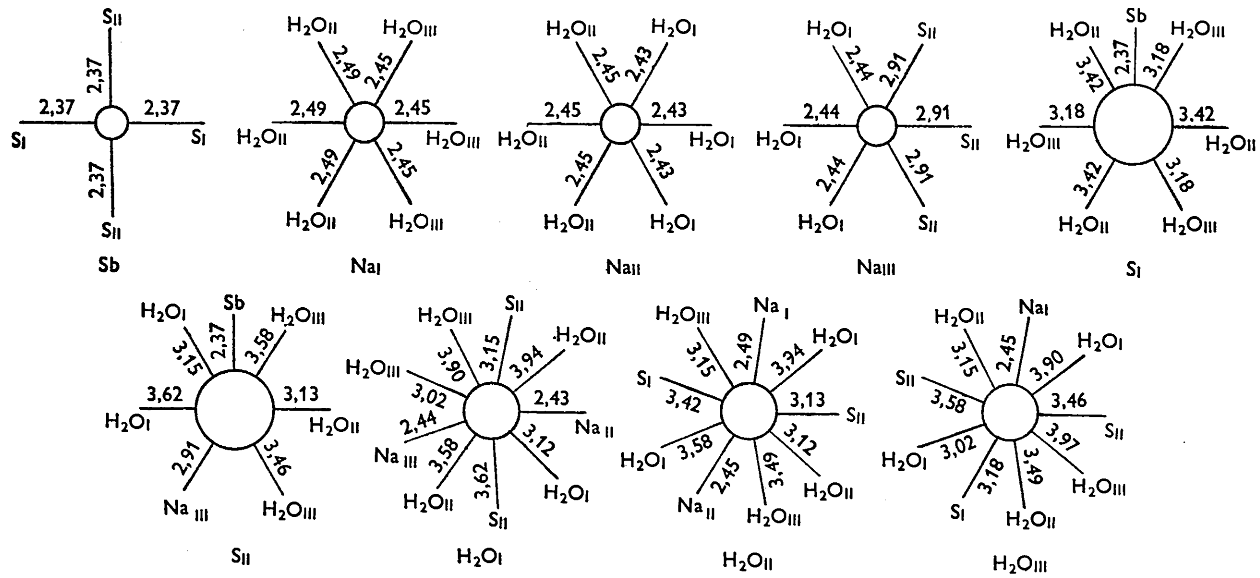

Fig. 3. Abstände (in A.) und nächste Nachbarn.

gleichmässige Ladungsverteilung gewahrt. Dies ist in Übereinstimmung mit der Tetraederanordnung des $[SbS_4]^{-3}$-Komplexions. Die Fig. 3 erläutert die Nachbarschaft jedes Atoms der Struktur.

Herrn Prof. Machatschki, der die Arbeit angeregt hat, sind wir für seine Hilfe zu grossem Dank verpflichtet.

Literatur

FEHER, F. & MORGENSTERN, G. (1937). *Naturwissenschaften*, **25**, 618.
Gmelins Handbuch der anorganischen Chemie (1928). 8. Aufl. Leipzig und Berlin: Verlag Chemie.
GRUND, A. & PREISINGER, A. (1949). *Anz. Akad. Wiss. Wien*, **86**, no. 5.
HOFMANN, W. (1933). *Z. Krystallogr.* **86**, 225.
HOFMANN, W. (1935). *Z. Krystallogr.* **92**, 176.
HUI, CH. Y. (1933). *Bull. Amer. Phys. Soc.* **8**, no. 24.
MACHATSCHKI, F. (1928). *Z. Krystallogr.* **68**, 204.
MARBACH, C. A. H. (1856). *Ann. Phys., Lpz.*, **99**, 451.
PAULING, L. (1934). *Z. Krystallogr.* **88**, 54.
RAMMELSBERG, C. (1841). *Ann. Phys., Lpz.*, **52**, 210.
RAMMELSBERG, C. (1855). *Handbuch der kristallographischen Chemie.* Berlin: Jeanrenaud.
VERHULST, A. (1933). *Bull. Soc. chim. Belg.* **42**, 359.
WEST, C. D. (1934). *Z. Krystallogr.* **88**, 97.
WYROUBOFF, G. (1886). *Ann. Chim. (Phys.)*, (6), **8**, 411.
ZINK, E., HARDER, A. & DAUTH, B. (1934). *Z. Elektrochem.* **40**, 588.

Acta Cryst. (1950). **3**, 366

A Graphical Method of Estimating Absorption Factors for Single Crystals

BY R. GWYNNE HOWELLS

Viriamu Jones Laboratory, University College, Cardiff, Wales

(*Received* 24 *August* 1949 *and in revised form* 23 *January* 1950)

An accurate method of estimating absorption factors for oscillation photographs of single crystals of constant cross-section is given, the computation being comparatively short for crystals of large absorbing power. The method is applicable to both zero and non-zero layer lines. It is also extended to zero-layer-line reflexions in two special cases of crystals of varying cross-section, viz. (1) that of a pyramidal form, and (2) that of a needle with its length perpendicular to the rotation axis.

1. Introduction

The observed intensity I'_{hkl} of a reflexion from a single crystal is related to the ideal intensity, I_{hkl}, by

$$I'_{hkl}=A_{hkl}\cdot I_{hkl},$$

where A_{hkl} is the absorption factor. It is of the form

$$A_{hkl}=\int_V \frac{\exp(-\mu x)\,dv}{V},$$

where μ is the absorption coefficient of the crystal for the X-rays used, x is the optical path in the crystal of rays reflected from an element dv, and V is the volume of the crystal. Simple approximate methods for computing this factor have been used for crystals of low absorbing power by Robinson (1933), by Robertson & White (1945) and by Albrecht (1939). Hendershot (1937) describes a method, involving considerable computation, for crystals of high absorbing power. The method given here is accurate and is not long, particularly in the case of crystals of high absorbing power bounded by a small number of faces.

marked on it, dividing the cross-section into four areas as in Fig. 1. For this reflexion, the angles ϕ and ψ marked in the figure have the values $\phi_1=30{\cdot}3°$, $\phi_2=21{\cdot}5°$, $\psi_1=54{\cdot}5°$ and $\psi_2=73{\cdot}7°$. In area (1), the loci of points of constant x are parallel to AB, and in area (3) they are parallel to AD. The loci in area (2) make intercepts on AB and AD proportional to $\sin\phi_1$ and $\sin\phi_2$ respectively, whilst those in area (4) make intercepts on BA and BC proportional to $\sin\psi_1$ and $\sin\psi_2$ respectively. The directions of these loci are all marked on the drawing as shown.

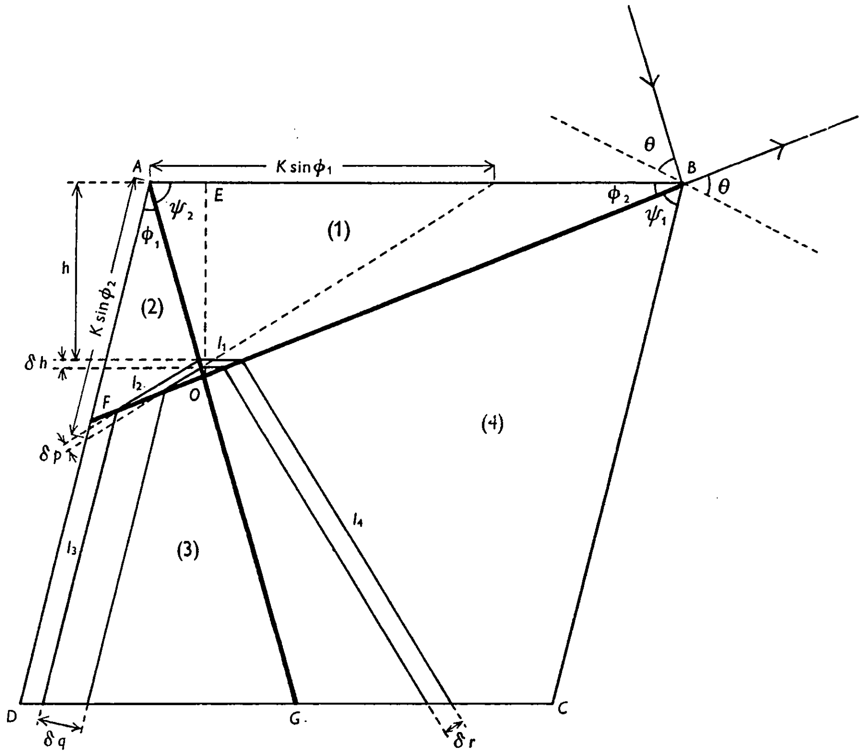

Fig. 1. Crystal cross-section showing loci for which $\exp(-\mu x)$ is constant.

2. Crystal of constant cross-section

2·1. *Zero layer line*

When the cross-section of the crystal, viewed along the axis of rotation, is constant, the equation for A_{hkl} becomes

$$A_{hkl}=\int_S \frac{\exp(-\mu x)\,ds}{S},$$

where ds is an elementary area of the cross-section, and S is the total cross-section. When the cross-section is bounded by straight lines, the loci of points for which x is constant are always straight lines. The method is best explained by a sample calculation, that of the computation of A_{038} for a crystal of mercury diphenyl, the cross-section of which is a rhombus of side $1{\cdot}60\times10^{-2}$ cm., and the interfacial angles of which are 76° and 104°. For cobalt $K\alpha$ radiation, μ is 446 cm.$^{-1}$ and the Bragg angle is 47·6°. A scale drawing of the cross-section is made and the directions of the incident and reflected rays are

Consider an elementary strip in area (1), parallel to AB, of width δh, and distant H from O. For all points in this strip the optical path lies between x and $x+\delta x$. Corresponding strips of width δp, δq and δr, distant P, Q and R respectively from O, exist in areas (2), (3) and (4). If the lengths of these strips are l_1, l_2, l_3 and l_4 respectively, then their area is

$$\begin{aligned}\delta s&=(l_1\delta h+l_2\delta p+l_3\delta q+l_4\delta r)\\&=\{l_1+l_2P/H+l_3Q/H+l_4R/H\}\{OE/(AO+OB)\}\\&\qquad\times\delta x\equiv f(x)\,\delta x,\end{aligned}$$

since $\delta p=(P/H)\,\delta h$ and $OE/(AO+OB)=\delta h/\delta x$. The contribution of these strips to A_{038} is $f(x)\exp(-\mu x)\,\delta x/S$. From the drawing we find that $P/H=1{\cdot}01$, $Q/H=4{\cdot}80$, $R/H=2{\cdot}70$ and $OE/(AO+OB)=0{\cdot}264$. Lengths l_1, l_2, l_3 and l_4 vary linearly with x between certain limits. In area (1), l_1 varies from $AB=1{\cdot}60\times10^{-2}$ cm. when $x=0$, to $l_1=0$ when $x=(AO+OB)=2{\cdot}13\times10^{-2}$ cm.

(by measurement). Putting this in tabular form, we have:

x (cm.)	l_1 (cm.)	$\dfrac{l_1 OE}{(AO+OB)}$ (cm.)
0	$1{\cdot}60\times10^{-2}$	$0{\cdot}422\times10^{-2}$
$2{\cdot}13\times10^{-2}$	0	0

These two points are plotted on a graph of

$$l_1OE/(AO+OB)$$

against x (Fig. 2). The straight line joining them (line (1)) represents the variation of $l_1OE/(AO+OB)$ with x.

In area (2), l_2 is at a maximum when it passes through F (Fig. 1). For this area, we have:

x (cm.)	l_2 (cm.)	$\dfrac{l_2P}{H}\dfrac{OE}{(AO+OB)}$ (cm.)
0	0	0
$1{\cdot}9\times10^{-2}$	$0{\cdot}372\times10^{-2}$	$0{\cdot}099\times10^{-2}$
$2{\cdot}13\times10^{-2}$	0	0

These three points are plotted giving lines (2) in Fig. 2. Similarly, lines (3) and (4) are obtained for areas (3) and (4). The ordinates of all four curves are added at each value of x at which a discontinuity appears in any of the curves. The resulting ordinates are joined by straight lines which represent the variation of $f(x)$ with x. For the first part of the curve of $f(x)$ against x, $f_1(x)=m_1x+c_1$, where m_1 and c_1 are constants. The contribution of this part of the curve to A_{038} is

$$\int_{x_1'}^{x_1''}(m_1x+c_1)\frac{\exp(-\mu x)\,dx}{S} = \frac{[(m_1x+m_1/\mu+c_1)\exp(-\mu x)]_{x_1''}^{x_1'}}{\mu S},$$

where x_1' and x_1'' are the abscissae of the ends of this straight line. From the graph, $x_1'=0$, $x_1''=1{\cdot}61\times10^{-2}$ cm., $m_1=0{\cdot}704/1{\cdot}61=0{\cdot}437$ and $c_1=0{\cdot}422\times10^{-2}$ cm. Substituting these values

$$\int_{x_1'}^{x_1''} f_1(x)\exp(-\mu x)\,dx = 4{\cdot}69\times10^{-2}.$$

As $\exp(-\mu x_1'')$ is negligibly small in this case, the remainder of the graph makes a negligible contribution and hence $A_{038}=4{\cdot}69\times10^{-2}$. For this reflexion, therefore, and for many others, it is unnecessary to plot more than the first parts of lines (1), (2) and (4), and it is unnecessary to sum the ordinates at more than one point, i.e. at $x=1{\cdot}61\times10^{-2}$ cm. This makes the computation quite short without introducing an appreciable error. If other parts of the graph have to be used, then clearly

$$A_{0kl}=\sum_{r=1}^{n}\int_{x_r'}^{x_r''}(m_rx+c_r)\frac{\exp(-\mu x)\,dx}{S},$$

the integration being performed in turn for each of the n straight lines comprising the graph of $f(x)$ against x.

If $AO<OF$ (Fig. 1) the maximum value of l_2 passes through O. In that case, x decreases as area (3) is traversed from left to right. The ratio Q/H cannot then be determined directly; the ratio Q/P must be found first. Point O will sometimes lie outside the cross-section and then only three areas have to be considered.

A simple construction for finding the directions of the loci in areas (2) and (4) has been pointed out by Dr D. Rogers. Consider area (4). Along OG, produced if necessary, mark off OT'' of length equal to OB. Draw $T''T$ parallel to AB to intersect BC, again produced if necessary, in T. Join OT. Then OT is parallel to the loci in area (4). This construction is very quick and eliminates the possibility of errors in marking off intercepts on the sides.

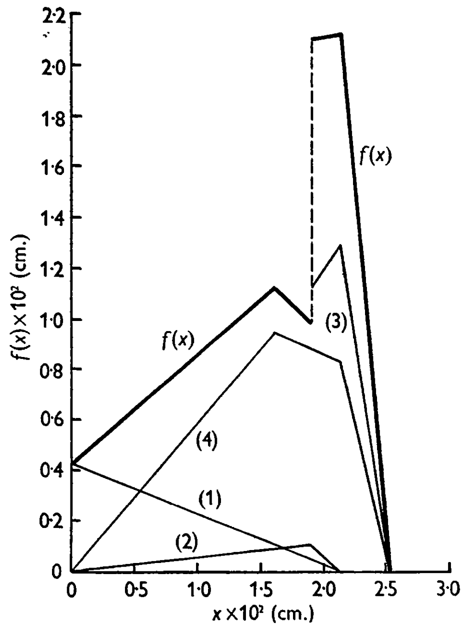

Fig. 2. Graph of $f(x)$ against x.

2·2. *Non-zero layer lines*

For non-zero lines, the reflected ray is inclined to the cross-section perpendicular to the rotation axis, whilst the incident ray lies in it. Line FOB in Fig. 1 now represents the projection of the reflected ray along the zone axis (which is not necessarily the rotation axis). If the length of the reflected ray from any point in areas (1) or (2) is d_1 and its projection is d_1', then $d_1=K_1'd_1'$, where K_1' is a constant which is easily determined. In area (1) the loci required are, as before, parallel to AB. The maximum value of x is now $(AO+K_1'OB)$ and $\delta h/\delta x=OE/(AO+K_1'OB)$. In area (2) the loci make intercepts proportional to $\sin\phi_1$ and $\sin\phi_2/K_1'$ respectively on AB and AD. The maximum length of x is now $K_1'FB$. Similar relations hold for areas (3) and (4) with some other proportionality constant K_2'. The remainder of the computation is performed as for zero-layer-line reflexions.

A similar method can be used for equi-inclination Weissenberg photographs, for which both incident and reflected rays are inclined to the cross-section perpendicular to the rotation axis.

Work may be saved by drawing the cross-section on paper, placing over it a celluloid sheet and marking all other lines on the celluloid in 'washable' ink. The celluloid is easily cleaned with a damp cloth before the next computation.

3. Crystals of varying cross-section

In special cases, it is possible to compute absorption factors for zero-layer-line reflexions from crystals of varying cross-section. Two such cases are dealt with below; others could be similarly treated.

3·1. *Pyramidal crystal terminating in a point*

If the pyramid is regular, the linear dimensions of the cross-section distant y from the vertex are proportional to y. The graph of $f(x)$ against x is constructed for the maximum cross-section corresponding to the base of the pyramid. The absorption factor is given by

$$A_{0kl} = V^{-1}\int_0^Y \left[\sum_{r=1}^{n}\int_{yX'_r/Y}^{yX''_r/Y} (m_r x + yC_r/Y) \times \exp(-\mu x)\,dx\right] dy,$$

where Y is the height of the pyramid, V its volume and X'_r, X''_r, C_r and m_r refer to the graph for the maximum cross-section. The explicit expression for A_{0kl} is long and the computation tedious unless $\exp(-\mu X'_r)$ and $\exp(-\mu X''_r)$ are small, in which case the expression is much simplified and the computation comparatively short.

3·2. *Long needle-shaped crystal*

If the needle length is perpendicular to the rotation axis, A_{0kl} can be computed for all reflexions for which the incident and reflected beams pass through the long faces of the needle (Fig. 3 (*b*)). A graph of $f(x)$ against x is not necessary. The loci of points of constant x are parallel to the needle length. Let us suppose that the cross-section perpendicular to the needle length is as shown in Fig. 3 (*a*). Consider a cross-section perpendicular to the rotation axis. If l is the length of the needle which is bathed in X-rays, and h is the distance from the crystal edge to an elementary strip of width ∂h, then the contribution of the strip to A_{0kl} is

$$l\exp(-\mu x)\,\delta h/S.$$

If x_1 is the length of an incident ray to the strip and x_2 the length of the ray reflected from it, then $x = x_1 + x_2$ and $\delta x = \delta x_1 + \delta x_2$. If X'_1, X'_2 and H' are the maximum values of x_1, x_2 and h respectively for the cross-section considered, then $\delta h = \delta x_1 H'/X'_1$ and $\delta h = -\delta x_2 H'/X'_2$, and we have $\delta x = \delta h(X'_1 - X'_2)/H'$. Thus the factor for this cross-section is

$$S^{-1}\int_{X'_2}^{X'_1} \frac{l\exp(-\mu x)\,dx\,H'}{(X'_1 - X'_2)}.$$

In sections (1) and (3) (Fig. 3 (*a*)), X'_1, X'_2 and H' are proportional to the distance y of the cross-section from the vertex. Thus the contribution to A_{0kl} from each of sections (1) and (3) is

$$V^{-1}\int_0^Y \left[\int_{yX_2/Y}^{yX_1/Y} \frac{l\exp(-\mu x)\,dx\,H}{(X_1 - X_2)}\right] dy,$$

where V is the volume of the crystal bathed in the X-ray beam, and X_1, X_2 and H are the respective values of X'_1, X'_2 and H' for the maximum cross-section. If Z is the

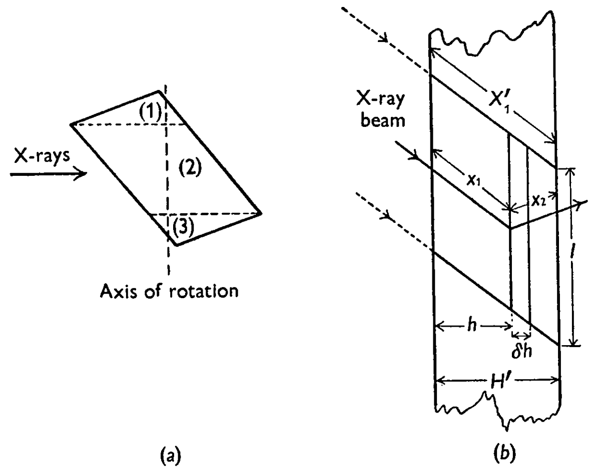

Fig. 3(*a*). Cross-section of needle perpendicular to axis of needle. (*b*) Cross-section of needle perpendicular to axis of rotation.

height of section (2), then its contribution to A_{0kl} is

$$\mu^{-1}V^{-1}lHZ\{\exp(-\mu X_2) - \exp(-\mu X_1)\}/(X_1 - X_2).$$

Hence

$$A_{0kl} = 2V^{-1}\int_0^Y \left[\int_{yX_2/Y}^{yX_1/Y} \frac{l\exp(-\mu x)\,dx\,H}{(X_1 - X_2)}\right] dy + \mu^{-1}V^{-1}lHZ\frac{\exp(-\mu X_2) - \exp(-\mu X_1)}{(X_1 - X_2)}.$$

This is quite easily evaluated using values of the constants obtained from measurements on a scale drawing. When μX_1 and μX_2 are large it reduces to

$$A_{0kl} = 2lHY/\mu^2 V X_1 X_2.$$

The author wishes to thank Dr A. J. C. Wilson for his continued interest and encouragement in the work, and Dr D. Rogers for a suggestion more fully acknowledged in the text.

References

Albrecht, G. (1939). *Rev. Sci. Instrum.* **10**, 221.
Hendershot, O. T. (1937). *Rev. Sci. Instrum.* **8**, 324.
Robertson, J. M. & White, J. G. (1945). *J. Chem. Soc.* p. 614.
Robinson, B. W. (1933). *Proc. Roy. Soc.* A, **142**, 435.