Der Approximationsfehler von (20) lässt sich in den nicht streng lösbaren Fällen an graphisch ermittelten Ellipsenwerten testen (Tabellen 2 und 3). Demnach liegt für das Achsenverhältnis $b/a = 1,8$ und für Absorptionswerte $\mu R \leqq 1,8$ der Fehler unter $\pm 2\%$. Der Fehler nimmt sicher ab für $b/a \to 1$. Die gegebene Abschätzung ist auch für dreiachsige Ellipsoide gültig, wobei anstelle von b/a jeweils das grösste Achsenverhältnis tritt.

Für $\mu R > 1,8$ kann der Approximationsfehler zunehmen. Bis $\mu R = 2,5$ zeigt sich jedoch noch kein indikativer Fehler, wie probeweise durchgeführte Extrapolationen der Tabellen 2 und 3 zeigen (Genauigkeit $\pm 3\%$). Da bei hohen μR für kreisnahe Achsenverhältnisse die Approximation zunehmend besser wird, ist es wahrscheinlich, dass auch für den mittleren Absorptionsbereich mit (20) brauchbare Werte entstehen. Der Beweis steht jedoch aus. Für alle μR hat man aber immer wieder Strahlengänge $v_\alpha = v_\beta$, die in allen Fällen genaue Werte und damit sichere Tabellenstützpunkte liefern. In dem untersuchten Bereich wird die Näherung (20) auch hohen Genauigkeitsansprüchen gerecht und ermöglicht es jetzt solche Kristalle eingehender zu untersuchen, bei denen es bisher nicht gelang einfachere Schleifkörper zu erhalten. In der Praxis werden die Messung der Achsenverhältnisse und die Bestimmung der Position des Ellipsoids zur Drehachse und zum Primärstrahl oft grössere Fehlerquellen darstellen, als die Näherung (20). Schliesslich ist bei photographischen Auswertemethoden zu beachten, dass in allen Fällen, in denen die Drehachse des Kristalls keine Rotationssymmetrieachse ist, die Interferenzpunkte auch bei gleichem θ unterschiedliche Form haben.

Die erhebliche Anzahl an Ellipsoidparametern bereitet einer sinnvollen allgemeinen Tabellierung beträchtliche Schwierigkeiten. Die hier gegebene Zurückführung auf die Kugel bzw. den Kreis dürfte daher von Interesse sein. In wenigen Stunden kann für ein gegebenes Problem eine vollständige Tabelle ohne besondere Rechenhilfsmittel aufgestellt werden.

Herrn Prof. Dr. R. Kern (Nancy) danke ich herzlich für Hinweise und für die Durchsicht eines Teils des Manuskriptes.

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On the Regularity of the Tetrahedra in Quartz

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(*Received* 20 *August* 1962)

By an analysis based on symmetry considerations it is possible to specify the conditions under which the SiO_4 tetrahedra in quartz can be strictly regular. For such a configuration the Si–O bond distance in α-quartz must be $(\sqrt{(3)}a - c)/2$, and c/a must be $< (3/2)(\sqrt{(3)} - 1)$; in β-quartz the axial ratio must be $(3/2)(\sqrt{(3)} - 1)$. Comparison of these quantities with published lattice constants shows quite clearly that in the vicinity of room temperature regular SiO_4 tetrahedra are not possible in α-quartz, nor are they possible in β-quartz. Hence, the small deviations from regularity reported in two recent refinements of α-quartz must be regarded as real.

Introduction

On the basis of early structural studies, it has been customary to assume that in quartz as well as in the other pure silica phases the SiO_4 tetrahedra are strictly regular; that any of the small deviations from regularity were simply the result of experimental errors in the diffraction data. Two recent refinements on α-quartz (Young & Post, 1962; Smith & Alexander, 1963) (hereafter designated YP and SA respectively) have yielded bond data which, however, are not entirely clear-cut in this regard; some of the bond data in Table 1 are consistent with the regular configuration, whereas for others the deviations from regularity are large enough to be statistically significant. Because of the importance of quartz in relation to the stereochemistry of the silicates, it is therefore of considerable interest to establish unambiguously whether or not the tetrahedra are to be considered regular within experimental error.

We shall show by an analytical approach that the existence of regular tetrahedra in quartz introduces relationships between the size of the tetrahedra and the unit cell dimensions, and that from the temperature dependence of the latter using the results of Jay (1933) some very definite conclusions can be drawn concerning the regularity of the tetrahedra at a number of temperatures.

Formulation of the constraint conditions

Fig. 1 shows the arrangement of a portion of the tetrahedra in α-quartz relative to both a right-handed primitive trigonal unit cell and to a right-handed centered orthogonal cell whose B axis coincides with the negative direction of a of the trigonal cell, and, by the convention of Wyckoff (1948), with a crystallographic two-fold axis. The trigonal cell contains one independent O in a general six-fold position and one Si in a three-fold special position on the two-fold axis; the space group is $P3_221$. The atoms O, O′ and Si of Fig. 1 have the following fractional coordinates, $(-1+x, y, z)$, $(\bar{y}, x-y, \frac{2}{3}+z-1)$ and $(-1+u, 0, 0)$ respectively along the trigonal axes, and the coordinates, $(y/2, 1-x+y/2, z)$, $(\frac{1}{2}(x-y), \frac{1}{2}(x+y), \frac{2}{3}+z-1)$ and $(0, 1-u, 0)$ respectively along the orthogonal axes.*

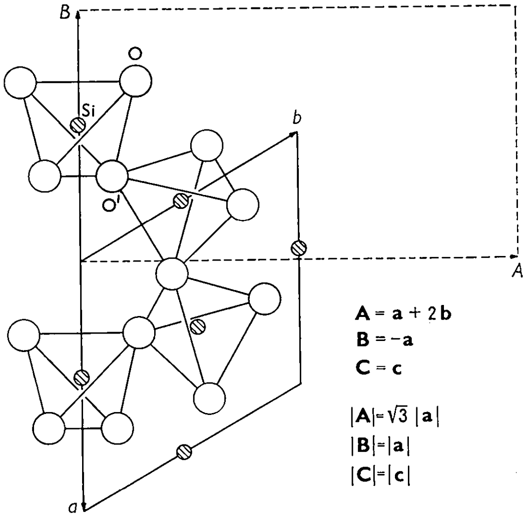

Fig. 1. The atomic arrangement in α-quartz seen in projection down the c-axis with the relationship between the trigonal and orthogonal unit cells also shown. The oxygen tetrahedra are outlined with solid lines.

With the change of variables: $X=\frac{1}{2}(x-y)$, $Y=\frac{1}{2}(x+y)$, $Z=\frac{2}{3}+z-1$ and $U=1-u$, the coordinates (in Å units) become

$$\begin{array}{llll} \text{O} & (\frac{1}{2}A(Y-X) & B(1-\frac{1}{2}(Y+3X)) & C(Z+\frac{1}{3})) \\ \text{O}' & (AX & BY & CZ) \\ \text{Si} & (0 & BU & 0)\,. \end{array} \qquad (1)$$

If this tetrahedron of oxygens is strictly regular, the two-fold axis through Si (along **a** or **B**) must become a $\bar{4}$ axis of symmetry for the SiO$_4$ group, and the angle O–Si–O′ must be equal to $\cos^{-1}(-\frac{1}{3})$. O would be related to O′ by a *clockwise rotation* (looking along the positive direction of **B**) of the $\bar{4}$ axis followed by *inversion* through the point $(0, BU, 0)$, (the reader is asked to bear in mind that $Z<0$). The coordinates (in Å units) for O resulting from this operation are

$$(-CZ, B(2U-Y), AX)\,. \qquad (2)$$

If the tetrahedron is to have $\bar{4}$ symmetry, these coordinates must be the same as those generated by the space group symmetry, or

$$-CZ=\tfrac{1}{2}A(Y-X) \qquad (3)$$

$$B(2U-Y)=B(1-\tfrac{1}{2}(Y+3X)) \qquad (4)$$

$$AX=C(Z+\tfrac{1}{3})\,, \qquad (5)$$

and if the tetrahedron be regular,

$$B(U-Y)=d\cos(\angle\ \text{O–Si–O}'/2)=d/\sqrt{3}\,, \qquad (6)$$

where

$d=$ Si–O bond distance $=(A^2X^2+B^2(U-Y)^2+C^2Z^2)^{\frac{1}{2}}$.

Subtracting (3) from (5) we obtain

$$X+Y=2C/(3A)=2c/(3\sqrt{(3)}a)=x\,. \qquad (7)$$

From (4) and (6) and making use of (7), we get

$$d=(A-C)/2\,, \qquad (8)$$

and the solution of (5) and

$$A^2X^2+C^2Z^2=d^2\sin^2(\angle\ \text{O–Si–O}'/2)=2d^2/3$$

for X yields

$$2AX=(C/3)\pm((4d^2/3)-(C^2/9))^{\frac{1}{2}}. \qquad (9)$$

From (8) we see that a solution to the system of linear equations set forth by equations (3) through (6) is only possible for prescribed values of the Si–O bond distance; for any other values the system of equations is *mathematically* inconsistent. At the same time, equation (9) requires

$$d^2\geq C^2/12 \quad \text{or} \quad d\geq(\sqrt{3}/6)c\,. \qquad (10)$$

Perhaps it is not surprising to encounter such restrictions on the bond distance since the coordinates required by the space group are generated by a three-fold screw axis, an operation which is not a symmetry element of a tetrahedron. Equations (8) and (10) therefore represent the constraints imposed on the size of the tetrahedron and the coordinate system (*i.e.* the unit cell dimensions) such that the coordinates generated by such divergent symmetry elements can be made identical.*

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* The coordinate transformation is $\mathbf{x}_{\text{orthog.}}=\overparen{\mathbf{R}^{-1}}\mathbf{x}_{\text{trig.}}$ where $\overparen{\mathbf{R}^{-1}}$ is the matrix $(0, \frac{1}{2}, 0/-1, \frac{1}{2}, 0/0, 0, 1)$.

* Any lack of conformity with the constraint conditions is clearly attributable to irregularities in the tetrahedra since there exists ample evidence for the space group, $P3_221$ (or its enantiomorph, $P3_121$).

The analysis of the situation in β-quartz is considerably simpler because of the higher site symmetry for Si. In terms of the space group $P6_222$, silicons occupy the $3c$ positions of 222 symmetry; oxygens are in the $6j$ positions with $x=0{\cdot}197$ (Wyckoff, 1948). The atoms in β-quartz corresponding to O, O′ and Si of Fig. 1 have the respective fractional coordinates $(-1+2x, x, \frac{1}{6})$, $(-x, x, -\frac{1}{6})$ and $(-\frac{1}{2}, 0, 0)$ relative to hexagonal axes. Transformation of these positions according to $\widetilde{\mathbf{R}^{-1}}$ yields the following coordinates in Å:

$$\begin{array}{llll} \mathrm{O} & (A(x/2), & B(1-3x/2), & C/6) \\ \mathrm{O}' & (A(x/2), & B(3x/2), & -C/6) \\ \mathrm{Si} & (0, & B/2, & 0)\,. \end{array} \qquad (11)$$

In β-quartz the three $\bar{4}$ axes of the hypothetical tetrahedron are either coincident with or parallel to axes of the orthogonal cell.

From the $\bar{4}$ axis coincident with $\mathbf{B}$, we require

$$A(x/2)=C/6 \quad \text{or} \quad x=C/(3A)\,. \qquad (12)$$

From the $\bar{4}$ axis parallel to $\mathbf{C}$ we require

$$A(x/2)=(B/2)-B(3x/2) \quad \text{or} \quad x=1/(3+\sqrt{3})=0{\cdot}2113\,. \qquad (13)$$

Equations (12) and (13) can be combined to read

$$c/a=\tfrac{3}{2}(\sqrt{3}-1)=1{\cdot}0981\,. \qquad (14)$$

Thus in order to have regular tetrahedra in β-quartz the axial ratio and the one variable positional parameter are required to be fixed numbers, independent of temperature. From (12) and (13) it is also evident that the Si–O bond distance for the atoms in (11) is required to be equal to $\sqrt{(3)}c/6$. Similarly, (8) and (10) can be combined to yield the relation

$$c/a \leq \tfrac{3}{2}(\sqrt{3}-1)\,, \qquad (15)$$

for the axial ratio in α-quartz. It follows then that the axial ratio in α-quartz should be less than or equal to the axial ratio in β-quartz, if regular SiO_4 tetrahedra are present.

Results

Table 1. *Interatomic distances and bond angles in α-quartz at room temperatures*

	Si–O		∠ Si–O–Si	
SA	1·617 Å	1·597 Å	144·0°	
YP	1·611	1·603	143·9	
	O · · · O		∠ O–Si–O	
SA	2·640 Å	2·637 Å	110·3°	109·5°
	2·614	2·604	109·2	108·8
YP	2·641 Å	2·635 Å	110·1°	110·0°
	2·613	2·613	109·2	108·7

Ave. e.s.d.'s from both studies: Si–O, 0·003Å; O · · · O, 0·004 Å; ∠ Si–O–Si, 0·2°; ∠ O–Si–O, 0·2°.

Numerical values for equations (8) and (10) together with values for the c/a ratio at various temperatures are given in Table 2; lattice constants reported originally in kX units by Jay (1933) have been multiplied by 1·00202 to effect the conversion to Å units. Jay's estimates of errors are: c, one part in 30,000; d_{100}, one part in 40,000; and c/a, one part in 20,000.

Reference to Table 2 shows that numerically the c/a ratio in quartz decreases steadily with increasing temperature and that this ratio is always higher in the α-phase than in the β-phase. Indeed from at least 18 to ~ 280 °C, the axial ratio actually exceeds the maximum value permitted by (15), and so in this temperature range (of perhaps greatest interest) we can at once conclude that the lattice constants *alone* are inconsistent with there being regular tetrahedra in α-quartz, due consideration being given to the experimental errors. At ~ 280 °C when the equal sign in (15) is applicable, regular tetrahedra nominally become possible. However, in such a case, the fractional coordinates as given by equations (9), (7), (6) and (5) become $(X, 3X, -\frac{1}{6})$ for O′ with $X=C/6A$ and $(0, \frac{1}{2}, 0)$ for Si, parameters which are identical with those demanded by the (hexagonal) β-quartz structure (see equation (11)). Thus if there were regular tetrahedra, the $\alpha \rightarrow \beta$ transformation would occur at ~ 280 °C instead of at ~ 580 °C as is actually the case. (Strictly speaking then, only the inequality signs in (10) and (15) prevail in the α-phase; we henceforth reserve the equality signs for the β-phase.)

We can use the magnitudes of the Si–O bond distances required by a regular tetrahedron in α-quartz to infer against such a configuration in the temperature range above 280 °C. In Table 2 all of the requisite bond distances are *shorter*, and significantly so, than any of the experimental distances in Table 1 obtained at room temperature. To put the position succinctly: the Si–O bond distance would have had to decrease with temperature, and then when a regular tetrahedron became established, *increase* with temperature in

Table 2. *Numerical results*

°C	c/a	$d=(3^{\frac{1}{2}}a-c)/2$	$d \geq 3^{\frac{1}{2}}c/6$	°C	c/a	$(3^{\frac{1}{2}}a-c)/2$	$3^{\frac{1}{2}}c/6$
18	1·1000	1·5525 Å	1·5601 Å	525	1·0952	1·5812	1·5700 Å
118	1·0994	1·5564	1·5615	567	1·0940	1·5881	1·5723
203	1·0987	1·5602	1·5628	579	1·0923	β-quartz*	
280	1·0980	1·5644	1·5640	590	1·0921		
366	1·0972	1·5690	1·5657	610	1·0921		
418	1·0965	1·5727	1·5667	665	1·0919		
494	1·0957	1·5782	1·5690	730	1·0919		

* Jay gives the α–β transformation temperature as 579 °C, and considers this within experimental error of the acknowledged temperature 575 °C.

accordance with the values in Table 2. Lastly, the observed axial ratios in β-quartz, while largely independent of temperature, deviate some 100σ from the required value of 1·0981; we can thus rule out the possibility of regular tetrahedra in β-quartz as well.

A further point can be answered by the present analysis. Equation (7), we note, is obtained under the condition that the tetrahedron has $\bar{4}$ symmetry, not necessarily the full symmetry of a regular tetrahedron (since (6) is not used in obtaining (7)). Accordingly, the x parameter of the independent oxygen is required to be $\frac{2}{3}C/A$, numerically 0·4234 at 25 °C using $a=4{\cdot}9032$ kX, $c=5{\cdot}3937$ kX (Lipson & Wilson, 1941). The experimental values of x are $0{\cdot}4152 \pm 0{\cdot}0007$ (YP) and $0{\cdot}4145 \pm 0{\cdot}0008$ (SA). Since 0·4234 minus either 0·4152 or 0·4145 is $\sim 10\sigma$, the experimental results at room temperature are therefore indicative of a (statistically) significant distortion from even $\bar{4}$ symmetry.

There are several other substances to which the present analysis can be directly applied. One polymorph of GeO_2 is found to have the α-quartz-type structure (Zachariasen, 1928). The GeO_4 tetrahedra cannot, however, be regular as the constraint conditions, (8) and (10), yield respectively $d=1{\cdot}498$ Å and $d>1{\cdot}630$ Å using $a=4{\cdot}987$ Å and $c=5{\cdot}652$ Å at 26 °C (Swanson & Tatge, 1953). On the other hand, the possibility of regular tetrahedra in BeF_2 is decidedly more favorable. Roy, Roy & Osborn (1953) report a transition temperature of 220 °C between α and β-quartz-like forms. From their graph of the temperature dependence of a and c we read $c/a=5{\cdot}16/4{\cdot}72=1{\cdot}093$ at 25 °C and a constant value of $c/a=5{\cdot}24/4{\cdot}77=1{\cdot}099$ in the β-phase. Hyde, O'Connor & Wait (1958) likewise report an axial ratio of 1·092 at 25 °C in the quartz form of BeF_2, so that the error in the above ratios may be as low as ±0·001. The prescribed Be–F bond distances would be $1{\cdot}50_8$ Å in the α-form at 25 °C and $1{\cdot}51_3$ Å in the β-form.

Discussion

Although the analysis is derived expressly for the situation in quartz, it is important to stress that only one general principle is involved; we have simply investigated the conditions whereby two symmetry operations, one required of an assumed molecular configuration and the other required by the space group, can be geometrically congruent. In doing so, it has not been necessary to postulate the atoms (or ions) as non-deformable and non-interpenetrating spheres packed according to some prescribed rule. Quite possibly, a similar analysis could be used to establish ratios and bond distances for other systems where differing atomic sizes and/or definite directional bonding can safely be assumed.

We observe that in quartz this analytical approach has considerable sensitivity in detecting small deviations from an ideal symmetry. Whereas the experimental bond data only conditionally* point to some degree of irregularity in the SiO_4 tetrahedra, the present analysis shows that at room temperature the bond distance required of a regular SiO_4 tetrahedron is numerically 1·55 Å, some 0·06 Å (or $\sim 20\sigma$) shorter than the average experimental value. Furthermore, when accurate lattice constants were available, we have already seen that in some cases we did not even need to compare the experimental and required bond distances; the values of the observed lattice constants alone were sufficient to rule out the possibility of a regular tetrahedron. From this it would seem that small deviations distributed among the several equivalent tetrahedra within the unit cell produced a concomitantly large effect on the lattice constants.

Conclusions concerning α-quartz

We have the results then that at room temperature the SiO_4 tetrahedron in α-quartz is neither regular nor does it have even $\bar{4}$ symmetry; nothing, however, in the present analysis excludes the possibility of equal Si–O bond distances. Nevertheless, in the absence of the higher site symmetry for the SiO_4 group, it is perhaps only appropriate to take the bond data of Table 1 strictly at face value. We can thus consider the independent Si–O bond distances of $1{\cdot}597 \pm 0{\cdot}003$ Å and $1{\cdot}617 \pm 0{\cdot}003$ Å reported by SA as significantly different from an average value of 1·607 Å. Although the bond distances found by YP deviate less pronouncedly, we suggest that α-quartz at 25 °C be considered to have two different types of Si–O bond lengths, one $1{\cdot}600 \pm 0{\cdot}003$ Å and the other $1{\cdot}614 \pm 0{\cdot}003$ Å, the mean values from the two refinements.

The author wishes to thank Dr Leroy E. Alexander for his kind interest and helpful advice during the present investigation.

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* The proper statistical approach in this case would be to subject the bond data to a generalized analysis which considers these structural parameters simultaneously and which takes into account their correlations (*International Tables for X-ray Crystallography*, Vol. II, p. 94). The regularity or lack of it at the given temperature would be established through the use of a multiparameter significance level test.