

## Secondary Extinction Corrections for Cylindrical Crystals\*

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A computer program for calculating secondary extinction corrections for crystals of arbitrary polyhedral shape is briefly described, and tables of the corrections for equatorial reflections from cylindrical crystals are presented.

### Introduction

The author in a previous publication (Hamilton, 1957, hereinafter referred to as I) has presented a formalism for calculating secondary extinction corrections for crystals of arbitrary shape. The corrections for cylindrical crystals were presented in I in the form of curves of  $I_o/I_c$  versus  $\sigma D$  for three scattering angles. The calculation of the points on these curves was carried out on a desk computer using a rather large grid size for the required two-dimensional numerical integration.

In the intervening four years, a fast computer program for the IBM 704/7090 has been developed for the calculation of absorption and secondary extinction corrections for convex polyhedral crystals of arbitrary shape. The availability of this program, which makes possible a much more accurate integration, and the requests that the author has received for tables of values for cylindrical crystals, have made it seem desirable to calculate and publish such a table.

### Method

The general method used is that of I, and the same notation will be used. A rectangular rather than a Gaussian mosaic spread distribution function has been used; the adequacy of this model has been demonstrated by its successful use in a number of problems in these laboratories.

If the power in the incident beam with direction  $n$  is denoted by  $P_o$  and that in the diffracted beam with direction  $m$  by  $P_H$ , the following pair of differential equations apply:

$$\partial P_H / \partial m = \gamma_{11} P_H + \gamma_{12} P_o \quad (1a)$$

$$\partial P_o / \partial n = \gamma_{21} P_o + \gamma_{22} P_H, \quad (1b)$$

where the  $\gamma$ 's are constants defined below. Rather than using the difference equations I-4 as an approximation to equations (1), a modified Euler integration scheme is used instead. In one dimension, the Euler formula is

$$f(x + \Delta x) = f(x) + (\Delta x/2)[f'(x) + f'(x + \Delta x)]. \quad (2)$$

In two dimensions, we construct a grid of points spanning the cross-section of the crystal. Let us denote the points  $(m, n)$ ,  $(m, n + \Delta n)$ ,  $(m + \Delta m, n)$ , and  $(m + \Delta m, n + \Delta n)$  by (00), (01), (10), and (11). If we choose  $\Delta n = \Delta m$  and define  $C_{ij} = \gamma_{ij} \Delta n/2$ , we may combine (2) and (1) to obtain

$$\begin{aligned} P_H(11) &= P_H(01) + C_{11}[P_H(01) + P_H(11)] \\ &\quad + C_{12}[P_o(01) + P_o(11)] \\ P_o(11) &= P_o(10) + C_{21}[P_o(10) + P_o(11)] \\ &\quad + C_{22}[P_H(10) + P_H(11)]. \end{aligned} \quad (3)$$

Since the boundary conditions for equations (1) are

$$P_o = 1^* \text{ at the incident boundary}$$

and

$P_H = 0$  at the boundary opposite to the direction of emergence of the diffracted beam, we must consider four types of boundary point in the application of the equations (3):

*Type I:* The point (11) is a boundary point with respect to both  $P_H$  and  $P_o$ . For this case

$$\begin{aligned} P_o(11) &= 1 \\ P_H(11) &= 0. \end{aligned} \quad (4)$$

*Type II:* The point is a boundary point with respect to  $P_H$  but not to  $P_o$ . The equations become

$$\begin{aligned} P_o(11) &= \frac{C_{22}}{1 - C_{21}} P_H(01) + \left( \frac{1 + C_{21}}{1 - C_{21}} \right) P_o(10) \\ P_H(11) &= 0. \end{aligned} \quad (5)$$

*Type III:* The point is a boundary point with respect to  $P_o$  but not to  $P_H$ . The equations become

$$P_o(11) = 1$$

$$P_H(11) = \frac{1 + C_{11}}{1 - C_{11}} P_H(01) + \frac{C_{12}}{1 - C_{11}} [1 + P_o(01)]. \quad (6)$$

*Type IV:* The point is not subject to the boundary conditions. The equations become on rearrangement

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\* The incident power is normalized to unity for convenience.

Table 1. *Reciprocal pure secondary extinction corrections for cylinder:  $1/E_s = I_c/I_o$* 

| $\sigma D \backslash 2\theta^\circ$ | $0^\circ$                | $22.5^\circ$   | $45^\circ$     | $67.5^\circ$   | $90^\circ$     | $112.5^\circ$  | $135^\circ$    | $157.5^\circ$  | $180^\circ$              |
|-------------------------------------|--------------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|--------------------------|
| 0.0                                 | 1.000                    | 1.000          | 1.000          | 1.000          | 1.000          | 1.000          | 1.000          | 1.000          | 1.000                    |
| 0.2                                 | 1.178                    | 1.178          | 1.177          | 1.176          | 1.173          | 1.172          | 1.170          | 1.169          | 1.169                    |
| 0.4                                 | 1.374                    | 1.372          | 1.368          | 1.362          | 1.354          | 1.346          | 1.341          | 1.337          | 1.336                    |
| 0.6                                 | 1.585                    | 1.581          | 1.571          | 1.556          | 1.538          | 1.523          | 1.511          | 1.504          | 1.501                    |
| 0.8                                 | 1.811                    | 1.804          | 1.785          | 1.757          | 1.727          | 1.701          | 1.682          | 1.670          | 1.666                    |
| 1.0                                 | 2.050                    | 2.038          | 2.007          | 1.963          | 1.917          | 1.879          | 1.852          | 1.836          | 1.830                    |
| 1.2                                 | 2.300                    | 2.283          | 2.236          | 2.173          | 2.108          | 2.057          | 2.022          | 2.001          | 1.993                    |
| 1.4                                 | 2.561                    | 2.536          | 2.471          | 2.385          | 2.301          | 2.236          | 2.192          | 2.165          | 2.156                    |
| 1.6                                 | 2.830                    | 2.796          | 2.710          | 2.599          | 2.493          | 2.415          | 2.362          | 2.330          | 2.318                    |
| 1.8                                 | 3.106                    | 3.062          | 2.952          | 2.814          | 2.686          | 2.593          | 2.531          | 2.493          | 2.480                    |
| 2.0                                 | 3.389                    | 3.333          | 3.196          | 3.030          | 2.880          | 2.772          | 2.700          | 2.657          | 2.641                    |
| 2.2                                 | 3.677                    | 3.608          | 3.443          | 3.247          | 3.073          | 2.951          | 2.869          | 2.820          | 2.802                    |
| 2.4                                 | 3.968                    | 3.886          | 3.690          | 3.463          | 3.266          | 3.129          | 3.038          | 2.983          | 2.963                    |
| 2.6                                 | 4.264                    | 4.167          | 3.939          | 3.680          | 3.459          | 3.308          | 3.207          | 3.146          | 3.123                    |
| 2.8                                 | 4.563                    | 4.449          | 4.188          | 3.897          | 3.653          | 3.486          | 3.376          | 3.309          | 3.284                    |
| 3.0                                 | 4.863                    | 4.733          | 4.437          | 4.113          | 3.846          | 3.664          | 3.545          | 3.471          | 3.444                    |
| 4.0                                 | 6.393                    | 6.163          | 5.684          | 5.196          | 4.812          | 4.556          | 4.387          | 4.283          | 4.143                    |
| 6.0                                 | 9.490                    | 9.037          | 8.172          | 7.358          | 6.741          | 6.335          | 6.070          | 5.900          | 5.832                    |
| 8.0                                 | 12.61                    | 11.90          | 10.65          | 9.515          | 8.667          | 8.110          | 7.752          | 7.516          | 7.416                    |
| 10.0                                | 15.75                    | 14.77          | 13.12          | 11.67          | 10.59          | 9.883          | 9.432          | 9.132          | 8.996                    |
| 12.0                                | 18.88                    | 17.62          | 15.59          | 13.82          | 12.51          | 11.65          | 11.11          | 10.75          | 10.58                    |
| 14.0                                | 22.02                    | 20.47          | 18.06          | 15.97          | 14.43          | 13.42          | 12.79          | 12.37          | 12.15                    |
| 16.0                                | 25.16                    | 23.32          | 20.52          | 18.12          | 16.35          | 15.19          | 14.46          | 13.98          | 13.73                    |
| 18.0                                | 28.30                    | 26.17          | 22.98          | 20.26          | 18.27          | 16.95          | 16.14          | 15.60          | 15.30                    |
| 20.0                                | 31.44                    | 29.01          | 25.44          | 22.41          | 20.18          | 18.72          | 17.81          | 17.22          | 16.88                    |
| 22.0                                | 34.58                    | 31.86          | 27.89          | 24.55          | 22.10          | 20.48          | 19.48          | 18.84          | 18.45                    |
| 24.0                                | 37.71                    | 34.70          | 30.35          | 26.69          | 24.01          | 22.24          | 21.15          | 20.47          | 20.03                    |
| 26.0                                | 40.86                    | 37.54          | 32.80          | 28.84          | 25.92          | 24.00          | 22.82          | 22.09          | 21.60                    |
| 28.0                                | 44.00                    | 40.38          | 35.25          | 30.98          | 27.83          | 25.76          | 24.49          | 23.71          | 23.17                    |
| 30.0                                | 47.14                    | 43.22          | 37.70          | 33.12          | 29.74          | 27.52          | 26.16          | 25.33          | 24.75                    |
| Limiting value                      | $\frac{1}{2}\pi\sigma D$ | $1.42\sigma D$ | $1.23\sigma D$ | $1.07\sigma D$ | $0.96\sigma D$ | $0.88\sigma D$ | $0.84\sigma D$ | $0.79\sigma D$ | $\frac{1}{4}\pi\sigma D$ |

$$\begin{aligned}
P_O(11) &= (1/K)[P_H(01)(1 + C_{11})C_{22} + P_O(01)C_{12}C_{22} \\
&\quad + P_H(10)C_{22}(1 - C_{11}) + P_O(10)(1 + C_{21})(1 - C_{11})] \\
P_H(11) &= (1/K)[P_H(01)(1 + C_{11})(1 - C_{21}) \\
&\quad + P_O(01)(1 - C_{21})C_{12} + P_H(10)C_{12}C_{22} \\
&\quad + P_O(10)(1 + C_{21})C_{12}] \quad (7)
\end{aligned}$$

with

$$K = (1 - C_{11})(1 - C_{21}) - C_{12}C_{22}.$$

If the linear absorption coefficient is denoted by  $\mu$  and the reflectivity by  $\sigma$  (see I), we have, for the case of non-zero extinction,

$$\begin{aligned}
C_{11} &= C_{21} = -(\mu + \sigma)\Delta n/2 \\
C_{12} &= C_{22} = \sigma\Delta n/2. \quad (8)
\end{aligned}$$

If extinction is considered to be negligible, and we are interested in calculating a pure absorption coefficient, we have

$$\begin{aligned}
C_{11} &= C_{21} = -\mu\Delta n/2 \\
C_{12} &= \sigma\Delta n/2 \\
C_{22} &= 0. \quad (9)
\end{aligned}$$

These equations are used in the program to integrate along lines of constant  $n$ , and the total diffracted power is integrated over the exit boundary:

$$P_H(T) = \sum_{n=n_{\min}}^{n_{\max}} P_H[m_{\max}(n)]. \quad (10)$$

To obtain the absorption-extinction correction,  $E_{sa}$  we divide  $P_H(T)$  by the ideal value for an extinction and absorption free crystal, namely

$$A = \sigma\Delta n \sum_{n=n_{\min}}^{n_{\max}} [m_{\max}(n) - m_{\min}(n)]. \quad (11)$$

[In (10) and (11),  $n$  and  $m$  refer to the integral indices of the grid points.] Thus

$$E_{sa} \equiv I_o/I_c = P_H(T)/A.$$

For the crystal of general shape, the program performs the integration over slices parallel to the  $mn$  plane, sums  $P_H(T)$  and  $A$  for the various planes and then divides to obtain  $E_{sa}$ . For equatorial reflections from a crystal with axial symmetry, in particular a cylindrical crystal, only one slice is necessary.

### Calculations for the table

The circular cross-section of the cylinder was approximated by a 30-gon of the same area as a circle with diameter  $D$ . The grid size for the integration was taken to be  $D/120$ , for  $45^\circ < 2\theta < 135^\circ$  and  $D/80$  for  $2\theta = 22.5^\circ$  and  $157.5^\circ$ . The values for  $2\theta = 0^\circ$  and  $180^\circ$  can be calculated by simpler methods than numerical integration. A series expansion was used to evaluate the integral in I-15 for  $2\theta = 0^\circ$  (equation I-18 should have a 2 in front of the summation sign); the following formulae were used for  $2\theta = 180^\circ$ :

$$a = \sigma D < 1, E_s = \frac{4}{\pi a} - \frac{2}{a^2} + \frac{8}{\pi a^2 (1-a^2)^{1/2}} \tan^{-1} \left( \frac{1-a}{1+a} \right)^{1/2}$$

$$a = D = 1, E_s = \frac{8}{\pi} - 2$$

$$a = \sigma D > 1, E_s = \frac{4}{\pi a} - \frac{2}{a^2} + \frac{4}{\pi a^2 (a^2-1)^{1/2}} \log \frac{(1+a)^{1/2} + (a-1)^{1/2}}{(1+a)^{1/2} - (a-1)^{1/2}}$$

The results are accumulated in Table 1. The quantity tabulated is  $1/E_s$ , i.e.  $I_c/I_o$ . To obtain an estimate of the accuracy of these numbers, calculations were made of a few pure absorption corrections, with the results compared in Table 2 with values from Vol. II of the *International Tables for X-ray Crystallography* (1959). For  $\mu D=3$ , the errors are no more than a few tenths of 1%. These increase to 2-3% at  $\mu D=30$ . This should be a tolerable error for any practical work where extinction or absorption is this severe.

Table 1 is extended to values of  $\sigma D$  where the reflected intensity is becoming independent of the

Table 2. Comparison of calculated pure absorption corrections with those tabulated in the *International Tables for X-ray Crystallography*

| $\mu R$ | $\theta$ | Calc. | Table | Relative error |
|---------|----------|-------|-------|----------------|
| 1.5     | 15       | 9.843 | 9.88  | 0.0037         |
|         | 25       | 8.766 | 8.79  | 0.0027         |
|         | 35       | 7.668 | 7.68  | 0.0015         |
|         | 45       | 6.722 | 6.74  | 0.0027         |
|         | 55       | 6.000 | 6.00  | —              |
|         | 65       | 5.453 | 5.45  | 0.0006         |
| 15.0    | 75       | 5.083 | 5.08  | 0.0006         |
|         | 15       | 711.5 | 731   | 0.027          |
|         | 25       | 321.3 | 313   | 0.027          |
|         | 35       | 179.9 | 176   | 0.022          |
|         | 45       | 117.6 | 115   | 0.023          |
|         | 55       | 84.95 | 82.7  | 0.027          |
|         | 65       | 65.86 | 64.8  | 0.016          |
|         | 75       | 54.43 | 54.1  | 0.006          |

structure factor, and the limiting values of  $1/E_s$  are also included in the table. The limiting values for  $2\theta=0^\circ$  and  $2\theta=180^\circ$  are exact; the others were obtained by extrapolation.

### References

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## Crystal Structure of $[\text{BrMn}(\text{CO})_4]_2$

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A three-dimensional structural analysis of  $[\text{BrMn}(\text{CO})_4]_2$ , a typical member of the group VII metal tetracarbonyl halides, has been carried out. Crystals of  $[\text{BrMn}(\text{CO})_4]_2$  possess space group symmetry  $P2_1/c$  and contain four dimeric molecules in a monoclinic unit cell of dimensions

$$a = 9.57 \pm 0.01, b = 11.79 \pm 0.02, c = 12.91 \pm 0.02 \text{ \AA}, \beta = 109^\circ 30' \pm 10'.$$

Isotropic least-squares refinement of all twenty atoms has yielded final discrepancy factors of  $R_1=10.0\%$  and  $R_2=10.9\%$ . The structure consists of discrete dimeric molecules formed by two octahedra joined at a common edge with bridging bromines equally shared between the manganese atoms. Within experimental error each molecular unit is of  $D_{2h}$  symmetry. The mean bond length for the four equivalent Mn-Br bonds is  $2.526 \pm 0.005 \text{ \AA}$ .

### Introduction

Although a large number of metal carbonyl halides are known, to date the structures of only two of them,  $[\text{ClRh}(\text{CO})_2]_2$  (Dahl, Martell & Wampler, 1961) and  $\text{I}_2\text{Ru}(\text{CO})_4$  (Dahl & Wampler, 1962), have been determined by X-ray diffraction. This paper reports the results of a three-dimensional X-ray investigation of a third such compound,  $[\text{BrMn}(\text{CO})_4]_2$ , which is a

representative member of the tetracarbonyl halides of the group VII transition metals.

The dimeric character of these compounds was first determined (Abel, Hargreaves & Wilkinson, 1958) from molecular weight measurements of the rhenium carbonyl halides. A structure of  $D_{2h}$  symmetry involving the connection of two octahedra at an edge with bridging halogen atoms was suggested as a most reasonable configuration. Other structures with