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Refinement of the Atomic Parameters of α-Quartz

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The positional and thermal parameters of α-quartz at room temperature have been redetermined accurately using Cu $K\alpha$ diffractometric intensities from a natural crystal showing unusually little primary extinction. Anisotropic refinement on the basis of the 112 observable independent $|F_o|$'s was performed by least squares and differential synthesis to final R values of 3·6 and 3·3% respectively. In good agreement with the results of Young & Post, the positional parameters are found to be $x = 0{\cdot}4145$, $y = 0{\cdot}2662$, $z = 0{\cdot}1189$, $u = 0{\cdot}4698$. The Si–O bond lengths are 1·597 and 1·617 (±0·003) Å, the O–O bond lengths range from 2·604 to 2·640 (±0·002 to 0·005) Å, and the Si–O–Si angle is 144·0 (±0·2)°. The dimensions and orientation of the thermal vibration ellipsoid of silicon agree well with the findings of Young & Post, the maximum r.m.s. vibrational amplitude, 0·080 Å, being parallel to c. For oxygen the agreement is not definite. The present study indicates that the maximum r.m.s. displacement, 0·132 Å, is perpendicular to the plane defined by a given oxygen atom and the two silicon atoms which it links.

1. Introduction

The rapid increase in recent years of the power of X-ray crystallographic techniques has promoted a revival in the study of silicate structures and led to heightened interest in the nature of chemical bonding in the silicates (for example, Cruickshank, 1961). This activity in the field of silicates in turn raises the need for a re-examination and refinement of the structures of α-quartz and the other pure silica phases. Current studies of the structures of organosilicon compounds in this laboratory have provided additional motivation for a redetermination of the positional and thermal parameters of α-quartz with a high order of accuracy. Finally, an immediate incentive for such a study was provided by the availability of some particularly suitable single crystals of quartz, as described below in Section 2.

Positional parameters for α-quartz were first determined with three-figure precision by Wei (1935) and later redetermined with greater accuracy by Brill, Hermann & Peters (1939, 1942), who used a milky quartz crystal to reduce the effect of primary extinction. Neither of these studies included an estimate of the thermal vibration parameters of the atoms. Recently Young & Post (1962) performed a precise redetermination of the positional parameters, using a synthetic quartz crystal and Mo $K\alpha$ counter-diffractometric intensities. They also determined the thermal parameters of the atoms at 155, 223 and 300 °K, compared the temperature dependence of these parameters with values predicted by the Debye–Waller theory, and computed the orientations of the thermal vibration ellipsoids of oxygen and silicon at room temperature.

Smith (1954) and Smith, Karle, Hauptman & Karle (1960) have emphasized the importance of an accurate knowledge of the Si–O bond lengths in silicate tetrahedra (1) as an aid in determining the amount of Al, Si substitutional solid solution present and (2) in relation to the nature of the linkage of the tetrahedra and the presence of neighboring cations. It is evident that α-quartz and the other 'pure' silica phases afford reference standards of particular value. Of possibly less practical, but great theoretical, interest is the characterization of the Si–O tetrahedron in a given structure as regular or irregular. Deviations from regularity are known to occur in a number of silicate structures, and evidence is now accumulating that deviations also occur in the three-dimensionally linked tetrahedra of the felspars (Jones & Taylor, 1961). Prior to the work of Young & Post (Young & Post, 1962; Hoffer, 1961) experimental evidence for departures from regularity in the several silica structures was lacking, and, in fact, it had been customary to assume the absence of any such deviations.

2. Nature of the quartz specimen

The crystal from which the X-ray intensity data were obtained was one of many of rather similar appearance removed from the inner surface of a geode collected by Andrew Carnegie in the Badlands of South Dakota in 1902. The crystal was clear and colorless, and in form it closely approximated a hexagonal bipyramid 0·14 mm from apex to apex and 0·06 and 0·08 mm in shortest and longest diameters respectively. An outstanding property of this crystal was the relative feebleness of primary extinction effects as revealed by the subsequent comparison of observed and calculated structure factors. This is unusual in a material normally as well-crystallized as quartz, and, of course, it rendered the specimen well suited to the purpose of this study.

Some of the crystals which were visually free of adhering matter and discoloration, and of rather similar size and appearance, were prepared as follows for spectrographic and X-ray powder analysis: (1) surface cleaned with hot concentrated hydrochloric acid for several hours, (2) washed in *aqua regia* for one hour, (3) rinsed thoroughly with deionized water, and (4) ground to a fine powder in a boron carbide mortar. Emission spectrographic analyses for impurity content were performed in sextuplicate, standards of similar composition ranging from 1 to 1000 parts per million (p.p.m.) being used. Generally accepted procedures of photographic photometry, background correction and internal standard calibration were used for all determinations. In p.p.m. the results with estimated probable errors are:

Al	88	(±10)	Li	4	(±1)
Ba	1		Mg	6	(±3)
Ca	285	(±20)	Mn	<1	
Fe	65	(±8)	Na	4	(±2)

Another portion of crystals was prepared for analysis in the manner just described except that, after the grinding, the powder was given an additional prolonged exposure to hot concentrated hydrochloric acid. This reduced the calcium content to 82 p.p.m.

A Debye–Scherrer pattern of the finely ground powder was prepared in a camera of 57·3 mm radius using Cu $K\alpha$ radiation and the asymmetric film position (Straumanis, 1949), and precise values of the lattice constants were derived by the extrapolation method of Taylor & Sinclair (1945) in conjunction with a procedure of successive approximations (Lipson & Wilson, 1941). The results at 25 °C uncorrected for refraction are:*

$$a = 4\cdot9039 \quad (\pm 0\cdot0001_5)\ \text{kX}$$
$$c = 5\cdot3943 \quad (\pm 0\cdot0001_5)\ \text{kX}$$
$$c/a = 1\cdot10000 \quad (\pm 0\cdot00005)$$

These values of a and c are both near the upper limits of the usual ranges observed for natural and synthetic quartz (Cohen & Sumner, 1958).

Some of the selected crystals were tested for the presence of color centers by X-irradiation with a Picker Industrial X-ray Unit and a Machlett AEG50T tungsten-target tube operated at 45 kVp and 35 mA. Two hours' irradiation failed to produce visible darkening. According to findings of Cohen (1960), aluminum may be incorporated into α-quartz either substitutionally or interstitially, but in either case it is accompanied by chemically equivalent amounts of alkali ion (Li^+ and/or Na^+), thus preserving electroneutrality. Visible color center phenomena in α-quartz are dependent upon the presence of substitutional, but not interstitial, aluminum; furthermore, interstitial aluminum produces a larger relative expansion of the a than of the c axis and, therefore, a decrease in the axial ratio c/a.

In the light of Cohen's findings, the analytical results reported above lead to the following conclusions concerning the character of the quartz crystals from the Carnegie geode: (1) Although the aluminum content is relatively high, only a small portion of it is actually incorporated into the α-quartz lattice, and this is mostly interstitial. (2) The greater part of the aluminum must be present chemically bound in a finely dispersed phase in the crystal. (3) The calcium, which is present in exceptionally high concentration, must also be present as a constituent of a dispersed phase.* The reduction in calcium content resulting from acid treatment of the powder is in keeping with this picture. It is also reasonable that such a dispersed phase would lead to the development of a highly mosaic structure such as is indicated in the present quartz crystals by the feebleness of primary extinction.

Two principal pure modes of twinning occur in α-quartz, Dauphiné and Brazilian, and furthermore Dauphiné–Brazilian or 'combined' twinning is also common (Frondel, 1945; Gault, 1949). Dauphiné twins are related as by a rotation of 180° about the c axis, while Brazilian twins are related as by reflection across $\{11\bar{2}0\}$. Whereas Brazilian twinning does not affect the diffracted intensities, Dauphiné twinning results in the superposition of a reflection $(\bar{h}\bar{k}\cdot l)$ of one component upon $(hk\cdot l)$ of the other, with the result that systematic discrepancies between calculated and observed structure factors are introduced. Thus Young & Post (1962) as a criterion of Dauphiné twinning have used deviations from the theoretical ratio $|F_c(\bar{h}\bar{k}\cdot l)|^2/|F_c(hk\cdot l)|^2$, in particular $|F_c(\bar{3}0\cdot1)|^2/|F_c(30\cdot1)|^2$, which has a calculated value of 734 for the parameters derived in the present study. Since the observed value is 385, and since, furthermore, $|F_o(\bar{3}0\cdot1)|$ is appreciably depressed by primary extinction (see Table 5), we may tentatively conclude that the effect of Dauphiné twinning upon the present intensity measurements is very minor although not necessarily negligible. From a more general point of view, the final very small value of the reliability index precludes the presence of any considerable amount of twinning.

A more specific and sensitive approach to this problem is to examine the $(|F_o|/|F_c|)_{hk\cdot l}$ values of all reflections for which $|F(hk\cdot l)|$ is relatively small, say less than 10, and for which $|F(\bar{h}\bar{k}\cdot l)|$ is large with respect to $|F(hk\cdot l)|$. Then, if a small but appreciable amount of Dauphiné twinning is present, the coincidence of the reciprocal lattice points $(hk\cdot l)_a$ and

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* The figures in parentheses indicate the order of precision with special reference to the results published by Cohen & Sumner (1958), which were obtained by identical techniques with the same camera.

* Powder from a completely opaque white quartz crystal from Pecos, Arizona showed, in addition to the normal powder pattern of α-quartz, the seven strongest lines of anhydrite, $CaSO_4$.

Table 1. *($|F_o|/|F_c|)_{hkl}$ ratios sensitive to Dauphiné twinning*

hkl			*h'k'l'*				
hkl	$10\|F_o\|$	$10\|F_c\|$	*h'k'l'*	$10\|F_o\|$	$10\|F_c\|$	$(\|F_o\|/\|F_c\|)_{hkl}$	Dauphiné correlation
301	26	21	031	504	559	1·24	+
501	43	38	051	128	129	1·13	+
321	40	34	231	321	324	1·18	+
421	86	84	241	125	126	1·02	+
402	67	59	042	187	184	1·14	+
232	58	59	322	198	196	0·98	−
052	35	42	502	387	396	0·83	−
103	40	29	013	275	275	1·38	+
413	97	94	143	276	280	1·03	+
033	59	59	303	163	155	1·00	
404	23	19	044	126	121	1·21	+
024	33	25	204	168	163	1·32	+
124	71	65	214	303	302	1·09	+
205	26	14	025	86	82	1·86	+
215	93	85	125	253	254	1·09	+
035	48	47	305	160	155	1·02	+
016	25	10	106	161	157	2·50	+
216	72	70	126	176	178	1·03	+

$(\bar{h}\bar{k}\cdot l)_b$ will result in the great majority of the $(|F_o|/F_c|)_{hk\cdot l}$ ratios being greater than unity, whereas in the absence of such twinning there should, on the average, be as many values smaller than unity as larger.

Table 1 presents the results of such an examination of the 18 weaker reflections to which this kind of analysis is applicable. Corresponding to each reflection $(hk\cdot l)$ of column 1, the reflection $(h'k'\cdot l')$ cited in column 4 is equivalent by Laue symmetry to the superposing reflection $(\bar{h}\bar{k}\cdot l)$ of the twin component. Of the $(|F_o|/|F_c|)_{hk\cdot l}$ data given, 15 values are larger and 2 values smaller than unity. This result clearly supports the existence of a small amount of Dauphiné twinning in the crystal from which the intensity data of the present study were collected.

3. Experimental procedure

The reflection intensities were measured with Cu $K\alpha$ radiation at room temperature, the single crystal described in Section 2 being used in a General Electric XRD-5 apparatus equipped with a single-crystal orienter and krypton-filled proportional counter. With this crystal the variation in the absorption factor over the ranges of θ and φ employed was less than $\pm 3\%$, and it was decided to neglect this source of error in the observed structure amplitude. All 112 independent reflections accessible with this experimental arrangement were observed with measurable intensity above background.

The integrated counting rates of the reflections were measured by the 2θ-scan technique, the scan range being increased stepwise with increasing 2θ so as to keep scan range corrections small except at the largest angles (Alexander & Smith, 1962). The background was measured by means of stationary counts at either end of the scan range and its mean value subtracted from the overall integrated counting rate to give a measure of the net integrated intensity. For all reflections of intermediate and strong intensity, sufficient counts were recorded to limit the standard deviation of counting to 1% or less. For the weak reflections, however, the σ's were necessarily larger; for two very feeble reflections σ exceeded 10%. To categorize the counting statistical errors more definitely:

For 90 reflections $\sigma < 1\%$
For 10 reflections $1 < \sigma < 3$
For 5 reflections $3 < \sigma < 6$
For 5 reflections $6 < \sigma < 10$
For 2 reflections $\sigma > 10$

Carefully calibrated nickel filters were used to attenuate the counting rates of the stronger reflections to within the linearity range of the counter. Long-period variations in the intensity of the direct beam were allowed for by periodic reference to the intensity of a standard reflection.

To minimize the adverse effect of anisotropy of the absorption factor and primary extinction upon the 112 independent experimental structure amplitudes,

Table 2. *Comparative peak reflection intensities of equivalent faces of the form* $\{10\bar{1}0\}$ *(natural quartz crystal)*

	Cu $K\alpha$ radiation			Mo $K\alpha$ radiation		
	N_p (c.p.s.)	δ (c.p.s.)	$\%\delta$	N_p (c.p.s.)	δ (c.p.s.)	$\%\delta$
	4979	+168	+3·5	3024	+26	+0·9
	4560	−251	−5·2	2975	−23	−0·8
	4895	+84	+1·8	3034	+36	+1·2
	4974	+163	+3·4	3009	+11	+0·4
	4540	−271	−5·6	2929	−69	−2·3
	4916	+105	+2·2	3018	+20	+0·7
$\langle N_p \rangle =$		4811			2998	
$\langle \delta \rangle =$		174			31	
$\sigma =$		187			36	
$\%\sigma =$		3·9			1·2	

all reflection intensities to be used in the refinement were measured within a φ range of 60°. Table 2 illustrates by means of data from the crystallographic form $\{10\bar{1}0\}$ the variation in peak reflection intensity among the six equivalent sets of planes as measured with Cu $K\alpha$ and Mo $K\alpha$ radiations. Each value of N_p in counts per second represents a total of approximately 580,000 recorded counts for Cu $K\alpha$ and 300,000 for Mo $K\alpha$. $\langle N_p \rangle$ = mean counting rate for all six sets of planes, δ = individual deviation from $\langle N_p \rangle$, and σ = standard deviation for all six sets of planes exclusive of counting statistics. The larger value of σ for Cu $K\alpha$ radiation is believed to be mainly attributable to the larger absorption coefficient of quartz for this wavelength.

4. Refinement by differential synthesis

The refinement of the positional and thermal parameters was begun with the positional parameters of Brill, Hermann & Peters (1939, 1942) and a single isotropic temperature coefficient $B = 0{\cdot}70$ Å^2. The first four rows of data in Table 3 trace the subsequent shift in positional parameters and resulting reduction in R from 9·5 to 3·3% during a course of refinement comprising 2 cycles of isotropic refinement and 4 cycles of differential synthesis with individual anisotropic temperature coefficients. Only one reflection, 01·1, displayed a conspicuous extinction effect, and this was allowed for by setting F_o equal to F_c in the several steps of differential synthesis and in the calculation of the reliability index.

The atomic scattering factors of silicon and oxygen employed in the present refinement procedures were those computed by Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955). The differential synthesis refinement of the positional and anisotropic thermal parameters of the atoms was performed with the aid of the I.B.M. 650 program of Shiono (1958). The indicated shifts in the thermal parameters as thus calculated by the method of Cruickshank (1956) proved to be much too large; it was therefore necessary to evaluate them instead on the basis of the criteria that

$$\varrho_o = \varrho_c \quad \text{and} \quad \frac{\partial^2 \varrho_o}{\partial x_i \partial x_j} = \frac{\partial^2 \varrho_c}{\partial x_i \partial x_j}$$

at each atomic site. Shiono's program was applied to the trigonal quartz structure after first transforming the primitive trigonal unit cell (T) to a C-centered monoclinic cell (M) as shown in Fig. 1. The axial transformation matrix $\mathbf{R}$ in $\mathbf{A}_M = \mathbf{R}\mathbf{A}_T$ is

$$\mathbf{R} = \begin{bmatrix} 1 & 2 & 0 \\ \bar{1} & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix},$$

and the coordinate transformation is $\mathbf{X}_M = \tilde{\mathbf{R}}^{-1}\mathbf{X}_T$.

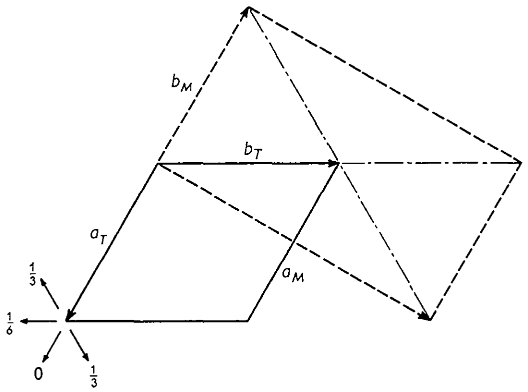

Fig. 1. Relationship between trigonal (T) and monoclinic (M) unit cells.

Table 3. *Principal stages in the refinement of the α-quartz structure*

(σ Values in parenthesis)

	x	y	z	u	Temp. factor (Å^2)	R (%)
1. Parameters of Brill *et al.*	0·415	0·272	0·120	0·465	Isotropic B = 0·70	9·5
2. Parameters of Brill *et al.*	0·415	0·272	0·120	0·465	B_O = 0·55 B_{Si} = 0·40	8·4
3. After 2 cycles of DS (isotropic)	0·4153	0·2666	0·1192	0·4695	B_O = 0·70 B_{Si} = 0·40	4·9
4. After 4 cycles of DS (anisotropic)	0·4146 (0·0008)	0·2662 (0·0008)	0·1190 (0·0006)	0·4699 (0·0003)	Anisotropic	3·3
5. After 2 cycles of LS (Hughes weights)	0·4129	0·2650	0·1180	0·4703	Anisotropic	4·6
6. After 2 cycles of LS ('Counter' weights)	0·4144 (0·0008)	0·2662 (0·0007)	0·1188 (0·0004)	0·4697 (0·0003)	Anisotropic	3·6
7. Suggested 'best' positional parameters from this study	0·4145	0·2662	0·1189	0·4698		
8. Young & Post's results	0·4152 (0·0007)	0·2678 (0·0006)	0·1184 (0·0004)	0·4705 (0·0003)	Anisotropic	8·1

$R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, DS = differential synthesis, LS = least squares.

Table 4. *Experimental temperature factors of α-quartz at room temperature*

A. From differential synthesis (monoclinic cell, Å^2 units)

$$\exp\,[-\tfrac{1}{4}\sum_{i=1}^{3}\sum_{j=1}^{3}B_{ij}h_ih_ja_i{}^*a_j{}^*] \text{ with } B_{ij}=B_{ji}$$

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Oxygen	0·710	0·900	1·140	0·038	0·020	−0·326
Silicon	0·510	0·360	0·410	0	0·018	0

B. From least squares (trigonal cell, dimensionless)

$$\exp\,[-\sum_{i=1}^{3}\sum_{j=1}^{3}\beta_{ij}h_ih_j] \text{ with } \beta_{ij}=\beta_{ji}$$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Oxygen	0·0140	0·0115	0·0087	0·0076	−0·0030	−0·0038
Silicon	0·0052	0·0029	0·0043	0	0·0002	0
	$\sigma(\beta_{11})$	$\sigma(\beta_{22})$	$\sigma(\beta_{33})$	$\sigma(\beta_{12})$	$\sigma(\beta_{13})$	$\sigma(\beta_{23})$
Oxygen	0·0017	0·0015	0·0008	0·0013	0·0010	0·0009
Silicon	0·0007	0·0008	0·0004		0·0002	

To facilitate comparison with the results of earlier investigations we employ the convention of Wyckoff that the twofold axis coincides with a_T of the trigonal cell (space group $P3_221$) and, of course, with b_M of monoclinic cell (space group $C2$). The anisotropic thermal coefficients based on monoclinic axes from the differential synthesis refinement are given in part A of Table 4. Following Shiono (1958) the temperature factor is expressed

$$\exp\,[-\tfrac{1}{4}\sum_{i=1}^{3}\sum_{j=1}^{3}B_{ij}h_ih_ja_i^*a_j^*]\,, \qquad (1)$$

wherein the B_{ij}'s have the dimensions Å^2 and $B_{ij}=B_{ji}$. The orientations of the thermal ellipsoids as derived from differential synthesis are described in Section 6.

5. Refinements by least squares

Least-squares refinement of the positional and anisotropic thermal parameters was carried out by minimizing the function $\Sigma w_{hkl}(|F_o|_{hkl}-|F_c|_{hkl})^2$ with the aid of an I.B.M. 704 Computer, the program of Busing & Levy (1959) being used. The starting parameters were those derived from 2 cycles of isotropic differential synthesis (Table 3, line 3). The refinement was performed in two ways, once with the familiar and simple weighting scheme originally suggested by Hughes (1941) for photographic intensity data, and again with a more complex weighting scheme designed to make the weights proportional to the reciprocals of the variances of the counter data. In each case two cycles of refinement sufficed to reduce the parameter shifts to a negligible level. The resulting positional parameters and values of the reliability index are given in rows 5 and 6 of Table 3. The anisotropic thermal coefficients derived on the basis of the 'counter' weighting scheme are reproduced in part B of Table 4. Here the temperature factor is expressed

$$\exp\,[-\sum_{i=1}^{3}\sum_{j=1}^{3}\beta_{ij}h_ih_j]\,, \qquad (2)$$

wherein the β_{ij}'s relate to the trigonal crystallographic axes and are dimensionless quantities, and $\beta_{ij}=\beta_{ji}$.

In the simple weighting scheme of Hughes (1941) employed by us in the first refinement, the weighting factor w_{hkl} is set equal to $1/F_{hkl}^2$ for F's more than four times the minimum observable F in any given range of θ and proportional to $(1/16)F_{\text{min}}^2$ for F's smaller than $4F_{\text{min}}$. In the second refinement the weights were taken as proportional to the reciprocals of the variances in the $|F_{hkl}|$'s as analytically expressed by the following equation:

$$\sigma_F^2=\frac{f_m}{4LP}\left(\frac{R}{2}\right)\left\{\frac{C_T/n_T+t^2C_B/n_B}{C_T-tC_B}+(C_T-tC_B)\,[E/n_E+D(m-1)^2+G]\right\}. \qquad (3)$$

The four terms of this expression have been formulated so as to represent in a semi-empirical but rational manner the effects of four sources of error, which are respectively from left to right: (1) counting statistics, (2) time-wise instability, (3) uncertainty in the attenuating factor of the absorbing filters, and (4) uncertainty in the factor for converting a peak intensity to an integrated intensity. The various symbols in the expression have the following meanings:

f_m = attenuating factor of m absorbing filters.
L = Lorentz factor.
P = polarization factor.
R = ratio for converting a peak intensity into an integrated intensity (equal to unity when the integrated intensity is measured directly).
C_T = number of counts recorded for a given reflection (hkl) in t_T seconds.
C_B = background counts recorded for reflection (hkl) in t_B seconds.

Table 5. *Observed and calculated structure amplitudes* (×10) *for α-quartz*

	ℓ = 0		ℓ = 1		ℓ = 2		ℓ = 3		ℓ = 4		ℓ = 5		ℓ = 6	
h k	$\|F_o\|$	$\|F_c\|$	$\|F_o\|$	$\|F_c\|$	$\|F_o\|$	$\|F_c\|$	$\|F_o\|$	$\|F_c\|$	$\|F_o\|$	$\|F_c\|$	$\|F_o\|$	$\|F_c\|$	$\|F_o\|$	$\|F_c\|$
0 0							184	189					249	252
1 0	303	285	452	470	333	340	40	29	365	382	215	211	161	157
2 0	344	346	266	245	181	170	564	626	168	163	26	14	175	170
3 0	180	175	26	21	413	431	163	155	127	121	160	155		
4 0	259	262	333	345	67	59	324	314	23	19				
5 0	26	8	43	38	387	396								
0 1			579	722	171	152	275	275	208	204	342	357	25	10
1 1	345	341	190	184	450	477	243	230	346	353	241	237	128	124
2 1			341	346	228	222	334	339	303	302	93	85	72	70
3 1			161	164	220	221	138	133	203	196	121	117		
4 1			288	289	143	132	97	94						
0 2			179	172	370	367	321	331	33	25	86	82	330	345
1 2	77	77	368	368	375	396	178	167	71	65	253	254	176	178
2 2	377	387	210	205	64	36	286	285	178	181	183	184		
3 2			40	34	198	196	12	16	133	128				
4 2			86	84										
0 3			504	559	286	287	59	59	181	174	48	47		
1 3	367	382	275	276	332	342	157	152	122	119	162	164		
2 3	217	213	321	324	58	59	28	29	302	315				
3 3	240	237	186	182	45	44								
0 4			113	110	187	184	238	237	126	121				
1 4	78	80	113	113	172	172	276	280						
2 4	250	250	125	126										
0 5			128	129	35	32								

t = t_T/t_B.

n_T, n_B = number of times C_T or C_B counts, respectively, were recorded for reflection (hkl) at one sitting.

n_E = number of sittings.

m = number of filters.

D = estimated variance in the knowledge of the filter factor for one filter, f_1.

E = time-wise variance of the diffracted intensities due to all experimental sources of instability. This quantity is estimated from periodic measurements of a standard reflection.

G = estimated variance in the knowledge of R (equal to zero when the integrated intensity is measured directly).

A much simpler formula incorporating fewer parameters has been applied by Busing & Levy (1957) to neutron diffraction data.

Table 5 compares the observed and calculated structure amplitudes on the basis of $F_{000} = 180$ for the 112 independent reflections as computed from the atomic parameters derived by least-squares refinement (line 6 of Table 3). With $F_o(01{\cdot}1)$ set equal to $F_c(01{\cdot}1)$ the final value of R was 3·6%. Differential synthesis refinement on the basis of the monoclinic unit cell described in Section 4 led to a very slightly larger scaling factor. The overall agreement between observed and calculated structure amplitudes was very similar to the results from least-squares refinement given in Table 5, and the final value of R was 3·3%.

6. Results and discussion

The variances in the experimental structure factors calculated by expression (3) and by the Hughes method are almost strictly proportional at intermediate and large values of $|F|$, but for small $|F|$'s the Hughes variance reaches a minimum and constant value whereas the 'counter' variance increases rapidly as $|F|$ approaches zero. That this difference in weighting has a significant effect upon the positional parameters can be seen from a comparison of lines 5 and 6 of Table 3. On the other hand, the results from differential synthesis refinement agree very well with those from least squares with 'counter' weighting factors, and the authors are inclined to regard these two sets of results as being equally reliable. Thus the suggested 'best' positional parameters are those given in line 7 of Table 3. They may be compared with the atomic positions derived by Young & Post (1962) for a synthetic quartz crystal given in line 8.

Table 6 summarizes the interatomic distances and bond angles from the present least-squares refinement

Table 6. *Interatomic distances and bond angles in α-quartz at room temperature*

(Standard deviations in parenthesis)

I. Bond angles (degrees)

Atoms	Angle	Average angle (SA)	Average angle (YP)
O–Si–O′	110·3 (0·2)	109·5	109·5
O′–Si–O‴	109·5 (0·2)		
O–Si–O″	109·2 (0·2)		
O–Si–O‴	108·8 (0·1)		
Si–O–Si′	144·0 (0·2)	144·0 (0·2)	143·9 (0·19)

II. Bond lengths (Å)

Atoms	Length	Average length (SA)	Average length (YP)
Si–O	1·597 (0·003)		1·603 (0·003)
Si–O′	1·617 (0·003)		1·611 (0·002)
O′–O‴	2·640 (0·005)	2·624	2·625
O–O′	2·637 (0·004)		
O–O‴	2·614 (0·002)		
O–O″	2·604 (0·004)		
Si–Si′	3·0572 (0·0002)		3·0565 (0·0002)

(SA = Smith & Alexander, YP = Young & Post, 1962).

Table 7. *Atomic thermal ellipsoids of α-quartz at room temperature as derived by least-squares refinement*

Silicon

	u_1 or φ_1	σ	u_2 or φ_2	σ	u_3 or φ_3	σ
u (Å)	0·051	0·007	0·080	0·004	0·074	0·005
u_x (Å)	0	0	0	0	−0·0736	0·0054
$u_{y'}$ (Å)	0·0508	0·0070	0·0078	0·0111	0	0
u_z (Å)	−0·0049	0·0070	0·0798	0·0040	0	0
φ_x (°)	90·0	0·0	90·0	0·0	180·0	0·0
$\varphi_{y'}$ (°)	5·6	7·9	84·4	7·9	90·0	0·0
φ_z (°)	95·6	7·9	5·6	7·9	90·0	0·0

Oxygen

	u_1 or φ_1	σ	u_2 or φ_2	σ	u_3 or φ_3	σ
u (Å)	0·132	0·006	0·084	0·008	0·102	0·007
u_p (Å)	−0·0083	0·0227	−0·0099	0·0262	0·1012	0·0083
u_q (Å)	−0·1305	0·0059	0·0102	0·0086	−0·0049	0·0180
u_r (Å)	−0·0151	0·0140	−0·0823	0·0077	−0·0127	0·0320
φ_p (°)	93·6	9·9	96·8	18·0	7·7	17·0
φ_q (°)	172·5	5·6	83·0	5·9	92·7	10·1
φ_r (°)	96·6	6·1	170·2	14·5	97·2	18·1

with 'counter' weights (hereafter designated SA) and compares their average values with the results of Young & Post (1962) (hereafter designated YP). It will be seen that the agreement is very good except for the Si–O and Si–O′ distances, which differ from each other more conspicuously in the present study, the deviations of 1·597 and 1·617 Å from their mean being more than 3σ. Of the four independent O–Si–O bond angles, the largest and smallest, 110·3° and 108·8°, deviate significantly from an average value of 109·5°, whereas the other two do not. A further indication of an inherent irregularity of the SiO$_4$ tetrahedron lies in the O–O distances. Each of the independent distances deviates by 3σ to 5σ from their overall mean of 2·624 Å. Elsewhere the non-regularity of the SiO$_4$ tetrahedron in α-quartz is discussed by one of us (Smith, 1963) in a more quantitative and conclusive fashion.

It may be observed that the mean Si–O distance of 1·607 Å falls somewhat below the midpoint of the range of values reported in the more accurate studies of silicate structures wherein no substitution of Al^{3+} for Si^{4+} occurs, namely 1·58–1·67 Å (for example Johansson, 1959; Smith, 1953; Krstanovic, 1958; Smith, Karle, Hauptman & Karle, 1960). The edge length of the SiO$_4$ tetrahedron varies much more widely in the silicates, evidently being sensitive to such factors as the mode of linking of the tetrahedra and the presence and nature of interstitial cations, so that it can only be said that the intramolecular O–O distances in α-quartz of 2·604 to 2·640 Å lie somewhat below the midpoint of the range observed in the silicates. The Si–O–Si bond angle of 144·0° lies almost precisely at the midpoint of the range of values observed in silicates containing linked tetrahedra; for example, in the felspars some of the reported ranges of the Si–O–Si angle are as follows: high albite 125–160° and low albite 128–155° (Ferguson, Taylor & Traill, 1958), microcline 130–155° (Bailey & Taylor, 1955), orthoclase 131–153° (Jones & Taylor, 1961). By X-ray radial distribution analysis of silica glass Zarzycki (1957) has deduced that the average Si–O–Si angle is 143°, but the precision of the method, ±17°, is not good enough to justify quantitative comparisons with crystalline systems.

The dimensions and orientations of the thermal vibration ellipsoids of the silicon and oxygen atoms from least-squares refinement are presented analytically in Table 7 and pictorially in Figs. 3 and 4. The figures also compare the dimensions and orientations of the principal axes with those of YP. The axes of reference are the same in both investigations. Thus the orientation of the silicon ellipsoid is referred to a set of orthogonal axes X, Y', Z, of which X and Z coincide respectively with the a and c trigonal axes, while Y' is perpendicular to both X and Z. Also X, or a, as explained earlier, coincides with a twofold axis in accordance with the convention of Wyckoff. The principal axes of the oxygen ellipsoid are referred to orthogonal axes p, q, r which are determined by

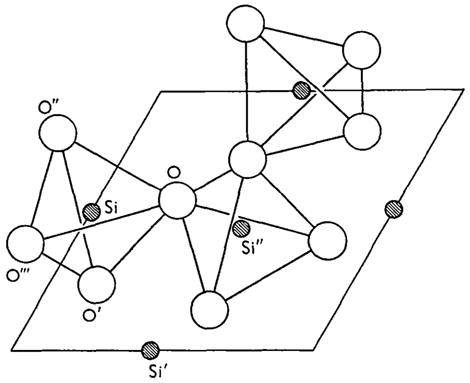

Fig. 2. C-axis projection of the atomic arrangement in α-quartz. The oxygen tetrahedra are outlined with solid lines.

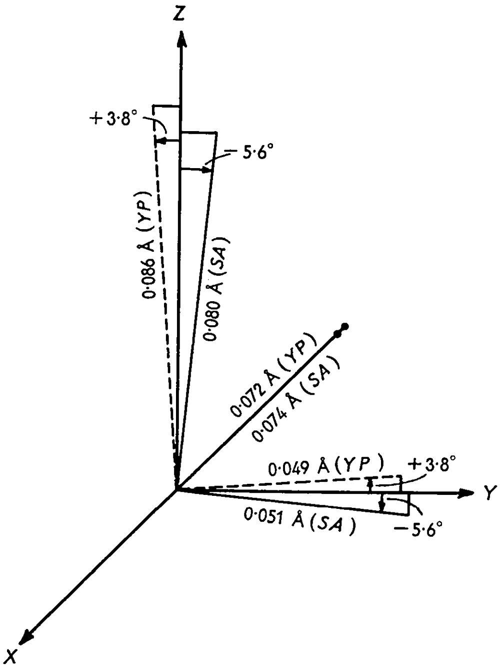

Fig. 3. Principal axes of thermal vibration ellipsoid of silicon from least-squares refinement. Distances in Å are the r.m.s. amplitudes. SA and YP refer respectively to the results of Smith & Alexander and of Young & Post.

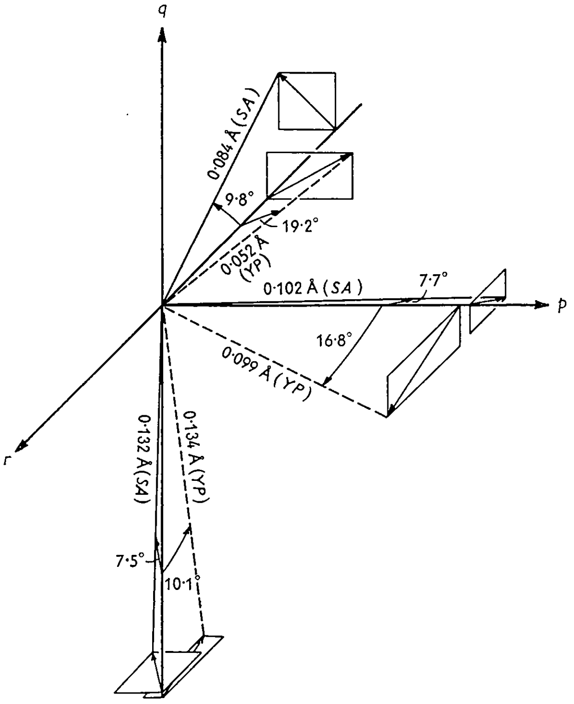

Fig. 4. Principal axes of thermal vibration ellipsoid of oxygen from least-squares refinement. Distances in Å are the r.m.s. amplitudes. See Fig. 5 for orientation of reference axes *p*, *r*, *q*. The angles of tilt are exaggerated for clarity. SA and YP refer respectively to the results of Smith & Alexander and of Young & Post.

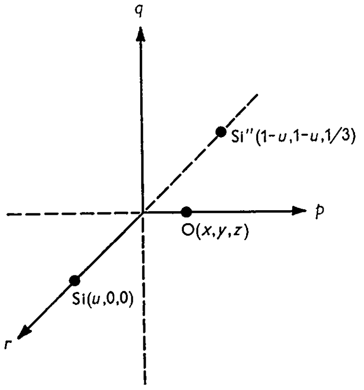

Fig. 5. Orientation of reference axes *p*, *r*, *q*. (See Fig. 4).

three atoms in the structure as shown in Fig. 5. The location of these reference atoms, Si, Si″ and O, with respect to the structure as a whole can be seen from the *ab* unit cell projection of Fig. 2.

Table 7 gives: (1) the r.m.s. amplitudes of thermal vibration, u_1, u_2, u_3, along the principal ellipsoid axes 1, 2, and 3 respectively; (2) the components of u_1, u_2, and u_3 on the reference axes (thus, $(u_1)_x$, $(u_1)_y$, $(u_1)_z$, *etc.* for silicon, $(u_1)_p$, $(u_1)_q$, $(u_1)_r$, *etc.* for oxygen); (3) the angles between each ellipsoid axis and the three reference axes (thus $(\varphi_1)_x$, $(\varphi_1)_y$, $(\varphi_1)_z$, *etc.* for silicon, $(\varphi_1)_p$, $(\varphi_1)_q$, $(\varphi_1)_r$, *etc.* for oxygen); (4) the standard deviations in the above quantities. From Fig. 3 it will be seen that the dimensions of the silicon ellipsoid from least-squares refinement are in good agreement with the YP results; the SA orientation, however, is opposite in sense to that of YP, being −5·6° compared with their mean value of +3·8°, where + denotes a clockwise rotation of axes 2 and 3 as one looks in the positive *X* direction. However, in both cases the departure from coincidence with the crystallographic axes *X*, *Y′*, *Z* is less than σ, which reaffirms the conclusion reached by Young & Post that the thermal ellipsoid axes actually coincide with *X*, *Y′*, *Z*, the maximum r.m.s. vibrational amplitude being parallel to *c* and the smallest amplitude perpendicular to both *a* and *c*.

Fig. 4 shows that the least-squares refinements of SA and YP lead to differences in one dimension, and in the orientation, of the oxygen thermal ellipsoid. There is very good concurrence in the magnitudes of the major and intermediate axes, 1 and 3 respectively, while the magnitude of the minor axis 2 found by SA is appreciably larger than that of YP (0·084 compared with 0·052 Å). In regard to the tilt of the ellipsoid with respect to the reference axes *p*, *q*, *r*, it is seen that (1) the magnitude of the tilt deduced by SA is considerably less than that found by YP, and (2) the senses of the YP and SA tilts are different with respect to axes *p* and *r* but the same with respect to *q*. In the light of the magnitudes of the σ's of the present

Table 8. *Comparison of atomic thermal ellipsoids for α-quartz from differential-synthesis and least-squares refinement*

Silicon

Differential synthesis	u_1 or φ_1	σ	u_2 or φ_2	σ	u_3 or φ_3	σ
u (Å)	0·043		0·072		0·068	
φ_x (°)	90·0		90·0		180·0	
$\varphi_{y'}$ (°)	3·9		86·1		90·0	
φ_z (°)	93·9		3·9		90·0	
Least squares						
u (Å)	0·051	0·007	0·080	0·004	0·074	0·005
φ_x (°)	90·0	0·0	90·0	0·0	180·0	0·0
$\varphi_{y'}$ (°)	5·6	7·9	84·4	7·9	90·0	0·0
φ_z (°)	95·6	7·9	5·6	7·9	90·0	0·0

Oxygen

Differential synthesis	u_1 or φ_1	σ	u_2 or φ_2	σ	u_3 or φ_3	σ
u (Å)	0·132		0·090		0·097	
φ_p (°)	100·2		96·3		12·1	
φ_q (°)	163·7		76·2		98·5	
φ_r (°)	102·5		164·8		98·6	
Least squares						
u (Å)	0·132	0·006	0·084	0·008	0·102	0·007
φ_p (°)	93·6	9·9	96·8	18·0	7·7	17·0
φ_q (°)	172·5	5·6	83·0	5·9	92·7	10·1
φ_r (°)	96·6	6·1	170·2	14·5	97·2	18·1

results, none of the SA φ's may be regarded as statistically significant, a conclusion not shared by YP on the basis of their results taken alone. We feel that the considerable disagreement between the modes of tilt derived in the two studies strongly supports the conclusion that the apparent tilts of YP and SA are both unreal and that the axes of the thermal ellipsoid actually coincide with p, q, r.

Table 8 compares the thermal ellipsoids derived in the present investigation from least-squares (LS) with those from differential synthesis (DS) refinement. The dimensions and angle of tilt of the silicon ellipsoid from DS are all only slightly smaller than those from LS, and the sense of tilt is the same in both cases. The overall agreement between the DS and LS results may be characterized as excellent. The oxygen ellipsoids from DS and LS agree well in dimensions and sense of tilt; however, the magnitude of the rotation from the reference axes p, q, r is considerably greater for DS than for LS. In the light of the magnitudes of the standard errors affecting these angles, this apparent difference between the DS and LS results can hardly be regarded as real. The inapplicability of standard statistical methods to the evaluation of the accuracy of thermal parameters from differential synthesis does not warrant a more intensive comparison of these DS results with the least-squares parameters of SA and YP.

Two points of interest emerge from the foregoing results on the thermal ellipsoid of oxygen. First of all, the order of the ease of vibration, as judged by the r.m.s. amplitudes along the principal axes, agrees with the expected order as predicted by the following analysis: If the Si–O–Si bond angle were 180°, vibrations normal to the Si–Si direction should be isotropic and of greater amplitude than those along the Si–Si direction since force constants for bending bonds are smaller than are those for vibrations along bond directions. Closure of the bond angle at oxygen to 144° results in the removal of the degeneracy normal to the Si–Si direction. In this case we would expect that $u_q > u_p > u_r$ since motion along p now requires some compression (and extension) of the Si–O bonds, but not as much as that along r, while motion along q still only involves bending of the Si–O bonds.

Secondly, the r.m.s. amplitudes along the principal axes are decidedly more isotropic than those found by YP (especially, note again the difference in the u_2 values cited earlier), and the principal axes make smaller angles with the reference cartesian axes, but have larger σ's associated with these angles. We wish to point out that this closer approach to isotropy should of its own accord result in such larger σ's. For, in the limiting case when the values of the r.m.s. amplitudes along two principal axes become identical, the location of the principal axes within the plane becomes meaningless. The conclusions are, of course, similar in the case of triple degeneracy, *i.e.*, complete isotropy of vibration. Also contributing to the higher σ's of SA is the fact that the present reflection data are confined to the Cu sphere; the analysis by Cruickshank (1960) indicates that the accuracy with which thermal parameters are determined is improved by extending the intensity data to higher $(\sin\theta)/\lambda$ values, the data otherwise being of equal quality.

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The Structure of *N*-(*p*-bromophenyl)sydnone

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The crystal structure of *N*-(*p*-bromophenyl)sydnone has been determined. The compound crystallizes in space group $P\bar{1}$, with two molecules in the unit cell. The sydnone ring system is found to be planar within the limits of accuracy. The *N*-phenyl bond is (almost) coplanar with the sydnone ring, but the phenyl ring is rotated about this bond so that the planes of the phenyl ring and the sydnone ring contain a dihedral angle of 27·6°.

Introduction

Meso-ionic compounds, and in particular the sydnones, have received considerable interest in recent years. The chemical properties of meso-ionic compounds have been reviewed by Baker & Ollis (1957). Physicochemical studies of sydnones include investigations of dipole moments (Hill & Sutton, 1953), of ultraviolet spectra (Hammick & Voaden, 1961), and of polarographic behaviour (Zuman, 1959), and the determina-

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