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Thermal Phonons in the Modified Two-Beam Description of Diffraction near a Three-Beam Point

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Abstract

The influence of thermal phonons on the dynamical diffraction **0H** near a third reciprocal-lattice point **L**, in an otherwise perfect crystal, is investigated theoretically. It is shown that in the first-order modified two-beam description [Juretschke (1984). *Acta Cryst.* A40, 379-389] all effects due to phonon transitions are governed by the usual Bessel functions, but only of arguments involving **H**. With this proviso, the first-order modified two-beam description of diffraction near **L** incorporates phonon coupling entirely in the standard manner of the strict two-beam case. Therefore typical phonon influences, such as the Debye-Waller factor or thermal diffuse scattering, can be discussed directly in the neighborhood of n-beam diffraction merely by using the modified parameters, *i.e.* structure factors, absorption coefficients *etc.* in a traditional two-beam formulation. Some additional implications of this result about the effect of other deviations from crystal perfection on the modified two-beam description are also pointed out.

Introduction

The first-order dynamical theory of the modified two-beam description of diffraction near a three-beam point, developed for perfect crystals (Juretschke, 1982, 1984; Høier & Marthinsen, 1983; Chang, 1984), has satisfactorily reproduced a variety of experimental data involving three-beam and higher interactions (Juretschke, 1984, 1986*a*; Juretschke & Wagenfeld, 1986). Such agreement suggests that the degree of crystal perfection does not crucially affect the main predictions of the theory, but it remains to be shown explicitly why this is so. In this paper we study the influence on the modified two-beam description of deviations from periodicity induced by thermal atomic motions. This mainly requires rederiving the basic equations of the modified two-beam approach in the presence of phonons, and then inspecting these equations for their predictions, specifically with respect to the dispersion surface, the Debye-Waller factor and thermal diffuse scattering.

It was originally expected that at finite temperature each structure factor entering into the theory would carry its own Debye-Waller factor. However, as shown below, this is not the case. Even though the modified two-beam formulation involves the structure factors of all coupled reciprocal-lattice points, temperature effects are governed entirely by the Debye-Waller factor of the primary interaction.

These results, correct in the asymptotic regime, of course also bear on the more general three-beam case at finite temperatures, a configuration for which the effect of phonon coupling apparently has not been worked out explicitly.

General formulation

In a three-beam interaction we describe propagation by the three propagation vectors $\mathbf{K}_0$, $\mathbf{K}_H$, and $\mathbf{K}_L$. If the primary diffraction is chosen to be *via* **H**, and the additional coupling occurs *via* **L**, then the usual two-beam phase matching now requires two conditions:

$$\mathbf{K}_H = \mathbf{K}_0 + \mathbf{H}; \quad \mathbf{K}_L = \mathbf{K}_0 + \mathbf{L}. \tag{1}$$

Maxwell's equations lead to six scalar equations for the field amplitudes, usually decomposed into the two principal polarizations σ and π with respect to the plane of incidence

$$(E_0^\sigma, E_H^\sigma; E_0^\pi, E_H^\pi; E_L^\sigma, E_L^\pi). \tag{2}$$

These equations involve the structure factors F_H, F_L and F_{L-H}, and the deviations ξ_i of the propagation vectors from their average value within the crystal

$$\xi_i = (\mathbf{K}_i \cdot \mathbf{K}_i)^{1/2} - k(1 - \tfrac{1}{2}\Gamma F_0), \quad i = \mathbf{0}, \mathbf{H}, \mathbf{L}, \tag{3}$$

where $k = \omega/c$, $\Gamma = e^2/(\varepsilon_0 m\omega^2 v_{\text{cell}})$.

The modified two-beam description applies when $\xi_L \gg \xi_0, \xi_H$, *i.e.* when **L** is still far from the Ewald sphere. In that case ξ_L is a known parameter (proportional to the distance of **L** from the Ewald sphere) and the two fields E_L^σ, E_L^π can be expressed in terms of the other four fields of (2), and ξ_L. The remaining four equations can then be recast into standard two-beam form, at least to terms including $1/\xi_L$ (Juretschke, 1984). In the notation of that paper, these equations are

$$\begin{aligned} 2\xi_0^\sigma E_0^\sigma + k\Gamma F_{H\bar{L}}^\sigma E_H^\sigma &= 0 \\ k\Gamma F_{HL}^\sigma E_0^\sigma + 2\xi_H^\sigma E_H^\sigma &= 0 \\ 2\xi_0^\pi E_0^\pi + k\Gamma F_{H\bar{L}}^\pi E_H^\pi &= 0 \\ k\Gamma F_{HL}^\pi E_0^\pi + 2\xi_H^\pi E_H^\pi &= 0, \end{aligned} \tag{4}$$

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which hold with respect to shifted Lorentz points given by

$$\begin{aligned}\xi_0^\sigma &= \xi_0 - \frac{\Pi_1}{4\xi_L}(k\Gamma)^2 F_L F_{\bar{L}} \\ \xi_H^\sigma &= \xi_H - \frac{\Pi_1}{4\xi_L}(k\Gamma)^2 F_{L-H} F_{\bar{L}-\bar{H}} \\ \xi_0^\pi &= \xi_0 - \frac{\Pi_4}{4\xi_L}(k\Gamma)^2 F_L F_{\bar{L}} \\ \xi_H^\pi &= \xi_H - \frac{\Pi_5}{4\xi_L}(k\Gamma)^2 F_{L-H} F_{\bar{L}-\bar{H}}\end{aligned} \tag{5}$$

and relative to the effective two-beam structure factors

$$\begin{aligned}F_{HL}^\sigma &= F_H - \frac{\Pi_1}{2\xi_L}(k\Gamma) F_L F_{\bar{L}-\bar{H}} \\ F_{HL}^\pi &= PF_H - \frac{\Pi_6}{2\xi_L}(k\Gamma) F_L F_{\bar{L}-\bar{H}}.\end{aligned} \tag{6}$$

Here $P = \cos 2\theta_B$, and the coefficients Π_i $(i = 1, \ldots, 6)$ are geometrical factors arising out of polarization projections, and are given by Juretschke (1984) and Høier & Marthinsen (1983). (Π_2 and Π_3 describe the coupling of σ and π modes, and only appear explicitly to order $1/\xi_L^2$.)

If, in addition, the crystal is traversed by N low-energy elastic modes described by rigid atomic displacements of the form

$$\mathbf{U}(\mathbf{r}) = \sum_{j=1}^{N} \mathbf{u}_j \sin(\mathbf{q}_j \cdot \mathbf{r} - \omega_j t + \varphi_j) \tag{7}$$

the set of fields (2) must be generalized to include all phonon couplings induced by the modes (7).

For simplicity, we will initially restrict the treatment to a single mode

$$\mathbf{u} \sin(\mathbf{q} \cdot \mathbf{r} + \varphi - \omega_p t) \tag{7'}$$

and all phonon transitions associated with it. Then the set of fields (2) becomes

$$(E_{l0}^\sigma, E_{lH}^\sigma; E_{l0}^\pi, E_{lH}^\pi; E_{lL}^\sigma, E_{lL}^\pi) \tag{8}$$

with the integer l running over all values $-\infty < l < \infty$, and the case $l = 0$ corresponds to the phonon-free central fields.

In the same manner, (1) is generalized to

$$\mathbf{K}_{lH} = \mathbf{K}_{l0} + \mathbf{H} = \mathbf{K}_{00} + l\mathbf{q} + \mathbf{H}; \quad \mathbf{K}_{lL} = \mathbf{K}_{l0} + \mathbf{L} \tag{9}$$

but, if all phonons of interest are of sufficiently low energy, the further condition of energy (frequency) conservation can be ignored, *i.e.* all dispersion surfaces can be constructed for a single energy, or frequency. At this common energy, however, as a consequence of (9), each l will lead to its own dispersion surface, so that we must also generalize (3) with this index: ξ_{l0}, ξ_{lH}, ξ_{lL}.

The coupling strengths between the various fields arise from the standard expansion

$$\begin{aligned}&\exp[i\mathbf{M} \cdot \mathbf{u} \sin(\mathbf{q} \cdot \mathbf{R} + \varphi)] \\ &\quad = \sum_l (-1)^l \exp(il\varphi) J_l(\mathbf{M} \cdot \mathbf{u}) \exp(il\mathbf{q} \cdot \mathbf{R})\end{aligned} \tag{10}$$

that enters in the Fourier expansion of the charge density (*e.g.* Köhler, Möhling & Peibst, 1974) in the presence of (7').

Despite these additional couplings, however, exactly the same procedure as was followed for the modified two-beam formulation in the absence of phonons can still be carried out. If $\mathbf{L}$ is sufficiently far from the Ewald sphere, we can assume that for all l of practical interest

$$\xi_{lL} \gg lq \tag{11}$$

so that all ξ_{lL} can be represented by the common value ξ_L.

Results

The outcome of carrying out the same set of manipulations outlined in the section above for obtaining the modified two-beam equations in the absence of phonons leads to expressions of which the following two, for σ polarization, are representative:

$$\begin{aligned}0 = {} & 2\xi_{l0} E_{l0}^\sigma + k\Gamma \sum_{l'} (-1)^{l'} \exp(il'\varphi) \\ & \times \Bigg\{ J_{l'}(\mathbf{H} \cdot \mathbf{u}) F_{\bar{H}} E_{(l-l')H}^\sigma \\ & - \frac{k\Gamma}{2\xi_L} \Bigg[F_L F_{\bar{L}} (\Pi_1 E_{(l-l')0}^\sigma - \Pi_2 E_{(l-l')0}^\pi) \\ & \times \sum_{l''} J_{l'-l''}(\mathbf{L} \cdot \mathbf{u}) J_{l''}(-\mathbf{L} \cdot \mathbf{u}) \\ & + F_{L-H} F_{\bar{L}} (\Pi_1 E_{(l-l')H}^\sigma + \Pi_3 E_{(l-l')H}^\pi) \\ & \times \sum_{l''} J_{l'-l''}(\mathbf{L} \cdot \mathbf{u}) J_{l''}([\mathbf{H} - \mathbf{L}] \cdot \mathbf{u}) \Bigg] \Bigg\}\end{aligned} \tag{12a}$$

$$\begin{aligned}0 = {} & 2\xi_{lH} E_{lH}^\sigma + k\Gamma \sum_{l'} (-1)^{l'} \exp(il'\varphi) \\ & \times \Bigg\{ J_{l'}(-\mathbf{H} \cdot \mathbf{u}) F_H E_{(l-l')0}^\sigma \\ & - \frac{k\Gamma}{2\xi_L} \Bigg[F_{\bar{L}-\bar{H}} F_L (\Pi_1 E_{(l-l')0}^\sigma - \Pi_2 E_{(l-l')0}^\pi) \\ & \times \sum_{l''} J_{l'-l''}([\mathbf{L} - \mathbf{H}] \cdot \mathbf{u}) J_{l''}(-\mathbf{L} \cdot \mathbf{u}) \\ & + F_{\bar{L}-\bar{H}} F_{L-H} (\Pi_1 E_{(l-l')H}^\sigma + \Pi_3 E_{(l-l')H}^\pi) \\ & \times \sum_{l''} J_{l'-l''}([\mathbf{L} - \mathbf{H}] \cdot \mathbf{u}) J_{l''}([\mathbf{H} - \mathbf{L}] \cdot \mathbf{u}) \Bigg] \Bigg\}.\end{aligned} \tag{12b}$$

When $\xi_L \to \infty$, these equations reduce to the standard form of the phonon contributions to the two-beam case (*e.g.* Köhler *et al.*, 1974). For finite but large ξ_L, the new contributions are characterized by the sums over products of Bessel functions. Each such product, as expected, involves as arguments the same two reciprocal-lattice points as those of the two structure factors it modifies. However, these are now to be summed over all l''. These sums can be carried out using a standard theorem (Abramowitz & Stegun, 1964) which states

$$J_l(x+y) = \sum_{l'} J_{l'-l}(x) J_{l'}(y) \tag{13}$$

such that

$$\begin{aligned} \sum_{l''} J_{l'-l''}(\mathbf{L}\,.\,\mathbf{u}) J_{l''}(-\mathbf{L}\,.\,\mathbf{u}) &= J_{l'}(0) = \delta_{l'0} \\ \sum_{l''} J_{l'-l''}(\mathbf{L}\,.\,\mathbf{u}) J_{l''}([\mathbf{H}-\mathbf{L}]\,.\,\mathbf{u}) &= J_{l'}(\mathbf{H}\,.\,\mathbf{u}). \end{aligned} \tag{13'}$$

With the reductions (13'), (12) can be rewritten, using (5) and (6), as follows

$$\begin{aligned} 0 = {} & 2\xi^{\sigma}_{l0} E^{\sigma}_{l0} + k\Gamma J_0(\mathbf{H}\,.\,\mathbf{u}) F^{\sigma}_{H\bar{L}} E^{\sigma}_{lH} \\ & + k\Gamma \sum_{l'\neq 0} (-1)^{l'} \exp(il'\varphi) J_{l'}(\mathbf{H}\,.\,\mathbf{u}) F^{\sigma}_{H\bar{L}} E^{\sigma}_{(l-l')H} \\ & + \frac{(k\Gamma)^2}{2\xi_L} \Pi_2 F_{\bar{L}} F_L E^{\pi}_{l0} - \frac{(k\Gamma)^2}{2\xi_L} \Pi_3 F_{\bar{L}} F_{L-H} \\ & \times \sum_{l'} (-1)^{l'} \exp(il'\varphi) J_{l'}(\mathbf{H}\,.\,\mathbf{u}) E^{\pi}_{(l-l')H} \\ 0 = {} & k\Gamma J_0(\mathbf{H}\,.\,\mathbf{u}) F^{\sigma}_{HL} E^{\sigma}_{l0} + 2\xi^{\sigma}_{lH} E^{\sigma}_{lH} \\ & + k\Gamma \sum_{l'\neq 0} (-1)^{l'} \exp(il'\varphi) J_{l'}(-\mathbf{H}\,.\,\mathbf{u}) F^{\sigma}_{HL} E^{\sigma}_{(l-l')0} \\ & - \frac{(k\Gamma)^2}{2\xi_l} \Pi_3 F_{\bar{L}-\bar{H}} F_{L-H} E^{\pi}_{lH} + \frac{(k\Gamma)^2}{2\xi_L} \Pi_2 F_{\bar{L}-\bar{H}} F_L \\ & \times \sum_{l'} (-1)^{l'} \exp(il'\varphi) J_{l'}(-\mathbf{H}\,.\,\mathbf{u}) E^{\pi}_{(l-l')0}. \end{aligned} \tag{14}$$

For completeness, we also list the corresponding equations obtained for the other polarization:

$$\begin{aligned} 0 = {} & 2\xi^{\pi}_{l0} E^{\pi}_{l0} + k\Gamma J_0(\mathbf{H}\,.\,\mathbf{u}) F^{\pi}_{H\bar{L}} E^{\pi}_{lH} \\ & - k\Gamma \sum_{l'\neq 0} (-1)^{l'} \exp(il'\varphi) J_{l'}(\mathbf{H}\,.\,\mathbf{u}) F^{\pi}_{H\bar{L}} E^{\pi}_{(l-l')H} \\ & + \frac{(k\Gamma)^2}{2\xi_L} \Pi_2 F_{\bar{L}} F_L E^{\sigma}_{l0} + \frac{(k\Gamma)^2}{2\xi_L} \Pi_2 F_{\bar{L}} F_{L-H} \\ & \times \sum_{l'} (-1)^{l'} \exp(il'\varphi) J_{l'}(\mathbf{H}\,.\,\mathbf{u}) E^{\sigma}_{(l-l')H} \\ 0 = {} & k\Gamma J_0(\mathbf{H}\,.\,\mathbf{u}) F^{\pi}_{HL} E^{\pi}_{l0} + 2\xi^{\pi}_{lH} E^{\pi}_{lH} \\ & - k\Gamma \sum_{l'\neq 0} (-1)^{l'} \exp(il'\varphi) J_{l'}(-\mathbf{H}\,.\,\mathbf{u}) F^{\pi}_{HL} E^{\pi}_{(l-l')0} \\ & - \frac{(k\Gamma)^2}{2\xi_L} \Pi_3 F_{\bar{L}-\bar{H}} F_{L-H} E^{\sigma}_{lH} - \frac{(k\Gamma)^2}{2\xi_L} \Pi_3 F_{\bar{L}-\bar{H}} F_L \\ & \times \sum_{l'} (-1)^{l'} \exp(il\varphi) J_{l'}(-\mathbf{H}\,.\,\mathbf{u}) E^{\sigma}_{(l-l')0}. \end{aligned} \tag{15}$$

In the limit $\mathbf{u} \to 0$, (14) and (15) agree with the three-beam expressions derived earlier [Juretschke (1984), equation (17)], and for $\mathbf{u} \neq 0$, but in the limit $\xi_L \to \infty$, they go over into the traditional two-beam equations in the presence of phonons.

Equations (14) and (15) represent the central result of this paper. Their generalization to N phonon modes follows the same procedure, without complications. It merely requires that each index l be replaced by the set of integers $[l_j] = (l_1, l_2, \ldots, l_j, \ldots, l_N)$ labelling the phonon number of each mode associated with a given field, and that each Bessel function labelled by $[l_j]$ be identified by a product of Bessel functions:

$$J_{[l_j]}(\mathbf{M}\,.\,\mathbf{u}) = \prod_j J_{l_j}(\mathbf{M}\,.\,\mathbf{u}_j).$$

The resulting equations can be exemplified by the first equation of (14) (ignoring the σ–π coupling terms)

$$\begin{aligned} 0 = {} & 2\xi^{\sigma}_{[l_j]0} E^{\sigma}_{[l_j]0} \\ & + k\Gamma \left[\prod_j J_0(\mathbf{H}\,.\,\mathbf{u}_j) \right] F^{\sigma}_{H\bar{L}} E^{\sigma}_{[l_j]H} \\ & + k\Gamma \sum_{[l'_j]\neq[0]} (-1)^{\sum l'_j} \exp(i \sum l'_j \varphi_j) \\ & \times \left[\prod_j J_{l'_j}(\mathbf{H}\,.\,\mathbf{u}_j) \right] F^{\sigma}_{H\bar{L}} E^{\sigma}_{[l_j - l'_j]H} \end{aligned} \tag{16}$$

and the other lines follow along the same pattern.

Discussion

The resultant equations (14) and (15) and their generalizations exemplified by (16) exhibit a number of notable features.

First of all, they mimic in all respects the true set of two-beam dynamical equations in the presence of phonons. This implies that, within the approximations inherent in the modified two-beam formulation, all thermal averaging procedures on the parameters in these equations can be taken over from those in the existing two-beam literature. Such transfers, of course, require that all results are referred to the modified dispersion surfaces governed by (5), and to the modified two-beam structure factors (6). A surprising aspect of the form of (14) to (16), however, is that only thermal factors associated with **H** appear, so that, for example, the structure factors F_L and F_{H-L} also contained in these equations, through (5) and (6), are not modified by phonons.

The main reason for this result must be that phonon-excited fields also find themselves in a three-beam situation and are subject to its coherent interaction, but now with the possibility of coupling through many more channels to each other. Nevertheless, it is surprising that all these couplings are entirely reflected in altering the modified two-beam formulation

for zero temperature. Hence all structure factors cannot be considered on the same footing.

In fact, (14) and (15) are exact three-beam equations in the limit $u = 0$. One must therefore raise the question of what additional approximations prevent them from being exact when $u \neq 0$, because, surely, sufficiently close to the three-beam point the other structure factors besides F_H must also undergo thermal modifications. The answer is to be found in the condition (11) - which breaks down before the other, implied, approximation $H \gg lq$ - whose breakdown requires that we consider all ξ_{lL} separately, since they differ by amounts of order lq. The detailed consequences of this breakdown remain to be investigated. But it should occur earlier at high temperature, where high values of l matter. At low temperature, (14) and (15) can be expected to remain valid over the whole range where ξ_L is a parameter rather than a dynamical variable.

A further implication of (14) and (15) is that in the next higher approximation in the approach to the three-beam point, in which the coupling between σ and π polarizations plays a role (Juretschke, 1986*b*), there appear new phonon-induced interactions in the last sums on the right side of these equations, while some of this coupling remains phonon independent. Whether or not these terms are incorporated into the standard form under the transformation introduced by Juretschke (1986*b*) remains to be seen.

More generally, (14) and (15) demonstrate that the modified dispersion surfaces and the modified structure factors of the modified two-beam formulation form the proper framework on which to impose any phonon coupling. This framework itself remains phonon independent, and therefore it constitutes a description of diffraction near a three-beam point that truly contains all the inherent features of exact two-beam theory. While for some purposes it may be useful to refer the modes of the modified description back to those of the pure two-beam case (Hümmer & Billy, 1986), for others, like those under consideration here, it is more consistent to treat the modified case as a two-beam case in its own right.

For the same reason one is led to expect that other deviations from crystal perfection, such as a weak mosaic structure, can be handled within the same framework merely by replacing the usual parameters by their modified equivalents. This remains to be tested theoretically, but it has gained support from a recent kinematic model based on double rather than single scattering in each block (Shen, 1986), where the modified structure factors (6) also emerge as the initial modification near a three-beam point. [Although, of course, (5) is beyond such kinematic approach.] Since the same modification occurs in both dynamical and kinematic models, and these two extremes are related exactly as in a strict two-beam case, it is reasonable to expect that the discussion of mosaic crystals also falls within the same pattern. In fact, the results of Kshevetskii, Mikhailyuk & Polyak (1985) show that the general broadening accompanying reflections from a mosaic crystal surface is also enhancing the many-beam features, although, as expected in the averaging over unsymmetric lines, their detailed structure can be modified significantly.

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The Refractive-Index Correction in Powder Diffraction

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Abstract

Throughout the history of powder diffraction practice there has been uncertainty about whether or not a refractive-index correction should be made to Bragg's law. High-precision Bragg-angle measurements have been performed with synchrotron radiation on SRM-640 silicon powders at glancing angles; it is found that little or no correction is necessary for the usual 2θ angle range.

1. Introduction

The question of the need to use a refractive-index correction for powder diffraction data has long been cloaked in uncertainty. The problem is discussed in this paper and is based on the theoretical background and recent measurements of a silicon-powder standard using synchrotron in high-resolution parallel-beam geometry.

When X-rays enter a material refraction at the surface causes a small shift of the observed Bragg reflection angles to larger 2θ values than indicated by Bragg's law. The shifts are normally much smaller than other sources of errors and corrections are not generally applied in the usual routine qualitative and quantitative powder diffraction analyses. The correction has been used mainly in precision lattice-parameter determination (*e.g.* Lipson & Wilson, 1941) but there is no general agreement, and some authors use it while others ignore it. In the 1960 IUCr round-robin test on the precision of lattice-parameter determination of powder samples with Cu $K\alpha$ radiation, the following values were added to the derived lattice parameters to correct for refraction: diamond 0·00004, silicon 0·00004 and tungsten 0·00016 Å (Parrish, 1960).

Synchrotron-radiation sources now provide improved resolution because high intensity and the narrow instrument functions can be simultaneously exploited (Hastings, Thomlinson & Cox, 1984; Parrish, Hart & Huang, 1986). The narrow symmetrical profiles and general absence of systematic errors open the possibility of higher precision and more reliable lattice-parameter determination (Parrish, Hart, Huang & Bellotto, 1987). The question of how one should correct powder data for X-ray refraction therefore becomes more important than it has been, especially because the move to synchrotron-radiation sources also means that wavelengths other than the 'standard' copper $K\alpha$ will be used.

In the growing field of grazing-incidence diffraction studies of thin films, the angular shifts are much larger than in conventional θ-2θ scanning and corrections are necessary for many of the analyses. This is described separately (Lim, Parrish, Ortiz, Bellotto & Hart, 1987).

2. Theoretical background

The index of refraction n of X-rays is slightly less than unity and is given by

$$n = 1 - \delta$$

where

$$\delta = (-e^2/2\pi mc^2)\lambda^2\rho; \qquad (1)$$

e is the charge on the electron, m is the electron mass, c is the velocity of light, λ is the wavelength in ångströms, and ρ is the number of electrons per unit volume. For wavelengths below about 2 Å, δ is of the order of 10^{-4} to 10^{-5}, depending on the density of the material.

Dynamical diffraction is usually associated with highly perfect single crystals. However, it is interesting to note that some of its concepts were required to analyze this powder problem. It should also be noted that a fundamental premise of kinematic diffraction theory is that all parts of the sample are illuminated by the full unattenuated primary beam; by definition therefore $n = 1$ and the question of refraction cannot arise. In the case of single-crystal diffraction it is well established, both theoretically and experimentally, that Bragg's law

$$2d \sin\theta_L = \lambda \qquad (2)$$

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