THE CRYSTAL STRUCTURE OF QUARTZ.

By Maurice L. Huggins.[1]

Synopsis.

The Structure of Quartz (SiO_2).—By means of the Lewis theory, a structure has been obtained for quartz which accounts in a satisfactory way for the crystalline form, crystal symmetry, optical rotation, hardness, high melting point, insolubility, and x-ray spectra of the substance. It is in strict accord with the conclusions of W. H. Bragg in regard to the structure. Furthermore, the distance between adjacent silicon and oxygen atoms, calculated from the dimensions of the lattice, as obtained by Bragg, is approximately equal to the sum of their atomic radii, obtained from other crystals.

The Arrangement of Atoms and Electrons.—Each silicon atom is surrounded by four pairs of electrons at tetrahedron corners, which act as bonds connecting it to four equidistant oxygen atoms. Each oxygen atom is also surrounded by four tetrahedrally oriented electronpairs, two of which serve as bonds connecting the oxygen to silicon atoms. *The crystal is thus not made up of SiO_2 units, but is a single molecule,* for all of the bonds around each silicon or each oxygen atom are of the same type—the usual type of bond which connects the atoms in a molecule.

QUARTZ crystals are placed by crystallographers in the trapezohedral class of the trigonal system, possessing three-fold symmetry about a vertical axis, but having neither plane of symmetry nor center of symmetry. They are enantiomorphic, being of two kinds, which are to each other as an object and its mirror image, and which rotate polarized light in opposite directions. The usual form of crystal is that of a hexagonal prism, terminated at each end by a pyramid, some of the corners, however, being modified by small faces of other types.

W. H. Bragg[2] has obtained x-ray reflections from several faces of a quartz crystal, his measurements being, in the main, such as would be

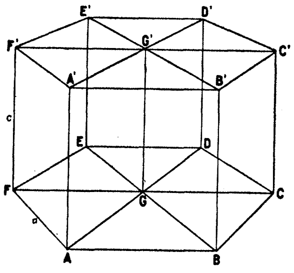

Fig. 1.

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[1] Dupont Fellow in Chemistry, University of California, 1921–22.

[2] W. H. Bragg, Proc. Roy. Soc., *A89*, 575 (1914); Bragg and Bragg, X-Rays and Crystal Structure, G. Bell and Sons, London, 1918, page 160.

obtained if the scattering centers were at the points of a triangular prism lattice (Fig. 1) of dimensions, $a = 4.89$ Å. (1 Ångstrom unit $= 10^{-8}$ cm.) and $c = 5.375$ Å. However, the reflections from the basal planes were such as to indicate a distance between planes just one-third of c, or 1.792 Å. Also it was calculated, from the density of the crystal, that three molecules of SiO_2 are associated with each point of the lattice. Bragg therefore reasoned that the structure is based on three interpenetrating lattices of the type shown, these being "so related that they can be derived from each other by a rotation of $2\pi/3$ about, and a translation $c/3$ along, an axis parallel to the c direction. Thus each trigonal axis of the structure has points arranged spirally around it, and since a spiral may be either right- or left-handed, we can understand the reason for the two forms of quartz."

This was as far as Bragg could go. He was not able to determine either the amount of the relative displacement of the interpenetrating lattices or the disposition of the atoms around the points of these lattices. It has been found possible, however, by means of the Lewis theory of valence and atomic structure,[1] which the author has successfully applied [2] to the structure of a large number of crystals, to obtain a complete solution of the structure, which is in entire accord with Bragg's conclusions.

According to the Lewis theory, there are sixteen valence electrons per SiO_2 group—six per oxygen atom and four per silicon atom. Each oxygen and each silicon atom tends to surround itself by four pairs of electrons, arranged at the corners of a tetrahedron. These pairs may act as bonds, in which case they each form a part of the valence shells of two atoms, or they may be "lone pairs"—pairs not acting as bonds between atoms. It seems highly probable, moreover, from a consideration of analogous substances, that in the quartz crystal the bonds are all $Si-O$ bonds.

If the above assumptions are correct—sixteen electrons per SiO_2 unit, a tetrahedron of pairs around each atom, and $Si-O$ bonds only—then each silicon must be bonded to four oxygen atoms, arranged at the corners of a tetrahedron, and each oxygen atom must be bonded to two silicon atoms, which are also at two of the corners of a tetrahedron. (We should not expect this tetrahedron to be regular, for two of the electron pairs around each oxygen atom are lone pairs and two are bond pairs. The magnitude of this distortion and the effect on the structure will be discussed later in this paper.)

The Quartz Structure.—With the aid of the foregoing ideas the author has obtained the structure for quartz represented in plan in Fig. 2. In

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[1] Lewis, J. Am. Chem. Soc., *38*, 762 (1916).

[2] Huggins, idem.

this figure there are shown three consecutive layers of atoms, each of which is normal to the trigonal axis. The atoms are numbered 1, 2 or 3, according to whether they are in the first, second or third layer from the bottom. The fourth layer is identical with the first, the fifth with the second, etc.; (3) means the layer, identical with 3, next below layer 1. The solid dots represent the centers of silicon atoms and the circles the centers of oxygen atoms. The double circle indicates that there are two oxygen atoms, in different layers, one over the other.[1] The bonds connecting the atoms are represented by full lines. These are of two lengths (in the diagram); the longer lines connecting atoms in the same layer; the shorter lines connecting atoms in different layers. (The actual distances between atomic centers are of course the same, or very nearly the same, in the two cases.) Each of these shorter lines is doubled, to represent, not a "double bond," but two single bonds, connecting a silicon in layer 2, for instance, with oxygens in layers 1 and 3, or a silicon in layer 1 with oxygens in layers (3) (below) and 2 (above).

Each silicon kernel is surrounded by four pairs of valence electrons, bonding it to four equidistant, tetrahedrally oriented, oxygen atoms, and each oxygen kernel by four tetrahedrally arranged electron pairs, two of which serve as bonds connecting the oxygen to two silicon atoms, the other two being lone pairs.

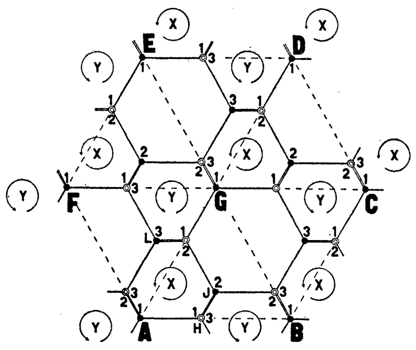

Fig. 2.

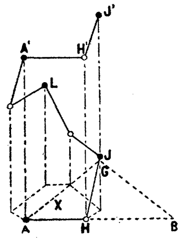

Fig. 3.

X and Y denote axes around each of which there is a spiral of silicon and oxygen atoms. One of these spirals is shown in Fig. 3. It may be readily seen from Fig. 2 that equivalent, similarly situated points in the structure (such as points X, or points A, B, C, D, E, F and G, the lettering in Figs. 1 and 2 corresponding) are at the points of a lattice of the type shown in Fig. 1. For each point of the lattice there are three silicon

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[1] This is not strictly true because of their distortions. See the later discussion on this subject.

and six oxygen atoms, arranged spirally in three similar layers, the vertical distance between layers being just one third the height of the unit prism. Thus the x-ray spectra, the crystalline form, the existence of right- and left-handed crystals, and the optical rotation of the substance are all accounted for.

Distortions from the Structure Described.—Let us now consider the distortion from the structure shown in Figs. 2 and 3. Of the four electron pairs surrounding each oxygen kernel only two are acting as bonds, hence their arrangement cannot be that of a *regular* tetrahedron. It seems reasonable to suppose that the bond pairs are further from the atomic center than the lone pairs, and that the angle formed by the imaginary lines connecting the atomic center with the bond pairs is somewhat greater than $109^\circ\, 28'$, its value if the electron pairs were at the corners of a regular tetrahedron.

Since we do not know this angle, it is impossible either to compare this structure quantitatively with the known dimensions of the lattice, as determined by Bragg, or to calculate directly the exact position of the atoms relative to each other. But by assuming this structure to be correct, and taking the distance between adjacent silicon and oxygen atomic centers as equal to the sum of their atomic radii, obtained from other crystals, the angle between silicon-oxygen bonds can be calculated from the lattice dimensions. If it proves to be some value somewhat greater than 109° and considerably less than 180°, then this constitutes a rough check on the structure. Or, we may do what amounts to the same thing—we may calculate the $\mathrm{Si}-\mathrm{O}$ distance on the assumption that the angle between bonds is $109^\circ\, 28'$; and this distance, if our reasoning is correct, should be a few per cent. greater than the distance calculated from the atomic radii. We shall see that this is the case.

If the angle between the two bonds connecting each oxygen to silicon atoms ($\angle AHJ$, Fig. 4) were $109^\circ\, 28'$, the distance between adjacent silicon and oxygen atom centers ($AH = HJ$), computed from the dimensions of the lattice, would be 1.97 Å. Now the radius of the silicon atom—the distance from atomic center to valence electron-pair—in a crystal of the element[1] is 1.17 Å. Bragg[2] computes the radius of the oxygen atom, from dimensions of the ZnSp, ZnS, and FeS_2 structures, to be 0.65 Å. Transferring these values of atomic radii to the quartz crystal, we get 1.82 Å. as the approximate distance between silicon and oxygen atomic centers.[3]

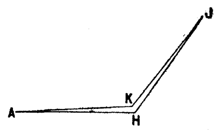

Fig. 4.

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[1] Debye and Scherrer, Phys. Zeit., *17*, 277 (1916); Hull, PHYS. REV., (2) ix, 566, 1917; Gerlach, Physik. Zeitsch., xxii 557. 1921.

[2] Phil. Mag., *40*, 169 (1920).

Each oxygen atom in the crystal is then displaced from the position *H* (Fig. 4) to a position *K*, about 1.82 Å. from the nearest silicon atoms. If we make the assumption that *K* is in the same plane as *A*, *H* and *J*, then the angle *AKJ* between the oxygen-silicon bonds can be calculated to be about 125°.

We are now in a position to calculate the relative positions of the silicon atoms (*e.g.*, of *J*, Figs. 2 and 3, relative to *AB*). The calculations are but a matter of geometry and simple trigonometry, but the results based on the Si–O distance 1.82 Å. and the angle $AKJ = 125°$, are of interest (although they must only be considered approximate). The projection of the silicon atom *J* on plane 1 is on the perpendicular bisector of the line *AB*, at a distance of 0.73 Å. from *AB*. Similarly, the projection of *L* is on the perpendicular bisector of *AG*, and 0.73 Å. from it, etc.

Discussion.—This structure agrees with the Lewis theory in every particular—in the number of valence electrons, in their tetrahedral arrangement around the silicon and oxygen atoms, and in the fact that each bond is in reality a pair of electrons in the shells of two atoms at the same time. It should be noted further that the Si–O bonds are single rather than double bonds[1] (as would be expected from the formula $O = Si = O$), this being in accordance with a generalization made by Lewis, and accounted for on theoretical grounds by the author,[2] that the elements which form double bonds readily (*e.g.*, carbon, nitrogen, oxygen) are all in the first row of the periodic table. The silicon and oxygen atoms do not occur in SiO_2 units, it being impossible to tell with what oxygen atoms a given silicon atom was "originally" bonded (before crystallization). Every atom in the crystal is connected to every other atom through bonds which are all of the usual type connecting atoms in a molecule; hence the whole crystal is a single molecule.

We might represent an isolated SiO_2 molecule in this way

$$\begin{array}{c} \cdot\cdot \qquad \cdot\cdot \\ :\mathrm{O}:\mathrm{Si}:\mathrm{O}: \\ \cdot\cdot \qquad \cdot\cdot \end{array}$$

the electronpairs around both the oxygen and silicon atoms being understood to be at tetrahedron corners. Now the tendency of the silicon

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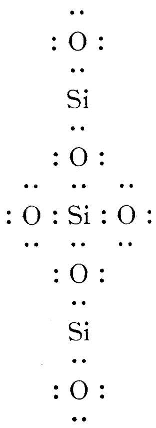
[1] A double bond being a bond in which *two* pairs of electrons hold together two atoms.

[2] J. Am. Chem. Soc., "Electronic Structures of Atoms," soon to be published.

[3] This must be considered only an approximation, for the distance from atomic center to bond electronpair is surely different in a crystal in which all four valence pairs are acting as bonds (ZnO) from that in a crystal in which only two of them are bonds (SiO_2). Also, the bond pairs in quartz may not be quite on the centerlines between atoms, but slight displacements such as might be expected would have a negligible effect on the interatomic distances. Considering everything, the value 1.82 Å. is probably too small.

atom to surround itself by *four* electronpairs is very great, and it does this by attracting the oxygen atoms from two more molecules, giving the structure



$$\begin{array}{ccc}
 & \cdot\cdot & \\
 & :\mathrm{O}: & \\
 & \cdot\cdot & \\
 & \mathrm{Si} & \\
 & \cdot\cdot & \\
 & :\mathrm{O}: & \\
\cdot\cdot & \cdot\cdot & \cdot\cdot \\
:\mathrm{O} & :\mathrm{Si}: & \mathrm{O}: \\
\cdot\cdot & \cdot\cdot & \cdot\cdot \\
 & :\mathrm{O}: & \\
 & \cdot\cdot & \\
 & \mathrm{Si} & \\
 & \cdot\cdot & \\
 & :\mathrm{O}: & \\
 & \cdot\cdot &
\end{array}$$

The new silicon atoms attract more oxygens, and this process is continued indefinitely, the tetrahedral arrangement of the bonds producing the structure of quartz.

Crystal formation in this case, then, as in the case of most minerals, consists chiefly of a reaction between an atom (O) containing a lone electronpair in its valence shell and another atom (Si) capable of holding on to that lone pair, the result being a stable single bond. The stability of these bonds, in the case of quartz, is evidenced by its hardness, high melting point, insolubility, etc., which would be difficult to account for if the crystal were composed of saturated molecules held together by secondary valence.

UNIVERSITY OF CALIFORNIA,
BERKELEY, CALIF.