INTRODUCTION TO THE APPLICATION AND LIMITS OF ANOMALOUS X-RAY DIFFRACTION IN THE DETERMINATION OF PARTIAL STRUCTURE FACTORS[*]

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ABSTRACT

The use of anomalous X-ray scattering to obtain the first differences and partial structure factors normally obtained with isotopic substitution neutron diffraction is described and compared with the neutron technique. Both the problems associated with the X-ray technique and the situations in which it is highly valuable are discussed.

1. Introduction

The availability of tunable, intense synchrotron radiation (SR) has made it possible to readily vary atomic form factors by varying the incident photon energy in X-ray scattering experiments. As a result, many isotopic substitution neutron diffraction techniques have become feasible, at least in principle, with X-rays. These include the determination of first differences [known as the differential structure factors (DSFs) and differential distribution functions (DDFs) of the differential anomalous scattering technique] and partial structure factors (PSFs) utilizing small-angle scattering and/or wide-angle scattering.

There are, however, distinct differences between the X-ray and the neutron experiments. Some of these serve to limit the accuracy and utility of the SR-determined PSFs considerably and are discussed in Sec. 3. Others, discussed in Sec.5, make the X–ray approach applicable to materials systems which cannot be readily studied with isotopic substitution neutron diffraction.

2. Anomalous X-ray Scattering and Partial Structure Factors

The atomic scattering factor is frequently expressed as:

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

where E is the photon energy, f_0 is the high photon energy limit of f, given by the Fourier transform of the atom's electron density, while f' and f" are the real and imaginary shifts arising from resonances when E is close to some excitation energy for atomic electrons.

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f" is simply related to the X-ray absorption coefficient, σ, by the relation

$$f''(E) = \frac{E}{4\pi\hbar c}\sigma(E)$$

(2)

f' is related to f" through the Kramers-Kronig relation, as the Cauchy principal value of

$$f'(E) = \frac{2}{\pi}\int_0^\infty \frac{E_0 f''(E_0)}{E^2 - E_0^2}dE_0 + \frac{E^{tot}}{mc^2}$$

(3)

Eq. (3) implies that the very large changes in f" near an X-ray absorption edge are translated into large changes in f' at energies in the same energy region. At approximately 100 eV below an edge, f' grows increasingly negative, peaking in magnitude at the edge energy. For Ge in amorphous Ge, the magnitude of f' reaches about 10, which is a large fraction of $f_o(0)=32$. The fraction increases considerably as q increases. Even larger fractional changes are achieved when L- and M-edges can be utilized.

Since SR sources provide a continuous spectrum, f' and f" may be varied by varying E in the scattering experiment, thus providing the different scattering cross-sections achieved in neutron diffraction experiments by varying the isotopes.

Consistent with the neutron situation, the total X-ray structure factor, S(q), may be written in terms of the partial structure factors, $s_{\alpha\beta}(q)$, as

$$S(q) = \sum_\alpha \sum_\beta \frac{c_\alpha c_\beta f_\alpha(q) f_\beta^*(q)}{|\langle f(q)\rangle|^2} s_{\alpha\beta}(q)$$

(4)

where c_α is the atomic fraction of species α and the compositionally averaged scattering factor is

$$\langle f(q)\rangle = \sum_\alpha c_\alpha f_\alpha(q)$$

(5)

Thus, all the isotopic substitution neutron diffraction procedures for obtaining differences and partials at both large and small scattering angles are potentially applicable with SR-based X–ray scattering. Typically, scattered intensities are measured at several photon energies *below* the absorption edge energy of each constituent species to obtain the independent S(q) while avoiding the strong fluorescence which would be produced if the measurements were made above the absorption edge energies.

Three features of this approach make the obtaining of PSF's with synchrotron radiation extremely attractive: (i) the scattering factor changes are achieved through photon energy changes, so that only a single sample need be prepared, (ii) the extremely high intensities mean that data acquisition times are short and (iii) very small sample volumes (e.g., thin films) are sufficient. It is also apparent, however, that the achievable changes in f are small compared the changes in nuclear cross-section which can be achieved in *some* isotopic substitution experiments. As a result, the condition numbers associated with the determination of the PSFs are large, so that errors in the total structure factor determinations or the scattering factors can large yield errors in the PSFs.

3. Some problems with the X-ray method
3.1 Low-Z problems

In the X-ray experiment, the photon energies must be chosen close to the absorption edges of the constituent elements of the material to be studied. Thus, for example, data cannot be obtained for q>10 for elements lighter than Ga, making data normalization difficult and high resolution pair distribution studies impossible for the lighter elements. No such limitation is present in the neutron diffraction experiments and quite high q-values are often obtained.

Small angle scattering studies can, of course, be performed at photon energies near the absorption edges of the lighter elements. These are typically limited by the vacuum paths and special monochromators required for soft X-ray research, but those difficulties are presently being addressed at various facilities.

3.2 Scattering factor problems
3.2.1 f_o problems

The nuclear cross sections utilized in isotopic substitution experiments are independent of scattering angle and the chemical state of the scattering species. Once measured for a specific isotope, they can be utilized in many different experiments. In contrast, f_o is dependent on angle, with a shape and magnitude which is dependent on the atom's chemical state, since it is the electrons, rather than the nuclei, which scatter the X–rays. Most experimentalists utilize tabulated f-values computed from computationally-derived electron wave functions for free atoms or ions. While these may be satisfactory for most structural studies, the large condition numbers make them suspect in PSF determination. Indeed, problems have been encountered in fitting the large-q scattering data to the atomic scattering factors for heavy elements by several workers, indicating that the computed f–values may be in error at high q for those elements in which relativistic effects are important. For example, in the poster presented by Wicks et al.[1] at this meeting, it was not possible to fit scattering data for a Ag-containing glass for $q > 10 \text{ Å}^{-1}$ to the calculated scattering curves.

3.2.2 f' problems

Similarly, f' depends on the ionic state *and the chemical environment* of each diffracting species. This strong dependence is made most evident by Eq. 3 and the knowledge that f' contains the X-ray absorption fine structure (XAFS) which is sufficiently strongly dependent on the local environment of the absorbing species near its absorption edge so that it is utilized to determine the environment. The resulting variations of f' with environment are greatest at photon energies just below the edge and decrease with increasing energy difference. Thus, most experienced workers measure $\sigma(E)$ at each edge for each sample to be studied and obtain f'(E) through the application of Eqs. 2 and 3. This procedure also yields the EXAFS, which also provides valuable structural information. This and other methods of determining f' are reviewed well by Lengeler[3].

A corollary of this dependence on environment is that a specific species may occupy quite different sites and have different chemical states in an amorphous material. As a consequence, f' would vary from site to site in a manner which is correlated with the environment. Experimental measurements yield $<f_\alpha>$, whereas Eq. 4 depends on $<f_\alpha^{\,2}>$ and $<f_\alpha f_\beta>$. This problem has not been investigated by simulations. Nevertheless, Fuoss' simulations[2] of errors in coordination distances and numbers calculated from partial distribution functions involving f' errors indicate that the former are rather small. There are, however, rotations in the three-dimensional space of the α–α, α–β and β–β distribution functions.

It should also be noted that the representation of f' and f" as scalars in Eqs. 1-5 is invalid generally, as discussed by Templeton and Templeton[4]. Instead, these quantities are the sum of different order tensors whose forms and components depend on the site symmetry as well as the directions of the polarization vector, the incident wave vector and the scattered wave vector of the X-rays. These authors have shown that representation of

the tensor f' by a site-independent scalar leads to small, but noticeable errors in the total distribution function. The presumably larger errors in the PSF determinations have not been evaluated. Simulations would be most valuable, although I believe the effects are likely to be small.

All the anomalous scattering PSF work that this author has seen assumes that f' is independent of scattering angle. This assumption is supported by the measurements of Zschack and Sparks[5] on Ga in GaAs, which indicate variations of the order of 1%. Theoretical calculations, however, of Kissel et al.[6] indicate that the angular dependence is sufficiently large to cause problems in PSF determination in Pb, while supporting the angular independence for the lighter elements. More theoretical calculations of the angular dependence at K-edges are needed to understand the impact of this effect on the elements between As and Pb. Also needed are L- and M-edge calculations, as well as simulations utilizing the results.

3.3 Compton Scattering problems

Still another, and perhaps the most serious, problem not faced in the neutron diffraction studies is the presence of Compton scattering in addition to the structure-dependent coherent X-ray scattering discussed above. The scattering is inelastic, with a distribution of energies at each scattering angle 2θ, which is peaked at

$$\Delta E \equiv E_0 - E'$$

$$\approx (E_0^2 / mc^2)[1 - \cos(2\theta)], \tag{6}$$

where E_o and E' are the initial and scattered photon energies, respectively. Thus, for example, there is a peak energy shift of 880 eV for 15 keV photons at $\theta=90^{\circ}$. The peak's energy width is determined by the electron momentum distribution in the solid. The intensity increases with increasing scattering angle, so that it is a major portion of the total scattering at high q-values for the lighter elements, but is less important for the very heavy elements.

The Compton scattering must be removed from the total scattering at each photon energy before the PSFs can be determined via Eq. (4). Three different approaches have been utilized for this purpose. In one, the scattered photons are detected utilizing a broad (>1 keV) pulse height window on the photon energy analyzer. As a consequence, all the Compton scattering is included in the measurement. It is then subtracted using tables constructed from theoretical calculations.

In the second, the narrowest window readily obtainable with solid-state detectors (~200 eV) is employed. As a result, the Compton scattering is counted at low scattering angles and eliminated at high angles. One then attempts to construct the bandpass in the intermediate region and eliminate all that was detected utilizing the theoretical tables. This approach, unfortunately, neglects the Compton scattering energy spreading at each scattering angle which is due to the electron momentum distribution.

In the third, a crystal monochromator is used[7] to eliminate virtually all the Compton scattering from the elastic scattering. The difficulty with this approach is the great reduction in measured intensity due to the small angular acceptance of such devices. With the availability of considerably more beam time on existing machines and the coming availability of the European Synchrotron Radiation Facility (ESRF) and other third generation X-ray sources, however, we may anticipate more general employment of these monochromators. It is likely that they will improve the quality of results markedly.

3.4 Fluorescence problems

Most anomalous scattering experiments are performed at photon energies just below the relevant absorption edge energies, so that significant backgrounds due to fluorescence would not be anticipated. Nevertheless, they are typically present in the form of resonant Raman scattering[8]. In this process, an incident photon whose energy is ΔE below the absorption edge is inelastically scattered, yielding a photon whose energy is ΔE below the corresponding emission energy. As a result, the difference between the energies of the incident and scattered photons is equal to the energy difference between the absorption edge and normal emitted photon energies.

The magnitude of this energy difference is readily seen by an example. The Ge K-edge energy is 11,103 eV while the $K\beta_1$ emission energy is 10,982 eV, leading to a difference in energy between the incident and the resonant Raman scattered photon of 121 eV. This difference is too small to allow for discrimination against resonant Raman scattered photons with the normally-employed solid-state detectors.

Two methods have been used commonly to deal with this problem. In the first, suggested by Fuoss[2], this scattering is treated as a smooth background which is eliminated in the normalization process. In the second, originated by Raoux and coworkers[9], the ratio of the $K\alpha$ to $K\beta$ fluorescent intensities is measured above the absorption edge, where the solid-state detector can distinguish readily the incident and the various fluorescent photon energies. It is then assumed that this ratio remains the same for the resonant Raman process. With measurements of the $K\alpha$ intensity, which can be obtained with the solid-state detector, the $K\beta$ intensity is obtained and subtracted from the total measured scattered intensity. Clearly, application of a diffracted beam monochromator will eliminate this problem, as well.

3.5 Storage Ring Stability Problems

Two features of the synchrotron radiation source, the storage ring, are worthy of discussion in this context. The first is that the synchrotron radiation intensity is not constant in time. Instead, the storage ring current and the corresponding intensity decay with a time constant of 2 to 60 hours, depending on the ring itself and the current. The storage ring is, therefore, refilled every few hours at some machines and daily at others. Between these fills, some rings are subject to instabilities which lead to sudden drops in intensity. Thus, it is critical that the incident intensity be monitored throughout the experiment.

In addition, the electron or positron orbit may vary from fill to fill, or shift within a fill. This is very serious for anomalous scattering experiments, because such shifts may lead to a change of the photons' angle of incidence upon the monochromator crystal and a resulting change in the photon energy of the beam reaching the sample. Given the very strong dependence of f' on photon energy near the edge - and the large condition numbers associated with the determination of the PSFs from the data, this is a serious problem. Indeed, most experienced workers do not work within 5 eV of the absorption edge as a result of this problem. It is also important, however, for experimenters to watch for orbit shifts while acquiring data. In addition, mathematical techniques[9,10] which search for inconsistent data sets are important in case the experimenter fails to observe the orbit shifts.

While such approaches are presently close to satisfactory, the ultimate solution of the orbit shift problem will be through greater orbit control. Such control is being developed and improved at almost all the synchrotron radiation facilities presently functioning and is being designed into the new machines.

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4. Present state of anomalous scattering studies

Raoux[9] reviews the present state of anomalous scattering studies in some detail. Here, let me make observations based on the work of my students and coworkers. Ludwig et al.[11] performed a critical test of differential anomalous scattering techniques in their study of liquid $GeBr_4$. The accuracies of first neighbor distances and coordination numbers were better than 0.01Å and 2%, respectively. Differential anomalous scattering is now used widely to obtain the environment of individual atomic species in complex amorphous materials. In addition, the Br-Br partial distribution function of Ludwig et al.[11] appeared to be of high accuracy. The Ge-Br and Ge-Ge PDFs showed clear indications of major problems, however. In particular, the solutions obtained through mathematical analysis of the data appeared to be linear combinations of the true solutions, so that there were deep negative minima in one PDF at the positions of apparently spurious maxima in the other. This situation was consistent with analysis of the linear equations yielding the PSFs from the observed data, but can also be understood intuitively with the observation that there are 4 Br atoms for each Ge atoms, and the two have approximately the same atomic numbers. As a result, one would expect the Br-Br PSF to dominate the scattering and to be obtained most accurately.

5. Why X-rays for PSFs?

As indicated above, anomalous scattering yields high quality DSFs and DDFs which provide a great deal of structural information. In addition, despite all the problems described above, there are good reasons for continuing efforts to obtain PSFs through anomalous X-ray scattering. As indicated earlier in this paper, dedicated synchrotron radiation beam time is becoming increasingly available and sources with two orders of magnitude greater brightness will soon be functional. Both will facilitate the use of diffracted beam monochromators to minimize problems associated with Compton scattering and fluorescence. Similarly, efforts are underway at the facilities to achieve greater orbit control, thus minimizing the problem of photon energy shifts. With this in mind, we turn to the types of problems which make continued development of the X-ray approach important.

5.1 Samples for which proper isotopes are not available

If proper isotopes are unavailable for the neutron experiment, and the atomic numbers of the elements in the sample are appropriate for the X-ray experiment, then X–rays are the only means of getting the PSF's.

5.2 Thin films or surfaces

The grazing incidence X-ray scattering (GIXS) technique has made it possible to determine[12] DSFs and DDFs from amorphous films as thin as 100Å, and efforts are underway to study liquid monolayers. These endeavors should advance markedly with the availability of the higher brightness X-ray sources, since GIXS is brightness limited.

5.3 Metastable and unstable materials

There is considerable interest currently in the structures of metastable and unstable materials. In many cases, one cannot be certain that 3 different samples, prepared with different isotopes, will have the same structure. As a result, the isotopic substitution neutron diffraction experiment is not feasible for such systems. In contrast, the anomalous X-ray scattering techniques are well suited to them, since only a single sample is needed.

6. Acknowledgements

7. References

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