

The criterion for the applicability of this limit is that the width of the Bragg resonance be large compared with the Bragg angle:

$$\left| \frac{2V_h}{\hbar^2 k_{||}^2 / 2m} \right| = \frac{\Delta\theta_B}{\theta_B} \gg 1.$$

For neutrons, $\Delta\theta_B/\theta_B$ is actually very small; consequently the angular structure is controlled by Bragg angles. For protons and α particles, on the other hand, $\Delta\theta_B/\theta_B$ is of the order of 10^3 , so that the limiting form is very closely approached. This form agrees quite well with the observed α -particle emission patterns and appears to be the proper classical limit for this problem.

In order to carry out the above investigations within the framework of the dynamical theory, it was necessary to employ computer solution of the basic matrix equations [cf. equations (2) and (3)]. However, our results strongly suggest that one should be able to treat the approach to the classical limit of particle motion in crystals within a relatively simple analytical framework. We are currently working to develop such a treatment, which then can be directly applied to the design and interpretation of experiments made with the heavier mass charged particles.

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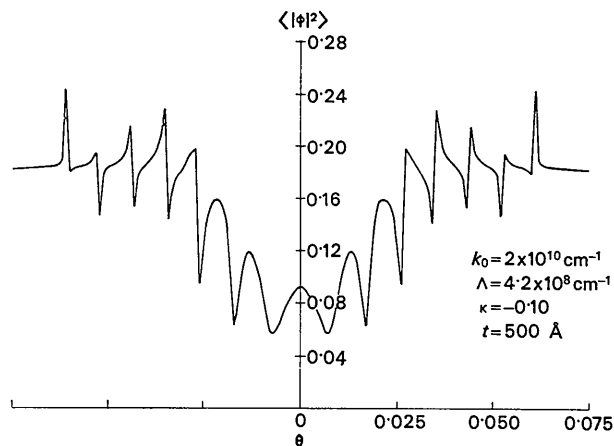


Fig. 9. Angular intensity variation for the positron. Ten-wave solution with attenuation.

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Experimental Tests of the General Formula for the Integrated Intensity of a Real Crystal

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The new formula for the integrated intensity of a real crystal has been tested experimentally with small crystal spheres of hambergite and of α quartz, and Mo $K\alpha$ as well as Cu $K\alpha$ radiation. Although both materials show very large extinction effects, excellent agreement is obtained between theory and experiment. Discrepancies between predicted and observed integrated intensities seem to be due to inadequately known atomic scattering powers and to experimental errors rather than to a failure of the theoretical formula. The mean radius of the perfect crystal domain was found to be 1.98×10^{-4} cm for the hambergite sphere and 0.47×10^{-4} cm for the quartz sphere.

Introduction

A new general formula for the integrated intensity, \mathcal{P} , of a real crystal was recently reported (Zachariasen, 1967*a,b*). It was hoped that this new intensity expression would be valid over the entire range from the ideally imperfect to the perfect crystal, and thus provide for significant improvement in the accuracy of experimental determinations of electron distributions, atomic scattering powers, and of the positional and thermal

parameters of the structure. However, in order to obtain even approximate solutions of the basic equations it was necessary to introduce a number of simplifications in the course of the derivation of the intensity formula. It is accordingly highly desirable to explore the validity of the approximations by comparisons with experiment for an assortment of crystal specimens. This paper gives the results of such tests for two crystals with large extinction effects, namely hambergite ($\text{Be}_2\text{BO}_3\text{OH}$) and α quartz.

Discussion of the intensity formula

The derivation of the intensity formula was based on Darwin's (1922) mosaic model of a real crystal. It was assumed that the perfect crystal domains, *i.e.* the mosaic blocks, were of roughly spherical shape with a mean radius, r , and that the orientations of the domains obeyed a Gaussian distribution law $W(A) = \sqrt{2g} \exp(-2\pi^2 g^2 A^2)$. In this manner the real crystal is characterized by only two parameters r and g . The assumed isotropy as to shape and orientation of the domains of this simple model may not be justified for some crystal specimens.

The integrated intensity does depend upon the shape of the crystal specimen even when ordinary absorption is negligible. The detailed intensity expression was developed for a crystal sphere of radius R completely immersed in the incident beam. If $r \ll R$, the intensity formula for a sphere with small or moderate absorption is

$$\begin{aligned} \mathcal{P} &= \mathcal{P}_c y = \mathcal{P}_c [1 + 2x]^{-\frac{1}{2}}, \\ \mathcal{P}_c &= \mathcal{I}_0 Q_0 Q_1 v A, \\ x &= (p_2/p_1) Q_0 \lambda^{-1} \bar{T} r^*, \\ Q_0 \lambda^{-1} &= |e^2 \lambda F_c / mc^2 V|^2 / \sin 2\theta, \\ p_n &= [1 + \cos^2 n 2\theta] / 2 \\ \bar{T} &= R A d A^* / d(\mu R) \\ r^* &= r [1 + (r/\lambda g)^2]^{-\frac{1}{2}}. \end{aligned} \quad (1)$$

\mathcal{I}_0 is the incident intensity, v the volume of the specimen, $A(\mu R)$ the transmission factor, $A^* = A^{-1}$ the absorption factor, while the other symbols have their usual meanings. Equation (1) assumes that the incident beam is unpolarized, and that the intensity is measured in the plane of incidence.

The extinction correction (which is $y = [1 + 2x]^{-\frac{1}{2}}$ for intensities) may be applied either to the 'calculated' structure factors $|F_c|$ or to the 'observed' structure factors $|F_o|$. In the former case one has

$$|F_o| = K |F_c| [1 + 2x]^{-\frac{1}{2}} \quad (2)$$

where K is the scale factor, and in the latter case

$$|F_c| = K^{-1} |F_o| \sqrt{x^* + \sqrt{1 + x^{*2}}} \quad (3)$$

where x^* is the value of x corresponding to a replacement of $|F_c|$ by $K^{-1} |F_o|$. The relationship between x and x^* is thus $x^* = x / \sqrt{1 + 2x}$.

The quantity x^* can be expressed in terms of \mathcal{P} instead of $|F_o|$ as follows

$$\begin{aligned} x^* &= C \beta \mathcal{P}, \\ \beta &= (p_2/p_1^2) d A^* / d(\mu R), \\ C &= (\mathcal{I}_0 v \lambda)^{-1} R r^*. \end{aligned} \quad (4)$$

The empirical correction formula (Zachariasen, 1963)

$$|F_c| \approx K^{-1} |F_o| [1 + C^1 \beta \mathcal{P}] \quad (5)$$

has been used with considerable success for crystals with high extinction. Since $\sqrt{x^* + \sqrt{1 + x^{*2}}} = 1 + \frac{1}{2}x^* + \frac{1}{8}x^{*2} - \frac{1}{16}x^{*3} + \dots$, it is seen that equation (5) is a good approximation to equation (3) for values $x^* \leq 2$.

Suppose that all structural parameters are known with high precision. The scale factor K for a given set of experimental $|F_o|$ values can be found from the weak reflections for which $x \neq 0$. Equation (2) can then be used to determine r^* from the strong reflections.

If the structure of the crystal is not known with sufficient accuracy, it becomes necessary to carry out least-square refinements based on equation (2) or on equation (3) with r^* as an additional parameter to be varied.

In order to find both quantities r and g characteristic of the crystal specimen independent determinations of the parameter r^* for two different wave lengths are needed. If r_1^* and r_2^* are the two values so obtained, one has

$$\left. \begin{aligned} r &= r_1^* r_2^* \sqrt{(\lambda_1^2 - \lambda_2^2) / (\lambda_1^2 r_2^{*2} - \lambda_2^2 r_1^{*2})}, \\ g &= (r_1^* r_2^* / \lambda_1 \lambda_2) \sqrt{(\lambda_1^2 - \lambda_2^2) / (r_1^{*2} - r_2^{*2})}, \end{aligned} \right\} \quad (6)$$

and it is seen that the ratio r_1^*/r_2^* must lie between the theoretical limits of λ_1/λ_2 and unity.

It is convenient to consider two special cases: type I crystals for which $r\lambda^{-1} \gg g$ (for both wavelengths employed, and type II crystals with $r\lambda^{-1} \ll g$. In type I crystals $r^* \approx \lambda g$ and in type II crystals $r^* \approx r$. In the former case one has thus $r_1^*/r_2^* = \lambda_1/\lambda_2$, and r cannot be determined beyond the qualitative statement $r \gg \lambda g$. In the latter case $r \approx r_1^* \approx r_2^*$ and $g \gg r\lambda^{-1}$.

Previous theoretical treatments of extinction have been valid only in the range $x \ll 1$ and have tacitly assumed the crystals to be of type I.

It should be remembered that both the observed set $|F_o|$ and the calculated set $|F_c|$ are inaccurate, the observed set because of experimental errors, the calculated set because of 'theoretical' errors. The greatest source of error in the $|F_c|$ values is due to the use of atomic scattering powers which have been calculated for atoms in free space with spherical symmetrical electron distribution. At small values of $\sin \theta/\lambda$ the errors in the $|F_c|$ values are probably greater than those in the $|F_o|$ values.

The expression $y = [1 + 2x]^{-\frac{1}{2}}$ for the extinction factor is an approximation. Although it is the theoretically preferable formula two other functional forms, *viz.* $y = \tanh \sqrt{3x}/\sqrt{3x}$ and $y = \tan^{-1} \sqrt{3x}/\sqrt{3x}$ have been proposed for consideration (Zachariasen, 1967a, b).

It is useful to discuss the variation of the extinction parameter x as function of the experimental conditions.

Since $x \propto R$ one should use a small sphere to reduce extinction effect. However, there is a practical power limit of about $R = 10^{-2}$ cm. The longer grinding needed to produce a smaller sphere can be expected to increase the imperfection in the specimen, thus to reduce r^* and lower x still further.

The greatest extinction effects occur at low scattering angles and hence one has $\sin 2\theta \propto \lambda$. Accordingly

$x \propto \lambda^2$ for type I and $x \propto \lambda$ for type II crystals, and the extinction will decrease with the wavelength. It should be remembered, however, that one needs to use two different wavelengths to determine both r and g .

The value of the quantity $Q\lambda^{-1}$ (for $\lambda=1 \text{ \AA}$) for the strongest reflections of a specimen is of the order of 10^6 cm^{-2} for crystals with simple structures, but will in general decrease with increasing complexity of the structure. Hence, for given R and r^* the extinction effects are generally greater for the simpler structures.

For $\lambda=1 \text{ \AA}$ and $R=10^{-2} \text{ cm}$ one must have $r^* \leq 10^{-6} \text{ cm}$ if extinction is to be negligible for a simple structure. This requires either $r \leq 10^{-6} \text{ cm}$ or $g \leq 10^2$. Conversely, extinction effects will be very severe ($x > 1$) if $r > 5 \times 10^{-5} \text{ cm}$ and simultaneously $g > 5 \times 10^3$.

Hambergite

A refinement of the hambergite structure to an R value of 0.040 using a sphere of radius $R=3.14 \times 10^{-2} \text{ cm}$ and Cu $K\alpha$ radiation was reported some years ago (Zachariassen, 1963; Zachariassen, Plettinger & Marezio, 1963). Extinction effects were very great (y values down to 0.246), but corrections were made successfully with the aid of the approximate formula of equation (5). The f curves for neutral atoms given in *International Tables for X-Ray Crystallography* were used.

Although the relationship $y=[1+2x]^{-2}$ is preferred theoretically, two other forms $y=\tanh \sqrt{3x}/\sqrt{3x}$ (case A) and $y=\tan^{-1} \sqrt{3x}/\sqrt{3x}$ (case B) have been suggested. It is useful to investigate which of the three forms is

Table 1. r^* values for large hambergite sphere

HK0	$ F_\sigma $	$ F_c $	y	$r^* \times 10^4 \text{ cm}$		
				Equation (2)	Case A	Case B
230	44.2	89.1	0.246	1.77	1.26	2.44
220	38.5	74.2	0.270	1.68	1.20	2.38
410	42.6	74.6	0.326	1.87	1.38	2.45
040	30.9	48.9	0.400	1.65	1.30	2.11
210	24.0	36.7	0.429	1.98	1.56	2.48
660	41.7	61.8	0.457	1.88	1.52	2.36
450	42.4	62.4	0.463	1.63	1.30	2.02
670	41.8	60.8	0.472	1.80	1.44	2.22
080	38.8	56.1	0.480	2.00	1.61	2.46
440	33.5	44.5	0.565	1.76	1.47	2.05
Mean				1.80	1.40	2.30

avored by experiment. Clearly, that functional dependence of y on x which makes r^* independent of y should be selected. Table 1 lists the y values for the ten strongest (HK0) reflections of hambergite and the r^* values obtained from equation (2) and for cases A and B. (The $|F_\sigma|$ and $|F_c|$ values are the same as given in the 1963 paper except for normalization to $K=1$ for the unit cell containing eight molecules.) It is seen that the r^* values for case A tend to decrease with y , with the reverse trend for case B, while equation (2) gives the most satisfactory results. In the following the validity of equations (1) and (2) will accordingly be assumed, although case B cannot be ruled out.

Observations with other wavelengths were not made on the hambergite sphere used in the 1963 study, and the sphere has been lost.

A second sphere of radius $R=2.00 \times 10^{-2} \text{ cm}$ was ground from another fragment of the original hambergite crystal, and the intensities of all reflections (HK0) with $\sin \theta/\lambda < 0.6$ were measured both with Cu $K\alpha$ and with Mo $K\alpha$ radiation. The resulting $|F_\sigma|$'s (scaled to $K=1$ with the aid of the very weakest reflections) for the ten strongest reflections are shown in Table 2 together with the corresponding y values and the r^* values as obtained from equation (2).

The two r^* values of $1.54 \times 10^{-4} \text{ cm}$ for Cu $K\alpha$ and of $0.98 \times 10^{-4} \text{ cm}$ for Mo $K\alpha$ substituted in equations (6) give

$$r = 1.98 \times 10^{-4} \text{ cm}, \quad g = 1.59 \times 10^4.$$

It is seen that the y values are smaller for the second crystal sphere. This is first of all due to the decrease in R from 3.14 to $2.00 \times 10^{-2} \text{ cm}$, and, secondly, to the reduction in r_1^* from 1.80 to $1.54 \times 10^{-4} \text{ cm}$, probably caused by the additional grinding needed to produce a smaller sphere.

α quartz

A refinement of the α -quartz structure was recently reported from this laboratory (Zachariassen & Plettinger, 1965). The sample was a sphere of radius $R=1.47 \times 10^{-2} \text{ cm}$, the radiation was Cu $K\alpha$, and equation (5) was used for the extinction correction. The imaginary part of the anomalous dispersion correction was ef-

Table 2. r^* values for small hambergite sphere

HK0	$ F_\sigma $	$ F_c $	y		$r^* \times 10^4 \text{ cm}$		
			Cu	Mo	Cu	Mo	
230	89.1	50.4	64.9	0.320	0.530	1.53	0.86
220	74.2	45.6	55.4	0.378	0.557	1.19	0.88
410	74.6	49.5	60.5	0.440	0.658	1.87	0.82
040	48.9	34.3	41.8	0.492	0.731	1.51	0.98
210	36.7	27.2	32.0	0.550	0.550	1.55	0.98
660	61.8	46.3	54.3	0.561	0.772	1.59	1.25
450	62.4	47.4	55.3	0.577	0.785	1.31	0.81
670	60.8	45.7	54.0	0.565	0.789	1.62	1.22
080	56.1	43.0	49.9	0.588	0.791	1.66	1.09
440	44.5	36.1	41.2	0.658	0.857	1.58	0.89
Mean						1.54	0.98

fectively eliminated by basing the $|F_{\sigma}|$ values on the mean intensity measured for pairs of reflections (HKL) and ($\bar{H}\bar{K}\bar{L}$). The real part of the anomalous dispersion correction was neglected, and the f_0 values given in column 1 of Table 3 were used. A small correction was applied for the indicated presence of 1.5% of the sample in a Dauphiné twin position. The three strongest reflections were omitted from the refinement; all other observations were included and weighed equally.

Table 3. f_0 values

sin θ/λ	1		2	
	Si	O	Si	O
0.10	12.16	7.25	11.79	7.80
0.15	10.79	6.48	10.63	7.02
0.20	9.59	5.86	9.61	6.06
0.25	8.77	5.02	8.81	5.14
0.30	8.14	4.18	8.16	4.24
0.35	7.62	3.42	7.64	3.50
0.40	7.15	2.96	7.21	3.05
0.45	6.74	2.66	6.79	2.75
0.50	6.24	2.34	6.34	2.45
0.55	5.78	2.14	5.88	2.21
0.60	5.31	1.94	5.43	2.02
0.65	4.89	1.82	5.00	1.87
0.70	4.47	1.71	4.60	1.76
0.75	4.11	1.64	4.22	1.67
0.80	3.75	1.57	3.89	1.59

A new set of intensity measurements using the same crystal sphere has since been made with Mo $K\alpha$ radiation. Indeed, it was the apparent discrepancy between the two sets of data when interpreted in accordance with the old intensity formula and the tacit assumption of a type I crystal that led the writer to re-examine the theory of extinction. The molybdenum data include all the reflections measured with copper radiation and 33 additional reflections not accessible with the longer wave length. The small correction for Dauphiné twinning was again applied. The scale factor (adjusted to $K=1$ per unit cell) was determined from the very weakest reflections not affected by the twinning corrections.

Table 4 gives the $|F_{\sigma}|$ and $|F_{\sigma}|$ values of the 1965 paper and the $|F_{\sigma}|$'s obtained with molybdenum radiation for the eight strongest reflections, the corresponding y values and the r^* values calculated from equation (2). The mean values of $r^*=0.56 \times 10^{-4}$ cm for Cu $K\alpha$ and of $r^*=0.54 \times 10^{-4}$ cm for Mo $K\alpha$ are the same

within experimental error, showing that the quartz sphere under study is a type II crystal with

$$r=0.56 \times 10^{-4} \text{ cm}, \quad g \geq 0.8 \times 10^4.$$

In order to test the sensitivity of the results to changes in the f curves new refinements were carried out, independently for the Cu $K\alpha$ and Mo $K\alpha$ data, using the f_0 values shown in columns 2 of Table 3. Cromer's (1965) values of $\Delta'=0.23$ for Cu $K\alpha$, $\Delta'=0.09$ for Mo $K\alpha$ were adopted for the real part of the anomalous dispersion correction for silicon, while the correction for oxygen was neglected. The extinction correction was based on equation (3) with the parameter r^* adjusted by a trial and error procedure based on the strongest reflections.

Table 5. Parameter values for quartz ($\times 10^4$)

	1965	Cu	1967	Cu	1967	Mo
	value	σ	value	σ	value	σ
μ	4697	2	4697	2	4697	2
β_{11}	71	4	84	5	84	3
$\beta_{22}=2\beta_{12}$	59	5	76	6	71	4
β_{33}	40	2	49	3	43	2
$\beta_{23}=\beta_{13}$	-2	3	-4	4	-4	2
x	4125	4	4127	5	4141	4
y	2662	4	2661	5	2676	4
$x-y$	1463		1466		1465	
z	1188	2	1190	3	1188	2
β_{11}	179	10	192	12	196	9
β_{22}	139	8	148	10	152	8
β_{33}	87	5	95	6	85	4
β_{12}	106	8	110	10	113	7
β_{13}	-23	6	-28	8	-25	5
β_{23}	-37	5	-33	6	-41	4
R	0.018		0.019		0.019	

Table 5 gives the 1965 parameter values and those resulting from the new refinements which included all observations weighed equally.

The large σ values and the lack of perfect agreement between the copper and molybdenum data for the x and y parameters of oxygen are due to a strong correlation between these two coordinates (the correlation coefficient is 0.53). Presumably the molybdenum set is more reliable since the data extend to larger values of sin θ/λ .

The r^* values for the eight strongest reflections resulting from the new refinements are shown in Table 6.

Table 4. r^* values for quartz. Old f curves

HKL	$ F_{\sigma} $	$ F_{\sigma} $		y		$r^* \times 10^4$ cm	
		Cu	Mo	Cu	Mo	Cu	Mo
10 $\bar{1}$	39.31	22.40	25.19	0.325	0.411	0.52	0.49
101	25.66	17.86	19.46	0.484	0.575	0.47	0.48
203	30.48	23.03	24.87	0.571	0.666	0.54	0.54
100	16.11	12.11	13.19	0.565	0.670	0.60	0.58
30 $\bar{1}$	26.75	20.79	22.54	0.604	0.710	0.59	0.56
112	23.73	18.80	20.08	0.628	0.716	0.53	0.50
110	17.90	14.32	15.34	0.640	0.734	0.62	0.57
102	17.39	14.24	15.09	0.671	0.753	0.62	0.58
Mean						0.56	0.54

Table 6. r^* values for quartz. New f curves

HKL	Cu $K\alpha$				Mo $K\alpha$			
	$ F_\sigma $	F_c	y	$r^* \times 10^4$ cm	$ F_\sigma $	$ F_c $	y	$r^* \times 10^4$ cm
10 $\bar{1}$	23.38	40.09	0.339	0.46	25.90	39.72	0.426	0.45
101	18.64	26.19	0.506	0.40	20.02	25.91	0.599	0.41
203	24.04	30.95	0.605	0.44	25.58	30.67	0.695	0.46
100	12.64	16.17	0.613	0.46	13.56	16.23	0.698	0.49
30 $\bar{1}$	21.70	27.18	0.638	0.48	23.18	27.15	0.729	0.49
112	19.62	24.21	0.658	0.44	20.65	23.85	0.750	0.44
110	14.94	18.31	0.667	0.51	15.78	18.13	0.758	0.53
102	14.86	17.76	0.701	0.50	15.52	17.35	0.803	0.46
Mean				0.46				0.47

It is seen that the r^* values are lower than in Table 4. This is due to the change in f_0 curves and the corresponding changes in scale factors. The new values for r and g are

$$r = 0.46 \times 10^{-4} \text{ cm}, \quad g \geq 0.7 \times 10.$$

The data of Tables 4 and 6 show that the fluctuation of an individual r^* value from the mean usually has the same sign for the copper as for the molybdenum measurement. This suggests that the fluctuations [which imply discrepancies between the two sides of equation (2)] are not due to experimental errors. The discrepancies are most probably caused by departures from spherical symmetry in the electron distributions of the atoms associated with the bond formation.

The assumed isotropy for the shape and orientation of the domains seems to be justified both for hambergite and for quartz since there is no systematic variation of r^* with the orientation of the reflecting plane. However, both of these crystals have three-dimensional network structures.

It has been demonstrated that equation (1) gives excellent agreement for the spherical specimens of hambergite and quartz. Individual discrepancies between observed and calculated intensities seem to be due to experimental errors and to lack of precise knowledge of

atomic scattering powers rather than to the approximate form of the theoretical intensity formula.

The tacit assumption in all previous theoretical work on extinction that real crystals are of type I with $r \gg \lambda g$ is shown to be incorrect both for the hambergite and the quartz specimens, and it has been demonstrated that both r and g can be found experimentally if the intensities are measured with two different wavelengths.

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