------------------|------------------|------------------|---|---|---------------------------------------|---------------------------------------|-------|-------|
| Sp-G | .0001<br>±.00001  | 28.538<br>±.000  | .4881<br>±.0000  | .9172<br>±.00001                        | .9171<br>±.00001                        |                                       |                                       | 1.0   | .000  |
| Sp-L | -.3553<br>±.00521 | 28.538<br>±.001  | 1.2764<br>±.0096 | 1.1915<br>±.0057                        | 1.1914<br>±.0057                        |                                       |                                       | .9997 | .0141 |
| Sp-V | .0000<br>±.0000   | 28.538<br>±.000  | .4064<br>±.0000  | .9172<br>±.0000                         | .9172<br>±.0000                         | .0000<br>±.0000                       | .0000<br>±.0000                       | 1.0   | .000  |
| Sp-P | -.0225<br>±.0010  | 28.538<br>±.000  | .5155<br>±.0012  | .931<br>±.022                           | .931<br>±.022                           | 13.13<br>±0.61                        | 13.13<br>±0.61                        | 1.0   | .002  |
| Sp-R | -.0751<br>±.0012  | 28.538<br>±.0006 | 1.9732<br>±.0012 | <u>A<sub>L</sub></u><br>11.619<br>±.073 | <u>A<sub>H</sub></u><br>11.621<br>±.073 | <u>B<sub>L</sub></u><br>95.63<br>±.97 | <u>B<sub>H</sub></u><br>95.62<br>±.97 | 1.0   | .0032 |

Sy = Symmetric, Sp = Split; G = Gaussian; L = Lorentzian; V = Voigt; P = Pearson VII; R = Rational function; S = Shape parameter for a symmetric function; S<sub>L</sub> and S<sub>H</sub> = Low and High angle side shape parameters.

In the test where the input data were generated in the form of a symmetric Lorentzian profile, the refinement using a Lorentzian function gave a perfect fit (results not shown) while a relatively poor fit occurred when a Gaussian function was used. Again the Voigt, Pearson VII and Rational functions were excellent model profiles.

## 2. Resolved XRD Profiles:

In example 2, experimental X-ray powder diffraction data collected for a  $\text{LaB}_6$  powder<sup>19</sup> (single input) was refined by using a split Pearson VII function. In the  $\text{LaB}_6$  pattern, each peak is well resolved and no overlap occurs. Therefore, the starting values for the FWHM,  $\gamma$ , of all the peaks were estimated by the program. The shape parameters, however, were set to 2.5 for both sides of the peak. Table 5 lists the refined profile parameters along with the  $2\theta$  positions (uncorrected for instrumental aberration). The intensity R factor for every peak is less than 2%, and most of them are around 1.5%, indicating an excellent fit. Figures 1 a-c show the quality of the fit for a low, intermediate and high  $2\theta$  peak.

From this example, it is clear that with the least-squares algorithm used in XRAYL, the P-VII function can fit real experimental diffraction data very well. Although the correlation of the refinement among different peaks is not yet clear at this stage, a good match for each individual peak may be obtained by an appropriate refinement. Moreover, smooth variations of the FWHM parameters versus  $2\theta$  are observed. This suggests that such fitting provides the possibility to establish a model of the profile parameters as a function of  $2\theta$ . Such dependencies of the profile parameters on  $2\theta$  would be very useful in generating a reference peak at any arbitrary  $2\theta$  position. To meet this need, a  $\text{LaB}_6$  powder for use as an instrumental profile standard reference material in X-ray powder diffraction analysis is being certified by NBS.

Table 5. Pearson VII Fitted Profile Parameters for  $\text{LaB}_6$

| Peak | $2\theta^\circ$ | $\gamma_L$ | $\gamma_H$ | $S_L$ | $S_H$ | COF   | R     |
|------|-----------------|------------|------------|-------|-------|-------|-------|
| 110  | 30.374          | .1461      | .0800      | 0.902 | 2.249 | .9995 | .0190 |
| 111  | 37.426          | .1314      | .0821      | 1.101 | 2.275 | .9993 | .0209 |
| 200  | 43.489          | .1171      | .0823      | 1.148 | 2.899 | .9995 | .0174 |
| 210  | 48.940          | .1246      | .0842      | 1.218 | 1.925 | .9996 | .0160 |
| 211  | 53.972          | .1270      | .0837      | 1.490 | 1.768 | .9997 | .0147 |
| 220  | 63.195          | .1305      | .0912      | 2.491 | 2.070 | .9996 | .0135 |
| 311  | 75.819          | .1328      | .0988      | 2.060 | 1.474 | .9996 | .0149 |
| 222  | 79.843          | .1342      | .1029      | 1.450 | 1.206 | .9995 | .0143 |
| 400  | 95.636          | .1330      | .1100      | 2.060 | 1.303 | .9997 | .0103 |
| 420  | 111.888         | .1418      | .1395      | 1.117 | 1.035 | .9997 | .0119 |
| 332  | 120.676         | .1559      | .1709      | 0.975 | 0.890 | .9997 | .0115 |
| 422  | 130.364         | .1821      | .1979      | 1.008 | 0.899 | .9996 | .0112 |
| 510  | 141.718         | .2177      | .2493      | 0.942 | 0.892 | .9995 | .0164 |

### 3. Overlapped XRD Profiles:

The material for this example is  $\text{GdBa}_2\text{Cu}_3\text{O}_7$ , a rare earth high  $T_c$  superconductor powder (SpGr=Pmmm,  $a= 3.8466$ ,  $b= 3.8958$ ,  $c= 11.6794 \text{ \AA}$ ).<sup>20</sup> In the pattern of this material, there are several overlapped peaks. Without appropriate peak separations, no diffraction profile analysis would be possible. Therefore, this material serves as a good example of using XRAYL to separate heavily overlapped peaks. Figure 2 shows the raw pattern of this material, the composite Pearson VII curve and the difference in the region of 32.5 degrees  $2\theta$  where peaks (013) and (103) are severely overlapped. The least-squares refinement was carried out by using split Pearson VII function. The starting values for this refinement are given in Table 6. In the refinement, two parameters, the slope of background intensity and the ratio of the  $\alpha_2$  to  $\alpha_1$  intensities, were held constant. It was noticed that the starting values of the  $2\theta$  positions of the two peaks are particularly important because altering the  $2\theta$  by  $0.05^\circ$  would cause the intensity R factor to increase dramatically. Table 6 also shows the refined parameters and their errors as well as the correlation of fit and the intensity R factor. Figure 3 shows the separated (013) peak and (103) peak along with their composite raw data curve. These two profiles were generated by using the fitted profile parameters with the background intensity removed.

From the results shown in Table 6 and the Figures 2 and 3, it can be concluded that a very severe overlapped pattern may still be separated into its component profiles. This separation is essential to the subsequent data analysis, such as crystallite size and residual microstrain. In our example, the refinement using a split P-VII function gave very good values for COF and the R factor (1.1%). These values suggest that the generated curves reliably represent the raw data curves very closely. It should be pointed out, however, the fitting errors of the high  $2\theta$  or "right" side shape parameter of the first peak, (013), and the low  $2\theta$  or "left" side shape parameter of the second peak, (103), are relatively large. This is due to the overlap because the shape parameter reflects mainly the tailing part of the profile and in this case, the right side tail of (013) and the left side tail of (103) are superimposed. Therefore, the refinement is less reliable. Such difficulties of refinement revealed in this example may suggest a further enhancement to XRAYL, namely, introducing constraints into the program. For example, if the shapes were assumed to be identical within the window, then the number of variables would be reduced and the ability to reasonably separate closely overlapped peaks enhanced.

Table 6. Profile Fitting the (013) and (103) Peaks of  $\text{GdBa}_2\text{Cu}_3\text{O}_7$ 

| <u>Parameters</u>         | <u>Line</u> | <u>Starting Values</u> | <u>Final Values</u> | <u>Fitting Errors</u> | <u>Fitting Control</u> |
|---------------------------|-------------|------------------------|---------------------|-----------------------|------------------------|
| B                         |             | .0523                  | .0498               | .0015                 | Fitted                 |
| m                         |             | .0031                  | .0031               | ---                   | Held constant          |
| $\alpha_2/\alpha_1$ Ratio |             | .50                    | .50                 | ---                   | Held constant          |
| $2\theta(^{\circ})$       | (013)       | 32.540                 | 32.548              | .002                  | Fitted                 |
| N                         | (013)       | .1042                  | .039                | .011                  | Fitted                 |
| $\gamma_L$                | (013)       | .5225*                 | .179                | .023                  | Fitted                 |
| $\gamma_H$                | (013)       | .5225*                 | .159                | .056                  | Fitted                 |
| $S_L$                     | (013)       | 1.000                  | 1.36                | .32                   | Fitted                 |
| $S_H$                     | (013)       | 1.000                  | 1.96                | 1.43                  | Fitted                 |
| $2\theta(^{\circ})$       | (103)       | 32.720                 | 32.769              | .001                  | Fitted                 |
| N                         | (103)       | .149                   | .073                | .007                  | Fitted                 |
| $\gamma_L$                | (103)       | .5225*                 | .203                | .033                  | Fitted                 |
| $\gamma_H$                | (103)       | .5225*                 | .143                | .007                  | Fitted                 |
| $S_L$                     | (103)       | 1.000                  | 1.51                | .52                   | Fitted                 |
| $S_H$                     | (103)       | 1.000                  | 1.85                | .16                   | Fitted                 |

Correlation of Fit: .9998      Intensity R factor: .0113

\*estimated in program

### V. Acknowledgements

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## VI. Appendix

The following is an example of the derivation to write the parametric functions in terms of their full width at half maximas (FWHM's). The function used in this example is a Gaussian:

$$I = \frac{1}{\sigma\sqrt{2\pi}} \cdot \exp\left(-\frac{x^2}{2\sigma^2}\right) \quad \text{-----} \quad (1)$$

From equation (1): when  $x=0$ ,  $I_o = \frac{1}{\sigma\sqrt{2\pi}}$  ; and

$$\text{when } x=x_f, I_f = \frac{1}{\sigma\sqrt{2\pi}} \cdot \exp\left(-\frac{x_f^2}{2\sigma^2}\right)$$

where  $x_f$  and  $I_f$  are the position and intensity at FWHM.

$$\text{Hence, } \frac{I_f}{I_o} = \frac{1}{2} = \exp\left(-\frac{x_f^2}{2\sigma^2}\right) \quad \text{-----} \quad (2)$$

and by definition,  $\text{FWHM} = 2x_f$ ,  $\therefore \text{FWHM}^2 = 8\sigma^2 \cdot \ln 2$

Then it follows that:

$$\sigma\sqrt{\pi} = \frac{\text{FWHM}}{2\sqrt{\ln 2}} \quad \text{-----} \quad (3)$$

$$\text{and } \sigma^2 = \frac{\text{FWHM}^2}{8\ln 2} \quad \text{-----} \quad (4)$$

Substituting (3) and (4) into (1) gives:

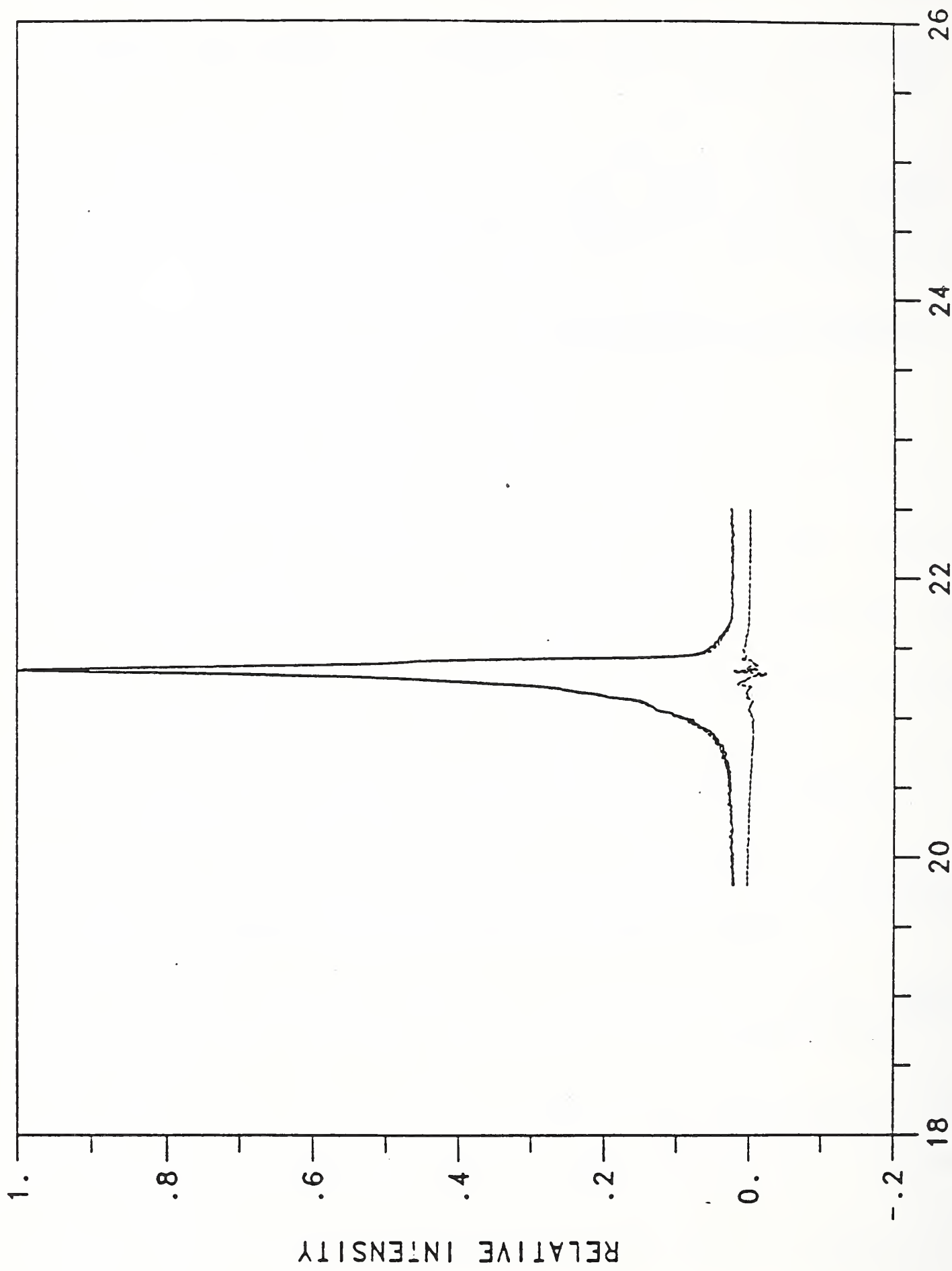
$$I = \frac{\sqrt{(4\ln 2)}}{\sqrt{\pi} \cdot \text{FWHM}} \cdot \exp\left[-4\ln 2 \cdot \left(\frac{X}{\text{FWHM}}\right)^2\right]$$

## VII. References

1. Taupin, D., (1973), J. Appl. Cryst., 6, p266
2. Parrish, W., Huang, T. C., and Ayers, G. L., (1976), Trans. Am. Crystallogr. Assoc., 12, p65
3. Mignot, J. and Rondot, D., (1976), J. Appl. Cryst., 9, p460
4. Hall, M. M. Jr., Veeraraghavan, V. G., Rubin, H., and Winchell, P. G., (1977), J. Appl. Cryst., 10, p66
5. De Keijser, Th. H., Langford, J. I., Mittermijer, E. J., Vogels, A. B. P., (1982), 15, p308
6. Rietveld, H. M., (1969), J. Appl. Cryst., 2, p65
7. Young, R. A. and Wiles, D. B., (1982), Profile Shape Functions in Rietveld Refinements, J. Appl. Cryst., 15, p430
8. Cagliotti, G., Paoletti, A. and Ricci, F. P., (1958), Nucl. Instrum., 3, p223.
9. Beech, F., Miraglia, S., Santoro, A. and Roth, R.S. (1987), Phys. Rev. B, 35, p 8778.
10. Hill, R. Presentation at the International Union of Crystallographers, Perth, Australia, 1987.
11. Howard, S.A. (1984), Ph.D Thesis "Incorporating (W\*G) Deconvolution in X-ray Rietveld Structure Refinement, Volume 1", Alfred University.
12. Zhang, Y., Stewart, J. M., Hubbard, C. R., Morosin, B., (1987), Advances in X-ray Line Profile Analysis to Determine Microstructure Information about Ceramics, in The Proceedings of the First International Conference on Ceramic Powder Processing Science, in press.
13. Zhang, Y., Stewart, J., Hubbard, C.R., Morrison, B., (1988), CRYSTZ: A Computer Code for X-ray Powder Diffraction Profile Analysis, paper in preparation.
14. Hubbard, C.R. and Snyder, R. L., (1988), Powder Diffraction, 3, p74.
15. Klug, H. P. and Alexander, L. E., (1974), X-Ray Diffraction Procedures, John Wiley and Sons, New York, N.Y., 2nd Edition.
16. National Bureau of Standards, (1984), Guide to Available Mathematical Software, NBSIR84-2824.

17. Zhang, Y., Stewart, J. M., Morosin, B., Graham, R. A., and Hubbard, C. R., (1987), X-ray line broadening study on shock-modified hematite, *Advances in X-ray Analysis*, in press.
18. Stewart, J. M., Zhang, Y., Hubbard, C. R., Morosin, B., (1988), A General Reference Material for X-Ray Powder Diffraction Profile Analysis, Paper in preparation.
19. Fawcett, T. G., Crowder, C. E., Brownell, S. J., Zhang, Y., Hubbard, C. R., Schreiner, W., Hamill, G. P., Huang, T. C., Sabino, E., and Langford, J. I., (1988), Establishing an Instrumental Calibration Standard for Powder Diffraction Analysis: International Round Robin Conducted by the JCPDS-ICDD and the U.S. National Bureau of Standards, *Powder Diffraction*, in press.
20. Paretzkin, B. and Wong-Ng W., private communication. Data to be submitted to Powder Diffraction.

RAW DATA CURVE OF INPUT REFERENCE PEAKS



THETA IN DEGREES

Fig. 1-(a)

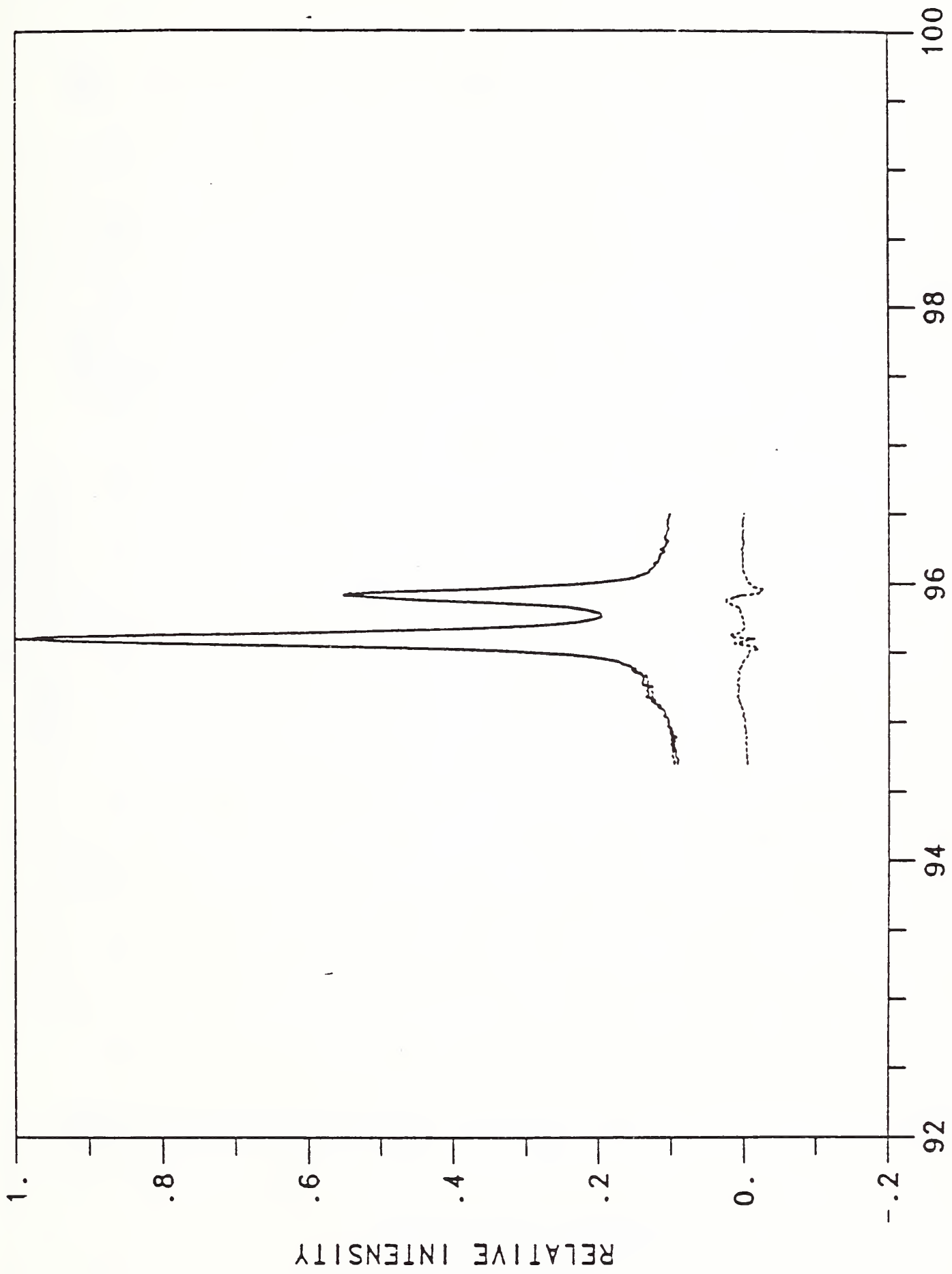


Fig. 1-(b) ;

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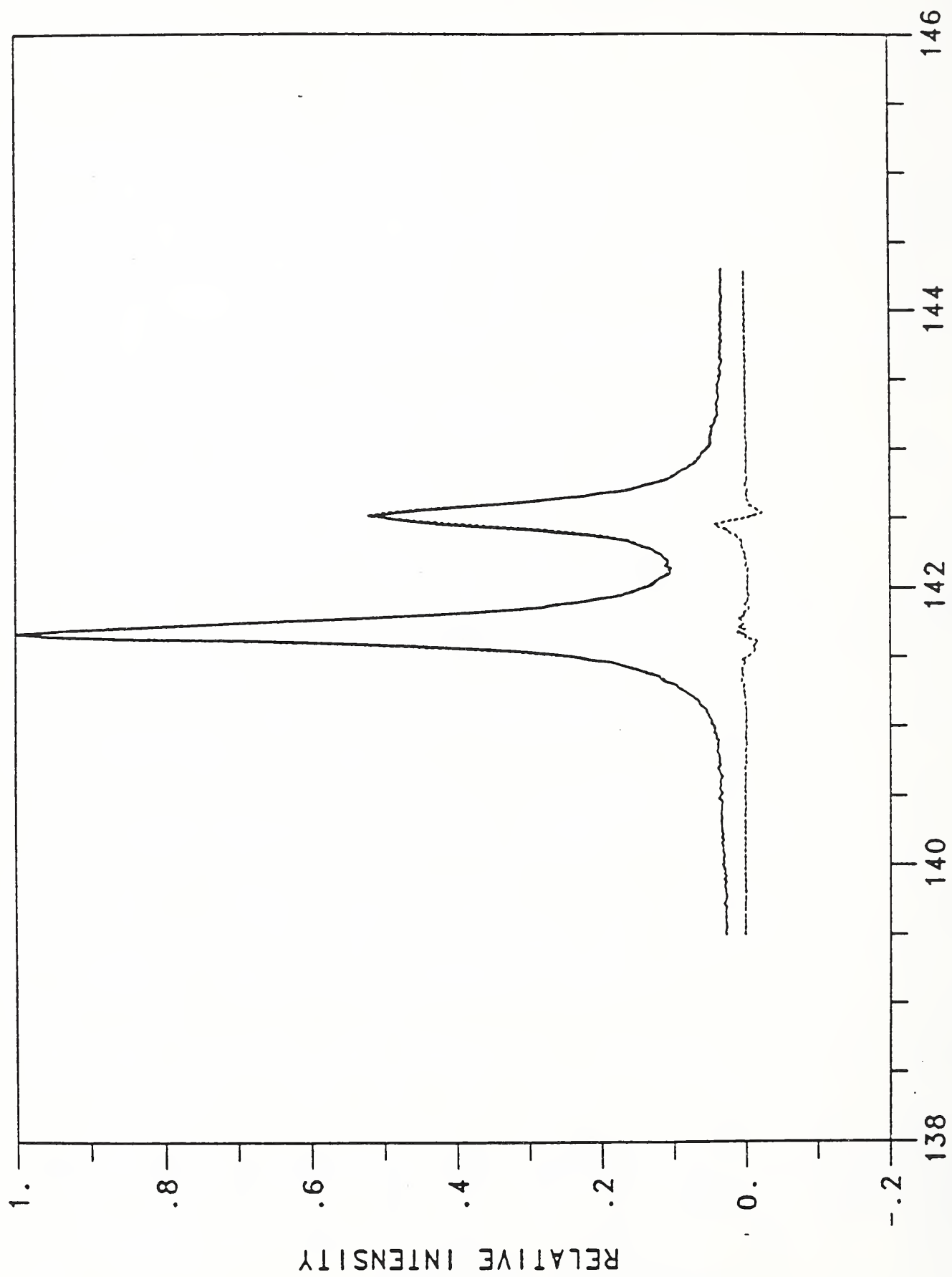
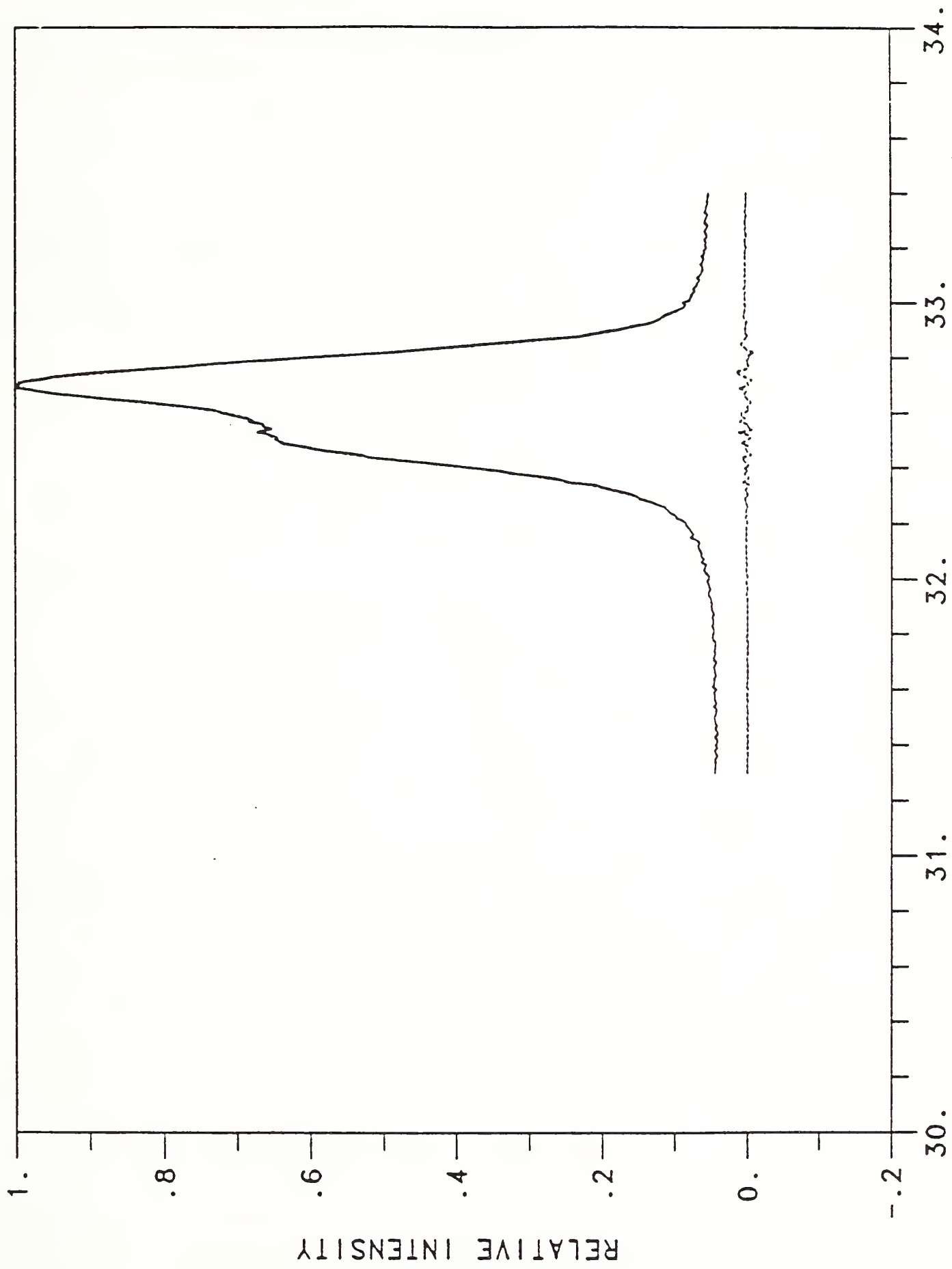


Fig. 1-(c)

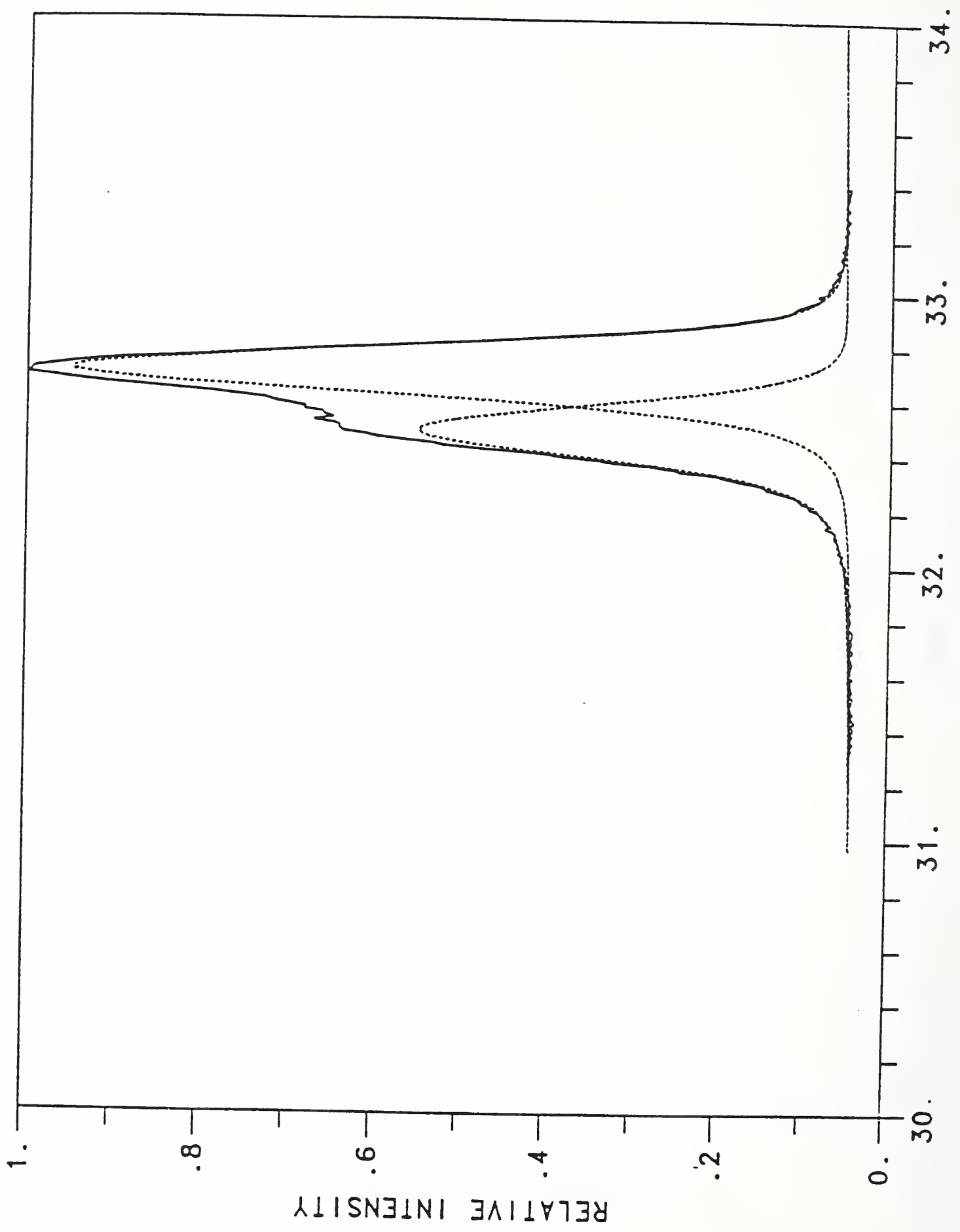
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Fig. 2

RAW AND GENERATED CURVES FOR REFERENCE DATA



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Fig. 3



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| 5. AUTHOR(S) J. M. Stewart and Y. Zhang, University of Maryland; C. R. Hubbard, National Bureau of Standards; B. Morosin and E. L. Venturini, Sandia National Laboratory  |  |  |                                    |                                     |
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| 10. SUPPLEMENTARY NOTES<br><br><input type="checkbox"/> Document describes a computer program; SF-185, FIPS Software Summary, is attached.  |  |  |                                    |                                     |
| 11. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)<br><br>In many applications of x-ray powder diffraction in material studies, when overlap occurs it is necessary to separate the total (or composite) profile into its components. A computer program, XRAYL, has been developed to fit analytical functions to powder diffraction lines. After fitting, the powder diffraction data, given as counts at steps in $2\theta$ , is represented, diffraction line by diffraction line, by parameters of a profile function. The resulting profile parameters may then be used to generate "idealized" powder diffraction lines, effectively free of statistical noise and contributions from overlapping lines, extending to background intensity on each side. Because of this capability XRAYL may be employed in x-ray powder diffraction profile analysis as a preprocessor program, that is, separating peaks and feeding the "resolved" data to subsequent analysis programs. This NBS-IR contains: (1) profile functions and the nonlinear least-squares algorithm utilized in XRAYL; (2) user options and execution of the program; and (3) several examples. |  |  |                                    |                                     |
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XRAYL: a powder diffraction profile refinement program

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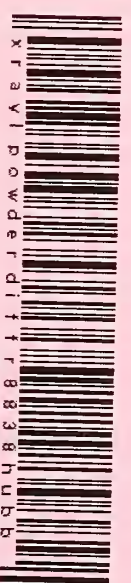
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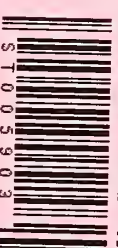
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