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Estimation of the Absorbing Power of Single Crystals for Weak and Medium Absorption

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The authors have studied an approximate method of quick application for the determination of the absorption of single crystals of low and medium absorbing power. The approximate formula employed by them, can be generally applied with graphic method and even more rapidly with analytical method, should the crystal sections be regular and simple. Approximation errors are reduced by means of an opportune nomogram.

Methods for reducing the work of estimating the absorption factors for single crystals have been studied in our laboratory. In a further note we shall describe methods applicable to heavily absorbing substances, but in this communication we confine ourselves to a method for the calculation of the absorption corrections for medium and weakly absorbing crystals. The method proves to be more rapid than either Albrecht's graphic method (1939) or the simplified procedure proposed by Bezzi, Frasson & Bua (1955) and by Rogers & Moffet (1956).

We have ascertained that, for weakly and medium absorbing single crystals, the estimation of the absorption factors may be measured quickly and with sufficient accuracy by means of the following approximate formula:

$$T_{(hkl)} \simeq \frac{1}{V^2}\int_v \exp(-\mu a)dv \cdot \int_v \exp(-\mu b)dv \qquad (1)$$

where:

T = transmission, V = volume of crystal, μ = linear absorption coefficient, a = optical path in the crystal of an incident ray and b = optical path in the crystal of a diffracted ray.

(a and b are considered not to and from dV, but as in Fig. 1.)

The degree of approximation is illustrated in Fig. 2. The expression (1) may be used either by transforming

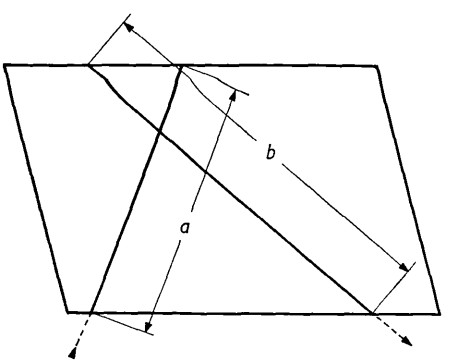


Fig. 1. Explanation of the symbols a and b.

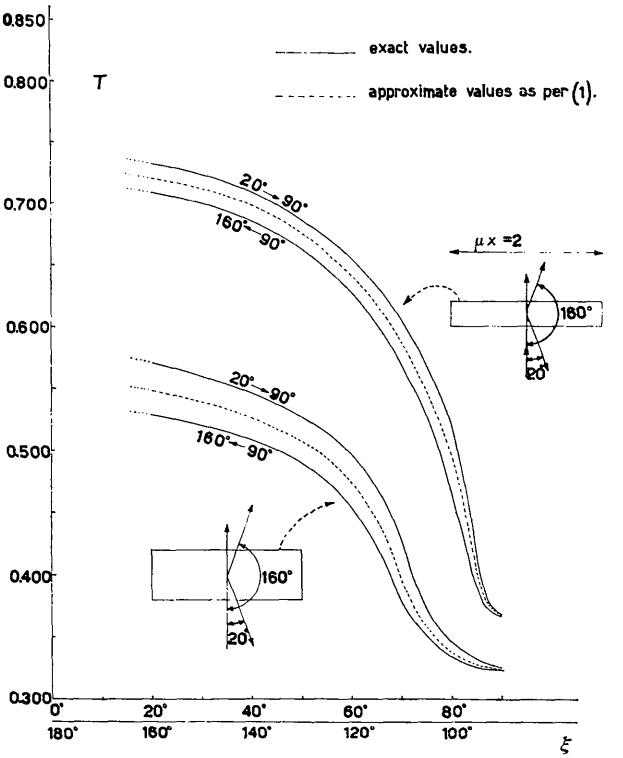


Fig. 2. Variation of crystal transmission for rectangular sections in function of ξ, angle between incident and diffracted ray $(180-\theta)$.

the integrals into summations or, in particular cases, by integration.

(*a*) *Graphical integration*

Equation (1) can be transformed to:

$$T_{(hkl)} \simeq \frac{\sum_{r=1}^{n}[1-\exp(-\mu a_r)]}{\sum_{r=1}^{n}\mu a_r} \cdot \frac{\sum_{s=1}^{n}[1-\exp(-\mu b_s)]}{\sum_{s=1}^{n}\mu b_s} \qquad (2)$$

or:

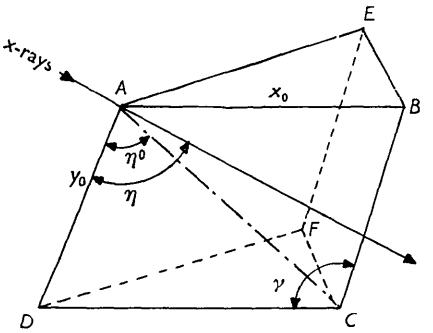
Table 1. *Values of T_a or T_b for common crystal shapes*

In this table $X = \mu x_0 \sin\gamma \operatorname{cosec}\eta$ and $Y = \mu y_0 \sin\gamma \operatorname{cosec}(\gamma-\eta)$

Prism: the symbols refer to the face parallel to the X-rays directions, the parallelogram $ABCD$

Parallelepiped: uniform cross-section is the parallelogram $ABCD$ parallel to the X-rays

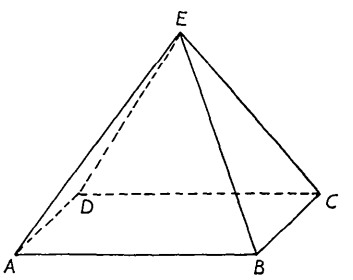
	Values of T_1	Values of T_2
$\eta = \gamma$	$\frac{2}{X} - \frac{2}{X^2}[1-\exp(-X)]$	$\frac{1}{X}[1-\exp(-X)]$
$\eta^\circ \leq \eta < \gamma$	$\frac{2Y+X-6}{XY} + 2\frac{X-Y+3}{X^2Y}[1-\exp(-X)]$	$\frac{2}{Y} + \frac{Y-X-2}{XY}[1-\exp(-X)]$
$0 < \eta \leq \eta^\circ$	$\frac{4X-Y-6}{X^2} + \frac{(Y-X)^2+4(Y-X)+6}{X^2Y}[1-\exp(-Y)]$	$\frac{2}{X} + \frac{X-Y-2}{XY}[1-\exp(-Y)]$
$\eta = 0$	$\frac{1}{Y}[1-\exp(-Y)]$	$\frac{1}{Y}[1-\exp(-Y)]$

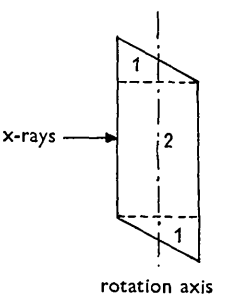


Pyramid: the symbols refer to the base, the parallelogram $ABCD$, parallel to the X-rays directions

Parallelepiped: non uniform cross-section parallel to the X-rays

	Values of T_3	Values of T_4
$\eta = \gamma$	$\frac{3(X+2)}{2X^2} - \frac{3(X+1)}{X^3}[1-\exp(-X)]$	$\frac{2T_1V_1+T_2V_2}{2V_1+V_2}$
$\eta^\circ \leq \eta < \gamma$	$\frac{3(XY+X^2-6X+2Y)}{2X^2Y} + 3\frac{X^2-XY+3X-Y}{X^3Y}[1-\exp(-X)]$	$\frac{2T_1V_1+T_2V_2}{2V_1+V_2}$
$0 < \eta \leq \eta^\circ$	$\frac{3(XY+Y^2-6Y+2X)}{2XY^2} + 3\frac{Y^2-XY+3Y-X}{XY^3}[1-\exp(-Y)]$	$\frac{2T_1V_1+T_2V_2}{2V_1+V_2}$
$\eta = 0$	$\frac{3(Y+2)}{2Y^2} - \frac{3(Y+1)}{Y^3}[1-\exp(-Y)]$	$\frac{2T_1V_1+T_2V_2}{2V_1+V_2}$





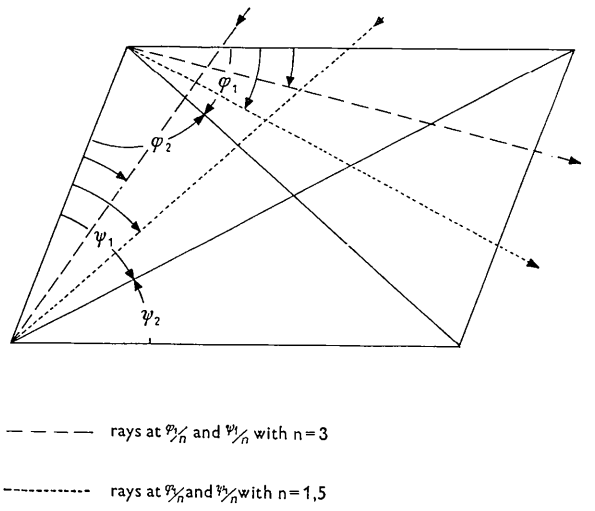


Fig. 3. Explanation of the symbols ψ_1, ψ_2, φ_1 and φ_2. Pairs of 'conjugate' rays are also drawn.

$$T_{(hkl)} \simeq T_a . T_b \qquad (3)$$

which can be applied to cross-sections of all shapes. It is sufficient to measure the lengths of a discrete number (10 to 20) of incident and diffracted rays represented by two sets of parallel equispaced lines placed on the section of the crystal. The very short time necessary for this graphical integration can be reduced considerably by using a transparent ruler graduated to read $[1-\exp(-\mu x)]$. Furthermore the terms $\Sigma\mu a$ and $\Sigma\mu b$ may be eliminated as they are equal and constant for all reflections.

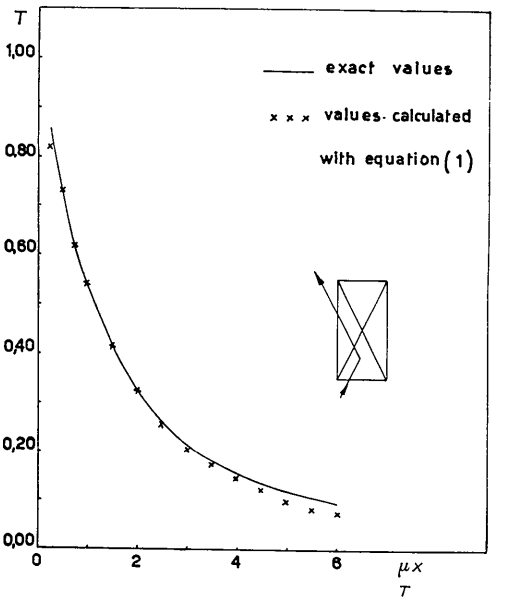


Fig. 4. Transmission for incident and diffracted rays parallel to the diagonals of a rectangle as a function of the diagonal length (x) and of μ.

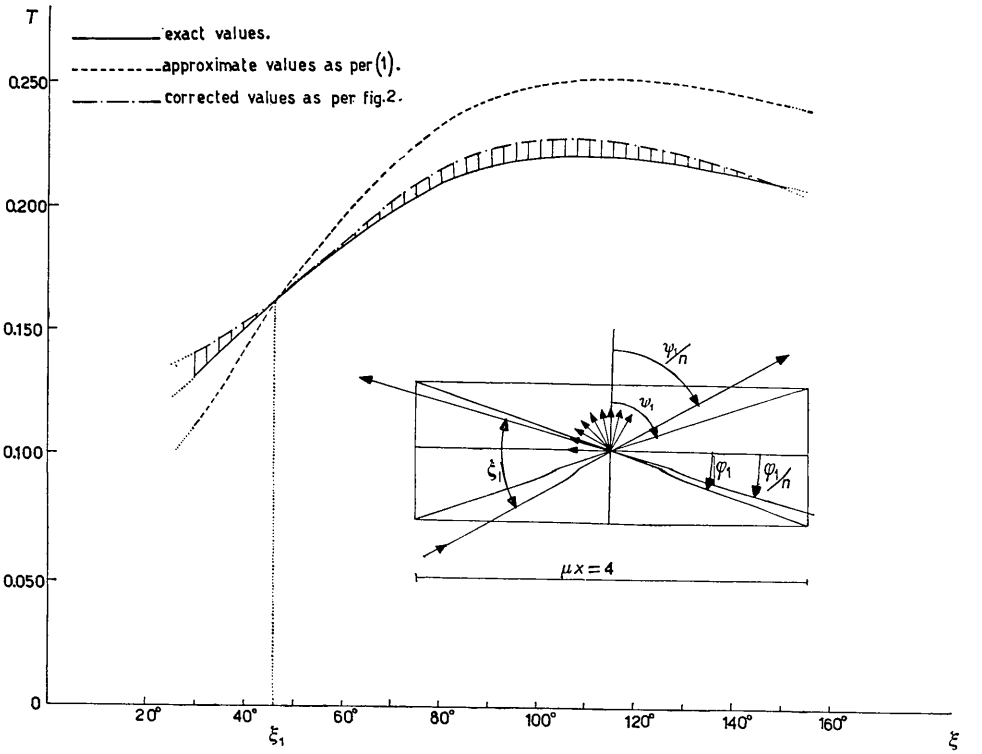


Fig. 5. Transmission values for a rectangular section as a function of ξ.

(*b*) *Analytical integration*

Table 1 lists the solutions of the single integrals in (1) for common crystal shapes.

Medium absorbing crystals

The method may be applied successfully to crystals of medium absorbing power if their cross-section is a parallelogram, for a correction of the approximation errors is then possible.

Whatever be the cross-section of the crystal, there always exist several pairs of directions for which the transmission value is independent of the direction of the incident and emergent rays. In a crystal with circular cross-section these pairs of directions, which we call 'conjugate', occur at right angles. In a crystal of any other cross-section, the angles between the incident and the emergent 'conjugate' rays varies with the cross-section and with the position of the rays with respect to the section. For a parallelogram section the pairs of conjugate rays may easily be found by the following rule. Define the angles ψ_1, ψ_2, φ_1 and φ_2 as in Fig. 3. If the direction of the incident ray lies in the ψ_1 angle, forming with the origin side of ψ_1 the angle $\psi_1/n (1 \leq n \leq \infty)$, the conjugate emergent ray forms with the origin side of φ_1 the angle φ_1/n. If the incident ray forms with the origin side of ψ_2 the angle ψ_2/n, the conjugate emergent ray forms with the origin side of φ_2 the angle φ_2/n and so on.

For conjugate rays traversing parallelogram sections we have empirically ascertained that formula (1) gives either exact or almost exact results. When $n = \infty$, the incident ray and the conjugate emergent ray are parallel to the two adjacent sides of the parallelogram, and it is evident that in this case formula (1) is exact. When $n = 1$, the conjugate rays are parallel to the two diagonals. Fig. 4 shows that in this case the error of formula (1) is very small up to $\mu x = 6$. Fig. 5 shows that, with an arbitrary direction of the incident ray—in other words with an arbitrary value of n—formula (1) gives almost exact results if the angle between the incident and the emergent ray is 45°. For all non-conjugate ray pairs formula (1) gives a value intermediate between the two exact ones which could be obtained by changing the path of either the emergent or the incident ray (see Figs. 2 and 8). The more the angle between the experimental rays differs from that between the conjugate rays, the bigger the approximation error.

We have therefore devised an empirical nomogram (Fig. 6) which enables us to determine quickly the approximate correction $\pm\Delta T$ as a function of ξ/ξ_1, where ξ is the angle between the two experimental rays $(180-2\theta)$ and ξ_1 the angle between the most

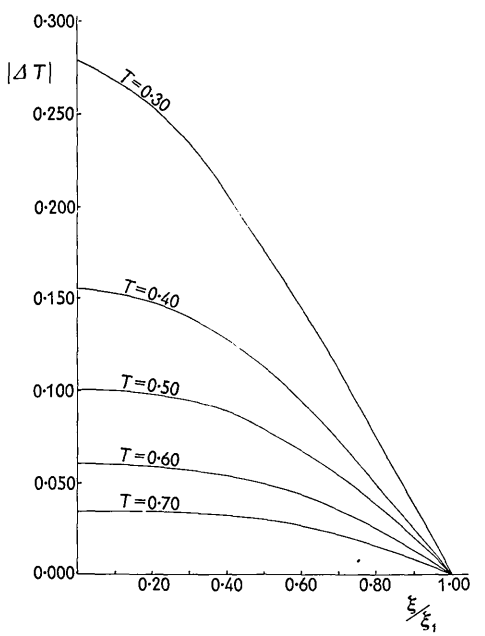


Fig. 6. Corrections $\pm|\Delta T|$ to be applied to various values of T determinated with equation (1) as a function of ξ and ξ_1.

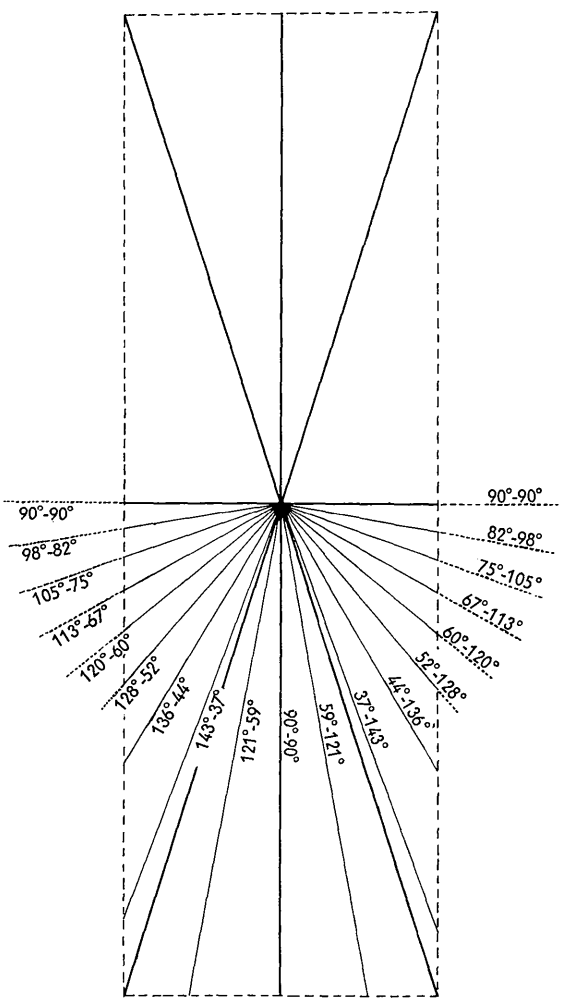


Fig. 7. Graph for reading the angle ξ_1 related to every direction on the section of the crystal.

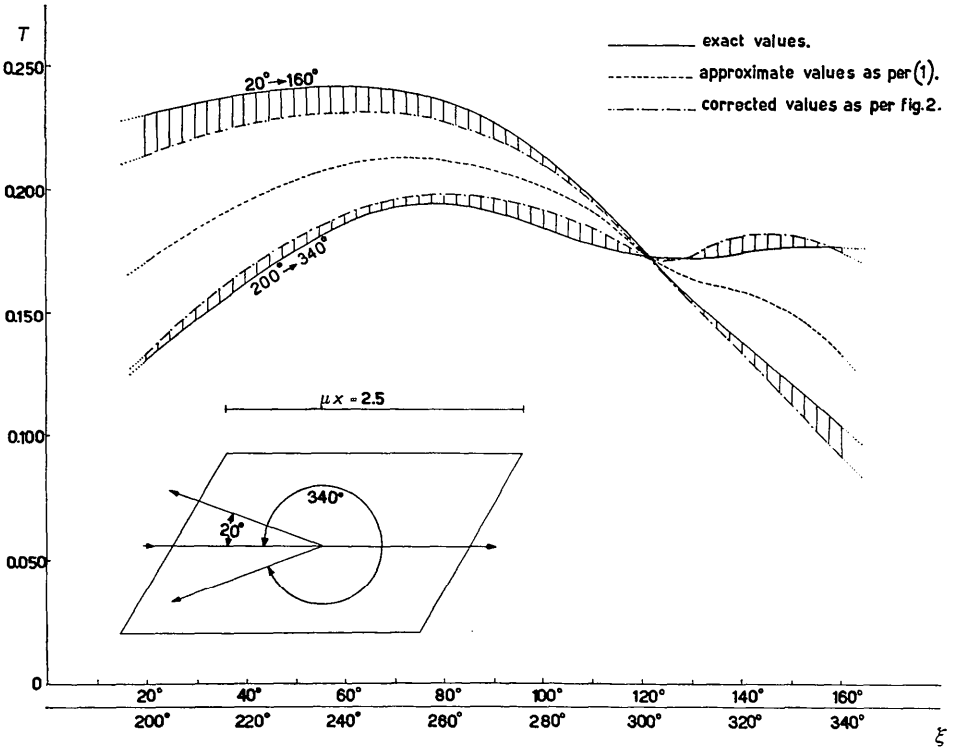


Fig. 8. Variation of the transmission of a crystal with a parallelogram section.

absorbing experimental ray and its conjugate ray. (Angles ξ_1 and ξ must contain the same semi-axis.) If $\xi < \xi_1$, the correction has the positive sign, if $\xi > \xi_1$ the correction has the negative sign; in this last case the abscissa must be determined by means of the supplements of the above angles. Equation (3) with correction then becomes:
either

$$T_{(hkl)} \simeq T_a . (T_b \pm \Delta T) \qquad (4)$$

or

$$T_{(hkl)} \simeq (T_a \pm \Delta T) . T_b .$$

The approximate determination of ξ_1 can be quickly performed by means of a diagram like that shown in Fig. 7. The angles ξ_1 are shown on some rays in the section which are directed radially from the centre. The first number refers to the angle between the ray and its conjugate measured in a clockwise direction, and the second refers to the angle ξ_1 measured in an anticlockwise direction. The position of the experimental ray with the smaller transmission may be recognised from Fig. 7. The value of ξ_1 is obtained by interpolation between either the first set of numbers when the angle between the above experimental ray and the other ray is in the clockwise direction, or between the second set of numbers when the angle ξ_1 is in the anticlockwise direction.

Figs. 5 and 8 compare the exact values of the transmission with the transmission calculated from (2) and the values after correction with the help of the nomogram of Fig. 6.

Rogers & Moffett state that 'if, for weakly absorbing crystals, the cross-section is fairly regular, the variation of A (absorption) throughout most of reciprocal space is smooth and slight. Sufficiently accurate values can therefore often be obtained by evaluating A at a few reciprocal-lattice points'. We have ascertained that this simplification may also be used when one dimension of the crystal is noticeably different from the other, provided that the interpolation is made on graphs of the transmission of reflections with two indices in common.

'La Gazzetta chimica italiana' will publish full details of this method and its application.

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