THE CRYSTAL STRUCTURE OF QUARTZ

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Abstract

Crystal structure of quartz.—Photographs by the powder method of X-ray crystal analysis have confirmed the *space-lattice* proposed by others. A careful study of 30 possible arrangements has shown that the *arrangement of atoms* which best fits the observed intensities of the lines in the pattern differs somewhat from those previously proposed, maintaining more clearly the identity of the molecule SiO_2. These molecules are obtuse-angled isosceles triangles (angle at Si atom-center, 115° 14′; distance between Si and O atom-centers, 1.631×10^{-8} cm) lying in the basal planes of each of three interpenetrating hexagonal space-lattices, so that the crystal may be considered as built up of layers of molecules, much closer together than adjacent molecules in the same layer.

PREVIOUS investigators have shown that the fundamental space-lattice of quartz is hexagonal (Γ_h) and that three molecules SiO_2 are to be associated with each unit of structure (pair of adjacent triangular right prisms, edge of base *a*, altitude *c*). A recent theoretical paper by Huggins [1] suggests a simple arrangement of atom-centers consistent with these facts and with the atomic radii for Si and O determined otherwise. Photographs by the powder method of X-ray crystal analysis have been taken, and a search has been made for an atomic arrangement consistent with the observed intensities of the lines in the pattern. The best arrangement differs in some respects from that suggested by Huggins and may prove to be of value in determining the shapes of the component atoms. Study of other crystalline forms of silica has been undertaken to throw additional light on this question.

The most general arrangement consistent with previous data is shown in Fig. 1 which gives two projections of a single unit of structure, outlined in dashes. The upper projection is on the basal plane (00.1)[2] and the lower on one of the lateral planes (01.0). The only elements of symmetry are the digonal rotation-axes, Q_1, Q_2, and Q_3, and the trigonal screw-axes, P_1, P_2, and P_3, the latter having translation-components, $c/3$.

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[1] M. L. Huggins, Phys. Rev. (2) **19**, 363–368 (1922).

[2] This notation for indices of form in the hexagonal system avoids including a derived index, the third being always the sum of the first and second with the sign changed. It also eliminates negative indices in the symbols for typical planes; *e.g.*, (01.0) for $(01\bar{1}0)$, and sets off the fourth index which is not of the same crystallographic value as the first three. Cf. A. W. Hull and W. P. Davey, Phys. Rev. (2) **17**, 549–570 (1921), on charts only.

The direction of the translation along the screw-axes determines whether the quartz is optically right- or left-handed. In the notation of Hilton[1] the symbol of the space-group is D_3^3 or D_3^5 and the symmetry is that of rhombohedral enantiomorphy in the hexagonal system.

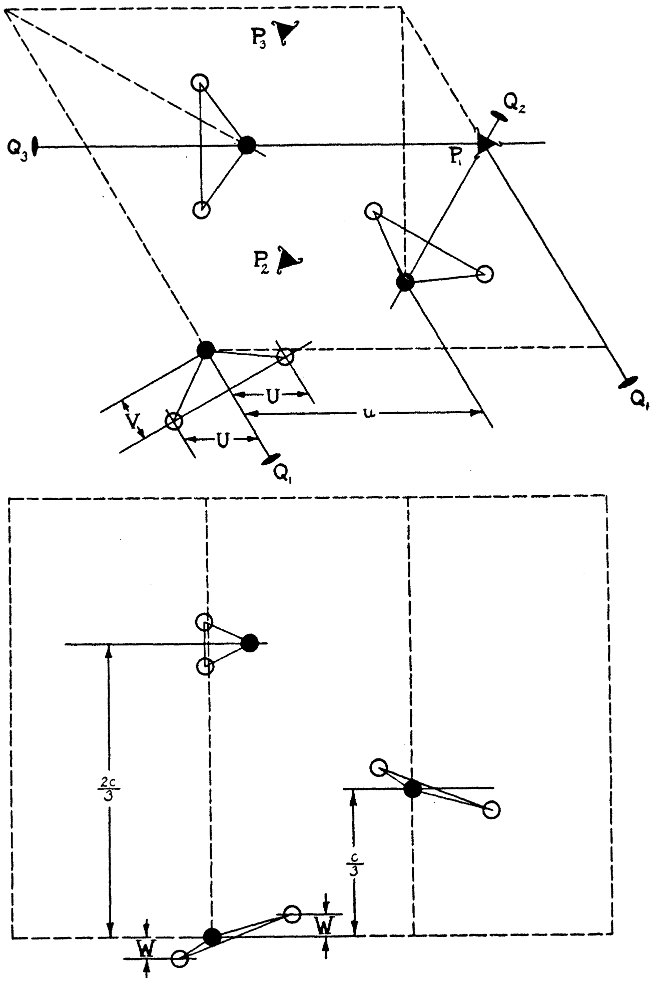

FIG. 1

For convenience in wording, we will speak of a molecule SiO_2, meaning thereby any silicon atom and the two nearest oxygen atoms. This will be ambiguous only in case more than two oxygen atoms are equally near, and in that case we will arbitrarily regard as a molecule any silicon atom and the two nearest oxygen atoms which lie nearest to the basal plane (00.1) through its center.

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[1] H. Hilton, Mathematical Crystallography, Oxford (1903).

The symmetry of the crystal now requires that:

(*a*) In each molecule the two O-atom-centers are equidistant from the Si-atom-center, so that the three atom-centers determine an isosceles triangle.

(*b*) Each Si-atom-center is equidistant from two O-atom-centers in adjacent molecules, the Si-atom-centers of which belong to different space-lattices from each other and from that of the Si-atom-center under consideration.

The special additional assumptions made by Huggins may be expressed in various ways. The reason for the choice here made will be evident when the experimental result is discussed. They are as follows:

(*c*) Each O-atom-center is equidistant from two Si-atom-centers, and the plane determined by these three points cuts the basal plane (00.1) of the space-lattice of one of its Si-atom-centers in one of its principal rows of points.

(*d*) The distance between the members of any adjacent pair of unlike atom-centers is 1.82×10^{-8} cm.

These assumptions completely fix the positions of both Si- and O-atom-centers for any particular values of the space-lattice parameters a and c. The values of a and c quoted by Huggins are due to the Braggs,[1] and are $a = 4.89 \times 10^{-8}$ cm, $c = 5.375 \times 10^{-8}$ cm. It is not at all difficult to compute the coördinates of the atom-centers and the angles between lines joining any atom-center to its neighbors. The following table gives the results of such calculations.

Table I

Crystal Constants Computed on Huggins' Assumptions

$a = 4.89 \times 10^{-8}$ cm, $c = 5.375 \times 10^{8}$ cm.

Coördinates of atom-centers, grouped by molecules.

Si	$[0, 0, 0]$	
O	$[0.381a, 0.025a, 0.041c]$	$[-0.381a, -0.356a, -0.041c]$
Si	$[0.591a, 0.182a, 0.333c]$	
O	$[0.566a, 0.538a, 0.374c]$	$[0.947a, 0.157a, 0.292c]$
Si	$[0.409a, 0.591a, 0.667c]$	
O	$[0.053a, 0.210a, 0.708c]$	$[0.434a, 0.972a, 0.626c]$

Angles at atom-centers between lines to adjacent atom-centers

At Si between lines to O of same molecule	127° 10′
At Si between lines to O of adjacent molecules	121° 09′
At O between lines to Si of same molecule and Si of adjacent molecule	118° 27′

Distance between Si- and O-atom-centers, either of same or of adjacent molecules, 1.82×10^{-8} cm.

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[1] W. H. Bragg and W. L. Bragg, X-Rays and Crystal Structure, London (1915).

The approximate relative intensities of the various possible reflections can be computed for any proposed arrangement of atoms by the formulæ

$$\begin{aligned} I &= md^3(A^2 + B^2), \\ A &= \sum_p \rho_p \cos 2\pi(hx_p + ky_p + lz_p), \\ B &= \sum_p \rho_p \sin 2\pi(hx_p + ky_p + lz_p), \end{aligned}$$

wherein h, k, l are the Miller indices of the reflecting planes (multiplied by the order of reflection), m is the number of families of such planes, d is the perpendicular distance between adjacent planes (divided by the order of reflection), ρ_p is the scattering power of the atom p, which has the coördinates x_p, y_p, z_p, in terms of the three principal parameters (in this case a, a, c). The values of ρ_p are in this case assumed to be the same for silicon with four electrons removed, and oxygen with two electrons added, it being thought reasonable to assume that the molecule SiO_2 is held together by the powerful electric forces which this exchange of electrons would create. The equations given above differ from those of Wyckoff[1] only by the factor md in the first formula, which takes care of the special circumstances of the powder method. The testing of any proposed arrangement consists then in the computation of I for the first few reflections, corresponding to the largest values of d, and a comparison with the relative intensities actually observed in the photographs. The values of I are surprisingly sensitive to small changes in the coördinates of the atom-centers.

In seeking a suitable arrangement, conditions (a) and (b) must of course be retained, so that the twenty-four coördinates of atom-centers not at the origin are by no means independent. There are, however, four variables at disposal, u, U, V, W in Fig. 1. The ranges in the values of these variables which have been examined cover the arrangements which do not put two oxygen atom-centers closer together than 1.30×10^{-8} cm, which appears to be a fair minimum value for the diameter of an oxygen atom. The arrangements tested included, of course, that proposed by Huggins. No attempt was made to locate the atom-centers with great apparent accuracy, since the number of uncertain factors, both theoretical and experimental, makes additional accuracy largely illusory. About thirty cases were worked out completely enough to check with the first six possible reflections. The best fit with the observed intensities was found for the values of coördinates given in Table II., and variations of as little as $0.02a$ or $0.02c$ from the preferred values make even the order of intensities different from that observed, so that the probable errors in the coördinates are thought to be somewhat less than this in magnitude.

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[1] R. W. G. Wyckoff, Am. J. Sci. 50, 317–360 (1920).

The parameters of the space-lattice determined from the positions of the lines differ so little from the Braggs' values that it would be merely confusing to substitute new values. The values of a and c used in Table I. have accordingly been used in computing the lower half of Table II.

TABLE II

Crystal Constants from These Experiments

$a = 4.89 \times 10^{-8}$ cm, $c = 5.375 \times 10^{-8}$ cm.

Coördinates of atom-centers, grouped by molecules.

Si	$[0, 0, 0]$
O	$[0.325a, -0.016a, 0][-0.325a, -0.341a, 0]$
Si	$[0.603a, 0.206a, 0.333c]$
O	$[0.619a, 0.547a, 0.333c][0.944a, 0.222a, 0.333c]$
Si	$[0.397a, 0.603a, 0.667c]$
O	$[0.056a, 0.278a, 0.667c][0.381a, 0.928a, 0.667c]$

Angles at atom-centers between lines to adjacent atom-centers

At Si between lines to O of same molecule	115° 14′
At Si between lines to O of adjacent molecules	111° 28′
At O between lines to Si of same molecule and Si of adjacent molecule	137° 50′

Distance between Si- and O-atom-centers

Of same molecule	1.631×10^{-8} cm
Of adjacent molecules	2.176×10^{-8} cm

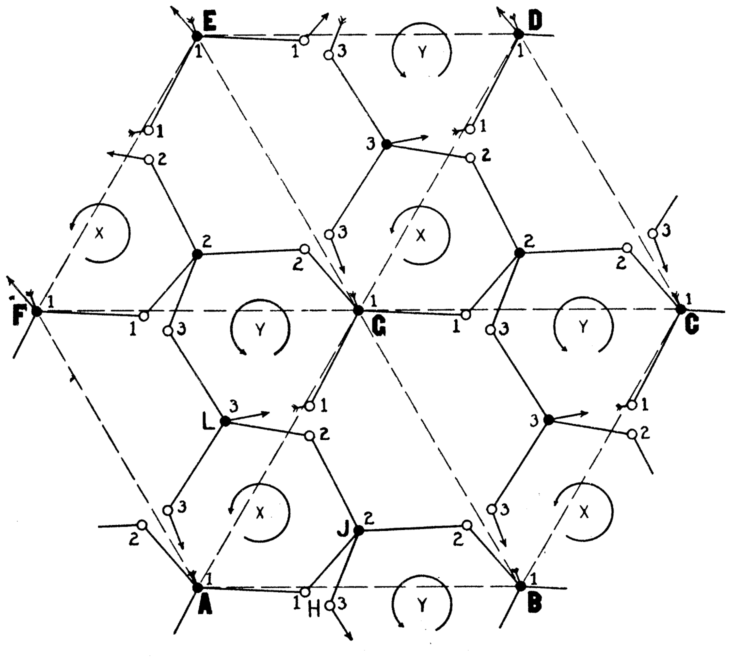

Fig. 2

The arrangement described in Table II. is illustrated in Fig. 2 which gives a projection of atom-centers on a basal plane and three projections of a unit of structure with the atoms represented by opaque spheres of arbitrary sizes. The lettering and numbering corresponds with that in Fig. 2 of Huggins' paper, with which it should be compared. It should be noted, however, that his preferred arrangement does not give oxygen atoms at different levels the same x and y coördinates, as shown by his figure here referred to. A striking peculiarity of the arrangement here proposed is the maintenance of identity of groups SiO_2 lying in basal planes. The crystal can be considered as built up of layers of molecules with their planes perpendicular to the hexagonal axis, so spaced, however, that adjacent layers are much closer together than adjacent molecules in the same layer.

It is interesting to compare the elbow-shaped molecule SiO_2, thus indicated, with the molecule CO_2, with which analogies might be expected. According to Rankine[1] the molecule CO_2 possesses symmetry about an axis and would therefore be expected to have relatively weak stray fields for maintenance of condensed phases. An irregular shape, even in cases of chemical saturation where symmetry is theoretically possible, thus appears able to prevent volatility in the case of the refractory SiO_2. Reëstablishment of symmetry in silicane, SiF_4, recently investigated by Rankine and Smith,[2] restores the low boiling point.

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[1] A. O. Rankine, Roy. Soc., Proc. A **98**, 369–374 (1921).

[2] A. O. Rankine and C. J. Smith, Phys. Soc., Proc. **34**, 181–186 (1922).