Acta Crystallographica Section A
Foundations of Crystallography
ISSN 0108-7673

Received 29 July 2002
Accepted 19 September 2002

Extension of the time-dependent dynamical diffraction theory to 'optical phonon'-type distortions: application to diffraction from coherent acoustic and optical phonons

Peter Sondhauss* and Justin. S. Wark

Department of Physics, Clarendon Laboratory, University of Oxford, Parks Road, Oxford OX1 3PU, England. Correspondence e-mail: p.sondhauss1@physics.ox.ac.uk

An extension of the time-dependent Takagi–Taupin theory to 'optical phonon'-type distortions is presented. By splitting the susceptibility into the contributions from each atom in a unit cell, modifications to the structure factor as well as lattice parameter are taken into account. The result is a compact, surprisingly simple, equation with a strong formal similarity to the classical Takagi–Taupin equation, with the latter included as a special case. Time dependence is explicitly retained and thus the analysis is applicable to situations where the crystal is modified on time scales comparable with that for the X-rays to traverse an extinction depth. A comparison is made between the influence of coherent acoustic and optical phonons on the diffraction of X-rays. Numerical and perturbative analytical solutions of the generalized Takagi–Taupin equation are presented in the presence of such phonons.

1. Introduction

Novel high-brilliance pulsed X-ray sources with pulse durations in the picosecond or subpicosecond domain have opened up a new and wide field of research. Processes such as chemical reactions, phase transitions and crystal lattice dynamics happen on time scales of the order of a few thermal oscillation periods, thus in the range of femto- to picoseconds. For more than two decades, they have been investigated predominantly with the help of short pulse optical lasers, using standard optical techniques such as ellipsometry, Brillouin or Raman scattering (Thomsen *et al.*, 1986; Ruhman *et al.*, 1988; Bloembergen, 1992; Reitze *et al.*, 1992; Wright, 1994). Visible light, however, inherently cannot resolve atomic scale features and it interacts mainly with valence and free electrons. In comparison, X-rays have sufficiently short wavelengths to resolve the atomic structure and interact with the more localized lower electron shells and are ideal for the investigation of structural dynamics.

The synchronous coupling of X-ray streak cameras to fourth-generation synchrotrons has enabled such sources to reach temporal resolutions of a few picoseconds (Larsson, 2001) whilst $K\alpha$ sources based on the electron beams present in laser plasmas have been demonstrated with pulse lengths below 300 fs (Rousse *et al.*, 1994). Furthermore, plans for sources based on free-electron laser technology promise hard X-rays with even shorter durations (Winick, 1995; Wiik, 1997).

So far a great variety of successful experiments utilizing time-resolved X-ray diffraction (TRXD) have been reported from fields as diverse as solid-state physics (Rischel *et al.*, 1997; Larsson *et al.*, 1998; Chin *et al.*, 1999; Rose-Petruck *et al.*, 1999; Siders *et al.*, 1999; Lindenberg *et al.*, 2000; Reis *et al.*, 2001; Sokolowski-Tinten *et al.*, 2001; Larsson *et al.*, 2002), chemistry (Neutze *et al.*, 2001) and biology (Srajer *et al.*, 1996; Perman *et al.*, 1998; Neutze *et al.*, 2000).

Many of the solid-state experiments have investigated the modification of nearly perfect crystals, using femtosecond optical lasers to induce coherent acoustic and optical phonons. These novel femtosecond X-ray sources allow the study of the diffraction from such phonons directly in the time domain (in contrast, for example, to the studies of thermal diffuse scattering, where incoherent phonons are studied in what is in effect the frequency domain). As single phonon modes, or narrow spectra of modes, are excited, with populations far greater than the thermal background, distinct temporal oscillations in the diffraction signal can be directly recorded. Coherent acoustic phonons with periods of a few picoseconds have been observed (Lindenberg *et al.*, 2000). More recently, coherent optical phonons with periods of a few hundred femtoseconds have also been observed in the time domain (von der Linde, 2002). Furthermore, it has been noted that the generation of coherent phonon or polariton distributions within crystals may provide a method for switching X-rays on time scales of order of the inverse of the phonon period (Bucksbaum & Merlin, 1999).

Given the highly perfect nature of the crystals used for many of the studies cited above, the theoretical background of such experiments (Chukhovskii & Colella, 1993; Tomov *et al.*, 1998) is based upon the *dynamical theory of X-ray diffraction*. As the investigated processes usually occur as distortions of

these perfect crystals, some variant of the Takagi–Taupin equation is often used (Takagi, 1962; Taupin, 1964; Klar & Rutichelli, 1973). Unfortunately, not all types of distortions are covered by the standard Takagi–Taupin theory. The standard theory can take into account strain – *i.e.* modifications to the local lattice parameter – and thus can be used to model diffraction from crystals that include low-frequency acoustic phonons. However, optical phonons principally modify the structure of the crystal, and as such do not fall within the standard treatment. As noted above, coherent optical phonons have already been the subject of interest in recent TRXD experiments with bismuth (von der Linde, 2002). Therefore, a theory that also covers this type of distortion is highly desirable. In this paper, such a theory is presented. If the crystal is modified on very short time scales, as it might be by a high-frequency coherent optical phonon or polariton for example, the time dependence of the diffraction process itself may become important (Wark & He, 1994; Chukhovskii & Förster, 1995; Wark & Lee, 1999; Graeff, 2002; Yamazaki & Ishikawa, 2002). We thus explictly keep time dependence in the treatment presented here.

The paper is laid out in the following manner. In §2, the generalized Takagi–Taupin equation is derived from first principles, and a discussion of it follows in §3. In §4, the generalized Takagi–Taupin equation for coherent single-mode acoustic and optical phonons is solved numerically, and a perturbative analytic solution is presented. The range of applicability of the perturbative solution is discussed.

2. Derivation of the generalized Takagi–Taupin equation

In classical Takagi–Taupin theory, the assumption is made that the atoms within a single unit cell are displaced uniformly, *i.e.* the atoms 1 to M within an M-atom unit cell are displaced by the same vector $\mathbf{u}_1 = \mathbf{u}_2 = \ldots = \mathbf{u}_M \stackrel{\text{def}}{=} \mathbf{u}$. This allows the susceptibility field of the distorted crystal $\chi(\mathbf{r}, t)$ to be related to the susceptibility of the perfect crystal $\chi^{(p)}(\mathbf{r})$:

$$\chi(\mathbf{r}, t) = \chi^{(p)}(\mathbf{r} - \mathbf{u}(\mathbf{r}, t)). \tag{1}$$

For this reason, the classical Takagi–Taupin equation cannot be applied directly to non-uniform distortions, by which we mean those where in principle each atom within a single unit cell can experience a different displacement (*e.g.* optical phonons). That is to say, in general $\mathbf{u}_1 \neq \mathbf{u}_2 \neq \ldots \neq \mathbf{u}_M$.

As the susceptibility in the case of an M-atom unit cell is well approximated by the sum of the single-atom susceptibilities, the susceptibility in the case of a non-uniform displacement can be expressed as

$$\chi(\mathbf{r}, t) = \sum_{N=1}^{M} \chi_N^{(p)}(\mathbf{r} - \mathbf{r}_N - \mathbf{u}_N(\mathbf{r}, t)), \tag{2}$$

with $\mathbf{r}_N$ being the atomic coordinates in a local unit-cell coordinate system. In what follows, unless stated otherwise, we will assume that $\mathbf{u}_N$ is a function of $\mathbf{r}$ and t.

The perfect-crystal susceptibilities $\chi_N^{(p)}(\mathbf{r})$ can be expanded as a spatial Fourier series which leads to

$$\chi(\mathbf{r}, t) = \sum_h \chi'_h(\mathbf{r}, t) \exp(-i\mathbf{G}_h \cdot \mathbf{r}), \tag{3}$$

where $\mathbf{G}_h$ is the reciprocal-lattice vector and

$$\chi'_h(\mathbf{r}, t) \stackrel{\text{def}}{=} \sum_{N=1}^{M} \chi_{Nh} \exp[i\mathbf{G}_h \cdot (\mathbf{r}_N + \mathbf{u}_N)], \tag{4}$$

where χ_{Nh} stands for the Fourier coefficients of the single-atom susceptibilities,

$$\chi_{Nh} \stackrel{\text{def}}{=} V_{\text{uc}}^{-1} \int \mathrm{d}V\, \chi_N^{(p)}(\mathbf{r}) \exp(i\mathbf{G}_h \cdot \mathbf{r})$$

and V_{uc} for the volume of the unit cell. In contrast to the classical Takagi–Taupin theory, the susceptibility component $\chi'_h(\mathbf{r}, t)$ is a function of space and time. Note that at this stage we have not yet made the assumption that the spatial variation of the displacement fields $\mathbf{u}_N(\mathbf{r}, t)$ from cell to cell is small. As the displacement of every atom in a unit cell is considered separately, one doesn't need the assumption of small spatial frequencies to ensure that the variation of the displacement vector within a single unit cell is small. At a later stage, we will make this assumption nevertheless, but for other reasons. Evidently, when we make the assumption of small spatial frequencies and further assume $\mathbf{u}_1 = \mathbf{u}_2 = \ldots = \mathbf{u}_M$, we recover results similar to those of Takagi and Taupin.

The wave equation for the X-ray dielectric displacement field $\mathbf{D}$ in a crystalline medium

$$\Delta\mathbf{D} - \frac{1}{c^2}\frac{\partial^2 \mathbf{D}}{\partial t^2} = -\mathrm{curl}\,\mathrm{curl}(\chi\mathbf{D}) \tag{5}$$

can be solved as is usual by applying the Bloch-type *ansatz*

$$\mathbf{D}(\mathbf{r}, t) = \sum_h \mathbf{D}'_h(\mathbf{r}, t) \exp[i(\omega t - \mathbf{k}_h \cdot \mathbf{r})], \tag{6}$$

with the speed of light in vacuum, c, the frequency of the X-rays, ω, the wave vector of the incident wave (in the crystal), $\mathbf{k}_0$, the wave vector of the diffracted wave, $\mathbf{k}_h = \mathbf{k}_0 + \mathbf{G}_h$, and

$$\mathbf{D}'_h(\mathbf{r}, t) \stackrel{\text{def}}{=} \sum_{N=1}^{M} \mathbf{D}_{Nh} \exp(i\mathbf{G}_h \cdot \mathbf{u}_N). \tag{7}$$

The X-ray field amplitudes $\mathbf{D}'_h$ here are, like the Fourier coefficients of the susceptibility, a sum over atomic terms. We now substitute (7) into the wave equation (5). The subsequent development and approximations are very similar to those leading to the classical Takagi–Taupin equation (Takagi, 1969; Authier, 2001) but are still worth showing to some level of detail. For the sake of clarity, we study this development for each of the three terms in (5) in turn:

1. *The* $\Delta\mathbf{D}$ *term:* If we assume that the displacement fields $\mathbf{u}_N(\mathbf{r}, t)$ and field amplitudes $\mathbf{D}_{Nh}(\mathbf{r}, t)$ at any time vary slowly in space then second-order derivatives of $\mathbf{u}_N$ and $\mathbf{D}_{Nh}$ can be neglected. Under this assumption, one obtains

$$\Delta\mathbf{D} = \sum_h \sum_{N=1}^{M} [-2i(\mathbf{k}'_{Nh} \cdot \nabla) - k'^2_{Nh}] \times \mathbf{D}_{Nh} \exp[i(\omega t - \mathbf{k}_h \cdot \mathbf{r} + \mathbf{G}_h \cdot \mathbf{u}_N)], \tag{8}$$

where $\mathbf{k}'_{Nh}$ stands for the *local wave vector*

$$\mathbf{k}'_{Nh} \stackrel{\text{def}}{=} \mathbf{k}_h - \nabla(\mathbf{G}_h \cdot \mathbf{u}_N). \tag{9}$$

In an analogous way to the assumptions made in Takagi–Taupin theory, by slow spatial variations in $\mathbf{u}_N(\mathbf{r}, t)$ we mean that the difference in the displacements of a particular atom in the basis between one unit cell and its neighbour should be small compared with the X-ray wavelength.

2. *The* $\partial^2\mathbf{D}/\partial t^2$ *term:* Typical temporal frequencies of diffractable X-rays lie around 10^{19} rad s^{-1}, thus far beyond the frequencies of phonons or any other kind of distortion. Therefore, terms of the order of $\ddot{\mathbf{D}}_{Nh}$, $\ddot{\mathbf{u}}_N$, $\dot{\mathbf{u}}_N^2$ and $\dot{u}_{Ni}\dot{D}_{Nhj}$ may be neglected. With this approximation the result reads:

$$\partial^2\mathbf{D}/\partial t^2 = \sum_h \sum_{N=1}^{M} [2i\omega\dot{\mathbf{D}}_{Nh} - 2\omega(\mathbf{G}_h \cdot \dot{\mathbf{u}}_N)\mathbf{D}_{Nh} - \omega^2\mathbf{D}_{Nh}] \times \exp[i(\omega t - \mathbf{k}_h \cdot \mathbf{r} + \mathbf{G}_h \cdot \mathbf{u}_N)]. \quad (10)$$

We would like to draw the reader's attention to the central term of the right-hand side of (10), which contains the time derivative of the displacement field. The temporal evolution of the X-ray field amplitudes $\mathbf{D}_{Nh}$ takes place on time scales of order of the *extinction depth traversal time*

$$\tau = \Lambda_{\rm ext}/c\gamma_0 \quad (11)$$

(Wark & He, 1994; Chukhovskii & Förster, 1995; Wark & Lee, 1999), where $\Lambda_{\rm ext}$ stands for the extinction depth and γ_0 for the direction cosine $\cos\psi_0$, with ψ_0 being the angle between $\mathbf{k}_0$ and the inner surface normal $\mathbf{n}$. One might initially expect that this time would be short compared with the evolution of the atomic displacement fields, and thus the central term can be neglected. However, for weak X-ray reflections, extinction depths can be large (tens or hundreds of μm), and thus the relevant time scales for the evolution of the X-ray field may approach or exceed 100 fs – *i.e.* the period of optical phonons. Thus there may well be situations in which this term must be retained. We keep it in the analysis presented here.

3. *The* $\mathrm{curl}\,\mathrm{curl}(\chi\mathbf{D})$ *term:* As the electric susceptibility, χ, for X-rays is very small ($10^{-6}-10^{-5}$), several approximations can be made here. As with standard Takagi–Taupin theory, we assume that first-order derivatives of $\mathbf{u}_N$ or $\mathbf{D}_{Nh}$ and higher can be neglected. Physically, this corresponds to the assumption that the spatial scales upon which these fields vary is large compared with the X-ray wavelength.

With such assumptions, we find:

$$\mathrm{curl}\,\mathrm{curl}(\chi\mathbf{D}) = k_h^2 \sum_{h,l} \chi'_{h-l}\mathbf{D}'_{l[h]} \exp[i(\omega t - \mathbf{k}_h \cdot \mathbf{r})] \quad (12)$$

with

$$\mathbf{D}'_{l[h]} \stackrel{\rm def}{=} \mathbf{D}'_l - \frac{\mathbf{k}_h}{k_h}\left(\frac{\mathbf{k}_h}{k_h} \cdot \mathbf{D}'_l\right). \quad (13)$$

This appears identical to the corresponding term in the classical Takagi–Taupin equation, but one has to bear in mind that χ'_{h-l} and $\mathbf{D}'_l$ are standing for the sums defined in (4) and (7).

Putting the above three parts together, and neglecting terms of the order of $\partial_i(\mathbf{G}_h \cdot \mathbf{u}_N)\partial_j\mathbf{D}_{Nh}$, we obtain the *generalized time-dependent Takagi–Taupin equation*:

$$2i(\mathbf{k}_h \cdot \nabla)\mathbf{D}'_h + k^2\frac{2i}{\omega}\frac{\delta\mathbf{D}'_h}{\partial t} + (k_h^2 - k^2)\mathbf{D}'_h = k_h^2 \sum_l \chi'_{h-l}\mathbf{D}'_{l[h]} \quad (14)$$

with $k \stackrel{\rm def}{=} \omega/c$ being the spatial frequency of the X-rays in vacuum. Note that all sums over N have disappeared owing to the definition of $\mathbf{D}'_h$ in (7). A discussion of this equation follows in §3.

3. Comparison with classical Takagi–Taupin theory

Equation (14) looks remarkably similar to the classical time-dependent Takagi–Taupin equation (Wark & He, 1994; Chukhovskii & Förster, 1995). In fact, the classical equation must be included as the special case for $\mathbf{u}_1 = \mathbf{u}_2 = \ldots = \mathbf{u}_M \stackrel{\rm def}{=} \mathbf{u}$. This will be demonstrated here, in order to prove consistency.

If the displacements $\mathbf{u}_N$ for all atoms N in a unit cell are the same, the phase factor $\exp(i\mathbf{G}_h \cdot \mathbf{u}_N)$ is identical for all terms in the sums in (4) and (7), which can thus be written

$$\chi'_h(\mathbf{r}, t) = \chi_h \exp(i\mathbf{G}_h \cdot \mathbf{u}), \quad \mathbf{D}'_h(\mathbf{r}, t) = \mathbf{D}_h \exp(i\mathbf{G}_h \cdot \mathbf{u}), \quad (15)$$

with $\mathbf{D}_h$ being the X-ray field amplitude as it is usually defined in classical Takagi–Taupin theory. Inserting these expressions into the generalized time-dependent Takagi–Taupin equation (14), one obtains

$$2i(\mathbf{k}_h \cdot \nabla)\mathbf{D}_h - 2(\mathbf{k}_h \cdot \nabla)(\mathbf{G}_h \cdot \mathbf{u})\mathbf{D}_h + k^2\frac{2i}{\omega}\frac{\partial\mathbf{D}_h}{\partial t} - k^2\frac{2}{\omega}(\mathbf{G}_h \cdot \dot{\mathbf{u}})\mathbf{D}_h + (k_h^2 - k^2)\mathbf{D}_h = k_h^2 \sum_l \chi_{h-l}\mathbf{D}_{l[h]}. \quad (16)$$

The above equation is identical to the time-dependent equation as derived previously (Wark & He, 1994; Chukhovskii & Förster, 1995; Wark & Lee, 1999) though care should be taken in comparison, as using the present notation the previous work presented equations for $\mathbf{D}'_h(\mathbf{r}, t)$.

Given that we have demonstrated that (14) describes X-ray diffraction from crystals with both uniform and non-uniform distortions, it is of interest to discuss the differences between the diffraction in the presence of the various distortion types. The only term where distortions leave their mark in (14) is the susceptibility coefficient χ'_{h-l}. In the case of uniform displacements, it has been shown in (15) that this just adds the phase $\mathbf{G}_h \cdot \mathbf{u}$ to the complex Fourier coefficient χ_h of the perfect crystal. Thus a uniform displacement field leads to a pure phase modulation of the susceptibility coefficient (it is this phase modulation that in the formulae presented here corresponds to the deviation from the local Bragg angle that strain introduces into the standard Takagi–Taupin equations). A non-uniform displacement, however, will not only change the phase but also the modulus (see Fig. 1).

A general expression for the displacement of coherent single-mode acoustic or optical phonons is given by

$$\mathbf{u}_N = \mathbf{p}_N \cos(\Omega t - \mathbf{q} \cdot \mathbf{r}), \quad N = 1, \ldots, M, \quad (17)$$

where $\mathbf{p}_N$ is a constant vector describing amplitude and polarization, Ω the phonon frequency and $\mathbf{q}$ the phonon wave

vector. In order to be able to take account of the non-uniform displacement of optical phonons, both displacement vector and polarization vector have an atomic index N. The susceptibility χ'_h can thus be written

$$\chi'_h = \sum_{N=1}^{M} \chi_{Nh} \exp(i\mathbf{G}_h \cdot \mathbf{r}_N) \exp[i\mathbf{G}_h \cdot \mathbf{p}_N \cos(\Omega t - \mathbf{q} \cdot \mathbf{r})]. \quad (18)$$

For small amplitudes $|\mathbf{p}_N|$, the second exponential function can be expanded as a Taylor series where terms of second order and higher are negligible, leading to

$$\chi'_h = \chi_h + \delta\chi_h \cos(\Omega t - \mathbf{q} \cdot \mathbf{r}), \quad (19)$$

where

$$\delta\chi_h \stackrel{\text{def}}{=} i \sum_{N=1}^{M} \mathbf{G}_h \cdot \mathbf{p}_N \chi_{Nh} \exp(i\mathbf{G}_h \cdot \mathbf{r}_N). \quad (20)$$

From this expression, it is evident that both optical and acoustic phonons do not affect the susceptibility coefficient χ'_h if the phonons are polarized parallel to the diffracting planes, *i.e.* $\mathbf{G}_h \cdot \mathbf{p}_N = 0$. In this case, the phonons will not be 'visible' in the rocking curve.

In addition, (19) and (20) reveal that an acoustic phonon, where $\mathbf{p}_1 = \mathbf{p}_2 = \ldots = \mathbf{p}_M \stackrel{\text{def}}{=} \mathbf{p}$ and

$$\delta\chi_h^{\text{ac}} = i\chi_h \mathbf{G}_h \cdot \mathbf{p}, \quad (21)$$

is incapable of lifting the ban of a forbidden reflection, because if $\chi_h = 0$, $\delta\chi_h^{\text{ac}}$ also vanishes. In contrast, an optical phonon can, in principle, lift the ban, as $\delta\chi_h$ is not necessarily zero if χ_h vanishes (see Fig. 1).

Finally, if one substitutes the expression for χ'_h from (19) into the Fourier series (3) of the susceptibility $\chi(\mathbf{r}, t)$, one receives

$$\chi(\mathbf{r}, t) = \chi^{(p)}(\mathbf{r}) + \tfrac{1}{2}\sum_h \delta\chi_h \exp[i\Omega t - i(\mathbf{G}_h + \mathbf{q}) \cdot \mathbf{r}] + \tfrac{1}{2}\sum_h \delta\chi_h \exp[-i\Omega t - i(\mathbf{G}_h - \mathbf{q}) \cdot \mathbf{r}]. \quad (22)$$

Besides the perfect-crystal susceptibility $\chi^{(\text{p})}(\mathbf{r})$, which has of course the periodicity of the lattice, there are two smaller terms, with slightly modified periodicities. The Laue condition for these terms reads

$$\mathbf{k} - \mathbf{k}_0 = \mathbf{G}_h \pm \mathbf{q}. \quad (23)$$

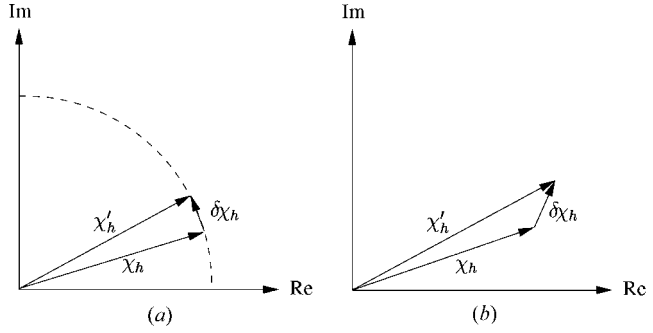

Figure 1
Effect of acoustic (*a*) and optical (*b*) single-mode phonons on the susceptibility coefficient χ'_h.

Thus, on either side of the rocking-curve peak ($\mathbf{k} - \mathbf{k}_0 = \mathbf{G}_h$, $\theta = \theta_B, \theta_B$: Bragg angle), smaller diffraction maxima appear at

$$\Delta\theta \stackrel{\text{def}}{=} \theta - \theta_B = \pm\frac{q}{G_h}(\cos\kappa \tan\theta_B + \sin\kappa) - \frac{\chi_{r0}(1-\gamma)}{2\sin(2\theta_B)}, \quad (24)$$

where q stands for the spatial frequency $|\mathbf{q}|$, G_h for the modulus of the reciprocal-lattice vector, κ for the angle between $\mathbf{q}$ and $\mathbf{G}_h$ (see Fig. 2) and γ for the asymmetry factor γ_h/γ_0 [$\gamma_h \stackrel{\text{def}}{=} \cos\psi_h$, $\psi_h \stackrel{\text{def}}{=} \angle(\mathbf{k}_h, \mathbf{n})$]. The last term in (24) represents the shift of the Bragg angle due to refraction. The periodic structures represented by terms 2 and 3 in (22) are not static. Obviously, the structure with reciprocal-lattice vector $\mathbf{G}_h + \mathbf{q}$ moves with the speed $\mathbf{v}^+ = \Omega(\mathbf{G}_h + \mathbf{q})/|\mathbf{G}_h + \mathbf{q}|^2$, and the other with $\mathbf{G}_h - \mathbf{q}$ with $\mathbf{v}^- = -\Omega(\mathbf{G}_h - \mathbf{q})/|\mathbf{G}_h - \mathbf{q}|^2$. This becomes important if the speed of sound is so high that relativistic Doppler effects have to be taken into account, as may be the case for *e.g.* polaritons. We discuss this further in the next section.

4. Perturbative analytical solution of the generalized Takagi–Taupin equation

In this section, a novel perturbative method to analytically solve the Takagi–Taupin equation in the presence of a small periodic distortion is presented. For such a small distortion, the susceptibility coefficient χ'_h can be separated into the susceptibility coefficient of the unperturbed crystal χ_h and a small perturbation term, *e.g.* $\delta\chi_h \cos(\Omega t - \mathbf{q} \cdot \mathbf{r})$ in the case of coherent single-mode phonons [see equation (19)]. Because one can expect that a small perturbation also only has a small effect on the X-ray field amplitudes $\mathbf{D}'_h$, it is useful to separate them as well: $\mathbf{D}'_h = \mathbf{D}_h^{(p)} + \delta\mathbf{D}'_h$, where $\mathbf{D}_h^{(p)}$ stands for the field amplitude in the perfect unperturbed crystal and $\delta\mathbf{D}'_h$ for a small perturbation (we return to these assumptions later in the section). Inserting these expressions into the generalized Takagi–Taupin equation (14), making use of the fact that $\mathbf{D}_h^{(p)}$ is the perfect-crystal solution and neglecting terms of the

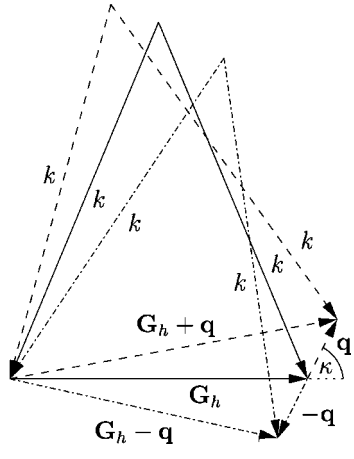

Figure 2
Laue condition for a crystal with single-mode phonons (wave vector $\mathbf{q}$).

order $\delta\chi_h\delta\mathbf{D}'_h$, one obtains the following non-homogeneous linear differential equation system for the perturbation terms $\delta\mathbf{D}'_h$:

$$\frac{2i}{k}(\mathbf{s}_h\cdot\nabla)\delta\mathbf{D}'_h+\frac{2i}{\omega}\frac{\partial(\delta\mathbf{D}'_h)}{\partial t}+\frac{k_h^2-k^2}{k^2}\delta\mathbf{D}'_h - \sum_l \chi_{h-l}\delta\mathbf{D}'_{l[h]}=\cos(\Omega t-\mathbf{q}\cdot\mathbf{r})\sum_l \delta\chi_{h-l}\mathbf{D}^{(p)}_{l[h]}. \quad (25)$$

What has been gained by this? In contrast to the Takagi–Taupin equation itself, this differential equation system has constant coefficients. The only space- and time-dependent term is the inhomogeneity. Therefore, the solution of this system is very straightforward. It will be demonstrated here for the case of two strong waves, where only a single diffracted wave field $\mathbf{D}'_h$ exists apart from the incident $\mathbf{D}'_0$, which corresponds to ordinary Bragg or Laue diffraction. The system of equations (25) can then be reduced to

$$\begin{aligned}\frac{2i}{k}\frac{\partial(\delta D'_0)}{\partial s_0}+\frac{2i}{\omega}\frac{\partial(\delta D'_0)}{\partial t}-C\chi_{\bar h}\delta D'_h &= \delta\chi_{\bar h}C\cos(\Omega t-\mathbf{q}\cdot\mathbf{r})D_h^{(p)}\\ \frac{2i}{k}\frac{\partial(\delta D'_h)}{\partial s_h}+\frac{2i}{\omega}\frac{\partial(\delta D'_h)}{\partial t}-C\chi_h\delta D'_0+2\beta_h\delta D'_h &= \delta\chi_h C\cos(\Omega t-\mathbf{q}\cdot\mathbf{r})D_0^{(p)}\end{aligned} \quad (26)$$

with s_0 and s_h being the in general non-orthogonal spatial coordinates whose axes are parallel to the wave vectors $\mathbf{k}_0$ and $\mathbf{k}_h$, C the polarization factor which is 1 for σ-polarized and $\cos(2\theta_B)$ for π-polarized X-rays, and finally

$$\beta_h \stackrel{\text{def}}{=} \frac{k_h^2-k^2}{2k^2}-\frac{\chi_0}{2}. \quad (27)$$

With the *ansatz*[1]

$$\delta D'_h = d_h^+\exp[i(\Omega t-\mathbf{q}\cdot\mathbf{r})]+d_h^-\exp[-i(\Omega t-\mathbf{q}\cdot\mathbf{r})], \quad (28)$$

the differential equation system can be written as an algebraic system for $d_h^\pm$ with the solution:

$$d_h^\pm=\frac{C}{2}\frac{\chi_h\delta\chi_{\bar h}CD_h^{(p)}\pm A_0\delta\chi_h D_0^{(p)}}{\pm A_0(\pm A_h+2\beta_h)-\chi_h\chi_{\bar h}C^2}, \quad (29)$$

with

$$A_0\stackrel{\text{def}}{=}(2/k)\mathbf{s}_0\cdot\mathbf{q}-2(\Omega/\omega),\quad A_h\stackrel{\text{def}}{=}(2/k)\mathbf{s}_h\cdot\mathbf{q}-2(\Omega/\omega). \quad (30)$$

The total solution

$$D_h(\mathbf{r},t)=D_h^{(p)}+d_h^+\exp[i(\Omega t-\mathbf{q}\cdot\mathbf{r})]+d_h^-\exp[-i(\Omega t-\mathbf{q}\cdot\mathbf{r})] \quad (31)$$

is the unperturbed rocking curve given by $D_h^{(p)}$ plus satellites on either side at $|\mathbf{k}-\mathbf{k}_0|=|\mathbf{G}_h\pm\mathbf{q}|$ with amplitudes $d_h^\pm$ oscillating with the phonon frequency Ω.

For the exact angular position of these satellites, refraction effects have to be taken into account. Therefore, in (27) the wave vectors $\mathbf{k}_0$ and $\mathbf{k}_h$ must be expressed by the vacuum wave vectors $\mathbf{k}_0^{(a)}$ and $\mathbf{k}_h^{(a)}$, *i.e.*

$$\mathbf{k}_0=\mathbf{k}_0^{(a)}+\frac{k\chi_0}{2\gamma_0}\mathbf{e}_z,\quad \mathbf{k}_h=\mathbf{k}_h^{(a)}+\frac{k\chi_0}{2\gamma_h}\mathbf{e}_z. \quad (32)$$

This leads to

$$\beta_h=-\Delta\theta^{(a)}\sin(2\theta_B)-\tfrac{1}{2}\chi_0(1-\gamma). \quad (33)$$

Attention has to be paid to the fact that the total solution is a sum of complex field amplitudes and therefore it is vital to use expressions for the perfect-crystal amplitudes $D_0^{(p)}$ and $D_h^{(p)}$ with the correct phases.

In Fig. 3, we show the results of the calculation of the rocking curve for Bragg reflection from 10 µm thick InSb 111 (angle of asymmetry $\phi=5^\circ$, $\lambda=1.5406$ Å, σ polarization) distorted by coherent longitudinal acoustic phonons propagating perpendicularly to the crystal surface with spatial frequency $|\mathbf{q}|=10^8$ rad m^{-1}, temporal frequency $\Omega=3.75\times10^{11}$ rad s^{-1} and strain amplitude $\eta_0=0.1\%$. The agreement between the perturbative solution and the full numerical solution of (14) is excellent – indeed, the difference between the two solutions lies within the accuracy of the numerical algorithms employed and cannot be seen on the scale of the graph.

One advantage of such an analytical solution is the ability to see immediately the influence of certain physical parameters. For example, the explicit time dependence represented by the time derivatives $\partial_t D_0$ and $\partial_t D_h$, which leads to the Ω/ω terms in A_0 and A_h, only plays a role if the phonon frequency Ω is of comparable order with the X-ray field frequency ω, *i.e.* if the phonon phase velocity is a non-negligible fraction of the speed of light. This could, for example, occur in the presence of polaritons. The major effect of these terms on the rocking curve is the angular shift of the satellites, either away or towards the centre of the rocking curve. The direction of shift depends on whether the phonon (polariton) has a velocity component parallel or anti-parallel in the direction of the reciprocal-lattice vector $\mathbf{G}_h$. If the component is anti-parallel, the satellites will move towards the central peak, if it is parallel they will move away. This effect can be understood in terms of the simple wave-vector-matching scheme introduced in §3. The structures with reciprocal-lattice vectors $\mathbf{G}_h\pm\mathbf{q}$ move

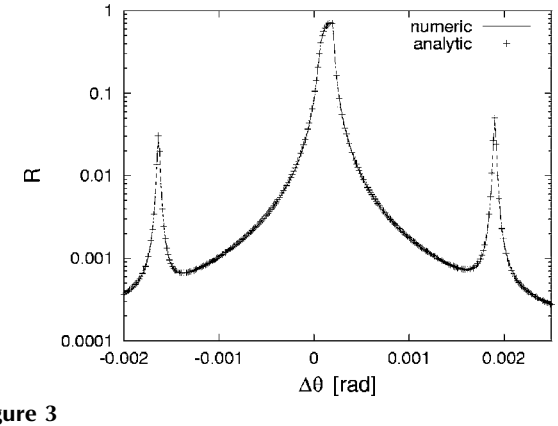

Figure 3
Comparison between the full numerical and the perturbative solution for Bragg diffraction from a single crystal in the presence of a coherent acoustic phonon for the conditions stated in the text.

[1] The index h stands here also for 0, *i.e.* the incident wave field.

now at a speed level that relativistic Doppler effects come into play. The structure with $\mathbf{G}_h + \mathbf{q}$ moves towards the crystal surface and sees a blue-shifted incident X-ray wave, the structure with $\mathbf{G}_h - \mathbf{q}$ moves into the crystal bulk and thus sees a red shift. In order to quantify this effect, one has to fulfil the Laue condition in the rest frame of each structure and then perform a Lorentz transformation into the rest frame of the crystal. The Laue condition in the respective rest frames

$$\mathbf{k}' - \mathbf{k}_0' = \mathbf{G}_h' + \mathbf{q}', \quad \mathbf{k}'' - \mathbf{k}_0'' = \mathbf{G}_h'' - \mathbf{q}'' \tag{34}$$

Lorentz transformed results in

$$\delta\mathbf{K}^{\pm} = \frac{2}{c^2}\frac{\mathbf{q} \pm \mathbf{G}_h}{|\mathbf{q} \pm \mathbf{G}_h|^2}\Omega(\omega - \Omega), \tag{35}$$

with the Doppler shift $\delta\mathbf{K}^{\pm} \stackrel{\text{def}}{=} \mathbf{K} - (\mathbf{G}_h \pm \mathbf{q})$ of the scattering vector $\mathbf{K} \stackrel{\text{def}}{=} \mathbf{k} - \mathbf{k}_0$. Under the assumption that $|\mathbf{q}| \ll |\mathbf{G}_h|$, this leads to the angular shift

$$\delta\theta^{\pm} = \pm 2\tan\theta_B[\Omega(\omega - \Omega)/(c^2 G_h^2)] \tag{36}$$

of the satellites. A more illustrative, but only qualitative, way of looking at the problem is from the viewpoint of the incident X-ray wave propagating 'only' at the speed of light. If the phonon moves at least partially into the same direction, the X-rays see a longer phonon wavelength because, in the time it takes the X-rays to travel *e.g.* from one amplitude maximum to another, the second maximum will have moved further away from the point where the X-rays have intercepted the first. Correspondingly, the X-rays will see a shorter phonon wavelength if the phonon moves towards the incident X-rays.

The analytic solution includes an arbitrary direction of propagation for the phonon. The numerical solution of this case is computationally expensive because the full spatially two-dimensional Takagi–Taupin equation has to be solved rather than a reduced one-dimensional variant for only depth-dependent strain (Klar & Rutichelli, 1973; Gronkowski, 1991). The analytic solution is in principle far simpler in such cases and may be of use in a study of the proposed phonon–Bragg switch (Bucksbaum & Merlin, 1999).

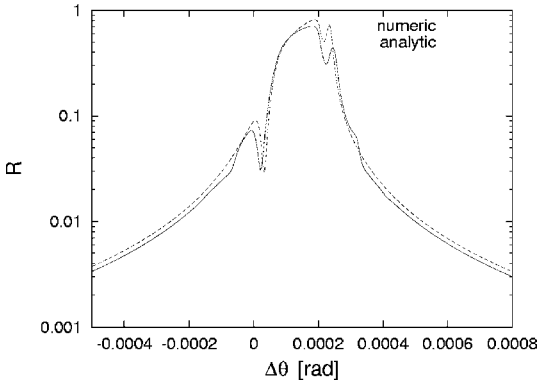

Figure 4
Comparison between the full numerical and the perturbative solution for Bragg diffraction from a single crystal in the presence of a low-frequency coherent acoustic phonon with $|\mathbf{q}| = 5 \times 10^6$ rad m^{-1}, $\Omega = 1.875 \times 10^{10}$ rad s^{-1}, and $\eta_0 = 0.01\%$. Otherwise, the parameters are the same as in Fig. 3.

Finally, the perturbative approach has the great advantage of allowing a direct decomposition of a measured rocking-curve profile into the contributions from coherent phonons in different modes. Because the differential equation (25) for $\delta\mathbf{D}_h' = \mathbf{D}_h' - \mathbf{D}_h^{(p)}$ is linear, the contributions from different modes simply superimpose. This allows us to use *e.g.* a least-squares algorithm to fit the modulus of a sum of those analytical solutions for a set of relevant phonon modes to a measured rocking curve, which directly reveals information about the modes' occupation numbers. The fitted solution may be ambiguous to a certain extent though, since the measured rocking curve lacks phase information.

Obviously, the perturbative solution becomes less accurate with increasing strain amplitude as the the realization of the basic assumption $|\delta\chi_h| \ll |\chi_h|$ gets worse. The assumption works well for strains up to a few tens of a percent, depending on where the satellites are located, *i.e.* what spatial frequency $|\mathbf{q}|$ the phonons have. In our studies to date, we have found that the perturbative solution is reasonable if the maximum intensity of the satellites does not exceed 10% of that of the main peak.

Care must also be taken in using the perturbative solution in the case where the sidebands are not well separated in angle from the main peak. This will clearly occur for phonons with wavelengths comparable to or longer than an extinction depth. Under such circumstances, the incident X-rays will not interact with many wavelengths of the periodic disturbance, and the solutions to the equations for the main peak cannot be decoupled from those of the sidebands. This can be seen in Fig. 4, where we show the perturbative and numerical solutions for low-frequency coherent single-mode acoustic phonons – evidently it is not safe to use the perturbative solution when the sidebands are only separated in angle from the main peak by of order a rocking-curve width.

Another case where the perturbative solution becomes inaccurate is if the crystal is thin enough to show Laue oscillations. In this case, the deviation is of the order of the Laue oscillation amplitude.

5. Conclusions

An extension of the Takagi–Taupin theory has been presented that can deal with distortions altering not only the lattice parameter but also the crystal structure. This is particularly important in the field of ultrafast molecular and interatomic dynamics, where optical phonons play an important role, *e.g.* in the form of soft modes during phase transitions or as a potential scheme for an ultrafast Bragg switch (Bucksbaum & Merlin, 1999). Fortunately, the generalized Takagi–Taupin equation turns out to be no more complex than the classical equation. It is even slightly more intuitive as the distortion affects directly the susceptibility, the parameter which defines the X-ray diffraction properties of a crystal.

In the case of small distortions, the generalized Takagi–Taupin equation can be solved analytically using a novel perturbative approach. This has been demonstrated for acoustic and optical phonons for the most important case of

two strong X-ray wave fields. In principle, this analytical solution can be used to directly decompose a measured rocking-curve profile into the contributions from different phonon modes. It shows that explicit time dependence of the X-ray wave fields has to be taken into account if the speed of sound is a non-negligible fraction of the speed of light, as *e.g.* can be the case for polaritons. The effect is a de- or increased effective spatial phonon frequency $|\mathbf{q}|$ owing to a simple Doppler effect which is also understandable in terms of simple wave-vector-matching considerations.

The authors would like to acknowledge the support of the European Commission through the Human Potential Programme.

References

Authier, A. (2001). *Dynamical Theory of X-ray Diffraction*, 1st ed. Oxford University Press.

Bloembergen, N. (1992). *Nature (London)*, **356**, 110–111.

Bucksbaum, P. & Merlin, R. (1999). *Solid State Commun.* **111**, 535–539.

Chin, A., Schoenlein, R., Glover, T., Balling, P., Leemans, W. & Shank, C. (1999). *Phys. Rev. Lett.* **83**, 336–339.

Chukhovskii, F. & Colella, R. (1993). *Phys. Rev. B*, **47**, 484–486.

Chukhovskii, F. & Förster, E. (1995). *Acta Cryst.* A**51**, 668–672.

Graeff, W. (2002). *J. Synchrotron Rad.* **9**, 82–85.

Gronkowski, J. (1991). *Phys. Rep.* **206**, 1–41.

Klar, B. & Rutichelli, F. (1973). *Nuovo Cimento B*, **13**, 249–271.

Larsson, J. (2001). *Meas. Sci. Technol.* **12**, 1835–1840.

Larsson, J., Allen, A., Bucksbaum, P., Falcone, R., Lindenberg, A., Naylor, G., Missalla, T., Reis, D., Scheidt, K., Sjörgen, A., Sondhauss, P., Wulff, M. & Wark, J. (2002). *Appl. Phys. A*, **75**, 467–478.

Larsson, J., Heimann, P., Lindenberg, A., Schuck, P., Bucksbaum, P., Lee, R., Padmore, H., Wark, J. & Falcone, R. (1998). *Appl. Phys. A*, **66**, 587–591.

Linde, D. von der (2002). Private communication.

Lindenberg, A., Kang, I., Johnson, S., Missalla, T., Heimann, P., Chang, Z., Larsson, J., Bucksbaum, P., Kapteyn, H., Padmore, H., Lee, R., Wark, J. & Falcone, R. (2000). *Phys. Rev. Lett.* **84**, 111–114.

Neutze, R., Wouts, R., von der Spoel, D., Weckert, E. & Hajdu, J. (2000). *Nature (London)*, **406**, 752–757.

Neutze, R., Wouts, R., Techert, S., Davidsson, J., Kocis, M., Kirrander, A., Schotte, F. & Wulff, M. (2001). *Phys. Rev. Lett.* **87**, 109–112.

Perman, B., Srajer, V., Ren, Z., Teng, T., Pradervand, C., Ursby, T., Bourgeois, D., Schotte, F., Wulff, M., Kort, R., Hellingwerf, K. & Moffat, K. (1998). *Science*, **279**, 1946–1950.

Reis, D., DeChamp, M., Bucksbaum, P., Clarke, R., Dufresne, E., Hertlein, M., Merlin, R., Falcone, R., Kapteyn, H., Murnane, M., Larsson, J., Missalla, T. & Wark, J. (2001). *Phys. Rev. Lett.* **86**, 3072–3075.

Reitze, D., Ahn, H. & Downer, M. (1992). *Phys. Rev. B*, **45**, 2677–2693.

Rischel, C., Rousse, A., Uschmann, I., Albouy, P.-A., Geindre, J.-P., Audebert, P., Gauthier, J.-C., Förster, E., Martin, J.-L. & Antonetti, A. (1997). *Nature (London)*, **390**, 490–492.

Rose-Petruck, C., Jimenez, R., Guo, T., Cavalleri, A., Siders, C., Ráski, F., Squier, J., Walker, B., Wilson, K. & Barty, C. (1999). *Nature (London)*, **398**, 310–312.

Rousse, A., Audebert, P., Geindre, J., Fallies, F., Gauthier, J., Mysyrowicz, A., Grillon, G. & Antonetti, A. (1994). *Phys. Rev. E*, **50**, 2200–2207.

Ruhman, S., Joly, A. & Nelson, K. (1988). *IEEE J. Quantum Electron.* **24**, 460–469.

Siders, C., Cavalleri, A., Sokolowski-Tinten, K., Tóth, C., Guo, T., Kammler, M., von Hoegen, M. H., Wilson, K., von der Linde, D. & Barty, C. (1999). *Science*, **286**, 1340–1342.

Sokolowski-Tinten, K., Blome, C., Dietrich, C., Tarasevitch, A., von Hoegen, M. H., von der Linde, D., Cavalleri, A., Squier, J. & Kammler, M. (2001). *Phys. Rev. Lett.* **87**, 225701.

Srajer, V., Teng, T., Ursby, T., Pradervand, C., Ren, Z., Adachi, S., Schildkamp, W., Bourgeois, D., Wulff, M. & Moffat, K. (1996). *Science*, **274**, 1726–1729.

Takagi, S. (1962). *Acta Cryst.* **15**, 1311–1312.

Takagi, S. (1969). *J. Phys. Soc. Jpn*, **26**, 1239–1253.

Taupin, D. (1964). *Bull. Soc. Fr. Minéral. Cristallogr.* **87**, 469–511.

Thomsen, C., Grahn, H., Maris, H. & Tauc, J. (1986). *Phys. Rev. B*, **34**, 4129–4138.

Tomov, I., Chen, P. & Rentzepis, P. (1998). *J. Appl. Phys.* **83**, 5546–5548.

Wark, J. & He, H. (1994). *Laser Particle Beams*, **12**, 507–513.

Wark, J. & Lee, R. (1999). *J. Appl. Cryst.* **32**, 692–703.

Wiik, B. (1997). *Nucl. Instrum. Methods Phys. Res. A*, **398**, 1–17.

Winick, H. (1995). *J. Electron Spectrosc. Relat. Phenom.* **75**, 1–8.

Wright, O. B. (1994). *Phys. Rev. B*, **49**, 9985–9988.

Yamazaki, H. & Ishikawa, T. (2002). *J. Appl. Cryst.* **35**, 314–318.