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Theory of Internal Strain Measurement in Zinc-Blende-Structure Crystals and a Reanalysis of Work on Gallium Arsenide

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Abstract

The internal strain parameter (or the bond-bending parameter) of zinc-blende-structure materials can be obtained from the stress dependence of the intensity of weak reflections in uniaxially stressed crystals. The theory, including dispersion and temperature effects, is presented and applied to the reanalysis of earlier work on gallium arsenide. The results are inconsistent, leaving the bond-bending parameter of this material unknown.

1. Introduction

The structural similarity of diamond and zinc blende makes it natural to turn from silicon (Cousins, Gerward, Olsen, Selsmark & Sheldon, 1982) and germanium (Cousins, Gerward, Nielsen, Olsen, Selsmark, Sheldon & Webster, 1982) to materials that crystallize in the zinc blende structure.

In this paper the opportunity is taken to show how the internal strain parameter $\bar{A}$ may be extracted from observations of the stress dependence of the intensities of X-ray reflections. Since there are no strictly forbidden reflections in the zinc blende structure the dispersion corrections to the atomic scattering factors must be fully included. This is particularly important in the case of the $h+k+l=4n+2$ class of reflection, where, under certain conditions, the intensity of a reflection can be due almost entirely to the difference between the imaginary parts of the dispersion correction. The inclusion of dispersion provides independent determinations of $|\bar{A}|$ and $\bar{A}$ from one data set, in contrast to the diamond case where only $|\bar{A}|$ is found.

The theory is applied to a reanalysis of earlier work on gallium arsenide by Koumelis & Rozis (1975, hereafter denoted KR) and Koumelis, Zardas, Londos & Leventouri (1976, hereafter KZLL). They appear to have incorporated neither temperature factors nor dispersion corrections. When these omissions are rectified it is found that the resulting value of $|\bar{A}|$ (or, equivalently, the bond bending parameter ζ) is increased by about 50%. On the other hand, the value of $\bar{A}$ is found to be ten times smaller and not inconsistent with the value zero. This in turn would imply vanishing dispersion corrections, for which there is no evidence. The reason for this is unknown.

2. The internal strain tensor in the zinc blende structure

The internal strain tensor in the zinc blende structure has the same form as the one in the diamond structure, namely

$$A=\bar{A}a\begin{bmatrix}0&0&0&1&0&0\\0&0&0&0&1&0\\0&0&0&0&0&1\end{bmatrix}, \tag{1}$$

where a is the lattice parameter and $\bar{A}$ is the single dimensionless measure of internal strain.

If a uniaxial stress σ (positive if tensile) is applied parallel to the unit vector $\mathbf{l}=[l_1, l_2, l_3]$ its components are given, in both contracted and uncontracted notation, by

$$\sigma_K=\sigma_{ij}=l_il_j\sigma, \tag{2}$$

where K is the Voigt contraction of ij.

The inner displacement of the two sublattices under stress is then given by

$$\delta_i=A_{iJ}S_{JK}\sigma_K, \tag{3}$$

where S is the compliance matrix of the crystal. From (1) and (2), (3) takes the form

$$\begin{bmatrix}\delta_1\\\delta_2\\\delta_3\end{bmatrix}=\bar{A}aS_{44}\sigma\begin{bmatrix}l_2l_3\\l_3l_1\\l_1l_2\end{bmatrix}. \tag{4}$$

3. Effect of inner displacement on the structure factor

In earlier work on germanium we corrected the free-atom scattering factors by including the real part of the anomalous dispersion correction using $f'=f^0+\Delta f'$, where $\Delta f'$ was obtained from the tables of Cromer & Liberman (1970) by interpolation. Neglect of $\Delta f''$ led to less than 0·6% error in our final result. In the present work we include the imaginary part of the anomalous dispersion correction, writing f''_α in

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place of the usual $\Delta f''_\alpha$. Thus the atomic scattering factor is now

$$f_\alpha = f'_\alpha + if''_\alpha, \qquad (5)$$

where $\alpha = 1$ corresponds to the cation (situated at the origin) and $\alpha = 2$ corresponds to the anion {situated at $\boldsymbol{\rho} = (a/4)[1, 1, 1]$}. The structure factor for Bragg diffraction from planes whose reflection vector is $\mathbf{H}$ is

$$F_\mathbf{H} = 4[f_1 + f_2 \exp(2\pi i \mathbf{H} . \boldsymbol{\rho})] \qquad (6)$$

and the square of the structure factor in the unstressed crystal takes the form

$$|F_\mathbf{H}|_0^2 = 16\{(f_1'^2 + f_1''^2) + (f_2'^2 + f_2''^2) + 2c_1 \cos\chi_\mathbf{H} + 2c_2 \sin\chi_\mathbf{H}\}, \qquad (7)$$

where

$$\chi_\mathbf{H} = 2\pi\mathbf{H} . \boldsymbol{\rho} = \frac{\pi}{2}(h + k + l),$$

and

$$\left.\begin{aligned} c_1 &= f'_2 f'_1 + f''_2 f''_1 \\ c_2 &= f'_2 f''_1 - f''_2 f'_1 \end{aligned}\right\} \qquad (8)$$

and the subscript zero denotes the unstrained crystal.

Under uniaxial stress the phase $\chi_\mathbf{H}$ is replaced by $\chi_\mathbf{H} + \psi_\mathbf{H}(\mathbf{l})$, where

$$\psi_\mathbf{H}(\mathbf{l}) = y_\mathbf{H}(\mathbf{l})\sigma \qquad (9)$$

with

$$y_\mathbf{H}(\mathbf{l}) = 2\pi \bar{A} S_{44}(hl_2l_3 + kl_3l_1 + ll_1l_2) \qquad (10)$$

and where the stress axis is $\mathbf{l} = [l_1, l_2, l_3]$. The effect of inner displacement is to increase the square of the structure factor by

$$\Delta|F_\mathbf{H}(\mathbf{l})|^2 = 32c_1\{\cos[\chi_\mathbf{H} + \psi_\mathbf{H}(\mathbf{l})] - \cos\chi_\mathbf{H}\} + 32c_2\{\sin[\chi_\mathbf{H} + \psi_\mathbf{H}(\mathbf{l})] - \sin\chi_\mathbf{H}\}.$$

Since $\psi_\mathbf{H}(\mathbf{l})$ is a small quantity the terms in $\chi_\mathbf{H} + \psi_\mathbf{H}(\mathbf{l})$ may be expanded with the result that, to second order in $\psi_\mathbf{H}(\mathbf{l})$ and thus also in σ,

$$\Delta|F_\mathbf{H}(\mathbf{l})|^2 = -16\{(c_1 \cos\chi_\mathbf{H} + c_2 \sin\chi_\mathbf{H})[\psi_\mathbf{H}(\mathbf{l})]^2 + 2(c_1 \sin\chi_\mathbf{H} - c_2 \cos\chi_\mathbf{H})\psi_\mathbf{H}(\mathbf{l})\}. \qquad (11)$$

If $P_{\mathbf{H}0}$ is the intensity of a particular reflection in an unstressed crystal and $\Delta P_\mathbf{H}(\sigma, \mathbf{l})$ is the change in intensity due to uniaxial stress, (11) can be rearranged, using (7) and (9), to give

$$\frac{1}{\sigma}\frac{\Delta P_\mathbf{H}(\sigma, \mathbf{l})}{P_{\mathbf{H}0}} = -\frac{1}{d_i}(c_1 \cos\chi_\mathbf{H} + c_2 \sin\chi_\mathbf{H})[y_\mathbf{H}(\mathbf{l})]^2\sigma - \frac{2}{d_i}(c_1 \sin\chi_\mathbf{H} - c_2 \cos\chi_\mathbf{H})y_\mathbf{H}(\mathbf{l}), \qquad (12)$$

where $d_i \equiv |F_\mathbf{H}|_0^2/16$ has the forms

$$\begin{aligned} d_0 &= (f'_1 + f'_2)^2 + (f''_1 + f''_2)^2 \quad \text{if } h + k + l = 4n \\ d_1 &= (f'_1 - f''_2)^2 + (f'_2 + f''_1)^2 \quad \text{if } h + k + l = 4n + 1 \\ d_2 &= (f'_1 - f'_2)^2 + (f''_1 - f''_2)^2 \quad \text{if } h + k + l = 4n + 2 \end{aligned} \qquad (13)$$

and

$$d_3 = (f'_1 + f''_2)^2 + (f'_2 - f''_1)^2 \quad \text{if } h + k + l = 4n + 3.$$

The d_i are always positive definite and there are no strictly forbidden reflections. Equation (12) is therefore the basis for analysing the stress dependence of any reflection from a zinc blende crystal. It yields two pieces of information:

$$m = -\frac{1}{d_i}(c_1 \cos\chi_\mathbf{H} + c_2 \sin\chi_\mathbf{H})[y_\mathbf{H}(\mathbf{l})]^2 \qquad (14)$$

and

$$I = -\frac{2}{d_i}(c_1 \sin\chi_\mathbf{H} - c_2 \cos\chi_\mathbf{H})y_\mathbf{H}(\mathbf{l}), \qquad (15)$$

both of which depend on $\bar{A}$. We see from (10) that $y_{\bar{\mathbf{H}}}(\mathbf{l}) = -y_\mathbf{H}(\mathbf{l})$ and therefore that the sign of I depends on the sign of $\bar{A}$. Since $\bar{A}$ has been chosen to represent the internal strain of the anion relative to the cation it is essential that the polarity of the crystal sample be determined so that the reflection $\mathbf{H}$ can be distinguished from the reflection $\bar{\mathbf{H}}$ and the correct sign of $\bar{A}$ can be unambiguously determined. In Fig. 1(*a*) we show (12) for a pair of reflections and in Fig. 1(*b*) the way in which a value for $\bar{A}$ is most easily deduced. The ordinate is $S = |m|^{1/2}$ and the abscissa is I. We list in Table 1 relevant expressions for the different classes of reflection. An experimental run on a specific reflection leads to a rectangular box in Fig. 1(*b*). From the geometry of the reflection and stress axis (10) can be used to provide a locus of compatible $|\bar{A}|$ values. The origin corresponds to $|\bar{A}| = 0$ and the end point to $|\bar{A}| = \frac{1}{4}$ (i.e. a bond-bending parameter $\zeta = 1$). If the line fails to intersect the box the experimental and theoretical results are incompatible. Conversely, if they intersect the magnitude and sign of $\bar{A}$ can be deduced by direct proportion.

Appropriate temperature factors must be included in f_1 and f_2. It is possible that two further factors may have an effect. These are the degree of ionicity and the shape, position and amount of bond charges. In this preliminary account only the temperature factors will be discussed.

3.1. *Temperature factors*

Each scattering factor should be modified by a factor that takes into account the thermal vibrations of the crystal. Thus, where f_α appears earlier it should be multiplied by T_α, where

$$T_\alpha = \exp[-B_\alpha(\sin\theta/\lambda)^2]. \qquad (16)$$

Table 1. *Factors governing the change of intensity of the hkl reflection in the zinc blende structure resulting from uniaxial stress σ acting in the direction* $\mathbf{l}=[l_1, l_2, l_3]$

$\psi \equiv \psi_{\mathbf{H}}(\mathbf{l})$ is given by equation (9), $y_{\mathbf{H}}(\mathbf{l})$ by (10), c_i by (8) and d_i by (13).

Reflection type $h+k+l$	$\cos\chi_{\mathbf{H}}$	$\sin\chi_{\mathbf{H}}$	$\lvert F_{\mathbf{H}}\rvert_0^2$	$\Delta\lvert F_{\mathbf{H}}(\mathbf{l})\rvert^2$	$S/\lvert y_{\mathbf{H}}(\mathbf{l})\rvert$	$I/y_{\mathbf{H}}(\mathbf{l})$
$4n$	1	0	$16d_0$	$-16(c_1\psi^2-2c_2\psi)$	$(c_1/d_0)^{1/2}$	$2c_2/d_0$
$4n+1$	0	1	$16d_1$	$-16(c_2\psi^2+2c_1\psi)$	$(\lvert c_2\rvert/d_1)^{1/2}$	$-2c_1/d_1$
$4n+2$	-1	0	$16d_2$	$16(c_1\psi^2-2c_2\psi)$	$(c_1/d_2)^{1/2}$	$-2c_2/d_2$
$4n+3$	0	-1	$16d_3$	$16(c_2\psi^2+2c_1\psi)$	$(\lvert c_2\rvert/d_3)^{1/2}$	$2c_1/d_3$

Reid (1983) has recently published Debye–Waller factors of zinc-blende-structure materials based on lattice dynamical calculations. He includes references to recent experimental results for the B_α.

In an approximation that treated the vibrations through a mean value of B all the factors relevant to the stress dependence of the intensity, such as the c_i and the d_i, would be modified in the same way. If, however, as seems physically more realistic, we use distinct temperature factors T_i then the c_i have one form of dependence, for example,

$$c_1=(f_1'f_2'+f_1''f_2'')T_1T_2 \tag{17}$$

whilst the d_i have a different dependence, for example

$$d_2=(f_1'T_1-f_2'T_2)^2+(f_1''T_1-f_2''T_2)^2. \tag{18}$$

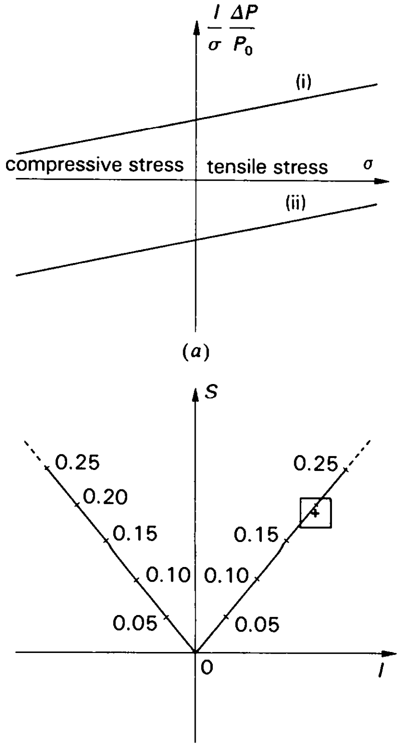

Fig. 1. (*a*) The variation of $(1/\sigma)$ $[\Delta P(\sigma)/P_0]$ as a function of σ for (i) a reflection $\mathbf{H}$ and (ii) a reflection $\bar{\mathbf{H}}$. (*b*) Plot of parameters derived from (*a*) enabling $|\bar{A}|$ and $\bar{A}$ to be related to a locus of theoretical values.

Table 2. *Atomic scattering factors, dispersion corrections and derived functions for* GaAs

Temperature factors and dispersion corrections are omitted from the values in parentheses.

	KR		KZLL
f_1^0 (Ga)	14·613		14·613
$\Delta f_1'$	−0·8548		−0·8158
f_1'	13·758		13·797
f_1''	0·9816		1·0154
f_2^0 (As)	16·194		16·194
$\Delta f_2'$	−0·5620		−0·5290
f_2'	15·632		15·665
f_2''	1·2690		1·3123
d_2	3·8675	(2·500)	3·8568
c_1	151·66	(236·64)	152·47
c_2	−1·4819	(0)	−1·5424

The temperature factors therefore influence both S and I in Table 1 and produce a distinct theoretical line in Fig. 1(*b*).

4. Reanalysis of earlier work

The theory presented in KR is in error in small details and incorrect values of ζ (*i.e.* $-4\bar{A}$) are shown in their Table 2. A factor of 3/2 was omitted and an incorrect value of S_{44} was used. The final corrected value was published as $\zeta=0{\cdot}77\,(4)$. This value is just a little larger than the values for silicon and germanium and thus appears quite reasonable. However, when we examine the expression used for $\Delta J/J$ (*i.e.* our $\Delta P/P_0$) it is clear that dispersion corrections have not been included and there is no evidence that temperature factors have been considered.

In KZLL the theory has been corrected but again only the $\lambda=0$ scattering factors have been employed. A value $\zeta=0{\cdot}764\,(9)$ is found.

It is possible to reanalyse the data in these two papers. The values of J are given in KR but have to be deduced from accurate measurements on Fig. 2 in KZLL. Equation (12) is the basis of analysis and we assume

$$\frac{1}{\sigma}\frac{\Delta J}{J_0}=S^2\sigma+I. \tag{19}$$

The initial value of J_0 is scanned and corresponding values of S^2 and I are obtained from a least-squares fitting routine. The value of J_0 corresponding to the best fit should be preferred to an experimental value when a strong reflection is under consideration. This is because the theory relates to an ideally imperfect crystal, the state to which the crystal tends on application of stress. The stress-free state may, in the case good crystals, correspond to the ideally perfect crystal. In the present case, however, the reflection is weak and the stress-free case is well represented by the ideally imperfect crystal.

The analysis in KR permits a value of ζ to be calculated for each data point and the final result is a weighted mean. So great is the range of the weighting factors that the final value is totally dominated by the point of highest stress. This is unfortunate because the intensity at stresses near to the breaking stress is often depressed due to the onset of damage in the crystal.

Since the polarity of the sample was irrelevant to the analysis originally undertaken we shall assume that both pieces of work refer to observations of the 006 reflection for which $\sin\theta/\lambda = 0{\cdot}53065$ Å^{-1}. The Debye–Waller factors deduced from the figures and tables in Reid (1983) are $B_1 = 0{\cdot}6853$ and $B_2 = 0{\cdot}5758$ Å^2 at 295 K. These lead to temperature factors $T_1 = 0{\cdot}8245$ and $T_2 = 0{\cdot}8503$. The stress axis is [111] in KR and y_{006} takes the value $0{\cdot}2126\,\bar{A}$. In KZLL there are two possibilities for the stress axis: either [110] with $y_{006} = 0{\cdot}3188\ \bar{A}$ or $[1\bar{1}0]$ with $y_{006} = -0{\cdot}3188\,\bar{A}$. The evidence of this analysis suggests the second of these, as this choice leads to $\bar{A}$ having the same sign in both KR and KZLL. The atomic scattering factors f_i^0 are taken from *International Tables of X-ray Crystallography* (1974) using the analytical approximations of Table 2.2*B*. These are displayed in Table 2 which also includes the dispersion corrections, calculated from a program of Cromer & Liberman (1970), appropriate to the energies 7·0580 keV (Fe $K\beta$) in KR and 6·9255 keV (Co $K\alpha$) in KZLL. The derived functions d_2, c_1 and c_2 are given together with the values they would have if dispersion and temperature were neglected.

In Table 3 the experimental and theoretical values of S and I are listed together with the values of $|\bar{A}|$ and $\bar{A}$ deduced therefrom. The lack of polarity information means that it is not known whether $\bar{A}$ relates to the internal strain of As with respect to Ga or *vice versa*. In Figs. 2(*a*) and (*b*) the results are plotted in the manner of Fig. 1(*b*).

The results in which dispersion and temperature are neglected agree with KR and KZLL and confirm the supposition of neglect. The errors assigned here are larger than those cited in the previous works and are based on estimates of the sensitivity of the values of S^2 and I to the initial value of J_0.

The results of the reanalysis including dispersion and temperature are strange and inconsistent. The values derived from S are 50% higher than the published values. A value of about unity for the bond-bending parameter is not impossible but a recent theoretical calculation (Cardona, Kunc & Martin, 1982) puts the value at $\zeta = 0{\cdot}72$. The values deduced from I are a factor of ten lower and the errors are large enough for consistency with a value zero. The implication of this is that the dispersion corrections are zero. Although the observations are made well below the $K\alpha$ absorption edges of gallium and arsenic there is no reason to suppose that the small remaining contributions to $\Delta f_i'$ and $\Delta f_i''$ are spurious.

Table 3. *Experimental and theoretical values of S and I, and the derived values of the internal strain parameter $\bar{A}$ and the bond-bending parameter ζ*

The second line of each S set contains no temperature or dispersion corrections. Units of S and I: 10^{-9} Pa^{-1}.

	S			
	Experiment	Theory	$\lvert\bar{A}\rvert$	$\lvert\zeta\rvert$
KR	0·40 (8)	$1{\cdot}3313\,\lvert\bar{A}\rvert$	0·30 (6)	1·20 (24)
		$2{\cdot}068\ \lvert\bar{A}\rvert$	0·19 (4)	0·77 (16)
KZLL	0·54 (4)	$2{\cdot}0044\,\lvert\bar{A}\rvert$	0·27 (2)	1·08 (8)
		$3{\cdot}102\ \lvert\bar{A}\rvert$	0·17 (1)	0·70 (4)

	I			
	Experiment	Theory	$\bar{A}$	ζ
KR	0·004 (14)	$-0{\cdot}1629\,\bar{A}$	−0·03 (9)	0·1 (3)
KZLL	−0·008 (8)	$0{\cdot}2550\,\bar{A}$	−0·03 (3)	0·1 (1)

It could be that other factors, neglected in this analysis, are important. So far it has been assumed that deformation has altered neither the electron distribution, the dispersion terms nor the Debye–Waller factors. Since spherical form factors are used, some degree of inaccuracy is already present in the zero-stress case. This is confined principally to the valence electrons which are actually subject to sp^3 hybridization and possibly a small ionic charge transfer. These effects should be considerably less than 10%, the ratio of valence electrons to total electrons. Similarly, the dispersion terms are calculated for forward scattering and there is little knowledge of how they change when

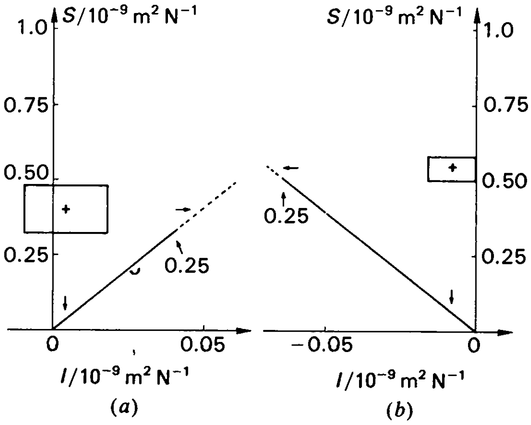

Fig. 2. The results for GaAs plotted as in Fig. 1(*b*). (*a*) for KR and (*b*) for KZLL.

the scattering angle $2\theta_B$ is non-zero. Nevertheless, these terms have proved satisfactory in many situations and thus constitute a good approximation. The greater parts of the corrections here come from scattering from the L shells, which belong to the atomic cores, and should not be greatly affected by pressure. As far as the Debye–Waller factors are concerned, a guess can be made for the effect of stress by comparing a fractional change in volume due to hydrostatic pressure with the same change due to temperature. A pressure of 0·1 GPa at room temperature is roughly equivalent to a reduction of 80 K from room temperature. This latter change would reduce B_1 and B_2 by 32%, corresponding to an increase in T_1 and T_2 of about 6%. All in all, the factors neglected might mean an uncertainty of ±5% in the values of S and I that are used to locate the end points (marked 0·25) of the theoretical lines in Fig. 2. The factors neglected are in no way large enough to account for the inconsistencies.

5. Conclusion

The theoretical basis for determining the internal strain in zinc-blende-structure materials has been presented and earlier work on gallium arsenide has been shown to have been inadequately analysed. Reanalysis in the manner of the present paper reveals strange inconsistencies.

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A Novel Approach to Dynamical Neutron Diffraction by a Deformed Crystal

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Abstract

The propagation of neutron waves in a deformed crystal is considered from the point of view of quantum mechanics. Instead of solving the Takagi–Taupin equations the probability of transitions, induced by the variation of the interaction potential, between quantum states corresponding to the two sheets of the dispersion surface is calculated. In this way transmission and reflection coefficients for an incident plane wave are obtained after a simple analytical calculation for a wide class of crystal deformations. The predictions of this theory are found to be in agreement with direct solutions of the Takagi–Taupin equations as well as with the experimental results.

1. Introduction

A large number of papers have appeared in the last two decades confined to the theoretical treatment of dynamical diffraction phenomena in deformed crystals. Starting from the pioneering works of Penning & Polder (1961) and Kato (1964) the theory has developed considerably after the amplitude-coupling equations for the propagation of the transmitted and reflected beams were formulated by Takagi (1962, 1969) and Taupin (1964). These equations, however, can be solved analytically only in the case of crystals with a constant strain gradient – for a complete treatment including an exhaustive list of references one should consult the paper of Chukhovskii & Petrashen (1977). The solution is a degenerated hypergeometric function being rather complicated for practical integrated intensity evaluation. Although a simplified asymptotic expression for the wave amplitudes is available, little insight into the process of wave propagation is obtained from this solution.

The theory of neutron diffraction by deformed crystals has been simply adopted from the X-ray literature

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