The integral can be easily evaluated if we consider each of the N known atoms to be enclosed in a sphere of radius R and centred at S_n, the total volume enclosed being U. Then

$$\int_U \exp\{2\pi i(\mathbf{p}-\mathbf{h})\,.\,\mathbf{x}\}\,.\,d\mathbf{x} = \frac{4\pi R^3}{3}\, G_{hp} \sum_{n=1}^{N} \exp\{2\pi i(\mathbf{p}-\mathbf{h})\,.\,S_n\}\,,$$

where

$$G_{hp} = \frac{3\,[\sin(2\pi HR) - (2\pi HR)\cos(2\pi HR)]}{(2\pi HR)^3}$$

and

$$H = |(\mathbf{p}-\mathbf{h})|\,.$$

Hence

$$\mathbf{f}_p = \frac{4\pi R^3}{3V} \sum_h \mathbf{F}_h G_{hp} \left[\sum_{n=1}^{N} \exp\{2\pi i(\mathbf{p}-\mathbf{h})\,.\,\mathbf{S}_n\}\right]. \quad (3)$$

The equations (3) are of the same form as the molecular replacement equations, although there will be many more significant terms per equation owing to the slower decrease of G as H increases. They express the relationship between the structure factors $\mathbf{F}_h$ when part of the cell is of known structure.

Now $\mathbf{f}_p$ can be calculated and an initial solution of the phases of $\mathbf{F}_h$ can be found from the usual heavy-atom techniques. Improvement of these phases can then be made by the methods described in the paper by Main (1967) in order to achieve better satisfaction of equations (3). Hence the heavy-atom phases may be improved without any chemical knowledge. An application of these equations may therefore be of help when a heavy atom is sufficiently weak not to permit easy recognition of chemical information, when resolution is too poor for recognition of chemical groups, or when approximate phases have been determined by means of poorly isomorphous derivatives.

This work was supported by N.S.F. grant GB-02905 and by N.I.H. grant GM-10704-03.

References

MAIN, P. & ROSSMANN, M. G., (1966). *Acta Cryst.* **21**, 67.
MAIN, P. (1967). *Acta Cryst.* **23**, 50.

Acta Cryst. (1967). **23**, 174

Proposed method of separating the particle size and distortion coefficients in line profile analysis.

By T. H. UNGÁR, *Eötvös University, Budapest* VIII, *Museum körut* 6–8, *Hungary*

(*Received* 30 *December* 1966)

The moments method in X-ray line-profile analysis described by Harrison yields automatically the so-called 'particle-size' coefficients besides the deformation moments. Simple matrix inversion gives the deformation moments multiplied by the particle-size coefficient and, since the zero-order moment has to be equal to one, the particle size coefficient can be obtained directly.

Harrison (1966) has described the possibility of determining the distribution of deformation on the basis of distortion coefficients obtained from X-ray diffraction lines. We should like to contribute to this work by showing that if we do not suppose that the deformation and particle-size coefficients have already been separated by some other method, then the moments method described by Harrison yields automatically the particle-size coefficients besides the deformation moments.

Using the notation of Harrison let us put down the Fourier coefficients of a diffraction line of a cubic crystal expanded by the deformation moments:

$$A_n = A_n^s - \frac{1}{2!}(2\pi h_0 L/a)^2 A_n^s \langle e_L^2 \rangle + \frac{1}{4!}(2\pi h_0 L/a)^4 A_n^s \langle e_L^4 \rangle - \ldots \quad (1)$$

$$B_n = -(2\pi h_0 L/a) A_n^s \langle e_L \rangle + \frac{1}{3!}(2\pi h_0 L/a)^3 A_n^s \langle e_L^3 \rangle - \ldots \quad (2)$$

where $\langle e_L^k \rangle$ denotes the kth moment of deformation e_L, index L denotes the averaging distance in the crystal, a is the length of the unit-cell edge in the direction of the diffraction and $h_0^2 = h^2 + k^2 + l^2$.

Harrison (1966) has shown that if the particle-size coefficients A_n^s are known, then by measuring a number of reflexions, say m, the deformation distribution can be determined with the help of equation systems (1) and (2).

Let us construct the vectors $\mathbf{a}_n$ and $\mathbf{b}_n$ from the coefficients A_n and B_n belonging to the same n suffixes but to different reflexions and the vectors $\mathbf{e}_e$ and $\mathbf{e}_o$ from the even and odd moments $\langle e_L^{2k} \rangle$ and $\langle e_L^{2k+1} \rangle$ (where $k = 0,1,2,\ldots m-1$). Here we have supposed that the $2m$th or higher deformation moments can be neglected. Let us further denote the following square matrices of order m by P_n and R_n

$$P_n = \begin{pmatrix} 1 & -\frac{1}{2!}(2\pi h_0 L/a)^2 & \ldots \\ 1 & -\frac{1}{2!}(2\pi h_0' L/a)^2 & \ldots \end{pmatrix} \quad (3)$$

$$R_n = \begin{pmatrix} -(2\pi h_0 L/a) & \frac{1}{3!}(2\pi h_0 L/a)^3 & \ldots \\ -(2\pi h_0' L/a) & \frac{1}{3!}(2\pi h_0' L/a)^3 & \ldots \end{pmatrix}, \quad (4)$$

where each row of the matrix belongs to a certain reflexion, the rows being arranged in increasing order of the reflexions downward.

The equation systems (1) and (2) can be written in the following form:

$$\mathbf{a}_n = A_n^s P_n \mathbf{e}_e \quad (5)$$

$$\mathbf{b}_n = A_n^s R_n \mathbf{e}_0\,. \quad (6)$$

If the P_n and R_n matrices are not singular they can be inverted and can be written

$$P_n^{-1}\mathbf{a}_n = A_n^s\mathbf{e}_e \qquad (7)$$

$$R_n^{-1}\mathbf{b}_n = A_n^s\mathbf{e}_0 \,. \qquad (8)$$

Because the first element of vector $\mathbf{e}_e$ is the zero-order moment of e_L (the matrix P_n has so been chosen) the first element of vector $P_n^{-1}\mathbf{a}_n$ defines the particle-size coefficients A_n^s. So by computing the inverse of matrix P_n it is possible to determine the particle-size coefficients A_n^s and the deformation moments $\langle e_L^k\rangle$ at the same time.

During the separation of particle-size and deformation coefficients it was supposed that the average crystal shape is spherical, *e.g.* that A_n^s is independent of h_0. If the particle shape cannot be supposed to be isotropic in this sense or if in case of anisotropy the explicit form of function $A_n^s(h_0)$ is unknown, the separation of particle-size and deformation coefficients has no physical meaning.

Obviously if in equation (1) only second-order terms are considered, the method described for separating particle size and deformation coefficients is identical with Warren's (1959) method.

The author wishes to thank Dr L. Zsoldos for comments on the manuscript.

References

HARRISON, J. W. (1966). *Acta Cryst.* **20**, 390.

WARREN, B. E. (1959). *Progr. Metal Physics*, **8**, 147. Oxford: Pergamon Press.

Acta Cryst. (1967). **23**, 175

The determination of strain distributions and particle-size coefficient by the moment method.

By J. W. HARRISON, *Metallurgy Division, Atomic Energy Research Establishment, Harwell, Didcot, Berks, England*

(*Received* 7 *February* 1967)

The moment method has previously been shown to yield the strain distribution in a crystal from measurements of broadened diffraction lines under the assumption that all broadening was due to strain. Ungár has pointed out that such an assumption is unnecessary, but his method involves sacrificing the determination of the highest strain moment consistent with the number of experimentally measured diffraction orders. It is shown in the present paper that such a sacrifice can lead to serious error in certain cases. A simple scheme is described which extracts the maximum amount of information from the observed data to give both the strain distribution and the particle-size coefficient.

In a previous paper (Harrison, 1966) it was shown that the strain distribution in a deformed crystal can be determined from measurements of broadened diffraction lines under the assumption that no particle-size effects contribute to the broadening. Ungár (1967) has since pointed out that such an assumption is unnecessary, but his method, which leads to a determination of the 'particle-size' coefficient, does so at the expense of determining one of the high-order deformation moments.

Summary of the previous methods

Harrison employed the truncated expansions

$$a'_i = 1 + \sum_{j=1}^{m} P_{i,j}\langle e^{2j}\rangle \qquad i=1,2,\ldots m$$

$$b'_i = \sum_{j=1}^{m} R_{i,j}\langle e^{2j-1}\rangle \qquad m = \text{number of observed diffraction orders}$$

to determine the deformation moments $\langle e^k\rangle$ of the strain distribution from the cosine and sine coefficients a'_i and b'_i of the Fourier expansion of the broadened diffraction line (the dashes denoting that the coefficients are from a line broadened by strain alone). The matrix elements $P_{i,j}$ and $R_{i,j}$ are given by

$$P_{i,j} = \frac{(-1)^j}{(2j)!}(2\pi L h_{i,0/a})^{2j}$$

$$R_{i,j} = \frac{(-1)^j}{(2j-1)!}(2\pi L h_{i,0/a})^{2j-1}$$

where $h_{i,0}^2 = h_i^2 + k_i^2 + l_i^2$ and the deformation moments are then computed by a process of matrix inversion to give

$$\langle e^{2j}\rangle = \sum_{i=1}^{m} P_{i,j}^{-1}(a'_i - 1) \qquad j=1,2,\ldots m$$

$$\langle e^{2j-1}\rangle = \sum_{i=1}^{m} R_{i,j}^{-1} b'_i$$

so that the first $2m$ moments may be obtained from measurements of m diffracted orders.

Ungár waives assumptions about the sources of strain broadening and writes

$$a_i = A_n^s + A_n^s \sum_{j=1}^{m-1} P_{i,j}\langle e^{2j}\rangle \qquad i=1,2,\ldots m$$

$$b_i = A_n^s \sum_{j=1}^{m} R_{i,j}\langle e^{2j-1}\rangle \qquad m = \text{the number of observed diffraction orders}$$

where the a_i and b_i are the measured Fourier coefficients and A_n^s is the particle size coefficient. The cosine expansion is now truncated at the $(2m-2)$th moment to enable A_n^s to be calculated with the first $m-1$ even moments from the m equations for a_i. The first m odd moments may then be calculated from the equations for the b_i. This method