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Reliability of partial structure factors determined by anomalous dispersion of x-rays

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The reliability of the partial structure factors determined by either of two x-ray scattering techniques using the effects of anomalous dispersion is considered. A comparison of the two experimental techniques is given for both binary and ternary systems. The recently proposed x-ray frequency-modulation technique is found to be about an order of magnitude better than the direct x-ray anomalous scattering method, and it is also found to be suitable for ternary systems. Experimental error is simulated by a pseudo-random-number generator which produces normally distributed numbers with a specified mean and standard deviation. Conditions corresponding to about 1% experimental error from data acquisition and processing are assumed.

I. INTRODUCTION

In the study of amorphous materials, whether liquid or solid, there is much interest in maximizing the amount of information that can be determined about such systems. The absence of long-range order makes this considerably more difficult than for crystalline materials. Consequently, when a new development in experimental capability occurs or is proposed, it becomes of interest to know what advantage or disadvantage could result from the new or modified technique. In particular, precisely this circumstance occurs in the study of amorphous systems by x-ray diffraction. The development of tunable high-intensity x-ray sources permits photon energies to be selected so that x rays can interact resonantly with bound electrons. The result is anomalous dispersion in the scattered beam which is distinct from the normal diffraction of x rays. In principle, each absorption edge of the atomic constituents of the sample could yield a distinct experimental result and, therefore, more information would be available for deducing structural details. This is especially important, for example, in the study of materials at high pressure since the possible alternatives, using neutron scattering to produce distinct experiments, are not currently performed with an apparatus such as the diamond anvil pressure cell. The advantages, though, are not limited to high-pressure studies. Given that the incident beam can be tuned, several distinct experiments become possible without a major change in the experimental apparatus, thereby yielding a considerable savings in both temporal and monetary costs. Furthermore, the feature of tunability opens the possibility of using frequency-modulation techniques to enhance the quality of the experimental results. The gain in the quantitative reliability of the deduced structural information is not so obvious, and it is this aspect of the use of anomalous dispersion that is investigated here.

The structure of a liquid or an amorphous material is often usefully expressed in terms[1-3] of a radial distribution function (RDF) or, more directly, in terms of a structure factor $\langle \sum_i \sum_j f_i f_j{}^* \exp(i\vec{s}\cdot\vec{R}_{ij}) \rangle$, where i, j are summed over all atoms, $\vec{R}_{ij}$ is the position vector from atom i to atom j, and $\vec{s}$ is the x-ray wave vector. When more than one type of atomic scattering species is present in the sample, the material is described by a set of partial RDF or a set of partial structure factors (PSF). For N distinct scattering species, there are $N(N+1)/2$ distinct PSF, and, correspondingly, that same number of experiments or pieces of information must be obtained to determine the set of PSF.

For x-ray scattering experiments, the methods[4-7] which can be used to generate the required number of different observations utilize the effects of anomalous dispersion. At the present time, the changes produced in the atomic scattering factors by means of the anomalous dispersion of x rays are not more than about 10% when standard x-ray tubes are used. This occurs because of the necessity of tuning to the particular energy of an absorption edge. For x-ray tubes, this tuning is limited to a selection among the available target electrodes. However, with a tunable x-ray source, such as the radiation from a synchrotron,[8] there arises the possibility of achieving larger changes in the scattering factors, perhaps in the range of

20–50%.

A question of some interest for the x-ray anomalous dispersion techniques is, how well can the PSF be determined in multicomponent systems? This question has been considered previously for particular experiments[9,10] on binary systems, subject to the usual uncontrolled conditions of error that occur in experimental processing. In this paper, the question is considered generally under controlled conditions of errors and for two alternative experimental techniques. To maintain controlled errors, a method of simulation is used in which the experimental errors are represented by means of a pseudo-random-number generator. The analysis is performed for binary and ternary systems in the context of two experimental techniques: (1) fixed-frequency (direct) x-ray scattering[4,5] with anomalous dispersion, and (2) frequency-modulated (derivative) x-ray scattering[6,7] with anomalous dispersion.

Consider a binary system for which there are three distinct PSF. In the case of direct x-ray scattering, the three required experiments[4,5] are produced by choosing three distinct frequencies for the incident x rays, one of which is removed from any absorption edge and two of which must be near the absorption edges. The three resulting equations can be written[2] as

$$W_{11}(s,\omega_m)I_{11}(s)+2W_{12}(s,\omega_m)I_{12}(s) + W_{22}(s,\omega_m)I_{22}(s)=I_m(s,\omega_m) \quad (1)$$

for $m=1,2,3$, where $s=4\pi\sin\theta/\lambda$, 2θ is the scattering angle, λ is the x-ray wavelength, ω is the x-ray frequency, I_{ij} is a PSF, I_m is the mth net observed interference function, and

$$W_{ij}(s,\omega)=\mathrm{Re}\left[\frac{c_i c_j f_i^*(s,\omega)f_j(s,\omega)}{\langle f\rangle^*\langle f\rangle}\right], \quad (2)$$

where c_i is the relative atomic concentration of species i, and $f_i(s,\omega)$ is the atomic scattering factor for species i which can be written as

$$f(s,\omega)=f_0(s)+\Delta f'(s,\omega)+i\Delta f''(s,\omega), \quad (3)$$

where i in Eq. (3) is the imaginary number $(-1)^{1/2}$. The compositional average value of f is

$$\langle f(s,\omega)\rangle=\sum_i c_i f_i(s,\omega). \quad (4)$$

The set of Eq. (1) will have a solution if the determinant of the coefficients does not vanish. To see the nature of the difficulty for the experimental conditions, suppose that each atom has an accessible absorption edge that is well separated from the other. Then, the determinant of the coefficients can be written as

$$\det = 2W_{11}(s)W_{12}(s)W_{22}(s) \times \left[\frac{\delta W_{11}(\omega_1)}{W_{11}}\frac{\delta W_{12}(\omega_1)}{W_{12}}+\frac{\delta W_{12}(\omega_1)}{W_{12}}\frac{\delta W_{22}(\omega)_2}{W_{22}} - \frac{\delta W_{11}(\omega_1)}{W_{11}}\frac{\delta W_{22}(\omega_2)}{W_{22}}\right], \quad (5)$$

where $W_{ij}(s,\omega)$ has been written as $W_{ij}(s)+\delta W_{ij}(s,\omega)$ when ω is near an absorption edge. The s dependence has been suppressed within the large parenthesis of Eq. (5). From Eq. (5), it is seen that det is second order in the variation of the W factors. From Eq. (2), $W\sim\frac{1}{4}$ while $|\delta W/W|\sim\frac{1}{10}$, so $|\det|\sim 10^{-4}$. The important point to note here is that $|\det| << W$. This circumstance is one indication that the set of equations is ill conditioned. The meaning of this statement can be seen as follows. The elements of the inverse coefficient matrix are of the order $W/\det$ which, in the above example, is about 10^3. Consequently, errors in the data can be greatly magnified in the process of forming a numerical solution. It should be emphasized that this is a spurious error that is a property of the numerical process and is not so much a matter of careful experimentation.

In general, for an N-species system,

$$|\det|\sim 4^{-N(N+1)/2}\times 10^{1-N(N+1)/2}.$$

For a ternary system, this is $\sim 10^{-9}$. In all cases, the elements of the coefficient matrix are of the same order of magnitude as given above. Consequently, the reliability of the solution set is expected to decrease rapidly as the number of scattering species increases.

The magnitude of the error in the determined partial structure factors can be expressed directly in terms of the error of the net observed interference functions. Let $M=N(N+1)/2$ and let the M-component column vector $\vec{I}_0$ be the required collection of M ideal error-free interference functions. The corresponding measured quantity $\vec{I}_x$ contains an element of error which can be expressed in terms of $\vec{I}_0$ by the relation

$$\vec{I}_x=(1+\underline{\epsilon})\vec{I}_0, \quad (6)$$

where $\underline{\epsilon}$ is the relative error matrix with M rows and M columns with elements $\epsilon_{mn}=\epsilon_m\delta_{mn}$. ($\delta_{mn}=1$ if $m=n$ and $=0$ otherwise.) For independent experiments, each ϵ_m is an independent random variable.

Likewise, the M distinct PSF can be represented by the ideal vector $\vec{P}_0$ and the experimentally determined vector $\vec{P}_x$. These vectors have the relation

$$\vec{P}_x=(1+\underline{\alpha})\vec{P}_0\ , \tag{7}$$

where $\underline{\alpha}$ is the relative-error matrix for the PSF. If the equation for the ideal vectors is written as

$$\underline{C}\vec{P}=\vec{I}_0\ , \tag{8}$$

then it follows directly that

$$\underline{\alpha}=\underline{C}^{-1}\underline{\epsilon}\,\underline{C}\ . \tag{9}$$

The matrix $\underline{\alpha}$ contains all of the information regarding the net error. The input error is contained in $\underline{\epsilon}$, and the spurious error due to possible ill conditioning is acquired through $\underline{C}^{-1}$.

A recently proposed alternative to the foregoing procedure is the use of the derivative of the intensity function obtained by a technique of frequency-modulated x-ray diffraction.[6] The significant feature of this method is that a time-dependent coherently scattered intensity can be Fourier analyzed. By examining the first harmonic of the modulation frequency, the derivative of the interference function with respect to the x-ray frequency enters the analysis. It is this species-selective derivative that is the important aspect of the anomalous dispersion method. (For this reason, this method is called, herein, the derivative method.)

The first experimental work[7] based on this anomalous dispersion technique was recently reported in a paper that should become an important reference in this field. While the partial RDF's were not determined, the Fourier transform of the energy derivatives of the scattering intensity did produce differential distribution functions (DDF) similar to RDF's. On the basis of the DDF's for amorphous GeSe and for GeSe_2, it proved possible to distinguish between two competing models for the structures of each of the two materials. This is a dramatic illustration of the potential and the importance of the anomalous dispersion methods. The present work considers how the derivative technique can contribute to the direct experimental resolution of the partial RDF and PSF components.

In particular, consider the first derivative of Eq. (8). Near the absorption edge ω_m of species i, this can be written in the form

$$\left[\frac{\partial I_m}{\partial\omega}\right]+\gamma_i I_m=\sum_j \gamma_{ij}I_{ij}\ , \tag{10}$$

where I_m is the appropriate component of $\vec{I}_0$, and

$$\gamma_i=\sum_j \gamma_{ij}\ , \tag{11}$$

$$\gamma_{ij}=\frac{2c_ic_j}{\langle f\rangle^2}\left[\frac{\partial\Delta f_i'}{\partial\omega}(f_{j0}+\Delta f_j')+\left[\frac{\partial\Delta f_i''}{\Delta\omega}\right]\Delta f_j''\right]\ . \tag{12}$$

The error relations can be obtained, as before, by writing

$$(I_m)_x=(1+\epsilon_m^{(1)})I_m$$

and

$$\left[\frac{\partial I_m}{\partial\omega}\right]_x=(1+\epsilon_m^{(2)})\left[\frac{\partial I_m}{\partial\omega}\right]\ ,$$

where the subscript x again denotes an experimental value. Then,

$$\epsilon_m^{(2)}\left[\frac{\partial I_m}{\partial\omega}\right]+\gamma_i\epsilon_m^{(1)}I_m=\sum_j \gamma_{ij}\alpha_{mj}I_{ij}\ . \tag{13}$$

Equations (9) and (13) form the basis of the discussion in the following sections.

II. SIMULATION

Equations (9) and (13) provide a means of examining quantitatively the reliability of the experimentally determined PSF. Recall that the matrix $\underline{\epsilon}$ represents the experimental error, and each of the diagonal elements of $\underline{\epsilon}$ is an independent random variable. As a consequence, $\underline{\epsilon}$ can be simulated by means of a pseudo-random-number generator. Then, given the coefficient matrix, the response error $\underline{\alpha}$ can be computed.

This method of simulation has the advantage that rather ideal conditions can be assumed in the construction of the coefficient matrix. One result of this advantage is that by repeating the procedure for many sets of random errors, it is possible to obtain a statistical estimate of the reliability of experimentally determined PSF. Another is that the response error can be considered as a continuous function of the magnitude of the anomalous dispersion effect. Thus, the question, by how much must the atomic scattering factors be changed to obtain a desired accuracy, can be answered.

For the purpose of simulation, the form of Eq. (13) is less convenient than Eq. (9) since it requires a knowledge of the ideal structure factors. However, if it is assumed that $\epsilon^{(1)}=\epsilon^{(2)}$, then it is possible to solve for α in the same form as in Eq. (9). (See Appendix.) This is not a serious approximation since the derivative term dominates the left-hand side of Eq. (13). Also, this approximation correlates the errors in such a way that the error is actually inflated in the simulated computations and, as can be seen in the following sections, this in no way detracts from the conclusions. Hence, $\epsilon^{(1)}=\epsilon^{(2)}$ is assumed in the following.

The construction of the coefficient matrix requires some discussion. It is assumed that each atom has an accessible absorption edge and that these edges are sufficiently well separated that, at most, only one edge is involved in the scattering of x rays of a given energy. Away from an edge, $\Delta f' = \Delta f''=0$ is used, and near an edge, the quantity $x=-\Delta f'(s)/f_0(s)$ is used as an independent error-free variable. For binary systems, $\Delta f''=0$ below an edge. For ternary systems, two of the three edges are used twice. It is then assumed that one experiment uses an x-ray energy below the edge and the second is above the edge. Below the edge, $\Delta f''=0$ and above the edge, $\Delta f''/\Delta f'$ is chosen to be a nonzero constant. The value of the constant is chosen by examining values of $\Delta f'$ and $\Delta f''$ in the literature.[11-13] The derivatives $\partial\Delta f'/\partial\omega$ and $\partial\Delta f''/\partial\omega$ are taken to be independent of x. For x-ray energies below an edge, $\partial\Delta f''/\partial\omega=0$. Nonzero values of the derivatives are estimated either by literature values or by means of the approximation of James.[14]

The values of the relative error matrix $\underline{\epsilon}$ are constrained such that, over many sets of values, each independent random variable is normally distributed with $\langle\epsilon\rangle=0$ and with a specified standard deviation $\sigma(\epsilon)$. It is assumed that each of the M required experiments are performed with the same accuracy. A result of this assumption is that

$$\operatorname{var}(\alpha_{KL})=\sigma^2(\epsilon)\sum_i (C_{Ki}^{-1})^2(C_{iL})^2 \;. \tag{14}$$

Since $\sigma(\lambda\epsilon)=\lambda\sigma(\epsilon)$ for a positive scale factor λ, it follows from Eq. (14) that it is sufficient to consider only one value of $\sigma(\epsilon)$. Other cases are simply scaled by the factor λ.

The analysis has been formulated in terms of relative errors and fractional changes in atomic scattering factors so that the results are essentially independent of the particular atoms that comprise the system. The relative scattering strengths are the important quantities for the determination of the response error, rather than the absolute strengths which are important for determining the input error (experimental error). This was verified by using several systems with different relative scattering strengths, as indicated in Table I.

When the response error is viewed as a function of $x=-\Delta f'(s)/f_0(s)$, the results are essentially independent of the value of s. This was verified by computations for values of s in the range $0<s<15$ Å^{-1}. Throughout this range, there were negligible differences.

III. ERROR ESTIMATION

From Eq. (9), the relative error of the Kth PSF is

$$(P_{K,X}-P_K)/P_k=\alpha_{KK}+\sum_{L\neq K}\alpha_{KL}P_L/P_K \;. \tag{15}$$

Equation (15) expresses the intuitively clear result that two very similar ideal partial structure factors are more difficult to resolve accurately than are two dissimilar PSF. Notice also that a strong scatterer (large P value) affects a weak scatterer (small P value) more significantly than vice versa,

TABLE I. Binary and ternary systems used to determine the relative-error matrix for the partial structure factors. The ratios of the atomic scattering factors at $s=0$ (rounded to the nearest whole numbers) are used as an indication of the relative scattering strengths of the atoms.

Binary		Ternary		
f_A/f_B	A-B	f_A/f_C	f_B/f_C	A-B-C
1	Cu-Ni, I-Sn, Gd-I	1	1	Ni-Fe-Cr, Gd-I-Sn
2	Sn-Mn, Sn-Cu	2	2	Gd-I-Ni, Sn-Ag-Mn
3	W-Ni, Au-Ni	3	2	W-Sn-Mn, Au-Ag-Ni

as should be expected.

According to Eq. (15), the best accuracy that should be expected for the Kth PSF is the average $|\alpha_{KK}|$. This component of the α matrix must underestimate the error since it ignores the coupling to other PSF. The detailed computations of the elements of $\underline{\alpha}$ show that, in fact, the off-diagonal elements are quite significant. Consequently, a more realistic estimate of the accuracy is given by the sum $\sum_L |\alpha_{KL}|_{\text{ave}}$, and it is this quantity that is used in the following discussion. In effect, this approximation yields results such that, for the best case, the error is worse than it should be, while for the worst case, the error is not yet as bad as it could be. Hence, the conclusions reached here are, again, understatements of the situation. This is entirely appropriate for the comparisons being made.

It should be recalled that the anomalous dispersion effect is represented by a continuous variable x. The experimentally accessible range of values is $0<x<0.3$, and for comparison the value $x=0.2$ can be used as a typical value. The computer calculations were carried out to $x=0.5$. In each case, the absolute values of the elements of the matrix $\underline{\alpha}$ were averaged over 45 replications of the simulated experiments. (Doubling the number of replications had a negligible effect on the results.) The standard deviation of the normally distributed input error was chosen to be 0.01 which corresponds to a net experimental measurement error of about 1%.

A. Binary systems

The results for the estimated relative errors for the partial structure factors of binary systems (AB) are illustrated in Fig. 1. In each case, atom A is assumed to have the larger atomic number, and with that convention, there are several observations that can be made.

(1) The error is smaller for the stronger scatterer.

(2) As the difference in the atomic numbers increases, the error curves become more widely spaced while retaining an approximately fixed centroid. In effect, the component for the stronger scatterer is determined more accurately at the expense of the weaker scatterer.

(3) The derivative results are about an order of magnitude better than the direct results.

(4) The error increases rapidly with decreasing x for the direct method and less so for the derivative technique.

(5) At $x=0.2$, the magnitude of the error is larger than might be anticipated *a priori*. For the direct method, the centroid indicates an error of

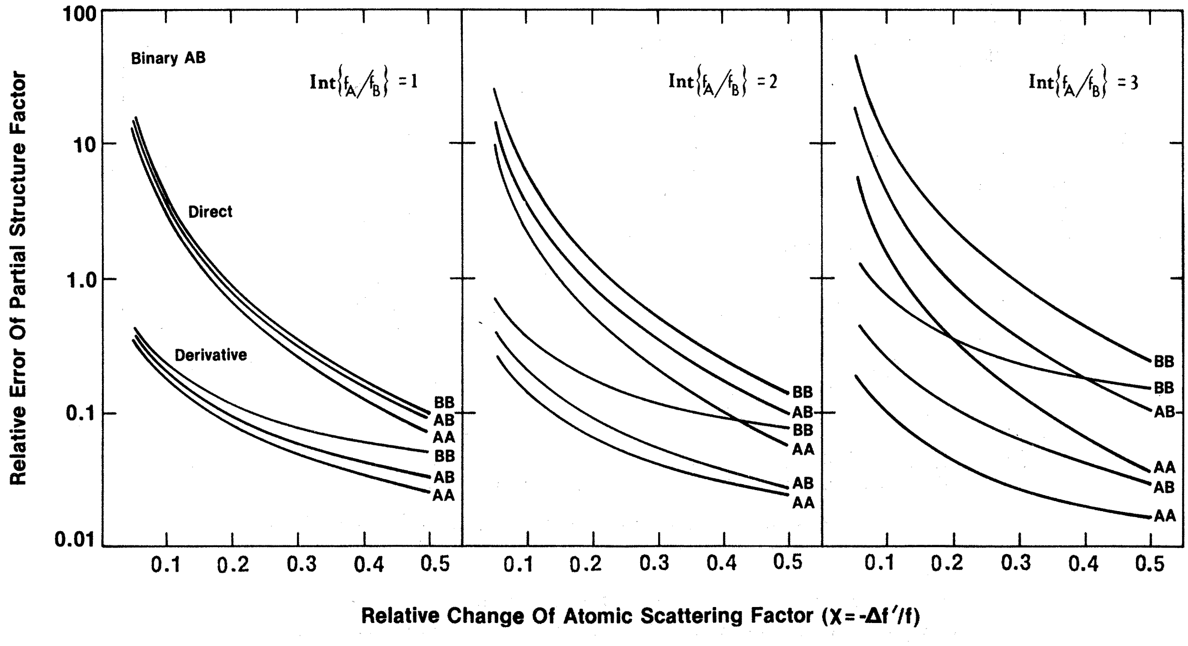

FIG. 1. Relative error of the component partial structure factors for typical binary systems AB as determined by computer simulation for input data having about 1% error, normally distributed. The system is composed of neutral atoms of equal concentrations. Three cases of relative scattering strengths are shown and are indicated by the ratios of the atomic scattering factors at $s=0$ rounded to the nearest integer. The experimentally accessible range is $0<x<0.3$.

about 80%, while for the derivative technique, it is about 8%.

B. Ternary systems

For the amorphous systems *ABC*, the results are illustrated in Fig. 2. The comments labeled (1)–(4) under binary systems apply here also. The principal difference is the larger magnitude of error. For example,

(5′) At $x = 0.2$, the centroid for the three cases occurs at about 500% error for the direct method and at about 50% for the derivative technique.

IV. CONCLUSION

The structure of a multicomponent amorphous substance can be given in terms of the component radial distribution functions which are expressed as Fourier transforms of the corresponding partial structure factors. The linear sequence of operations which relate the scattering experiment to the RDF involves several steps: data accumulation, data processing, determination of PSF, and transformation of PSF to RDF. Each step involves the generation and propagation of error. The present paper is concerned with the error resulting from the third step, and, hence, the errors from the first two steps are regarded here as input

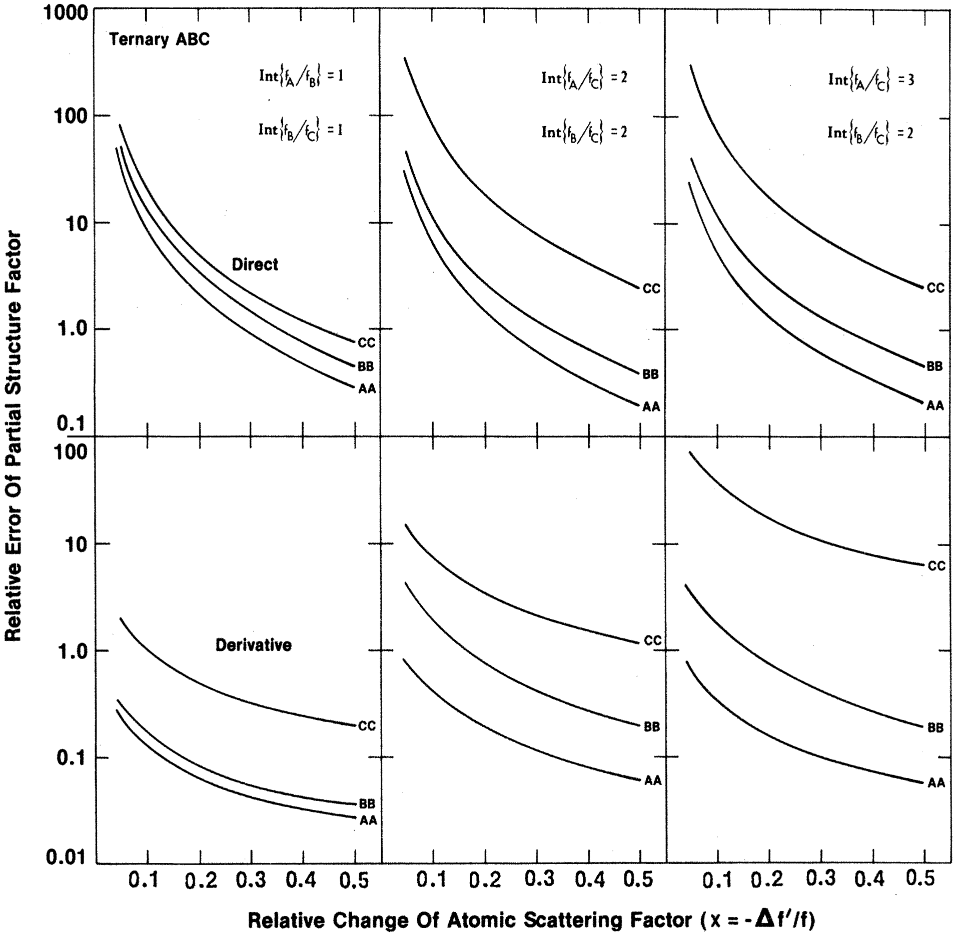

FIG. 2. Relative error of the component partial structure factors for typical ternary systems *ABC* using input data with a normally distributed random error of about 1%. Three cases of relative scattering strengths are shown. These are indicated by the ratios of the atomic scattering factors at $s = 0$ rounded to the nearest integer. Only the components *AA*, *BB*, and *CC* are shown for clarity. The components *AB*, *AC*, and *BC* occur somewhat unpredictably between the curves for *AA* and *CC*. The system is composed of neutral atoms having equal concentrations. The experimentally accessible range is $0 < x < 0.3$.

error. Incorporated into the input error are effects due to the primary beam characterization, absorption and polarization corrections, detector efficiency and counting statistics, background subtraction, matching of spectra taken over different s ranges, and normalization of the resultant interference functions to physical units. An optimistic value of 1% has been used as the net result of these contributing factors. What is not measured by the input error is the effect of the imposition of *a priori* constraints which are not readily expressed analytically. These constraints can involve qualitative characteristics of the final RDF, features of structural models, or specific quantitative information derived from other experiments. It is generally argued that the imposition of such constraints reduces the error in the results. A comparison with published RDF works in which such constraints have been used suggests that as much as a factor-of-2 reduction in the response error can result from their use, and possibly more than a factor of 2 with a derivative technique.

For a simulated input error of about 1%, the results given in Figs. 1 and 2 indicate that a very large amplification of the error can occur in the determination of the component PSF. Most apparent in the figures is the improvement that can be obtained by the derivative technique that has recently been proposed.[6,7] This method appears to be more accurate, does not require very large changes in the atomic scattering factors, and achieves for ternary systems an accuracy comparable to that of the direct method when it is used for binary systems.

The numbers seen in Figs. 1 and 2 are rather large and need to be put into their proper perspective. The response error refers to the amplitudes of the partial structure factors, and this, in turn, determines the uncertainty in the RDF amplitudes. In the simplest case, the two uncertainties would be the same. Large errors in amplitude, as is well known, destroy the possibility of determining coordination numbers. The important question that needs to be considered here is how the uncertainties in the nearest-neighbor distances are affected by the uncertainties in amplitudes. This relationship can be estimated rather easily.

Consider a curve, as in Fig. 3, with a peak at point P. If the y coordinate is uncertain by an amount δy, P could actually be as low as P'. Likewise, points another δy below P' could be as high as P'. Consequently, the uncertainty δx in the x coordinate is not worse than $(x_B - x_A)/2$ and not better than $(x_D - x_C)/2$. Using $(x_B - x_A)/2$ as the worst case, it is easy to see that

$$\delta x = (4 y_P / |d^2 y/dx^2|_{x=x_P})^{1/2} \alpha^{1/2} , \qquad (16)$$

where $\delta y = \alpha y_P$ has been used.

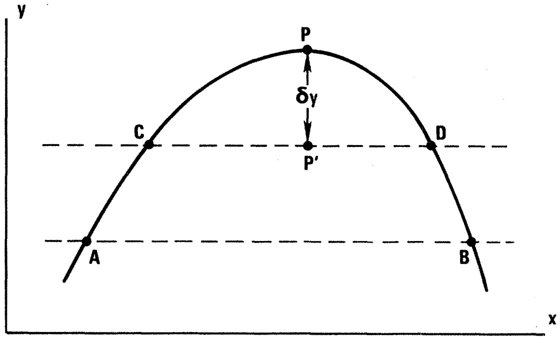

FIG. 3. Diagram to estimate the uncertainty in x given the uncertainty δy in y.

The coefficient of $\alpha^{1/2}$ in relation (16) can be estimated by examining published RDF's of monatomic materials for which there are not partial components to decouple. The coefficient is found to vary by only a small amount from one material to another. For example, for Hg at 25 °C the coefficient is about 0.52, while for Pb at 600 °C it is about 0.66. Hence, for a rough estimation an average value of 0.6 has been used for Fig. 4.

As an example, consider the 80% response error for a fixed-frequency experiment on a binary system. From Fig. 4, this would yield about 17% uncertainty in the nearest-neighbor distance. If a factor of 2 is allowed for nonanalytic constraints, the uncertainty in distance is reduced to about 12%. These numbers are to be compared to the corre-

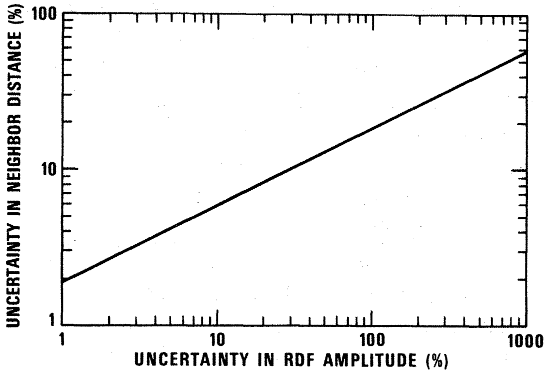

FIG. 4. Estimated relation between the uncertainty (in %) of neighbor distance and the uncertainty in amplitude, based on Fig. 3 and published RDF curves of monatomic materials.

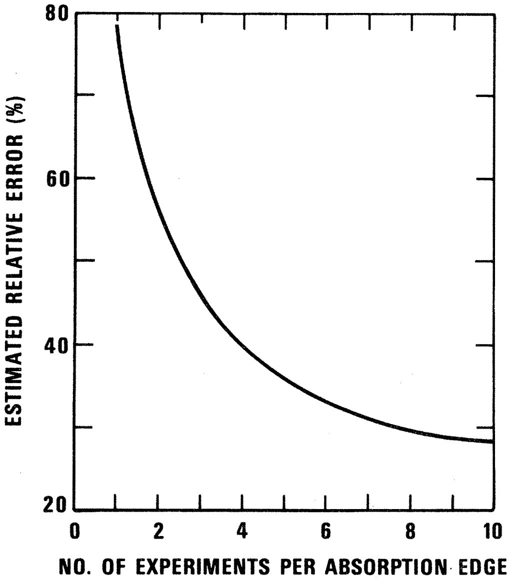

FIG. 5. Example of the fixed-frequency response error for a binary system as a function of the number of experiments performed at each absorption edge.

sponding results for the 8% response error of the derivative technique. In the latter case, the uncertainty in distance is about 4%−5%.

If the nearest-neighbor distance is desired as a function of temperature or pressure, then it is desirable to have an uncertainty that is smaller than the variation that is to be measured. Clearly, the results of the derivative technique become very attractive for this purpose. With an uncertainty as large as 5%, it would still be feasible to perform meaningful experiments at high pressure.

Another question that could be asked is what improvement in the fixed-frequency technique would result if more than one set of experiments could be used. This can be simulated as before, and the case of 80% response error is shown in Fig. 5 as an example. The plot of response error versus number of experiments (N) at each absorption edge shows an error decreasing by approximately a factor $N^{-1/2}$. Consequently, four sets of experiments at each edge could reduce the error by about $\frac{1}{2}$. Adding to this another factor $\frac{1}{2}$ for nonanalytic constraints would reduce the 80% error to 20%, and from Fig. 4, the uncertainty in the nearest-neighbor distance would be reduced to about 9%. This is still twice the error of the derivative technique.

Perhaps as a final remark it should be emphasized again that the present work relates to the determination of partial RDF and PSF components without *a priori* subjective interpretations of the measured quantities. Prior to the derivative technique, such direct unbiased determinations could not be found to be of much value. While subjective interpretations will always be important, the exciting aspect of the derivative technique is that it becomes possible to resolve ambiguities in structural models directly[7] and even to determine the PSF directly with useful accuracy.

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APPENDIX

The relative-error matrix for the derivative method can be put into the form of Eq. (9) as in the following example for a binary system. With reference to Eqs. (6)−(13), we can write

$$\left[\frac{\partial I}{\partial \omega}\right]_1+\gamma_1 I_1=\gamma_{11}P_1+\gamma_{12}P_2\,, \tag{A1}$$

$$\left[\frac{\partial I}{\partial \omega}\right]_2+\gamma_2 I_2=\gamma_{21}P_2+\gamma_{22}P_3\,, \tag{A2}$$

$$I_3=C_{31}P_1+C_{32}P_2+C_{33}P_3\;. \tag{A3}$$

With the following definitions, we have

$$\left[\frac{\partial I}{\partial \omega}\right]_3\equiv 0,\quad \gamma_3\equiv 1\,, \tag{A4}$$

$$Q_k\equiv\left[\frac{\partial I}{\partial \omega}\right]_k+\gamma_k I_k\,, \tag{A5}$$

$$\vec{Q}=\begin{bmatrix}\gamma_{11} & \gamma_{12} & 0\\ 0 & \gamma_{21} & \gamma_{22}\\ C_{31} & C_{32} & C_{33}\end{bmatrix}\begin{bmatrix}P_1\\ P_2\\ P_3\end{bmatrix}=\underline{C}\vec{P}\;. \tag{A6}$$

We can also write

$$Q=\left[\frac{\partial I}{\partial \omega}\right]+\vec{\gamma} I\,, \tag{A7}$$

$$\left[\frac{\partial I}{\partial \omega}\right]_x=(1+\underline{\epsilon}^{(1)})\left[\frac{\partial I}{\partial \omega}\right]_0\,, \tag{A8}$$

$$(\vec{\gamma} I)_x=(1+\underline{\epsilon}^{(2)})(\gamma I)_0\,, \tag{A9}$$

$$\vec{P}_x=(1+\underline{\alpha})\vec{P}_0\;. \tag{A10}$$

Upon setting $\underline{\epsilon}^{(1)}=\underline{\epsilon}^{(2)}=\underline{\epsilon}$, there follows from substitution

$$\underline{\alpha}=\underline{C}^{-1}\underline{\epsilon}\,\underline{C}\,, \tag{A11}$$

which is the same form as Eq. (9).

[1] H. P. Klug and L. E. Alexander, *X-ray Diffraction Procedures* (Wiley, New York, 1974), pp. 791 ff.

[2] C. N. J. Wagner, in *Liquid Metals,* edited by S. Z. Beer (Dekker, New York, 1972), pp. 257 ff.

[3] R. F. Kruh, Chem. Rev. 62, 319 (1962).

[4] J. Krogh-Moe, Acta. Chem. Scand. 20, 2890 (1966).

[5] T. G. Ramesh and S. Ramaseshan, J. Phys. C 4, 3029 (1971).

[6] N. J. Shevchik, Philos. Mag. 35, 805 (1977); 35, 1289 (1977).

[7] P. H. Fuoss, P. Eisenberger, W. K. Warburton, and A. Bienenstock, Phys. Rev. Lett. 46, 1537 (1981).

[8] A. Bienenstock, IEEE Trans. Nucl. Sci. 26, 3780 (1979).

[9] Y. Waseda and S. Tamaki, Philos. Mag. 32, 951 (1975).

[10] Y. Waseda and S. Tamaki, Commun. Phys. 1, 3 (1976).

[11] D. T. Cromer, Acta. Crystallogr. 18, 17 (1965).

[12] D. T. Cromer and D. Liberman, J. Chem. Phys. 53, 1891 (1970).

[13] D. T. Cromer, Acta. Crystallogr. A 32, 339 (1976).

[14] R. W. James, *The Optical Principles of the Diffraction of X-rays* (Cornell University, Ithaca, 1965).