A.22

Machine Computation	(a)	(b (i))	(b (ii))	(b (iii))	(c)
FMLS	2:53	1:25	4:15	4:05	12:20
BDLS	1:17	0:46	2:10	2:21	5:02
DMAP	0:55	0:43	2:17	2:10	4:52

The Weitek 3167 coprocessor is twice as fast as the 80387 and the IBM version on a 3090/200 is more than 20 times as fast as the VAX version.

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RAD, a program for analysis of X-ray diffraction data from amorphous materials for personal computers.

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Abstract

RAD is an interactive computer program for radial distribution analysis of X-ray diffraction data from amorphous materials. *RAD* has been written in Fortran 77 and runs on IBM PC/XT/AT or compatible computers.

1. Introduction

The radial distribution function $4\pi r^2 \rho(r)$ (RDF) is used to characterize amorphous structures. It represents the number of atoms in a spherical shell of radius r and unit thickness. The function is zero for values of r less than the hard-sphere diameter of the atoms and modulates about $4\pi r^2 \rho_0$ for larger values of r, where ρ_0 is the average atomic density of the amorphous material. Peaks in the RDF(r) indicate frequently occurring atom–atom distances; the area under a peak is equal to the average number of atom pairs within a particular range of distances (Klug & Alexander, 1954).

The reduced RDF, $G(r) = 4\pi r[\rho(r) - \rho_0]$, is associated by a Fourier transformation with the interference function $i(s)$, which is the structure-dependent part of the experimental X-ray diffraction data. In the program *RAD* the interference function is defined, following Pings & Waser (1968), as

$$i(s) = \left[I_a^{\mathrm{coh}}(s) - \sum_{i=1}^n x_i f_i^2(s) \right] \Bigg/ \left[\sum_{i=1}^n x_i f_i(s) \right]^2 \quad (1)$$

where $s = 4\pi(\sin\theta)/\lambda$, 2θ is the scattering angle, λ the wavelength, f_i are the atomic scattering factors, x_i the molar fractions of components, n the number of atomic species, and $I_a^{\mathrm{coh}}(s)$ is the coherently scattered intensity in electron units.

The aim of the radial distribution analysis is to evaluate the RDF(r) as the Fourier transform of the $i(s)$, which in turn can be obtained from the experimental intensities $I(s)$. The total scattered intensity $I(s)$ is related to $I_a^{\mathrm{coh}}(s)$ (Wagner, 1969a), neglecting the small-angle and multiple scattering, by

$$I_a^{\mathrm{coh}}(s) = \beta[I(s) - I_b(s)]/[P(s)A(s)] - M(s)I_a^{\mathrm{inc}}(s) \quad (2)$$

where β is an unknown normalization constant, $I_b(s)$ is the background scattering (from air, substrate *etc.*), $P(s)$ and $A(s)$ are the appropriate polarization and absorption factors respectively, $M(s)$ is the monochromator attenuation function, and $I_a^{\mathrm{inc}}(s)$ is the incoherent scattering in electron units scaled to one structural unit.

2. Outline of the program

The program consists of a main part and four subroutines (*SETUPD, DATRED, NORM, CALCRD*), where separate steps in processing the experimental intensities are performed.

The main program consists of input–output and control statements corresponding to the different options.

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The subroutine *SETUPD* creates the X-ray diffraction data file, which includes scattering angles and up to 750 intensity values, and a parameter data file, supplied by the user. The parameter data file includes the number of atomic species (up to ten) constituting the sample, the corresponding molar fractions x_i and the atomic numbers Z_i, the atomic scattering-factor coefficients (Cromer & Mann, 1968), anomalous-dispersion corrections (Cromer, 1965), the wavelength λ, the linear absorption factor of the sample, the average atomic density of the amorphous material, the counter dead time, some control flags determined from the experimental configuration (geometry and monochromatization type) and the monochromator attenuation function (Ruland, 1964). Some of the numbers (density ρ_0 for instance) are not crucial in the data processing and can be neglected in the data file.

The subroutine *DATRED* uses as input data the X-ray diffraction data file and a parameter data file. The experimental data undergo the following treatments:

(i) Subtraction of background scattering according to Warren & Mozzi (1970) and Wagner (1969b).

(ii) Correction for counter dead time (Klug & Alexander, 1954).

(iii) Correction for polarization (Wagner, 1978; Thijsse, 1984) depending on the type of monochromatization.

(iv) Correction for absorption (Wagner, 1969a) depending on the geometry.

(v) The missing values between $2\theta = 0$ and the first experimental data are derived by linear extrapolation to the origin.

(vi) The corrected XRD data are smoothed (Savitzky & Golay, 1964), calculated in steps of $\Delta s = 0.05$ from $s = 0$ to $s_{max} = 4\pi(\sin\theta_{max})/\lambda$ by means of a cubic spline interpolation and stored as a new data file.

The subroutine *NORM* uses a corrected data file from *DATRED* and the parameter data file as input. The independent coherent scattering,

$$\sum_{i=1}^{n} x_i f_i^2(s), \tag{3}$$

the sharpening factor,

$$\left[\sum_{i=1}^{n} x_i f_i(s)\right]^2, \tag{4}$$

and the incoherent scattering,

$$I_a^{inc} = (\lambda/\lambda')^2 \sum_{i=1}^{n} x_i Z_i (b_i s)^{a_i} / [1 + (b_i s)^{a_i}], \tag{5}$$

where a_i, b_i are semi-empirical expressions (Thijsse, 1984) and λ' is a modified wavelength, are here calculated.

The corrected X-ray diffraction data are scaled into electron units by the so-called high-angle method (Wagner, 1978):

$$\beta_{HA} = \int_{s_{min}}^{s_{max}} \left[\sum_{i=1}^{n} x_i f_i^2(s) + M(s) I_a^{inc}(s)\right] ds$$

$$\times \left\{\int_{s_{min}}^{s_{max}} [I(s) - I_b(s)][P(s)A(s)]^{-1} ds\right\}^{-1}; \tag{6}$$

and the interference function $i(s)$ is calculated. As an independent check the integral

$$\int_{s_{min}}^{s_{max}} s^2 i(s) \, ds = -2\pi^2 \rho_0 \tag{7}$$

is computed according to the so-called sum rule (Wagner, 1978). When a satisfactory normalization is reached, by varying the low limit of integration s_{min} ($s_{max}/2 < s_{min} < s_{max}$), the $i(s)$ data are stored as a new file.

The subroutine *CALCRD* uses as input an interference function data file and again the parameter data file. The reduced RDF $G(r)$ is calculated, properly damped (Klug & Alexander, 1954), as a Fourier transform of the $i(s)$:

$$G(r) = (2/\pi) \int_{s=0}^{s_{max}} si(s) \sin(sr) \exp(-bs^2) \, ds, \tag{8}$$

where b is the damping factor. A straight line is fitted to the $G(r)$ in the range $r = 0-1$ Å to obtain an estimate for the average atomic density ρ_0, on the basis of the expression

$$G(r) = -4\pi\rho_0 r \tag{9}$$

which holds only for small values of r. The RDF is calculated and the reduced RDF or optionally the RDF is stored as a new data file.

Residual errors in the $i(s)$, due to incorrect normalization of the data, may introduce spurious oscillations in the corresponding $G(r)$ in the region between the origin and the first peak. In order to avoid such errors a correction may be performed by means of repeated Fourier transformations (Kaplow, Strong & Averbach, 1965) and a new extended file (up to $2s_{max}$) with corrected $i(s)$ values may be created. This file may be used as an input data file in the subroutine *CALCRD*.

RAD has been tested using published X-ray diffraction data for silica glass (Konnert & Karle, 1973). Fig. 1 shows the agreement between $si(s)$ values computed by *RAD* and by *RADILS* (Konnert & Karle, 1973). The program *RAD* proved to be useful for analysis of X-ray diffraction data from metallic glasses (Petkov, Apostolov & Skumryev, 1989).

3. Implementation of *RAD*

RAD consists of 1500 statements written in Microsoft Fortran 77 occupying about 110 Kbyte of core memory. It runs on IBM PC/XT/AT under PC-DOS 3.1. DOS utilities
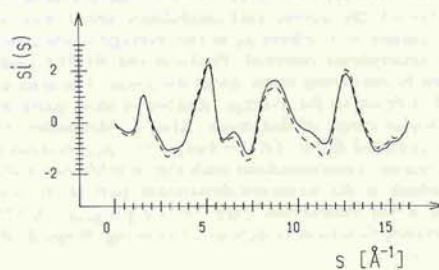

Fig. 1. Interference functions $si(s)$ for silica glass. Full line after *RAD* (multiplied by a proper constant factor because of the different sharpening factors used); broken line after *RADILS* (with permission from J. Karle).

and commands can be easily performed without leaving *RAD*.

During the data processing the raw data, the corrected data, the independent coherent and the incoherent scattering, the interference function $i(s)$, the reduced RDF and the RDF can be displayed by means of built-in graphic routines, if the computer is equipped with a CGA graphics card.

A Fortran source code is available from the author on a floppy disk upon request.

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*SIR*88 – a direct-methods program for the automatic solution of crystal structures.

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Abstract

*SIR*88 is an integrated package of computer programs for the solution of crystal structures. The package is based on the estimation of one- and two-phase structure seminvariants and three- and four-phase structure invariants according to the theory of representations [Giacovazzo (1977). *Acta Cryst.* A33, 933–944; (1980). *Acta Cryst.* A36, 362–372]. The program works in all the space groups and in most cases it is able to provide the correct solution without user intervention. Some prior information like the availability of a partial structure or of pseudotranslational symmetry is easily exploited to obtain the structure solution.

Introduction

The *SIR* (semi-invariants representations) package has been developed for solving crystal structures by direct methods. Its establishment was initiated some years ago. The present release, *SIR*88, is the second which we consider suitable for distribution and includes new features with respect to the previous version, *SIR*85. Even though *SIR*85 has been distributed by the authors to many laboratories worldwide over the last three years and has contributed to the determination of several difficult crystal structures, hitherto no published description of *SIR* has been available, except for the abstract presented at the IX ECM Meeting (Cascarano, Giacovazzo, Burla, Nunzi, Polidori, Camalli, Spagna & Viterbo, 1985).

The theoretical basis of *SIR* is the theory of representations (Giacovazzo, 1977, 1980a, b) according to which, for any structure invariant or seminvariant Φ, the set of diffraction magnitudes may be arranged in a sequence of subsets in order of their expected effectiveness (in the statistical sense) for the estimation of Φ. Thus different formulas can be used for estimating a given Φ, each exploiting a different subset of diffraction magnitudes, and therefore a different amount of prior information (faster access to this subset is guaranteed by storing all the reciprocal lattice in the central memory). In *SIR*88 one- and two-phase seminvariants and three- and four-phase invariants are estimated according to various formulas and subsequently used in the phasing process. Symmetry is used by *SIR*88 in a general way, so allowing the use of phase relationships in all space groups. A further goal of *SIR*88 is to minimize the amount of expertise the user has to bring to solving a crystal structure. To this end all decisions concerning data manipulations or appropriate choice of parameters can be assumed by the program. Therefore scientists untrained in direct methods or experienced people prepared to trust the *SIR*88 default mode can often solve crystal structures without personal intervention. However a large range of options is available to experienced crystallographers for choosing their own way of solving crystal structures.