Aust. J. Phys., 1988, **41**, 469–76

Simple Method for Estimating the Contribution of Neighbouring *n*-beam Interactions to Two-beam Structure Factors*

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Abstract

Unless special precautions are taken, the experimental determination of two-beam structure factors to better than 1% may include contributions from neighbouring *n*-beam interactions. In any particular experimental configuration, corrections for such contributions are easily carried out using the modified two-beam structure factor formalism developed recently (Juretschke 1984), once the full indexing of the pertinent *n*-beam interactions is known. The method is illustrated for both weak and strong primary reflections and its applicability in special cases, as well as for less than perfect crystals, is discussed.

1. Introduction

The determination of two-beam X-ray structure factors relies on the possibility of establishing, by suitable choice of wavelength and azimuthal angle, a region free of multiple-beam interactions around the primary reflection under study (e.g. Mills and Batterman 1980). Traditionally, this condition has been assumed to be met if, for example, neighbouring *n*-beam interactions are of the order of a degree away, because the range of such interactions has generally been taken to be at most a few seconds of arc. While this is certainly true for a measure such as their half-width, this criterion has to be reconsidered in precision determinations of structure factors where the *tails* of these interactions may still play a role at angular distances of the order of degrees.

This paper calls attention to a simple procedure for evaluating the level of influence of such neighbouring multiple-beam interactions within a measured two-beam structure factor, for any given experimental configuration. The procedure follows from the solution of the standard two-beam X-ray problem when neighbouring weak excitations are taken into account as a perturbation. The corresponding approach in electron diffraction is of long standing, where it is characterised by the Bethe potentials, but only recently has the method been generalised systematically and explicitly for vector waves. This generalisation can deal with the different polarisations of X-rays, and includes both changes in the structure factor and changes in extinction brought about by such interactions.

* Paper presented at the International Symposium on Accuracy in Structure Factor Measurement, held at Warburton, Australia, 23–26 August 1987.

0004-9506/88/030469$03.00

As shown below, for weak structure factors these corrections are absolutely essential, because they can easily produce changes in integrated intensity of the order of 100%. Similarly, for strong structure factors it is difficult to keep their influence below the 10^{-3} level. Therefore, any structure factor determinations aiming at such accuracy must address an evaluation of these corrections to insure that they do not contribute a significant systematic error. The need for such correction procedures has been voiced over the years (e.g. Wagenfeld 1972), although only the recent advent of precision experimentation has made it unavoidable.

The correction procedures follow from a dynamical treatment for perfect crystals, but they apply to imperfect crystals as well, since many of the same results are also contained in a kinematical approach.

2. Theoretical Background

The perturbation treatment of the dynamical two-beam problem for X-rays was developed independently about five years ago by Høier and Marthinsen (1983) and by Juretschke (1982, 1984). Its method and its results are summarised here using the notation of Juretschke, keeping in mind that there exist fully corresponding expressions in Høier and Marthinsen.

Both formulations start with a primary reflection $0H$, with a third reciprocal lattice point L far from the Ewald sphere. In terms of the excitation errors ξ_0, ξ_H, ξ_L of the three-beam problem, this condition is expressed by

$$\xi_L \gg \xi_0, \xi_H. \tag{1}$$

Because of (1), ξ_L is not a truly dynamical variable, but becomes a parameter in the three-beam problem. One can then seek solutions of the remaining (two-beam) dynamical problem involving ξ_0 and ξ_H in a power expansion of $1/\xi_L$, with the coefficients in the expansion involving the additional structure factors F_L and F_{H-L}. To order $1/\xi_L$ such solutions can be described most succinctly as a simple transformation of the original two-beam dispersion surface to a new modified or effective two-beam dispersion surface. The structure factor, measuring the midpoint separation of the dispersion surface sheets, moves from F_H (PF_H for π-polarisation) to the value

$$F^{\sigma}_{HL} = F_H - \frac{k\Gamma\Pi_1}{2\xi_L} F_L F_{\bar{L}-\bar{H}}, \qquad F^{\pi}_{HL} = PF_H - \frac{k\Gamma\Pi_6}{2\xi_L} F_L F_{\bar{L}-\bar{H}}, \tag{2a, b}$$

where $P=\cos 2\theta_B$, and Π_1 and Π_6 are geometrical factors related to polarisation projections. These are defined in both the original sources mentioned above.

The corresponding excitation errors also shift from their original ξ_0, ξ_H to

$$\xi^{\sigma}_0 = \xi_0 - \frac{(k\Gamma)^2}{4\xi_L}\Pi_1 F_L F_{\bar{L}}, \qquad \xi^{\sigma}_H = \xi_H - \frac{(k\Gamma)^2}{4\xi_L}\Pi_1 F_{L-H} F_{\bar{L}-\bar{H}}, \tag{3a, b}$$

$$\xi^{\pi}_0 = \xi_0 - \frac{(k\Gamma)^2}{4\xi_L}\Pi_4 F_L F_{\bar{L}}, \qquad \xi^{\pi}_H = \xi_H - \frac{(k\Gamma)^2}{4\xi_L}\Pi_5 F_{L-H} F_{\bar{L}-\bar{H}}, \tag{3c, d}$$

indicative of shifts of the Lorentz point, i.e. the centre between the sheets of the dispersion surface. This implies a change in the average value of the index of refraction. It is different for the two polarisations.

In terms of (2) and (3), the transformation has completely reduced the approximate three-beam problem to a standard two-beam case. Hence, the entire arsenal of the two-beam literature can now be applied to treat the primary $0H$ diffraction in the presence of L. Conversely, experimental results must be interpreted as referring to the parameters of the modified or effective two-beam case.

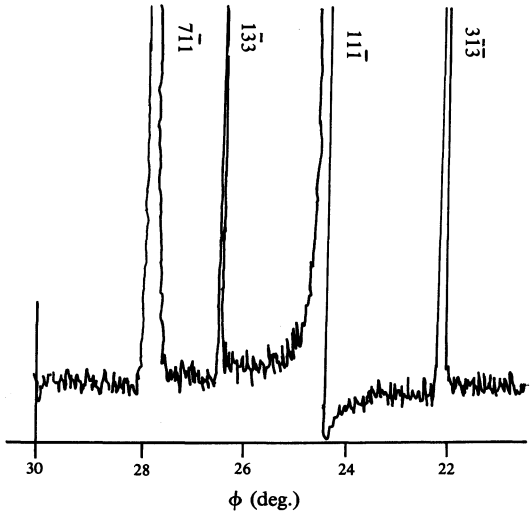

Fig. 1. Experimental Renninger chart for Ge $222/L$, Cu Kα. [From Nicolosi (1982).]

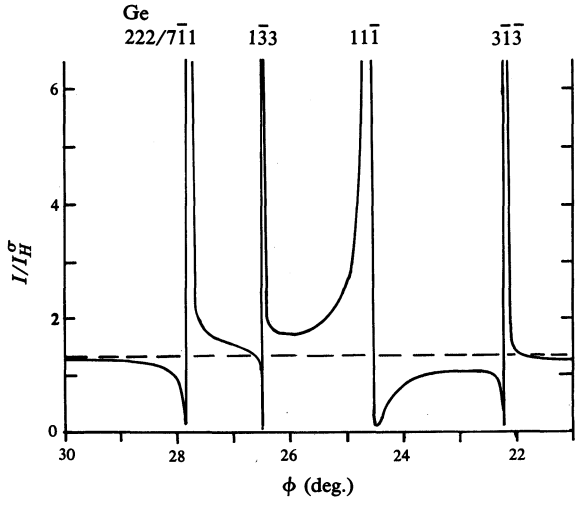

Fig. 2. Theoretically predicted Renninger chart for the four peaks of Fig. 1 using the modified two-beam approximation. The integrated intensity for unpolarised incident radiation is normalised to the pure 222 intensity for σ-polarisation. The dashed line is the level expected in the absence of all n-beam interactions.

Two additional comments are in order: (a) some of the limitations of the above conclusions were discussed by Juretschke (1984), and cases requiring special treatment were also taken up (Juretschke 1986*a*, 1986*b*); (b) the transformation to a modified two-beam case can actually be extended to second order in $1/\xi_L$ under appropriate conditions (Juretschke 1986*c*), although this is only of interest if the separation between n-beam points becomes small.

Finally, the generalisation of (2) and (3) to include more than one additional reciprocal lattice point near the Ewald sphere is straightforward. To order $1/\xi_L$ these effects are simply additive so that, for example, the modified structure factor in such a situation becomes

$$F^{\sigma}_{HLM\ldots} = F_H - \frac{k\Gamma\Pi_1^L}{2\xi_L} F_L F_{\bar{L}-\bar{H}} - \frac{k\Gamma\Pi_1^M}{2\xi_M} F_M F_{\bar{M}-\bar{H}} - \ldots . \tag{4}$$

Thus, a six-beam case is merely the superposition of four three-beam cases.

3. Illustrative Examples

We illustrate the effect of n-beam interactions with two examples, one dealing with a weak, the other with a strong primary reflection.

(a) Ge(222) for Cu Kα

This case has been discussed extensively by Juretschke (1984, 1986*a*), and the figures above are adapted from the first reference. The Renninger scan shown in Fig. 1 exemplifies the difficulty of finding a region between interaction peaks that can be identified with the true F_{222}. While the integrated intensity may remain constant over a given range of azimuthal angles, this constant value is not the same between different neighbouring peaks. On the other hand, the theoretical prediction of the modified two-beam method shown in Fig. 2 is capable of giving a quite faithful reproduction of the experimental data. In this case it includes five interaction peaks L, the four of Fig. 1 plus the image $3\bar{5}1$ of the point $L = 7\bar{1}1$ beyond $\phi = 30°$. In principle, therefore, it is possible to correct the measured intensity between peaks by calculating the contribution of the neighbouring peaks. As shown in Table 1, though, it is not sufficient to just consider nearest neighbours. The net effect is a sum of contributions of both signs, and even the occurrence of a true two-beam structure factor in some angular region of Fig. 1 may, in fact, be due to the accidental cancellation of such terms. Obviously, a systematic correction can be carried out only if all possible multiple interaction points, as shown on a Renninger chart, are properly known and indexed, so that they can be included in equation (4). Indeed, from this point of view, the entry for the total ΔF at $\phi = 30°$ shown in Table 1 is deficient. It takes into account only the five interaction peaks listed. But since $\phi = 30°$ is a mirror plane, there should be four additional contributions besides $L = 3\bar{5}1$ from beyond the mirror. If they are taken into account we obtain twice the sum of the first four interactions, to give $\Delta F^{\sigma} = 0$ and $\Delta F^{\pi} = 0{\cdot}010$. A similar deficiency is probably present at the other extreme of the angular range, $\phi = 21°$. Therefore, at these extremes there remain additional corrections to the theoretical curve shown in Fig. 2.

Exactly the same correction technique has recently been applied by Shen (1986) in describing the weak Si $442/\bar{1}1\bar{1}$ reflection, using eight interaction peaks.

Table 1. Contributions to structure factor F_{222} from neighbouring n-beam interactions L, at selected angles ϕ of Fig. 2 between the n-beam peaks

For each value of ϕ the first and second rows give the σ and π polarisations respectively

ϕ (deg.)	L					Total
	$3\bar{1}\bar{3}$	$11\bar{1}$	$1\bar{3}3$	$7\bar{1}1$	$3\bar{5}1$	ΔF
21	0·013	−0·035	0·001	0·006	−0·004	−0·019
	0·008	−0·028	0·003	0·003	−0·002	−0·016
23	−0·020	−0·079	0·001	0·009	−0·005	−0·094
	−0·012	−0·063	0·005	0·004	−0·002	−0·068
26	−0·004	0·091	0·010	0·024	−0·007	0·114
	−0·003	0·071	0·037	0·010	−0·003	0·112
27	−0·003	0·053	−0·010	0·054	−0·008	0·086
	−0·002	0·038	−0·037	0·022	−0·003	0·018
30	−0·002	0·023	−0·001	−0·020	−0·020	−0·020
	−0·001	0·019	−0·005	−0·008	−0·008	−0·003

(b) Si(12 12 0) for Ag Kα

This example was chosen to explore the possible influence of multiple interactions in the recent high precision measurements by Deutsch and Hart (1985). Since no azimuthal position was reported in this work, we selected two particular regions of ϕ. The first is around the azimuthal point of $(12\,6\,\bar{6})$, which would be encountered if the crystal is cut relative to a common growth direction. The second is the most extensive angular range free of significant multiple peaks. The results for both polarisations are shown in Table 2, where the influence of all the neighbouring interaction points listed is included to find the relative change of the structure factors for points in between. In the first region, it appears that the effects can be sufficiently large, depending critically on the precise azimuthal angle chosen, to have to be taken into account at the 0·1% level of accuracy. In the second region, the effects stay below 5×10^{-4}, so that their influence at this level will be marginal. While (in the absence of a known ϕ) not having a direct bearing on the reported results, Table 2 clearly illustrates the desirability of having a record of the azimuth, or of all (well-indexed) multiple interactions in the neighbourhood of the chosen scattering plane in all high accuracy experiments, so that an assessment of their influence can be carried out.

The question has been raised of how the correction effect of multiple interactions scales with wavelength. A first order argument may go as follows: The product $k\Gamma/\xi_L$ varies as λ^2, while the number of interaction points goes like $1/\lambda^2$, so that at best, the effect is independent of λ. However, since contributions of both signs are more and more equally likely, their cancellation will be more complete at shorter wavelengths, so that there the net correction should become less important (see e.g. Graf and Schneider 1986). In any case, it would probably still be prudent to verify this conclusion by a detailed evaluation of the corrections as they apply to the specific experimental configuration at hand.

4. Discussion

These illustrations exemplify both the need for assessing the influence of neighbouring multiple-beam interactions and the ease, via (4), with which a quantitative measure of this influence can be calculated, once a full and consistent indexing of the pertinent reciprocal lattice points is known.

Table 2. Relative changes of $F_{12\,12\,0}$ for Si Ag Kα due to neighbouring interactions L in two ranges of ϕ

All interactions L shown are included with their weight proper to all equivalent three-beam points as indicated

ϕ (deg.)	$(\Delta F/F)_\sigma$ ($\times 10^{-4}$)	L	$(\Delta F/F)_\pi$ ($\times 10^{-4}$)	ϕ (deg.)	$(\Delta F/F)_\sigma$ ($\times 10^{-4}$)	L	$(\Delta F/F)_\pi$ ($\times 10^{-4}$)
34·46		2(7 15 $\bar{9}$)		59·06		2(0 0 $\bar{8}$)	
34·56	4·4		3·3	59·17		2(1 9 5)	
34·66	2·4		1·2	59·40	4·5		6·7
34·76	1·7		0·4	59·50	3·4		5·2
34·86	1·3		0·4	59·60	2·7		4·2
34·97		1(3 9 7)		59·70	2·3		3·7
35·06	−1·4		−7·7	59·80	2·1		3·6
35·16	−5·4		−13·7	59·90	1·9		3·3
35·26		4(12 6 $\bar{6}$)		60·00	1·8		3·2
35·36	12·3		17·1	60·10	1·9		3·5
35·46	9·5		10·2	60·20	2·4		4·7
35·56	8·9		9·3	60·34		2(12 2 $\bar{6}$)	
35·67		1($\bar{3}$ 15 1)		60·40		2(1 7 5)	
35·76	18·8		16·2	60·47		1(7 5 $\bar{13}$)	
35·84		2(3 $\bar{1}$ 3)		60·68		2(3 1 $\bar{11}$)	
36·30		2(9 1 $\bar{1}$)		60·71		2(12 2 $\bar{2}$)	

In addition, these examples emphasise that if the experiment uses an unpolarised source the traditional polarisation correction is not applicable, and such corrections must be done separately for each mode. This is brought out most strongly in those cases where the corrections for the two polarisations caused by the same peak have opposite sign, which can occur under certain conditions (Juretschke 1986*a*).

Along the same lines, a further comment is in order. It would appear from (2) that if one or the other of the connecting structure factors F_L or F_{L-H} vanishes, there is no correction whatsoever. This is certainly true as far as F_{HL} is concerned, but the shift in the Lorentz point implied in (3) carries with it also a correction of the linear absorption coefficient (Juretschke and Wagenfeld 1986), given for σ-polarisation in centrosymmetric crystals by

$$\mu^\sigma = k\Gamma\left(F_0'' - \Pi_1 \frac{k\Gamma}{\xi_L}(F_L' F_L'' + F_{L-H}' F_{L-H}'')\right). \tag{5}$$

Modifications in this term alter any correction of the integrated intensity for primary extinction (Juretschke 1986*b*). In most situations, this adjustment may be negligible but, in any case, it can easily be taken into account using (5) for any specific experimental configuration.

Finally, one may ask about the extent of the usefulness of the proposed corrections, derived essentially from dynamical theory for perfect crystals, when dealing with realistically less than perfect materials. While a complete answer is not yet available, two recent studies suggest that the modifications discussed here can be incorporated directly into the typical averaging procedures used to interpret diffraction from mosaic structures. In other words, the modified structure factors (2) and absorption coefficients (5) truly characterise diffraction near L, and any mosaic structure merely

broadens but does not destroy this response. It may, of course, be important to take into account that these modified parameters are also functions of the angles over which the mosaic spread is to be averaged.

One study bearing on this conclusion is the recent work by Shen (1986), who carried the kinematic response in the presence of L to second order and found precisely the same answer as given in (2). [Being purely kinematical it, of course, cannot incorporate absorption, and say anything about equation (5).] The other study is a generalisation of the modified two-beam approach to include phonons (Juretschke 1988). There, it is found explicitly that the same transformed structure of the dispersion surface described for perfect crystals above persists fully, and is merely broadened by thermal effects characteristic of the primary reflection. In the sense that phonons and weak mosaic structure have similar consequences in diffraction, the same argument should apply to weakly imperfect crystals. Thus, with the corrections having justification both in the kinematical limit, and in the limit of weak imperfections in perfect crystals, it is very likely that they apply equally well also over the intermediate range of mosaicity.

This conclusion is further reinforced by the fact that in the closely related problem of invariant phase determination using the neighbourhood of multiple-diffraction peaks, it has been possible to observe effects due to (2) in highly mosaic crystals (Thorkildsen and Mo 1983). More recently Kshevitskii *et al.* (1985) have shown, by a deliberate roughening of a Ge surface, that many of these effects are indeed enhanced and broadened when the crystal becomes less than perfect.

In conclusion, we want to re-emphasise that, apart from many other corrections necessary at the 0·1% level of accuracy of structure factors, those arising from neighbouring multiple-beam interactions may not be negligible, and that in any particular experimental two-beam configuration their influence can be assessed rather simply. This, of course, is possible only if the geometry of the two-beam experiment is fully embedded in reciprocal space, so that all other interactions are fully indexable. We end with a plea that experimental reports on accurate structure factor determination should at least provide such indexing information.

Acknowledgments

We acknowledge the assistance of Mr Ross Piltz, Melbourne University, in providing a full listing of significant multiple interactions with Si(12 0 0). One of us (H.J.J.) was supported in part by JSEP Contract No. F49620-85-C-0078.

References

Deutsch, M., and Hart, M. (1985). *Phys. Rev.* B **31**, 3846–58.
Graf, H. A., and Schneider, J. R. (1986). *Phys. Rev.* B **34**, 8629–37.
Høier, R., and Marthinsen, K. (1983). *Acta Cryst.* A **39**, 854–60.
Juretschke, H. J. (1982). *Phys. Rev. Lett.* **48**, 1487–9.
Juretschke, H. J. (1984). *Acta Cryst.* A **40**, 379–89.
Juretschke, H. J. (1986*a*). *Phys. Status Solidi* (*b*) **135**, 455–66.
Juretschke, H. J. (1986*b*). *Acta Cryst.* A **42**, 405–6.
Juretschke, H. J. (1986*c*). *Acta Cryst.* A **42**, 449–56.
Juretschke, H. J. (1988). *Acta Cryst.* A **44**, 189–92.

Juretschke, H. J., and Wagenfeld, H. K. (1986). *Z. Phys.* B **62**, 407–11.
Kshevitskii, S. A., Mikhailyuk, I. P., and Polyak, M. I. (1985). *Sov. Phys. Cryst.* **30**, 145–7.
Mills, D., and Batterman, B. W. (1980). *Phys. Rev.* B **22**, 2887–97.
Nicolosi, J. (1982). Ph.D. Thesis, Polytechnic Institute of New York.
Shen, Q. (1986). *Acta Cryst.* A **42**, 525–33.
Thorkildsen, G., and Mo, F. (1983). Abstract 4.02-P, p. 258, 8th European Crystallographic Meeting, Liège, Belgium.
Wagenfeld, H. K. (1972). Invited Lecture, German Physical Society, Freudenstadt (unpublished).

Manuscript received 30 September, accepted 13 November 1987