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THE CORRECTION FOR ABSORPTION FOR ROD-SHAPED SINGLE CRYSTALS

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Abstract

There is a simple relation between the forms of the transmission factors for upper levels and the zero levels for rod-shaped specimens. When the equi-inclination technique is used, the several ray paths for a given Υ have lengths x_j for the zero level, while the ray paths for the upper level at the same Υ are $x_j/\cos\nu$. If the form of the transmission factor for the zero level is known, the form for the upper level is therefore the same for the same value of Υ, except that the geometrical scale of the cross-section is increased by the factor $1/\cos\nu$. The resulting correction for absorption for all levels is especially easy to apply if the cross-section of the crystal is circular.

Introduction

If a material has a linear absorption coefficient μ_l, then, after traversing a path of length x, a beam of original intensity I_0 is reduced[1] to

$$I = I_0 e^{-\mu_l x}. \tag{1}$$

If the crystal has a shape such that the various paths have different lengths, x, then (1) must be integrated over the volume of the crystal.

The transmission factor is defined as the ratio of the intensity which is diffracted by the specimen to the intensity which would be diffracted if the specimen had no absorption. Let K be the fraction of the intensity of the direct beam diffracted by a crystal in a particular spectrum. Then the transmission factor for that spectrum is

$$\begin{aligned} T &= \frac{KI}{KI_0} \\ &= \frac{\int^V I dV}{\int^V I_0 dV} \\ &= \frac{\int^V e^{-\mu_l x} dV}{V}. \end{aligned} \tag{2}$$

What is termed the transmission factor here is ordinarily called the

[1] M. J. Buerger. X-ray crystallography. John Wiley and Sons, New York, (1942) 181–182.

"absorption" factor. But, as Joel et al.[2] have pointed out, that usage is confusing. The fraction transmitted is I/I_0, whereas the fraction absorbed is its complement $(I_0-I)/I_0$.

Claasen,[3] and later Bradley,[4] solved (2) for cylindrical samples by graphical integration. As a result, the transmission factor for cylindrical samples is available[4,9] tabulated as a function of the Bragg angle θ and the product $\mu_l R$, where R is the radius of the cylinder. Evidently the transmission factor for a single crystal which has been ground to circular cylindrical form can be treated in the same way[3–8] provided that the correction is required only for reflections from planes parallel to the cylinder axis, and provided that the incident x-ray beam is normal to the cylinder axis. But this corresponds to correcting only the zero level for normal-beam or equi-inclination techniques.

Transmission Factors for the General Case

Fig. 1 shows a cross-section of a crystal ground to circular cross-section. The path of the primary ray to the element of volume dV is x_1, and the path of the diffracted ray from the element of volume is x_2. From this point of view (2) can be written

$$T = \frac{1}{V}\int^{V} e^{-(\mu_l x_1+\mu_l x_2)}dV. \tag{3}$$

In the general case, Fig. 2, the primary ray makes an angle μ, and the diffracted ray makes an angle ν, with a plane normal to the cylinder axis. The diffracted ray is more completely defined by cylindrical direction coordinates ν (the angular component in the plane of the cylinder axis)

[2] N. Joel, R. Vera, and I. Garaycochea. A method for the estimation of transmission factors in crystals of uniform cross section. *Acta Cryst.*, 6 (1953) 365–468.

[3] A. Claassen. The calculation of absorption in x-ray powder photographs and the scattering power of tungsten. *Phil. Mag.* (7) 9 (1930) 57–65.

[4] A. J. Bradley. The absorption factor for the powder and rotating-crystal methods of x-ray crystal analysis. *Proc. Phys. Soc.*, **47** (1935) 879–899.

[5] H. Kersten and W. Lange. Method of preparing crystals for rotation photographs. *Rev. Sci. Instr.* (**12**) 3 (1932) 790–791.

[6] C. A. Beevers and W. Hughes. The crystal structure of Rochelle salt (sodium potassium tartrate tetrahydrate, $NaKC_4H_9O_6 \cdot 4H_2O$. *Proc. Roy. Soc., London* (A) **177** (1941) 251–259.

[7] Ray Pepinsky. Method of cutting and shaping fragile crystals. *Rev. Sci. Instr.*, **24** (1953) 403.

[8] F. Barbieri and J. Durand. Method of cutting cylindrical crystals. *Rev. Sci. Instr.*, **27** (1956) 871–872.

[9] C. Hermann. Internationale Tebellen zur Bestimmung von Kristallstrukturen, Vol. II. Gebrüder Borntraeger, Berlin, (1935) 584.

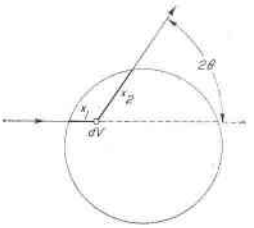

FIG. 1. Crystal ground to a circular cross-section.

and Υ (the angular component in a plane normal to the cylinder axis). Both μ and ν are setting coordinates for any method involving a rotating crystal; Υ is a setting coordinate for a quantum-counter apparatus,[10] also is the coordinate on the Weissenberg film normal to the center line of the film. Now, if one compares the situation for a general level at a value of Υ equal to the 2θ of Fig. 1, it is evident that for the general case, the path x_1 is replaced by $x_1/\cos\mu$ and the path x_2 is replaced by the path $x_2/\cos\nu$. Therefore the transmission factor for the upper level for this reflection has the form similar to equation (3), namely

$$T = \frac{1}{V}\int^{V} e^{-(\mu_l x_1/\cos\mu + \mu_l x_2/\cos\nu)}dV. \tag{4}$$

The integration is equivalent to an integration of x_1 and x_2 over segments of two ellipses, respectively, and then integrating over a change of location of the join of the ellipses.

ABSORPTION FACTORS FOR EQUI-INCLINATION AND ANTI-EQUI-INCLINATION

Relation (4) has a simple solution when $\nu = -\mu$ (equi-inclination, general level) or when $\nu = +\mu$ (anti-equi-inclination, zero level only). In these cases

$$\begin{aligned} T &= \frac{1}{V}\int^{V} e^{-(\mu_l x_1 + \mu_l x_2)/\cos\nu}dV. \\ &= \frac{1}{V}\int^{V} e^{-\mu_l x/\cos\nu}dV. \end{aligned} \tag{5}$$

This is exactly the same as (2) except that every ray path is increased by the factor $1/\cos\nu$.

[10] M. J. Buerger. New single-crystal counter-tube technique. *Acta Cryst.*, **9** (1956) 834.

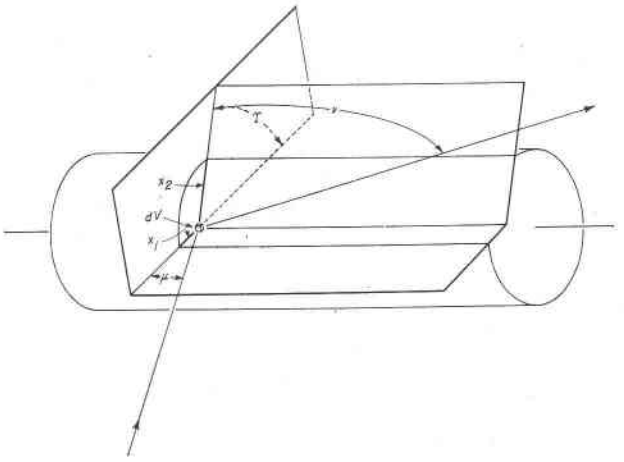

FIG. 2. General case: primary ray makes an angle μ, and the diffracted ray makes an angle ν, with the plane normal to the cylinder axis.

To correct the upper-level equi-inclination reflection for absorption, therefore, one applies the same correction that would be applied at the same value of Υ for the zero level (where $\Upsilon = 2\theta$), except that it should not be looked up under the value of R, but rather $R/\cos\nu$.

This analysis neglects an end effect (for which there is less absorption) for the ends of the cylinder in Fig. 2. This end effect is negligible if the length-to-diameter ratio of the cylinder is large. (If the absolute length of the cylinder is so large that the ends are not in the x-ray beam, then there is no end effect, but there must be a correction for the volume intercepted by the beam. This is proportional to $1/\cos\nu$, so that the "integrated intensity" must be corrected by $\cos\nu$ if the x-ray beam does not bathe the full length of the cylinder.)

EXTENSION TO RODS OF NON-CIRCULAR CROSS-SECTION

If the zero-level transmission factor is found for any rod-shaped specimen of uniform cross-section, it follows from the above discussion that the transmission factor for the upper levels is the same as that of the zero level for the same value of Υ, except that the scale of the cross-section (or else the absorption coefficient) must be regarded as increased by the factor $1/\cos\nu$, provided equi-inclination is used. The simplicity of the absorption correction for equi-inclination provides one more reason for using that technique whenever possible.

Example

To illustrate the importance of making a correction for absorption in data taken from upper levels, an example is given here of the computation of the correction and its application: Three-dimensional data were obtained from a small crystal of wollastonite. The average diameter was 0.0076 cm. The linear absorption coefficient, calculated as outlined elsewhere,[1] is $\mu_l = 215$ cm.$^{-1}$ for CuKα. Thus $\mu_l R = 0.81$. Table 1 shows the computation of the transmission factor. For each level there is derived a

Table 1. Calculation of Correction for Absorption for Rod-Shaped Crystal of Wollastonite

($\mu_l = 215$ cm.$^{-1}$ for CuKα; Radius, $R = .0038$ cm)

	Transmission factor, T								
Υ	level:	0	1	2	3	4	5	6	7	8
	ν:	0°	6°03′	12°10′	18°25′	24°55′	31°47′	39°12′	47°31′	57°26′
	cos ν:	1	.994	.978	.949	.907	.850	.775	.675	.538
	$\mu_l R/\cos \nu$:	.81	.815	.828	.853	.893	.954	1.045	1.20	1.505
0		.264	.262	.257	.248	.233	.213	.185	.146	.088
45°		.274	.272	.267	.258	.243	.224	.198	.160	.103
90°		.302	.300	.295	.287	.273	.255	.230	.195	.141
135°		.334	.332	.328	.320	.307	.291	.268	.235	.181
180°		.353	.351	.347	.339	.326	.308	.285	.251	.199

[11] N. Niizeki and M. J. Buerger. The crystal structure of livingstonite, $HgSb_2S_8$. *Zeit. Krist.*, **109**, 129–157 (1957).

value of $\mu_l R/\cos \nu$. For each of these values, the transmission factor is found by interpolation from the corresponding value of $\mu_l R$ in standard tables.[4,9] To make actual use of these sample values of the transmission, they should be plotted and connected by curves as shown in Fig. 3. Then the transmission factor T for any reflection on any level can be read when the value of Υ for the reflection is known. Since this is a Weissenberg coordinate, and also a setting coordinate for the single-crystal Geiger-counter instrument[10] the value is known for each reflection.

Fig. 3 brings out the importance of making appropriate corrections for absorption in upper-level intensity data. The transmission factors for the higher levels differ so widely from those of the zero level that only a poor residual factor, R, can be expected if the zero-level correction is applied to all levels.[11] The crystal in the example is about as small as can be handled conveniently, yet the transmission factor falls in the range 8% to 35% for CuKα radiation. For MoKα, the value $\mu_l R$ is of the order of only 10% of that for CuKα, and the corresponding transmissions are in the range 90%–100%.

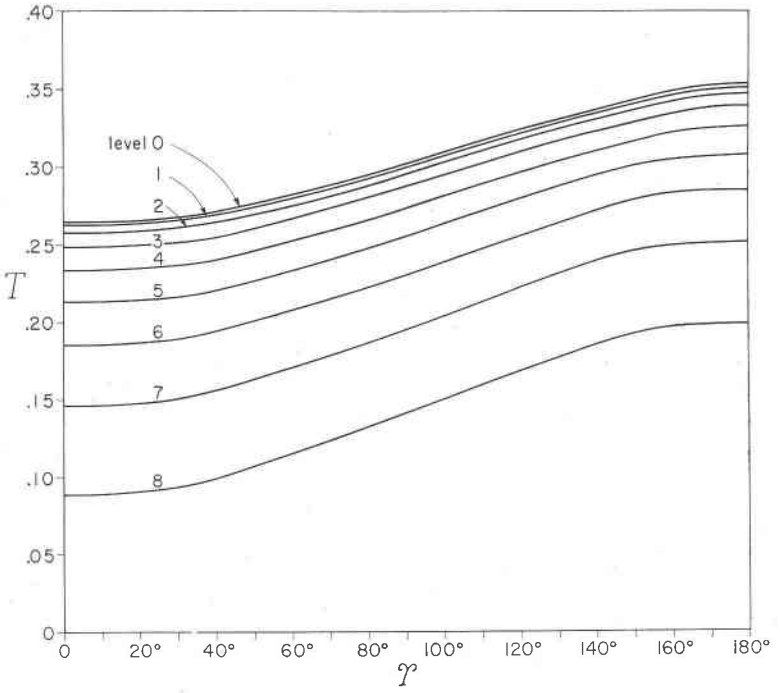

FIG. 3. Transmission factor T plotted against values of τ for various levels.

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