Let us indicate, by $\mathbf{A}_m$, the $\mathbf{A}$ matrix corresponding to the minimum rotation around the $c$ axis. The groups with 6 or $\bar{3}$ axes must contain either binary (180°) rotation or inversion respectively; one $\mathbf{A}$ matrix is therefore $-\mathbf{I}_{(2\times 2)}$, and the determinant of the corresponding $\mathbf{A}-\mathbf{I}$ is $-4$. Because of points (*a*) and (*g*), the determinant of $\mathbf{A}_m-\mathbf{I}$ cannot be other than $\pm 1$, since 3 and $-4$ must be integer multiples of it. Therefore, in this case the application of point (*f*) becomes possible, as for non-hexagonal space groups. For groups with a $\bar{6}$ or 3 axis, this symmetry element can be alone [and then we can apply points (*a*) and (*g*)] or combined with other symmetry elements. In the latter case, each new symmetry element is relative to a series of rotation matrices, one of which (let us call it $\mathbf{R}_o$) has rows as in non-hexagonal groups (see *International Tables for X-ray Crystallography*, 1952); the others are combinations of this operation and rotations around $c$. Let us now examine which $\mathbf{A}$ matrices can be related to $\mathbf{R}_o$. Omitting singular matrices, the identity, and $-\mathbf{I}$ (which would bring us back to $\bar{3}$ or 6 axes), and moreover considering that, since $a$ and $b$ are oblique, no rotations are possible which leave either $x$ or $y$ unchanged, we end up with:

$$\pm\begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix} \quad \pm\begin{bmatrix}0 & 1\\ \bar{1} & 0\end{bmatrix},$$

the rows of the corresponding $\mathbf{A}-\mathbf{I}$ matrices being only $\pm[\bar{1}1]$ and $[\bar{1}\bar{1}]$. The latter is already a row of the $\mathbf{A}-\mathbf{I}$ matrix corresponding to a rotation of 120°; the former rows, if present, can be combined with the row $[1\bar{2}]$ (of the 120° rotation) to give a new $2\times 2$ matrix, whose determinant is $\pm 1$. Consequently, we can always build a matrix $\mathbf{M}'$ such that the determinants of all the others are its integer multiples, making the application of (*f*) possible even in this case.

The fundamental part of this theory was developed at the C.E.C.A.M. meeting on direct methods (September–October 1970), where a computer routine working essentially to this scheme was written (in *FORTRAN* language). Accordingly, we want to thank the Italian Consiglio Nazionale delle Ricerche and the French Conseil National de la Récherche Scientifique for making it possible to carry out this work. The kind hospitality at C.E.C.A.M., extended by Dr Carl Moser, is also gratefully appreciated. We thank Dr Gremlich and Professor Wondratschek for useful criticism.

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# Calculation of the Intensity of Secondary Scattering of X-rays by Noncrystalline Materials. II. Moving Sample Transmission Geometry

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Equations that require numerical integration over only one variable were derived for calculating the intensity of secondary scattering of X-rays for noncrystalline samples in the case of a transmission geometry, in which the sample is rotated so that the incident and diffracted beams are always at equal angles with respect to a normal to the faces of the slab of sample. Tables are given that allow the intensity ratios of secondary-to-primary scattering to be determined without making lengthy calculations.

## Introduction

The first paper of this series (Dwiggins & Park, 1971) gives the background material, general theory, and nomenclature section needed to follow this paper.

The transmission geometry is best visualized by considering a slab of sample in a reflection geometry diffractometer to be rotated by 90° from the reflection position when the instrument is set for zero total scattering angle. It is then apparent that the incident and diffracted X-ray beams will form equal scattering angles with a normal to the sample faces at all scattering angles. In comparison with the more usual transmission geometry, where the sample remains fixed and normal to the incident X-ray beam, this type of transmission geometry has the advantages that the

Table 1. *Values of* $Q\{b,q,2\theta,\mu t\}\times 10^4$

$\mu t=0{\cdot}20$

| $2\theta$ | $b=10$ | $b=20$ | $b=40$ | $b=60$ | $b=80$ | $b=100$ |
|---|---|---|---|---|---|---|
| | | | $(q=0)$ | | | |
| 0·20 | 59·64 | 29·44 | 14·61 | 9·74 | 7·31 | 5·86 |
| 15·00 | 58·99 | 28·41 | 13·41 | 8·52 | 6·11 | 4·69 |
| 30·00 | 57·42 | 26·06 | 11·09 | 6·50 | 4·37 | 3·17 |
| 45·00 | 55·75 | 23·65 | 9·16 | 5·05 | 3·25 | 2·29 |
| 60·00 | 54·72 | 21·88 | 7·91 | 4·19 | 2·63 | 1·82 |
| 75·00 | 54·53 | 20·85 | 7·19 | 3·72 | 2·30 | 1·57 |
| 90·00 | 54·55 | 20·28 | 6·81 | 3·48 | 2·13 | 1·45 |
| 105·00 | 54·02 | 19·86 | 6·61 | 3·36 | 2·05 | 1·39 |
| 120·00 | 53·07 | 19·57 | 6·55 | 3·34 | 2·05 | 1·39 |
| 130·00 | 52·55 | 19·52 | 6·60 | 3·39 | 2·09 | 1·42 |
| 140·00 | 52·34 | 19·65 | 6·75 | 3·50 | 2·17 | 1·49 |
| 150·00 | 52·70 | 20·02 | 7·00 | 3·67 | 2·29 | 1·58 |
| | | | $(q=0{\cdot}05)$ | | | |
| 0·20 | 73·50 | 39·42 | 21·64 | 15·51 | 12·37 | 10·45 |
| 15·00 | 73·06 | 38·59 | 20·62 | 14·46 | 11·33 | 9·44 |
| 30·00 | 72·13 | 36·81 | 18·76 | 12·81 | 9·90 | 8·19 |
| 45·00 | 71·55 | 35·28 | 17·44 | 11·83 | 9·17 | 7·63 |
| 60·00 | 72·15 | 34·75 | 17·01 | 11·60 | 9·06 | 7·61 |
| 75·00 | 74·16 | 35·37 | 17·39 | 11·97 | 9·43 | 7·96 |
| 90·00 | 76·61 | 36·64 | 18·26 | 12·69 | 10·06 | 8·53 |
| 105·00 | 77·99 | 37·77 | 19·17 | 13·46 | 10·72 | 9·12 |
| 120·00 | 78·18 | 38·57 | 20·00 | 14·19 | 11·36 | 9·68 |
| 130·00 | 78·17 | 39·12 | 20·62 | 14·74 | 11·85 | 10·12 |
| 140·00 | 78·42 | 39·84 | 21·39 | 15·43 | 12·46 | 10·67 |
| 150·00 | 79·37 | 40·91 | 22·38 | 16·32 | 13·27 | 11·41 |
| | | | $(q=0{\cdot}10)$ | | | |
| 0·20 | 90·06 | 52·67 | 32·33 | 25·09 | 21·33 | 19·00 |
| 15·00 | 89·83 | 52·05 | 31·50 | 24·22 | 20·46 | 18·15 |
| 30·00 | 89·54 | 50·84 | 30·11 | 22·97 | 19·38 | 17·22 |
| 45·00 | 90·07 | 50·24 | 29·47 | 22·54 | 19·12 | 17·08 |
| 60·00 | 92·34 | 51·03 | 29·99 | 23·08 | 19·68 | 17·65 |
| 75·00 | 96·59 | 53·40 | 31·63 | 24·48 | 20·94 | 18·82 |
| 90·00 | 101·46 | 56·58 | 33·88 | 26·34 | 22·56 | 20·27 |
| 105·00 | 104·69 | 59·24 | 35·92 | 28·02 | 24·01 | 21·57 |
| 120·00 | 105·91 | 61·01 | 37·55 | 29·42 | 25·22 | 22·63 |
| 130·00 | 106·32 | 62·06 | 38·64 | 30·39 | 26·08 | 23·40 |
| 140·00 | 106·96 | 63·28 | 39·93 | 31·56 | 27·14 | 24·36 |
| 150·00 | 108·45 | 65·00 | 41·60 | 33·12 | 28·58 | 25·69 |
| | | | $(q=0{\cdot}20)$ | | | |
| 0·20 | 131·28 | 88·97 | 64·67 | 55·71 | 50·96 | 47·99 |
| 15·00 | 131·48 | 88·77 | 64·24 | 55·22 | 50·45 | 47·49 |
| 30·00 | 132·47 | 88·77 | 63·88 | 54·87 | 50·19 | 47·31 |
| 45·00 | 135·26 | 90·13 | 64·79 | 55·78 | 51·13 | 48·27 |
| 60·00 | 140·96 | 93·81 | 67·57 | 58·27 | 53·46 | 50·51 |
| 75·00 | 149·84 | 100·01 | 72·22 | 62·29 | 57·13 | 53·93 |
| 90·00 | 159·59 | 107·22 | 77·63 | 66·89 | 61·25 | 57·73 |
| 105·00 | 166·32 | 112·84 | 81·98 | 70·55 | 64·46 | 60·64 |
| 120·00 | 169·23 | 116·20 | 84·90 | 73·02 | 66·59 | 62·51 |
| 130·00 | 170·21 | 117·94 | 86·64 | 74·55 | 67·93 | 63·69 |
| 140·00 | 171·40 | 119·91 | 88·71 | 76·44 | 69·65 | 65·25 |
| 150·00 | 173·85 | 122·76 | 91·59 | 79·16 | 72·19 | 67·64 |

absorption correction for primary scattering is less and the upper limit of total scattering angle is extended from 90 to 180°. Also, it would be predicted that the ratio of secondary-to-primary scattering would be less than for the more usual transmission geometiy.

## Theory

The six position variables of equation (2) of the first paper of this series were transformed to a set of three cartesian coordinates fixed with respect to the sample, and to a set of three spherical coordinates in terms of the vector **r**. After introducing boundary conditions for the sample shape and explicit expression of terms, it was possible to integrate analytically over five of the six position variables. Solving equation (1) of the first paper allows the primary intensity to be obtained. It is assumed that the detector views a portion of the sample larger than $V_1$.

Results are given in terms of the $Q$ function by

Table 1 (*cont.*)

$\mu t=0{\cdot}50$

| $2\theta$ | $b=10$ | $b=20$ | $b=40$ | $b=60$ | $b=80$ | $b=100$ |
|---|---|---|---|---|---|---|
| | | | $(q=0)$ | | | |
| 0·20 | 130·39 | 67·73 | 34·82 | 23·54 | 17·80 | 14·33 |
| 15·00 | 128·75 | 65·16 | 31·82 | 20·49 | 14·81 | 11·42 |
| 30·00 | 124·67 | 59·28 | 26·07 | 15·46 | 10·47 | 7·65 |
| 45·00 | 120·05 | 53·14 | 21·22 | 11·84 | 7·68 | 5·43 |
| 60·00 | 116·33 | 48·34 | 17·97 | 9·64 | 6·10 | 4·24 |
| 75·00 | 113·57 | 44·94 | 15·93 | 8·34 | 5·20 | 3·58 |
| 90·00 | 110·31 | 42·24 | 14·56 | 7·52 | 4·65 | 3·18 |
| 105·00 | 105·63 | 39·79 | 13·56 | 6·98 | 4·31 | 2·94 |
| 120·00 | 101·05 | 37·94 | 12·96 | 6·69 | 4·14 | 2·83 |
| 130·00 | 99·30 | 37·38 | 12·86 | 6·67 | 4·14 | 2·84 |
| 140·00 | 99·63 | 37·68 | 13·08 | 6·83 | 4·26 | 2·94 |
| 150·00 | 104·39 | 39·63 | 13·88 | 7·30 | 4·58 | 3·17 |
| | | | $(q=0{\cdot}05)$ | | | |
| 0·20 | 155·38 | 86·24 | 48·12 | 34·52 | 27·45 | 23·09 |
| 15·00 | 154·20 | 84·13 | 45·56 | 31·88 | 24·84 | 20·55 |
| 30·00 | 151·52 | 79·52 | 40·83 | 27·71 | 21·23 | 17·41 |
| 45·00 | 149·20 | 75·28 | 37·32 | 25·12 | 19·28 | 15·91 |
| 60·00 | 148·76 | 73·01 | 35·78 | 24·22 | 18·77 | 15·63 |
| 75·00 | 150·14 | 72·73 | 35·82 | 24·53 | 19·20 | 16·12 |
| 90·00 | 151·04 | 73·18 | 36·60 | 25·39 | 20·05 | 16·95 |
| 105·00 | 149·32 | 73·10 | 37·33 | 26·23 | 20·88 | 17·73 |
| 120·00 | 146·43 | 72·82 | 38·04 | 27·07 | 21·71 | 18·52 |
| 130·00 | 145·67 | 73·27 | 38·88 | 27·91 | 22·49 | 19·24 |
| 140·00 | 147·54 | 75·03 | 40·43 | 29·27 | 23·71 | 20·35 |
| 150·00 | 155·68 | 79·86 | 43·60 | 31·83 | 25·93 | 22·34 |
| | | | $(q=0{\cdot}10)$ | | | |
| 0·20 | 184·94 | 110·32 | 67·72 | 52·11 | 43·87 | 38·74 |
| 15·00 | 184·24 | 108·70 | 65·61 | 49·90 | 41·67 | 36·59 |
| 30·00 | 182·96 | 105·39 | 61·97 | 46·66 | 38·87 | 34·17 |
| 45·00 | 182·97 | 103·14 | 59·95 | 45·27 | 37·95 | 33·59 |
| 60·00 | 185·89 | 103·56 | 60·34 | 45·94 | 38·80 | 34·53 |
| 75·00 | 191·51 | 106·59 | 62·77 | 48·20 | 40·93 | 36·56 |
| 90·00 | 196·58 | 110·32 | 65·93 | 51·02 | 43·49 | 38·92 |
| 105·00 | 197·70 | 112·54 | 68·37 | 53·27 | 45·54 | 40·80 |
| 120·00 | 196·32 | 113·64 | 70·24 | 55·10 | 47·24 | 42·36 |
| 130·00 | 196·46 | 115·02 | 71·93 | 56·71 | 48·72 | 43·73 |
| 140·00 | 199·87 | 118·26 | 74·83 | 59·31 | 51·09 | 45·92 |
| 150·00 | 211·61 | 126·25 | 80·73 | 64·24 | 55·61 | 50·07 |
| | | | $(q=0{\cdot}20)$ | | | |
| 0·20 | 257·79 | 175·26 | 125·85 | 107·13 | 97·07 | 90·72 |
| 15·00 | 258·03 | 174·61 | 124·68 | 105·82 | 95·73 | 89·40 |
| 30·00 | 259·59 | 174·01 | 123·39 | 104·65 | 94·81 | 88·71 |
| 45·00 | 264·41 | 176·01 | 124·76 | 106·17 | 96·49 | 90·52 |
| 60·00 | 274·27 | 182·30 | 129·75 | 110·82 | 100·95 | 94·85 |
| 75·00 | 288·61 | 192·56 | 137·86 | 118·03 | 107·62 | 101·14 |
| 90·00 | 302·10 | 203·20 | 146·42 | 125·54 | 114·46 | 107·51 |
| 105·00 | 308·57 | 209·84 | 152·30 | 130·72 | 119·12 | 111·79 |
| 120·00 | 309·67 | 213·17 | 156·00 | 134·10 | 122·16 | 114·54 |
| 130·00 | 311·35 | 216·10 | 159·12 | 137·00 | 124·82 | 116·99 |
| 140·00 | 317·83 | 222·30 | 164·77 | 142·18 | 129·63 | 121·49 |
| 150·00 | 337·42 | 237·49 | 177·16 | 153·29 | 139·94 | 131·22 |

$$\frac{I_2}{I_1}=\frac{(\sum Z_j^2)^2 Q}{J\{2\theta\}\sum A_j\mu_j\{m\}}\,. \qquad (1)$$

Working equations for the $Q$ function and terms contained in it follow:

$$Q\{b,q,2\theta,\mu t\}$$
$$=G\left[\int_{\gamma=-\pi/2}^{0} W_{-}M\mathrm{d}\gamma+\int_{\gamma=0}^{\pi/2} W_{+}M\mathrm{d}\gamma\right] \qquad (2)$$

$$W_{+}=\frac{\exp(-\mu t\sec\theta)}{1-\sin\gamma\sec\theta}+\left[\frac{\sin\gamma}{\mu t(1-\sin\gamma\sec\theta)^2}\right]$$
$$\times\left[\exp(-\mu t\,\mathrm{cosec}\,\gamma)-\exp(-\mu t\sec\theta)\right]$$

$$W_{-}=\frac{\exp(-\mu t\sec\theta)}{1-\sin\gamma\sec\theta}+\left[\frac{\sin\gamma\exp(-\mu t\sec\theta)}{\mu t(1-\sin\gamma\sec\theta)^2}\right]$$
$$\times\left[1-\exp\{-\mu t(\sec\theta-\mathrm{cosec}\,\gamma)\}\right]$$

Table 1 (*cont.*)

| $2\theta$ | $b=10$ | $b=20$ | $\mu t=1{\cdot}00$ $b=40$ | $b=60$ | $b=80$ | $b=100$ |
|---|---|---|---|---|---|---|
| | | | ($q=0$) | | | |
| 0·20 | 232·89 | 126·23 | 66·82 | 45·69 | 34·78 | 28·10 |
| 15·00 | 229·71 | 121·20 | 60·89 | 39·65 | 28·84 | 22·33 |
| 30·00 | 221·79 | 109·67 | 49·53 | 29·69 | 20·22 | 14·82 |
| 45·00 | 212·57 | 97·55 | 39·92 | 22·50 | 14·68 | 10·42 |
| 60·00 | 204·55 | 87·81 | 33·41 | 18·10 | 11·52 | 8·04 |
| 75·00 | 197·36 | 80·40 | 29·12 | 15·40 | 9·66 | 6·67 |
| 90·00 | 188·33 | 73·97 | 26·02 | 13·58 | 8·45 | 5·81 |
| 105·00 | 177·08 | 68·10 | 23·64 | 12·69 | 7·63 | 5·24 |
| 120·00 | 168·67 | 64·25 | 22·26 | 11·59 | 7·21 | 4·96 |
| 130·00 | 168·58 | 64·03 | 22·23 | 11·61 | 7·24 | 4·99 |
| 140·00 | 178·31 | 67·51 | 23·47 | 12·28 | 7·67 | 5·30 |
| 150·00 | 215·98 | 81·09 | 28·04 | 14·65 | 9·15 | 6·32 |
| | | | ($q=0{\cdot}05$) | | | |
| 0·20 | 269·93 | 154·51 | 87·58 | 62·96 | 49·98 | 41·91 |
| 15·00 | 267·61 | 150·36 | 82·50 | 57·72 | 44·79 | 36·85 |
| 30·00 | 262·18 | 141·16 | 73·06 | 49·38 | 37·56 | 30·56 |
| 45·00 | 257·01 | 132·45 | 65·90 | 44·07 | 33·56 | 27·47 |
| 60·00 | 254·57 | 127·08 | 62·34 | 41·93 | 32·25 | 26·67 |
| 75·00 | 254·14 | 124·76 | 61·48 | 41·88 | 32·58 | 27·20 |
| 90·00 | 251·55 | 123·17 | 61·67 | 42·65 | 33·55 | 28·24 |
| 105·00 | 244·81 | 120·77 | 61·81 | 43·39 | 34·49 | 29·23 |
| 120·00 | 239·79 | 119·72 | 62·68 | 44·63 | 35·78 | 30·50 |
| 130·00 | 243·13 | 122·33 | 64·91 | 46·61 | 37·57 | 32·14 |
| 140·00 | 260·07 | 131·54 | 70·52 | 50·99 | 41·29 | 35·44 |
| 150·00 | 317·81 | 160·49 | 86·32 | 62·61 | 50·84 | 43·73 |
| | | | ($q=0{\cdot}10$) | | | |
| 0·20 | 313·24 | 190·54 | 117·20 | 89·56 | 74·79 | 65·51 |
| 15·00 | 311·77 | 187·27 | 112·97 | 85·14 | 70·38 | 61·19 |
| 30·00 | 308·87 | 180·48 | 105·57 | 78·55 | 64·68 | 56·27 |
| 45·00 | 307·82 | 175·33 | 101·09 | 75·42 | 62·54 | 54·82 |
| 60·00 | 311·10 | 174·60 | 100·89 | 76·00 | 63·58 | 56·14 |
| 75·00 | 317·59 | 177·72 | 103·96 | 79·17 | 66·73 | 59·23 |
| 90·00 | 321·53 | 181·20 | 107·84 | 82·98 | 70·37 | 62·69 |
| 105·00 | 319·23 | 182·29 | 110·58 | 85·91 | 73·22 | 65·41 |
| 120·00 | 317·54 | 184·02 | 113·72 | 89·13 | 76·31 | 68·33 |
| 130·00 | 324·46 | 189·68 | 118·51 | 93·39 | 80·19 | 71·93 |
| 140·00 | 349·22 | 205·39 | 129·43 | 102·48 | 88·25 | 79·30 |
| 150·00 | 429·06 | 252·37 | 159·58 | 126·72 | 109·37 | 98·45 |
| | | | ($q=0{\cdot}20$) | | | |
| 0·20 | 418·64 | 285·83 | 202·98 | 170·76 | 153·21 | 142·06 |
| 15·00 | 418·90 | 284·36 | 200·53 | 168·05 | 150·46 | 139·33 |
| 30·00 | 421·10 | 282·55 | 197·50 | 165·33 | 148·25 | 137·62 |
| 45·00 | 428·51 | 285·00 | 199·13 | 167·42 | 150·78 | 140·47 |
| 60·00 | 443·66 | 294·38 | 206·87 | 174·87 | 158·06 | 147·61 |
| 75·00 | 464·50 | 309·42 | 219·30 | 186·21 | 168·70 | 157·74 |
| 90·00 | 481·75 | 323·75 | 231·70 | 197·46 | 179·14 | 167·60 |
| 105·00 | 488·13 | 331·86 | 239·95 | 205·17 | 186·34 | 174·36 |
| 120·00 | 492·93 | 339·10 | 247·71 | 212·53 | 193·25 | 180·87 |
| 130·00 | 507·47 | 351·51 | 258·42 | 222·26 | 202·30 | 189·41 |
| 140·00 | 549·67 | 382·61 | 282·81 | 243·85 | 222·23 | 208·22 |
| 150·00 | 679·82 | 473·61 | 351·10 | 303·39 | 276·94 | 259·79 |

$$G=\left[\frac{e^4}{m^2c^4}\right]\left[\frac{2N}{(1+\cos^2 2\theta)\exp(-\mu t\sec\theta)}\right]$$

$$M=M'\cos\gamma$$

$$M'=\pi q^2(2A+B+3C/4)+[1-q+q\alpha]\,[2\pi(1-q)]$$
$$\times\left[\frac{4A}{\alpha\beta}+\left\{\frac{4(1+\cos^2\gamma)\cos^2\theta}{b^2}\right\}\left\{\frac{\alpha}{\beta}-1\right\}+\frac{2\alpha^3}{\beta b^4}-\frac{2\alpha^2}{b^4}-\frac{\sin^2\theta\cos^2\gamma}{b^2}\right]$$

$$A=\tfrac{1}{2}(\cos^4\theta\sin^4\gamma-4\sin^2\theta\cos^2\theta\cos^2\gamma+1)$$

$$B=\cos^2\gamma\cos^2\theta\sin^2\theta(1+\cos^2\gamma)$$

$$C=\tfrac{1}{2}(\sin^4\theta\cos^4\gamma)$$

$$\alpha=2+b(1-\cos\theta\sin\gamma)$$

$$\beta=(\alpha^2-b^2\sin^2\theta\cos^2\gamma)^{1/2}$$

Table 1 (*cont.*)

$\mu t = 2{\cdot}00$

| $2\theta$ | $b=10$ | $b=20$ | $b=40$ | $b=60$ | $b=80$ | $b=100$ |
|---|---|---|---|---|---|---|
| | | | ($q=0$) | | | |
| 0·20 | 410·23 | 232·67 | 127·11 | 88·05 | 67·52 | 54·82 |
| 15·00 | 404·54 | 223·11 | 115·58 | 76·22 | 55·82 | 43·41 |
| 30·00 | 390·50 | 201·28 | 93·52 | 56·73 | 38·87 | 28·61 |
| 45·00 | 374·39 | 178·44 | 74·95 | 42·70 | 28·02 | 19·98 |
| 60·00 | 360·58 | 160·13 | 62·38 | 34·13 | 21·84 | 15·30 |
| 75·00 | 348·06 | 146·03 | 54·02 | 28·83 | 18·17 | 12·60 |
| 90·00 | 332·26 | 133·71 | 47·87 | 25·20 | 15·75 | 10·87 |
| 105·00 | 315·71 | 123·55 | 43·44 | 22·72 | 14·16 | 9·76 |
| 120·00 | 316·58 | 121·51 | 42·28 | 22·05 | 13·74 | 9·46 |
| 130·00 | 347·68 | 131·70 | 45·43 | 23·62 | 14·69 | 10·11 |
| 140·00 | 357·45 | 169·92 | 57·62 | 29·70 | 18·36 | 12·59 |
| 150·00 | 976·27 | 350·03 | 114·37 | 57·67 | 35·11 | 23·78 |
| | | | ($q=0{\cdot}05$) | | | |
| 0·20 | 462·75 | 274·40 | 158·67 | 114·57 | 90·94 | 76·12 |
| 15·00 | 458·61 | 266·48 | 148·74 | 104·26 | 80·70 | 66·10 |
| 30·00 | 449·07 | 248·99 | 130·33 | 87·86 | 66·41 | 53·63 |
| 45·00 | 440·20 | 232·39 | 116·29 | 77·35 | 58·43 | 47·44 |
| 60·00 | 436·26 | 221·90 | 109·06 | 72·88 | 55·61 | 45·64 |
| 75·00 | 435·58 | 216·77 | 106·75 | 72·26 | 55·84 | 46·33 |
| 90·00 | 431·37 | 213·02 | 106·42 | 73·20 | 57·29 | 47·99 |
| 105·00 | 424·69 | 210·11 | 107·08 | 74·85 | 59·25 | 50·05 |
| 120·00 | 438·71 | 217·94 | 113·08 | 80·10 | 64·00 | 54·41 |
| 130·00 | 489·43 | 242·92 | 126·85 | 90·35 | 72·49 | 61·83 |
| 140·00 | 652·31 | 320·80 | 166·98 | 119·00 | 95·61 | 81·67 |
| 150·00 | 1409·62 | 676·25 | 344·97 | 243·90 | 195·29 | 166·63 |
| | | | ($q=0{\cdot}10$) | | | |
| 0·20 | 523·20 | 326·12 | 201·85 | 153·44 | 127·16 | 110·50 |
| 15·00 | 520·62 | 319·86 | 193·55 | 144·71 | 118·43 | 101·93 |
| 30·00 | 515·61 | 306·81 | 178·97 | 131·62 | 107·04 | 92·06 |
| 45·00 | 514·12 | 296·72 | 169·90 | 125·15 | 102·52 | 88·92 |
| 60·00 | 520·33 | 294·58 | 168·76 | 125·63 | 103·98 | 90·97 |
| 75·00 | 531·87 | 299·13 | 173·47 | 130·79 | 109·28 | 96·27 |
| 90·00 | 539·64 | 304·62 | 179·90 | 137·37 | 115·72 | 102·50 |
| 105·00 | 543·21 | 309·59 | 186·47 | 144·05 | 122·20 | 108·73 |
| 120·00 | 571·35 | 328·61 | 201·23 | 156·94 | 133·93 | 119·61 |
| 130·00 | 643·57 | 370·88 | 228·60 | 179·08 | 153·28 | 137·20 |
| 140·00 | 865·20 | 495·87 | 305·48 | 239·71 | 205·58 | 184·37 |
| 150·00 | 1888·52 | 1062·59 | 647·01 | 506·54 | 434·73 | 390·64 |
| | | | ($q=0{\cdot}20$) | | | |
| 0·20 | 667·88 | 459·57 | 323·07 | 268·27 | 237·96 | 218·50 |
| 15·00 | 668·42 | 452·66 | 318·14 | 262·81 | 232·39 | 212·99 |
| 30·00 | 672·65 | 452·81 | 311·75 | 257·00 | 227·60 | 209·17 |
| 45·00 | 686·32 | 456·59 | 313·93 | 260·16 | 231·68 | 213·93 |
| 60·00 | 713·65 | 472·68 | 327·20 | 273·11 | 244·46 | 226·56 |
| 75·00 | 750·81 | 498·66 | 348·88 | 293·15 | 263·45 | 244·77 |
| 90·00 | 783·68 | 524·71 | 371·65 | 314·18 | 283·25 | 263·65 |
| 105·00 | 808·91 | 547·31 | 392·52 | 333·68 | 301·69 | 281·26 |
| 120·00 | 868·14 | 592·66 | 429·60 | 367·05 | 332·78 | 310·76 |
| 130·00 | 989·03 | 677·04 | 493·10 | 422·51 | 383·79 | 358·88 |
| 140·00 | 1345·11 | 918·54 | 669·92 | 575·33 | 523·72 | 490·64 |
| 150·00 | 2983·01 | 2015·68 | 1465·38 | 1261·03 | 1151·41 | 1082·08 |

Indeterminate forms can be avoided by careful selection of the increments in $\gamma$ for the numerical integration, or l'Hôpital's rule can be used.

Detailed derivations are available from the author.

### Results

Values of the $Q$ function are given in Table 1. The first paper of this series describes the meaning and use of this table.

Double-precision source programs for calculation of $Q$ that are written in 360 *Fortran* IV (*H* level) are available from the author. Only 74 seconds of computing time were required to compile the source program and calculate 576 values of $Q$.

The $Q$ functions, and thus the ratios of secondary-to-primary scattering, at all angles higher than zero are less than the corresponding values in the more usual transmission case given in the first paper of this series. The $Q$ functions at zero scattering angle agree with those given in the first paper, because the two types of transmission geometry become identical at zero scattering angle.

## Discussion

The portions of the discussion in the first paper of this series that apply for transmission geometry also apply to the present case.

The type of transmission geometry described in this paper can often be used by only slight modification of a reflection geometry diffractometer. The sample holder is rotated by 90° so that the surface of the sample is normal to the incident X-ray beam at zero scattering angle. The slits of the diffractometer may have to be changed in some cases.

A comparison of the three forms of geometry considered in this and the first paper of the series is interesting. For very large scattering angles, reflection geometry often is superior from the standpoints of secondary scattering, primary scattering, and the magnitude of the absorption correction. For intermediate scattering angles, the type of transmission geometry described in this paper and reflection geometry often are both satisfactory. At small scattering angles, either type of transmission geometry is usually superior to reflection geometry. At extremely small angles, the usual transmission geometry described in the first paper is superior, because fewer moving parts are required in the diffractometer.

If a sample cannot be made thin enough to yield a small calculated ratio of secondary-to-primary intensity, the calculated secondary intensity can be used to obtain an approximation of primary coherent intensity, using the normalization procedure described in the first paper. An improved value of secondary intensity can then be calculated using the approximate coherent experimental intensity. However, this procedure would require a very large amount of work. Very careful design of the scattering experiment will usually allow such problems to be avoided.

## Nomenclature

| | |
|---|---|
| $A_j$ | Atomic weight of element $j$. |
| $b,q$ | Parameters used to approximate scattering in $J=[\sum Z_j^2]\,[q+(1-q)/(1+b\sin^2\theta)]$. |
| $c$ | Velocity of light. |
| $e$ | Electronic charge. |
| $I_1$ | Total intensity of primary scattering. |
| $I_2$ | Total intensity of secondary scattering. |
| $J$ | Intensity of primary scattering in electron units. |
| $m$ | Rest mass of electron. |
| $N$ | Avogadro's number. |
| $\mathbf{r}$ | Vector from first to second scattering point in the case of secondary scattering. |
| $t$ | Sample thickness. |
| $V_1$ | Volume of sample illuminated by incident X-ray beam. |
| $Z_j$ | Atomic number of element $j$. |
| $2\theta$ | Total scattering angle for primary scattering. |
| $\mu$ | Linear absorption coefficient at the wavelength of incident radiation. |
| $\mu'$ | Linear absorption coefficient at the wavelength of incoherent radiation as a function of scattering angle. |
| $\mu_j\{m\}$ | Mass absorption coefficient of element $j$. |

## APPENDIX

Normalization can be done in the same manner as described in the appendix of the first paper of this series, if the expressions for $\mathcal{F}_2$ and $\mathcal{F}_3$ are used as given below.

$$\mathcal{F}_2=[\mu t\exp(-\mu t\sec\theta)]/[\cos\theta\sum A_j\mu_j\{m\}]$$

$$\mathcal{F}_3=\frac{\mu[\exp(-\mu t\sec\theta)-\exp(-\mu' t\sec\theta)]}{[\mu'-\mu]\sum A_j\mu_j\{m\}}\left(\frac{\nu'}{\nu}\right)^2$$

### Reference

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# Application of Constraints to Derivatives in Least-Squares Refinement

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The effect of imposing constraints on the parameters of a least-squares refinement is considered, and a general equation is presented that relates the derivatives for the calculated, unconstrained parameters to those of the constrained parameters.

A problem which is frequently encountered in the least-squares refinement of positional and thermal parameters for crystal-structure analyses is the imposition of constraints to account for the interdependence of such parameters. The constraints usually arise from the imposition of known symmetry or geometry for parts