will be no charge for electronic mail distribution - contact should be made with D.Bird@uk.ac.bath.gdr. Distribution by floppy disc will be in the form of $5\frac{1}{4}$ in discs on PCs running under DOS. In this case there will be a handling charge of US $20.

5. Discussion

Subroutine *ATOM* provides a simple means of constructing elastic and absorptive potentials from individual atomic contributions. How useful are the results likely to be? For the elastic potential, the use of atomic potentials is known to be an excellent approximation. Even for the lower-order V_g, where effects due to bonding can be observed, the difference between the actual and neutral-atom potential coefficients is very small (*e.g.* Zuo, Spence & O'Keeffe, 1988). For the absorptive potential, the use of atomic potentials is certain to be a poorer approximation, but it is very difficult to be quantitative about this. It also has to be recognized that TDS is only one contribution to V'_g, and that the use of isotropic Debye-Waller factors introduces further inaccuracy. (The question of what is the best average Debye-Waller factor to use in any given situation when working with anisotropic crystals is rather difficult and we do not attempt to address it here). Our view is that the calculations presented here are about the best that can be done in a general fashion. We expect that they will reliably reflect trends in the absorptive potential as a function of s and M, and will show the correct behaviour of the ratio of elastic to absorptive potential for light and heavy atoms. In this way our results should provide a much better guide to the form of the absorptive potential than any *ad hoc* rule. Given that they can be incorporated into diffraction calculations in a very straightforward way, we suggest that they should be used, if only to see whether the inclusion of absorption in a rather more rigorous fashion makes any significant difference to the final results.

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Acta Cryst. (1990). A**46**, 208-214

Absorption in High-Energy Electron Diffraction from Non-Centrosymmetric Crystals

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(*Received* 30 *July* 1989; *accepted* 17 *October* 1989)

Abstract

The influence of absorptive potentials on high-energy electron diffraction amplitudes is analysed, with an emphasis on effects which are specific to diffraction from non-centrosymmetric crystals. It is shown that the phase difference which then exists between the elastic and absorptive potential coefficients can give rise to a significant asymmetry between +g and −g reflections. This phase difference is calculated for a number of important III-V semiconductors. In many diffraction calculations it is assumed that the phase difference is zero - it is argued here that such calculations cannot be truly quantitative. The inclusion of absorption by perturbation theory is shown to be valid, but only if the change in the eigenvectors as well as the eigenvalues is taken into account. It is shown that within two-beam theory the +g, −g

0108-7673/90/030208-07$03.00

asymmetry in non-centrosymmetric crystals arises purely from changes in the eigenvectors.

1. Introduction

The aim of most dynamical diffraction calculations is to compute a set of diffracted wave amplitudes from which intensities may be derived and compared with experiment. In this paper we ask the simple question - how are these amplitudes affected by absorption? In a previous paper (Bird & King, 1990) the construction of realistic absorptive potentials was discussed - here we make use of those results to make quantitative statements about the influence of absorption on diffracted amplitudes. Many previous authors have considered this question (*e.g.* Hirsch, Howie, Nicholson, Pashley & Whelan, 1977; Humphreys, 1979; Dederichs, 1972). The new work presented here is a discussion of those effects which are specific to non-centrosymmetric crystals. In this case, the Fourier coefficients $V_{\mathbf{g}}$ and $V'_{\mathbf{g}}$ of the elastic and absorptive potentials repectively are both complex numbers and there is no reason in principle why the phases, $\varphi_{\mathbf{g}}$ and $\varphi'_{\mathbf{g}}$, of these coefficients should be the same (Gevers, Blank & Amelinckx, 1966; Snykers, Serneels, Delavignette, Gevers, Van Landuyt & Amelinckx, 1977; Bird, James & King, 1989; Bird & King, 1989). However, in the vast majority of diffraction calculations it is assumed that the absorptive potential is directly proportional to the elastic potential, in which case the phase difference, $\Delta\varphi_{\mathbf{g}}=\varphi_{\mathbf{g}}-\varphi'_{\mathbf{g}}$, vanishes.

Bird & King (1990) used the Einstein model of lattice vibrations to calculate the thermal diffuse scattering (TDS) contribution to the absorptive potential. For reflections other than $\mathbf{g}=\mathbf{0}$, TDS provides the major source of absorption (*e.g.* Radi, 1970) and although the Einstein model is by no means exact, it can provide a useful estimate of $\Delta\varphi_{\mathbf{g}}$ for any non-centrosymmetric structure. In § 2 we present results for a number of important III-V semiconductors. It is shown that a non-zero $\Delta\varphi_{\mathbf{g}}$ makes a significant difference to the kinematic diffraction intensity because it produces corrections of order $|V'_{\mathbf{g}}/V_{\mathbf{g}}|$, while if $\Delta\varphi=0$ (as it is in centrosymmetric structures), the correction is of order $|V'_{\mathbf{g}}/V_{\mathbf{g}}|^2$. Another important point is that this first-order correction changes sign for $\mathbf{g}\rightarrow-\mathbf{g}$. It follows that in non-centrosymmetric crystals an asymmetry exists between $+\mathbf{g}$ and $-\mathbf{g}$ reflections which arises entirely through absorption, *via* the phase difference $\Delta\varphi_{\mathbf{g}}$. In § 3 a more general analysis of absorption is presented, based on a perturbation expansion in the ratio $|V'_{\mathbf{g}}/V_{\mathbf{g}}|$. We find that this approach is valid, but only if changes in the eigenvectors (*i.e.* Bloch wave coefficients) are taken into account, as well as changes in the eigenvalues (*i.e.* the dispersion surface). In many perturbative calculations only the effect on the eigenvalues is included (*e.g.* Humphreys, 1979). In fact, an analysis of two-beam theory shows that the $\Delta\varphi$-induced asymmetry between $+\mathbf{g}$ and $-\mathbf{g}$ reflections is contained *entirely* within the perturbation of the eigenvectors. Two basic conclusions are drawn from this work. The first is that quantitative diffraction calculations should include absorption either by a full perturbation treatment or non-perturbatively, *via* computation of the complex non-Hermitian eigenvalue problem. The second is that even if this is done it is essential to allow for the phase difference $\Delta\varphi_{\mathbf{g}}$ in non-centrosymmetric crystals. As electron microscopy becomes increasingly quantitative (*e.g.* Zuo, Spence & O'Keeffe, 1988; Bird, James & Preston, 1987; Zuo, Spence & Høier, 1989) it is expected that the accurate inclusion of absorption into diffraction calculations will become of major importance.

To end the introduction we run quickly through the fundamentals of dynamical theory in order to set up the equations that will be used and to introduce our notation. Within the forward-scattering and projection approximations the basic equation governing the fast electron wavefunction Φ is (*e.g.* Howie, 1966; Berry, 1971; Bird, 1989)

$$[-\nabla^2_{\mathbf{R}}+U(\mathbf{R})]\Phi(\mathbf{r})=2ik\,\partial\Phi/\partial z, \qquad (1)$$

where k is the magnitude of the incident electron wavevector. The division of $\mathbf{r}$ into transverse, $\mathbf{R}$, and longitudinal, z, coordinates is made explicit in (1). z is the direction of projection, and the $\mathbf{R}$ plane is perpendicular to this. This equation is exactly analogous to the time-dependent Schrödinger equation where $\mathbf{R}$ is the spatial coordinate and z takes the place of time - this similarity will be exploited in the perturbation theory of § 3. $U(\mathbf{R})$ is the effective 'potential' which is related to the actual projected potential $V(\mathbf{R})$ by

$$\begin{aligned}U(\mathbf{R})&=(2\gamma m_0/\hbar^2)\,V(\mathbf{R})\\&=\sum_{\mathbf{G}}U_{\mathbf{G}}\exp(i\mathbf{G}\,.\,\mathbf{R}). \qquad (2)\end{aligned}$$

We have expressed the periodic potential as a sum over Fourier coefficients, $U_{\mathbf{G}}$, here; the $\mathbf{G}$ represents the two-dimensional set of zero-layer reciprocal-lattice vectors. The solutions to (1) are separable and can be expressed in the form of Bloch waves, $\Phi^{(j)}$, each of which has an excitation amplitude $\varepsilon^{(j)}$:

$$\begin{aligned}\Phi^{(j)}&=\sum_{\mathbf{G}}C^{(j)}_{\mathbf{G}}(\mathbf{K})\exp[i(\mathbf{K}+\mathbf{G})\,.\,\mathbf{R}]\\&\quad\times\exp[-is^{(j)}(\mathbf{K})z/2k] \qquad (3a)\\\Phi&=\sum_{j}\varepsilon^{(j)}\Phi^{(j)}. \qquad (3b)\end{aligned}$$

The Bloch wave coefficients $C^{(j)}_{\mathbf{G}}$ and transverse energies $s^{(j)}$ are the eigenvectors and eigenvalues respectively of the many-beam equations

$$\sum_{\mathbf{G}'}\{[(\mathbf{K}+\mathbf{G})^2-s^{(j)}]\delta_{\mathbf{G},\mathbf{G}'}+U_{\mathbf{G}-\mathbf{G}'}\}C^{(j)}_{\mathbf{G}'}=0, \qquad (4)$$

where $\mathbf{K}$ is chosen to match the component of the incident wavevector parallel to the specimen surfaces. Finally, for a non-absorbing potential, the boundary condition at the entrance surface, $z=0$, is satisfied by setting $\varepsilon^{(j)}=C_0^{(j)*}$.

So far, nothing has been said about the form of the potential $U(\mathbf{R})$. We now write it as a total potential, U^{tot}, which is divided into elastic, U, and absorptive, U', parts

$$U^{\text{tot}}(\mathbf{R})=U(\mathbf{R})+iU'(\mathbf{R}). \tag{5}$$

The potential coefficients in (2) can therefore be expressed as

$$U_{\mathbf{G}}^{\text{tot}}=-|U_{\mathbf{G}}|\exp(i\varphi_{\mathbf{G}})-i|U'_{\mathbf{G}}|\exp(i\varphi'_{\mathbf{G}}), \tag{6}$$

where the coefficients are written out explicitly in terms of their magnitudes, $|U_{\mathbf{G}}|$ and $|U'_{\mathbf{G}}|$, and phases, $\varphi_{\mathbf{G}}$ and $\varphi'_{\mathbf{G}}$. The minus signs are included for convenience in (6) to indicate that the potential felt by the fast electrons is basically attractive and therefore negative. In non-centrosymmetric crystals there is no reason why $\varphi_{\mathbf{G}}$ should equal $\varphi'_{\mathbf{G}}$, although, as discussed above, it is often assumed that this is so.

2. Application to III–V semiconductors

We start by re-writing the potential coefficients (6) in terms of their overall amplitude and phase. This proceeds as follows:

$$\begin{aligned}
U_{\mathbf{G}}^{\text{tot}}&=-|U_{\mathbf{G}}|\exp(i\varphi_{\mathbf{G}})-i|U'_{\mathbf{G}}|\exp(i\varphi'_{\mathbf{G}})\\
&=-|U_{\mathbf{G}}|\exp(i\varphi_{\mathbf{G}})[1+R_{\mathbf{G}}\sin(\Delta\varphi_{\mathbf{G}})\\
&\quad+iR_{\mathbf{G}}\cos(\Delta\varphi_{\mathbf{G}})]\\
&\simeq-|U_{\mathbf{G}}|\exp(i\varphi_{\mathbf{G}})[1+R_{\mathbf{G}}\sin(\Delta\varphi_{\mathbf{G}})]\\
&\quad\times[1+iR_{\mathbf{G}}\cos(\Delta\varphi_{\mathbf{G}})]\\
&\simeq-|U_{\mathbf{G}}|\exp(i\varphi_{\mathbf{G}})[1+R_{\mathbf{G}}\sin(\Delta\varphi_{\mathbf{G}})]\\
&\quad\times\exp[iR_{\mathbf{G}}\cos(\Delta\varphi_{\mathbf{G}})]\\
&=-[|U_{\mathbf{G}}|+|U'_{\mathbf{G}}|\sin(\Delta\varphi_{\mathbf{G}})]\\
&\quad\times\exp\{i[\varphi_{\mathbf{G}}+R_{\mathbf{G}}\cos(\Delta\varphi_{\mathbf{G}})]\},
\end{aligned} \tag{7}$$

where $\Delta\varphi_{\mathbf{G}}=\varphi_{\mathbf{G}}-\varphi'_{\mathbf{G}}$ (as in § 1) and $R_{\mathbf{G}}=|U'_{\mathbf{G}}/U_{\mathbf{G}}|$. In the third and fourth steps it is assumed that $R_{\mathbf{G}}$ is small - the final expression is correct to order $R_{\mathbf{G}}$. To this order, therefore, the amplitude and phase of the $\mathbf{G}$ coefficient are corrected by absorption by additive factors $|U'_{\mathbf{G}}|\sin(\Delta\varphi_{\mathbf{G}})$ and $R_{\mathbf{G}}\cos(\Delta\varphi_{\mathbf{G}})$ respectively. It can be seen that the phase difference $\Delta\varphi_{\mathbf{G}}$ plays a vital role in these expressions. This will be discussed in more detail later, but we note at this stage that $\Delta\varphi_{\mathbf{G}}$ is independent of the choice of origin and is therefore a phase-invariant quantity (*e.g.* Bird, James & Preston, 1987). It is also interesting to distinguish between the $\mathbf{G}=\mathbf{0}$ and $\mathbf{G}\neq\mathbf{0}$ components. In writing $U_{\mathbf{G}}^{\text{tot}}$ in the form (7) in may seem that the physical meaning of absorption in terms of loss of electron flux has been lost, because we have lost the distinction between real and imaginary potentials. This can be overcome if it is remembered that U_0 and U'_0 can be incorporated directly (and exactly) into the transverse energy $s^{(j)}$ with a change of definition $s^{(j)}\rightarrow s^{(j)}-|U_0|-i|U'_0|$. The U'_0 term then gives a uniform attenuation to all Bloch waves (3*a*). The $\mathbf{G}\neq\mathbf{0}$ (*i.e.* anomalous absorption) terms act in a different way and in a sense do not contribute to overall absorption - instead (at least to lowest order) they simply redistribute intensity between the different Bragg reflections.

An important feature of (7) is that $+\mathbf{G}$ and $-\mathbf{G}$ behave differently. Without absorption $U_{\mathbf{G}}^{\text{tot}}=U_{-\mathbf{G}}^{\text{tot}*}$; with absorption this is still true separately of the real and absorptive parts (*i.e.* $|U_{\mathbf{G}}|=|U_{-\mathbf{G}}|$, $\varphi_{\mathbf{G}}=-\varphi_{-\mathbf{G}}$, and similarly for $U'_{\mathbf{G}}$) but when combined we find (to first order in $R_{\mathbf{G}}$)

$$\begin{aligned}
U_{\mathbf{G}}^{\text{tot}}U_{-\mathbf{G}}^{\text{tot}}&\simeq|U_{\mathbf{G}}|^2\exp[2iR_{\mathbf{G}}\cos(\Delta\varphi_{\mathbf{G}})]\\
|U_{\mathbf{G}}^{\text{tot}}|^2&\simeq|U_{\mathbf{G}}|^2+2|U_{\mathbf{G}}U'_{\mathbf{G}}|\sin(\Delta\varphi_{\mathbf{G}}).
\end{aligned} \tag{8}$$

The second of these is the modulus squared of the potential coefficient and is the quantity that governs the intensity of diffraction into reflection $\mathbf{G}$ within the kinematic (*i.e.* single-scattering) approximation. For $-\mathbf{G}$, $\sin(\Delta\varphi_{\mathbf{G}})$ changes sign, so the magnitude of the $+\mathbf{G}$ and $-\mathbf{G}$ coefficients are different, as are the $+\mathbf{G}$ and $-\mathbf{G}$ kinematic intensities. Equation (8) reveals two important properties of this asymmetry - first, it enters to order $R_{\mathbf{G}}$ and, second, it is found only for non-centrosymmetric structures. For centrosymmetric crystals, $\Delta\varphi_{\mathbf{G}}$ must equal zero or π in which case the $+\mathbf{G}$ and $-\mathbf{G}$ intensities are the same. This is true to all orders in $R_{\mathbf{G}}$, as can be seen in (7) before it is approximated. Absorption does change the magnitude of $U_{\mathbf{G}}^{\text{tot}}$ in centrosymmetric structures, but only to order $R_{\mathbf{G}}^2$ and with no $+\mathbf{G}$, $-\mathbf{G}$ asymmetry.

How important are these effects due to a non-zero $\Delta\varphi_{\mathbf{G}}$? To answer this it is necessary to calculate both $R_{\mathbf{G}}$ and $\Delta\varphi_{\mathbf{G}}$ for the non-centrosymmetric structure under consideration. As an example we have evaluated the absorptive potential for four important III–V semiconductors using the method described by Bird & King (1990). The results for the magnitude of $U_{\mathbf{G}}/U_0$ (expressed as a percentage), $R_{\mathbf{G}}$ (at an accelerating voltage of 200 kV, and expressed as a percentage) and the magnitude of $\Delta\varphi_{\mathbf{G}}$ (in degrees) are shown in Table 1. Values have been calculated at two temperatures, 80 and 300 K; the relevant Debye–Waller factors are taken from Reid (1983). It can be seen that $R_{\mathbf{G}}$ is a rapidly varying function of $\mathbf{G}$, being largest for the weaker $h+k+l=4n+2$ type (where n is an integer) reflections. As a rough guide, its value at 80 K is about half that at 300 K. The $\Delta\varphi_{\mathbf{G}}$ values are insensitive to temperature and are non-zero only for the *hkl*-odd-type reflections. The common assumption in electron-diffraction calculations is that

Table 1. *Values of the potential coefficients for the lowest-order reflections in* GaAs, GaP, InAs *and* InP *at* 80 *and* 300 K

	GaAs (300 K)			GaAs (80 K)			GaP (300 K)			GaP (80 K)		
g	$\lvert U_g/U_0\rvert$	$\lvert R_g\rvert$	$\lvert\Delta\varphi_g\rvert$	$\lvert U_g/U_0\rvert$	$\lvert R_g\rvert$	$\lvert\Delta\varphi_g\rvert$	$\lvert U_g/U_0\rvert$	$\lvert R_g\rvert$	$\lvert\Delta\varphi_g\rvert$	$\lvert U_g/U_0\rvert$	$\lvert R_g\rvert$	$\lvert\Delta\varphi_g\rvert$
000	100·0	2·6	0·0	100·0	1·4	0·0	100·0	1·6	0·0	100·0	0·9	0·0
111	45·2	3·9	0·9	45·7	2·1	0·8	43·2	2·9	20·8	43·6	1·6	19·8
200	3·1	5·4	0·0	3·2	2·9	0·0	6·7	12·0	0·0	6·7	6·4	0·0
220	41·8	5·6	0·0	43·0	3·1	0·0	37·9	3·9	0·0	38·9	2·2	0·0
311	24·9	6·4	1·6	25·9	3·5	1·6	22·6	5·0	16·6	23·4	2·8	15·5
222	1·2	12·5	0·0	1·3	6·7	0·0	6·4	11·7	0·0	6·5	6·4	0·0
400	28·3	7·5	0·0	29·9	4·2	0·0	24·6	5·4	0·0	25·8	3·1	0·0
331	18·0	8·0	2·5	19·2	4·5	2·5	16·0	6·4	13·6	17·0	3.6	12.9
420	0·4	28·7	0·0	0·6	14·6	0·0	5·8	11·8	0·0	6·1	6·5	0·0
422	21·8	8·8	0·0	23·7	5·0	0·0	18·5	6·5	0·0	19·9	3·8	0·0
333	14·2	9·3	3·0	15·6	5·3	3·0	12·6	7·5	11·9	13·6	4·3	10·8
440	17·7	9·9	0·0	19·8	5·7	0·0	14·9	7·4	0·0	16·4	4·3	0·0
531	11·7	10·2	3·1	13·2	5·9	3·1	10·3	8·4	11·1	11·4	4·9	9·9
600	0·1	104·9	0·0	0·2	35·1	0·0	4·5	13·1	0·0	4·9	7·5	0·0
	InAs (300 K)			InAs (80 K)			InP (300 K)			InP (80 K)		
000	100·0	3·8	0·0	100·0	2·0	0·0	100·0	3·2	0·0	100·0	1·7	0·0
111	48·1	5·7	13·8	48·7	3·1	13·6	47·9	5·7	22·0	48·5	3·1	21·3
200	9·2	15·8	0·0	9·6	8·3	0·0	18·4	13·1	0·0	18·9	6·9	0·0
220	45·7	7·3	0·0	47·1	4·0	0·0	42·6	6·6	0·0	43·9	3·6	0·0
311	27·8	8·8	12·3	29·1	4·8	12·1	26·9	9·0	18·3	28·2	5·0	17·4
222	6·3	20·2	0·0	6·9	10·7	0·0	13·0	16·4	0·0	14·0	8·7	0·0
400	31·3	9·6	0·0	33·3	5·4	0·0	28·2	8·9	0·0	30·0	5·0	0·0
331	20·2	10·9	11·4	21·8	6·1	11·2	19·2	11·3	16·1	20·8	6·4	15·0
420	4·7	23·4	0·0	5·6	12·5	0·0	10·3	18·6	0·0	11·6	10·1	0·0
422	24·0	11·4	0·0	26·4	6·4	0·0	21·1	10·6	0·0	23·2	6·1	0·0
333	15·8	12·5	11·1	17·6	7·2	11·0	14·8	13·1	15·0	16·7	7·5	13·8
440	19·4	12·7	0·0	22·0	7·4	0·0	16·7	12·1	0·0	19·0	7·1	0·0
531	12·9	13·9	11·2	14·9	8·1	11·2	12·0	14·7	14·7	13·9	8·6	13·3
600	2·7	31·5	0·0	3·7	16·8	0·0	6·7	22·8	0·0	8·3	12·7	0·0

$R_G = 10\%$ and $\Delta\varphi_G = 0$. A glance at Table 1 shows that this is a very crude approximation.

The behaviour of $\Delta\varphi_G$ can be understood if the potential coefficients are written in the form (Bird & King, 1990)

$$\begin{aligned} U_G &\propto f_A(G) + f_B(G)\exp[-i(h+k+l)\pi/2] \\ U'_G &\propto f'_A(G) + f'_B(G)\exp[-i(h+k+l)\pi/2] \end{aligned} \tag{9}$$

where $f_{A,B}$ and $f'_{A,B}$ are the elastic and absorptive form factors respectively for the group III element (A) at (0, 0, 0) and the group V element (B) at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$. For *hkl*-even reflections, both U_G and U'_G are real, so the phase difference $\Delta\varphi_G$ is zero. For *hkl*-odd reflections both U_G and U'_G have phases which are not equal to one another. The magnitude of the phase difference depends only on the magnitude of **G** (Table 1), but its sign is a rather more subtle quantity. In calculations of the absorptive potential (*e.g.* Bird & King, 1990, and references therein), it is generally found that the absorptive form factor increases more rapidly with atomic number than the elastic contribution, that is, f'/f increases with Z. (This result must be used with care, however, because the Debye-Waller factor also plays an important role, and lighter atoms with a large thermal vibration amplitude may have a larger f'/f.) From (9), $\Delta\varphi_G$ for *hkl*-odd reflections can be written

$$\Delta\varphi_G = \pm\left[\tan^{-1}\left(\frac{f_B}{f_A}\right) - \tan^{-1}\left(\frac{f'_B}{f'_A}\right)\right], \tag{10}$$

where the plus sign corresponds to reflections with $h+k+l = 4n-1$ and the minus sign to those with $h+k+l = 4n+1$. If the group III element is the heavier atom (as in InP, GaP and InAs), then $\Delta\varphi_G$ will be positive for $4n-1$ type reflections and negative for $4n+1$ type reflections because f'_B/f'_A is smaller than f_B/f_A. The converse is true if the group V element is heavier (as in GaAs). This also explains why $\Delta\varphi_G$ is much larger in InP than in GaAs, because the more different the atomic species, the greater is the difference to be expected between the two terms in (10). A similar effect is expected to be observed in other non-centrosymmetric structures.

From (8) and the data of Table 1 we can calculate the difference in kinematic intensity between +**G** and −**G** reflections (or between any $4n+1$ and $4n-1$ type reflections in a given family of {**G**}s). The relative difference is given by

$$(\Delta I_G/I_G)_{\text{kin}} \simeq 4R_G \sin(\Delta\varphi_G). \tag{11}$$

For InP at 300 K this becomes 8·5, 11·3, 12·5, 13·6 and 14·9% for the 111, 311, 331, 333 and 531 reflections respectively. These represent the largest values, for the other materials in Table 1 the values will be smaller (especially for GaAs) and will decrease at lower temperatures. However, the data in Table 1 show that a 10% difference between ±**G** is by no means exceptional. Although this refers to the squared modulus of the potential coefficients, it still means that the amplitudes themselves can differ by around 5%. In truly quantitative work it is clear that effects of this magnitude should be taken into account.

3. Perturbation theory

We now turn to a more general treatment of absorption which involves including the absorptive potential by perturbation theory. The aim is to derive expressions for the change in elastic diffraction amplitudes to first order in the absorptive potential. In order to show exactly where the results come from, the problem is tackled using both time-dependent and time-independent methods. They yield the same results, but only if the effect on the eigenvectors is taken into account as well as the more familiar change in the eigenvalues (see also Rez, 1979).

In a time-dependent formalism we go back to the original diffraction equation (1) with $U(\mathbf{R})$ being the elastic potential. The absorptive potential $U'(\mathbf{R})$ is to be included as a perturbation which causes scattering of the original Bloch states into other states, thus leading to a formulation of the problem in terms of z- (*i.e.* 'time-') dependent Bloch wave amplitudes. In this approach the Bloch waves remain those of the elastic potential, but their amplitude varies with depth. Without the perturbing potential, of course, these amplitudes would be constant. Green's function methods (*e.g.* Schiff, 1968) are used to include the absorption. The total wavefunction is written

$$\begin{aligned}\Phi(\mathbf{R}, z) = \Phi_0(\mathbf{R}, z) + \int \mathrm{d}\mathbf{R}'\,\mathrm{d}z'\,\mathscr{G}(\mathbf{R}, z; \mathbf{R}', z')\\ \times iU'(\mathbf{R}')\Phi_0(\mathbf{R}', z') + \ldots,\end{aligned} \tag{12}$$

where Φ_0 is the unperturbed elastic wavefunction

$$\begin{aligned}\Phi_0 = \sum_j C_{\mathbf{0}}^{(j)*} \sum_{\mathbf{G}} C_{\mathbf{G}}^{(j)}(\mathbf{K}) \exp\left[i(\mathbf{K}+\mathbf{G}) . \mathbf{R}\right]\\ \times \exp\left[-is^{(j)}(\mathbf{K})z/2k\right]\end{aligned} \tag{13}$$

and $i\mathscr{G}U'\Phi_0$ is the first-order correction. The Green function obeys

$$\begin{aligned}\left[-\nabla_{\mathbf{R}}^2 + U(\mathbf{R}) - 2ik\partial/\partial z\right]\mathscr{G}(\mathbf{R}, z; \mathbf{R}', z')\\ = -\delta(\mathbf{R}'-\mathbf{R})\delta(z'-z)\end{aligned} \tag{14}$$

and is given by

$$\begin{aligned}\mathscr{G}(\mathbf{R}, z; \mathbf{R}', z') = (2ik)^{-1}(4\pi^2)^{-1}\Theta(z-z')\\ \times \sum_{j'\mathbf{G}\mathbf{G}'} \int \mathrm{d}\mathbf{K}'\,C_{\mathbf{G}}^{(j')}(\mathbf{K}')C_{\mathbf{G}'}^{(j')*}(\mathbf{K}')\\ \times \exp\left[i(\mathbf{K}'+\mathbf{G}) . \mathbf{R}\right]\\ \times \exp\left(-is^{(j')}z/2k\right)\\ \times \exp\left[-i(\mathbf{K}'+\mathbf{G}') . \mathbf{R}'\right]\\ \times \exp\left(is^{(j')}z'/2k\right)\end{aligned} \tag{15}$$

where the $\mathbf{K}'$ integral is over one Brillouin zone of the zero-layer reciprocal lattice. $\Theta(z)$ is the step function, $\Theta(z) = 0$ for $z < 0$ and $\Theta(z) = 1$ for $z > 0$. Equations (12), (13) and (15) are then combined to give the amplitude at the exit surface $z = t$:

$$\begin{aligned}A_{\mathbf{G}} = \sum_j C_{\mathbf{0}}^{(j)*}C_{\mathbf{G}}^{(j)} \exp\left(-is^{(j)}t/2k\right)\\ -\sum_{jj'} \left(U'_{jj'}t/2k\right)C_{\mathbf{0}}^{(j)*}C_{\mathbf{G}}^{(j')}\\ \times \exp\left[-i(s^{(j)}+s^{(j')})t/4k\right]\\ \times \{\sin\left[(s^{(j)}-s^{(j')})t/4k\right]/\left[s^{(j)}-s^{(j')}\right]t/4k\}\end{aligned} \tag{16}$$

where the matrix element of the absorptive potential is given by

$$U'_{jj'} = {\sum_{\mathbf{G}\mathbf{G}'}}' C_{\mathbf{G}'}^{(j')*}|U'_{\mathbf{G}'-\mathbf{G}}| \exp\left(i\varphi'_{\mathbf{G}'-\mathbf{G}}\right)C_{\mathbf{G}}^{(j)}. \tag{17}$$

In accordance with our discussion in § 2 it is assumed that U'_0 has been absorbed into s and so the $\mathbf{G} = \mathbf{G}'$ term is omitted from the double sum in (17) (hence the prime). The first term in (16) is the familiar elastic-diffraction amplitude, the second is the first-order correction due to absorption. This will provide a good approximation to total absorptive effect provided $U'_{jj'}t/2k \ll 1$ for all j and j'. Absorptive potentials are usually considerably weaker than the elastic potential (*e.g.* Table 1), and so in fairly thin crystals it is not difficult to meet this condition. For any thickness, of course, the correct amplitudes can be obtained by a full diagonalization of the non-Hermitian many-beam equations. Before discussing the first-order correction in detail, we show how it can also be derived using time-independent perturbation theory.

Here we look at the effects on the Bloch waves themselves, and derive a set of perturbed $\Phi^{(j)}$ which still propagate with constant amplitude. It must be remembered, however, that this excitation amplitude will also be perturbed from its elastic value of $C_{\mathbf{0}}^{(j)*}$. The standard results of first-order perturbation theory (*e.g.* Schiff, 1968) applied to the many-beam equations (4) give corrections $\delta C_{\mathbf{G}}^{(j)}$ and $\delta s^{(j)}$ to the Bloch wave coefficients and transverse energies respectively, where

$$\delta C_{\mathbf{G}}^{(j)} = -i \sum_{j' \neq j} \left[U'_{jj'}/(s^{(j)}-s^{(j')})\right]C_{\mathbf{G}}^{(j')}$$

and (18)

$$s^{(j)} = -iU'_{jj}$$

and the matrix elements are defined in (17). The first-order change in the diffraction amplitude can therefore be built up from the first-order changes in $C_{\mathbf{G}}^{(j)}$, $s^{(j)}$ and the excitation amplitudes, $\delta\varepsilon^{(j)}$. $A_{\mathbf{G}}$ now becomes

$$\begin{aligned}A_{\mathbf{G}} = \sum_j C_{\mathbf{0}}^{(j)*}C_{\mathbf{G}}^{(j)} \exp\left(-is^{(j)}z/2k\right)\\ +\sum_j \left[(-iz/2k)C_{\mathbf{0}}^{(j)*}C_{\mathbf{G}}^{(j)}\delta s^{(j)}\right.\\ \left. + C_{\mathbf{0}}^{(j)*}\delta C_{\mathbf{G}}^{(j)} + \delta\varepsilon^{(j)}C_{\mathbf{G}}^{(j)}\right]\\ \times \exp\left(-is^{(j)}z/2k\right) + \ldots.\end{aligned} \tag{19}$$

$\delta\varepsilon^{(j)}$ is determined by the boundary condition that at the entrance surface $z=0$ the first-order correction term must vanish. This is satisfied provided

$$\sum_j C_{\mathbf{0}}^{(j)*}\delta C_{\mathbf{G}}^{(j)} = -\sum_j \delta\varepsilon^{(j)} C_{\mathbf{G}}^{(j)} \tag{20}$$

from which we find [using (18) and the orthogonality of the Bloch waves]

$$\delta\varepsilon^{(j)} = -i \sum_{j'\neq j} [U'_{j'j}/(s^{(j)}-s^{(j')})]C_{\mathbf{0}}^{(j')*}. \tag{21}$$

Equations (18), (19) and (21) can then be combined to give the total first-order change in $A_{\mathbf{G}}$ which, not surprisingly, agrees with (16). We note in passing that it is more usual to put the change in the transverse energy into the $\exp(-is^{(j)}z/2k)$ factor rather than expand this to first order, as in (19). Although this may be a useful approximation, the resulting amplitudes cannot be more accurate than first order in $U'(\mathbf{R})$; to go beyond this it would be necessary to consider higher-order corrections to both the Bloch wave coefficients and the transverse energies. To make the link between time-dependent and time-independent treatments it is important to compare like with like, and so we must work in both cases with the genuine first-order correction.

Although the result is the same, the time-independent derivation shows clearly where the terms in (16) arise. In (19), both $\delta C_{\mathbf{G}}^{(j)}$ and $\delta\varepsilon^{(j)}$ contain sums over j', so these terms are the origin of the $j\neq j'$ contributions in (16). These terms arise from the perturbation of the eigen*vectors* in (18). The $j=j'$ terms in (16) come from the $\delta s^{(j)}$ part of (19) and therefore arise from the perturbation of the eigen*values*. It follows that if, as is often the case, only the perturbation of the eigenvalues is considered, a substantial part of the overall first-order change of the diffraction amplitudes is neglected. Rez (1979) makes a similar point but his analysis concentrates on application to centrosymmetric crystals. The difference between the $j=j'$ and $j\neq j'$ terms is very closely related to the dependent/independent Bloch wave result in inelastic scattering theory (*e.g.* Bird & Wright, 1989, and references therein). The $j=j'$ terms (independent waves) tend to dominate in thicker crystals because these terms increase linearly with thickness, while the $j\neq j'$ terms oscillate. However, in specimens whose thickness is less than the significant extinction distances (*i.e.* when $t<4k/|s^{(j)}-s^{(j')}|$ for the important j and j') the $j\neq j'$ term (dependent waves) can provide an equally significant contribution.

The different effects of the $j=j'$ and $j\neq j'$ terms in (16) are clearly demonstrated in two-beam theory (see also Gevers *et al.*, 1966; Snykers *et al.*, 1977). Here, the many-beam equations (4) reduce to the 2×2 equation

$$\begin{pmatrix} W+s^{(j)} & U\exp(-i\varphi_{\mathbf{G}}) \\ U\exp(i\varphi_{\mathbf{G}}) & -W+s^{(j)} \end{pmatrix}\begin{pmatrix} C_{\mathbf{0}}^{(j)} \\ C_{\mathbf{G}}^{(j)} \end{pmatrix} = 0 \tag{22}$$

where the deviation parameter is given by $W=\mathbf{G}\,.\,(\mathbf{K}+\mathbf{G}/2)$ and $U=|U_{\mathbf{G}}|$. The Bloch wave coefficients become

$$\left.\begin{aligned} C_{\mathbf{0}}^{(1)} &= 2^{-1/2}[1+W/(U^2+W^2)^{1/2}]^{1/2} \\ C_{\mathbf{0}}^{(2)} &= 2^{-1/2}[1-W/(U^2+W^2)^{1/2}]^{1/2} \\ C_{\mathbf{G}}^{(1)} &= +\exp(i\varphi_{\mathbf{G}})C_{\mathbf{0}}^{(2)} \\ C_{\mathbf{G}}^{(2)} &= -\exp(i\varphi_{\mathbf{G}})C_{\mathbf{0}}^{(1)} \end{aligned}\right. \tag{23a}$$

with corresponding eigenvalues

$$s^{(1)} = -(U^2+W^2)^{1/2}, \qquad s^{(2)} = (U^2+W^2)^{1/2}. \tag{23b}$$

These expressions can be used in (16) and (17) to produce the first-order change in the two-beam amplitude. The matrix elements (17) become

$$U'_{1,1} = -U'_{2,2} = [UU'/(U^2+W^2)^{1/2}]\cos(\Delta\varphi_{\mathbf{G}}) \tag{24a}$$

$$\begin{aligned} U'_{1,2} = U'^{*}_{2,1} &= iU'\sin(\Delta\varphi_{\mathbf{G}}) \\ &\quad -[WU'/(U^2+W^2)^{1/2}]\cos(\Delta\varphi_{\mathbf{G}}) \end{aligned} \tag{24b}$$

where $U'=|U'_{\mathbf{G}}|$. The diffracted amplitude, correct to first order in U', is then

$$\begin{aligned} A_{\mathbf{G}} = {} & iU\exp(i\varphi_{\mathbf{G}}) \\ & \times\sin[(U^2+W^2)^{1/2}t/2k]/(U^2+W^2)^{1/2} \\ & \times\{1+(U'/U)\sin(\Delta\varphi_{\mathbf{G}}) \\ & +i[W^2/(U^2+W^2)](U'/U)\cos(\Delta\varphi_{\mathbf{G}})\} \\ & -\{\exp(i\varphi_{\mathbf{G}})(U'z/2k)[U^2/(U^2+W^2)] \\ & \times\cos[(U^2+W^2)^{1/2}t/2k]\cos(\Delta\varphi_{\mathbf{G}})\}. \end{aligned} \tag{25}$$

The factor of 1 in the first term represents the unperturbed amplitude, the remainder of this term is the absorption correction which arises from the perturbation of the eigen*vectors* [*i.e.* from the off-diagonal terms, (24*b*)]. The second term is produced by the diagonal matrix elements in (24*a*) which represent the contribution from perturbation of the eigen*values*. This term is exactly what is obtained if we take the standard expressions for absorption-affected two-beam amplitudes, which include only eigenvalue changes (*e.g.* Hirsch *et al.*, 1977), and expand them to first order in U'. To find the diffracted intensity we take the modulus squared of (25). Because this expression is correct only to first order in U', the same must be true of the intensity. To this order, only the $\sin(\Delta\varphi_{\mathbf{G}})$ part of the first term contributes because the remaining parts are out of phase with the basic amplitude by a factor of i. We therefore obtain

$$\begin{aligned} I_{\mathbf{G}} \simeq {} & [U^2+2UU'\sin(\Delta\varphi_{\mathbf{G}})] \\ & \times\sin^2[(U^2+W^2)^{1/2}t/2k](U^2+W^2)^{-1}. \end{aligned} \tag{26}$$

The two-beam intensity is simply modified by a corrected value for U^2, which is precisely the first-order expression for $|U_{\mathbf{G}}^{\text{tot}}|^2$ in (8). The same $+\mathbf{G}$, $-\mathbf{G}$ asymmetry in non-centrosymmetric crystals is therefore found in two-beam theory and, importantly, is found to be contained *entirely* within the first-order changes to the eigenvectors (Snykers *et al.*, 1977). It follows that even if an absorptive potential is used which allows for the phase difference $\Delta\varphi_{\mathbf{G}}$, its full effects will be observed only if absorption is included non-perturbatively, or if changes to the eigenvectors are taken into account.

4. Discussion

Although perturbation theory may provide an excellent approximation, is it useful to include absorption this way? The analysis of § 3 shows that it is essential to include the effect on the eigenvectors, in which case it is necessary to evaluate the matrix element $U'_{jj'}$, (17), for every j and j'. In an N-beam calculation there are N^2 of these, each of which involves N^2 sums over reciprocal-lattice vectors. First-order perturbation theory therefore becomes an N^4 procedure, which, as N increases, exceeds the N^3 operations required for matrix diagonalization. This N^3 dependence is the same for non-Hermitian and Hermitian matrices; thus we conclude that as the size of a many-beam calculation increases, it becomes more time consuming to use perturbation theory than to diagonalize the non-Hermitian matrix. It follows that for a general-purpose program to compute diffracted intensities it will almost certainly be best to include absorption non-perturbatively.

Our analysis of the influence of a non-zero $\Delta\varphi_{\mathbf{G}}$ in non-centrosymmetric crystals has concentrated on two-beam theory. To go beyond this in any general way is very difficult - Snykers *et al.* (1977) and Bird, James & King (1989) discuss particular examples of the effect in three-beam diffraction. It is for this reason in § 2 that we concentrated on the change which $\Delta\varphi_{\mathbf{G}}$ induces in the basic Fourier coefficients. In any dynamical diffraction situation it is these coefficients which control the strength of scattering between different reflections, and if this changes by the order of a few percent it is reasonable to assume, just as we found in two-beam theory, that the diffracted intensities will change by similar amounts. There is a clear need to perform dynamical calculations, to simulate both images and diffraction patterns, on a range of non-centrosymmetric crystals in order to see just how important the effects of a non-zero $\Delta\varphi_{\mathbf{G}}$ can be.

I thank J. A. Eades and A. R. Preston for helpful discussions and Q. A. King for help with the computing.

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