Effective Structure Factors in Many-Beam X-ray Diffraction – Use of the Second Bethe Approximation

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Abstract

An analytical expression for the effective structure factor, $F_{h0}^{n,p}$, generally valid for each polarization direction p in the many-beam X-ray case, is derived. The second Bethe approximation is utilized with the additional assumption that certain small $\sigma.\pi$-type terms may be neglected. It is shown that the many-beam effects observed in both plane-wave- and integrated-intensity-type experiments may be described by the existing standard two-beam expressions provided the effective structure factor is introduced. Examples based on three- and four-beam interactions are given with focus on the absorption-independent effects. In particular, the deviation of $F_{h0}^{3,p} F_{0h}^{3,p}$ in the general three-beam case from the corresponding two-beam value is shown to depend on the three-phase structure invariant and the deviation parameter of the coupled beam. The results which agree with full three-beam calculations may be applied to determine invariants experimentally from any type of three-beam experiment in principle. Applications to *Pendellösung* and mosaic-crystal experiments are briefly discussed. The accuracy of the method is evaluated from calculated dispersion surfaces in three- and four-beam examples.

Introduction

The interest in many-beam diffraction effects reflects the application of such effects in structure studies through the possible experimental determination of structure factors and structure invariants (*e.g.* Kambe, 1957; Hart & Lang, 1961; Gjønnes & Høier, 1969; Terasaki, Watanabe & Gjønnes, 1979; Post, 1979; Chapman, Yoder & Colella, 1981; Høier & Aanestad, 1981; Chang, 1982; Thorkildsen & Mo, 1982). Single crystals have as a rule been studied theoretically, and the interpretation of the effects observed has typically been on a qualitative scale by means of plane-wave theory. Even then the interpretation has to be built on rather detailed numerical calculations as analytical solutions may only be found in very special cases. Approximated analytical solutions are therefore highly

desirable for studying the dependence of the observed intensity on the various experimental parameters, in plane-wave cases, but especially in integrated-intensity-type experiments with X-rays.

It is clear from available numerical many-beam calculations of the dispersion surface and excitation coefficients (Høier & Aanestad, 1981) that the main intensity contributions may be ascribed to the particular dispersion-surface branches which are excited also in the corresponding two-beam case. The minimum distances between these branches, however, are in many-beam experiments different from the two-beam values, being dependent on the deviation parameters of the simultaneously excited beams. This variation in the gap width may be associated with a corresponding structure-factor variation, and the effective structure factor thus defined is larger or smaller than the standard value as shown by, for example, Watanabe, Uyeda & Fukahara (1968) and Gjønnes & Høier (1971) or Høier & Aanestad (1981) for the electron and X-ray diffraction cases, respectively.

In the present studies we have focused on the determination of analytical expressions for the effective structure factors which then generally may be introduced in existing two-beam X-ray expressions. The method utilized is the second Bethe approximation (Bethe, 1928; Cowley, 1975) originally developed for the electron diffraction case. The necessary additional assumptions for the application of this approximation in the many-beam X-ray case as well are discussed. Some preliminary results have been given by Marthinsen (1981).

Theory

The crystal wave field is found from the fundamental equation (Pinsker, 1978)

$$\frac{\mathbf{k}_n^2 - K^2}{\mathbf{k}_n^2} D_{np} - \sum_{\substack{m \\ p'}} \chi_{nm}^{pp'} D_{mp'} = 0, \tag{1}$$

where m and n are the interacting beams, and the polarization unit vectors $\mathbf{p}_n$ and $\mathbf{p}_m'$ are either σ or π.

Further, $\chi_{nm} = \chi_{n-m}$ and

$$\chi_{nm}^{pp'} = \chi_{nm}\, \mathbf{p}_n \cdot \mathbf{p}'_m, \tag{2}$$

where

$$\chi_{nm} = -\frac{r_e \lambda^2}{\pi V_c} F_{nm}. \tag{3}$$

Here r_e, V_c and F_{nm} are the classical electron radius, the unit-cell volume and the structure factor, respectively. The wave field is written

$$\mathbf{D} = \sum_n \mathbf{D}_n \exp\,[2\pi i(\nu t - \mathbf{k}_n \cdot \mathbf{r})], \tag{4}$$

where

$$\mathbf{D}_n = D_{n\sigma}\, \boldsymbol{\sigma}_n + D_{n\pi}\, \boldsymbol{\pi}_n. \tag{5}$$

The incident-beam direction $\mathbf{K}_0$ is determined by the parameter $\mathbf{y}_0 = \mathbf{LP}$ or alternatively by the vector $\boldsymbol{\xi}$ in Fig. 1. The latter quantity is preferred in cases where the operating reflections originate from one zone only. The $\boldsymbol{\xi}$ plane is parallel to the reciprocal plane considered through the Laue point as shown schematically in Fig. 1. $\boldsymbol{\xi}$ is thus the vector from L to the projection of P on the ζ plane. This single parameter determines all the deviation parameters s_n (or $\Delta\theta_n$) for all the interacting beams, viz.

$$s_n = \boldsymbol{\xi} \cdot \mathbf{n}/K. \tag{6}$$

s_n, which is the distance from the reciprocal point n to the Ewald sphere, is positive when n is inside the sphere. The *Anpassung*

$$K\delta = \mathbf{PA} \tag{7}$$

is positive along the inward-directed normal to the entrance surface. The alternative quantity

$$\Gamma = -K\delta - K\chi_{0r}/2\gamma_0 \tag{8}$$

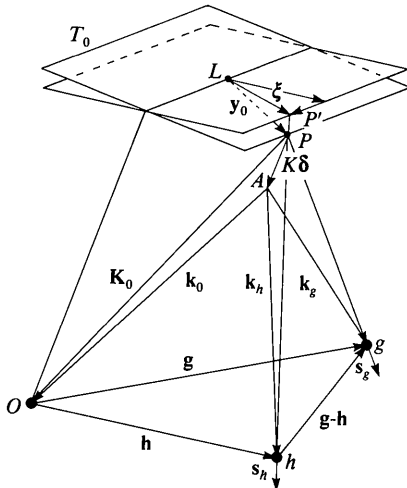Fig. 1. Three-beam geometry with definitions of $K\delta$, s_h and $\boldsymbol{\xi}$.

was used in a previous paper (Høier & Aanestad, 1981), where Γ is positive in the direction of negative δ and χ_{0r} is the real part of χ_0. Here and below γ_0 and γ_n are the direction cosines of $\mathbf{K}_0$ and $\mathbf{K}_n$, respectively.

For generality we introduce (Pinsker, 1978)

$$B_{np} = \sqrt{\gamma_n}\, D_{np}, \tag{9}$$

thus transforming the fundamental equation to the following form

$$\sum_{\substack{m \\ p'}} G_{nm}^{pp'}\, B_{mp'} = K\delta B_{np}, \tag{10}$$

where

$$G_{nm}^{pp'} = -\frac{1}{\sqrt{\gamma_n\, \gamma_m}}\, [s_m\, \delta_{nm}^{pp'} + \tfrac{1}{2}K\chi_{nm}^{pp'}]. \tag{11}$$

The quantity $\delta_{nm}^{pp'}$ is equal to unity when $n = m$ and $p = p'$ and equal to zero otherwise.

Following Bethe (1928) the incident-beam direction is now assumed to be such that one Bragg condition is nearly or exactly fulfilled. We thus have two strong beams 0 and h, i.e. the direct and the primary beam, respectively. The other beams g are termed secondary beams and are far enough from the Bragg condition to be considered weak, but close enough to be non-negligible. The weak-beam amplitudes may thus be found from (10) as functions of the strong components only, assuming $K\delta \simeq -K\chi_0/2\gamma_0$:

$$B_{gp} = -\frac{\gamma_g}{s_g + \tfrac{1}{2}K\chi_0(1 - \gamma_g/\gamma_0)} \sum_{\substack{m=0,h \\ p'}} \frac{K\chi_{gm}^{pp'}}{2\sqrt{\gamma_g\, \gamma_m}}\, B_{mp'}. \tag{12}$$

Utilizing (10), the resulting eigenvalue problem for the strong beams 0 and h has the following interaction matrix elements:

$$H_{nm}^{pp'} = G_{nm}^{pp'} + \Delta G_{nm}^{pp'}$$

$$= -\frac{1}{\sqrt{\gamma_n\, \gamma_m}} \left[s_m\, \delta_{nm}^{pp'} + \tfrac{1}{2}K\chi_{nm}^{pp'} - \tfrac{1}{4}K^2 \right.$$

$$\left. \times \sum_{\substack{g \neq 0,h \\ p''}} \frac{\chi_{ng}^{pp''}\, \chi_{gm}^{p''p'}}{s_g + \tfrac{1}{2}K\chi_0(1 - \gamma_g/\gamma_0)} \right]. \tag{13}$$

Generally this problem may not be solved analytically due to the presence of the $\boldsymbol{\sigma}_h \cdot \boldsymbol{\pi}_g$-type terms. Available calculations (Høier & Aanestad, 1981) show, however, that their influence may be considered small and only of importance for incident-beam directions of very limited angular extent. These terms are hence neglected giving $\Delta G_{nm}^{pp'} = 0$ for $p \neq p'$ and otherwise

$$\Delta G_{nm}^{pp} \simeq \frac{K^2}{4\sqrt{\gamma_n\, \gamma_m}} \sum_{g \neq 0,h} \frac{\chi_{ng}^{pp}\, \chi_{gm}^{pp}}{s_g + \tfrac{1}{2}K\chi_0(1 - \gamma_g/\gamma_0)}. \tag{14}$$

With the polarization system used in standard two-beam theory, the 4×4 matrix is reduced to two 2×2 blocks representing the two polarization systems $p = \sigma$ or π. The following elements are obtained:

$$H_{00}^{pp} = -\frac{1}{2\gamma_0} K\chi_0 + \Delta G_{00}^{pp}$$

$$H_{0h}^{pp} = -\frac{1}{2\sqrt{\gamma_0\,\gamma_h}} K\chi_{0h}\, \mathbf{p}_0\cdot\mathbf{p}_h + \Delta G_{0h}^{pp}$$

$$H_{h0}^{pp} = -\frac{1}{2\sqrt{\gamma_h\,\gamma_0}} K\chi_{h0}\, \mathbf{p}_h\cdot\mathbf{p}_0 + \Delta G_{h0}^{pp}$$

$$H_{hh}^{pp} = -\frac{1}{\gamma_h} s_h - \frac{1}{2\gamma_h} K\chi_0 + \Delta G_{hh}^{pp}. \tag{15}$$

It follows that the minimum distance between the dispersion-surface branches, *i.e.* the dispersion-surface gap width, is ξ dependent and appears for an incident-beam direction which as a rule differs from the one found in the two-beam case.

The nondiagonal elements of the interaction matrix derived lead to the definition of an effective structure factor for each polarization direction in the many- or n-beam case. From (15) we obtain, using (3),

$$F_{h0}^{n,p} = F_{h0}\, \mathbf{p}_h\cdot\mathbf{p}_0 + \frac{r_e}{2\pi K V_c}\sum_{g\neq 0,h}\frac{F_{hg}F_{go}\, \mathbf{p}_h\cdot\mathbf{p}_g\, \mathbf{p}_g\cdot\mathbf{p}_0}{s_g + \frac{1}{2}K\chi_0(1 - \gamma_g/\gamma_0)}. \tag{16}$$

This *effective structure factor*, $F_{h0}^{n,p}$, may generally replace $F_{h0}\,\mathbf{p}_h\cdot\mathbf{p}_0$ in all the existing two-beam expressions provided the weak-secondary-beam assumption is valid.

Many-beam examples

The three-beam case

The effective structure factor is found from (16):

$$F_{h0}^{3,p} = F_{h0}\, \mathbf{p}_h\cdot\mathbf{p}_0 + \frac{r_e}{2\pi K V_c}\frac{F_{hg}F_{g0}\, \mathbf{p}_h\cdot\mathbf{p}_g\, \mathbf{p}_g\cdot\mathbf{p}_0}{s_g + \frac{1}{2}K\chi_0(1 - \gamma_g/\gamma_0)}, \tag{17}$$

giving the following dispersion-surface gap width:

$$K\delta^2 - K\delta^1 = \frac{r_e}{\pi K V_c(\gamma_0\,\gamma_h)^{1/2}}(F_{h0}^{3,p} F_{0h}^{3,p})^{1/2}. \tag{18}$$

From now on we shall neglect absorption and in this special case denote the gap width $\varepsilon_h^{n,p}$. With three beams we thus obtain

$$\varepsilon_h^{3,p} = a|F_{h0}^{3,p}|$$

$$= a\left(\left[\;|F_{h0}|\,\mathbf{p}_h\cdot\mathbf{p}_0\right.\right.$$

$$+ \frac{r_e|F_{0g}|\,|F_{gh}|\,\mathbf{p}_0\cdot\mathbf{p}_g\,\mathbf{p}_g\cdot\mathbf{p}_h}{2\pi K V_c[s_g + \frac{1}{2}K\chi_0(1 - \gamma_g/\gamma_0)]}$$

$$\left.\times \cos\,(\varphi_{h0} + \varphi_{0g} + \varphi_{gh})\right]^2$$

$$+ \left\{\frac{r_e|F_{0g}|\,|F_{gh}|\,\mathbf{p}_0\cdot\mathbf{p}_g\,\mathbf{p}_g\cdot\mathbf{p}_h}{2\pi K V_c[s_g + \frac{1}{2}K\chi_o(1 - \gamma_g/\gamma_0)]}\right\}^2$$

$$\left.\times [1 - \cos^2\,(\varphi_{h0} + \varphi_{0g} + \varphi_{gh})]\right)^{1/2}, \tag{19}$$

where $a = r_e/[\pi K V_c(\gamma_0\gamma_h)^{1/2}]$ and φ_{h0} is the phase of F_{h0}.

In addition to the constant term this general expression has terms which are either symmetric or antisymmetric in s_g. For structurally forbidden reflections $|F_{h0}| = 0$ and $\varepsilon_h^{3,p}$ falls off as $|s_g|^{-1}$, thus explaining the double-scattering effect.

For $|F_{h0}| \neq 0$ the gap depends on the phase sum. When this quantity is $\pi/2$, $\varepsilon_h^{3,p}$ is again symmetric in s_g. A phase sum of 0 or π results in an asymmetric gap which is seen to be larger than the two-beam gap when the cosine term and s_g have the same sign and smaller otherwise. This effect corresponds to the rule suggested by Chang (1982).

The angular extent of the three-beam effect is from (19) seen to depend on the size of the structure factors involved through the product $|F_{0g}|\,|F_{gh}|/|F_{h0}|$. The effect is thus most easily observed in a weak beam which is strongly coupled to a strong beam in agreement with previous conclusions (Gjønnes & Høier, 1969).

For a *centrosymmetric* crystal we obtain, from (19) for $|F_{h0}| \neq 0$,

$$|F_{h0}^{3,p}| = |F_{h0}|\,\mathbf{p}_h\cdot\mathbf{p}_0\left[1 + \frac{\cos\,(\varphi_{h0} + \varphi_{0g} + \varphi_{gh})}{[s_g + \frac{1}{2}K\chi_0(1 - \gamma_g/\gamma_0)]}\right.$$

$$\left.\times \frac{r_e|F_{0g}|\,|F_{gh}|\,\mathbf{p}_0\cdot\mathbf{p}_g\,\mathbf{p}_g\cdot\mathbf{p}_h}{2\pi K V_c|F_{h0}|\,\mathbf{p}_h\cdot\mathbf{p}_0}\right]. \tag{20}$$

The phase dependence of (20) corresponds to the one found previously in the electron diffraction case by, for example, Kambe (1957).

The dependence on the experimental parameters may also be seen from the values of the deviation parameters s_g and s_h for which the dispersion-surface gap width is zero. From (20) we get

$$s_g = -\frac{1}{2}K\chi_0(1 - \gamma_g/\gamma_0)$$

$$- \frac{r_e\cos\,(\varphi_{h0} + \varphi_{0g} + \varphi_{gh})\,|F_{0g}|\,|F_{gh}|\,\mathbf{p}_0\cdot\mathbf{p}_g\,\mathbf{p}_g\cdot\mathbf{p}_h}{2\pi K V_c|F_{h0}|\,\mathbf{p}_h\cdot\mathbf{p}_0}$$

$$\tag{21}$$

with the accompanying deviation parameter for the primary beam:

$$s_h = -\tfrac{1}{2}K\chi_0(1 - \gamma_h/\gamma_0)$$

$$- \frac{r_e|F_{h0}|\,[|F_{hg}|^2\,(\mathbf{p}_h\cdot\mathbf{p}_g)^2 - |F_{g0}|^2\,(\mathbf{p}_g\cdot\mathbf{p}_0)^2\,\gamma_h/\gamma_0]}{2\pi K V_c \cos(\varphi_{h0} + \varphi_{0g} + \varphi_{gh})\,|F_{g0}|\,|F_{hg}|}$$

$$\times\ \mathbf{p}_h\cdot\mathbf{p}_0/\mathbf{p}_g\cdot\mathbf{p}_0\,\mathbf{p}_h\cdot\mathbf{p}_g. \tag{22}$$

It should be noted that although (21) and (22) illustrates correctly a general diffraction effect (Gjønnes & Høier, 1971), the expression for s_g may be invalid for special structure-factor combinations. This happens, for example, in three-beam cases with mirror symmetry as the one discussed below. Here the correct value of s_g is zero and the assumption on which (21) is based is consequently invalid.

The dependence of $\varepsilon_h^{3,p}$ and thus also $|F_h^{3,p}|$ on the various parameters is of course reflected in any type of three-beam diffraction experiment. The possible observation of the effects is, however, strongly experiment dependent. One very favourable case is the Kikuchi-line pattern observed in electron diffraction where three-beam effects have already been discussed by Shinohara (1932). In these patterns the observed line width is known to be a direct mapping of the dispersion-surface gap width $\varepsilon_h^{n,p}$. The extensive intensity anomalies observed near crossing points between two or several lines in these patterns (Gjønnes & Høier, 1969) correspond therefore to the gap variations derived from (19). The observed contrast anomalies close to $s_g = 0$ demonstrate clearly, however, the limitations of the present approximations for such diffraction conditions.

In the particular X-ray case discussed by Høier & Aanestad (1981), i.e. the 000, $h = 2\bar{2}0$, $g = 0\bar{2}2$ three-beam case in Si with $\gamma_h = \gamma_g = \gamma_0$, the gap is found for $s_h = 0$. The relative gap width may thus in the present approximation be written ($s_g \neq 0$)

$$\frac{|F_{h0}^{3,p}|}{|F_{h0}|\,\mathbf{p}_h\cdot\mathbf{p}_0} = 1 + \frac{r_e|F_{h0}|\,\mathbf{p}_0\cdot\mathbf{p}_g\,\mathbf{p}_g\cdot\mathbf{p}_h}{2\pi K V_c\,s_g\,\mathbf{p}_0\cdot\mathbf{p}_h}. \tag{23}$$

Comparison of the dependence of this expression on s_g with the corresponding dependence found in the full three-beam calculations shows that the long-range influence of the secondary beam, g, is remarkably well reproduced, and even at relatively small deviation parameters the correspondence is good.

A four-beam case

The 000, $h = \bar{2}20$, $g = \bar{3}11$, $f = \bar{1}\bar{1}1$ case in Si using Mo $K\alpha$ radiation will be taken as an example. The direction cosines are equal and absorption is neglected. Further, $s_h = 0$ and $s_g = s_f = s$. The polarization directions for the 0 and h beams are chosen equal to the ones in the standard 0, h two-beam case. σ_f and σ_g are

parallel and orthogonal to $\mathbf{h}$. From (16) the following effective structure factor is found for the primary beam $h = \bar{2}20$:

$$F_{h0}^{4,p} = F_{h0}\,\mathbf{p}_h\cdot\mathbf{p}_0 + \frac{r_e}{2\pi K V_{cs}}\,(F_{hg}F_{g0}\,\mathbf{p}_h\cdot\mathbf{p}_g\,\mathbf{p}_g\cdot\mathbf{p}_0$$

$$+ F_{hf}F_{f0}\,\mathbf{p}_h\cdot\mathbf{p}_f\,\mathbf{p}_f\cdot\mathbf{p}_0). \tag{24}$$

The dispersion surface resulting from a full four-beam calculation is shown in Fig. 2, while the result from the present approximate treatment is shown in Fig. 3. The unit of ξ is $10^{-6}\,\text{Å}^{-1}$ in both figures corresponding to an angular deviation parameter of $0\cdot15''$. The figures show the variation with ξ of the quantity $\Gamma_s = \gamma_0\Gamma$ [see (8)] corrected for a distance corresponding to PP' in Fig. 1.

Calculated excitation coefficients show that the important branches in Fig. 2 are the pairs 1 and 4 or 2 and 3 for $\xi < 0$ and the pairs 5 and 8 or 6 and 7 for $\xi > 0$ (Marthinsen, Aanestad & Høier, 1983). These
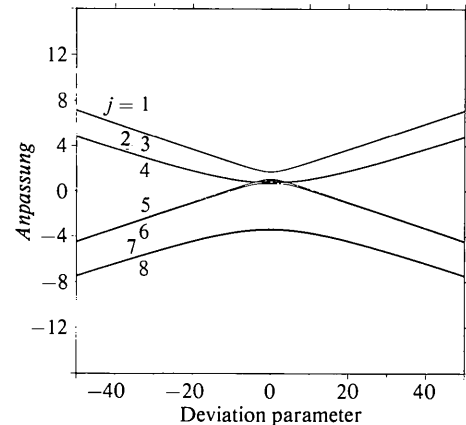

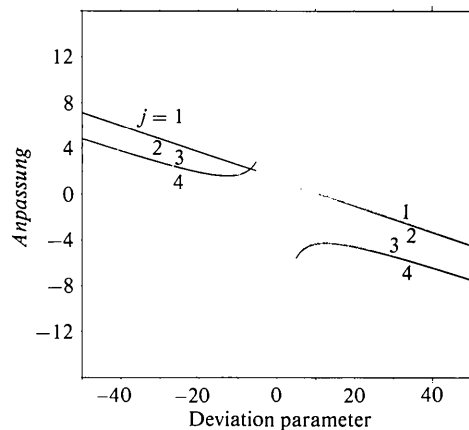Fig. 2. Calculated four-beam dispersion surface as a function of ξ in units of $10^{-6}\,\text{Å}^{-1}$.

Fig. 3. Calculated perturbed two-beam dispersion surface as a function of ξ in units of $10^{-6}\,\text{Å}^{-1}$. Present approximations.

correspond to the two-beam branches. The narrow gaps found at the dispersion surface near $\xi = 0$ are due to the $\sigma_h \cdot \pi_g$-type terms and will be discussed elsewhere.

As the branch distance is proportional to the effective structure factor, Fig. 2 clearly demonstrates the dependence of $|F_{h0}^{4,p}|$ on the sign of ξ (or s). With the particular structure-factor combination chosen the gap is larger or smaller than the two-beam value when ξ is positive or negative, respectively. The same dependence on the sign of ξ is found in Fig. 3 as well. A comparison between Figs. 2 and 3 shows that the gap widths correspond to within 0·5% when $|\xi| \gtrsim 50$ and approximately to within 6% when $|\xi| \gtrsim 20$. The Bethe gap is larger or smaller than the one found in Fig. 2 when ξ is positive or negative, respectively.

Comparison of the variation in Fig. 3 with the two-beam gap shows that the difference is larger than 34 or 1% when $|\xi|$ is smaller than approximately 20 or 600, respectively. The four-beam effect may thus be significant even at relatively large deviation parameters. As the angular extent of this effect depends on the experimental parameters, it should be noted that the structure-factor combination used in the examples is not favourable for the demonstration of this particular effect.

Applications

The present approximation may profitably be utilized in integrated-intensity-type experiments as demonstrated in the following two examples where absorption is neglected.

Pendellösung fringes

If s_g is taken as constant, the observed integral power in the many-beam case may be written

$$R_h^{n,p} = \frac{\pi \gamma_h}{2K \sin 2\theta \, A_h^{n,p}} \int_0^{2\pi t / A_h^{n,p}} J_0(x) \, dx, \qquad (25)$$

where we in the standard two-beam expression have introduced the *effective extinction distance*:

$$A_h^{n,p} = 1/\varepsilon_h^{n,p}. \qquad (26)$$

In addition to being proportional to the thickness, $R_h^{n,p}$ is, for $t \ll A_h^{n,p}$, i.e. the *kinematic* many-beam case, seen to be proportional to $(\varepsilon_h^{n,p})^2$ and may be written

$$R_h^{n,p} \propto |F_{h0}^{n,p}|^2. \qquad (27)$$

The dependence on the phase and size of the structure factors involved as well as the deviation parameters may thus in principle be extracted from the observed intensity variations. With three beams these variations correspond to the ones found above in the discussion of (17) to (23).

At large thicknesses, on the other hand, the essential variation of $R_h^{n,p}$ is determined by a cosine factor with argument

$$\alpha_h^{n,p} = \frac{2\pi t}{A_h^{n,p}} + \frac{\pi}{4}. \qquad (28)$$

This expression shows the well-known displacement $\pi/4$ of the fringe position as compared with plane-wave theory. The important point in this connection, however, is the appearance of the effective extinction distance, (26), which varies inversely with the gap width. It follows that near positions on the photographic plate which correspond to many-beam diffraction conditions, the fringe position or intensity is in general modified as compared with the two-beam values.

With three beams the dependence of $\alpha_h^{3,p}$ on the experimental parameters follows the one found above in (17) to (23). If we take a centrosymmetric crystal as an example the fringe displacement is therefore asymmetric with respect to a sign shift in s_g. When this sign is fixed, however, the fringe bending from the two-beam position is towards larger or smaller crystal thickness depending on the three-phase structure invariant. In conclusion, the three-beam effect is observable at any crystal thickness, and (25) explains the variation observed in the fringe position and intensity by Hart & Lang (1961) and Høier & Aanestad (1981).

Scattering from mosaic crystals

In structure analysis the intensity expression used includes a convolution between the perfect-block scattering function and the block-orientation distribution function. Following standard procedure and taking the former to have a much more rapid variation with the scattering angle than the latter, we find that the essential variation in the integrated power is given by the two-beam intensity expression (e.g. Zachariasen, 1945). This treatment may also be applied with many beams if we replace the standard structure factor by the effective one using (16). As above, the integrated power in the *kinematic* thickness region is proportional to the dispersion-surface gap width squared. We thus obtain, in the n-beam case

$$P_h^{n,p} \propto |F_{h0}^{n,p}|^2. \qquad (29)$$

With three beams this n-beam expression simplifies considerably as shown above. From (29) it is found that $P_h^{3,p}$ has a similar variation with the experimental parameters as the one found for $\varepsilon_h^{3,p}$ in connection with the discussion of (17) to (23). $P_h^{3,p}$ is, for example, larger than the two-beam value when the cosine factor and s_g in (27) [see (19)] have the same sign and smaller otherwise. The influence of the third beam is further dependent on the size of the structure factors involved.

Such effects have been observed by Thorkildsen & Mo (1982).

Conclusions

Available numerical three- and four-beam calculations show that a variety of the effects observed can be understood from a perturbed two-beam point of view. This is also the original basis of the Bethe approximation, which in the present studies has been shown to be applicable in the X-ray case provided one additional assumption is added, *i.e.* to neglect the $\sigma_h \cdot \pi_g$-type coupling terms between the strong beams and the weak secondary beams. These terms are, however, only of importance at relatively small deviation parameters of the secondary beams where the weak-beam assumption is already invalid. The resulting interaction matrix includes absorption, but is in the present work applied to derive analytical solutions relevant to essentially absorption-independent many-beam effects. The utilization of absorption-dependent effects in structure studies has been discussed by, for example, Post (1979).

The effective structure factor introduced for each polarization direction may generally be applied for the interpretation and prediction of many-beam effects. As defined $F_{h0}^{n,p}$ is valid for $s_g \neq 0$ for centrosymmetric as well as non-centrosymmetric absorbing crystals, and in the special case of three beams the results of Juretschke (1982) are included.

The accuracy of the effective structure factor can be seen from the calculated dispersion-surface gap. The deviation of the gap width from the one found in a full many-beam calculation is less than 0·5% for deviation parameters corresponding to $|\Delta\theta_g| \geq 7''$ in the examples studied and may thus in practice be neglected.

For each polarization direction the observed intensity depends on the product $F_{h0}^{n,p} F_{0h}^{n,p}$ and the two examples given show that all the basic parameters are included in this quantity. Of special interest experimentally is the three-beam case where the three-phase structure invariant appears explicitly leading to a product which is larger than, smaller than or equal to the two-beam value depending on the phase sum. It should also be noticed that $F_{h0}^{3,p} F_{0h}^{3,p}$ may be zero for a particular s_h, s_g combination. Although the appearance of this effect is generally correct in the three-beam case, (21) is invalid for cases where $s_g \simeq 0$ and the Bethe approach fails. Here more dispersion-surface branches have to be taken into account as may be seen from the corresponding effects observed near Kikuchi-line intersections (Gjønnes & Høier, 1969). Preliminary studies have shown that some particular reducible many-beam cases may give additional information for these incident-beam directions.

In one way or another the effective structure factor, or the dispersion-surface gap, is projected out in any type of experiment, *e.g.* section topographs, plane-wave cases, mosaic-crystal or *Pendellösung* experiments. In the latter case the fringe displacement near the three-beam condition follows from (25) provided s_g can be considered constant. This assumption is, however, only partly valid, primarily due to the finite anode height. The consequence of the accompanying vertical divergence in standard experimental setups is that each point on the crystal will diffract according to a range of incident-beam directions. The local observed intensity therefore follows from an integration over the corresponding range in s_g, thus smearing out the effect.

In structure analysis and from a methodic point of view the possible experimental determination in three-beam cases of a large number of three-phase structure invariants from very small crystallites or from mosaic crystals is of great importance. In the former case, where electron diffraction methods have to be used, systematic work in this particular direction is still lacking (*e.g.* Gjønnes, 1981). With mosaic crystals and standard X-ray diffraction methods two experimental parameters seem to influence the experimental possibilities, *i.e.* the spread in s_g due to the vertical divergence and the width of the mosaic distribution function. An integration over the actual width Δs_g is expected to smear out the effect in this case as well. The effects may be observed, however, as shown by Thorkildsen & Mo (1982).

In addition to the phase dependence the intensity observed in any type of three-beam experiment is from (19) seen to depend on the size of the structure factors involved. The structurally forbidden reflections are here explained through the double-scattering terms, and otherwise the relative variation in the primary beam with s_g is seen to depend on $|F_{0g}| |F_{gh}| |F_{h0}|^{-1}$. It is thus found that the phase invariant is most easily determined experimentally in a primary beam which is strongly coupled to a secondary beam with much larger structure factor, in accordance with previous electron diffraction results (Gjønnes & Høier, 1969).

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A Note on Practical Aspects of the Application of *DIRDIF*, a Procedure for Structure Elucidation When a Part of the Structure is Known

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Abstract

The *DIRDIF* procedure (*dir*ect methods applied to *dif*ference structures) has been tested on a variety of structures. It is shown that errors in the atomic positions of approximately 0·3 Å are acceptable, that the minimum size of the known molecular fragment is about 10% of the total scattering power, and that lack of knowledge about the unit-cell contents is not deleterious

Introduction

When part of a structure is known, the *DIRDIF* method (Beurskens *et al.*, 1982) can be effectively used to solve the unknown part of the structure. Although the various *DIRDIF* procedures include unique features designed for solving enantiomorph and super-symmetry problems (see Prick, Beurskens & Gould, 1983, and references therein), the general *DIRDIF* method has proved to be a very efficient tool for routine crystal-structure analyses, particularly if the known part is only barely sufficient to solve the structure. The automatic computer program uses observed structure amplitudes and positions of the known atoms as input to a structure-factor calculation and scaling routine. This is followed by a weighted tangent refinement of the difference structure factors, to yield a greatly improved electron density map.

To explore the effects of errors or lack of information, we pose the following questions:

*Q*1. How small may the known part be so that *DIRDIF* is still helpful?

*Q*2. How much error can be tolerated in the positional coordinates of the known atoms?

*Q*3. What are the effects of 'incorrect atoms' in an otherwise correct molecular fragment?

*Q*4. What is the effect of unknown chemical composition?

We investigated these aspects using a few known crystal structures as test cases. The results are summarized in this note.

Calculations

All calculations were performed by the program *DIRDIF* using default executional parameters. A scaling procedure (Gould, Van den Hark & Beurskens, 1975) leads to the determination of the scale factor, SC, B_p the (overall) isotropic temperature parameter of the known part (heavy atom or 'partial structure'), and B_r the (overall) isotropic temperature parameter of the unknown part of the structure ('rest structure').

The contribution of the known part to the total scattering power is defined by the *a priori* scattering fraction:

$$p_Z^2 = \sum_p Z_p^2 / \sum_l Z_l^2,$$

where Z is the atomic number, $\sum_p$ denotes summation over the known atoms, and $\sum_l$ denotes summation over all atoms in the unit cell.

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