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CRYSIZ: A Program for Computing Crystallite Size and Strain from the Broadening of Powder Diffraction Lines

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C. R. Hubbard, B. Morosin,† and J. M. Stewart‡

ABSTRACT

The program **CRYSIZ** is designed to take the powder diffraction line profiles for a well-crystallized sample, called a reference pattern, and for a sample of the same substance, called a broadened pattern, to produce measures of the mean crystallite size, the distribution of crystallite sizes, and the root mean square residual microstrain in the broadened sample. The data required are the two powder patterns and a series of directives to signal the calculations and plots to be done during the execution of the program. The program loads files containing the background corrected powder diffraction intensity data for both the reference and broadened patterns. Preliminary calculations are done to find the centroids, full width at half maximums, integral breadths, spans over sum, and second moments. Two methods of deconvoluting the profile to calculate size and strain are allowed. Either the "direct" or the Stokes Fourier coefficient method of deconvolution may be chosen. In the direct method the profiles are extracted by numerical fitting. This method is slower but produces unfolded profiles free of ringing and the "hook effect." In this case the Fourier coefficients required for Warren-Averbach analysis are produced from the deconvoluted profile. In the Stokes method the diffraction pattern of each reference and broadened profile is Fourier transformed to produce a set of Fourier coefficients. The Fourier coefficients of the broadened profiles are divided by those of the reference pattern. The resulting coefficients are the "Stokes" coefficients. The Stokes coefficients are then smoothed by a least-squares procedure in order to remove noise and quell ringing and hooking. Once the filtering of the Stokes coefficients has been carried out, they are used as input to a reverse Fourier transform. This transform produces an "unfolded powder line," which is a best estimate of the broadened profile with the reference profile and noise removed. The deconvolution of the reference profile is assumed to give a broadened profile due only to the crystallite size and strain. Whichever method of deconvolution is chosen, all the various measures of line width are calculated for the "unfolded" profile. These may be used as measures of the broadness of the unfolded powder lines in a Hall-Williamson analysis. Before the unfolding of the coefficients is carried out from the reverse Fourier transform, the Stokes coefficients themselves are used in the Warren-Averbach procedure as an alternative means of determining size and strain.

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INTRODUCTION

Klug and Alexander give the basis and detailed description of the calculations carried out by the program **CRYSIZ**.[1] They define the various profiles referred to in this report. Following their symbolism, the profile $g(\epsilon)$ is the profile that arises from the broadening due to instrumental and physical factors. The profile $f(\epsilon)$ is due to the effects of the microstructure of the sample itself. The function $h(\epsilon)$, the experimentally measured profile, is the convolution of $f(\epsilon)$ and $g(\epsilon)$. The object of **CRYSIZ** is to extract $f(\epsilon)$ from $h(\epsilon)$ using $g(\epsilon)$ and then, by various types of analysis, determine mean crystallite size and residual microstrain by use of $f(\epsilon)$. The function $f(\epsilon)$ can yield information such as the size of the coherent crystalline domains, commonly referred to as the mean crystallite size; the distribution of crystallite sizes; and the nature and extent of lattice imperfections.

In the documentation which follows, the profile $g(\epsilon)$ is referred to as the "reference" profile. It is ideally* determined experimentally by taking a powder pattern of a well-annealed large crystallite sample (≥ 0.1 μm) of the material to be analyzed on the same instrument and over the same 2θ scan range as that used for the "broadened" profile, $h(\epsilon)$. The function $f(\epsilon)$ may be deconvoluted from $h(\epsilon)$ by either of two methods: direct or Stokes. The deconvoluted $f(\epsilon)$ is also called the "unfolded" profile. These methods are summarized in *The International Tables for X-Ray Crystallography, Volume III*, Sects. 5.2.3.1 and 5.2.3.2 (ref. 2). In **CRYSIZ** the direct method is the default. In the direct method the deconvolution is carried out by separating the reference pattern from the broadened pattern by successive approximations.[3] This method is computationally intensive. It has the advantage of producing a very good approximation of $f(\epsilon)$, the unfolded profile. The result is that the Fourier coefficients, $F(\zeta)$, for the Warren-Averbach analysis are well behaved. They do not produce ringing or a hook in the final plots. When this method is used, the $F(\zeta)$ are produced by the forward Fourier transform of the deconvoluted $f(\epsilon)$.

---

*In the absence of a "reference" profile from the material under study, another substance, such as a material like LaB_6 (SRM 660 for instrument profile determination), can be used to measure lines to estimate the missing $g(\epsilon)$.

The alternative method is the Fourier method which is also called the Stokes method in this report. In this method Fourier transforms are made of both measured profiles, $g(\epsilon)$ and $h(\epsilon)$. These transforms produce two sets of Fourier coefficients, $G(\zeta)$ and $H(\zeta)$. From the ratio of $H(\zeta)/G(\zeta)$, a set of Fourier coefficients $F(\zeta)$ of the profile $f(\epsilon)$ is formed. The $F(\zeta)$ coefficients are the Stokes coefficients which yield, through a reverse Fourier transform, the unfolded profile $f(\epsilon)$ which represents the microstructural nature of the sample. It is the various measures of the broadness of this function that are used in the classical Hall-Williamson plotting methods for size and strain.[4-8] The Stokes coefficients are the basis for the more modern Warren-Averbach approach to size and strain analysis.[9-15]

The computer code for carrying out the numerical deconvolution was originally written by Dr. John Konnert of the Laboratory for the Structure of Matter at the Naval Research Laboratory in Washington, D.C.[16]

MEASURES OF LINE BROADENING

The calculations carried out for each measured *h, k, l* line by **CRYSIZ** to determine the broadness of the unfolded profile are as follows:

First, A, the sum of all the intensities, I, within the scan over N points in 2θ space is found:

$$A = \sum_{j=1}^{N} I_j \, . \tag{1}$$

Then a weighted sum, B, where each intensity is multiplied by one less than its position in the scan is found:

$$B = \sum_{j=1}^{N} (j - 1) I_j \, . \tag{2}$$

The ratio B/A gives a number with its decimal fraction approximately one less than the interval in the scan in which the center of the profile, representing 2θ of the maximum intensity, exists. NINT is the FORTRAN nearest integer function, used to create an integer pointer, j_c , to the maximum intensity point in the scan:

$$j_c = NINT\left(\frac{B}{A}\right) + 1 \ . \tag{3}$$

The second moment of the profile is found by computing a sum, S, formed by weighting the intensity at each point by the square of the distance from the central point:

$$S = \sum_{j=1}^{N} (j - 1 - j_c)^2 I_j \ . \tag{4}$$

The second moment of the profile is S/A. To produce another measure of profile broadening, we introduce the scaled function:

$$second\ moment\ breadth = \frac{(8ln2)^{1/2} \cdot (S/A)^{1/2}}{(N-1)} \ . \tag{5}$$

A third measure of breath, the integral breadth, is determined from the area, A, of the intensity scan divided by the maximum intensity:

$$integral\ breadth = \frac{A}{I_{j_c}} \ . \tag{6}$$

The span over sum is closely related to the integral breadth but is computed from the Fourier coefficients, F, which were used to produce the unfolded profile:

$$span/sum = \frac{0.5}{0.5 + \sum_{j=1}^{N} F_j} \ . \tag{7}$$

The last measure of peak breadth, the full width at half maximum (FWHM), is the most common choice for very well-defined profiles as it is an easy measure of line broadening to comprehend. It is determined by establishing the location and intensity of the unfolded profile and then searching the profile from both extremes to locate the position of the 2θ of half-maximum intensity on each side of the peak maximum. The difference, $|2\theta_h - 2\theta_l|$, is the FWHM measure of line broadening.

CLASSIC PLOTTING METHODS

Three of the four line width measures, $LW_{r,j}$, described above, are each multiplied by a cosine term and used to form nine distinct plots. Each plot contains points for all the reflections, r, measured for the sample. The *span/sum* is not used since it is equivalent to the *integral breadth.* The three measures of broadening, *integral breadth, second moment breadth,* and FWHM, are designated LW and used with three distinct plotting methods as follows:

Three "Cauchy" plots:

$(LW_{r,j})*(COS(\theta_r)/\lambda)$ versus $SIN(\theta_r)/\lambda$

Three "Gauss" plots:

$[(LW_{r,j})*(COS(\theta_r)/\lambda)]^2$ versus $[SIN(\theta_r)/\lambda]^2$

Three "Cauchy-Gauss" plots:

$(LW_{r,j})*(COS(\theta_r)/\lambda)$ versus $[SIN(\theta_r)/\lambda]^2$

Each of these plots may be used, with appropriate use of the square root, to obtain a domain size parameter from the y-axis intercept and a strain parameter from the slope of the line through the plotted points.[4-7] The program determines a least-squares line through all the reflection data supplied and prints out the values implied by the regression line. These values should **not** be relied upon unless the plots have been carefully inspected for "outliers." These methods constitute the classical size and strain part of **CRYSIZ.** Using these plots is often referred to as a Hall-Williamson analysis. The results are based on all lines supplied in the powder pattern. Since many materials exhibit anisotropic behavior, that is, different grain size or strain in

different crystal directions, there will often be considerable scatter in these plots. A careful analysis of the data with regard to the Miller indices of each powder line should be carried out.

The various plotting methods described above are based on different assumptions of how the combination of size and residual strain broadens diffraction profiles. In addition to this underlying consideration, there is the problem of finding a good measure of the width of a profile. The FWHM is the most obvious choice for very well-defined profiles. In addition, it is an easy measure of line broadening to comprehend. It is determined by establishing the location and intensity of the center of the unfolded profile and then searching the profile from both extremes to locate the half-maximum intensity. Extremely erratic measures of slope and intercept may result when a sample is very anisotropic with respect to crystallite size and residual strain. Each reflection contributes a measure of the size and strain that is dependent on a specific direction through the crystallites. From extensive testing of the plotting methods, we have observed that the regression line is very sensitive to shoddy data or serious anisotropy in the crystallites. Because the crystallite size is determined by an extrapolation of the least-squares line, the coefficients of the line are very sensitive to data that do not satisfy the presumed linear relationship. The Warren-Averbach method described below appears to be much more consistent in the measures produced. However, careful examination of the plots may reveal interesting anisotropic effects in the crystallite size as a function of direction through the crystals. The Warren-Averbach method usually produces size values smaller than those predicted by the plotting methods.

The various plotting methods described above are based on different assumptions of how the combination of size and strain broadens diffraction profiles. It is important that the measure of line broadening used be as reliable as possible. Since each measure described above has some limitation, the program presents all those shown and leaves to the user the choice appropriate to the analysis at hand. Rather extensive examples obtained by an earlier version of this program when used on ceramic materials can be seen in Morosin.[17]

THE WARREN-AVERBACH METHOD

The other major method for estimating domain size and root mean square strain (rms strain) coded in **CRYSIZ** is the Warren-Averbach procedure.[10-15] The input lines are searched for those sets that are orders of one another, e.g., (1, 1, 1) and (2, 2, 2). When such sets are detected, the value of ϵ, the rms strain, and average coherence length or crystallite size are obtained as a function of crystallographic direction. The effective crystallite size is derived from the slope of another function, the size coefficients derived from the Stokes coefficients versus the column length. The results from this method are printed and plotted.

USING THE PROGRAM CRYSIZ

In order to use the program **CRYSIZ,** it is necessary to have two input files: one with the reference data and one with the broadened data. In these files each crystallographic line must be supplied separated from all other nonsymmetrically overlapping lines. Exact superposition of lines (e.g., cubic {5,1,1} and {3,3,3}) must be treated as a single line as the lines cannot be separated. The program **XRAYL** is used to prepare these data files. The files will be "opened" if they have the designation <*identity*>.IDL, where <*identity*> is a name chosen by the user for the data sets; for example: NaClrf.IDL for the reference pattern and NaClb1.IDL for broadened sample one. The contents and structure of these *ASCII* files are given in Appendix A. In the program <*identity*> is restricted to no more than 11 characters. Note, however, that certain machines upon which the program may be run will limit the number of characters. Disk operating system (DOS) on a personal computer (PC), for example, will require <identity> to be four characters or less.

Besides the data files, instructions for the run must be given either interactively, or more conveniently, by preparation of an <*identity*>.CIN file. Whichever method is chosen, the options to be specified concern which methods are to be carried out, the plots to be generated, the extent of the printed details, and the reflections from the .IDL to be included in the analysis. In the interactive mode the options are presented as a set of tedious questions to be answered in turn.

The **CRYSIZ** program will open and process a number of prepared files and produce output files in the process. Each file type is defined by an "extension" mnemonic following a period. Before the period, an up-to-11-character code, here called the *<identity>*, is prefixed. The *<identity>* code should be mnemonic of the data set being treated. The extension codes are fixed by the program while the identities are chosen by the user.

FILE TYPES

.CIN	Program input instructions file. Program may be run interactively, but the use of this file prepared by a local line editor is much more productive.
.IDL	Input files containing the separated, idealized input profiles.
.IDM	Optional input files like .IDL but with least-squares parameters displaced by a specified number of standard deviations down from the best result.
.IDP	Optional input file like .IDM but with the parameters displaced up from the best result.
.CPN	Output file containing summary of run suitable for printing.
.CPL	Optional output file containing crude line printer plots for inspection.
.CEX	Optional output file containing raw plot data for use with local plotting software.

STRUCTURE OF THE .CIN FILE

This file, which specifies the calculations to be done and the results to be displayed, must consist of a series of "lines" with defining titles which are parsed in fields defined by blanks (spaces). These lines may be prepared by means of a line editor and then used repeatedly to drive the program. The first field of every line defines the function of the line in setting options. The six types of lines and the order in which they must be supplied in the file are:

OPTIONS *(required)*

QUANTITIES *(optional)*

STOKES *(optional, forces use of Fourier rather than numerical deconvolution)*

REFLEC *(optional, if none supplied all reflections in file will be used)*

WARREN *(optional)*

END *(required)*

The **OPTIONS** line and the **END** line are mandatory. The other lines are optional, depending on the result desired. If they are not supplied, default actions will be taken as described below. The benefit of using a **.CIN** file is that it may be edited with the local line editor for use with other problems or samples. In **CRYSIZ** these lines are parsed by explicit code so that the quotation marks (for example, in 'REGIN_2_THETA' or 'N') required in **XRAYL** for alphanumeric strings must not be used.

FORMATS OF THE .CIN INPUT LINES

OPTIONS line -- y/n implies do (y) or do not (n)

Field	Contents	Purpose of field	Usual choice
1	OPTIONS		
2	y/n	Print out the Fourier coefficients produced from the input line profiles.	n
3	y/n	Print out the Stokes coefficients of the line profiles.	n
4	y/n	Print out the **A** values of the line profiles.	n
5	y/n	Calculate and print out the Warren-Averbach size and strain values.	y
6	y/n	Plot the input line profiles.	n
7	y/n	Print all intermediate results (voluminous dump!).	n
8	y/n	Plot the Stokes coefficients of the line profiles.	n
9	y/n	Plot the unfolded line profile derived from the Stokes coefficients.	y
10	y/n	Determine the size and strain and produce the plots for the Cauchy plotting method of Hall-Williamson, using the sum of coefficients as a measure of broadening.	y
11	y/n	As in 10, but using integral breadth as the measure of broadening.	y
12	y/n	As in 10, but using FWHM as the measure of broadening.	y
13	y/n	Determine the size and strain and produce the plots for the Gauss plotting method, using the sum of coefficients as a measure of broadening.	y
14	y/n	As in 13, but using integral breadth.	y
15	y/n	As in 13, but using FWHM.	y
16	y/n	Determine the size and strain and produce the plots for the Cauchy-Gauss plotting method, using the sum of coefficients as a measure of broadening.	y
17	y/n	As in 16, but using integral breadth.	y
18	y/n	As in 16, but using FWHM.	y
19	y/n	Plot the effective crystallite size plot of the Warren-Averbach method.	y
20	y/n	Plot the average strain as a function of column length of the Warren-Averbach method.	y
21	y/n	Plot the Stokes Fourier coefficients as a function of $[1/d]^2$ for three l values of the Warren-Averbach method.	y

QUANTITIES line -- two successive blanks terminate scanning of line

Field	Contents	Purpose of field	Usual Choice
1	QUANTITIES		
2	Integer	The number of points in the Stokes coefficient tables. If zero, the default will be 120, the maximum allowed. The maximum column length treated will be the column length step size of field 7 times this integer.	100
3	Integer	The number of points at each end of the raw profile data that are used to establish background intensity. If zero, the default is 20. No fewer than three points should be specified.	10
4, 5, 6	Reals	The three values of '*l*,' in Angstroms, which are to be used in preparing the Warren-Averbach plots of Stokes Fourier coefficients versus $[1/d]^2$. If supplied as zero, the values 50.0, 100.0, and 150.0 will be used.	50., 100., 150.
7	Real	The column length step size to be used in the Warren-Averbach method. The default is 10.0A.	10.0

STOKES line -- parameters for controlling the damping of Stokes coefficients. If used, there must be one STOKES line for each reflection in the **.IDL** files. The presence of a Stokes line switches the deconvolution procedure from direct to Fourier methods.

Field	Contents	Purpose of field	Usual choice
1	STOKES		
2	0/1/2	Zero directs a *log* decay, fit by least squares to the Stokes coefficients. One directs the application of a linear decay to zero in the noise region. Two directs that no smoothing be done.	0
3	Real	A weight control parameter for the Stokes coefficient fitting process. If it is near 1.0, the fit will be to all regions of column length, *'l.'* If it is near 4.0, the fit will be weighted to short column lengths.	1.0

REFLEC line -- selects reflections from the **.IDL** data files. One reflection is specified per line. When these lines are omitted, all reflections will be included.

Field	Contents	Purpose of field
1	REFLEC	
2	Integer	The *h* index of the reflection.
3	Integer	The *k* index of the reflection.
4	Integer	The *l* index of the reflection.

WARREN line -- selects reflections to be associated in a Warren-Averbach analysis. One reflection is specified per line. Each associated group must be terminated with a "WARREN -99" line. When these lines are omitted, associations will be made of all reflections in the **.IDL** files which are orders of one another, e.g., (1, 1, 1) with (2, 2, 2). The use of WARREN lines allows superseding of this choice.

Field	Contents	Purpose of field
1	**WARREN**	
2	Integer	The *h* index of the reflection or -99 to signal end of group.
3	Integer	The *k* index of the reflection.
4	Integer	The *l* index of the reflection.

END line -- this line is not optional and must be the last line in the **.CIN** file.

EXAMPLES OF .CIN FILES

```
1.)
OPTIONS N N Y Y Y N N Y Y Y Y N N N N N N Y Y N
QUANTITIES 100 10 25 50 100 10
END

2.)
OPTIONS N N Y Y Y N N Y Y Y Y N N N N N N Y Y N
QUANTITIES 100 10 25 50 100 10
WARREN 2 0 0
WARREN 3 0 0
WARREN 4 0 0
WARREN -99
WARREN 1 1 1
WARREN 2 2 2
WARREN -99
END
```

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APPENDIX A - Format of the *<identity>* .DA and *<identity>* .IDL files

The structure of the input **.IDL** files read by program **CRYSIZ** is as shown below. These *ASCII* files contain the intensity measurements from regions of 2θ in steps of 2θ generated by program **XRAYL**. The format of these records is identical to those of the **.DA** files. The distinction is that the region of 2θ in the **.DA** files specifies a window which may contain up to five reflections. These may be both reflections of the phase under study and of impurities. The structure of the input **.IDL, .IDM,** and **.IDP** files written by the program **XRAYL** is as follows. The same format is used for both reference and broadened patterns which are distinguished by the *<identity>* portion of the file name. The program limit on the number of characters in *<identity>* is eleven. Some operating systems may restrict the number of characters in *<identity>* further.

Record	Format	Contents
1	A53	Title; up to the first 11 characters may be the *<identity>* used to identify the files of the compound
1	A19	Time/date as bhh:mm:ssbdd/MMM/yy where "b" represents a blank space
2	I4	h index of reflection
2	I4	k
2	I4	l
2	I4	Number of type 3 records of intensity data, NREC, which must be > 15 and < 1023
2	F10.2	Counting time per intensity point
2	F10.4	Beginning 2θ for intensity measurements
2	F10.4	Ending 2θ for intensity measurements
2	F10.4	2θ step size, lower limit 0.001°
2	F10.6	Wave length of $K\alpha_1$ used for measurement
3 through 2 + NREC	F10.2	Intensity at measured point

The pattern of records shown above repeats for each reflection or window of the sample. The end of all reflections is marked by an end-of-file.

APPENDIX B - History of the authorship of programs XRAYL, POWTES, and CRYSIZ

These programs were first proposed in the summer of 1984 by Dr. Bruno Morosin of Sandia National Laboratories. In the summers of 1984 and 1985, the initial coding was undertaken, at Sandia, by Professor James M. Stewart of the University of Maryland in College Park. In 1986, Dr. Camden Hubbard, then at the National Institute for Science and Technology (formerly The National Bureau of Standards), undertook to advise Dr. Yuming Zhang, then a graduate student, and Professor Stewart in combining the original Sandia codes with codes that Dr. Hubbard had written. These codes, written by Hubbard, Stewart, Morosin, Zhang, and Venturini, are documented in NBS IR-88-3850. The present code is a modification and enhancement of this long, collaborative effort. Many details and examples of the use of the programs and the extensive references to the methods coded in them can be found in Dr. Zhang's 1988 thesis," Advances in X-Ray Powder Diffraction Analysis and its Application in Ceramic Material Studies," a dissertation submitted to the faculty of the graduate school of The University of Maryland. The direct convolution features were added to **CRYSIZ** by Dr. John Konnert of the Naval Research Laboratory in 1996.

XRAYL serves to separate overlapped powder profiles by fitting with analytical functions, while **CRYSIZ** combines the classic plotting methods and the Warren-Averbach methods for the determination of crystallite size and strain. **POWTES, POWTE2, POWCON, POWLAP,** and **RDCON** were written by Hubbard and Stewart as an aid to testing and for converting data to the required input format. **POWWID and POWTRY** were written by Konnert and Stewart to produce simulated broadened patterns using direct convolution of an instrument (reference) profile and a broadening profile of known spread for testing **CRYSIZ.**

APPENDIX C - Example runs

This appendix is a summary of the results which may be seen in detail by printing or viewing the files supplied on the distribution diskette "EXAMPLES." On it there are several examples which illustrate various features of the program **CRYSIZ**.

The first group of examples has been run using synthetic data generated by the program **POWTRY**. These data have been generated by convoluting a reference (instrumental) pattern, $g(\epsilon)$, with a broadened pattern, $f(\epsilon)$, to produce a broadened (experimental) pattern, $h(\epsilon)$, to be analyzed. The $f(\epsilon)$ pattern is generated from chosen values of D, the size, and ϵ, the strain parameters. Six reflections for cubic silicon are used for the trials: {1,1,1}, {2,2,0}, {2,2,2},* {3,3,1}, {4,2,2}, and {6,2,0}. The example shown on the next page was generated with D = 250Å, $\epsilon = 0.002$. The broadening is generated using the Gaussian profile form and, thus, should follow the Cauchy functional relationship. This implies that the "true" values should be returned from **CRYSIZ** from the Cauchy Hall-Williamson analysis. It is interesting to note that the Warren-Averbach results as produced by the automatic analysis of the Fourier coefficients produce significantly lower values for size and strain. A second set of examples has been run on experimental data measured at Sandia National Laboratories using a sample of shock-loaded zirconia. These tests show the effect of experimental noise and systematic errors on the determination of size and strain. All the tests done to date emphasize that the reference files must be generated using well-annealed samples. If the patterns for the reference material are broadened due to size and strain, the deconvolution process and the results produced by **CRYSIZ** will be seriously compromised. If no sufficiently pure and well-annealed sample of the material under study is available, one can use a substance such as LaB_6 (SRM660) to get the instrumental broadening. Once the broadening for the certified material is known, a reference pattern for the material under study can be generated to a good approximation using the program **POWTES** supplied with **XRAYL** and **CRYSIZ**.

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*The {2,2,2} reflection of Si is exceedingly weak. Only the asymmetry of the bonds contributes to it. It was included as a significant reflection in this generated data in order to demonstrate a feature of **CRYSIZ**. The program automatically finds and displays reflections which are orders of one another for the Warren-Averbach analysis.

TESTS USING GENERATED PATTERNS

CRYSIZ produces estimates of the size and strain parameters in the following format. This snapshot of the output is taken from file TR3T33.CPN.

```
CASE 1  SPANOSUM .. CAUCHY
PARAMETER <D(A)> =     233.8 ANGSTROMS.
PARAMETER EPSILON = 0.21327E-02

CASE 2  SEC MOM  .. CAUCHY
PARAMETER <D(A)> =     248.3 ANGSTROMS.
PARAMETER EPSILON = 0.20067E-02

CASE 3  FWHM     .. CAUCHY
PARAMETER <D(A)> =     248.3 ANGSTROMS.
PARAMETER EPSILON = 0.20074E-02

CASE 4  SPANOSUM .. GAUSS
PARAMETER <D(A)> =     190.1 ANGSTROMS.
PARAMETER EPSILON = 0.35448E-02

CASE 5  SEC MOM  .. GAUSS
PARAMETER <D(A)> =     201.9 ANGSTROMS.
PARAMETER EPSILON = 0.33360E-02

CASE 6  FWHM     .. GAUSS
PARAMETER <D(A)> =     201.9 ANGSTROMS.
PARAMETER EPSILON = 0.33366E-02

CASE 7  SPANOSUM .. CAUCHY-GAUSS
PARAMETER <D(A)> =     186.1 ANGSTROMS.
PARAMETER EPSILON = 0.24333E-02

CASE 8  SEC MOM  .. CAUCHY-GAUSS
PARAMETER <D(A)> =     197.7 ANGSTROMS.
PARAMETER EPSILON = 0.22896E-02

CASE 9  FWHM     .. CAUCHY-GAUSS
PARAMETER <D(A)> =     197.7 ANGSTROMS.
PARAMETER EPSILON = 0.22903E-02

******** WARREN-AVERBACH RESULT ********************
***EFFECTIVE CRYSTALLITE SIZE      165.4 ANGSTROMS**
***USING POINTS  3 TO  16 IN A(L) CURVE
***AVERAGE STRAIN VALUE IN SIZE RANGE  0.2679E-02 *****
***FROM INTERVAL  2 TO  17. STEP LENGTH  10.0 ANGSTROMS**
***STRAIN AT L =  50 ANG  0.2890E-02
***STRAIN AT L = 100 ANG  0.2543E-02
***STRAIN AT L = 200 ANG  0.1733E-02
***OF REFLECTIONS....     1  1  1     2  2  2

******** WARREN-AVERBACH RESULT ********************
***EFFECTIVE CRYSTALLITE SIZE      158.6 ANGSTROMS**
***USING POINTS  2 TO  13 IN A(L) CURVE
***AVERAGE STRAIN VALUE IN SIZE RANGE  0.2509E-02 *****
***FROM INTERVAL  2 TO  16. STEP LENGTH  10.0 ANGSTROMS**
***STRAIN AT L =  50 ANG  0.2688E-02  ***STRAIN AT L = 100 ANG  0.2322E-02  ***STRAIN AT L = 200 ANG  0.1538E-02
***OF REFLECTIONS....     1  1  1     2  2  0     2  2  2     3  3  1
```

Table C.1 shows a summary of the results of **XRAYL** and **CRYSIZ** runs on files labeled as shown in the column headed FILES. The column headed GENERATED shows the values of D and ϵ used in **POWTRY** to generate the broadened profiles from the reference profiles. The column HALL-WILLIAMSON shows the results from the plotting methods using the following codes: I - *span/sum*, S - *second moment*, and F - FWHM. The column headed WARREN-AVERBACH shows the D and ϵ derived from that analysis. These values are given in detail in the *.CPN files on the examples diskette.

The authors believe that in using **CRYSIZ** it is very important to view the various plots produced for an analysis before drawing any conclusions concerning the validity of the printed size and strain parameters. In Appendix D, selected plots extracted from the *.CEX files produced by **CRYSIZ** are shown. These plots were prepared by editing the appropriate lines from the *.CEX files into *.TXT files which were then imported into **KaleidaGraph™** and edited into the illustrations.

Figure D.1 (see Appendix D) shows the Hall-Williamson Cauchy plot for test TR3T33. This ideal data produces an ideal result. Figures D.2 and D.3 (see Appendix D) show the Warren-Averbach plots for size and strain. The results from this analysis give a 36% smaller D value and a 25% larger ϵ value when compared to the Hall-Williamson result. Examination of Table C.1 will show this difference to be common. Figures D.4 and D.5 (see Appendix D) illustrate a very interesting problem and generate a warning to users of **CRYSIZ**. The test is TR4T24. In this test the reference pattern is as broad as the broad pattern for several of the lowest-order reflections. The result can be seen in the plots. Notice that the compromised unfolding has made the full width at half maximum (FWHM) a poor measure of broadening compared to the second moment. Note also that the Warren-Averbach result produces a D value 29% lower and an ϵ value 240% higher than the generating values. Another consequence of processing this data set is the fact that the convergence of the convolution using the direct numerical method was very slow. Using Stokes Fourier methods was quicker but led to even poorer results. Perusal of Table C.1 reveals that as the broadening gets less and less the results of the analysis are poorer and poorer. It must be realized that these results were obtained using generated Gaussian profiles with no unequal backgrounds or counting noise. Notice, too, that as

Table C.1. A summary of generated tests

FILES T11.XIN, T11.CIN+	GENERATING		HALL-WILLIAMSON						WARREN-AVERBACH	
			Cauchy		Gauss		Cauchy-Gauss			
	D	ϵ		D	ϵ	D	ϵ	D	ϵ	D	ϵ
TRR.DA, T11.DA	750	0	I	701	3.5e-7	701	2.3e-5	701	4.8e-7	602	0.000015
			S	745	9.4e-8	745	1.7e-5	745	2.8e-7		
			F	743	0.0	743	0.0	743	0.0		
TRR.DA, T21.DA	500	0	I	468	8.9e-7	497	2.7e-5	497	4.8e-7	405	0.000038
			S	497	3.7e-7	497	2.7e-5	497	4.8e-7		
			F	497	0.0	497	0.0	497	0.0		
TRR.DA, T31.DA	250	0	I	234	3.4e-6	234	1.1e-4	234	3.7e-6	204	0.000082
			S	249	1.3e-6	249	6.9e-5	249	1.5e-6		
			F	249	1.3e-6	249	7.0e-5	249	1.5e-6		
TRR.DA, T12.DA	10000	0.0001	I	2764	0.0	2813	0.0	2815	0.0	3782	0.000046
			S	3463	1.0e-5	3438	5.8e-5	3431	1.4e-5		
			F	2428	0.0	2542	0.0	2540	0.0		
TR4.DA, T14.DA	10000	0.0001	I	1.0e+8	3.7e-4	3392	3.0e-4	5023	2.6e-4	10076	0.00021
			S	1.0e+8	3.7e-4	4803	2.6e-4	11440	2.6e-4		
			F	1.0e+8	4.9e-4	3781	3.4e-4	10926	3.7e-4		
TR4.DA, T24.DA	750	0.0001	I	614	3.0e-5	607	1.7e-4	607	2.3e-5	531	0.00024
			S	775	1.2e-4	732	3.5e-4	730	1.1e-4		
			F	551	0.0	566	0.0	566	0.0		
TR4.DA, T34.DA	250	0.0001	I	233	1.0e-4	230	5.5e-4	230	8.8e-5	201	0.00046
			S	248	9.7e-5	244	5.1e-4	244	8.2e-5		
			F	247	8.9e-5	243	4.9e-4	243	7.6e-5		
TR3.DA, T13.DA	10000	0.002	I	9060	2.1e-3	1983	2.2e-3	828	2.5e-3	529	0.0011
			S	9745	2.0e-3	2114	2.1e-3	880	2.3e-3		
			F	9268	2.0e-3	2076	2.1e-3	878	2.3e-3		
TR3.DA, T23.DA	750	0.002	I	701	2.0e-3	440	2.7e-3	396	2.5e-3	312	0.0017
			S	744	2.0e-3	467	2.5e-3	421	2.3e-3		
			F	744	2.0e-3	467	2.5e-3	421	2.3e-3		
TR3.DA, T33.DA	250	0.002	I	234	2.1e-3	190	3.5e-3	186	2.5e-3	158	0.0025
			S	248	2.0e-3	202	3.3e-3	198	2.3e-3		
			F	248	2.0e-3	211	3.3e-3	198	2.3e-3		

the broadening increases the reliability increases as well. The comparative results are, in general, in the correct order.

If it seems advisable to be able to estimate the reliability of the size and strain produced by **CRYSIZ, XRAYL** contains provisions for calculating estimated errors by means of multiple files. These files, in which the generated profiles are narrowed and broadened by specified multiples of the estimated error in FWHM, may be used as input to multiple runs of **CRYSIZ.**

EXAMPLE USING ZIRCONIA DATA

The data for a sample of zirconia are included on the examples diskette. This sample was reported on in the paper by B. Morosin, R. A. Graham, Y. Zhang, J. M. Stewart, and C. R. Hubbard, "X-ray Line Broadening Study on Shock-modified Zirconia," *Aust. J. Phys.* **41**, 251 (1988). The sample chosen for this example was 8G820 which appeared to have the most broadened pattern. The {1,1,0} and {0,1,1} reflections are overlapped in the shocked sample so they illustrate the use of **XRAYL** to separate overlapped profiles. The details of this separation can be seen in file ZRFZR5.XPN of the examples diskette. The zirconia reference pattern is in file ZRF.IDL. It was generated by means of the program **POWTES.** Because of this generation of the reference pattern, there is no ZRF.DA file. A somewhat broadened pattern ZRR.DA was used to get the initial reflection 2θ values and an estimate of the instrumental broadening used in the generation. This was done because the files of the well-annealed reference pattern could no longer be located. Attempts were made to use the data ZRR.DA for a reference pattern with disastrous results. The results found in ZRFZR5.CPN show the analysis of size and strain. These values agree closely with those published in the paper. The figures in Appendix D show a sample of the figures in the paper. Figure D.6 (see Appendix D) shows the superimposed plots of the observed broadened {-1,1,1} reflection, its Pearson VII idealized trace, and the difference between them. These plots were produced by **XRAYL.** Figure D.7 (see Appendix D) shows the numerically deconvoluted profile produced by **CRYSIZ** for the analysis. Figure D.8 (see Appendix D) shows one line of Fig. 2 of the paper. This figure shows the Warren-Averbach Fourier coefficients as a function of interplanar spacing, d. In Fig. D.8, only the data for L = 50 Å are shown. The straight lines for each L value yield an intercept which gives an "average"

size Fourier coefficient and a slope an "average" mean-square strain value. These strain values are printed in ZRFZR5.CPN with the results of the Warren-Averbach analysis. The importance of examining the graphs is to ensure oneself that all the reflections are "in line." If there are bad data or large anisotropy for a sample, these plots, and the others shown here, will reveal it. Figure D.9 (see Appendix D) is a Hall-Williamson plot using FWHM as the measure of broadening and the assumption that the relationship is Gaussian. This plot was not published in the paper. It shows that the deconvolution process does not yield profiles that are well represented by the FWHM. Figure D.10 (see Appendix D), on the other hand, corresponds to Fig. 3 in the original paper. The second moment gives a much smoother progression of points so that it was chosen as representing the best "plotting" result. Figures D.11 and D.12 (see Appendix D) correspond to Figs. 4 and 5 of the original paper. These are the Warren-Averbach plots for determining size and strain. In these plots one can see the improvement due to the use of the slower, but smoother, direct numerical deconvolution. The original paper was written using the Stokes Fourier method which was the only one programmed at that time.

APPENDIX D - Samples of plotted output from example runs

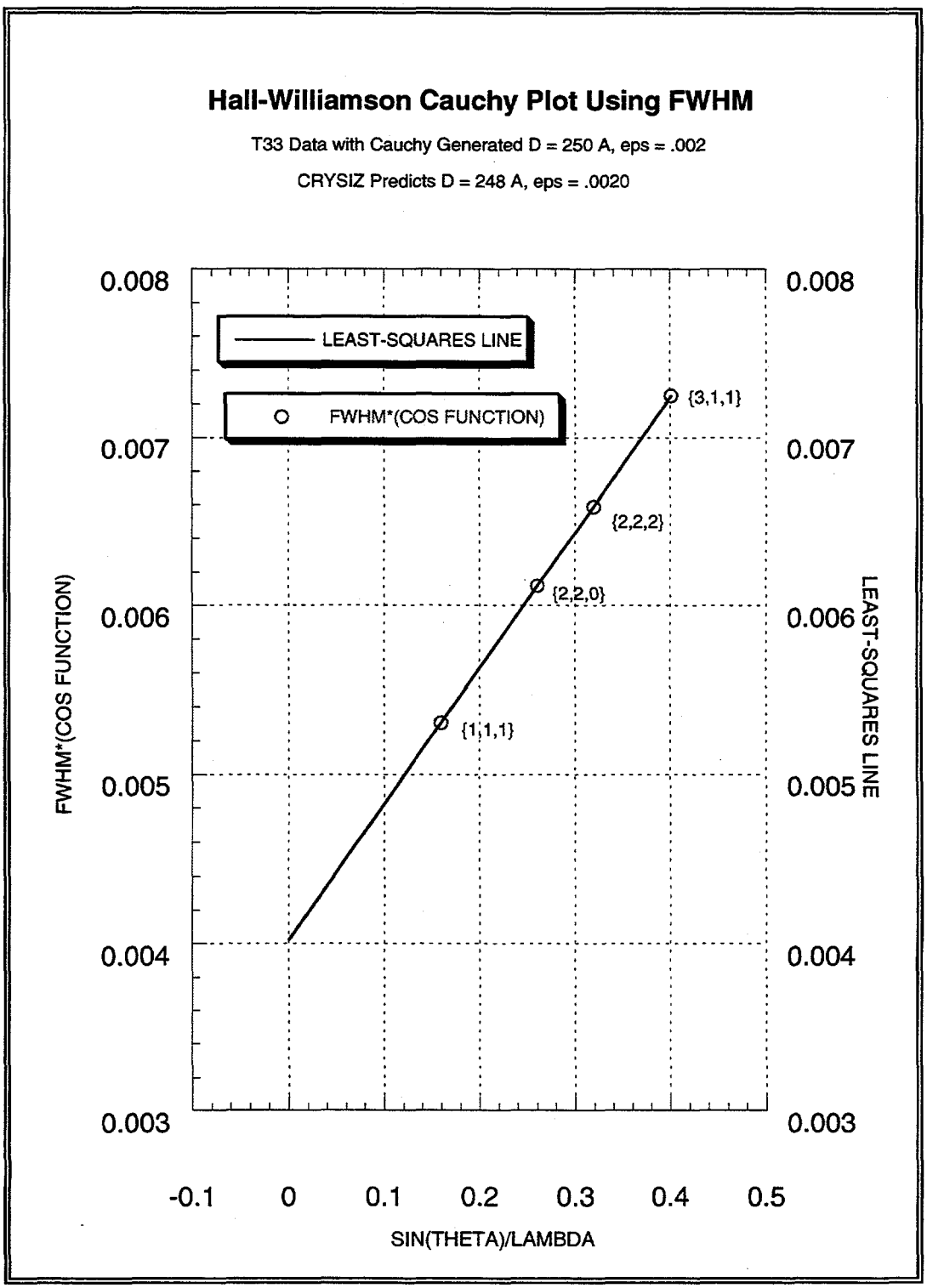

Fig. D.1. Hall-Williamson Cauchy plot for test TR3T33.

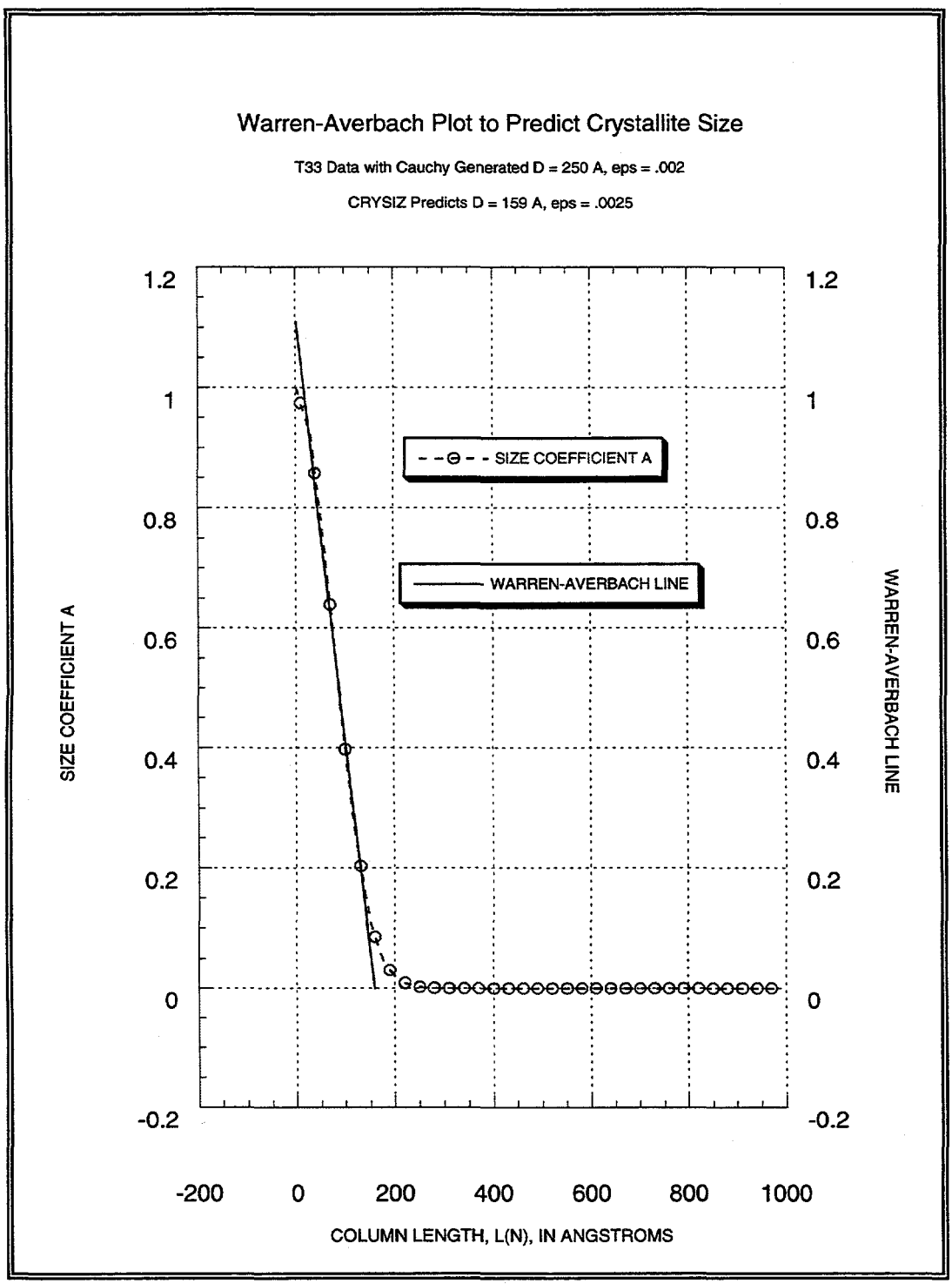

Fig. D.2. Warren-Averbach plot for crystallite size, test TR3T33.

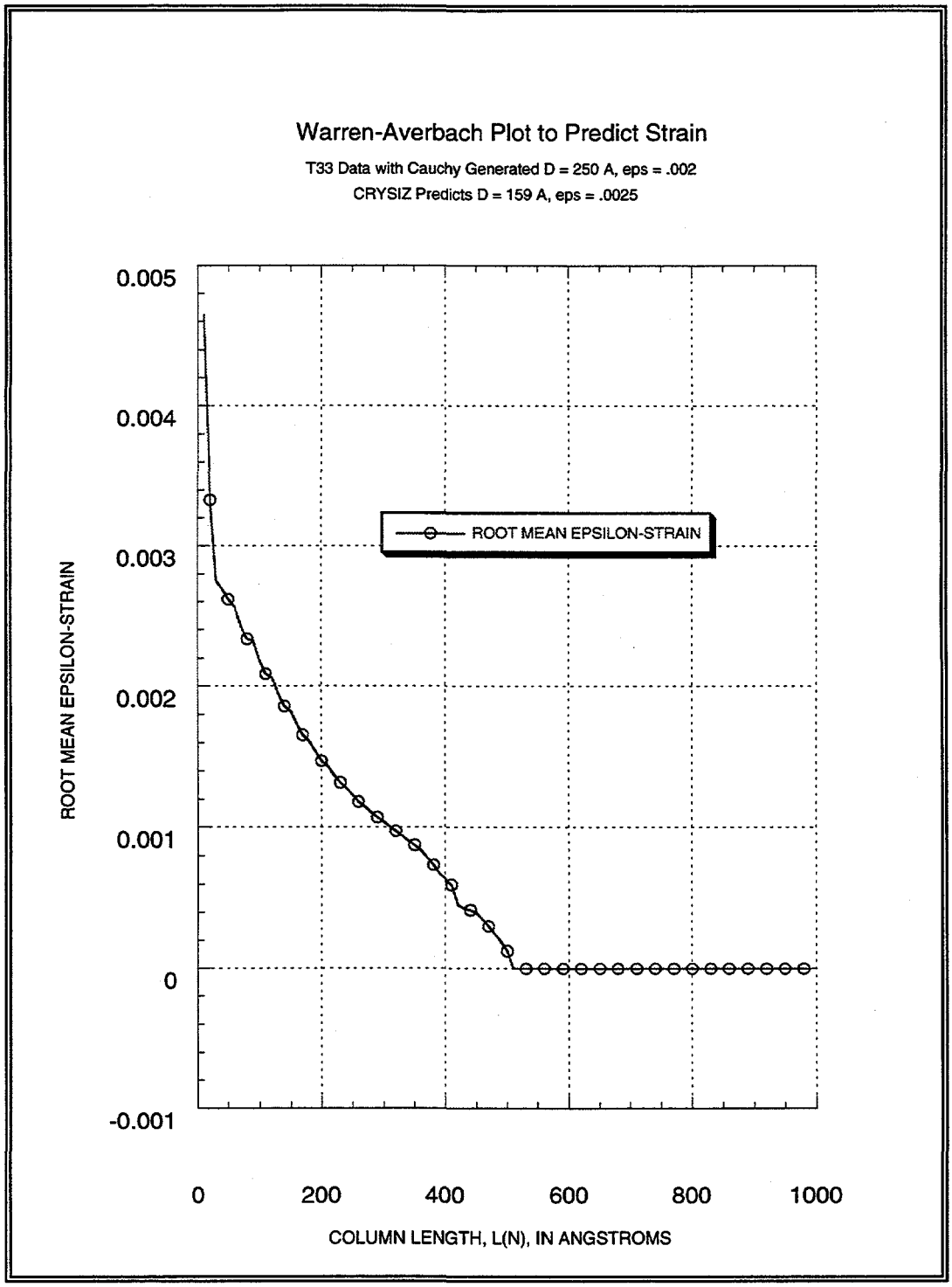

Fig. D.3. Warren-Averbach plot for strain, test TR3T33.

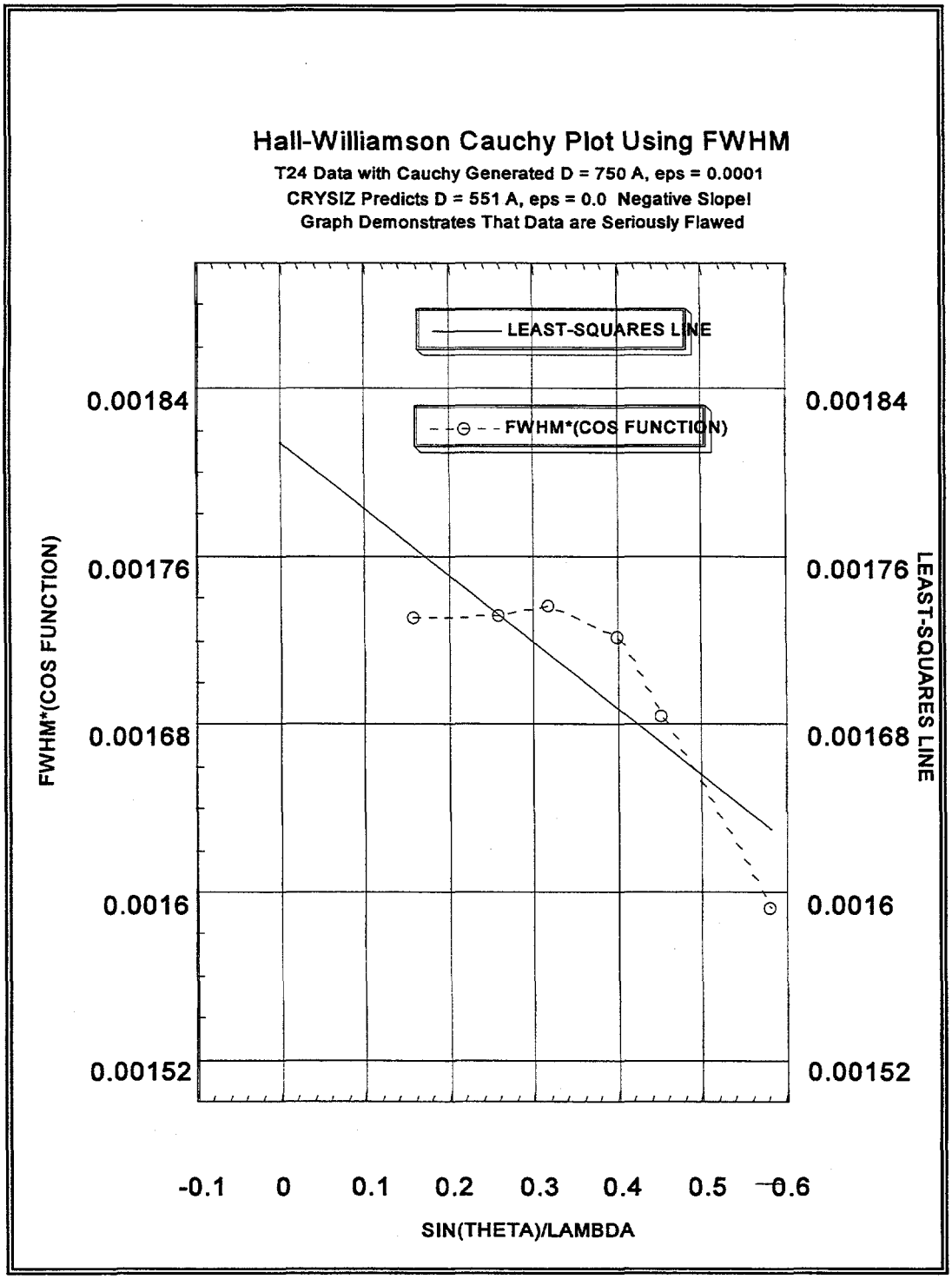

Fig. D.4. Hall-Williamson Cauchy plot for test TR4T24 with flawed data.

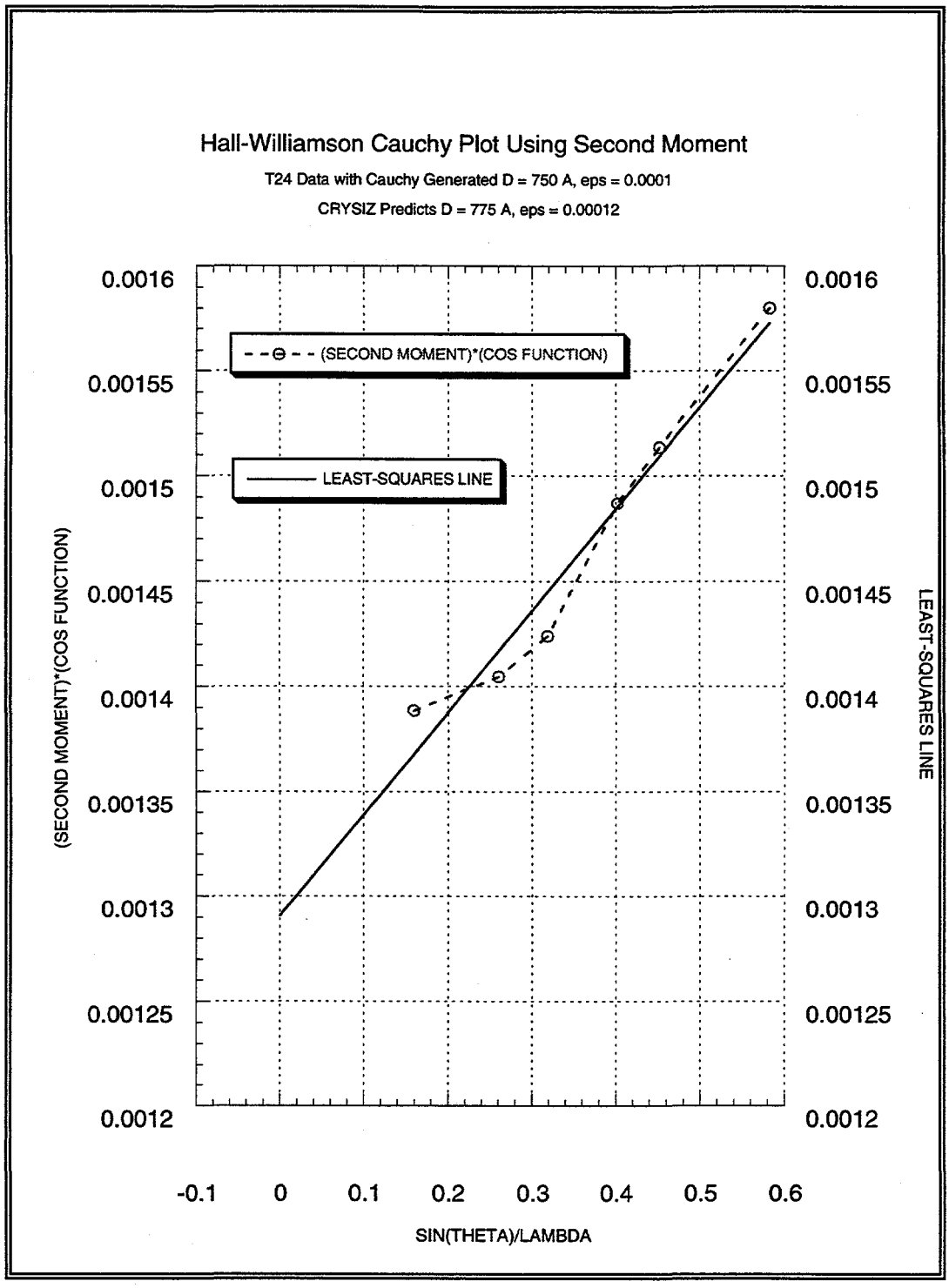

Fig. D.5. Hall-Williamson Cauchy plot for test TR4T24.

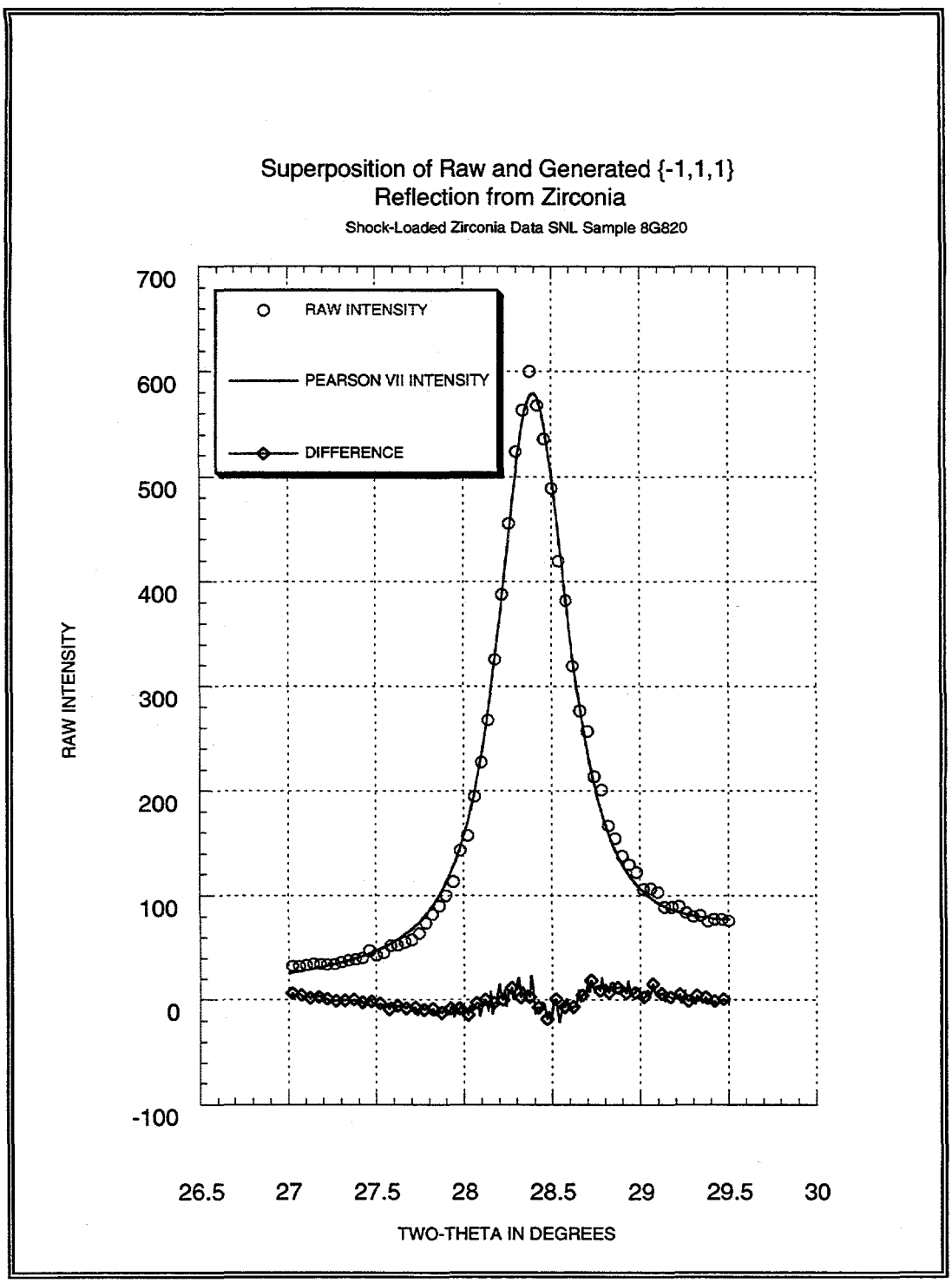

Fig. D.6. Superimposed plots of broadened {-1,1,1} reflection: raw intensity, Pearson VII fitting, and difference between them.

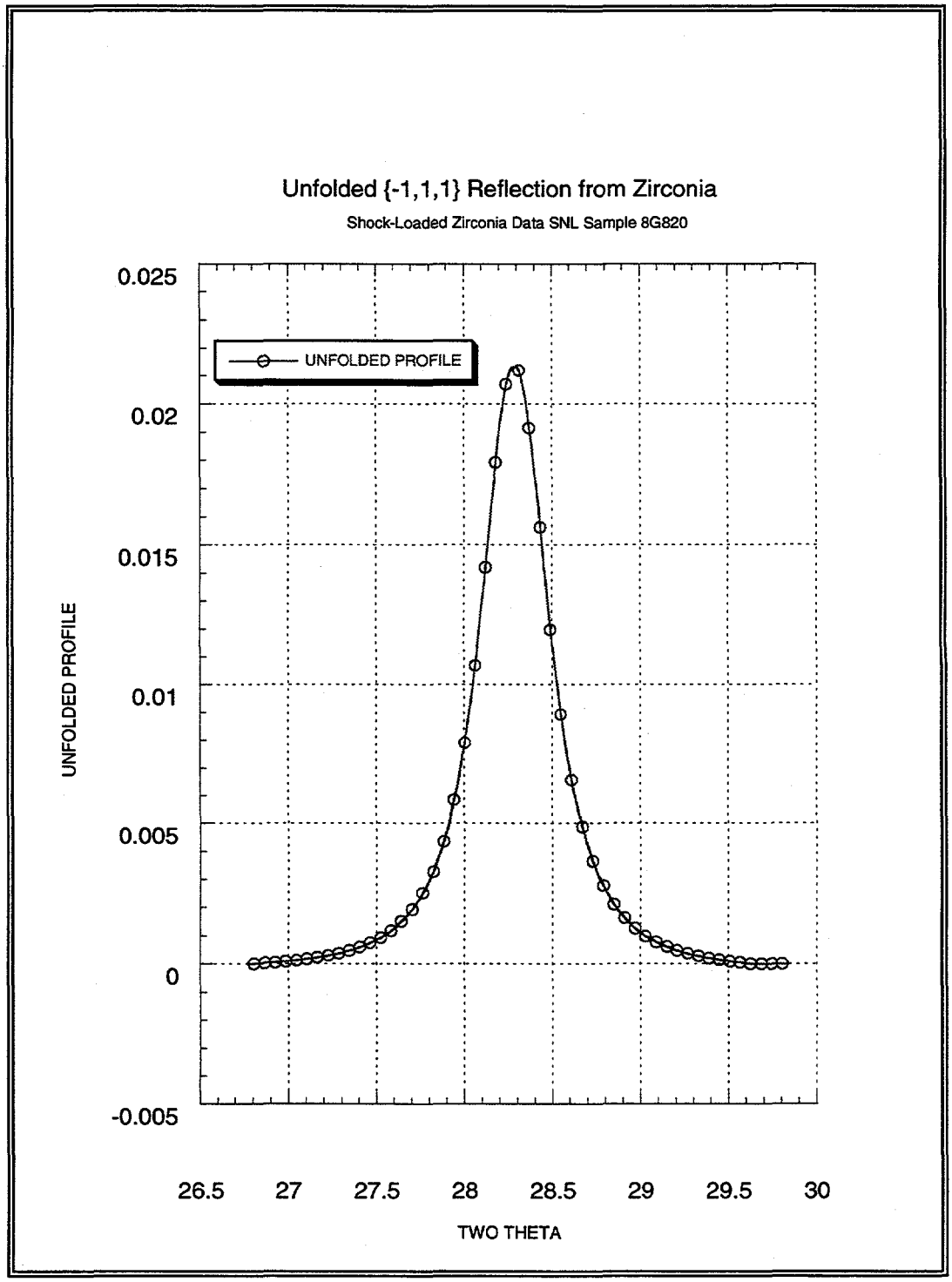

Fig. D.7. Numerically deconvoluted profile produced by CRYSIZ.

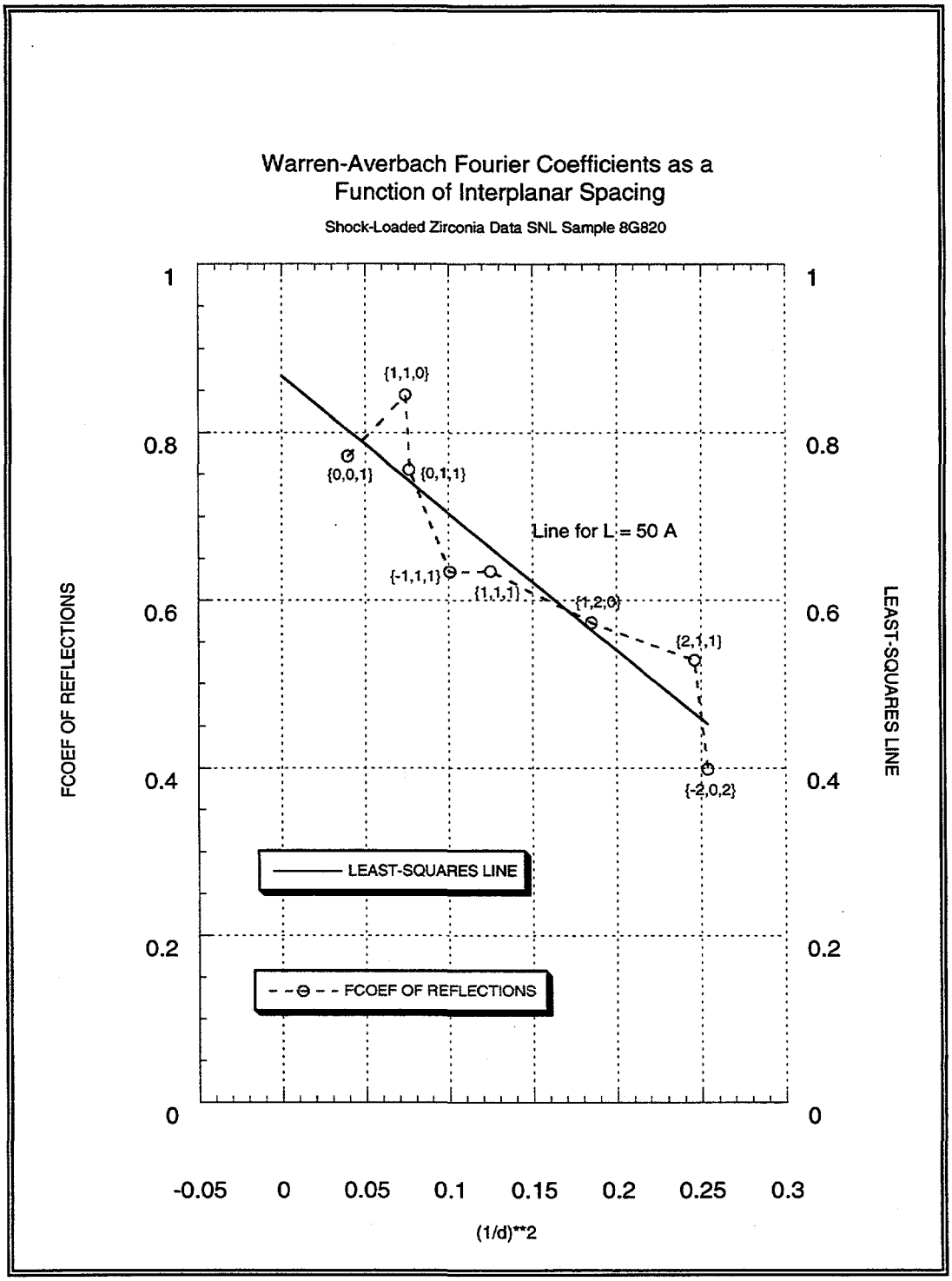

Fig. D.8. Warren-Averbach Fourier coefficients as a function of interplanar spacing.

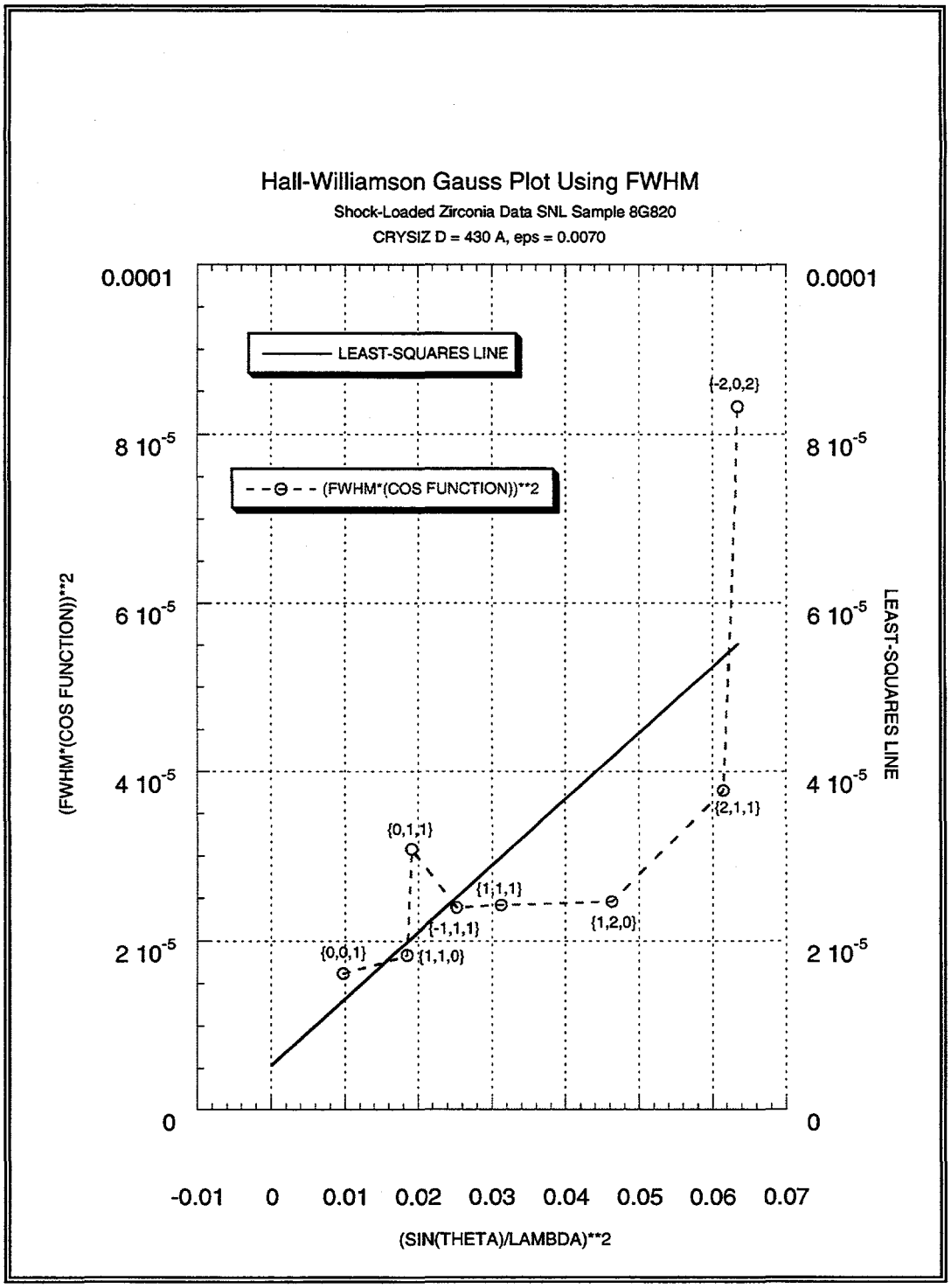

Fig. D.9. Hall-Williamson Gauss plot using full width at half maximum.

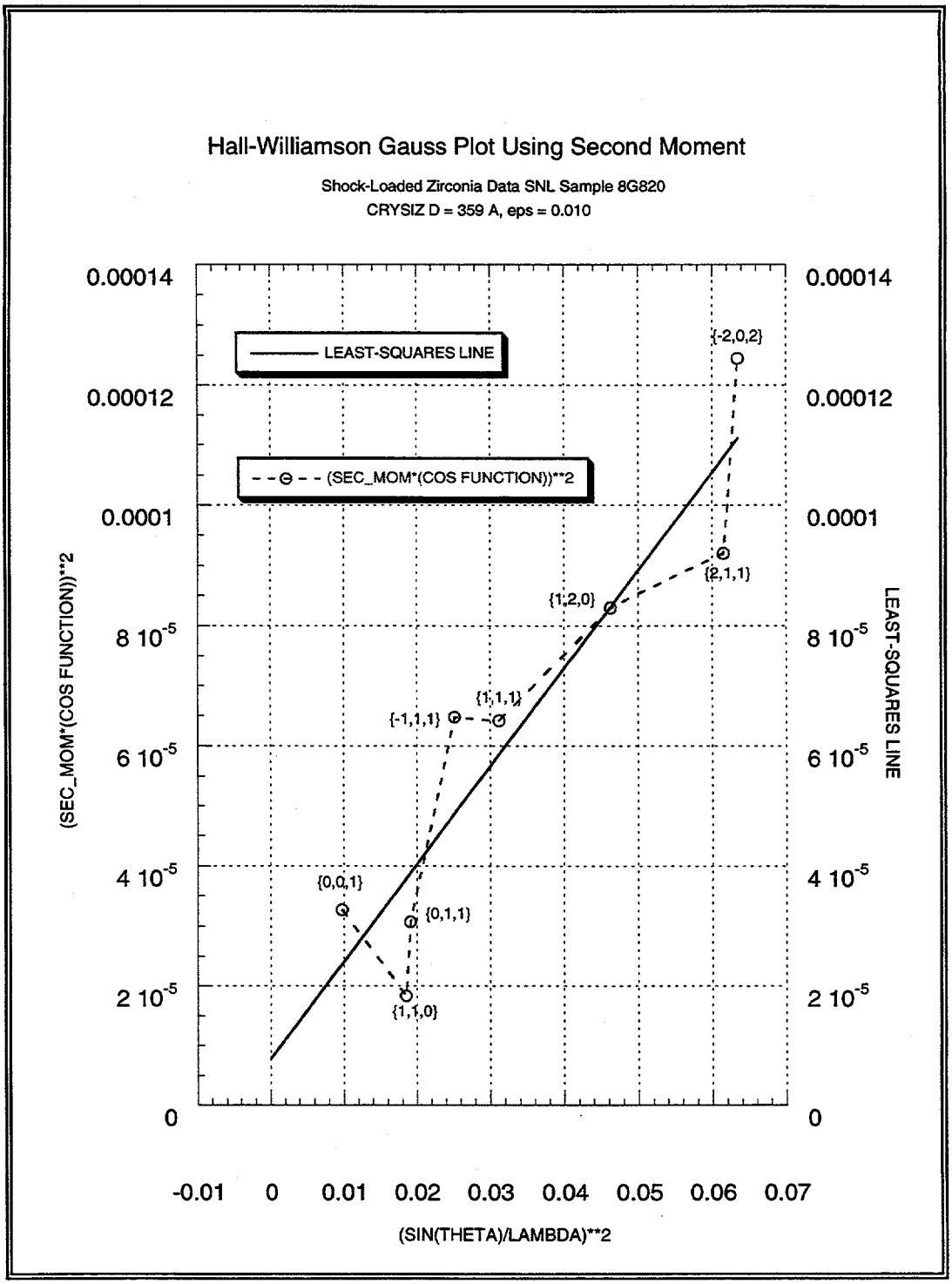

Fig. D.10. Hall-Williamson Gauss plot using second moment.

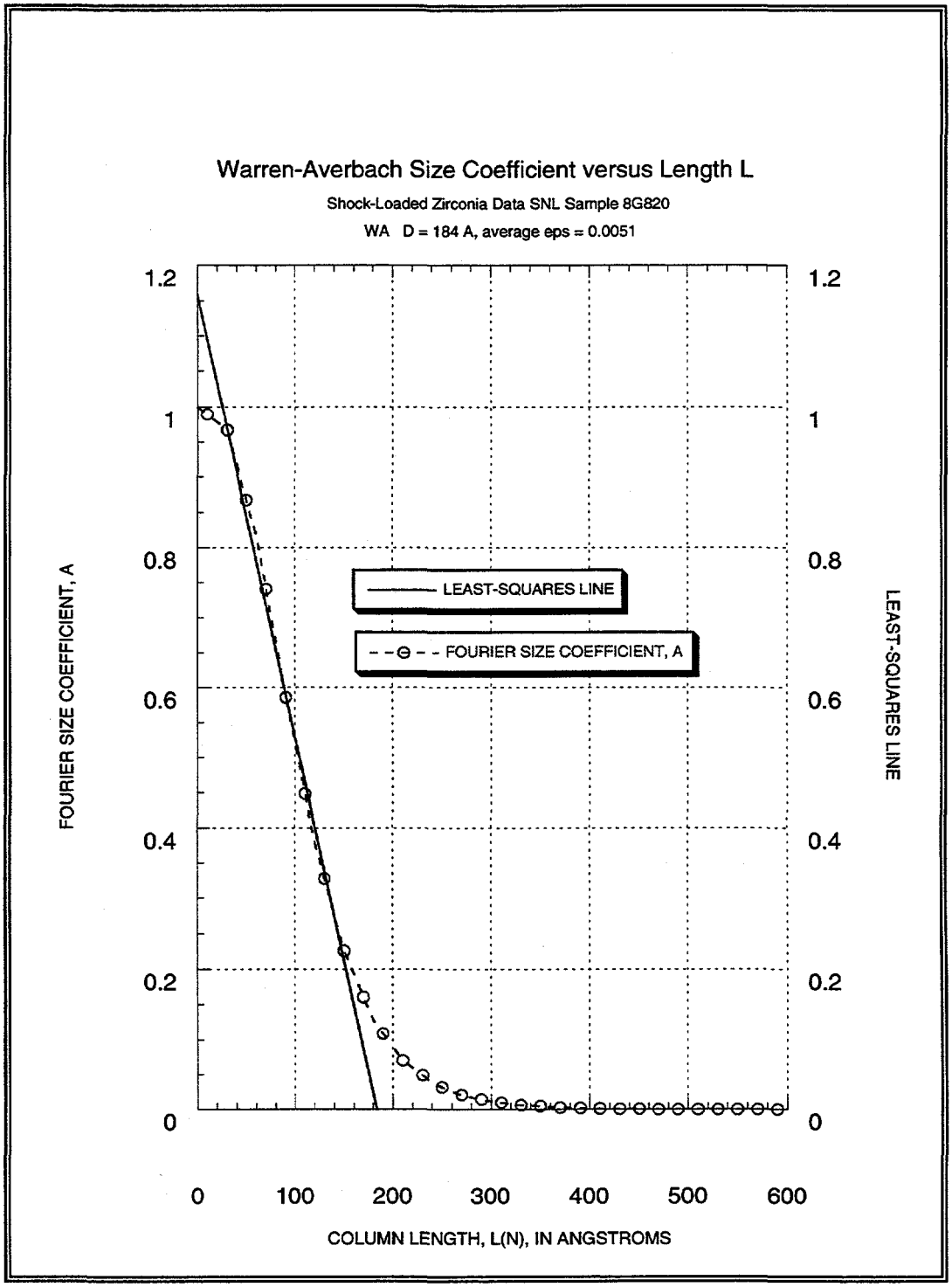

Fig. D.11. Warren-Averbach plot for determining size.

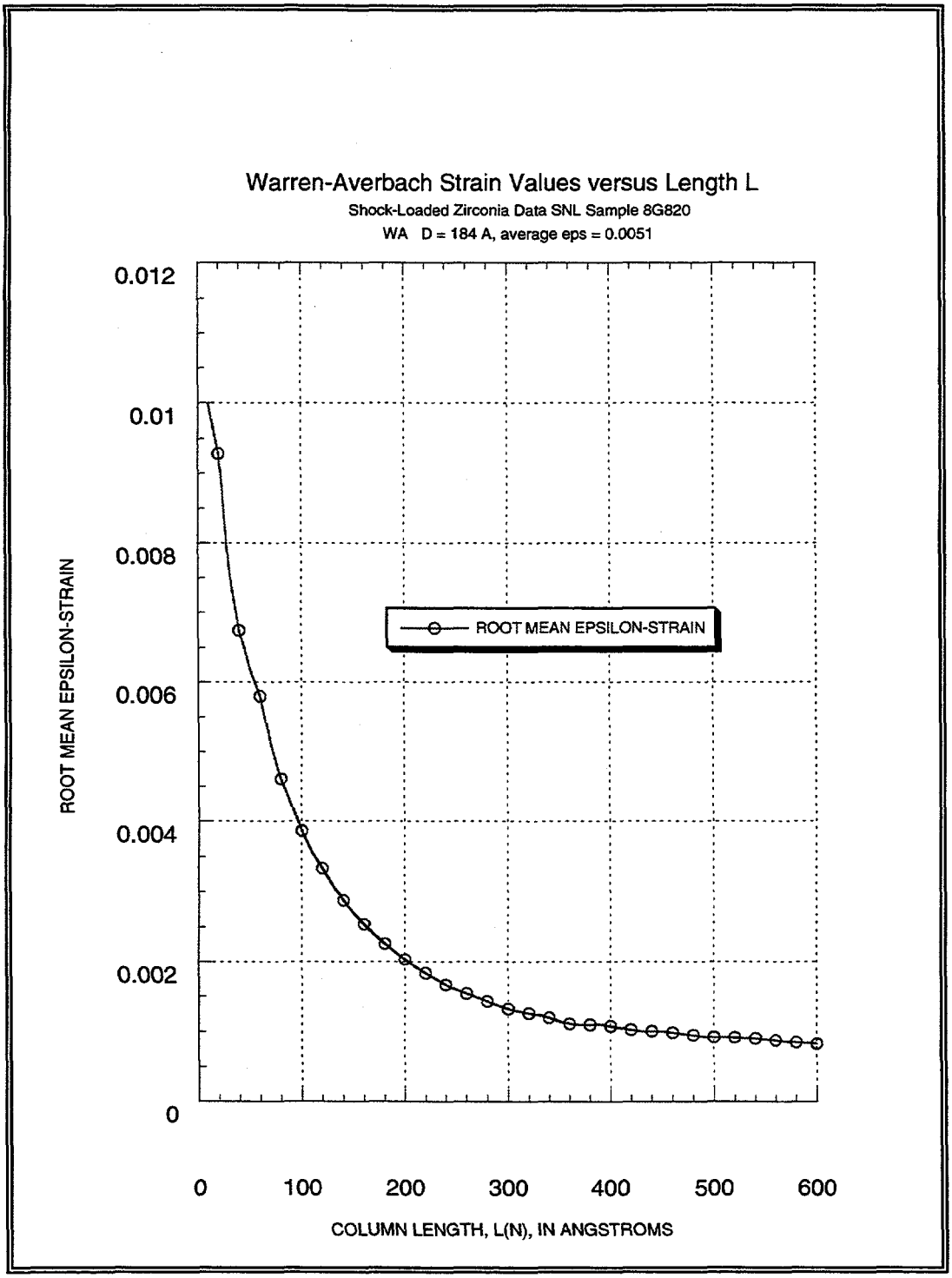

Fig. D.12. Warren-Averbach plot for determining strain.

APPENDIX E - Source code listings on diskette

The attached diskettes contain:

```
The volume label in drive A is CRYSIZ.
Directory of A:\

CRYSIZ96.FOR   TAGFOR.FOR    TIMDAT.FOR    CRYSIZ.LST
     4 file(s)    575606 bytes used
                  879616 bytes free

The volume label in drive A is PSEUDODATA.
The Volume Serial Number is 0000:1BDE.
Directory path listing
Path:        \PSEUDODA
Subdirectories: None
[.]          [..]         T31.DA       TR3.DA       T11.DA
T21.DA                    TRR.DA       T12.DA       T22.DA       T32.DA
T13.DA                    T23.DA       T33.DA       TR4.DA       T14.DA
T24.DA                    T34.DA       T3P.XIN      T11.XIN      T33.XIN
T3Q.CIN                   T11.CIN      T55.CIN      TR.IDL       T1.IDL
T11.IDL                   T21.IDL      T31.IDL      TRR.IDL      T12.IDL
T22.IDL                   T32.IDL      TR3.IDL      T13.IDL      T33.IDL
T23.IDL                   TR4.IDL      T14.IDL      T24.IDL      T34.IDL
T25.IDL                   T35.IDL
    42 file(s)    893072 bytes used
                  307200 bytes free

Path:        \PSEUDOOP
Subdirectories: None
Directory of A:\pseudoop
[.]          [..]         TR3T33.XPN    TR3T33.CPN    TR3T33.CPL
TR3T33.CEX
     6 file(s)    223545 bytes used
                  306688 bytes free

The volume label in drive A is ZIRCONIADAT.
Directory path listing
Path:        \ZIRCONIA
Subdirectories: None
[.]          [..]         ZRR.DA       ZRR.IDL      ZRR.FIT
ZR5.DA                    ZR5.IDL      ZR5.XIN      ZR5.CIN
     9 file(s)    73290 bytes used
                  208896 bytes free

Path:        \ZROUTPUT
Subdirectories: None
[.]          [..]         ZRRZR5.XPN    ZRRZR5.XEX    ZRRZR5.XPL
ZRRZR5.CPN     ZRRZR5.CPL     ZRRZR5.CEX
     8 file(s)   1161835 bytes used
                  208384 bytes free
```

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