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Kinematic diffraction on a structure with periodically varying scattering function

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A theory is developed to describe the kinematic diffraction response of a crystal when it is subjected to a periodically varying external perturbation. It is shown that if a part of the local electron density varies linearly with an external stimulus, the diffracted signal is not only a function of the stimulation frequency Ω, but also of its double 2Ω. These frequency components can provide, under certain conditions, selective access to partial diffraction contributions that are normally summed up in the interference pattern. A phasing process applied to partial diffraction terms would allow recovery of the substructure actively responding to the stimulus. Two ways of frequency filtering are discussed (demodulation and correlation) with respect to extracting information from such an experiment. Also considered is the effect of the variation of different structural parameters on the diffraction intensity that have to be accounted for while planning modulation-enhanced experiments. Finally, the advantages and limitations of the proposed concept are discussed, together with possible experiments.

1. Introduction

Periodic stimuli applied to a crystal have been used to study the effects of dynamic scattering by ultrasonic modulation (Punegov *et al.*, 2010; Remhof *et al.*, 1997), or to study kinetics *via* pump–probe experiments (Techert *et al.*, 2001). Here we consider the kinematic diffraction response to a periodic perturbation of a crystal where only a subset of the atoms (active atoms) is periodically changing its properties. We also analyse the possible implications for diffraction in general. This idealized case may provide a general model for many processes where the scattering power of a certain constituent of the crystal structure can be periodically modified by an external stimulus. Adsorption/desorption in framework materials, reversible ion intercalation in organic/inorganic matrices for battery applications, and polarization- or magnetization-induced displacements by electric or magnetic fields in a multiferroic may serve as examples.

Modulation techniques have been successfully applied in spectroscopy (Urakawa *et al.*, 2008) and recently they have also been adopted for powder diffraction (van Beek *et al.*, 2010). First diffraction data sets collected in modulation mode have just been reported (Urakawa *et al.*, 2011), but there is still no clear understanding of what kind of information can be safely extracted from such an experiment. A general theory of the modulation approach applied to diffraction is not yet available and this makes further experiments and their analysis difficult. The formulation of the corresponding theoretical background is the main goal of this paper.

X-ray diffraction has become, after 100 years of development, a very successful experimental tool for structural characterization of condensed matter. There are, however, a few fundamental limitations of this technique that we want to discuss with respect to the modulation approach. Diffraction is an interference phenomenon and the intensity on a detector does not allow one to separate contributions from different atomic subsets; for neutron diffraction this is possible, but only for a very limited number of isotopes (Trunov *et al.*, 1991; Herren *et al.*, 1980). The very same interference nature also does not permit a direct measurement of the phase of the diffracted waves, and this problem is sometimes called 'the phase problem of crystallography'. Here we show that in some cases these two fundamental crystallographic problems can be solved, or at least greatly reduced, with the help of the modulation-enhanced diffraction (MED) technique.

The text is organized as follows. First, we give an introduction to the theory of MED. Second, we derive the periodic diffraction response for the case when only one subset of atoms in a multi-atomic structure is responding to an external periodic stimulus. Then we consider a general case of correlation between the periodic diffraction response and the external stimulus. Finally, we discuss new options and limita-

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tions imposed by the MED technique, together with possible practical applications of the modulation approach.

2. Basics of modulation-enhanced diffraction

In MED (see the generic scheme in Fig. 1) diffraction data are collected as a function of time $[I(t,\, 2\Theta)]$, while a periodic external stimulus $[S(t)]$ with period $T = 2\pi/\Omega$ is also recorded, Ω being the frequency of modulation. The total time of data collection covers many periods of modulation. The diffraction response $I(t,\, 2\Theta)$, being correlated with a periodic stimulus (a sine function in the simplest case), suppresses background scattering and enhances the diffraction signal conjugated with the modulated property. This is similar to other modulation techniques, such as reverse time-of-flight Fourier spectroscopy (Hiismaki, 1997) and modulated anomalous X-ray scattering proposed by Jemian *et al.* (1993).

If a crystal is subjected to an external stimulus alternating with time, the electron density can be decomposed into responding (active, 'A') and non-responding (silent, 'S') components:

$$\rho(\mathbf{r}, t) = \rho_{\rm S}(\mathbf{r}) + \rho_{\rm A}(\mathbf{r}, t) = \rho_{\rm S}(\mathbf{r}) + \overline{\rho_{\rm A}(\mathbf{r})} + \delta\rho_{\rm A}(\mathbf{r}, t).$$

Here $\overline{\rho_{\rm A}(\mathbf{r})}$ is the time-averaged value of the electron density of the active part and $\delta\rho_{\rm A}(\mathbf{r}, t)$ represents its variation with time from the averaged value; we also assume the system to be ergodic.

Let us now associate a subset of atoms in a multi-atomic structure with the active contribution to the electron density. We also assume here that the diffraction intensity is already corrected for absorption, Lorentz and polarization, and detector-specific aberrations. Such integrated intensity measured at the Bragg node $\mathbf{Q} = \mathbf{Q}_{HKL}$ reads

$$\begin{aligned} I(t) &= \left| \sum_1^{\rm A} \mu_j f_j \exp\big(i\mathbf{Q}\mathbf{R}_j\big) + \sum_1^{\rm S} \mu_j f_j \exp\big(i\mathbf{Q}\mathbf{R}_j\big) \right|^2 \\ &= \big|F_{\rm A}(t) + F_{\rm S}\big|^2 = \big|\big[\overline{F_{\rm A}} + \delta F_{\rm A}(t)\big] + F_{\rm S}\big|^2, \qquad (1) \end{aligned}$$

where A and S stand for actively responding and silent substructures, respectively, and f_j, $\mathbf{R}_j$, μ_j indicate scattering power (atomic form factor for X-ray or Fermi scattering length for neutron diffraction), positional vector and occupancy of the different atoms, respectively. The time-dependent response of the active substructure (A) assumes that f_j, $\mathbf{R}_j$, μ_j may all vary reproducibly with time to the external stimulus.

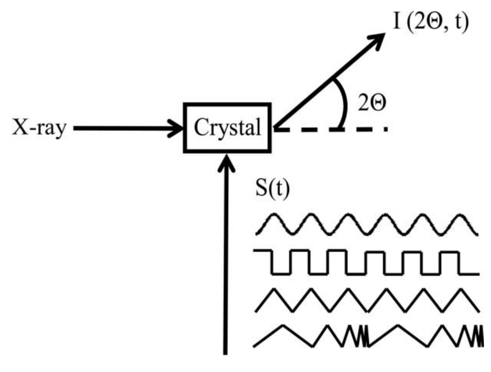

Figure 1
A scheme of the modulation-enhanced diffraction experiment. The incoming X-ray beam is diffracted by a crystal, which is subjected to an external periodic perturbation $S(t)$. Sinusoidal, square and triangular waves are shown as examples of possible trends of the external stimuli.

Different external stimuli will affect different components in equation (1). For example, the temperature may induce atomic displacements in the A substructure, thus changing $\mathbf{R}_j$ and/or the $\mathbf{B}_j$ matrix describing the thermal motion (see §6.4). Filling empty voids in a porous structure as a function of temperature or pressure would mostly affect μ_j if the temperature/pressure range is small so that the other parameters can be assumed constant, while the variation of the energy of the incoming X-ray beam near an absorption edge would change f_j for the resonant atoms.

Since the structure factor F is a complex number, the intensity may also be expressed in the following way:

$$I(t) = \big|F_{\rm A}(t)\big|^2 + \big|F_{\rm S}\big|^2 + F_{\rm A}(t)F_{\rm S}^* + F_{\rm A}^*(t)F_{\rm S}, \qquad (2a)$$

where * stands for complex conjugate. After separating time-dependent and -independent terms, equation (1) reads

$$\begin{aligned} I(t) = {} & \big|\overline{F_{\rm A}} + F_{\rm S}\big|^2 + \big|\delta F_{\rm A}(t)\big|^2 + \delta F_{\rm A}^*(t)\big(\overline{F_{\rm A}} + F_{\rm S}\big) \\ & + \delta F_{\rm A}(t)\big(\overline{F_{\rm A}^*} + F_{\rm S}^*\big). \qquad (2b) \end{aligned}$$

The first term does not depend on the external stimulus, the second corresponds to the diffraction response of the active substructure and the last two terms represent the interference between active and silent substructures.

The diffraction signals from different substructures, $\big|F_{\rm S}\big|^2$ and $\big|F_{\rm A}\big|^2$, cannot be measured separately, since the interference factor $F_{\rm S}F_{\rm A}^*(t) + F_{\rm S}^*F_{\rm A}(t)$ is an unknown part of the measured intensity. With MED this problem may be overcome by Fourier transforming the diffraction intensity from time to frequency domain, thus leaving only the time-dependent terms and suppressing the time-independent contributions:

$$\begin{aligned} \tilde{I}(\omega) = {} & {\rm FT}\Big[\big|\delta F_{\rm A}(t)\big|^2\Big] + \big(\overline{F_{\rm A}} + F_{\rm S}\big){\rm FT}\big[\delta F_{\rm A}^*(t)\big] \\ & + \big(\overline{F_{\rm A}^*} + F_{\rm S}^*\big){\rm FT}\big[\delta F_{\rm A}(t)\big], \qquad (3) \end{aligned}$$

where

$${\rm FT}[f(t)] = \int_0^T f(t)\exp(i\omega t)\,{\rm d}t.$$

Equation (3) suggests a way of separating the different contributions. By analysing the frequency response one could separate the contributions from the interference term $\delta F_{\rm A}^*(t)\big(\overline{F_{\rm A}} + F_{\rm S}\big) + \delta F_{\rm A}(t)\big(\overline{F_{\rm A}^*} + F_{\rm S}^*\big)$ and from that of the active substructure $\big|\delta F_{\rm A}(t)\big|^2$.

For the sake of illustration, let us consider a straightforward case. Equation (3) becomes very simple if we assume a cosine-shaped stimulus and a proportional response: $\delta F_{\rm A}(t) = \delta F_{\rm A}^*(t) \propto S(t) = A\cos(\Omega t)$. Here A is the amplitude of the external stimulus.

Under these assumptions equation (3) reads

$$\tilde{I}(\omega) \propto (\pi A^2/2)[\delta(\omega)+\delta(\omega-2\Omega)+\delta(\omega+2\Omega)] + 2\pi A\big[\mathrm{Re}\big(\overline{F_{\rm A}}\big)+\mathrm{Re}\big(F_{\rm S}\big)\big][\delta(\omega-\Omega)+\delta(\omega+\Omega)].$$

This simple derivation illustrates a very important property of the frequency spectrum of the modulated diffraction signal: perturbing a component of the crystal with frequency Ω by modulating the scattering factor, the diffraction signal responds with two frequencies, Ω and 2Ω. By extracting the different frequency components one could, therefore, at least for the case considered, separate different contributions normally merged into one diffracted intensity.

Thus, having shown the main idea of using modulation in diffraction techniques, we will formulate a general theory for an arbitrary periodic stimulus and response, derive the analytical tools and methods to extract structural information, and also enumerate the limitations to be accounted for in a real experiment.

3. Stimulus and response expressed as Fourier series

Both $S(t)$ and $\delta F_{\rm A}(t)$ may be much more complex than a simple cosine function but, as long as they are periodic, they can always be expressed as Fourier series:

$$\begin{aligned}\delta S^{\omega}(t) &= S(t)-\overline{S(t)} = S_0\sum_{-\infty}^{\infty} p_r \exp(ir\omega t)\\ \delta F_{\rm A}^{\omega}(t) &= F_0\sum_{-\infty}^{\infty}\hat{q}_r\exp(ir\omega t)\end{aligned}\qquad (4a)$$

with

$$\begin{aligned}p_r &= \frac{1}{S_0T}\int_0^T \delta S^{\omega}(t)\exp(ir\omega t)\,{\rm d}t\\ \hat{q}_r &= \frac{1}{F_0T}\int_0^T \delta F_{\rm A}^{\omega}(t)\exp(ir\omega t)\,{\rm d}t.\end{aligned}\qquad (4b)$$

Here F_0 and S_0 are the amplitudes of the response and the stimulation, respectively, and F_0 corresponds to the active substructure, r stands for integers and the superscript ω highlights that our expressions depend parametrically on frequency. $\delta S^{\omega}(t)$ is set to be symmetric with respect to $t=0$, so that p_r are real numbers and $p_r = p_{-r}$; this condition can be easily realized for many external perturbations. Note that $q_0 = p_0 = f_0 = 0$ since $\overline{\delta F_{\rm A}^{\omega}(t)} = \overline{\delta S^{\omega}(t)} = 0$. For $\delta F_{\rm A}^{\omega}(t)$ one also has to account for a possible time delay of response with respect to stimulus:

$$\delta F_{\rm A}^{\omega}(t) = F_0\sum_{-\infty}^{\infty} q_r\exp(ir\omega t)\exp(ir\omega\tau_{\rm A})\qquad (4c)$$

where $\tau_{\rm A}$ denotes the corresponding time delay and $q_r\exp(ir\omega\tau_{\rm A}) = \hat{q}_r$. $\delta F_{\rm A}^{\omega}(t)$ is symmetric with respect to $t=-\tau_{\rm A}$ and therefore $q_r = q_{-r}$.

It is also useful to derive the corresponding expansion for $\left|\delta F_{\rm A}^{\omega}(t)\right|^2$,

$$\left|\delta F_{\rm A}^{\omega}(t)\right|^2 = \left|F_0\right|^2\sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty} q_rq_n\exp\big[i\omega\tau_{\rm A}(r+n)\big] \times\exp[i\omega t(r+n)].\qquad (4d)$$

Now we introduce an important assumption that could be tentatively called 'linear response'. By doing so we imply that only the first linear term is considered in the following Taylor series and the contributions from the higher terms are negligible:

$$\delta F_{\rm A} = \frac{\partial F_{\rm A}}{\partial S}\delta S + \frac{\partial^2 F_{\rm A}}{\partial S^2}(\delta S)^2 + \ldots.$$

Here $\delta F_{\rm A}$ is the variation of the structure amplitude of the active substructure, δS is the variation of the external stimulus and the derivative $\partial F_{\rm A}/\partial S$ is considered as a constant. It immediately follows that for such a linear response $q_r \propto p_r$; in other words, if the stimulus function consists of only odd harmonics such as sinusoidal-, square- and triangle-wave shapes (Fig. 1), the response does not contain any components at even harmonics. Concerning equation (4*d*), r and n are both odd, as occurred in the simple example considered in the previous section. This result is general and does not depend on the shape of the stimulus, as long as it can be expressed in a Fourier series and the linear response hypothesis holds, which is typically valid when δS is sufficiently small.

4. Separating out contributions summed into diffraction intensity

We start from a scheme very similar to the one used in spectroscopy (Urakawa *et al.*, 2008), based on the calculation of the following integrals by introducing a new variable τ, resulting in the conversion of $I(t)$ to $I(\omega,\tau)$:

$$\begin{aligned}I(\omega,\tau) &= \int_0^{T_{\rm exp}} {\rm d}t\, I(t)\exp[i\omega(t-\tau)]\\ &= \int_0^{T\,\rm exp} {\rm d}t\left|\delta F_{\rm A}\right|^2\exp[i\omega(t-\tau)]\\ &\quad + A\int_0^{T\,\rm exp} {\rm d}t\,\delta F_{\rm A}\exp[i\omega(t-\tau)]\\ &\quad + A^*\int_0^{T\,\rm exp} {\rm d}t\,\delta F_{\rm A}^*\exp[i\omega(t-\tau)]\end{aligned}\qquad (5)$$

with $A = \big(\overline{F_{\rm A}}+F_{\rm S}\big)$; $T_{\rm exp}$ denotes the time taken by the experiment, which is assumed to be much longer than the period T of the stimulus, and many experimental data sets are collected during each period. Assuming that equation (4*c*) holds for $\delta F_{\rm A}$, the result only contains the cross-terms related to A and A^*, and reads

$$I(\omega,\tau) = q_1F_0\big\lfloor A\exp\big[i\omega(\tau_{\rm A}+\tau)\big] + A^*\exp\big[-i\omega(\tau_{\rm A}+\tau)\big]\big\rfloor.\qquad (6)$$

Here we recall that

$$\int_0^{T\exp} \mathrm{d}t \exp\{i\omega[(r+1)t]\} = \begin{cases} 1 \to (r+1) = 0 \\ 0 \to (r+1) \neq 0 \end{cases}.$$

Note that the first integral containing $|\delta F_{\rm A}|^2$ in equation (5) goes to zero; however the corresponding term takes non-zero values after the following double frequency transformation:

$$\begin{aligned} I(2\omega,\tau) &= \int_0^{T_{\rm exp}} \mathrm{d}t\, I(t) \exp[i2\omega(t-\tau)] \\ &= \int_0^{T\exp} \mathrm{d}t\, |\delta F_{\rm A}|^2 \exp[i2\omega(t-\tau)] \\ &\quad + A \int_0^{T\exp} \mathrm{d}t\, \delta F_{\rm A} \exp[i2\omega(t-\tau)] \\ &\quad + A^* \int_0^{T\exp} \mathrm{d}t\, \delta F_{\rm A}^* \exp[i2\omega(t-\tau)], \end{aligned} \tag{7}$$

$$I(2\omega,\tau) = |F_0|^2 \sum_{-\infty}^{\infty} q_n q_{n+2} \exp[-i2\omega(\tau_{\rm A}+\tau)]. \tag{8}$$

Higher-frequency terms $I(N\omega,\tau)$, $N>2$ can be similarly derived but they are assumed minor and negligible because of the lower amplitude of high-frequency terms contained in the stimulus and thus have no practical use for the separation of partial diffraction contributions.

For a fixed frequency of modulation $\omega = \Omega$, $I(\Omega,\tau)$ and $I(2\Omega,\tau)$ could therefore be used to separate $|\delta F_{\rm A}|^2$ and $\delta F_{\rm A}$ contributions from time-dependent modulated diffraction data. It is important to realize that in the linear response case the 2Ω component only represents the active substructure signal, provided that no even frequency terms are present in the stimulus. For example, with a sinusoidal-wave stimulus of a frequency Ω, under the linear-response assumption the active substructure signal appears exclusively at 2Ω frequency. We call the calculation of integrals [equations (5) and (7)] 'demodulation' to distinguish it from the 'correlation' procedure described in the next section. The 'demodulated' intensity as a function of τ is a wave with period $2\pi/\Omega$ and phase $\Omega\tau_{\rm A}$. The range $0 \le \tau \le T = 2\pi/\Omega$ defines the irreducible part of the phase space.

5. Correlation of stimulus and response

Equations (5) and (7) are particular cases of a convolution integral correlating the exponential function with diffraction intensity. Let us now consider a convolution of the diffraction response $I(t)$ with a periodic external stimulus $S(t)$, taking both functions in the general form of the corresponding Fourier series:

$$\begin{aligned} \langle I, \delta S\rangle_\tau^\omega &= \int_0^{T\exp} \mathrm{d}t \Big[|\overline{F_{\rm A}} + F_{\rm S}|^2 + |\delta F_{\rm A}(t)|^2 + \delta F_{\rm A}^*(t)(\overline{F_{\rm A}} + F_{\rm S}) \\ &\quad + \delta F_{\rm A}(t)(\overline{F_{\rm A}^*} + F_{\rm S}^*) \Big] \delta S(t-\tau) \\ &= \left\langle |\delta F_{\rm A}|^2, \delta S \right\rangle_\tau + \langle \delta F_{\rm A}, \delta S\rangle A^* + \langle \delta F_{\rm A}^*, \delta S\rangle A. \end{aligned} \tag{9}$$

Using equation (4*a*), one derives

$$\begin{aligned} \langle \delta F_{\rm A}, \delta S\rangle^\omega &= \int_0^{T_{\rm exp}} \delta F_{\rm A}^\omega(t) \delta S^\omega(t-\tau)\, \mathrm{d}t \\ &= F_0 S_0 \sum_{-\infty}^{\infty} p_r q_{-r} \{ A \exp[ir\omega(\tau_{\rm A}+\tau)] \\ &\quad + A^* \exp[-ir\omega(\tau_{\rm A}+\tau)] \}. \end{aligned} \tag{10}$$

If we also select $\delta S^\omega(t) = S_0 \sum_{-\infty}^{\infty} p_r \exp(ir\omega t)$ to be such that only odd harmonics are non-zero, then, according to equation (6), the interference terms would not contribute to the total response at 2Ω.

Now we could apply the same approach used to calculate the first term in equation (5), and derive the convolution of the modulated diffraction intensity from the active substructure with the external modulation, $\langle |\delta F_{\rm A}|^2, \delta S\rangle$:

$$\begin{aligned} \left\langle |\delta F_{\rm A}|^2, S \right\rangle^\omega &= \int_0^{T_{\rm exp}} |\delta F_{\rm A}^\omega(t)|^2 S^\omega(t-\tau)\, \mathrm{d}t \\ &= F_0^2 S_0 \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} q_r q_n p_m \exp\{i\omega[-m\tau + (r+n)\tau_{\rm A}]\} \\ &\quad \times \int_0^{T_{\rm exp}} \exp[i(r+m+n)\omega t]\, \mathrm{d}t \\ &= F_0^2 S_0 \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} q_r q_n p_{-(n+r)} \exp\{i\omega[(\tau_{\rm A}+\tau)(r+n)]\}. \end{aligned} \tag{11}$$

There are contributions like $q_n q_n p_{-2n} \exp[i2n\omega(\tau_{\rm A}+\tau)]$ which are zero for the selected $S^\omega(t)$. If, as before, we assume a linear response of the active substructure, implying also odd r and n, the entire term $\langle |\delta F_{\rm A}|^2, S\rangle^\omega$ remains zero.

The final form of the correlated diffraction intensity therefore contains only cross-terms and reads

$$\begin{aligned} \langle I, S\rangle_\tau^\omega &= F_0 S_0 \sum_{-\infty}^{\infty} p_r q_{-r} \{ A \exp[ir\omega(\tau_{\rm A}+\tau)] \\ &\quad + A^* \exp[-ir\omega(\tau_{\rm A}+\tau)] \}. \end{aligned} \tag{12}$$

At variance with the demodulated intensity [equation (6)], its correlated analogue [equation (12)] does not give a wave but a sum of many waves with frequencies $r\omega$ and intensities proportional to $p_r q_r$.

Similarly to the demodulated form, the convolution of the diffracted intensity with $S^{2\omega}(t-\tau)$, *i.e.* with an external perturbation taken at doubled frequency, does not contain a contribution from the interference term and only represents the active substructure:

$$\begin{aligned} \left\langle |\delta F_A|^2, S \right\rangle^{2\omega} &= |F_0|^2 S_0 \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} q_r q_n p_{-(n+r)/2} \\ &\quad \times \exp\{i\omega[(\tau_{\rm A}+\tau)(r+n)]\}. \end{aligned} \tag{13}$$

The correlation approach offers an important advantage that has been implemented before in a specific neutron time-of-flight technique – namely the reverse time-of-flight (RTOF) method (Hiismaki, 1997). If one varies the modulation frequency during an experiment from zero to $\Omega^{\max}$ such that the time during which the system stays at a certain frequency

Ω_n is proportional to a weight function $g(\Omega_n)$ that obeys the normalization condition

$$\int_0^{\Omega_{\max}} \mathrm{d}\omega\, g(\omega) = 1, \tag{14}$$

then integration of equation (12) over frequency using the weight function $g(\omega)$ results in

$$\begin{aligned}
\langle I, S\rangle_\tau &= \int_0^{\Omega_{\max}} \langle I, S\rangle_\tau^\omega g(\omega)\,\mathrm{d}\omega \\
&= F_0 S_0 \sum_{-\infty}^{\infty} p_r q_{-r} \big\{AR\big[r(\tau_{\rm A}+\tau)\big] + A^* R^*\big[r(\tau_{\rm A}+\tau)\big]\big\} \\
R\big[r(\tau_{\rm A}+\tau)\big] &= \int_0^{\Omega_{\max}} \mathrm{d}\omega\, g(r\omega) \exp\big[ir\omega(\tau_{\rm A}+\tau)\big] \\
R^*\big[r(\tau_{\rm A}+\tau)\big] &= \int_0^{\Omega_{\max}} \mathrm{d}\omega\, g(r\omega) \exp\big[-ir\omega(\tau_{\rm A}+\tau)\big].
\end{aligned} \tag{15}$$

If $g(\omega)$ is now also chosen such that its Fourier transform is a sharp peak, then all the information in the phase space (τ) is condensed in a peak centred at $\tau_{\rm A}$. $R(r\tau)$ may now be considered as an instrumental resolution function in phase space. A schematic illustration of a few frequency windows and corresponding resolution functions is shown in Fig. 2. For simple frequency windows like Gaussian or Dirichlet, the width of the resolution function is inversely proportional to the maximal frequency (Hiismaki, 1997). Integration of the peak profile is now a measure of F_0 for a given Bragg reflection.

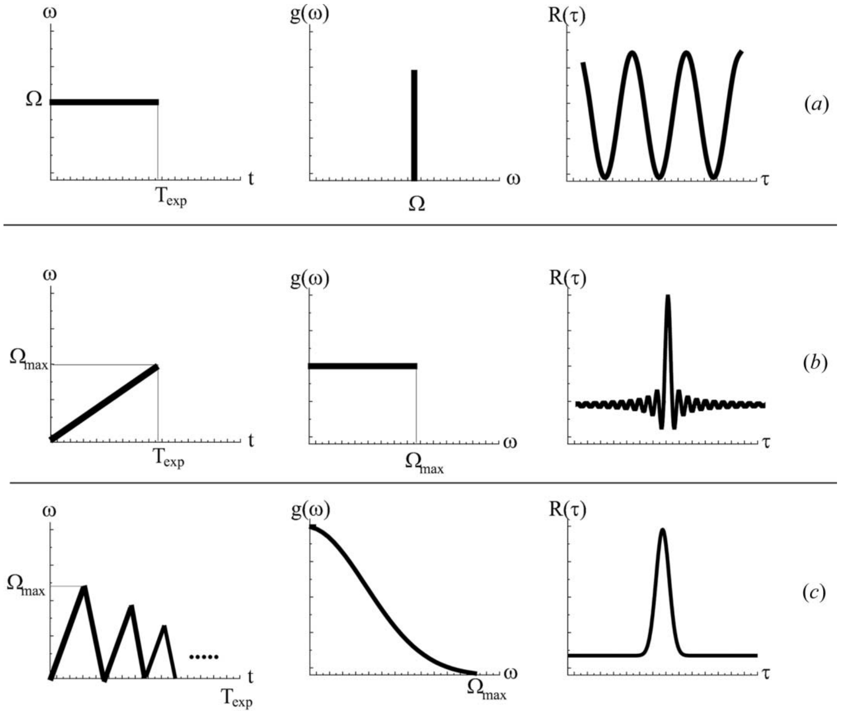

Figure 2
Modulation frequency as a function of time (left), corresponding frequency window (middle) and resolution function in phase space (right). Case (*a*) assumes constant frequency of modulation, the demodulated or convoluted signal is a periodic wave in the phase space; case (*b*) implies a linear variation of the modulation frequency with time thus giving a Dirichlet frequency window together with a peaked but still oscillating signal produced by convolution; case (*c*) illustrates a Gaussian frequency window and a well defined peak in the phase space.

Integrating equation (13) over frequency gives

$$\begin{aligned}
\Big\langle \big|\delta F_{\rm A}\big|^2, S\Big\rangle &= \int_0^{\Omega_{\max}} \langle I, S\rangle_\tau^{2\omega} g(\omega)\,\mathrm{d}\omega \\
&= \big|F_0\big|^2 S_0 \sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty} q_r q_n p_{-(n+r)/2} R\big[(\tau_{\rm A}+\tau)(r+n)\big].
\end{aligned} \tag{16}$$

The area of the corresponding peak would give an estimate of $\big|F_0\big|^2$. In other words, the shape of $g(\omega)$ together with the maximum modulation frequency allows us to gain control over the shape and width of the peak in the phase space in close similarity with neutron diffraction (Kudryashev *et al.*, 1999). At variance with the demodulation approach, where the filtered signal is periodically distributed in phase space, the convolution condenses information in a peak that may be used to increase accuracy.

6. Modulation of structural parameters and diffraction response

In the above sections we have formulated the basic hypothesis and two ways of obtaining structural information from modulated data. Here we discuss some intrinsic limitations of the modulation technique that have to be accounted for while planning real experiments.

We restrict ourselves by considering the electron density as the sum of all the electron densities of the atoms or ions and neglecting possible variations of the deformation density. Fourier transformation of the electron density is shown in equation (1).

Based on $S^\omega(t) = S_0 \sum_{-\infty}^{\infty} p_r \exp(ir\omega t)$ as the periodic external stimulus and on the crystal structure as modelled by equation (1), we consider all possible changes induced in the diffraction signal by the stimulus affecting active atoms. The four different cases are: (*a*) occupancy of atomic positions, (*b*) atomic form factor, (*c*) coordinates and (*d*) atomic displacement parameters for active atoms.

6.1. The stimulus affects the occupancy of the active atoms

Let us suppose that the occupancy of the active atoms changes in time according to the following law:

$$\mu_j(t) = \overline{\mu_j} + \delta\mu_j \sum_{-\infty}^{\infty} q_r \exp[ir\omega(t+\tau)],$$

where the occupancy of site j varies between $\overline{\mu}_j + \delta\mu_j$ and $\overline{\mu}_j - \delta\mu_j$. In this case the structure factor for the active atoms may be written as

$$\begin{aligned} F_{\rm A}(t) &= \sum_{1}^{\rm A} \left\{ \overline{\mu_j} + \delta\mu_j \sum_{-\infty}^{\infty} q_r \exp[ir\omega(t+\tau)] \right\} f_j \exp\big(i\mathbf{QR}_j\big) \\ &= \sum_{1}^{\rm A} \overline{\mu}_j f_j \exp\big(i\mathbf{QR}_j\big) + \sum_{1}^{\rm A} \delta\mu_j f_j \exp\big(i\mathbf{QR}_j\big) \\ &\quad \times \sum_{-\infty}^{\infty} q_r \exp[ir\omega(t+\tau)] \\ &= \overline{F_{\rm A}} + \delta F_{\rm A}(t). \end{aligned} \qquad (17)$$

Therefore the total intensity can be written in the form of equation (2*b*). For a single active sublattice $\delta F_{\rm A}(t) = (\delta\mu/\overline{\mu})\overline{F_{\rm A}} \sum_{-\infty}^{\infty} q_r \exp[ir\omega(t+\tau)]$ and to have a linear response, one has to make sure experimentally that $q_r \propto p_r$. For this case one could apply both demodulation and convolution techniques to recover $(\delta\mu/\overline{\mu})\overline{F_{\rm A}}$ and $|(\delta\mu/\overline{\mu})\overline{F_{\rm A}}|^2$ for odd and even frequencies, respectively. Note that these values differ from $\overline{F_{\rm A}}$ and $|\overline{F_{\rm A}}|^2$ by the scale factors $\delta\mu/\overline{\mu}$ and $|\delta\mu/\overline{\mu}|^2$.

To give an idea of the possible magnitude of the demodulated intensities, we consider the modulation of the occupancy of lithium positions in $\rm LiCoO_2$ cathode material. The diffraction contribution from lithium is very weak with respect to the scattering from cobalt and oxygen, and the Li content can be varied electrochemically in a broad range (Laubach *et al.*, 2009). Taking the 113 Bragg reflection as an example, for an X-ray wavelength of 0.65 Å, $\delta\mu = 0.25$ and $\overline{\mu} = 0.75$ the demodulated intensity $|(\delta\mu/\overline{\mu})\overline{F_{\rm Li}}|^2$ could be extracted at the level of 0.2% from the total; for a complete removal and insertion of the intercalated lithium this value takes its maximal value of ~2%. In spite of the smallness of the extracted values, the demodulated intensities after scaling are the same as those in the diffraction pattern calculated for the active Li sublattice alone. As an illustration, we have carried out a simple simulation of a MED experiment with a sinusoidal modulation of Li occupancy, assuming linear response and zero time delay. A total of 60 powder patterns of $\rm Li_xCoO_2$, with x = 0.3–0.5, have been calculated with the help of the *TOPAS* software and Fig. 3(*a*) illustrates the time evolution of the diffraction pattern. For the sake of simplicity we have neglected the variation of the unit-cell dimensions and oxygen displacement, since they are expected to be small (Laubach *et al.*, 2009). The comparison of the Li contribution with the total intensity from $\rm Li_xCoO_2$ is illustrated in Fig. 3(*b*). The extraction of the demodulated diffraction intensities at 2Ω has been carried out with a locally developed script calculating the integral in equation (7) with $\tau = 0$ and the comparison with the diffraction pattern of the Li sublattice alone is shown in Fig. 3(*c*); the patterns are the same as expected.

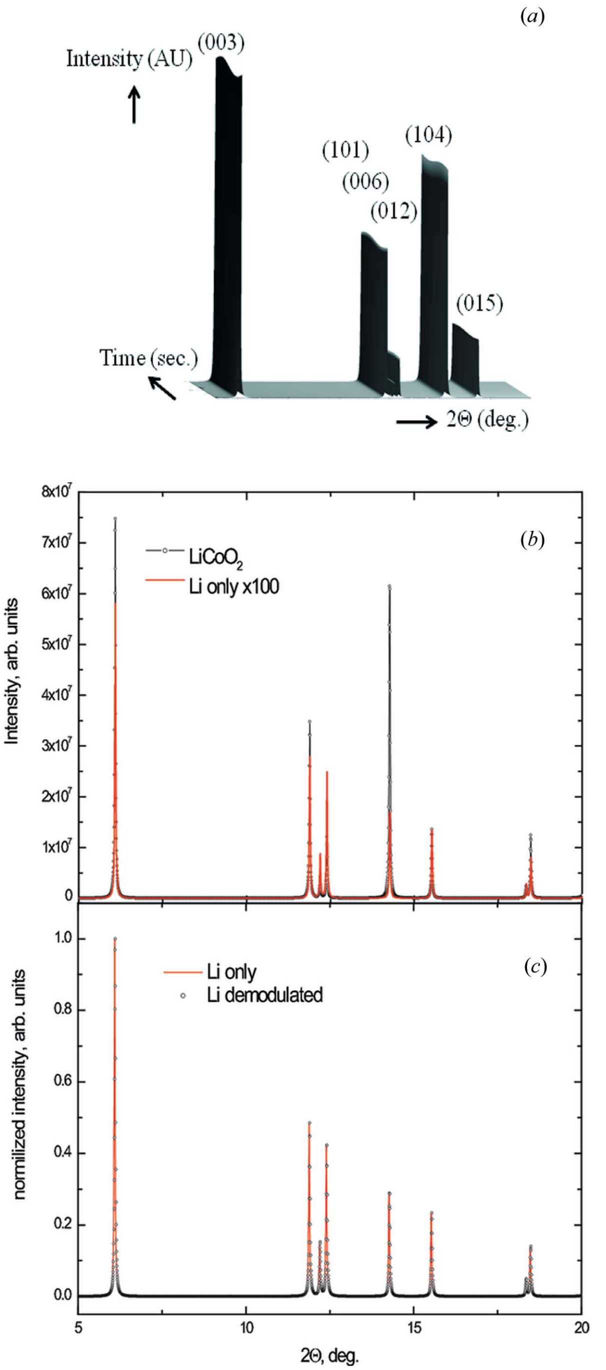

Figure 3

(*a*) Time evolution of the diffraction pattern of $\rm LiCoO_2$ induced by a sinusoidal modulation of Li occupancy. (*b*) Simulated diffraction from Li atoms only (red) (*i.e.* a structural analogue of $\rm LiCoO_2$ with occupancy of Co and O set to zero) compared with the total diffraction from $\rm LiCoO_2$ (black). (*c*) Simulated (red) and demodulated (black) powder patterns of the Li sublattice, normalized to the same scale.

6.2. The stimulus affects the scattering factor of the active atoms

Let us suppose that the scattering factors of some atoms of the crystal structure change in time according to the following law:

$$f_j(t) = \overline{f_j} + \delta f_j \sum_{-\infty}^{\infty} q_r \exp[ir\omega(t+\tau)]$$

where the atomic scattering factor varies between $\overline{f} + \delta f$ and $\overline{f} - \delta f$. This could be obtained by modulating either the oxidation state of the *i*th atom or the wavelength of the X-ray beam. In the latter case, if the wavelength induces resonant scattering effects, the scattering factor changes in time according to the law

$$f_j(t) = \overline{f_j} + \left(\delta f_j' + i\delta f_j''\right) \sum_{-\infty}^{\infty} q_r \exp[ir\omega(t+\tau)], \qquad (18)$$

where $\delta f_j'$ and $\delta f_j''$ are the variations of the real and imaginary dispersion corrections for the jth atom, respectively. The structure factor for the active atoms may then be written as

$$\begin{aligned} F_{\rm A}(t) &= \sum_1^{\rm A} \mu_j \overline{f_j} \exp\left(i\mathbf{QR}_j\right) + \sum_1^{\rm A} \mu_j \left(\delta f_j' + i\delta f_j''\right) \\ &\quad \times \exp\left(i\mathbf{QR}_j\right) \sum_{-\infty}^{\infty} q_r \exp[ir\omega(t+\tau)] \\ &= \overline{F_{\rm A}} + \delta F_{\rm A}(t). \end{aligned}$$

When an active sublattice is present and a linear response is assumed, both demodulation and convolution techniques would recover $[(\delta f' + i\delta f'')/\overline{f}]\overline{F_{\rm A}}$ and $\left|[(\delta f' + i\delta f'')/\overline{f}]\overline{F_{\rm A}}\right|^2$ for odd and even frequencies, respectively. Note that, at variance with occupancy modulation, such values are not simply proportional to $\overline{F_{\rm A}}$ and $\left|\overline{F_{\rm A}}\right|^2$ but differ in $\mathbf{Q}$ dependence. Taking again $\rm LiCoO_2$ as an example (Laubach *et al.*, 2009) and varying the X-ray wavelength between 0.4 and 0.7 Å, one finds that the demodulated intensity from the Co sublattice represents ∼0.17% of the total intensity for the 113 reflection.

6.3. The stimulus affects the position of the active atoms

Let us suppose that the position of active atoms changes in time according to the following law:

$$\mathbf{R}_j(t) = \overline{\mathbf{R}}_j + \delta\mathbf{R}_j \sum_{-\infty}^{\infty} q_r \exp[ir\omega(t+\tau)],$$

where $\overline{\mathbf{R}}_j$ is the average position of the atom j, and $\delta\mathbf{R}_j$ defines the direction and amplitude of the atomic displacement. In this case the structure factor for active atoms is

$$\begin{aligned} &F_{\rm A}(t) \\ &= \sum_1^{\rm A} \mu_j f_j \left(\exp\left(i\mathbf{Q}\overline{\mathbf{R}}_j\right) \exp\left\{ i\mathbf{Q}\delta\mathbf{R}_j \sum_{-\infty}^{\infty} q_r \exp[ir\omega(t+\tau)] \right\} \right). \end{aligned} \qquad (19a)$$

For small displacements $\mathbf{Q}\delta\mathbf{R}_j \sum_{-\infty}^{\infty} q_r \exp[ir\omega(t+\tau)]$ is also small and series expansion for the corresponding exponent gives

$$\begin{aligned} &\exp\left\{ i\mathbf{Q}\delta\mathbf{R}_j \sum_{-\infty}^{\infty} q_r \exp[ir\omega(t+\tau)] \right\} \\ &\simeq 1 + i\mathbf{Q}\delta\mathbf{R}_j \sum_{-\infty}^{\infty} q_r \exp[ir\omega(t+\tau)] \\ &\quad - \frac{1}{2} \left\{ \mathbf{Q}\delta\mathbf{R}_j \sum_{-\infty}^{\infty} q_r \exp[ir\omega(t+\tau)] \right\}^2 + \ldots . \end{aligned} \qquad (19b)$$

Keeping only the two first terms we obtain an approximation of the structure amplitude,

$$\begin{aligned} F_{\rm A}(t) &\simeq \sum_1^{\rm A} \mu_j f_j \exp\left(i\mathbf{Q}\overline{\mathbf{R}}_j\right) \left\{ 1 + i\mathbf{Q}\delta\mathbf{R}_j \sum_{-\infty}^{\infty} q_r \exp[ir\omega(t+\tau)] \right\} \\ &= \overline{F_{\rm A}} + \delta F_{\rm A}(t). \end{aligned}$$

To have a valid linear response, for the variation

$$\delta F_{\rm A}(t) = \sum_{-\infty}^{\infty} q_r \exp[ir\omega(t+\tau)] i\mathbf{Q} \sum_1^{\rm A} \mu_j f_j \delta\mathbf{R}_j \exp\left(i\mathbf{Q}\overline{\mathbf{R}}_j\right)$$

one again has to make sure that $q_r \propto p_r$. If we additionally assume that all the active atoms move coherently in the same direction (translation movement), then $\delta F_{\rm A}(t) = i\overline{F}_{\rm A}\mathbf{Q}\delta\mathbf{R} \sum_{-\infty}^{\infty} q_r \exp[ir\omega(t+\tau)]$. For this particular case one could apply both demodulation and convolution techniques to recover $\overline{F_{\rm A}}\mathbf{Q}\delta\mathbf{R}$ and $\left|\overline{F_{\rm A}}\mathbf{Q}\delta\mathbf{R}\right|^2$ for odd and even frequencies, respectively.

If the assumption of small atomic shifts does not hold, one would not be able to separate squared and cross-terms [equation (2*b*)] on the sole basis of their frequency response. Thus, also for a linear response of the atomic shifts [equation (19*a*)], the response at the level of structure amplitude and diffraction intensity is in general nonlinear as a result of the nonlinearity of the exponential function.

6.4. The stimulus affects the atomic displacement parameters (ADPs) of the active atoms

Smearing of atomic positions due to thermal motion and/or static structural distortions is conveniently modelled by a tensor of atomic displacement parameters (Trueblood *et al.*, 1996). Here we consider the modulation effect in an isotropic approximation, thus treating only the trace of the ADP matrix; a more detailed consideration assumes similar treatment applied to all the elements of the ADP matrix.

Let us suppose that the isotropic ADP is modulated by the following law:

$$B_j(t) = \overline{B_{j0}} + \delta B_0 \sum_{-\infty}^{\infty} q_r \exp[ir\omega(t+\tau)].$$

Then the structure factor for the active atoms may be written:

$$\begin{aligned} F_{\rm A}(t) &= \sum_1^{\rm A} \mu_j f_j^0 \exp\left(- \left\{ \overline{B_j} + \delta B_0 \sum_{-\infty}^{\infty} q_r \exp[ir\omega(t+\tau)] \right\} |\mathbf{Q}|^2 \right) \\ &\quad \times \exp\left(i\mathbf{QR}_j\right), \end{aligned} \qquad (20a)$$

where f_j^0 is the atomic scattering factor for the atom without thermal motion. Provided that $\delta B_j(t)|\mathbf{Q}|^2 \ll 1$ the above expression can be simplified:

$$\begin{aligned} F_{\rm A}(t) &= \sum_1^{\rm A} \mu_j f_j^0 \exp\left(-\overline{B_j}|\mathbf{Q}|^2\right) \exp\left(i\mathbf{QR}_j\right) \\ &\quad \times \exp\left(-\delta B_0 \left\{ \sum_{-\infty}^{\infty} q_r \exp[ir\omega(t+\tau)] \right\} |\mathbf{Q}|^2 \right) \\ &\simeq \sum_1^{\rm A} \mu_j f_j^0 \exp\left(-\overline{B_j}|\mathbf{Q}|^2\right) \exp\left(i\mathbf{QR}_j\right) \\ &\quad \times \left(1 - \delta B_0 \left\{ \sum_{-\infty}^{\infty} q_r \exp[ir\omega(t+\tau)] \right\} |\mathbf{Q}|^2 + \ldots \right) \\ &= \overline{F_{\rm A}} + \delta F_{\rm A}(t). \end{aligned} \qquad (20b)$$

The linear response of the isotropic B factor can be anticipated for a temperature region where $B_j(t) \propto k_B T(t)$, but the diffraction response $\delta F_{\rm A}(t)$ will stay linear only for small variations of $B_j(t)$.

7. Discussion – advantages and pitfalls of the MED technique

While the application of the MED method is limited with respect to normal diffraction, this approach opens up new opportunities compared to traditional experiments. The problems to be studied with MED may be broadly split into two, which we shall refer to here as direct and inverse.

The *direct problem* of MED may be formulated as a recovery of structural information from modulated diffraction intensity. The problem can be solved assuming or designing an experiment such that a subset of the atoms responds and the response is described by a linear function in terms of structure amplitudes, which is also typically achieved by decreasing the amplitude of the stimulus.

Jemian *et al.* (1993) presented the theory and a simulated study on modulated anomalous X-ray scattering for a liquid solution. We have shown here that demodulated and correlated diffraction intensities calculated at odd and even frequencies separately represent contributions from different terms summed up in the normal diffraction intensity. This conclusion contradicts the conjecture of Jemian *et al.* (1993) that all frequency components other than the modulation frequency do not need to be taken into account. Combining periodic external modulations with demodulation or correlation procedures allows one to separate the interference term information from both silent and active atoms from the diffraction contribution of the active substructure; this is not possible for standard diffraction experiments. This statement has, however, to be taken with a grain of salt – the information we could extract is limited to a set of Fourier coefficients q_n; their number and the accuracy of each of them would define the quality of $\left|\delta F_{\rm A}^{\omega}(t)\right|$ and $\left|\delta F_{\rm A}^{\omega}(t)\right|^2$.

The information derived from the demodulation procedure, *e.g.* $I(\omega, \tau)$, is a wave in the τ space, and structural information is proportional to the amplitude of the wave. It could be difficult to extract structural information using the demodulation procedure where the information is spread in a wave in phase space. In contrast, the convolution procedure may provide a more accurate measure for the structural information together with the delay of the structural response, $\tau_{\rm A}$. To do so, the convolution procedure has to be combined with proper frequency windowing; Gaussian-shaped windows may be taken as an example, providing a sharp δ-like resolution function in the phase space. The peak is centred at $\tau_{\rm A}$, its intensity is a measure of the structural information and its width is a function of the maximum modulation frequency, but also contains information on the spread of the delay in the structural response.

The diffraction intensity extracted at double frequency can be used for solving the structure of the active sublattice using the same algorithms developed so far for normal diffraction experiments. However, access to the interference term *via* demodulation at single frequency may be used for developing new phasing tools. Further discussion of the application of MED data for structure solution will be reported elsewhere.

However MED is not limited to the solution of the phase problem but may also serve to characterize the kinetics of a process induced by the stimulus. We define the *inverse problem* of MED as the recovery of time evolution of a structural response through frequency analysis of the diffracted intensity. Such a recovery assumes that the structural changes induced by the external periodic modulation are known. The procedure may be considered as the calculation of the Fourier coefficients, $\hat{q}_r$, followed by reconstruction of the time evolution of the crystal structure. The inverse problem therefore deals with a structural response that is not necessarily linear; this approach may be of interest with respect to kinetic and *in situ* studies of non-equilibrium systems.

Until now we have only discussed diffraction intensities, but the diffraction experiment also provides information on the position of Bragg reflections and therefore on unit-cell dimensions. Note that lattice deformations and changes of atomic positions may be very different at certain timescales, as recently shown for an electric field acting on a piezoelectric crystal (Gorfman *et al.*, 2010). However, slow adiabatic variation of unit-cell dimensions may be considered as characteristic for the equilibrium state. Cell dimensions, at variance with intensities, are linearly proportional to atomic shifts and may, therefore, serve as an independent test of the linearity of the structural response.

The position of Bragg reflections may also be correlated with Bragg intensities and the external stimulus. Such an internal linearity test approach, as well as combination of different experimental probes, needs to be further developed and should be based on a detailed analysis of the physical processes involved in the stimulus.

8. Conclusions

When an external stimulus is applied to a crystal, its structure may respond and this response is commonly studied by diffraction techniques. We have formulated the necessary theoretical basis for the modulation-enhanced technique when a *periodically* varying stimulus is applied. We have shown that with the help of this technique one may selectively extract partial diffraction intensities. This option has already been realized in the case of neutron diffraction and for a limited number of isotopes, but it is lacking in the case of X-rays. We propose two methods – demodulation of diffracted intensity and its convolution with an external modulation – to facilitate the extraction of the necessary information from the diffraction signal. The theoretical description assumes that the inverse problem could also be addressed to allow recovery of the time response when the structural changes are known.

Taking into account the four possible ways to affect structural parameters and the respective response in terms of diffracted intensities, we would like to conclude this theoretical work with some comments on possible experiments. On the one hand, some external perturbations, like temperature, may trigger a variety of processes affecting the structure: partial gas pressure and concentration variations in a multicomponent mixture, chemical reactions, and structural phase transitions, to mention a few. A complex structural response has therefore to be decomposed into a set of coupled processes where coupling is a function of microscopic mechanisms involved in the structural evolution. On the other hand, some of the external variations, such as the energy of the incoming X-ray beam for a structure containing resonant atoms, may be considered as a 'safe' stimulus selectively addressing a certain set of atoms and providing linear response. The other, almost ideal, external modulation is a magnetic field combined with neutron diffraction on a compound in which the magnetic structure could be altered by a periodic perturbation. Resonant diffraction with X-rays and modulated magnetic neutron diffraction could therefore be considered as good candidates to test the proposed theoretical schemes for the solution of the direct problem.

Finally, we have shown here only the first step towards the theory of modulation effects in kinematic diffraction, which could also be expanded to dynamic scattering and diffuse scattering problems related to thermal or static structural disorder. This paper describes the basic ideas and formulas of the general MED theory. Forthcoming theoretical steps should deal with simulated experiments, error analysis, and applications to solve the phase problem and to perform kinetic analyses. Recommendations on the required statistics and sampling have also to be worked out for the test diffraction experiments.

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