X-RAY DIFFRACTION STUDY OF THE STRUCTURE OF GLASS[1]

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CONTENTS

I. INTRODUCTION

Glass is usually called an undercooled liquid, the name suggesting that, although it has many of the mechanical properties of a true solid, it differs from the crystalline form of matter by not having passed through a sharp or definite transition in solidifying from the melt. From the x-ray studies we shall conclude that glass is similar to a liquid in that both are amorphous forms of matter. In one respect, however, their structures differ: in a glass each atom has permanent neighbors at a fairly definite distance, while in a liquid the neighbors about any atom or molecule are continually changing.

The x-ray diffraction pattern of a glass consists of one or more broad diffuse rings. It is distinctly different from the powder pattern of a crystalline material, which shows a large number of fairly sharp rings. Most of the early attempts to analyze amorphous patterns approached the problem from the point of view of crystalline diffraction, and tried to explain the diffraction bands as Bragg reflections from layers of atoms such as the planar layers in crystalline structures. Only recently have x-ray workers realized that an x-ray scattering pattern showing maxima

and minima can be produced solely by the existence of a few fairly definite interatomic distances in the sample material.

With the development of the Fourier method of analysis, it is now possible to carry through a straightforward and rigorous analysis of the x-ray pattern of a glass. From this type of analysis one gets directly the interatomic distances in the glass and the number of neighboring atoms about each kind of atom. From these results certain important conclusions can be drawn, and for the simple glasses the results are often sufficient to establish a fairly definite picture of the structure.

A wide variety of materials can be brought into the glassy state. Among the elements selenium is the well-known example; in the inorganic field the silicates, borates, and phosphates are ready glass formers, and in the field of organic chemistry glasses are formed by many substances, particularly by molecules containing a fair number of hydroxyl radicals. The diffraction patterns of the inorganic glasses are the simplest to interpret;
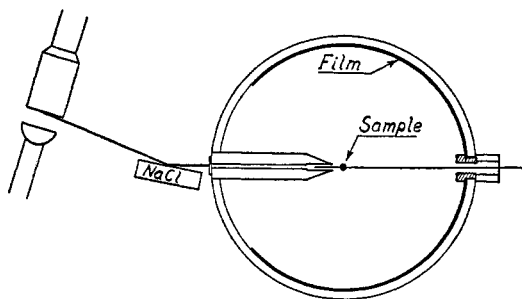

FIG. 1. Camera for x-ray diffraction patterns of glass

furthermore, these are the glasses of practical interest. Accordingly, the discussion in this paper will be confined to silicate and borate glasses.

II. EXPERIMENTAL METHODS

X-ray diffraction patterns of glass are usually made in a cylindrical camera of about 5 cm. radius. The schematic arrangement is shown in figure 1. A highly monochromatic beam is obtained by allowing the radiation from a molybdenum or copper target tube to fall upon a rock salt crystal set at the correct angle to reflect the K_α line. The monochromatic reflected beam passes through a collimating system and falls upon the glass sample, which is usually in the form of a rod about 0.5 to 1.0 mm. in diameter. The diffracted radiation is recorded on a photographic film placed inside the cylindrical camera. To eliminate the scattering of the main beam by air, the camera is evacuated during the exposure. Figures 2 and 3 are typical x-ray diffraction patterns of glass.

The diffraction patterns are microphotometered and the microphoto-meter records changed to intensity curves in the usual way. The final experimental result is a curve giving the intensity of x-ray scattering (in arbitrary units) as a function of the angle of scattering. Intensity curves for vitreous silica and for a series of soda–silica compositions are shown in figures 4 and 9.
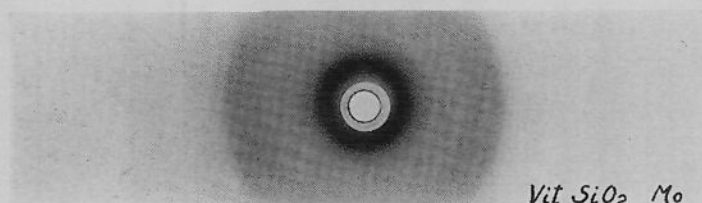

Vit SiO₂ Mo

FIG. 2. X-ray pattern of vitreous silica taken with Mo K_α radiation ($\lambda = 0.710$ Å.)

B₂O₃ Mo

0.114 Na₂O

0.225 Na₂O

0.333 Na₂O
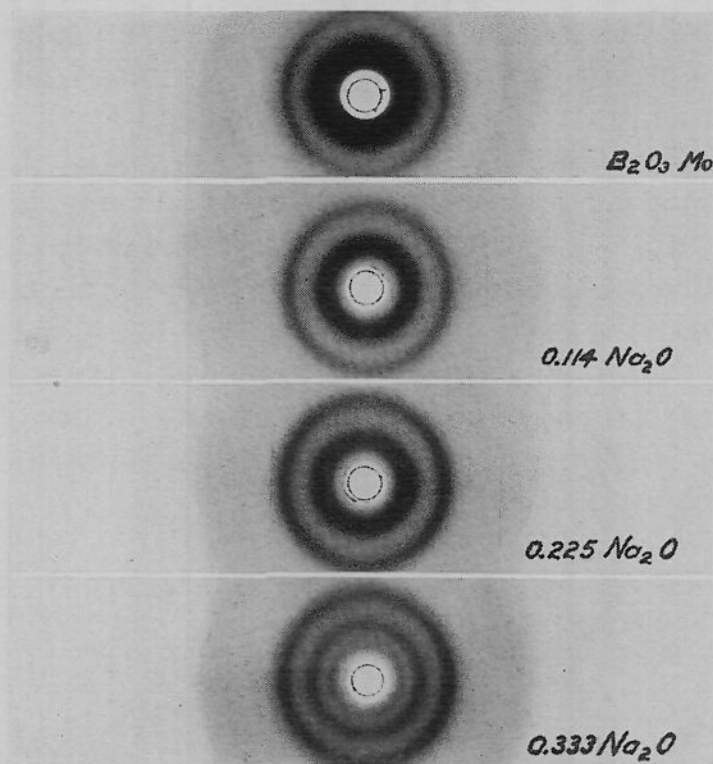
FIG. 3. X-ray patterns of soda–boric oxide glass taken with Mo K_α radiation ($\lambda = 0.710$ Å.)

III. THEORY OF FOURIER ANALYSIS

From a typical glass diffraction pattern, containing three or four diffuse rings, the only quantity which can be determined directly and uniquely is the radial distribution function. This is obtained from a Fourier analysis of the experimental x-ray scattering curve, and gives directly the average number of atoms to be found at any distance from a given atom. The method of Fourier analysis is equally applicable to a liquid,

a glass, or a powdered crystalline material, so that in using this method one is not making any *a priori* assumptions as to the structure of the material in question.

For simplicity, the theory of the method of Fourier analysis will be developed here for the simple case of a material containing only one kind of atom. A monochromatic x-ray beam falls upon an array of atoms, and the radiation scattered at an angle 2θ to the direction of the primary beam is observed at a point P. The amplitude of the unmodified scattered radiation is given in electron units (using the radiation scattered by a single electron according to classical theory as the unit) by equation 1.

$$E_p = \sum_n f_n \, e^{2\frac{\pi i}{\lambda}(\bar{S}-\bar{S}_0)\cdot\bar{r}_n} \tag{1}$$

Σ indicates summation over all the atoms in the sample, $\bar{r}_n$ is a vector giving the position of atom n, f_n is the atomic scattering factor of atom n, and $\bar{S}$ and $\bar{S}_0$ are unit vectors giving the direction of the scattered and primary radiation.

For a crystalline material the summation of equation 1 can be carried out, and an expression secured for the resultant amplitude and intensity. This intensity expression will show sharp maxima in the usual directions given by the Bragg law. If one is not at liberty to assume the material to be crystalline, it is not possible to carry out the summation indicated in equation 1. Multiplying equation 1 by its conjugate complex quantity, and then averaging the resulting expression for intensity, as the rigid array of atoms is allowed to take all possible orientations in space, one obtains the Debye equation (4):

$$I = \sum_m \sum_n \frac{f_m f_n \sin Sr_{mn}}{Sr_{mn}} \tag{2}$$

$$S = \frac{4\pi\sin\theta}{\lambda}$$

r_{mn} = distance from atom m to atom n

In applying equation 2 to a glass, it is obviously not necessary actually to rotate the sample, since any configurations which may exist will be found many times with all possible orientations. For a material consisting of only one kind of atom, and with the assumption that on the average each atom is surrounded in the same way as every other atom, equation 2 becomes

$$I = Nf^2 \sum_n \frac{\sin sr_n}{sr_n} \tag{3}$$

where N is the effective number of atoms in the sample.

Introducing a radial distribution function such that $4\pi r^2 \rho(r) \, dr$ is the number of atoms between distances r and $r + dr$ from any atom, equation 3 becomes

$$I = Nf^2 \left\{ 1 + \int_0^\infty 4\pi r^2 \rho(r) \, \frac{\sin sr}{sr} \, dr \right\} \tag{4}$$

Rearranging this gives

$$s\left(\frac{I}{Nf^2} - 1\right) = 4\pi \int_0^\infty r(\rho - \rho_0) \sin sr \, dr + 4\pi \int_0^\infty r\rho_0 \sin sr \, dr \tag{5}$$

Except for very small values of s, the second integral is zero. Inverting the rest of the equation by the Fourier integral theorem, we obtain finally

$$4\pi r^2 \rho(r) = 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_0^\infty si(s) \sin rs \, ds \tag{6}$$

$$i(s) = \left(\frac{I}{Nf^2} - 1\right)$$

$\rho_0 =$ average density of the sample, in atoms per unit volume

The quantity $si(s)$ is obtained directly from the experimental scattering curve. The integration involved in equation 6 is then carried out for a number of different values of r. The resulting values of $4\pi r^2 \rho(r)$ plotted against r give the radial distribution of atoms about any average atom. Equation 6 was first derived by Zernike and Prins (14), and was first applied by Debye and Menke (5) in an x-ray study of liquid mercury.

For a material containing more than one kind of atom, such as vitreous silica, equation 6 takes the more general form (12):

$$\sum K_m 4\pi r^2 \rho_m = \sum K_m 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_0^\infty si(s) \sin rs \, ds \tag{7}$$

Σ indicates summation over an assumed unit of composition, K_m is the effective number of electrons in atom m, ρ_m is the electron density surrounding atom m, and ρ_0 is the average number of electrons per unit volume.

The weighted radial distribution function $\Sigma K_m 4\pi r^2 \rho_m$ given by equation 7 is obtained from the experimental x-ray scattering curve. The result is unique, in that no assumptions as to structure or crystallinity are involved. The significance of the distribution function is best explained in terms of the specific examples which follow.

IV. FOURIER ANALYSIS OF VITREOUS SILICA

A simple stable glass, and one that is very convenient for x-ray study, is vitreous silica (fused quartz). For the details of the x-ray analysis of

vitreous silica, reference should be made to the original paper (12). The diffraction patterns were made in an evacuated camera of radius 4.40 cm., using Cu K_α and Mo K_α radiation monochromated by reflection from a rock salt crystal. Intensity curves were obtained from the microphotometer records of the diffraction patterns. The intensity curves were put upon an absolute basis (electron units per SiO_2) by consideration of the fact that at large values of $\sin\theta/\lambda$ the experimental curve must approach the curve for independent scattering by the atoms. The experimental curve must be corrected for absorption, polarization, and Compton modi-
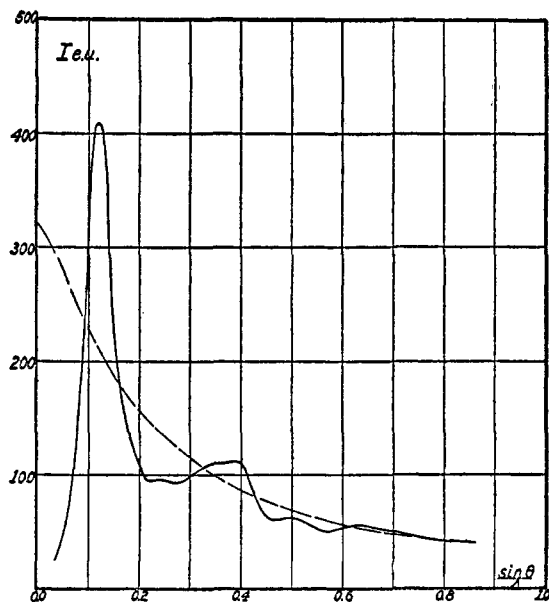

FIG. 4. X-ray intensity curve for vitreous silica in electron units per SiO_2. Dashed line, independent scattering per SiO_2.

fied scattering. The final intensity curve for vitreous silica is shown in figure 4.

From the intensity curve the quantity $si(s)$ is calculated and plotted as a function of s. The integration involved in equation 7 is then carried out for about forty different values of r ranging from 0 to 8 Å. The integration can be done either graphically or with a harmonic analyzer. The result is a series of values of $\Sigma K_m 4\pi r^2 \rho_m$. These values plotted against r give the radial distribution curve for vitreous silica shown in figure 5.

Since there are two kinds of atoms in silica, the curve of figure 5 is really two distribution curves superimposed,—the distribution of neigh-

boring atoms about a silicon atom, and the distribution about an oxygen atom.   The positions of the peaks give the distances of neighboring atoms from a silicon or an oxygen atom.   From the area under a peak, it is generally possible to calculate the number of neighbors at that distance. The significance of the different peaks is established by comparing the interatomic distances given by the radial distribution curve with the various known interatomic distances determined from crystalline structures.

The first peak of figure 5 occurs at about 1.62 Å.   Since this is the silicon–oxygen distance which has been found in all crystalline forms of silica and in crystalline silicates, the peak is identified as representing the
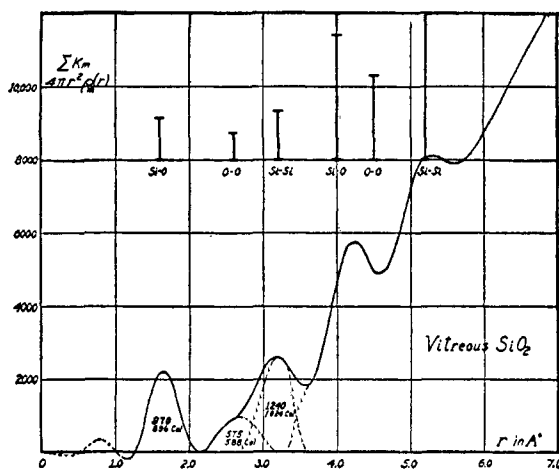

FIG. 5. Radial distribution curve for vitreous silica

silicon–oxygen distance in the glass.   From the area under the first peak we can calculate the number of oxygens about each silicon.   If there are n oxygens bonded to each silicon, there must be $n/2$ silicons bonded to each oxygen.   From the atomic scattering factors for silicon and oxygen, it is found that the best average value for the effective number of electrons per atom is for silicon $K = 16.0$ and for oxygen $K = 7.0$.   The area under the first peak will be

$$A = 1 \times 16 \times n \times 7.0 + 2 \times 7.0 \times (n/2) \times 16$$

Equating this to the observed peak area 970 elect[2], and solving for n:

$$n = \frac{970}{1 \times 16.0 \times 7.0 \times 2} = 4.3 \sim 4$$

[2] For a discussion of early work bearing on this question see reference 6.

Since the silicon atom is always found tetrahedrally surrounded by four oxygens at a distance of about 1.62 Å. in all crystalline silicates, the measured value 4.3 is interpreted as meaning 4 within the limits of experimental error. If each silicon is tetrahedrally surrounded by four oxygens, then from the composition of the glass each oxygen must be bonded to two silicons. Assuming that the four oxygens about a silicon are tetrahedrally arranged, the oxygen–oxygen distance should be

$$O{-}O = 1.62 \sqrt{8/3} = 2.65 \text{ Å.}$$

The second and third peaks are not well resolved, but the existence of a peak at about 2.65 Å., of about the right area to correspond to six oxygen neighbors about each oxygen, is clearly indicated on the distribution curve.

If the two bonds to an oxygen are roughly diametrically opposite, the silicon–silicon distance will be approximately twice the silicon–oxygen distance, or about 3.2 Å. A distinct peak at 3.2 Å. shows that this is the case. The first three peaks indicate that each silicon is tetrahedrally surrounded by four oxygens at a distance of 1.62 Å. and each oxygen is bonded to two silicons, the two bonds being roughly diametrically opposite. So far as concerns the satisfying of these requirements, the relative orientation of one tetrahedral group with respect to a neighboring group, around the direction of the connecting Si—O—Si bond, can be practically random. In spite of this randomness, a number of definite interatomic distances exist. These distances are indicated on figure 5 by a series of vertical lines, the heights of the lines being proportional to the expected peak areas. The oxygen–second oxygen distance depends upon the relative orientation of two tetrahedral groups about their connecting Si—O—Si bond, and the value 4.5 Å. which is given represents only an average distance. The peak at 4.2 Å. in the experimental curve is interpreted as an unresolved average of the Si—O peak at 4.0 Å. and the average O—O separation at 4.5 Å. For distances greater than the silicon–second silicon distance of 5.2 Å., the various interatomic distances depend upon the relative orientation of the tetrahedral groups, and the distribution curve rapidly smooths out.

It should be pointed out that the distribution curve of figure 5 is a unique result for vitreous silica, since the application of the Fourier method of analysis involves no assumption as to whether the material is truly amorphous or crystalline. The x-ray results are completely explained by picturing glassy silica as a random network in which each silicon is tetrahedrally surrounded by four oxygens and each oxygen is bonded to two silicons, the two bonds to an oxygen being roughly diametrically opposite. The orientation of one tetrahedral group with respect to a neighboring group about the connecting Si—O—Si bond can be practically

random. This is the simplest picture of silica glass, free from all specialized assumptions, which will completely explain the x-ray diffraction pattern. There is a definite scheme of structure involved: each atom has a definite number of nearest neighbors at a definite distance, but no unit of structure repeats itself identically at regular intervals in three dimensions, and hence the material is not crystalline. This is essentially the picture of an oxide glass which Zachariasen (13) deduced from consideration of the chemical composition. Figure 6, taken from Zachariasen's paper, illustrates schematically in two dimensions the irregular structure of a glass as distinguished from the regularly repeating structure of a crystal.
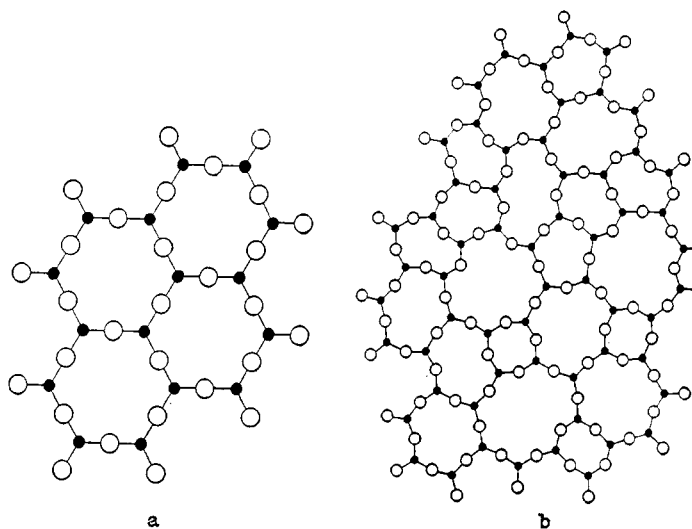

Fig. 6. Schematic representation in two dimensions of the difference between a crystal and a glass: a, crystal; b, glass. (W. H. Zachariasen.)

It should be emphasized that there is no such thing as an SiO_2 molecule in silica glass. Instead, the glass is a high-polymer random network in which each silicon is bonded to four oxygens and each oxygen is bonded to two silicons. The non-existence of an SiO_2 molecule in silica glass should not be surprising, since the extensive x-ray studies of crystalline silicates have shown that the fundamental law of structural silicate chemistry is the tetrahedral bonding of four oxygens about each silicon, and that molecules have no existence in silicate structures.

V. THE CRYSTALLITE THEORY OF GLASS

While the Fourier analysis gives uniquely the coördination scheme, that is, the number of neighbors and their distances, it does not answer the

specific question as to whether or not the material can be considered crystalline. A number of workers have interpreted the x-ray diffraction patterns of vitreous silica as due to extremely small crystals of the high-temperature crystalline form of silica, cristobalite (6, 8).

Figure 7 shows the diffraction patterns of vitreous silica and cristobalite taken under identical conditions. Figure 8 shows the microphotometer records of these patterns. The strongest ring in the cristobalite pattern comes at very nearly the position of the first broad peak in the vitreous silica pattern. Since the breadth of the lines on a crystal powder pattern increases continuously with decreasing size of crystalline particles, it is evident that if one postulates in vitreous silica cristobalite crystals sufficiently small, the strong peak of cristobalite would broaden out to give
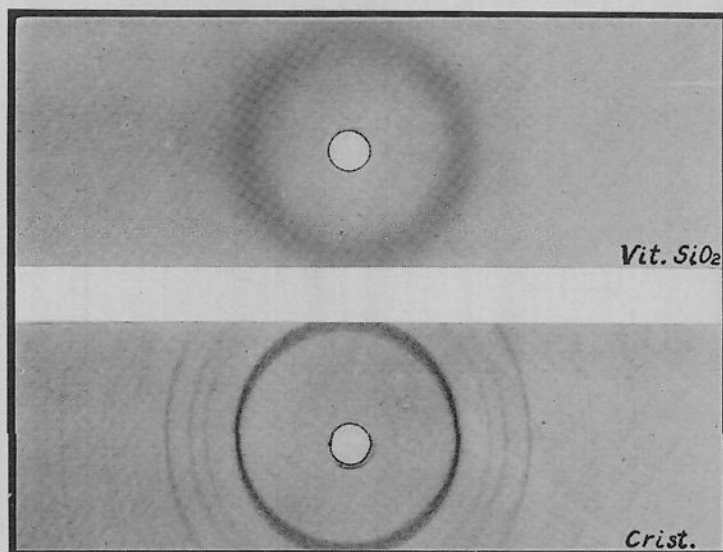

FIG. 7. X-ray diffraction patterns: above, vitreous silica; below, cristobalite

the appearance of the vitreous pattern. From a formal point of view this interpretation is perfectly sound, and since cristobalite is the stable form of silica through the temperature range in which glassy silica stiffens up, it is not at all unreasonable to expect cristobalite crystals in the glass.

If we assume tentatively that the x-ray pattern of vitreous silica is due to small cristobalite crystals, the size of these assumed crystallites can be calculated from the line breadth. Changing the microphotometer record to an intensity curve, and measuring the half-intensity breadth of the strong peak, the average particle dimension is calculated by the Bragg particle size equation (3)

$$L = \frac{0.89\lambda}{B \cos \theta} = \frac{0.89 \times 1.54}{0.181 \times 0.98} = 7.7 \text{ Å} \qquad (8)$$

The edge of the unit cell of cristobalite is about 7.0 Å., and the crystallite hypothesis has therefore forced us to postulate cristobalite crystals scarcely larger than one unit cell in order to explain the observed peak width.

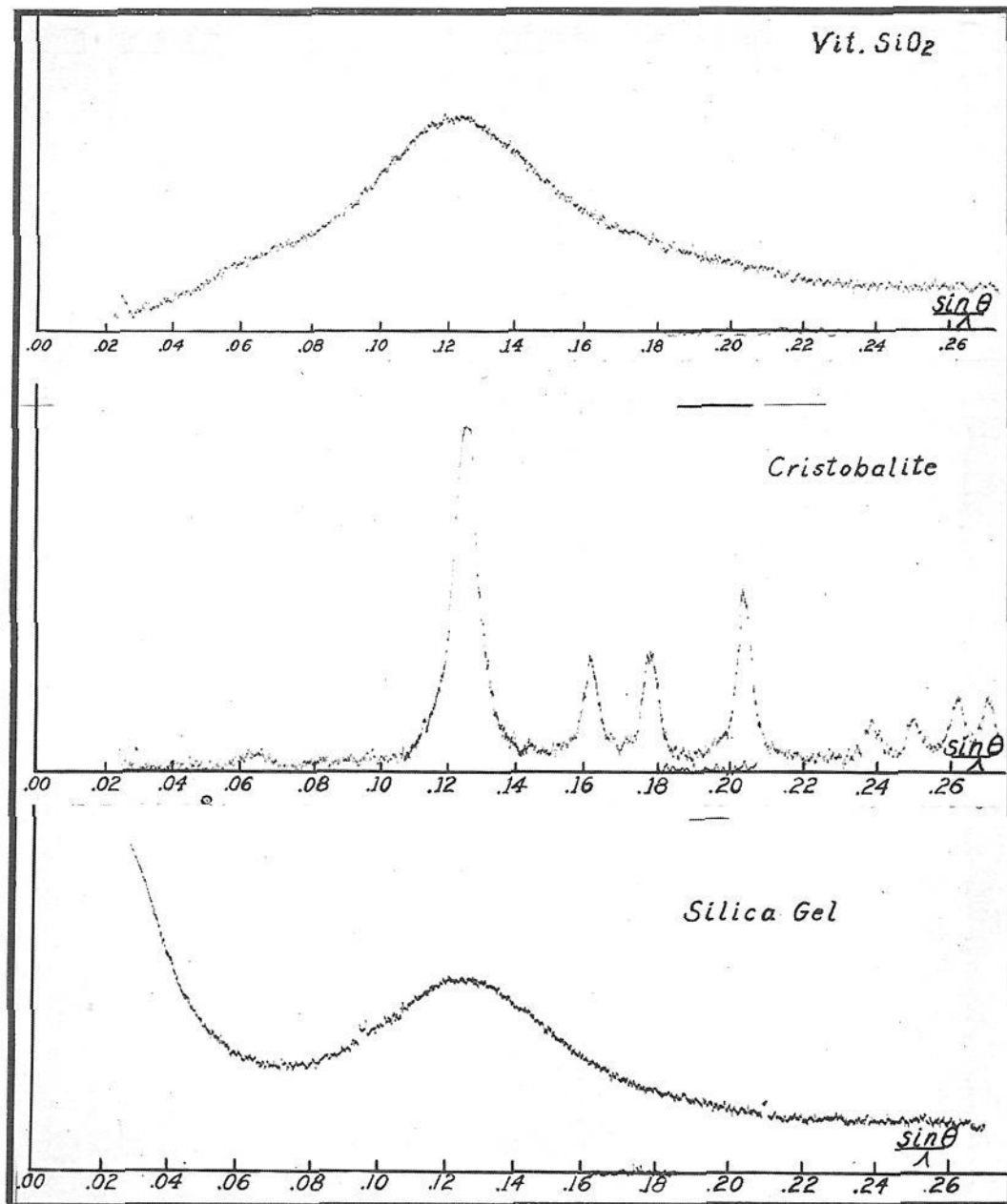FIG. 8. Microphotometer records of x-ray diffraction patterns: a, vitreous silica; b, cristobalite; c, dried commercial silica gel.

The essence of the idea of crystallinity is regular repetition, and in a particle containing only one unit cell repetition does not exist. There is then a very real objection to the cristobalite crystallite description of silica glass (9, 10). In order to conform to the experimental facts, it

requires the extension of the term "crystal" to blocks of matter so small that the term ceases to have any meaning.

Another question of interest concerns the homogeneity of glass. Is glass an aggregation of small groups of atoms with breaks and voids between these groups, or is it a homogeneous medium with a continuous scheme of bonding? In other words, is glass like a pail full of pebbles or a pail full of water? This question can be answered by comparing the small angle scattering of silica glass and silica gel shown on figure 8. The main peak is the same for both the silica glass and the silica gel, but whereas for the glass the intensity falls to zero at small scattering angles, for the gel it rises to high values.

Small angle scattering is due to large scale inhomogeneities in the sample (large with respect to atomic dimensions). The diffraction patterns indicate that the dried silica gel comprises silica particles having about the same structure as the glass, but with gaps and voids between these particles of the order of 10 to 100 Å. In marked contrast to the gel, the pattern of silica glass shows no small angle scattering, indicating a completely homogeneous medium without discrete particles, gaps, or voids. This means that the random tetrahedral network is one in which there is a continuous scheme of bonding.

The x-ray data for vitreous silica are completely explained on the basis of the random tetrahedral network picture of the glass. However, x-ray analysis does not prove that there is no crystalline cristobalite in glassy silica. Here and there one would expect to find the cristobalite configuration existing for a short distance, as one of a continuous variety of configurations. The x-ray analysis does, however, prove that the major part of the material cannot be in the form of cristobalite crystals of sufficient size to give the term any meaning. The devitrification of vitreous silica to cristobalite, over a wide range of temperatures, is probably facilitated by the presence of a small amount of crystalline cristobalite acting as seed material. Trostel (7) has found that a silica glass containing a small trace of quartz can be devitrified at about 1300°C. to give mainly quartz as the devitrification product.

The scheme of coördination about each atom is the same in silica glass and in crystalline cristobalite. If a man sitting on a silicon atom could look no farther than the nearest and next nearest atoms, he would not know whether he was in a piece of silica glass or in a cristobalite crystal. The glass is a form of matter in which the coördination scheme is the same as in the crystalline phase, but which cooled too rapidly from a viscous melt to allow any disentangling and subsequent rebuilding of an orderly structure.

VI. STRUCTURE OF SODA–SILICA GLASS

Soda–silica glass can be formed with compositions ranging from pure silica to the equimolal composition $Na_2O \cdot SiO_2$. The soda–silica glasses form an interesting binary system of great practical importance. X-ray intensity curves for a series of compositions are given by figure 9. It should be noted that the change in the intensity curves is a perfectly continuous change with increase in soda content. From a Fourier analysis
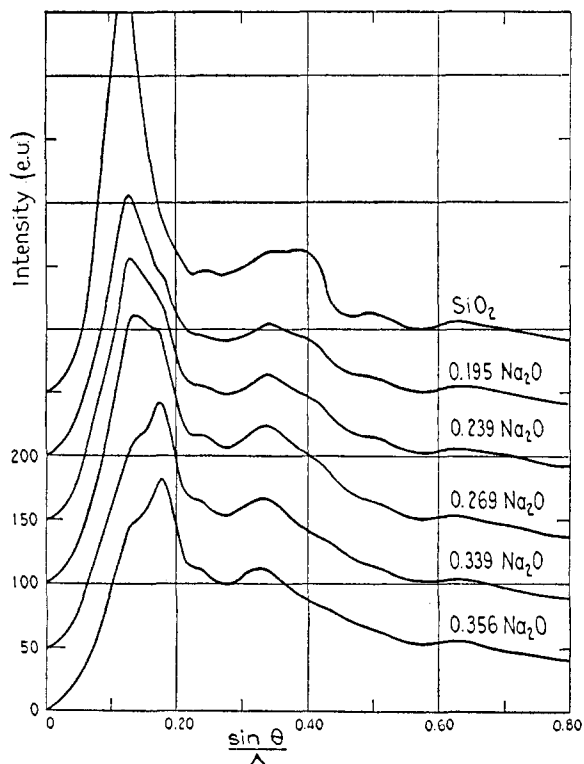

FIG. 9. X-ray intensity curves for soda–silica glass

of the intensity curves, the radial distribution curves of figure 10 are obtained (11).

For each composition the first peak occurs at about 1.62 Å., corresponding to the well-known silicon–oxygen distance in silicates. The number of oxygens around a silicon can be calculated from the area under the peak. The values obtained are shown in figure 10. Although the values run a little above 4, it is assumed that they should be interpreted as 4 within the limits of experimental error. Of course it might be argued that a

value of 4.5 could be interpreted as indicating part of the silicons sur-
rounded by four oxygens and part by five oxygens. However, this idea
is dismissed as completely improbable, in view of the well-established
tetrahedral bonding of four oxygens about each silicon in all silicates so
far studied.
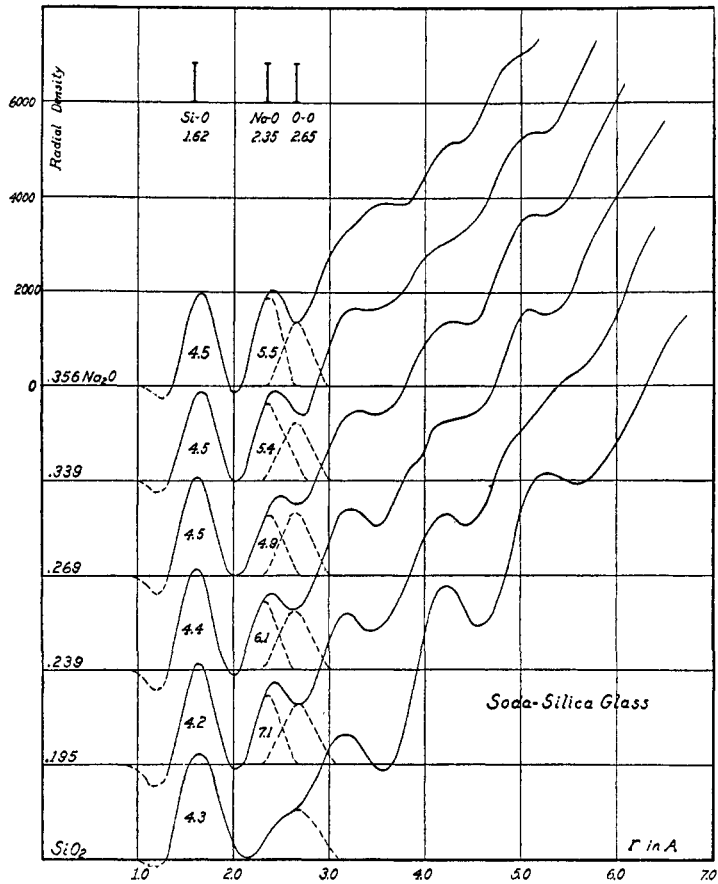
FIG. 10. Radial distribution curves for soda–silica glass

The next two distances, Na—O and O—O, are too close together to
give resolved peaks. From the known tetrahedral bonding and the
composition of the glass, the area of the O—O peak at 2.65 Å. can be
calculated. These peaks, which are shown dotted on figure 10, are sub-
tracted from the distribution curve, leaving a peak at about 2.35 Å. These
residual peaks are interpreted as representing the Na—O separation, since

the distance 2.35 Å. corresponds to the sum of the atomic radii for Na^+ and O^{--}. From the area of the residual peaks the number of oxygens about a sodium atom is readily calculated. The values listed on figure 10 have an average of about 6, which is a reasonable coördination number for oxygen atoms about a sodium atom.

A soda–silica glass is not a structure comprising silica molecules, SiO_2, and soda molecules, Na_2O. The sodium exists as the ion Na^+, and all of the oxygen in the composition takes part in forming the tetrahedral coördination of four oxygens about each silicon. Since the total number of oxygens is greater than twice the number of silicons, it is not possible
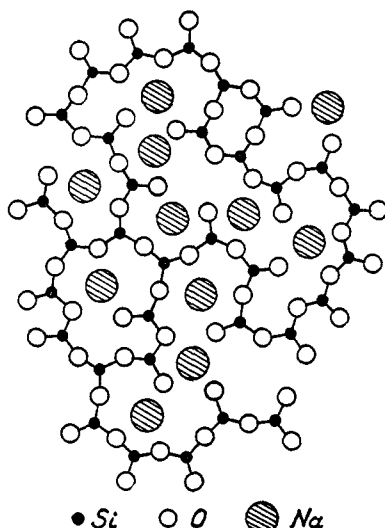

● Si ○ O ◎ Na

FIG. 11. Schematic representation in two dimensions of the structure of soda–silica glass.

for each oxygen to be bonded to two silicons. Part of the oxygens must be bonded to two silicons and part bonded to only one silicon.

Figure 11 represents schematically in two dimensions the structure of soda–silica glass as deduced from the present x-ray study. Because the real structure exists in three dimensions, it is necessary to take certain liberties in making a schematic two-dimensional representation. In three dimensions, each silicon is tetrahedrally surrounded by four oxygens, and in the two-dimensional representation each silicon is shown surrounded only by three oxygens. The oxygens are correctly represented, some of them bonded between two silicons, and others bonded only to one silicon. The sodium ions, Na^+, are shown in various holes in the irregular silicon–

oxygen network. This figure represents very well the essential scheme of structure in a soda–silica glass. There is a definite scheme of co-ordination,—each silicon tetrahedrally surrounded by four oxygens and part of the oxygens bonded between two silicons and part only to one silicon. The sodium ions are held rather loosely in the various holes in the silicon–oxygen network and are surrounded on the average by about six oxygens. Although it is a perfectly definite scheme of structure, there is no regular repetition in the pattern and the structure is non-crystalline.

Because there is no regular repetition, it is evident why soda–silica glass has no definite chemical composition. Starting with vitreous silica, there is a random network in which each silicon is tetrahedrally surrounded by four oxygens and each oxygen is bonded between two silicons. As the soda content is increased, the number of oxygens becomes greater than twice the number of silicons, and hence more and more of the oxygens are bonded only to one silicon. The sodium ions take the best places they can find in the various openings in the silicon–oxygen network.

Electrical conduction is readily understood in terms of figure 11. Owing to the temperature motion, the atoms of the silicon–oxygen network are oscillating about mean positions. Under the influence of the electric field, the loosely bound sodium ion falls step-fashion from one network hole to another as conditions make the step possible.

The lowering of the softening temperature of silica glass by addition of soda is also understood from figure 11. In vitreous silica there is a complete system of bonding in three dimensions, each silicon to four oxygens and each oxygen to two silicons. With the addition of soda, breaks occur in the silicon–oxygen framework, owing to some of the oxygens being bonded only to one silicon. With more and more breaks in the strong silicon–oxygen network, the structure is no longer rigidly braced in three dimensions. Displacements and changes in configuration in the silicon–oxygen network can take place at temperatures which are still too low for disrupting any appreciable number of silicon–oxygen bonds.

Because there is no scheme of repetition in the glass, no two points are exactly identical. There are points with widely varying degrees of weakness, at which flow or breaking can occur at a continuous variety of temperatures. It is readily understood, therefore, why glass gradually softens, rather than having a definite melting point as a crystal does.

Vitreous silica has an extremely small coefficient of thermal expansion and is a very stable glass. For many purposes it would be the ideal glass to use, if it were not for the fact that the temperatures required to make and work it are inconveniently high. Soda is added to silica merely to

soften the glass and to bring the working temperature down into a convenient range. From the atomic point of view this softening of the glass by addition of soda results from the extra oxygen introduced by the soda, which produces single-bonded oxygens. Each single-bonded oxygen represents a break or weak spot in the strong three-dimensional silicon-oxygen network. The more of these breaks, the weaker the glass and the lower the temperature at which the glass can be worked.

VII. BORATE GLASSES

The oxide B_2O_3 readily forms a glass; in fact, crystallization can be produced only by taking very special precautions. The x-ray analysis (12) of vitreous boric oxide leads to the result that each boron is triangularly surrounded by three oxygens and each oxygen is bonded to two borons. Except for the lower coördination number, the same sort of random network is formed as in the case of vitreous silica.

In boric oxide–silica compositions (1) it is found that each boron is triangularly surrounded by three oxygens, each silicon is tetrahedrally surrounded by four oxygens, and each oxygen is bonded to two cations, either two borons, two silicons, or a boron and a silicon. The structure is a continuous three-dimensional random network. The addition of boric oxide to silica produces a softer glass by putting in boron, which bonds to the rest of the structure in only three directions, in place of silicon which bonds itself tetrahedrally in four directions to the surrounding atoms. A slight softening of silica glass by the addition of boric oxide is the basis of the familiar Pyrex chemical glasses.

In the soda–boric oxide (2) and the soda–boric oxide–silica glasses, a change in the coördination number of the boron atom is responsible for maxima and minima found in various physical properties. The boron atom can exist in either threefold triangular coördination or fourfold tetrahedral coördination, and is actually found in both kinds of bonding in crystalline borates. When soda is added to a glass containing boric oxide, the extra oxygen introduced by the soda furnishes the necessary extra oxygen for part of the borons to change to fourfold tetrahedral coördination. The effect of adding soda to a boric oxide glass is just opposite to the effect of adding soda to silica glass. When soda is added to silica, the coördination number of silicon remains 4, the extra oxygen produces single-bonded oxygens in the silicon–oxygen network, and the breaks in the network result in a weaker or softer glass. On the other hand, when soda is added to a boric oxide glass, over certain ranges of composition, the extra oxygen is taken up by the increase in the coördination number of the boron, and the increase in the number of bonds results in a strengthening or hardening of the glass.

VIII. DISCUSSION OF THE GLASSY STATE

The remarkable glass-forming properties of silica are due to two features which result from the coördination scheme. Even in the melt, there is probably a strong tendency for each silicon to surround itself by four oxygens, and hence for each oxygen to bond between two silicons. Although any such bonding must be continually forming and breaking, it will nevertheless put enough linkages into the melt to stiffen it up and to give the high viscosity which prevents the atoms from rearranging themselves in the orderly fashion necessary for crystallization. It is this factor which prevents crystallization on cooling. The fact that each oxygen is bonded to only two silicons puts such a flexibility into the scheme of structure that the random network is almost as stable as a crystalline arrangement. It is this flexibility which allows a random type of linkage to form and exist in the melt.

Zachariasen (13) has discussed the conditions for glass-forming ability among the oxides, and has pointed out the importance of the condition that each anion shall be bonded to not more than two of the glass-forming cations. The compounds SiO_2, GeO_2, and BeF_2 are ready glass formers, and all have the same structure in which the anion is bonded to two cations. Similarly in vitreous B_2O_3 the oxygens are bonded to only two cations. On the other hand, BeO is not a glass-forming oxide, because although the beryllium atom surrounds itself tetrahedrally by four oxygens, the composition requires that each oxygen be bonded to four beryllium atoms. Four bonds to each oxygen do not allow enough flexibility for a random network to be comparable in stability with the crystalline form. Enough flexibility in structure to allow the existence of a fairly stable random network is the essential requirement for glass-forming properties.

The oxides which are found in a commercial glass can be fairly well classified in two groups,—network formers and modifiers. The oxides SiO_2, B_2O_3, P_2O_5, and GeO_2 are the standard network formers. Oxides such as Na_2O, K_2O, CaO, BaO, and PbO modify the properties of the glass by changing the ratio of total oxygen atoms to network-forming cations.

In the organic field, glass-forming properties are most pronounced with materials such as sugar or glycerol, where the molecule contains a large number of hydroxyl groups. A random type of hydroxyl bonding between hydroxyl groups on neighboring molecules results in the necessary random linkages to produce a viscous melt. Here again it is the fact that there is a wide flexibility in the way in which the bonding can take place which allows the random type of network necessary for glass-forming properties.

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