$$\bar{P}_i \simeq I_0 v A(\mu_0)[Q_i + C_i g T]$$

where I_0 is the incident intensity, $v = ST$ (S the cross section of the incident beam) the irradiated volume and $A(\mu_0) = e^{-\mu_0 T}$ the absorption factor. C_i is the appropriate factor given in equations (1c)–(4c).

The approximate solutions for a crystal of arbitrary shape can be given in analogous form as

$$\bar{P}_i \simeq I_0 v A(\mu_0)[Q_i + C_i g \bar{T}] \tag{12}$$

where $\bar{T} = A \, dA^*/d\mu_0$, $A^* = A^{-1}$ being the appropriate absorption factor.

The specific expression of equation (12) for single diffraction (with polarization included) becomes

$$\bar{P}_1 \simeq I_0 v A \left[Q_1 p_1 - g Q_1^2 p_{11}(0) A \frac{dA^*}{d\mu_0} \right]. \tag{13}$$

Apart from a difference in notation this result is identical with equation (13) of a recent paper (Zachariasen 1963).

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Extinction in Quartz

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Extinction effects in a quartz sphere have been studied with the use of Cu $K\alpha$ radiation. It is shown that extinction varies with scattering angle in accordance with the modified rather than the Darwin formula for the extinction correction.

The data indicate that the quartz specimen contained 1·5 % of material in the Dauphiné twin position, and it is suggested that it may be difficult or impossible to find quartz crystals (natural or synthetic) entirely free of such twinning.

As a by-product of the extinction study all structural parameters of quartz were obtained with greater accuracy than hitherto reported and corresponding to $R = 0.02$.

Introduction

This investigation was undertaken to check experimentally the revised formula for the extinction correction. It was believed that quartz would be a suitable crystal for the purpose because of simple structure, great hardness and high extinction.

The study was carried out with Cu $K\alpha$ radiation and a carefully selected, seemingly flawless, natural crystal which had been ground into a nearly perfect sphere of radius $r = 0.147$ mm, corresponding to $\mu r = 1.35$.

In the course of the work unexpectedly large dispersion effects were observed, the intensities I_H and $I_{\bar{H}}$ differing by as much as fifty per cent for some weak reflections. For the purpose of the extinction study the dispersion effects were eliminated by neglecting the imaginary part of the dispersion corrections to the atomic scattering powers and by using the mean intensity $(I_H + I_{\bar{H}})/2$ to obtain the experimental structure factors. The observed differences $I_H - I_{\bar{H}}$ will be discussed and interpreted in the following paper.

The intensities were measured with a proportional counter to a precision of two per cent for the very weakest, one per cent or less for the strong reflections. Because of the high symmetry multiple diffraction is not uncommon, and special care was taken to avoid making the intensity measurements under such conditions.

Dauphiné twinning

According to the Dauphiné twinning law the (HKL) plane of one individual coincides with the $(HK\bar{L})$ plane of the other. Ratios $I_{HK\bar{L}}/I_{HKL}$ as low as 0·02 were observed for the pairs $10\bar{6}/106$ and $50\bar{2}/502$, and until the last stages of the investigation it was therefore believed that the specimen contained no twinned material. However, the observed structure factors for the weak components of pairs $HKL/HK\bar{L}$ were consistently larger than the calculated values. These discrepancies could not be removed by modifications of parameters, extinction or f curves; but they could be explained by the presence of a small amount of twinned material (assumed to be uniformly distributed throughout the medium for mathematical convenience).

A correction for Dauphiné twinning was accordingly applied. If I'_{HKL} and $I'_{HK\bar{L}}$ are the actually observed

values, the corrected intensities I_{HKL} and $I_{HK\bar{L}}$ are given as follows

$$I_{HKL} = I'_{HKL} + a(I'_{HKL} - I'_{HK\bar{L}})$$
$$I_{HK\bar{L}} = I'_{HK\bar{L}} - a(I'_{HKL} - I'_{HK\bar{L}})$$

(1)

where $a = y/(1-2y)$, y being the fraction of the sample in the twinned position. The best fit was obtained with $a = 0.015$.

The experimental data given in two recent papers on quartz by Young & Post (1962) and Smith & Alexander (1963) also indicate the presence of a small amount of Dauphiné twinning in their specimens, as was, indeed, suggested by Smith & Alexander. Thus, if the proposed explanation is correct, it would seem that it is difficult, if not impossible, to find quartz crystals entirely free of twinning.

Extinction

The first order correction for (secondary or primary) extinction can be given in the form (Zachariasen, 1963)

$$|F|_{\text{corr}} = |F|_{\text{obs}}[1 + C\beta I_{\text{obs}}]$$

(2a)

$$\beta = \frac{2(1+\cos^4 2\theta)}{(1+\cos^2 2\theta)^2} \cdot \frac{A^{*'}(2\theta)}{A^{*'}(0)},$$

(2b)

where $A^{*'} \equiv dA^*/d\mu$, A^* being the absorption factor.

An approximate value for the parameter C was readily found by comparing observed structure factor ratios for neighboring reflections with those calculated from Smith & Alexander's parameters. A least-squares refinement varying all other structure parameters was then made and a revised value for C obtained. A few repetitions of this process led to a stationary value for C.

At the end of the investigation, when presumably very precise values of $|F|_{\text{calc}}$ had been obtained, equation (2a) was solved for $C\beta$ on the assumption that $|F|_{\text{corr}} = |F|_{\text{calc}}$, and the results compared with the theoretical function of equation (2b). This comparison (using the data of Table 2 with $C = 1.65 \times 10^{-3}$) is shown in Fig. 1.
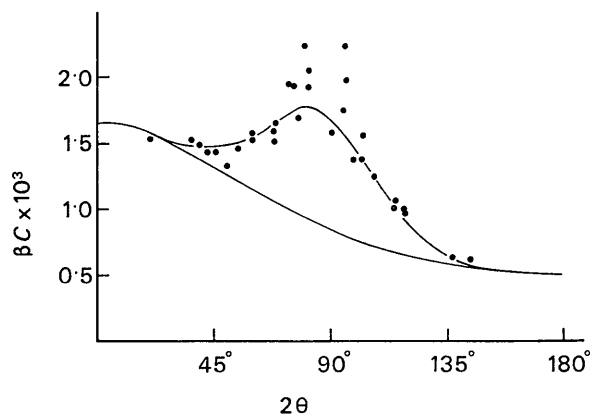

Fig. 1. Variation of βC with scattering angle. The lower curve gives the functional relation according to Darwin's formula, the upper curve according to equation (2). The experimental points are indicated by small circles.

The least-square refinements

The Busing–Levy IBM-704 least-squares refinement program was used, initially with the f curves for neutral atoms given in *International Tables for X-Ray Crystallography*. Slightly modified f curves were used in the last refinement. These adjustments were

$\sin \theta/\lambda$	0.20	0.25	0.30	0.35	0.40	0.45
Si	−0.08	−0.08	−0.08	−0.08	−0.05	−0.03
0	0.23	0.21	0.09	−0.07	−0.05	−0.01.

The structure factors for the three innermost reflections (100, 101, 10$\bar{1}$) were not used in the refinements because the extinction corrections were too large and the f values too uncertain. All other structure factors were included with unit weight.

The cell dimensions of quartz were assumed to be $a = 4.9128$, $c = 5.4042$ Å. The absolute atomic configuration according to the dispersion observations was 3Si in (1): $(u\,0\,0)$; (2): $(1-u, 1-u, \frac{1}{3})$; (3): $(0\,u\,\frac{2}{3})$6 0 in (1): (xyz); (2): $(y-x, \bar{x}, \frac{1}{3}+z)$; (3): $(1-y, x-y, z-\frac{1}{3})$; (4): $(x-y, \bar{y}, \bar{z})$; (5): $(1-x, y-x, \frac{1}{3}-z)$; (6): $(y, x, \frac{2}{3}-z)$.

Anisotropic temperature factor exponents $M = \mathbf{H} \cdot \boldsymbol{\beta} \cdot \mathbf{H}$, $\mathbf{H} = \Sigma H_j \mathbf{b}_j$, $\boldsymbol{\beta} = \Sigma\Sigma \beta_{jk} \mathbf{a}_j \mathbf{a}_k$ were used. Since the Si(1) atom lies on the twofold axis $\mathbf{a}_1$, the silicon tensor $\boldsymbol{\beta}$ must satisfy the condition $\boldsymbol{\beta} \cdot \mathbf{a}_1 || \mathbf{a}_1$, and this requires $2\beta_{12} = \beta_{22}$, $2\beta_{13} = \beta_{23}$. (In Smith & Alexander's paper $\beta_{12} = \beta_{23} = 0$, which is incorrect. It is not clear from Young & Post's article whether or not the proper conditions were imposed on the coefficients β_{12} and β_{23}).

Results

The parameter values resulting from the last two refinements are shown in Table 1 together with those obtained by Young & Post and Smith & Alexander. The figures in column I correspond to the ideal , those of column II to the modified f curves for neutral atoms.

Table 1. *Parameters* ($\times 10^4$)

	This study				Young & Post		Smith & Alexander	
	I		II					
Si	Value	σ	Value	σ	Value	σ	Value	σ
u	4696	2	4697	2	4705	3	4697	3
β_{11}	73	5	71	4	49	4	52	7
β_{22}	58	6	59	5	27	5	29	8
β_{33}	40	3	40	2	49	3	43	4
β_{12}	(29)		(29)		?		0	
β_{13}	(−1)		(−1)		−1	2	2	2
β_{23}	−1	4	−2	3	?		0	
O								
x	4126	6	4125	4	4152	7	4144	8
y	2663	5	2662	4	2678	6	2662	7
z	1190	3	1188	2	1184	4	1188	4
β_{11}	170	13	179	10	143	11	140	17
β_{22}	140	11	139	8	81	9	115	15
β_{33}	82	6	87	5	90	6	87	8
β_{12}	102	11	106	8	85	9	76	13
β_{13}	−19	8	−23	6	−32	7	−30	10
β_{23}	−32	7	−37	5	−42	5	−38	9
$R, \%$	2.3		1.8		8.1		3.6	

There are several sources of error in Young & Post's and Smith & Alexander's investigations: extinction was not treated properly, no correction was made for Dauphiné twinning, and an incorrect form may have been used for the silicon thermal vibration tensor. Smith & Alexander, who also used Cu $K\alpha$ radiation, made no reference to dispersion and possible errors due to this effect.

The complete set of data is given in Table 2. I' is the observed mean intensity $\frac{1}{2}(I_H + I_{\bar{H}})$, I the corrected value according to equation (1) and $|F|_{\mathrm{obs}}$ is the

Table 2. Structure factors

HKL	I'	I	$|F|_{\mathrm{obs}}$	$|F|_{\mathrm{corr}}$	$|F|_{\mathrm{calc}}$
100	214		12.11	16.16	16.11
101	563	560	17.86	27.67	25.60
10$\bar{1}$	564	567	22.40	41.91	39.21
110	164		14.32	17.84	17.90
102	147	149	14.24	17.55	17.39
10$\bar{2}$	45.1	45.6	7.70	8.12	8.25
111	57.0		8.89	9.64	9.50
200	138		14.26	17.15	17.09
201	31.7	32.4	11.50	12.90	12.85
20$\bar{1}$	39.5	33.8	7.90	8.34	8.35
112	198		18.90	24.31	23.75
003	40.04		8.54	9.04	8.71
202	363	35.0	8.32	8.76	8.91
20$\bar{2}$	120	121	15.42	18.23	18.15
103	2.77	2.73	1.86	1.86	1.56
10$\bar{3}$	71.7	72.7	12.04	13.36	13.60
210	8.67		4.23	4.29	3.80
211	96.8	96.6	14.49	16.63	16.62
21$\bar{1}$	109	109	15.43	18.00	18.10
113	49.7		10.76	11.62	11.23
300	26.7		7.99	8.34	8.25
212	43.4	42.5	10.23	10.94	10.64
21$\bar{2}$	105	106	16.18	18.96	18.98
203	212	214	23.03	31.00	30.48
20$\bar{3}$	82.2	80.2	14.10	15.91	15.90
301	4.77	2.27	2.37	2.38	1.51
30$\bar{1}$	171	174	20.79	26.61	26.75
104	94.6	95.5	15.84	18.43	18.30
10$\bar{4}$	35.7	34.8	9.53	10.07	10.02
302	108	109	17.08	20.30	20.70
30$\bar{2}$	58.6	57.9	12.47	13.73	13.99
220	94.5		16.03	18.70	18.61
213	71.5	72.2	14.10	15.94	16.38
21$\bar{3}$	23.9	23.2	7.99	8.32	8.17
221	31.7		9.35	9.89	10.02
114	80.8		14.95	17.13	17.28
310	86.4		15.46	17.86	18.20
311	19.8	19.4	7.35	7.60	7.71
31$\bar{1}$	49.2	49.6	11.73	12.74	13.09
204	21.4	21.7	7.76	8.06	8.01
20$\bar{4}$	0.85	0.54	1.22	1.23	1.39
222	1.33		1.93	1.96	1.69
303	19.4	19.6	7.37	7.61	7.53
30$\bar{3}$	2.98	2.73	2.75	2.76	2.68
312	36.9	36.3	9.98	10.61	10.44
31$\bar{2}$	77.0	77.6	14.59	16.49	16.52
400	46.1		11.18	12.01	12.14
105	38.4	37.6	10.01	10.60	10.52
10$\bar{5}$	88.6	89.4	15.44	17.63	17.86
401	73.0	73.9	14.02	15.66	16.34
40$\bar{1}$	11.3	10.3	5.26	5.35	5.12
214	64.3	65.2	13.10	14.39	14.78
21$\bar{4}$	5.01	4.13	3.29	3.32	3.04
223	62.7		12.67	13.84	13.76
402	3.30	2.91	2.68	2.68	2.81
40$\bar{2}$	29.5	29.9	8.56	8.90	8.87
115	49.6		10.99	11.75	11.84
313	16.9	16.8	6.39	6.53	6.54
31$\bar{3}$	21.6	21.7	7.26	7.48	7.34
304	14.6	14.4	5.85	5.97	5.82
30$\bar{4}$	28.5	28.7	8.26	8.57	8.54
320	39.9		9.75	10.26	10.30
205	0.32	0.21	0.70	0.70	0.55
20$\bar{5}$	7.57	7.68	4.20	4.24	4.14

Table 2 (cont.)

HKL	I'	I	$|F|_{\mathrm{obs}}$	$|F|_{\mathrm{corr}}$	$|F|_{\mathrm{calc}}$
321	1.70	1.41	1.85	1.87	1.54
32$\bar{1}$	94.5	9.7	17.07	15.47	15.46
410	8.73		5.72	5.75	5.71
322	9.7	9.2	8.30	9.25	9.35
32$\bar{2}$	4.80	2.4	2.79	2.80	2.45
40$\bar{3}$	97.0	98.	14.81	15.15	15.16
40$\bar{3}$	61.2	60.4	10.84	11.51	11.56
411	80.1	81.1	17.57	13.59	13.65
41$\bar{1}$	15.3	14.5	5.27	5.55	5.05
224	77.2		8.40	8.70	8.66
004	7.3		11.85	12.67	12.75
215	10.4	9.9	4.07	4.11	3.97
21$\bar{5}$	75.3	74.5	11.63	12.46	12.50
11$\bar{5}$	9.5	10.7	9.01	9.65	9.62
11$\bar{5}$	0.9	20.5	5.85	5.95	5.97
10$\bar{6}$	6.6	7.1	7.71	7.94	7.97
10$\bar{6}$	0.7	0.5	0.54	0.54	0.59
41$\bar{1}$	25.5	25.5	6.35	6.40	6.42
41$\bar{2}$	8.5	9.7	7.84	8.04	8.12
405	8.7	9.2	7.40	7.56	7.80
405	4.0	4.15	2.22	2.40	2.46
324	0.40	0.45	0.74	0.74	0.63
42$\bar{2}$	0.97	0.97	1.15	1.16	1.23
130	0.02		0.20	<0.20	0.04
116	30.5		6.11	6.24	6.25
501	3.05	2.67	1.77	1.78	1.80
50$\bar{1}$	73.5	73.9	5.83	5.95	5.99
404	1.21	0.76	0.90	0.92	0.87
40$\bar{4}$	31.0	31.4	5.91	6.03	6.02
306	66.5	64.2	3.16	8.50	8.61
20$\bar{6}$	21	25	15.20	17.33	17.36
413	22.0	20.1	4.46	4.52	4.52
41$\bar{3}$	152	156	12.44	13.63	13.49
330	125		10.71	11.51	11.20
502	299	303	15.85	18.62	18.82
50$\bar{2}$	6.30	1.91	1.25	1.27	1.33
225	90.4		8.61	9.06	9.03
331	86.9		8.34	8.76	8.62
420	162		10.86	11.88	11.78
315	49.7	48.9	5.53	5.68	5.76
31$\bar{5}$	94.4	95.2	7.71	8.13	8.00
421	25.7	25.4	3.93	3.99	3.92
42$\bar{1}$	54.6	55.0	5.78	5.96	6.05
324	64.7	60.9	5.77	5.95	6.17
32$\bar{4}$	314	319	13.15	15.44	15.19
216	25.5	23.6	3.31	3.36	3.42
21$\bar{6}$	149	151	8.59	9.07	8.87
332	8.5		1.91	1.92	1.92

corresponding structure factor. $|F|_{\mathrm{corr}}$ is obtained from $|F|_{\mathrm{obs}}$ using equation (2) with $C = 1.65 \times 10^{-3}$, and $|F|_{\mathrm{calc}}$ is the calculated structure factors based on the parameters of set II of Table 1.

The interatomic distances and bond angles are listed in Table 3. The σ values were 0.0001 Å for Si–Si, 0.002 Å for Si–O, 0.003 Å for O–O distances, and 0.04–0.09° for the bond angles.

Table 3. Interatomic distances and bond angles

Distances

Si(1)–O(1)	1·603 Å
Si(1)–O(3)	1·616 Å
O(1)–O(4)	2·604 Å
O(1)–O(3)	2·648 Å
O(1)–O(5)	2·618 Å
O(3)–O(5)	2·632 Å
Si(1)–Si(2)	3·0570 Å

Angles

Si(1)–O(1)–Si(2)	143·52°
O(1)–Si(1)–O(4)	108·63°
O(1)–Si(1)–O(3)	110·70°
O(1)–Si(1)–O(5)	108·88°
O(3)–Si(1)–O(5)	109·03°

Table 4 gives the r.m.s. amplitudes of thermal vibration, w_j, along the principal axes s_j, as well as the angles between s_j and the axes $XY'Z$ of a righthanded cartesian system for which X and Z coincide with the corresponding crystallographic directions. It is seen that vector s_3 for silicon is along the X axis, whereas Young & Post and Smith & Alexander found s_2 in this direction.

Table 4. *Root mean square amplitudes* (Å) *and angles* (°) *with $XY'Z$ axes*

Atom j		w_j	σ	X	Y'	Z
Si	1	0·073	0·003	90	26 ± 23	64 ± 23
	2	0·078	0·002	90	116 ± 23	26 ± 23
	3	0·083	0·003	0	90	90
O	1	0·086	0·005	115 ± 6	43 ± 3	58 ± 5
	2	0·111	0·004	42 ± 7	93 ± 6	48 ± 7
	3	0·138	0·003	59 ± 5	47 ± 3	122 ± 5

Let u_1 and u_2 be unit vectors along the bonds O(1)→Si(1) and O(2)→Si(2). The (rpq) system used by Young & Post and Smith & Alexander to describe the orientation of the oxygen ellipsoid corresponds to the directions $u_1 - u_2$, $u_1 + u_2$, $u_1 \times u_2$. The angles between the s_j axes of oxygen and the rpq axes are given in Table 5. Thus there is excellent agreement with Young & Post and with Smith & Alexander as to the orientation of the oxygen thermal vibration tensor.

Table 5. *Angles with rpq axes*

j	w_j	r $u_1 - u_2$	p $u_1 + u_2$	q $u_1 \times u_2$
1	0·086	8	96	90
2	0·111	84	11	100
3	0·138	89	81	7

Discussion of extinction

As shown in Fig. 1 the observed variation of the extinction correction with scattering angle agrees well with the prediction of the modified theory of extinction.

On the assumption that the intensity scale factor has been found, equation (2) can be put in the form

$$|F_c| \simeq |F|_o\{1 + \tfrac{1}{2}g_2(p_2/p_1^2)\,(Q_{p_1}^*\bar{T})\} \qquad (3)$$

where $\bar{T} \equiv AdA^*/d\mu$ and Q^* refers to the observed rather than the calculated value Q, i.e. $Q^* = Q|F|_o^2/|F|_c^2$. Thus the extinction coefficient $g_2 \equiv \int W_{(A)}^2 dA$ can be determined. Table 6 gives the individual values of g_2 as obtained from equation (3) and the strongest reflections of Table 2. The average value $g_2 = 4·3 \times 10^3$ corresponds to a half width of 0·014°.

According to the method of derivation equation (3) is a first order approximation. It is surprising therefore, as shown in Tables 2 and 6, that good agreement is obtained even when the correction term approaches unity. The same observation was made with hambergite (Zachariasen, 1963). The exact form of the extinc-

Table 6. *Values of g_2*

HKL	J_0/J_c	$g_2 \times 10^{-3}$	HKL	J_0/J_c	$g_2 \times 10^3$
100	0·565	4·2	213	0·741	5·3
101	0·484	3·4	114	0·748	4·8
10$\bar{1}$	0·325	3·8	310	0·722	4·8
110	0·640	4·4	31$\bar{2}$	0·780	4·3
102	0·671	4·3	401	0·736	4·3
200	0·696	4·3	10$\bar{5}$	0·747	4·8
201	0·801	4·1	214	0·785	5·4
112	0·628	3·3	223	0·848	4·0
20$\bar{2}$	0·722	4·3	32$\bar{1}$	0·817	4·4
10$\bar{3}$	0·784	5·0	403	0·830	4·1
211	0·760	4·3	411	0·848	4·6
21$\bar{1}$	0·727	4·3	006	0·861	4·5
203	0·571	3·8	21$\bar{5}$	0·866	4·6
20$\bar{3}$	0·787	4·1	20$\bar{6}$	0·767	4·3
30$\bar{1}$	0·604	4·2	41$\bar{3}$	0·850	3·7
104	0·170	5·0	502	0·709	4·4
302	0·681	4·7	420	0·850	3·8
30$\bar{2}$	0·794	5·0	32$\bar{4}$	0·750	3·9
220	0·742	4·1			

tion correction will depend both on the shape of the crystal and on the distribution function W. It must hence be regarded as an accident that equation (3) is a better approximation for spherical crystals than one has a right to expect from the derivation.

As already shown (Zachariasen, 1963) the extinction problem can be solved exactly for a plane parallel plate. The result was given as a series expansion involving extinction coefficients $g_n \equiv \int W^n dA$. However, if the extinction is high, the series will converge very slowly and is not suited for practical use.

The simplest assumption as to a distribution function W is: $W = g_2$ for $-\tfrac{1}{2}g_2 \leq A \leq +\tfrac{1}{2}g_2$ and $W = 0$ everywhere else. Under these circumstances the integrated intensity expression for the symmetrical Laue case of a plane parallel plate becomes

$$\begin{aligned} J_0 &= J_c y \\ y &= (y_\perp + y_\parallel \cos^2 2\theta)/(1 + \cos^2 2\theta) \\ y_\perp &= (1 - e^{-2x})/2x \qquad (4) \\ y_\parallel &= (1 - e^{-2x\cos^2 2\theta})/2x \cos^2 2\theta \\ x &= g_2 Q_0 T . \end{aligned}$$

With this choice of W one has $g_n = g_2^{n-1}$, and it is readily verified that the result is in agreement with the general expansion formula (equation (9) of Zachariasen, 1963).

It is of interest to note that J_0 approaches a limiting value $J_0 = I_0 e^{-\mu T} V/g_2$ as the extinction increases.

Equation (4) (using $\bar{T} = AdA^*/d\mu$ instead of T) gives less good agreement for quartz than does equation 3. For example J_0 for the strongest reflection (10$\bar{1}$) is fifty per cent higher than predicted by equation (4).

Throughout this paper the term extinction has been used intentionally without distinction between primary and secondary type. If there is no secondary and only primary extinction one has

$$J_0 = I_0 Q_0 p_1 A V\, Q'/Q$$

where Q'/Q is the primary extinction correction. For the plane parallel plate and small primary extinction one has

$$\frac{Q'}{Q} = 1 - a_1 \frac{p_2}{p_1^2}(Q_0 p_1) + a_2 \frac{p_3}{p_1^3}(Q_0 p_1)^2 + \cdots$$

where

symmetrical Laue case

$$a_1 = 2t_0^2 \tan \theta / 3\lambda \qquad a_2 = \tfrac{33}{40} a_1^2$$

symmetrical Bragg case

$$a_1 = 2t_0^2 \cotan \theta / 3\lambda \qquad a_2 = \tfrac{6}{5} a_1^2 ,$$

t_0 being the thickness of a single mosaic block. Thus the primary and secondary extinction corrections are of the same form and it is difficult, if not impossible, to make an experimental distinction.

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Dispersion in Quartz

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With Cu $K\alpha$ radiation diffraction intensities I_H and $I_{\bar{H}}$ of quartz were found to differ by as much as fifty per cent.

The observations gave a value of $\Delta = 0.31 \pm 0.01$ for the imaginary dispersion correction of silicon and are in good agreement with theory.

Introduction

A convenient experimental measure of the dispersion effect in asymmetric crystals is the dimensionless quantity $, X_H$, defined by

$$X_H = \frac{I_H - I_{\bar{H}}}{\tfrac{1}{2}(I_H + I_{\bar{H}})} = \frac{|F'_H|^2 - |F'_{\bar{H}}|^2}{\tfrac{1}{2}(|F'_H|^2 + |F'_{\bar{H}}|^2)}. \qquad (1)$$

As stated in the preceding paper (Zachariasen & Plettinger, 1965) large deviations from Friedel's rule were found for quartz and Cu $K\alpha$ radiation. Indeed, values of $|X_H|$ up to 0·5 were observed for some reflection pairs. The magnitude of the dispersion effects was greater than anticipated, for the Cu $K\alpha$ wave length is less than one fourth that of the nearest critical absorption edge. Moreover, the recent study of quartz by Smith & Alexander (1963), in which also Cu $K\alpha$ radiation was used, does not report any intensity differences $I_H - I_{\bar{H}}$. For these reasons it seemed desirable to demonstrate that the observed dispersion effects were in agreement with theory.

The formal treatment of dispersion in X-ray diffraction theory is well known and has been given in various text books (see for instance sections III, 4, 5, 9, 12 of Zachariasen, 1945). However, it will be useful to give some of the general theoretical results in detailed form so as to facilitate comparison with experiment.

Theoretical considerations

The atomic scattering power is of the form $f' = f_0 + \Delta' + i\Delta = f + i\Delta = f(1 + i\delta)$. The imaginary term implies true absorption, the corresponding atomic absorption coefficient, μ_a, being

$$\mu_a = \frac{2e^2 \lambda}{mc^2} \Delta. \qquad (2)$$

On the assumption that true absorption is the predominant process equation (2) can be used to calculate Δ from the empirical value for μ_a which is reliably known for most atoms for many wave lengths.

The structure factor corresponding to f' is $F'_H = F_H + i\Psi_H$, where F_H is associated with the f's and Ψ_H with the Δ's. It is convenient to write $F_H = \Sigma F_j$, $\Psi_H = \Sigma \delta_j F_j$, F_j being the contribution to F_H due to the atoms of the jth chemical species. It is readily shown that

$$P_H \equiv \tfrac{1}{2}\{|F'_H|^2 + |F'_{\bar{H}}|^2\} = |F_H|^2 + |\Psi_H|^2 =$$
$$= \Sigma\Sigma(1 + \delta_j \delta_k)|F_j| |F_k| \cos(\alpha_k - \alpha_j) \qquad (3a)$$

$$D_H \equiv |F'_H|^2 - |F'_{\bar{H}}|^2 = 4F_H|\Sigma\delta_j F_j| \sin(\alpha - \alpha_j) =$$
$$= 2\Sigma\Sigma(\delta_j - \delta_k) |F_j| |F_k| \sin(\alpha_k - \alpha_j) \qquad (3b)$$

where α is the phase of F_H, α_j of F_j. The experimental quantity X_H introduced in equation (1) is given by