

exponentials and the displacement distribution functions are not known. Also, the geometric growth in the number of terms in the Taylor expansion severely restricts the order to which this expansion can be successfully applied to real diffraction data. Therefore, when the displacements are large, the Taylor expansion must be abandoned in favour of methods based on direct simulation of the defects or perhaps other (nonlinear) descriptions of the diffuse intensity, for instance one based on a cumulant expansion of the exponential.

The displacement correlation parameters that arise naturally in the Taylor-expansion description should not be forgotten entirely even in such instances, because these parameters are convenient to use in the *qualitative* description of displacement disorder and can thus aid understanding of the origins of many diffuse features. For example, the Warren size-effect intensity contains parameters that describe the deviations of pair distances from the long-range average and give rise to an easily interpreted diffuse asymmetry. The forms of the displacement correlation parameters associated with the intensity I_2 have also recently been used to describe successfully the diffuse absences that are evident in some diffraction patterns, such as those present in the diffraction image of Fig. 1(a) (Butler, Withers & Welberry, 1992).

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script. The diffuse-scattering images of Figs. 1(a) and (d) were computed on a Fujitsu VP-2200 supercomputer using a grant from the Australian National University Supercomputer Facility.

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Modulated Anomalous X-ray Scattering*

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Abstract

To determine the partial structure associated with a particular element in a multicomponent system, contrast variation is proposed based on the use of modulated anomalous X-ray scattering (MAXS).

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The photon energy of the X-ray beam incident on the sample is modulated over a range of energies below an absorption edge of the selected element. Because of anomalous dispersion, measurement of the scattered-intensity gradient with respect to the energy gives the required information. MAXS can be used in both small-angle and wide-angle diffraction and is applicable, in principle, to crystalline, amorphous and liquid materials. Energy modulation obtained by oscillating the Bragg angle of the monochromator by a small amount, followed by phase-sensitive detection, leads to a significant reduction of both systematic and statistical errors. Results of a

simulation study of MAXS from an aqueous solution of NiCl_2 under extreme conditions of dilution and scattering contrast are presented.

I. Introduction

Diffraction experiments are effective in probing the microscopic nature of the short- and intermediate-range order in disordered materials. A single diffraction experiment yields a *total structure factor*, $S(Q)$; in a sample containing n different elements, $S(Q)$ is expressed in terms of $n(n+1)/2$ distinct *partial structure factors*, $S_{\alpha\beta}(Q)$, each weighted by the appropriate contrast. These partial structure factors contain crucial information needed to fully resolve the structure. Similar methods may be used for crystalline materials where conventional reciprocal-space methods, such as profile-refinement analysis, are inapplicable or inadequate.

Contrast-variation methods such as isomorphous replacement, isotopic substitution, magnetic scattering and anomalous dispersion can be used to derive directly the partial structure factors. Excellent reviews have been written of the first two methods (Soper, Neilson, Enderby & Howe, 1977; Skipper, Neilson & Cummings, 1989). We focus our attention on the X-ray anomalous-dispersion method, in which the atomic scattering factor of a single element A in the sample is varied by changing the incident photon energy near an absorption edge of the element. In this way, the *environmental structure factor*, $S_A(Q)$, associated with element A , consisting of a weighted sum of the $S_{A\beta}(Q)$ for different β 's, can be determined. The distinct $S_{AB}(Q)$ can then be derived from a combination of several such measurements.

A standard approach to the determination of $S_A(Q)$ (Fuoss, Eisenberger, Warburton & Bienenstock, 1981) has been to conduct two experiments under monochromatic conditions, each at a different energy near the absorption edge. The first-order intensity difference yields the scattering caused by interactions with the chosen element. Gradient methods that combine three or more monochromatic experiments (Munro, 1982; Ludwig, Warburton, Wilson & Bienenstock, 1987; Jemian, Weertman, Long & Spal, 1990; Jemian, Weertman & Long, 1993) have been shown to reduce the systematic errors. Further improvements can be achieved if the incident photon energy is modulated in a periodic fashion just below the absorption edge; the derivative of the scattered intensity with respect to time is then dominated by contributions from the selected element (Cardona, 1969; Shevchik, 1977) owing to the anomalous dispersion. This method, referred to as *modulated anomalous X-ray scattering* (MAXS), has the advantage that partial structure information can be derived from a single experiment.

A schematic of the MAXS experimental set-up is shown in Fig. 1. A synchrotron X-ray source (a) generates a beam with a broad spectrum of photon energies, from which the monochromator (b) selects a narrow band. When the Bragg angle of the monochromator crystals is varied using a piezoelectric device, the energy is modulated with time in a periodic fashion. Owing to anomalous-dispersion effects, the atomic scattering factors of the elements in the sample (c) change with the photon energy. The modulated scattered intensity is registered on a detector (d) that is phase locked to the modulation of the monochromator.

The object of the present work was to obtain numerical estimates for counting times and environmental parameters needed to provide the required precision in $S_A(Q)$ in a specific situation. The case chosen was the measurement of $S_{\text{Ni}}(Q)$ in a one molal (1 m) sample of NiCl_2 in H_2O , a situation for which data are available from neutron diffraction with isotope substitution. Computer simulation was used to obtain the numerical estimates and explore the effects of changes in the various parameters. Other practical aspects of the use of the technique are also considered.

II. Theory

An X-ray diffraction experiment using a single incident photon energy provides information about the local environment around the average atom in a sample. The scattered intensity, $I(Q, E)$, is a weighted sum of the constituent partial structure factors:

$$I(Q, E) = \sum_{\alpha} c_{\alpha} |f_{\alpha}(Q, E)|^2 + \sum_{\alpha} \sum_{\beta} c_{\alpha} c_{\beta} f_{\alpha}(Q, E) f_{\beta}^*(Q, E) [S_{\alpha\beta}(Q) - 1], \quad (1)$$

where $Q = (4\pi/\lambda)\sin\theta$; 2θ is the scattering angle; λ and E are the wavelength and energy of the incident photons, respectively; c_{α} and $f_{\alpha}(Q, E)$ are the concentration and scattering factor of atom α , respectively; $S_{\alpha\beta}(Q)$ is the partial structure factor of the (α, β) atom pair. In general, three terms comprise the atomic scattering factor:

$$f(Q, E) = f_0(Q) + f'(E) + if''(E). \quad (2)$$

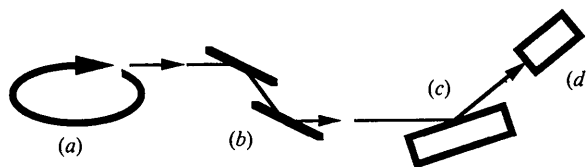


Fig. 1. Schematic for MAXS experiments: (a) X-ray synchrotron; (b) monochromator; (c) sample; (d) constant- Q detector with ms resolution.

Here, $f_0(Q)$ is the limiting form at high energy (Cromer & Mann, 1967) and $f'(E)$ and $f''(E)$ are the anomalous-dispersion corrections, which can be significant even for photon energies far removed from the vicinities of absorption edges. Thus, it is necessary to consider f' and f'' for all elements in the system.

Gradient information about the local atomic environment of one of the elements, A , can be obtained by contrast-variation methods. With MAXS (Shevchik, 1977), the incident photon energy is modulated near an absorption edge of A as a function of time at frequency ω_0 :

$$f'_A(E) \approx g_b \ln |1 - (E/E_b)|, \quad (3)$$

where g_b is the oscillator strength (James, 1965) of the core electron and E_b is the absorption-edge energy. [A relativistic quantum-mechanical method for calculating f' and f'' has been given elsewhere (Cromer & Liberman, 1970).] When the energy range of modulation is kept just below the absorption edge, $f''(E)$ is relatively small and independent of E . Modulation of the photon energy incident on the sample produces a modulation of $f_A(Q, E)$, for example:

$$f_A[Q, E(t)] = \bar{f}_A(Q) + \Delta f_A \sin(\omega_0 t), \quad (4)$$

where $\bar{f}_A(Q)$ is the mean atomic scattering factor and Δf_A is the amplitude of the scattering-factor modulation. Consequently, the scattered intensity will also be modulated, with amplitude ΔI , which can be calculated as follows:

$$\text{corr}(I, \omega_0) \equiv \int_0^\infty I[Q, E(t)] \sin(\omega_0 t) dt. \quad (5)$$

All frequency components in $I[Q, E(t)]$ other than ω_0 give a vanishing contribution to (5). This includes all of the partial structure factors of elements other than A and most of the Compton-scattering background. Replacement of the upper limit of integration with N periods of equal length, $\tau_0 = 2\pi/\omega_0$, gives

$$\text{corr}_N(I, \omega_0) = N\tau_0 \Delta I / 2 + \sum_{i=1}^N R_i(\omega_0), \quad (6)$$

where $R_i(\omega_0)$ is the amplitude of noise for the i th period at ω_0 . For random noise and large N , the first term in (6) becomes dominant.

An *environmental* structure factor around A can be defined by

$$S_A = \sum_{\beta} c_{\beta} \Re(f_{\beta} S_{A\beta}) / \sum_{\beta} c_{\beta} \Re(f_{\beta}). \quad (7)$$

The amplitude modulation is given to the first order, assuming $\Delta f'_A = 0$ and $\Delta f_{\beta} = 0$ ($\beta \neq A$), by

$$\Delta I = \Delta f_A \left. \frac{\partial I}{\partial f_A} \right|_{Q, f_{\beta}}, \quad (8)$$

Table 1. Atomic fractions, c_{α} , and scattering factors, $f_{\alpha}(Q=0)$, of a 1 molal aqueous NiCl_2 solution

α	H	O	Cl^-	Ni^{2+}
c_{α}	0.6549	0.3273	0.0118	0.0059
$f_{\alpha}(Q=0)$	1	8	18	26

with

$$\left. \frac{\partial I}{\partial f_A} \right|_{Q, f_{\beta}} = 2c_A \left\{ \Re(f_A) + \sum_{\beta} c_{\beta} [\Re(f_{\beta}^* S_{A\beta}) - \Re(f_{\beta})] \right\}. \quad (9)$$

With the above approximations, the intensity gradient is constant over the modulation range of the experiment. S_A is then derived as

$$S_A = 1 + \{[\Delta I - 2c_A \Delta f_A \Re(\bar{f}_A)] / 2c_A \Delta f_A \Re(\langle f \rangle)\}, \quad (10)$$

where $\langle f \rangle = \sum_{\alpha} c_{\alpha} f_{\alpha}$.

The convergence of the mathematical correlation is demonstrated by (6). If S_A^N is the estimate resulting from N iterations and S_A is the limiting value as $V \rightarrow \infty$, then, from (6) and (10),

$$S_A^N \rightarrow S_A + (\text{noise}/N). \quad (11)$$

Further extension of this technique to second-order terms, *i.e.* measurement of S_A for different $\{f_{\beta}\}$, can provide estimates of the $S_{A\beta}$.

III. Simulation

A computer simulation of MAXS can answer some practical questions about its feasibility. Three issues will be addressed: (1) the number of modulation periods required to achieve a specified precision in S_A for a given Δf_A ; (2) the minimum practical Δf_A for a MAXS experiment; and (3) the effect of the source intensity on the number of periods required.

Simulations were carried out for the case of an X-ray diffraction experiment from a very dilute sample, 1 mol kg^{-1} of NiCl_2 in H_2O , at photon energies near the nickel K -absorption edge. The relevant atomic fractions and the scattering factors are given in Table 1. This system was chosen because: (1) the partial structure factors have been measured by neutron diffraction using isotropic substitution (Neilson & Enderby, 1978; Soper & Phillips, 1986; Enderby *et al.*, 1987; Skipper *et al.*, 1989); (2) the extreme dilution is a challenging test of the limits of applicability of MAXS; (3) it will allow comparison between the neutron and X-ray precisions in yielding partial structure factors.

The intensity was calculated from (1) and (4) for a time-channel width $\Delta = 1$ ms with a modulation period $\tau_0 = 100$ ms and scaled for a typical incident

intensity I_0 , detector solid angle Ω and instrumental efficiency ε . Gaussian noise of zero mean and $I^{1/2}$ standard deviation was added to the data. Shown in Fig. 2 are several periods of the calculated intensity for $\Delta f_{\text{Ni}} = 0.26$ e.u. (1 e.u. = $4.184 \text{ J K}^{-1} \text{ mol}^{-1}$).

The nickel environmental structure factor, S_{Ni} , is given by

$$S_{\text{Ni}} = AS_{\text{NiH}} + BS_{\text{NiO}} + CS_{\text{NiCl}} + DS_{\text{NiNi}}, \quad (12)$$

where the weighting factors are

$$\begin{aligned} A &= c_{\text{H}}f_{\text{H}}/\langle f \rangle, & B &= c_{\text{O}}f_{\text{O}}/\langle f \rangle, & C &= c_{\text{Cl}}f_{\text{Cl}}/\langle f \rangle, \\ D &= c_{\text{Ni}}f_{\text{Ni}}/\langle f \rangle. \end{aligned} \quad (13)$$

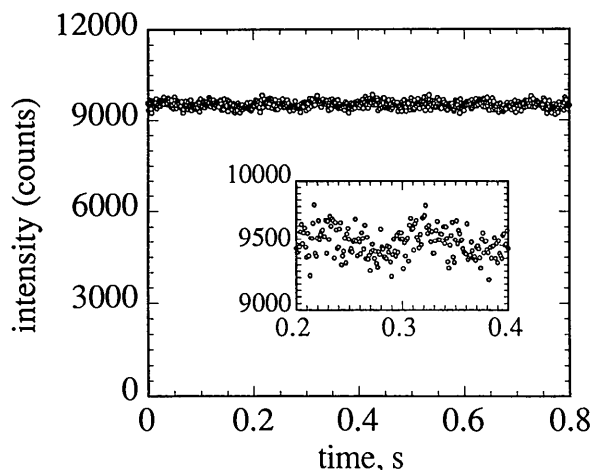


Fig. 2. Simulated time dependence of the modulated intensity, $I(t)$, of a 1 molal aqueous NiCl_2 solution. The inset figure enlarges the time and intensity scales for several periods. Here, $I_0 = 10^{11}$ photons, $Q = 3.4 \text{ \AA}^{-1}$, $\Delta f_{\text{Ni}} = 0.26$ e.u., $\Omega = 10^{-5}$ sr, $\varepsilon = 100\%$, $\tau_0 = 0.1$ s and $\Delta t = 0.001$ s.

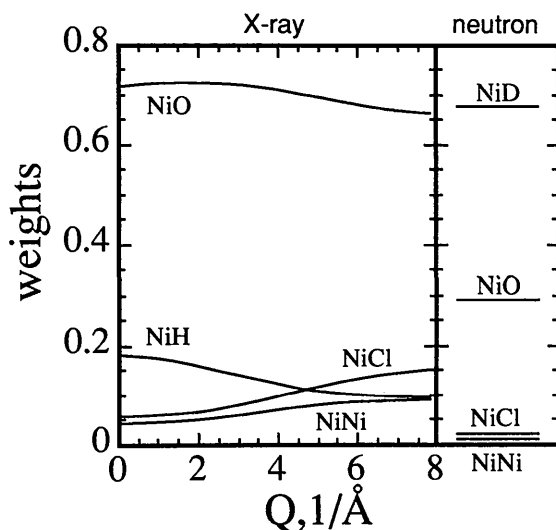


Fig. 3. Weighting of the partial structure factors contributing to the nickel environmental structure factor, S_{Ni} , for X-rays (Q dependent) and neutrons (Q independent).

The weighting factors calculated for both X-rays and neutrons are plotted in Fig. 3 as functions of Q . For X-rays, the NiO partial structure factor dominates S_{Ni} , while for neutrons both NiD (deuterium) and NiO partial structure factors are important. Thus, a MAXS experiment near the Ni K edge will yield information mainly on S_{NiO} .

A plot of S_{Ni}^N versus N is reproduced in Fig. 4(a) for $Q = 3.4 \text{ \AA}^{-1}$. As illustrated in Fig. 4(b), the effect of random noise on the correlation diminishes as $1/N$. In our calculations, convergence was accepted when the standard deviation of the 30 most recent S_{Ni}^N had fallen below 0.002 for 40 consecutive periods. In the figure shown, 221 periods, corresponding to a measurement time of ~ 22 s, were needed to achieve a satisfactory convergence.

Fig. 5 gives the number of periods, N_c , required for convergence of S_{Ni}^N to ± 0.002 at $Q = 3.4 \text{ \AA}^{-1}$ as a function of Δf_{Ni} . Five repetitions were made at each Δf_{Ni} to improve the statistical estimates. Empirically, $N \propto (\Delta f_{\text{Ni}})^{-2/3}$. For $N_c = 300$ periods

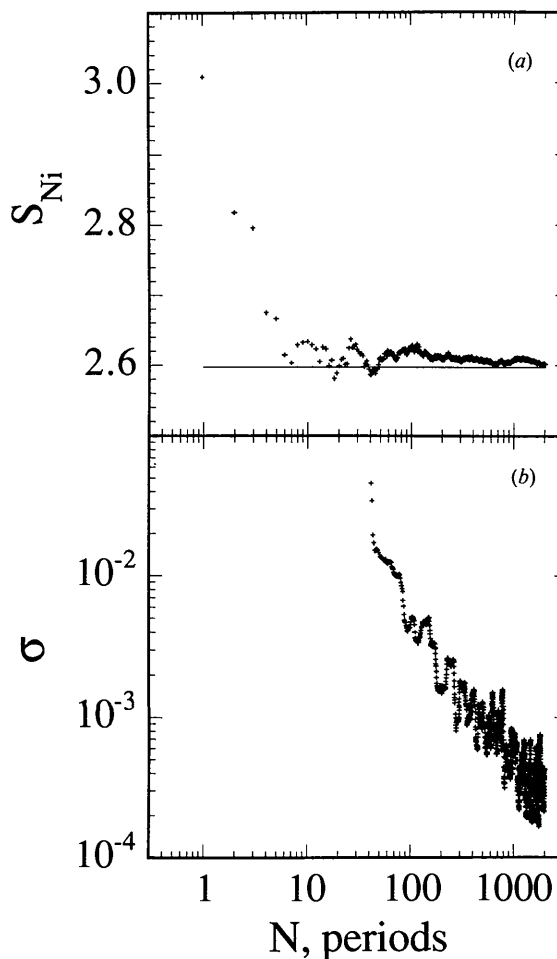


Fig. 4. Convergence of the environmental structure factor as a function of the number of periods of integration, N , at $Q = 3.4 \text{ \AA}^{-1}$. (a) S_{Ni}^N , $- S_{\text{Ni}}$. (b) $+ \text{e.s.d. of } S_{\text{Ni}}^N$, denoted by σ .

(30 s), it can be seen that the amplitude of Δf_{Ni} must be between about 0.4 and 0.7 e.u. to give convergence.

Fig. 6 shows a plot of N_c as a function of $I_0\Omega\varepsilon$ for $\Delta f_{\text{Ni}} = 0.26$ e.u. Four repetitions were made at each $I_0\Omega\varepsilon$ to account for the use of the random-number generator. Empirically, $N_c \propto (I_0\Omega\varepsilon)^{-1/3}$. It is found that $I_0\Omega\varepsilon$ must be 10^5 counts or greater for convergence to be reached in 300 periods. Consequently,

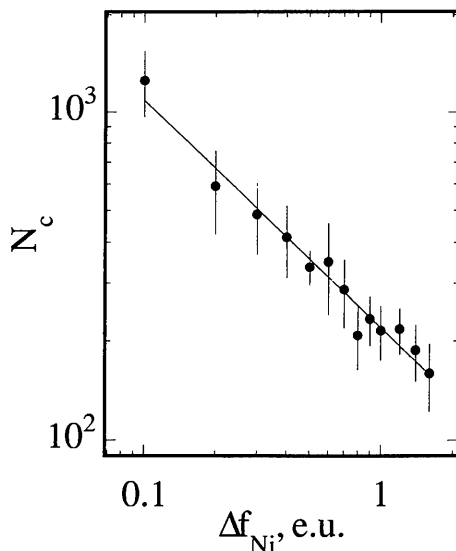


Fig. 5. Number of periods required for convergence, N_c , of S_{Ni}^N to ± 0.002 at $Q = 3.4 \text{ \AA}^{-1}$ as a function of the amplitude of the scattering-factor modulation, f_A .

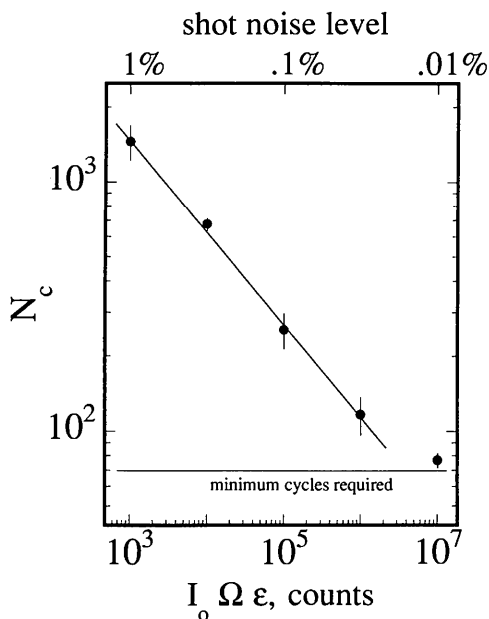


Fig. 6. Number of periods required for convergence, N_c , of S_{Ni}^N to ± 0.002 at $Q = 3.4 \text{ \AA}^{-1}$ as a function of the product of incident intensity, detector solid angle and instrumental efficiency, $I_0\Omega\varepsilon$.

an incident intensity of 10^{10} photons per data point (10^{13} counts s^{-1}) is required, assuming an instrument efficiency of 100% and $\Omega = 10^{-5}$ sr.

The calculated S_{Ni} as a function of Q is shown in Fig. 7. The product $I_0\Omega\varepsilon$ was set to 10^3 , corresponding to a shot-noise level of 1% at $Q = 3.4 \text{ \AA}^{-1}$, $N = 300$ periods and $\Delta f_{\text{Ni}} = 0.26$ e.u. The points correspond to the MAXS simulation while the solid line marks the exact values. The agreement is quite satisfactory at the ± 0.01 level.

IV. Discussion

MAXS has been shown to be capable of isolating the scattering associated with an element in solution, even when the dilution is extreme. A potential source of difficulty is that the maximum accessible value of Q is determined by the energy of the absorption edge. Thus, in cases of amorphous systems where values of $Q_{\text{max}} \geq 12 \text{ \AA}^{-1}$ are required, elements lighter than selenium for the K edges and lighter than gold for the L_{III} edges) could still be studied but with lower spatial resolution. The finite energy bandpass of the X-ray optical elements affects the selection of the photon energies for anomalous scattering experiments. For a double-crystal monochromator at an X-ray synchrotron, the intensity in the tails of the photon energy spectrum at energy E_s is proportional to $1/(E - E_s)^4$. Fluorescence is eliminated by using phonon energies below the absorption edge. The incident photon energy E should be allowed no closer to E_b than two or three monochromator resolution elements, which represents a compromise between maximization of the possible variation in $f_A(E)$, on the one hand, and minimization of the resonant Raman scattering (RRS), which occurs with

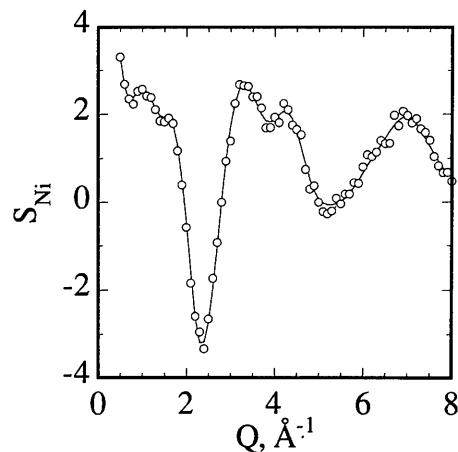


Fig. 7. Comparison of exact and simulated environmental structure factors resulting from phase-sensitive detection of $I(t)$ and mathematical correlation with $\sin(\omega_0 t)$. \circ S_{Ni}^N , where $N = 300$ periods; — exact S_{Ni} .

incident energies near and below the absorption edge, and avoidance of fluorescence from the high-energy tail of the incident energy spectrum, on the other hand. The photon energy farthest from the edge is a compromise between obtaining the maximum difference in $f'_A(E)$ and minimizing of the variation in the scattering factors of all the other elements in the system. For the K edges of the $3d$ transition metals, these two energies can be as far apart as 200 eV.

Monochromator resolution, $\Delta E/E$, is important for precise definition of the f'_A as a function of energy. From (3), it can be seen that the gradient df'_A/dE is strongest at energies near E_b . However, the singularity of (3) is broadened by the lifetime of the core hole to the order of a few electronvolts. The core-hole lifetime also limits the depth of the $f'(E)$ well. For K electrons, the maximum depth of the well is approximately $Z/3$, where Z is the atomic number. The *absolute* precision in the determination of f'_A is about 0.3 e.u. for nickel near the K edge (8333 eV). The *relative* precision that can be measured for two different f'_A near the same absorption edge is about three times smaller than the absolute precision (0.1 e.u.). From Fig. 5, it is seen that, even when $\Delta f_{\text{Ni}} \approx 0.1$ e.u., convergence of S_{Ni}^N at the ± 0.002 level is obtained. In (1), the atomic fraction and the atomic scattering factor appear as a product, $c_{\alpha}f_{\alpha}$, so that the arguments about the dependence on c_{Ni} of the number of cycles to convergence are similar to those for Δf_{Ni} . The atomic fraction of nickel in the aqueous solution is 0.0059, which, when taken together with $\Delta f_{\text{Ni}} \approx 0.1$ e.u., represents an extreme lower bound to the range of concentrations and contrasts possible in a MAXS experiment.

An upper limit on the required energy resolution of the monochromator can be gauged from the $\Delta f'_A$ precision given above. The energy resolution at the ± 0.1 e.u. level for the Ni K edge is $\Delta E/E \approx 0.00025$. With respect to monochromators using perfect single crystals as optical elements, the energy resolution of the 111 reflection from silicon is approximately 0.00015, sufficient to achieve the desired resolution of f'_A . In comparison, the energy resolution of the Ge111 reflection is about 0.00031. Furthermore, germanium optics are restricted to the energy range below the Ge K -absorption edge (11 103 eV), owing to fluorescence. A consequence of the fine $\Delta E/E$ required for the precision of scattering factors is that $\Delta Q/Q$, which is comparable to $\Delta E/E$, is much greater than the values required to obtain reliable structural information from liquid and amorphous systems. However, it may be useful in crystal materials.

The monochromator is the critical piece of experimental equipment required to enable time-modulated anomalous-dispersion experiments. The requisite photon-energy modulation, on the order of 1%, is well beyond the elastic strain limit for crystal optics.

Thus, it is not possible to adjust the crystal d spacing using mechanical or thermal strain. Only a mechanical oscillation of the Bragg angle of the diffracting planes will produce the desired energy range. If the energy range is moderate ($\leq 1\%$), piezoelectric transducers can be used to provide the necessary motion. An example of such a two-crystal monochromator where the modulation frequency is in the MHz-to-GHz range has been demonstrated for neutron diffraction at a reactor source (Bakshi, 1990). The exact waveform of the scattering-factor modulation is arbitrary and may be chosen for the convenience of the monochromator design. Factors influencing the selection of the frequency of photon-energy modulation, ω_0 , are the frequency of slow drifts in the experiment, source instabilities, microphonics and the electrical supply frequency.

In MAXS, the momentum transfer Q varies as the photon energy is modulated when the detector is at a fixed single scattering angle 2θ . The condition of constant Q must be maintained at the detector, especially in the case of diffraction from ordered or partially ordered materials, to avoid correlating the effects of the Q dependence of the scattering. The 2θ position must be corrected to maintain this condition, either in real time by using a position-sensitive detector and coupling the detector 2θ calibration to the monochromator Bragg-angle oscillation in a phase-locked loop or during the analysis stage by applying the appropriate numerical corrections.

The correlation given in (5) removes all terms independent of f'_A , including parasitic background and most of the Compton scattering as well as elastic scattering, fluorescence and RRS unrelated to the element A . The energy dependence of the Compton scattering is relatively weak and can be calculated if necessary. As discussed above, fluorescence associated with element A is avoided by choosing photon energies just below the absorption edge. The RRS associated with element A remains and must be corrected for. This requires energy analysis of the scattered beam, which in principle can be done in two ways. A crystal analyzer can be placed in the scattered beam and modulated in phase with the monochromator to select out the elastic scattering. To discriminate against the $K\beta$ as well as the $K\alpha$ RRS, the energy resolution of the analyzer must be comparable to that of the monochromator, requiring high collimation of the scattered beam and considerable loss in intensity. A more practical solution is to follow the method used in previous anomalous X-ray scattering studies (*e.g.* Ludwig, 1986), incorporating an energy-sensitive photon detector. In this case, the energy resolution is usually adequate to resolve the $K\alpha$, but not the $K\beta$, RRS. Because the $K\alpha:K\beta$ intensity ratio is rather insensitive to incident photon energy, the ratio can be measured in an ancillary scan at an energy away from the absorption

edge. The $K\alpha$ signal measured and $K\beta$ signal thus inferred can then be subtracted from the MAXS data.

Finally, the measured difference signal must be related to the ΔI of (10) in absolute terms by appropriate normalization. This requires, in effect, a determination of the intensity factor $I_0\Omega\varepsilon$ at the energy of the MAXS measurement, which has been taken as a given quantity for the computer simulations. This factor can be obtained by recording the total signal as a function of Q at some energy E_r within the modulation range and applying the usual normalization conditions to the derived $I(Q, E_r)$ [(1)]. We again follow previous workers (Fuoss, 1980; Ludwig, 1986) and adopt either the Krogh-Moe normalization condition (Norman, 1957), which requires that the pair distribution functions $g_{\alpha\beta}(r)$ are zero at small r , or the condition that $I(Q, E_r)$ oscillates about the self-scattering term $\sum_{\alpha} c_{\alpha} |f_{\alpha}(Q, E)|^2$ at large r . It has been assumed in this paper that $I_0\Omega\varepsilon$ is constant over the limited range of photon energy used in the modulation. However, this assumption can be checked by applying the normalization condition at several values of E_r and any small variations in the normalization constant can be allowed for by applying an appropriate correction in the correlation calculation, (5).

V. Concluding remarks

Information about the local atomic environment of a single element in a multicomponent material can be obtained from a single MAXS experiment. An advantage of MAXS is that most of the experimental background present in single-wavelength X-ray diffraction experiments is removed by the mathematical correlation.

A MAXS experiment has been simulated for scattering from a 1 molal aqueous NiCl_2 solution, an extreme case of dilution and low contrast for anomalous scattering, near the Ni K -absorption edge. The results show that the nickel environmental structure factor, S_{Ni} , can be reconstructed at the rate of *circa* 30 s per Q value, given a scattering-factor modulation amplitude $\Delta f_{\text{Ni}} = 0.26$ e.u. with $I_0\Omega\varepsilon = 10^5$ sr. If $\varepsilon = 100\%$ and $\Omega = 10^{-5}$ sr, an incident intensity of 10^{13} photons s^{-1} is needed, which is about three decades higher than presently available. Longer

counting times, by a factor $(I_0\Omega\varepsilon)^{-1/3}$, are required to produce equivalent results at existing sources.

Practical considerations relating to optimal modulation frequencies, energy ranges relative to the absorption edge, RRS corrections and normalization procedures are being explored in the course of work in progress. The results and conclusions of this work will be reported subsequently.

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