be unity, *i.e.*

$$h = n/f^3g^2 = c_{1j}c_{2j}c_{3j},$$

and q_3 is the characteristic function of the cube-free integers, *i.e.* $q_3(n) = 0$ if n is divisible by a cube and $q_3(n) = 1$ otherwise.

Only a small fraction of these lattices have truly three-dimensional structures with $f > 1$ (Rutherford, 1993), and since the general formulae for the numbers of subgroups are complex, these cases were considered individually.

Concluding remarks

After applying Polya's theorem, and removing by recursion the patterns of lower true index, we find $K(n, m)$. Table 1 contains the relevant results for indices up to 20. These may be combined with the number of lattices belonging to each colour lattice group, given in Tables 1 and 2 of Rutherford (1993), to give the total number of patterns; for example, for $n = 5$ and $m = 2$ in two dimensions, we have

$$2\sigma_1(5) = 2 \times 6 = 12$$

possible patterns. These are shown in Fig. 2.

A more complex example in two dimensions is $n = 18$, $m = 6$. Here, there are 36 lattices belonging to colour lattice group C_{18} and 3 to $C_6 \times C_3$. For the former and $m = 6$, the total number of patterns is 1026, the latter 1024. This gives as the total number:

$$(36 \times 1026) + (3 \times 1024) = 40\,008.$$

The number of patterns in three dimensions is considerably larger still; for example, for $n = 16$, $m = 8$, we have

$$(448 \times 800) + (168 \times 792) + (28 \times 792) + (7 \times 778) = 519\,078.$$

I wish to thank Professor Y. Billiet for suggesting improvements to, and correcting some errors in, the original manuscript.

References

Bertaut, E. F. & Billiet, Y. (1979). *Acta Cryst.* **A35**, 733–745.
Billiet, Y. & Bertaut, E. F. (1983). *International Tables for Crystallography*, Vol. A, edited by T. Hahn, pp. 814–817. Dordrecht: Kluwer Academic Publishers.
Billiet, Y. & Rolley-Le Coz, M. (1980). *Acta Cryst.* **A36**, 242–248.
Fujita, S. (1990). *J. Math. Chem.* **5**, 99–120.
Hardy, G. H. & Wright, E. M. (1979). *An Introduction to the Theory of Numbers*, 5th ed. Oxford Univ. Press.
Harker, D. (1978). *Proc. Natl Acad. Sci. USA*, **75**, 5264–5267.
Kucab, M. (1981). *Acta Cryst.* **A37**, 17–21.
McLarnan, T. J. (1978). *J. Solid State Chem.* **26**, 235–244.
McLarnan, T. J. (1981). *Z. Kristallogr.* **155**, 227–246.
McLarnan, T. J. & Moore, P. B. (1981). *Structure and Bonding in Crystals*, Vol. II, edited by M. O'Keeffe & A. Navrotsky, pp. 133–165. New York: Academic Press.
Moore, P. B. & Araki, T. (1976). *Am. Mineral.* **61**, 1226–1240.
Polya, G. (1937). *Acta Math.* **68**, 145–254.
Polya, G. & Read, R. C. (1987). *Combinatorial Enumeration of Groups, Graphs and Chemical Compounds*. New York: Springer-Verlag.
Rutherford, J. S. (1990). *Acta Cryst.* **B46**, 289–292.
Rutherford, J. S. (1991). *Trans. Am. Crystallogr. Assoc.* **27**, 315–321.
Rutherford, J. S. (1992). *Acta Cryst.* **A48**, 500–508.
Rutherford, J. S. (1993). *Acta Cryst.* **A49**, 293–300.

Acta Cryst. (1995). **A51**, 679–683

The Validity of Approximations Made in Differential Anomalous X-ray Scattering

By James R. Fishburn and Scott W. Barton*

Polymer Science and Engineering Department, University of Massachusetts at Amherst, Amherst, MA 01003, *USA*

(*Received* 2 *December* 1994; *accepted* 22 *March* 1995)

Abstract

Approximations of weighting-factor functions are used when determining coordination numbers from differential anomalous scattering (DAS) experiments. The accuracy of two single-value approximations for the weighting functions are tested using non-interacting hard-sphere models of systems that have been studied previously with DAS. The first approximation is an average of the weighting-factor function over the experimental wave-vector range. The second is the weighting-function value at the wave vector that is related to a peak position in the corresponding differential radial distribution function (dRDF). It was found that the first approximation introduced up to 10% error into calculated coordination numbers. The second weighting-factor approximation introduced minimal error into the coordination-number calculations and is simple to use.

---

* Author to whom correspondence should be addressed.

Acta Crystallographica Section A
ISSN 0108-7673 ©1995

I. Introduction

Differential anomalous X-ray scattering (DAS) is an important technique used to probe the local structure surrounding specific atoms in multicomponent amorphous materials. The method has been used to study binary metal alloys (Fuoss, Eisenberger, Warburton & Bienenstock, 1981; Fuoss, Warburton & Bienenstock, 1980; Aur *et al.*, 1983; Fischer-Colbrie, Bienenstock, Fuoss & Marcus, 1988; Tonnerre, DeLima & Raoux, 1989), molecular liquids (Ludwig, Warburton, Wilson & Bienenstock, 1987; Schultz, Bertagnolli & Frahm, 1990; Mager, Schultz, Bertagnolli & Frahm, 1990; Mager, Bertagnolli, Degenhardt & Frahm, 1991) and salt solutions (Ludwig, Warburton & Fontaine, 1987; Dreier & Rabe, 1986). We have used the technique to study the chemical and structural environment of salts dissolved in polymer matrices, such as $ZnBr_2$ in poly(propylene oxide) (Fishburn & Barton, 1995).

The atomic scattering factor is expressed as (James, 1982)

$$f(k,E)=f_0(k)+f'(E)+if''(E), \tag{1}$$

where f_0 is the energy-independent component and f' and f'' are the anomalous scattering corrections. Both f' and f'' vary slowly with energy, except very close to an absorption edge; the DAS method exploits this rapid change in the vicinity of the edge. In Fig. 1, $f''(E)$ and $f'(E)$ are shown for Zr. Note that strong changes in f' are observed within a few hundred eV of the K-shell absorption edge at 17.998 keV. Suppose that one has a multicomponent sample in which Zr is present and that two separate scattering experiments are performed using different X-ray energies E_a and E_b, where E_a is far from the Zr absorption edge and E_b is very close to the absorption edge. The difference between the coherent X-ray scattering intensities at E_a and E_b, as a function of the wave vector $k=(4\pi\sin\theta)/\lambda$, is a weighted sum of only partial structure factors that contain Zr as one of the atoms. From the intensity difference, one determines a differential structure factor (dSF) and this can be Fourier sine transformed into a real-space differential radial distribution function (dRDF) describing the chemical environment around the Zr atom.

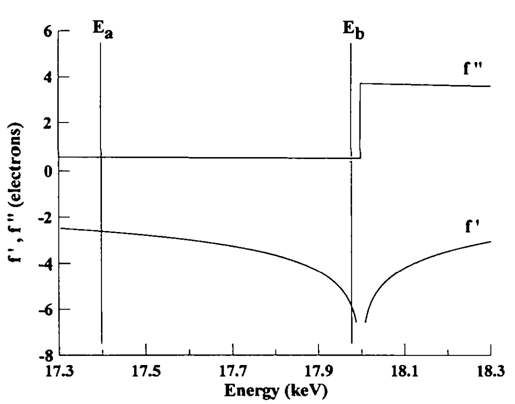

Fig. 1. Anomalous scattering factors, $f'(E)$ and $f''(E)$, for an isolated Zr atom near the K-shell absorption edge. E_a and E_b are the two energies at which the model structure factors are calculated.

We questioned the validity of certain approximations made in obtaining coordination numbers from the dRDF. Since the coordination numbers are of central importance in most scattering studies, including our own, we feel a need to explore this problem in more depth.

Below, we first provide a more specific statement of the problem. Next, we model a DAS experiment by a hard-sphere binary liquid in which the size and concentration of the two components is varied. We then make a comparison between the exact dRDF and the dRDFs calculated from the partial structure factors using different approximations. We show that the exact dRDF can be reproduced using an approximation slightly different from that previously reported (Ludwig, Warburton & Fontaine, 1987; Dreier & Rabe, 1986).

A. Statement of the problem

Consider a multicomponent amorphous solid or liquid containing atoms of type 1, 2, 3, ..., n. With the absorbing species labeled as atom 1, the intensity difference is written explicitly as (Dreier & Rabe, 1986)

$$\begin{aligned}\Delta I^{\rm abs}&=I^{\rm coh}_{E_a}(k)-I^{\rm coh}_{E_b}(k)\\&=2c_1\Delta f'_1\sum c_j{\rm Re}(\bar{f}_j)[a_{1j}(k)-1],\end{aligned} \tag{2}$$

where Δ signifies the difference between the values at E_a and E_b, $\bar{f}_j$ is averaged between the two energies, and c_j is the atomic fraction of species j. $[a_{1j}(k)-1]$ is a Faber–Ziman partial structure factor (Faber & Ziman, 1965), defined by the partial pair correlation functions, $g_{1j}(r)$:

$$k[a_{1j}(k)-1]=4\pi\rho_o\int\limits_0^\infty r[g_{1j}(r)-1]\sin(kr)\,{\rm d}r, \tag{3}$$

where $g_{1j}(r)$ is related to the partial density distribution

$$\rho_{1j}(r)=4\pi r^2c_j\rho_o g_{1j}(r). \tag{4}$$

In the above notation, $\rho_{1j}(r)$ is the density of j-type atoms surrounding an atom of type 1 and ρ_o is the sample average density.

In any system of N different atom types, the real-space structure is described by a set of $N(N+1)/2$ distinct partial pair correlations. Since we have designated one atom in each pair as type 1, there are now only N contributions to the real-space distribution. We define the differential structure factor (dSF), $a_1(k)$, by

$$[a_1(k)-1]=\sum_{j=1}^{N}[c_j{\rm Re}(\bar{f}_j)/{\rm Re}(\langle\bar{f}\rangle)][a_{1j}(k)-1], \tag{5}$$

where

$$\langle\bar{f}\rangle=\sum_i c_i\bar{f}_i,$$

which is related to the scattered intensity by (2) (Schultz, Bertagnolli & Frahm, 1990; Mager, Schultz, Bertagnolli & Frahm, 1990; Mager, Bertagnolli, Degenhardt & Frahm, 1991; Dreier & Rabe, 1986).

$$[a_1(k) - 1] = \Delta I^{\rm abs}/2c_1 \Delta f_1' \,{\rm Re}\langle \bar{f} \rangle. \qquad (6)$$

The differential structure factor obtained for the DAS experiment is the inteference function arising from the average packing of atoms around the type-1 atom in the system.

To obtain the real-space representation, the dSF is Fourier sine transformed into the differential radial distribution function (dRDF) (Schultz, Bertagnolli & Frahm, 1990; Mager, Schultz, Bertagnolli & Frahm, 1990; Mager, Bertagnolli, Degenhardt & Frahm, 1991; Dreier & Rabe, 1986):

$$\begin{aligned} {\rm dRDF} &= 4\pi r^2 \rho_o g_1(r) \\ &= 4\pi r^2 \rho_o + (2r/\pi) \int_0^\infty k[a_1(k) - 1] \sin(kr)\, {\rm d}k, \end{aligned} \qquad (7)$$

where the transform of $a_1(k) - 1$ is actually the sum of the convolutions

$$\begin{aligned} {\rm dRDF} = {} & 4\pi r^2 \rho_o + (2r/\pi) \\ & \times \sum_j \left[\int_0^\infty k[a_{1j}(k) - 1] \sin(kr)\, {\rm d}k \right] \\ & * \left[\int_0^\infty c_j[{\rm Re}(f_j)/{\rm Re}(\langle f \rangle)] \sin(kr)\, {\rm d}k \right]. \end{aligned} \qquad (8)$$

More thorough descriptions of the DAS method were documented by Tonnerre, DeLima & Raoux (1989), Dreier & Rabe (1986) and Fishburn & Barton (1995).

Each peak in the dRDF corresponds to a coordination shell around atom type 1. If it is known that only type-j atoms occupy a coordination shell between r_1 and r_2, then the coordination number of j atoms is approximated by

$$N_{1j} \simeq \left\langle {\rm Re}\langle \bar{f} \rangle / {\rm Re}(\bar{f}_j) \right\rangle \int_{r_1}^{r_2} 4\pi r^2 \rho_o g_1(r)\, {\rm d}r, \qquad (9)$$

where $\left\langle {\rm Re}\langle \bar{f} \rangle / {\rm Re}(\bar{f}_j) \right\rangle$ must be averaged in order to interpret the real-space data. Because the main usefulness of the DAS method is the determination of coordination numbers, our problem is to determine the accuracy of the averaging approximation for $\left\langle {\rm Re}\langle \bar{f} \rangle / {\rm Re}(\bar{f}_j) \right\rangle$. We approach the problem by first generating a dSF from a set of model partial structure factors using (5). Equation (7) is then used to calculate the dRDF for the model. This 'exact' dRDF is then compared with two dRDFs generated from dSFs in which the weighting factor, $\left\langle {\rm Re}(\bar{f}_i) / {\rm Re}(\langle \bar{f} \rangle) \right\rangle$ [(5)], is: (1) averaged over the k range of the data; and (2) a fixed value at $k_p = 2\pi/r_p$, where r_p is the position of the coordination peak of interest. We find that the k averaging can introduce errors as large as 10% for simple binary systems but that fixing the weighting factor at the k_p value produces a dRDF almost identical to that obtained using the exact expression.

II. Modeling

We modeled DAS experiments for the systems Mo_xNi_{1-x} (Aur *et al.*, 1983) and Ni_2Zr (Tonnerre, DeLima & Raoux, 1989), for which previous studies are reported. In Mo_xNi_{1-x}, the atoms are of similar size and, in Ni_2Zr, there is enough of a size difference to partially separate the contributions to the first peak of the dRDF. Because there is no way to extract the individual partial structure factors from the experimental dSFs accurately, we are unable to access the accuracy of the approximations using the existing experimental data. Therefore, we modeled the experimentally determined dRDFs using non-interacting hard spheres in a two-component liquid (Ashcroft & Langreth, 1967; Islam, 1981). The model was dependent on only three variables: (1) η, the fraction of the total volume occupied by the spheres; (2) x, the atomic fraction of the larger spheres; and (3) α, the ratio of the sphere diameters, σ_1/σ_2, where sphere type 2 always represents the larger sphere. The atomic fraction used was the same as in the experiments and the sphere diameters were taken from tables of metallic radii (Shriver, Atkins & Langford, 1990).

We first calculated the partial structure factors of (3) and the weighting factors, ${\rm Re}(\bar{f}_j)/{\rm Re}\langle \bar{f} \rangle$, in (5) based on the hard-sphere model. The differential structure factors, $[a_1(k) - 1]$, were then calculated [(5)] using three sets of weighting factors: (1) the correct k-dependent functions; (2) the average value of the weighting factor over all k-space data; and (3) the value of the weighting factor at $k_p = 2\pi/r_p$. The dRDFs were then calculated for each case from (7). The dRDF transform from the dSF using the correct weighting factors is referred to as the exact dRDF. For clarity, the two approximations will be called the k-averaged case and the k-peak case.

A. *Example* 1, Mo_xNi_{1-x}

The first system modeled is amorphous Mo_xNi_{1-x} (Aur *et al.*, 1983), where the two atoms are very similar in size, $d_{\rm Mo} = 2.80$ and $d_{\rm Ni} = 2.50$ Å. We model the DAS from the Mo K edge at $E_a = 19.781$ and $E_b = 19.959$ keV as in the original experiment, with the modeling parameters listed in Table 1. In calculating the weighting factors, the values for f_0 are calculated from the fitting parameters of Cromer & Mann (1968) and the f' values are calculated by a Kramers–Kronig inversion (Kawamura & Fukamachi, 1978; Hoyt, de Fontaine & Warburton, 1984) of the X-ray cross-section data found in the McMaster tables (McMaster, del Grande, Mallett & Hubbell, 1969). A k range of $0.073 \le k \le 19.491$ Å^{-1} is used.

Table 1. *Parameters used in calculating the hard-sphere-model structure factors*

The parameters are: η, the occupied volume; x, the atomic fraction of the larger spheres; and α, the ratio of the sphere diameters (Ashcroft & Langreth, 1967).

Model	η	x	α
$Mo_{50}Ni_{50}$	0.460	0.500	0.893
Ni_2Zr	0.460	0.333	0.781

While only an experiment with $x_{Mo} = 0.50$ is reported, the Mo concentration in the modeling is varied to determine the effect, if any, of concentration in the approximations. Regardless of concentration, the use of a k-averaged or k-peak weighting factor makes little difference in the first peak of the dRDF which contains contributions from both Mo–Ni and Mo–Mo pairs. This fortuitous agreement between the exact and approximated solutions is due to a simultaneous overestimation of $\rho_{MoNi}(r)$ and underestimation of $\rho_{MoMo}(r)$ in the vicinity of the first peak as shown in Figs. 2(*a*) and (*b*).

The first coordination peak from the weighted Mo–Ni pair distribution using the k-averaged weighting factor is larger than the same peak in the exact distribution while the first Mo–Ni peak in the k-peak dRDF is essentially identical to the corresponding peak in the exact distribution (Fig. 2*a*). But the first coordination peak in the Mo–Mo weighted pair distribution created using the k-averaged weighting factor is smaller than the peak from the exact distribution function, while the first peak using the k-peak approximation is again identical to the exact case (Fig. 2*b*). This is true for $x = 0.25$, 0.50 and 0.75.

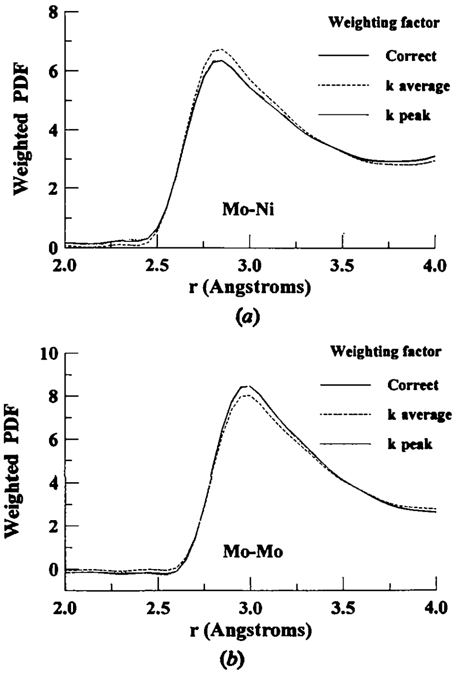

Fig. 2. Weighted pair distribution functions calculated from the Mo edge of the $Mo_{50}Ni_{50}$ model. First coordination peaks of (*a*) the Mo–Ni and (*b*) the Mo–Mo pair coordinations. Solid lines: exact distributions; dashed lines: k-averaged approximated distributions; dotted lines: k-peak approximated distributions.

By choosing a system with a greater difference of atomic sizes, the 1–1- and 1–2-type coordinations are separated in r and errors introduced by approximating the weighting factors become more visible in the dRDF.

B. Example 2, Ni_2Zr

The second system modeled was amorphous Ni_2Zr (Tonnerre, DeLima & Raoux, 1989) with the metallic radii $d_{Ni} = 2.50$ and $d_{Zr} = 3.20$ Å. We model the DAS from the Zr K edge between the scattering curves measured at 17.398 and 17.987 keV from $k = 0.073$ to 17.447 Å^{-1}. The model parameters are listed in Table 1.

The behavior observed in the Mo_xNi_{1-x} model also occurs with the Ni_2Zr model. When using the k-averaged weighting factors, the first Zr–Ni coordination peak is larger than the corresponding peak in the correct dRDF, while the first Zr–Zr peak is smaller than the Zr–Zr peak in the correct dRDF (Fig. 3). The dRDF created with the k-peak weighting factors is in excellent agreement with the exact dRDF (Fig. 3).

III. Discussion

How do these examples relate to the experimental case where one always interprets the exact dRDF? It is the inverse of the weighting factor that is used to extract the coordination numbers from the peak area in (9). Therefore, an overestimation of the weighting factor corresponds to an underestimation of the calculated coordination numbers. In the two examples given, the 1–2 weighting factor is too large and the 1–1 weighting factor is too small with the k-averaged approximation. One expects, then, that for both models the 1–2 coordination number calculated using (9) is artificially low while that for the 1–1 coordination is too large.

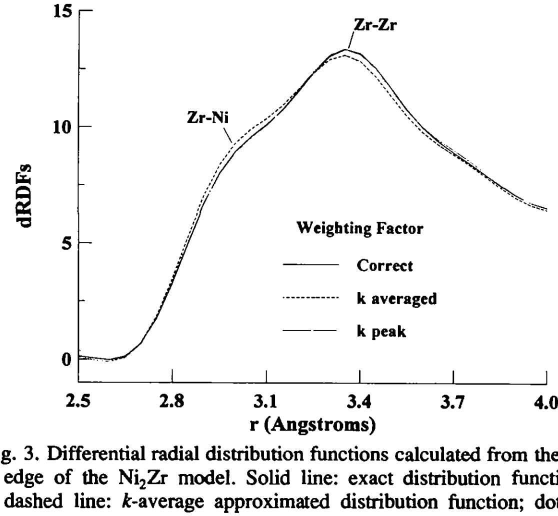

Fig. 3. Differential radial distribution functions calculated from the Zr edge of the Ni_2Zr model. Solid line: exact distribution function; dashed line: k-average approximated distribution function; dotted line: k-peak approximated distribution function.

Table 2. *Coordination numbers calculated using the two approximations to the weighting factor in equation* (9)

The Ni_2Zr coordination numbers are determined from the model distribution function while the $[PPO]_6ZnBr_2$ coordination numbers are determined from experimental data (Fishburn & Barton, 1995).

Sample	Coordination	*k* averaged	*k* peak
Ni_2Zr			
	Zr–Ni	3.76	3.92
	Zr–Zr	4.99	4.45
$[PPO]_6ZnBr_2$			
	Zn–O	2.04	1.90
	Zn–Br	1.67	1.83
	Br-Zn	1.17	1.31

However, no significant deviations from the exact solution are observed when using the *k*-peak weighting factor. Therefore, there is negligible error introduced into the coordination-number calculations from use of this approximation:

$$N_{ij} \simeq [\mathrm{Re}\overline{f(k_p)}/\mathrm{Re}\overline{f_i(k_p)}] \int_{r_1}^{r_2} 4\pi r^2 \rho_o g_1(r)\,\mathrm{d}r. \qquad (10)$$

In Table 2, the coordination numbers are estimated from the exact dRDFs of the Ni_2Zr model using a two-Gaussian fit for $g_1(r)$. The coordination numbers could not be calculated for the $Mo_{50}Ni_{50}$ model because unphysical results are produced for the fitting of two Gaussian curves to the first peak in the correct dRDF with the peak positions obtained from the weighted partial distribution functions.

The effect on the coordination numbers is just as anticipated from the above analysis. The Zr–Ni coordination number decreased by 4.3% while the Zr–Zr coordination number increased by 12% when using the *k*-average approximation as opposed to the *k*-peak approximation. We note that, in calculating the peak areas, the Guassian curve is fit to the low-*r* side of the peak. This cannot be accurately determined for the Zr–Zr peak because the low-*r* side is obscured by the Zr–Ni coordination peak.

Also listed in Table 2 are the coordination numbers calculated from our recent DAS experiments on the polymer electrolyte $[PPO]_6ZnBr_2$ (Fishburn & Barton, 1995). In our original analysis, we used the *k*-averaged approximation of the weighting factors. The coordination numbers changed slightly when using the *k*-peak approximation. The refined coordination numbers better support our conclusion that, on average, each Zn^{2+} cation is coordinated with two Br and two O atoms.

IV. Concluding remarks

With the use of *k*-averaged weighting factors, coordination numbers can be over- or underestimated by as much as 10%. This could be a serious obstacle in proposing structures for the coordination numbers calculated with the DAS method. We have shown that using *k*-peak values is, by contrast, an excellent approximation.

References

ASHCRFOT, N. W. & LANGRETH, D. C. (1967). *Phys. Rev.* **156**, 685–692.

AUR, S., KOFALT, Y., WASEDA, Y., EGAMI, T., WANG, R., CHEN, H. S. & TEO, B. K. (1983). *Solid State Commun.* **48**, 111–115.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.

DREIER, P. & RABE, P. (1986). *Rev. Sci. Instrum.* **57**, 214–220.

FABER, T. E. & ZIMAN, J. M. (1965). *Philos. Mag.* **11**, 153–173.

FISCHER-COLBRIE, A., BIENENSTOCK, A. I., FUOSS, P. H. & MARCUS, M. A. (1988). *Phys. Rev. B*, **38**, 12388–12403.

FISHBURN, J. & BARTON, S. W. (1995). *Macromolecules*, **28**, 1903–1911.

FUOSS, P. H., EISENBERGER, P., WARBURTON, W. K. & BIENENSTOCK, A. I. (1981). *Phys. Rev. Lett.* **46**, 1537–1540.

FUOSS, P. H., WARBURTON, W. K. & BIENENSTOCK, A. I. (1980). *J. Non-Cryst. Solids*, **35/36**, 1233–1238.

HOYT, J. J., DE FONTAINE, D. & WARBURTON, W. K. (1984). *J. Appl. Cryst.* **17**, 334–351.

ISLAM, M. (1981). *Comput. Phys. Commun.* **23**, 43–50.

JAMES, R. W. (1982). *The Optical Principles of the Diffraction of X-rays*, pp. 135–192. Woodbridge, CN:Oxbow Press.

KAWAMURA, T. & FUKAMACHI, T. (1978). *Jpn J. Appl. Phys.* Suppl. **17-2**, 224–226.

LUDWIG, K. F., WARBUTON, W. K. & FONTAINE, A. (1987). *J. Chem. Phys.* **87**, 620–629.

LUDWIG, K. F., WARBURTON, W. K., WILSON, L. & BIENENSTOCK, A. I. (1987). *J. Chem. Phys.* **87**, 604–612.

MCMASTER, W. H., DEL GRANDE, N. K., MALLET, J. H. & HUBBELL, J. H. (1969). *Compilation of X-ray Cross Sections.* Available from National Technology Information Service, Springfield, VA, USA. Ref. UCRL-50174, Sec. II, Rev. 1.

MAGER, T., BERTAGNOLLI, H., DEGENHARDT, D. & FRAHM, R. (1991). *Mol. Phys.* **73**, 587–601.

MAGER, T., SCHULTZ, E., BERTAGNOLLI, H. & FRAHM, R. (1990). *Ber. Bunsenges. Phys. Chem.* **94**, 703–709.

SCHULTZ, E., BERTAGNOLLI, H. & FRAHM, R. (1990). *J. Chem. Phys.* **92**, 667–672.

SHRIVER, D. F., ATKINS, P. W. & LANGFORD, C. H. (1990). *Inorganic Chemistry*, p. 26. New York: W. H. Freeman.

TONNERRE, J. M., DELIMA, J. C. & RAOUX, D. (1989). *J. Chim. Phys.* **86**, 1509–1522.