

Refinement of the Crystal Structure of Low-Quartz

BY YVON LE PAGE AND GABRIELLE DONNAY

Department of Geological Sciences, McGill University, Montreal, Quebec, H3C 3G1, Canada

(Received 4 December 1975; accepted 22 January 1976)

The positional and thermal parameters of low-quartz have been redetermined accurately with graphite-monochromated Mo $K\alpha$ radiation and a synthetic crystal, a fragment from a (0110) plate grown at the Bell Telephone Laboratory and tested there for the absence of twinning and of strain. Only the strongest reflexion, 0111, had to be omitted. Least-squares refinement of the 342 observed structure factors led to a residual of 1.71%. Dauphiné twinning, probably stress-induced, is present. Correction of intensities for 0.009 volume fraction of crystal II led to a final unweighted residual of 1.57%. The extinction correction was evaluated to be insignificant and was therefore not applied. Crystal-structure results: space group $P3_221$, origin at $0, 0, \frac{1}{3}$; O in 6(c): $x=0.4141$ (2), $y=0.2681$ (2), $z=0.1188$ (1); Si in 3(a): $u=0.4699$ (1). The agreement of crystal-structure parameters with those obtained by Zachariasen & Plettinger [*Acta Cryst.* (1965), **18**, 710–714] is excellent, except for oxygen coordinates.

Introduction

Professor R. F. Stewart of the Carnegie–Mellon University pointed out to us that a better refinement of the low-quartz crystal-structure parameters was needed for his study of the absolute electron density in the Si–O bond in low-quartz.

Positional parameters for low-quartz were first determined with three-figure precision by Wei (1935) and later redetermined with greater precision by Brill, Hermann & Peters (1939, 1942) who used a milky quartz crystal to reduce the effect of primary extinction. Then Young & Post (1962) performed a careful redetermination of the positional and thermal parameters using spheres of synthetic quartz and obtained a 6.0% residual on more data (309 reflexions) collected with Mo $K\alpha$ radiation. A severe extinction correction was applied to their data. Smith & Alexander (1963) obtained results of comparable precision on a natural quartz crystal with limited data collected with Cu $K\alpha$ radiation: they attained a 3.3% residual on 112 independent reflexions. Only the 0111 reflexion was seriously affected by extinction and left out of their refinement. Zachariasen & Plettinger (1965) applied corrections for twinning and for primary and secondary extinction to data collected with Cu $K\alpha$ on a small sphere. They attained a 2.3% residual, on 109 reflexions, which was further lowered to 1.8% after adjustment of the atomic scattering curves.

Crystal sample

The sample used was a small chip taken from a 0.08 mm thick wafer of a synthetic crystal, cut approximately parallel to (01.0) by Dr Robert L. Barns at the Bell Telephone Laboratories. He determined the sample to be free from electrical and optical twinning* and also free from strain.

* For the correlation of the physical tests and resulting terminology with the crystallographic classification of quartz twins, see Donnay & Le Page (1975).

The chip is irregular in shape with dimensions $0.08 \times 0.15 \times 0.26$ mm. The longest dimension, making an angle of about 10° with c , was mounted along the axis of the goniometer head.

The cell dimensions used (Table 1) are the mean values of those determined by Cohen & Sumner (1958) on three different samples of synthetic quartz from Bell Telephone.

Table 1. *Crystal data*

Cell dimensions after Cohen & Sumner (1958).

$a = 4.9134 \text{ \AA}$	Chemical formula: SiO_2
$c = 5.4052$	Space group: $P3_221$
$V = 113.01 \text{ \AA}^3$	$Z = 3$
Temperature 293K	

Linear absorption coefficient for Mo $K\alpha = 9.71 \text{ cm}^{-1}$
[from *International Tables for X-ray Crystallography* (1974)].

For a Gaussian distribution of intensity measurements, the *mean deviation* from the mean of a normal variate is $\sigma\sqrt{2/\pi} = 0.80\sigma$ (*International Tables for X-ray Crystallography*, 1959). For the present intensities the value is 0.88σ . This is close enough to the theoretical value to show that counting statistics are the only important single source of uncertainty in these intensity data. The low linear total absorption coefficient of 9.71 cm^{-1} (Table 1) and the irregular shape of the fragment, which would have made an accurate absorption correction impossible, led to the decision to omit the absorption correction.

A spherical crystal was not used because the synthetic wafer was not thick enough to give a sphere of sufficient volume. A 'Herkimer diamond' (gem-quality quartz crystal from Herkimer Co., New York) had been used first. It was ground into a sphere of 0.2 mm radius. An intensity test of the sphere showed pronounced extinction effects and about 1.5 vol. % of Dauphiné twinning. Other twin laws, likely to be present, could not be identified on the sphere. The

natural spherical sample thus gave intensities greatly inferior to those of the synthetic crystal fragment.

Experimental procedure

The reflexion intensities were measured on an automated 4-circle Picker diffractometer, using graphite-monochromated Mo $K\alpha$ radiation. The θ - 2θ scan method was used and the crystal was turned through the angle θ at $0.5^\circ \text{ min}^{-1}$. All reflexions, up to $2\theta=90^\circ$, were collected in the hemisphere $l \geq 0$. The indices h and k ranged from -9 to $+9$ and the index l from 0 to 10 .

The intensities of the six symmetry-equivalent reflexions in Laue group $\bar{3}2/m$ were averaged and showed a 2.6% mean deviation of the square root of the intensity, permitting a residual as low as 1.1% to be significant. We measured 397 independent intensities, of which 342 were observed. The criterion for observation was $I_{\text{obs}} > 3\sigma(I_{\text{obs}})$, where the variance of the intensity was based on counting statistics.

Refinement of the crystal structure

We used the *DATRDN* program of the X-RAY 70 system of programs (Stewart, Kundell & Baldwin, 1970) to correct intensities for Lorentz and polarization factors. The atomic Si and O mean scattering factors and the Si dispersion correction were taken from *International Tables for X-ray Crystallography* (1962). To facilitate comparison with the results of earlier investigations, we employed the space-group positions of Wyckoff (1931) and the coordinates of Smith & Alexander (1963), but we used space group $P3_221$ (D_3^2) (all screw axes are left screws) which is equivalent* to Wyckoff's $P3_121$ (D_3^3).

Like Wyckoff, but unlike *International Tables for X-ray Crystallography* (1952, p. 259), we take the origin of the coordinate system at the intersection of the 3_2 axis with the twofold axis along the x direction. With that origin, the silicon atoms are in the special position $3(a) u, 0, 0$, and the oxygen atoms are in general position $6(c) x, y, z$. Least-squares refinement of atomic coordinates and anisotropic thermal parameters was performed by use of the *CRYLSQ* program. We gave unit weights to the $F_{\text{obs } hkl}$ and obtained an unweighted residual of 2.0% for observed reflex-

ions only. A survey of observed and calculated structure factors showed that the $01\bar{1}1$ reflexion, having the second lowest 2θ value (12.20°) and much the highest F_{obs} value, was computed to be 38.73 electrons while it was observed to be 34.22 electrons. After taking it out of the list of structure factors, the residual dropped to 1.71%.

Dauphiné twinning in our sample

Although the crystal wafers sent to us were ascertained to be free from any twinning, some Dauphiné twinning [$6'22'=(3.2')22'$] could have been produced by breaking the chip off the wafer. We are not concerned here with the Brazil twinning [$\bar{3}'2/m'=(3.1')2/m'$] since its effect would not change the X-ray data, which are centrosymmetric by Friedel's law (Laue class $\bar{3}2/m$), nor with the combined twinning ($\bar{6}'2m'=3/m'2m'$), which Friedel's law transforms like Dauphiné twinning into $6'/m'2/m'2'/m'$. Note that the latter twin symmetry does not imply Laue class $6/m2/m2/m$ nor does it simulate diffraction symmetry $6/m2/m2/m$. Brazil twinning is an example of 'twinning by merohedry of class I', while Dauphiné twinning and combined twinning illustrate 'class II' (Catti & Ferraris, 1976).

One of the twin operations that can be used to describe Dauphiné twinning in quartz is a 180° rotation around the threefold axis. It superposes, on the reciprocal lattice node $hk.l$ of crystal I, the node $h\bar{k}.l$ of crystal II, which by Laue symmetry is equivalent to node $kh.l$ in the same crystal II. Whenever $F_{hk.l}$ is sufficiently different from $F_{h\bar{k}.l}$, the pair becomes an indicator of Dauphiné twinning. Either member of the pair may give the more intense reflexion. The above treatment was first proposed by Young & Post

Table 2. List of the most significant Dauphiné-twinning indicators

	10 $ F_{\text{obs}} $	10 $ F_{\text{calc}} $		10 $ F_{\text{obs}} $	10 $ F_{\text{calc}} $
3 0.1	23	12	5 0.4	17	14
0 3.1	268	272	0 5.4	134	134
4 0.1	161	164	2 1.4	148	146
0 4.1	54	52	1 2.4	32	30
5 0.1	18	18	4 1.4	105	105
0 5.1	57	57	1 4.4	31	30
6 0.1	89	91	5 1.4	17	17
0 6.1	30	29	1 5.4	59	59
7 0.1	16	15	4 3.4	68	68
0 7.1	86	87	3 4.4	18	16
3 2.1	20	15	3 0.5	74	74
2 3.1	153	153	0 3.5	24	22
5 2.1	22	22	5 0.5	90	91
2 5.1	111	113	0 5.5	24	23
3 2.2	91	91	7 0.5	74	75
2 3.2	28	27	0 7.5	17	15
1 0.3	20	14	2 1.5	41	40
0 1.3	137	135	1 2.5	123	123
4 1.3	45	44	4 1.5	20	20
1 4.3	134	136	1 4.5	98	99
2 0.4	82	81	5 2.5	50	51
0 2.4	14	15	2 5.5	15	13
4 0.4	11	10	4 1.6	89	90
0 4.4	60	60	1 4.6	17	15

* The confusion stems from the very definition of a screw axis: the old convention (Wyckoff, 1922, 1931, 1963; Friedel, 1926) used clockwise rotation as seen when looking in the $-Z$ direction, accompanied by a translation component in the $+Z$ direction, so that C_3^3 , which designated a 3_1 axis, was a left screw; *International Tables for X-ray Crystallography* (1952) recognized the left screw, kept the C_3^3 symbol, but interpreted the screw axis as a 3_2 because the sense of the rotation was changed to counterclockwise (the 'direct' or 'trigonometric' sense of the mathematicians). Donnay (1964), in a review of Wyckoff's (1963) volume, mentions the discrepancy. Parthé (1964) still refers low-quartz to ' $D_3^3-P3_121$ ', which should read ' $D_3^2-P3_221$ '.

(1962) and carried out by Smith & Alexander (1963). We write the well-known equation:

$$|F_{hk.l}|_{\text{obs}}^2 = (1-x)|F_{hk.l}|_I^2 + x|F_{hk.l}|_{II}^2,$$

in which x is the volume fraction of crystal II in the twin. The list of the most significant pairs (Table 2) shows that Dauphiné twinning is present in our sample, but in a small amount ($x=0.009$).

In the same way, we evaluate the relative volume of crystal II to be 0.013 for Smith & Alexander and 0.056 for Young & Post.

We then evaluate the observed contribution of structure I to the observed structure factor of the twin:

$$|F_{\text{obs } hk.l}|_I^2 = |F_{\text{obs } hk.l}|^2 - x|F_{\text{obs } kh.l}|^2.$$

With the observed structure factors of crystal I as input data, the structure of quartz refines to a final residual of 1.57%, a very significant improvement.*

The above treatment is equivalent to the correction used by Zachariasen & Plettinger (1965) in the treatment of the same problem. Their volume fraction of crystal II was 0.015.

Correction for extinction

Zachariasen (1963) establishes that the structure factor corrected for extinction, F_{corr} , is given by $F_{\text{corr}} = KF_{\text{obs}}[1 + \beta(2\theta)CI_{\text{obs}}]$, where F_{obs} is the observed structure factor, I_{obs} the observed integrated intensity and $\beta(2\theta)$ is a geometric factor depending only on the 2θ angle. K and C are constants to be adjusted. In an effort to evaluate K and C , we draw the graph $F_{\text{corr}}/F_{\text{obs}} = f[\beta(2\theta)I_{\text{obs}}]$. It should be a straight line of slope KC intersecting the ordinate axis at K . We

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31645 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

obtain $K=0.995$ and $C=0$ within our experimental accuracy. K corresponds to a scale factor. Its value is not 1 because the scale factor is evaluated from least squares and not from the mean value. Therefore no extinction correction has to be made.

Comparison of our results with the results of previous authors

Table 3 summarizes the results of this study together with those of Young & Post (1962), Smith & Alexander (1963) and Zachariasen & Plettinger (1965). Following Cruickshank (1965), we give, not β_{ij} but the U_{ij} thermal parameters. The silicon atom is in a special position 3(a): $u, 0, 0$, on a twofold axis extending in the x direction. The constraints on the thermal parameters for such a site symmetry are: $U_{12} = \frac{1}{2}U_{22}$ and $U_{13} = \frac{1}{2}U_{23}$ (Johnson & Levy, 1974).*

The agreement between our results and the results of Zachariasen & Plettinger is so good for all parameters except the x and y coordinates of oxygen that we are very baffled by the large discrepancies of these parameters. While we agree within 1σ on most of the other parameters, the discrepancy is 4σ on the x coordinate and 4.5σ on the y coordinate. This could follow from a systematic error due to the use of a limited $(\sin \theta)/\lambda$ range. Smith & Alexander, who also used $\text{Cu K}\alpha$ radiation, find the same y coordinate as Zachariasen. Zachariasen & Plettinger had found thermal parameters very different from those of Smith & Alexander who agreed with Young & Post. We agree completely with Zachariasen & Plettinger and we find that the r.m.s. displacements of the silicon atom in the directions of the principal axes of the

* The zero values of β_{12} and β_{23} in Table 4 of Smith & Alexander (1963) are a misprint. These values, as well as the blank values given by Young & Post (1962), must be interpreted as $\beta_{12} = \frac{1}{2}\beta_{22}$ and $\beta_{23} = 2\beta_{13}$ (Smith, 1975).

Table 3. *The crystal structure parameters after refinement*

The thermal parameters are in \AA^2 and multiplied by 100. They have the form:

$$T = \exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})].$$

	This study		Zachariasen & Plettinger (1965)		Smith & Alexander (1963)		Young & Post (1962)	
	342 Obs. refl., R=1.57% a=4.9134, c=5.4052 Å		109 Obs. refl., R=1.8% a=4.9128, c=5.4042 Å		112 Obs. refl., R=3.3% a=4.9138, c=5.4052 Å		309 Obs. refl., R=6.0% a=4.9128, c=5.4052 Å	
	Si	O	Si	O	Si	O	Si	O
x	0.46987 (9)	0.4141 (2)	0.4697 (2)	0.4125 (4)	0.4698 (3)	0.4145 (8)	0.4705 (3)	0.4152 (7)
y	0*	0.2681 (2)	0	0.2662 (4)	0	0.2662 (7)	0	0.2678 (6)
z	0*	0.1188 (1)	0	0.1188 (2)	0	0.1189 (4)	0	0.1184 (4)
U_{11}	0.66 (1)	1.56 (4)	0.65 (4)	1.63 (9)	0.48 (6)	1.28 (16)	0.45 (4)	1.31 (10)
U_{22}	0.51 (2)	1.15 (3)	0.54 (5)	1.27 (8)	0.27 (7)	1.05 (14)	0.25 (5)	0.74 (8)
U_{33}	0.60 (1)	1.19 (3)	0.59 (3)	1.28 (7)	0.63 (6)	1.28 (12)	0.72 (4)	1.33 (9)
U_{12}	$\frac{1}{2}U_{22}$ *	0.92 (3)		0.97 (8)		0.69 (12)		0.78 (8)
U_{13}	$\frac{1}{2}U_{23}$ *	-0.29 (3)		-0.27 (7)		-0.35 (12)		0.37 (8)
U_{23}	-0.03 (1)	-0.46 (2)	-0.02 (3)	-0.43 (6)	0.04 (4)	-0.44 (10)	-0.02 (4)	0.49 (6)

* Value imposed by symmetry.

thermal vibration ellipsoid are: 0.084 (1), 0.077 (1) and 0.071 (1) Å, respectively, in the direction of x , the direction perpendicular to x making a 14° angle with z in the clockwise direction, and the direction perpendicular to the previous two. The thermal vibration ellipsoid is very close to a sphere, a result which is expected for an atom in a nearly perfect tetrahedral coordination.

The accuracy of the structure parameters, when judged on the basis of σ 's on all parameters, is about three times better in our study than the studies of Young & Post, and Smith & Alexander, and two times better than in Zachariasen & Plettinger. The fact that we did not have to perform extinction corrections and that our specimen contained a comparatively small volume-fraction of the Dauphiné twin, gives us confidence in the present results. Due to the accuracy of the structure refinement, some interesting details are now better resolved. For example, there are two non-equivalent Si–O bonds (Table 4). The agreement of their mean value is good: 1.6065 Å in Young & Post, 1.607 Å in Smith & Alexander, 1.6095 Å in Zachariasen & Plettinger and 1.609 Å in this study. However, the difference between the two bond lengths is more variable. The same authors find, respectively: 0.008(5), 0.020(6), 0.013(4) and 0.004 (2) Å. Silicate groups are known to be quite regular groups. Each time the bond lengths differ significantly in a given tetrahedron, the bond-valence analysis (Donnay & Allmann, 1970) can find the origin of this distortion in a non-equivalent surrounding of the silicate group. In this case, the site-symmetry of Si is 2, but it approximates $\bar{4}$ very closely if we include the neighbouring silicate groups. Therefore, we do not expect the two symmetry-independent Si–O bonds to be significantly different. Any value of the difference between these two bond lengths larger than 0.01 Å is subject to doubt.

Table 4. Distances (Å) and angles (°)

Si–O	1.607(1)	O–Si–O'''	108.70(4)
Si–O'	1.611(1)	O'–Si–O''	108.70(4)
Si–O–Si'	143.68(9)	O'–Si–O'''	109.57(6)
O–Si–O'	110.39(4)	O''–Si–O'''	110.39(4)
O–Si–O''	109.07(6)		

The most prominent peaks on the final Fourier difference map have a height of 0.3 e Å⁻³. They are halfway between Si and O and can possibly be ascribed to the covalent part of the Si–O bond. The two unshared electron pairs of O which are expected in a

tetrahedral direction with respect to the two O–Si bonds are not discernible.

Dr G. S. Smith gave us invaluable help with the temperature corrections. We thank Dr R. L. Barns, Bell Telephone Laboratories, who provided the sample for study. We also thank Professor J. D. H. Donnay who read the manuscript critically and suggested many improvements.

References

- BRILL, R., HERMANN, C. & PETERS, C. (1939). *Naturwissenschaften*, **27**, 676–677.
- BRILL, R., HERMANN, C. & PETERS, C. (1942). *Ann. Phys. Lpz.* **41**, 233–244.
- CATTI, M. & FERRARIS, G. (1976). *Acta Cryst.* **A32**, 163–165.
- COHEN, A. J. & SUMNER, G. G. (1958). *Amer. Min.* **43**, 58–68.
- CRUICKSHANK, D. W. J. (1965). *Acta Cryst.* **19**, 153.
- DONNAY, G. & ALLMANN, R. (1970). *Amer. Min.* **55**, 1003–1015.
- DONNAY, J. D. H. (1964). *Anal. Chem.* **36**, 212.
- DONNAY, J. D. H. & LE PAGE, Y. (1975). *Canad. Mineral.* **13**, 83–85.
- FRIEDEL, G. (1926). *Leçons de Cristallographie*. Paris: Berger–Levrault.
- International Tables for X-ray Crystallography* (1952). Vol. I. Birmingham: Kynoch Press.
- International Tables for X-ray Crystallography* (1959). Vol. II, p. 87. Birmingham: Kynoch Press.
- International Tables for X-ray Crystallography* (1962). Vol. III, pp. 202, 215. Birmingham: Kynoch Press.
- International Tables for X-ray Crystallography* (1974). Vol. IV, p. 35. Birmingham: Kynoch Press.
- JOHNSON, C. K. & LEVY, H. A. (1974). *International Tables for X-ray Crystallography*, Vol. IV, p. 327. Birmingham: Kynoch Press.
- PARTHÉ, E. (1964). *Crystal Chemistry of Tetrahedral Structures*, p. 139. New York: Gordon & Breach.
- SMITH, G. S. (1975). Private communication.
- SMITH, G. S. & ALEXANDER, L. (1963). *Acta Cryst.* **16**, 462–471.
- STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The X-RAY 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- WEI, P. (1935). *Z. Kristallogr.* **92**, 355–362.
- WYCKOFF, R. W. G. (1922). *The Analytical Expression of the Results of the Theory of Space Groups*. Publication No. 18, Carnegie Inst., Wash.
- WYCKOFF, R. W. G. (1931). *The Structure of Crystals*. New York: The Chemical Catalog Co. Inc.
- WYCKOFF, R. W. G. (1963). *The Structure of Crystals*. Vol. I. New York: Interscience.
- YOUNG, R. A. & POST, B. (1962). *Acta Cryst.* **15**, 337–346.
- ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.
- ZACHARIASEN, W. H. & PLETTERING, H. A. (1965). *Acta Cryst.* **18**, 710–714.