

X-RAY DETERMINATION OF THE STRUCTURE OF GLASS*

By B. E. WARREN

ABSTRACT

A method has been developed for analyzing the X-ray diffraction patterns of amorphous solids, and the atomic arrangement in two simple glasses has been completely worked out. In SiO_2 , for example, each silicon is tetrahedrally surrounded by 4 oxygens at a distance 1.60 Å, and each oxygen is shared between two such tetrahedral groups. The mutual orientation of the two groups about their common direction of bonding is random, and hence it is a random three-dimensional network which is built up. The configuration does not repeat at regular intervals and hence is noncrystalline; it is this feature which distinguishes the glassy state from the crystalline.

I. Introduction

X-ray diffraction patterns of glass are readily obtained by passing a fine X-ray beam through a thin slab of glass and registering the diffraction pattern upon a photographic film placed several centimeters behind the sample. X-ray studies of glass have been reported by a number of workers.¹ In most cases one or more broad diffuse rings were obtained, similar to the rings generally obtained with liquids. Except for two of the recent papers (see footnotes 1e and 1g) however, there has been very little done in the way of a serious attempt to interpret the X-ray diffraction patterns of glass.

It is the purpose of this paper to summarize the results so far obtained in the intensive program of X-ray diffraction study of glass, which has been started at the Massachusetts Institute of Technology. The most promising method of attack appeared to be in making a careful study of the diffraction patterns of one or two of the simplest glasses to obtain a completely

satisfactory quantitative interpretation of the diffraction patterns. Once the method of interpretation of glass diffraction patterns is firmly established by the preliminary work on simple glasses, the program can then be extended to include the more complex compositions of interest to glass technology.

Vitreous silica, SiO_2 , is one of the simplest forms of glass, and was therefore selected as a suitable material with which to begin the study. Not only is the chemical composition simple, but from the large number of crystalline silicates² which have been worked out, the interatomic distances and arrangements of the silicon and oxygen atoms to be expected are quite well known.

II. Experimental Method

Although glass diffraction patterns are readily obtained by this simple set-up, it was found necessary to use a more refined apparatus to

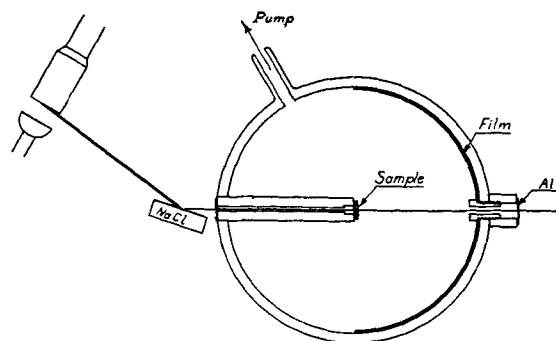


FIG. 1.—Vacuum camera with monochromator for making X-ray diffraction patterns of glass.

obtain really reliable quantitative diffraction data. The present apparatus is represented schematically in Fig. 1. The radiation from a copper target X-ray tube is monochromatized by reflection from a rock-salt crystal set to reflect the $K\alpha$ -line. The reflected beam is collimated by a brass tube and then passed through the thin glass sample. The diffraction pattern is registered on a photographic film held against the wall of the cylindrical camera, which is of the radius 4.40 centimeters, and evacuated during the run to eliminate the scattering of the

* Presented at the Annual Meeting, AMERICAN CERAMIC SOCIETY, Cincinnati, Ohio, February 14, 1934 (Glass Division). Received March 8, 1934.

¹ (a) P. Debye and P. Scherrer, *Nachr. kgl. Ges. Wiss. Göttingen*, p. 16 (1916). (b) R. W. G. Wyckoff and G. W. Morey, "X-Ray Diffraction Measurements on Some Soda-Lime-Silica Glasses," *Jour. Soc. Glass Tech.*, **9**, 265 (1925). (c) N. J. Seljakow, L. V. Strutinski, and A. J. Krasnikow, *Z. Phys.*, **33**, 53 (1925). (d) C. W. Parmelee, G. L. Clark, and A. E. Badger, "The Diffraction of X-Rays by Ordinary Glass Subject to Various Treatments," *Jour. Soc. Glass Tech.*, **13**, 285 (1929); G. L. Clark and C. R. Amberg, "X-Ray Investigations of Feldspar Glasses," *ibid.*, p. 290 (1929). (e) J. T. Randall, H. P. Rooksby, and B. S. Cooper, "The Structure of Glasses: Evidence of X-Ray," *Z. Krist.*, **75**, 196 (1930); *Jour. Soc. Glass Tech.*, **14**, 219 (1930). (f) I. Levin and E. Ott, "X-Ray Study of Opals (Natural), Silica, Glass, and Silica Gel," *Z. Krist.*, **85**, 305 (1933). (g) B. E. Warren, *Z. Krist.*, **86**, 349 (1933).

² W. L. Bragg, "The Structure of Silicates," *Z. Krist.*, **74**, 237 (1930); *Jour. Soc. Glass Tech.*, **14**, 295 (1930).

X-ray beam in the air path between the sample and film. By these two precautions, *viz.*, monochromatizing the beam by crystal reflection so that a completely monochromatic beam is obtained and evacuating the camera to eliminate air scattering, one eliminates completely the

troublesome background blackening which is otherwise so difficult to correct for.

For the sample of vitreous SiO_2 , a piece of fused quartz tubing was used, and for vitreous GeO_2 , 5 grams of powdered oxide were melted in a Vitreosil crucible. In both cases, the thin sample was obtained by blowing a bubble of the material and then picking out a chip of about three-fourths the optimum thickness. With the tube running at 20 milliamperes and 30 kilovolts peak, exposures of 30 hours were found to be sufficient. The microphotometer records of the films were changed to intensity curves by the usual method of making calibration blackening steps on the films.

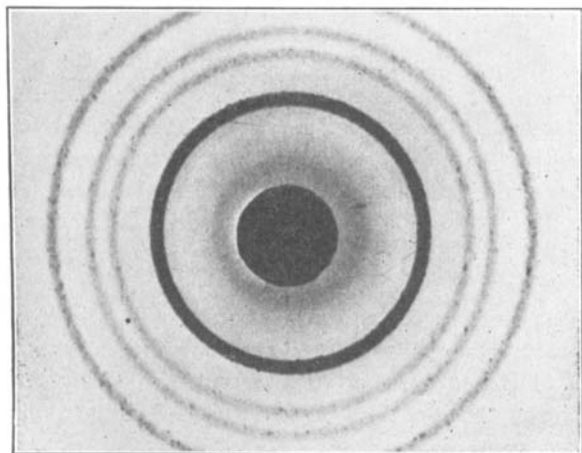
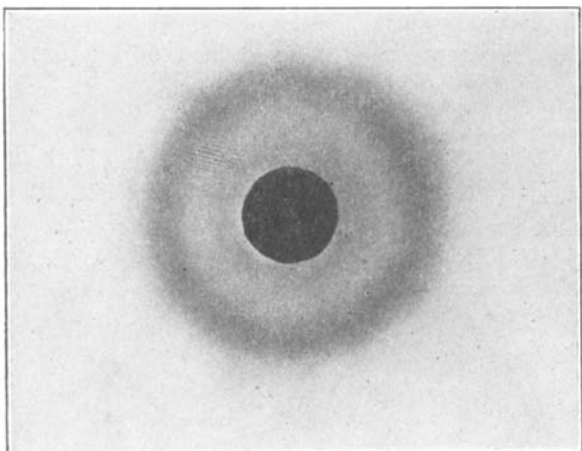
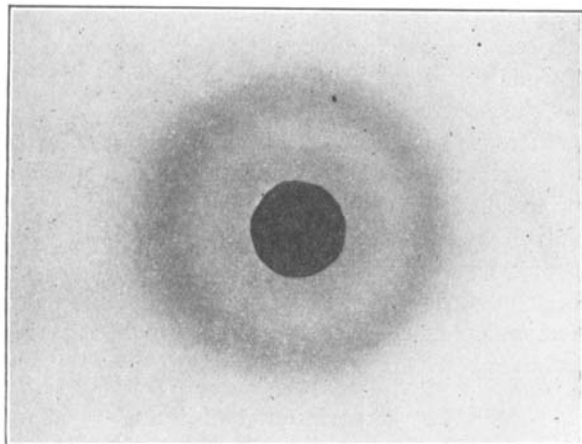


Fig. 2.—X-ray diffraction pattern: (*top*) Pyrex-brand resistance glass; (*center*) vitreous silica; (*bottom*) cristobalite.

(1) **Methods of Interpretation of SiO_2 Pattern** Figure 2 (*center*) shows the diffraction pattern of vitreous silica. The pattern consists of a strong but diffuse ring whose peak occurs at a scattering angle 2θ which would correspond to a spacing $d = 4.32 \text{ \AA}$ in the Bragg law. There is also another much weaker peak at about $d = 1.30 \text{ \AA}$, but this second peak occurs at too large an angle to be included on the reproduction in Fig. 2 (*center*).

Two methods of interpretation of the pattern suggest themselves.

(a) Crystallite hypothesis: The pattern is due to the diffraction of X-rays in extremely small crystals.

(b) Random network hypothesis: The ring is due to the scattering of X-rays in a noncrystalline network of silicon and oxygen atoms.

(a) **Crystallite Hypothesis** If a sample of vitreous silica is held at 1500°C for several hours it devitrifies completely to cristobalite.

The diffraction pattern of this material is shown in Fig. 2 (*bottom*). The very strong ring is the (111) reflection of cristobalite, and occurs at roughly the same scattering angle as the peak from vitreous silica. It suggests itself at once that the diffraction pattern of silica can be interpreted as due to extremely tiny crystals of cristobalite, the observed strong diffuse ring being the strong (111) reflection of cristobalite, and the individual crystals being so small that a broad diffuse ring is produced, rather than the sharp one which is characteristic of crystals of appreciable size. This is the conclusion reached by Randall, Rooksby, and Cooper,^{1e} who found that the breadth of the diffuse ring was satisfactorily accounted for by postulating cristobalite crystals of about 15 \AA size. The idea that vitreous silica should be

made up of extremely tiny crystals of cristobalite is not at all unreasonable, since cristobalite is the stable form of SiO_2 in the temperature range through which the vitreous silica solidified.

There are, however, certain serious objections to the crystallite hypothesis. For one thing, the spacing obtained from the vitreous silica ring is 4.32 Å, while that obtained from large cristobalite crystals (low-temperature form³) is 4.05 Å, a discrepancy of 6%.

Another objection to the crystallite hypothesis comes from the fact that cristobalite undergoes a marked volume change between 200°C and 300°C, whereas vitreous silica shows no such change.

What is probably the most serious objection to the crystallite hypothesis has to do with the behavior of the material under heat treatment. If samples of the material are held for various lengths of time at high temperature, it would be expected that the tiny cristobalite crystals would grow and that the broad diffraction peak would gradually narrow. Actually, however, the broad peak of vitreous silica goes over abruptly into the sharp displaced ring of cristobalite. Furthermore, for tiny crystals of the size postulated, the width of the diffraction peak should be extremely sensitive not only to heat treatment, but also to previous history and origin of the material. It was found, however, that samples of vitreous silica of quite different origin and others having undergone heat treatment as drastic as possible without producing devitrification all showed broad diffraction bands of the same width. These objections to the crystallite interpretation of the diffraction pattern of vitreous silica seem to be sufficiently serious to make it worth while to look for another interpretation.

(b) Random Network Hypothesis

The alternative interpretation is that based upon X-ray scattering from a noncrystalline random network. It is reasonable to suppose that even in such a noncrystalline arrangement, the interatomic distances and coordination will be essentially the same as found in the crystalline forms of silica. Each silicon will be tetrahedrally surrounded by four oxygens with an silicon-oxygen distance of about 1.60 Å, and each oxygen will be shared

between two silicon atoms. Assuming that each oxygen lies very nearly upon the straight line between the two silicons to which it is bonded, then the distance between nearest silicons will be 3.20 Å. Although this distance between neighboring tetrahedral groups is perfectly definite, the relative orientations of the two tetrahedral groups around the common direction of bonding is completely random. The resulting 3-dimensional network which is built up is a random network; it does not repeat itself at regular intervals, and the material is accordingly noncrystalline.

The only rigid conditions which it is assumed are maintained in the glass network are those having to do with the silicon-oxygen distance, the grouping of four oxygens about each silicon, and two silicons about each oxygen. Except for these conditions the network is completely random, but in spite of its random nature, the distances from any one atom to the nearest, next nearest, and next next nearest neighbors are perfectly definite, and it turns out that it is just these definite interneighbor distances which determine the X-ray diffraction patterns of the glass.

A method has been developed for calculating the diffraction pattern of a noncrystalline solid such as a glass.¹⁸ The intensity of scattering is given as a function of the angle by the expression

$$I = \sum_m \sum_n f_m f_n \frac{\sin sr_{mn}}{sr_{mn}} \quad s = \frac{4\pi \sin \theta}{\lambda} \quad (1)$$

where f_n is the X-ray scattering factor for atom n , and r_{mn} is the distance from atom m to atom n . It appears from equation (1) that the intensity depends only on the distances from each atom to all the other atoms and that, if these distances are known, the intensity can be immediately written down as a function of the angle of scattering.

The next step is to tabulate the number of neighbors and their distances about any one atom. About any one silicon there will be 1 Si at distance 0, 4 oxygens at 1.60 Å, 4 Si at 3.20 Å, 12 oxygens at 4.00 Å, and 12 Si at 5.20 Å. Thus far, the number of neighbors and their distances are perfectly definite, regardless of the orientations of the tetrahedral groups. Next come 36 oxygens at a distance which is not quite definite,

³ T. F. W. Barth, "The Cristobalite Structure, II. Low Cristobalite," *Amer. Jour. Sci.*, **24**, 97 (1932).

but varies from 5.0 Å to 6.6 Å, depending on the orientation of the groups. Beyond this the distances become quite indefinite, and a continuous distribution of scattering matter can be assumed and the summation can be carried out by direct integration. Beginning with the 12 Si at 5.20 Å, it is a considerable simplification to replace the discreet array of atoms by spherical SiO₂ scattering units,⁴ comprising one Si at the center and two oxygens spread uniformly over the surface of a sphere of radius Si-O = 1.60 Å. The complete distribution of neighbors is listed in Table I.

1 silicon surrounded by		2 oxygens each surrounded by	
1 Si at	$r = 0$	1 O at	$r = 0$
4 O	= 1.60 Å	2 Si	= 1.60 Å
4 Si	= 3.20 Å	$6 \times 1/2 = 3$ O	= 2.62 Å
$12 \times 1/2 = 6$ O	= 4.00 Å	6 SiO ₂	= 4.00 Å
12 SiO ₂	= 5.20 Å		
Continuous distribution beyond $R_1 = 6.05$ Å		Continuous distribution beyond $R_2 = 4.55$ Å	

The integration over the continuous distribution is readily carried out, making the obvious assumption that the outer limits are indefinite and hence give rise to no effect.

$$\int_R^\infty 4\pi r^2 \rho f \frac{\sin sr}{sr} dr = -\frac{4}{3}\pi R^3 \rho f \Phi(sR) \quad (2)$$

where ρ is the density in SiO₂ molecules per cubic centimeter and

$$\Phi(x) = \frac{3}{x^2} \left[\frac{\sin x}{x} - \cos x \right]$$

The intensity of scattering for vitreous SiO₂ is now written out as a function of the scattering angle by inserting the numerical values from Table I into equation (1).

$$\begin{aligned} \frac{I}{N} = & f_{si} \left\{ f_{si} + 4f_o \frac{\sin 1.60s}{1.60s} + 4f_{si} \frac{\sin 3.20s}{3.20s} + 6f_o \frac{\sin 4.00s}{4.00s} \right. \\ & + 12f \frac{\sin 5.20s}{5.20s} - 17f\Phi(6.05s) \left. \right\} + 2f_o \left\{ f_o + 2f_{si} \frac{\sin 1.60s}{1.60s} \right. \\ & + 3f_o \frac{\sin 2.62s}{2.62s} + 6f \frac{\sin 4.00s}{4.00s} - 8f\Phi(4.55s) \left. \right\} \quad (3) \end{aligned}$$

Equation (3) is plotted against $\frac{\sin \theta}{\lambda}$ in Fig. 3a

⁴ While this is only a rough approximation, it is nevertheless a sufficiently good one for the small angles of scattering considered. The appropriate scattering factor for such a spherical unit is given by $f = f_{si} + 2f_o \frac{\sin 1.60s}{1.60s}$.

and compared with the experimental intensity curve derived from the microphotometer record of the film. Since the experimental intensity is in arbitrary units, the scale of ordinates has been arbitrarily chosen so that the maximum height of the experimental and calculated curves shall be the same. The agreement between the calculated and experimental curves is quite satisfactory, both with respect to the position of the peak and the general shape of the curve. If the calculated intensity curve is carried out to larger values of $\frac{\sin \theta}{\lambda}$, the term $8f_{si}f_o \frac{\sin 1.60s}{1.60s}$ in equation (3) gives rise to another weaker peak at $\frac{\sin \theta}{\lambda} = 0.38$. This is the weak outer peak mentioned above.

The agreement between calculated and experimental intensity curves is so completely satisfactory that the proposed picture of the atomic arrangement in vitreous silica can be taken as completely substantiated. On the crystallite hypothesis it was impossible to understand the constant width of the diffraction peak regardless of origin or treatment of the material. On the random network hypothesis of the vitreous state, however, it follows immediately, for the scattering curve is determined solely by equation (3) which contains no sensitive variable quantity such as particle size.

(2) Check Example, Vitreous GeO₂

An excellent check upon the correctness of the proposed picture of the atomic arrangement in a simple glass such as SiO₂ is obtained from a study of vitreous GeO₂. From the similarity in the crystalline forms of SiO₂ and GeO₂ it would be expected that the atomic arrangement in vitreous GeO₂ would be essentially the same as in SiO₂. This turns out to be the case. The interatomic distance is slightly larger: Ge-O = 1.65 Å, but otherwise the scheme of grouping is the same.

The intensity of scattering for vitreous GeO₂ is given by an expression of the same form as equation (3), with f_{si} replaced by f_{Ge} and the fundamental cation-anion distance 1.65 Å instead of 1.60 Å. When this intensity expression is plotted and compared with the experimental intensity curve for GeO₂, it is found that the main peak agrees very well, but that the second peak in the calculated curve is somewhat too

strong and occurs at too large an angle. A careful analysis of the intensity equation shows that the discrepancy is due wholly to the second order maximum of the strong term $12f_{\text{Ge}}f_{\text{Si}} \frac{\sin(5.35s)}{5.35s}$ and that a satisfactory agreement between the calculated and experimental curves can be obtained only if the distance from Ge to

obtained between calculated and experimental intensity curves as seen in Fig. 3*b*.

It appears possible that from a more careful and detailed comparison of the calculated and experimental curves, it would be possible to determine not only the kind of atomic grouping and interatomic distances in glass, but also the degree of regularity in the grouping. While a similar variation in the distance to neighboring atoms, due to the two bonds to any oxygen not being exactly diametrically opposite, must also be present in vitreous SiO_2 , the effect does not show up so markedly in the diffraction pattern due to the smaller scattering of silicon relative to oxygen. That vitreous SiO_2 and GeO_2 should have the same atomic arrangement and yet give quite different scattering patterns is due to the relative difference in the scattering power of the atoms.

III. Results on Other Glasses

Three other simple glasses, vitreous BeF_2 , B_2O_3 , and P_2O_5 , are being studied by C. F. Hill of this laboratory. BeF_2 has the same atomic arrangement as vitreous SiO_2 and GeO_2 , each Be being tetrahedrally surrounded by 4F, building up the same nonrepeating random network. The analysis of the B_2O_3 and P_2O_5 patterns is not yet completed.

A start has been made on the soda-silica series of glasses⁵ by Mr. Loring and the author. Seven samples with progressively increasing soda content have been X-rayed. The diffraction patterns show a continuous variation with increase in the soda content. Starting with 100% SiO_2 , there is a strong peak at $\frac{\sin \theta}{\lambda} = 0.12$, as mentioned

above in the discussion of the silica pattern. As the soda content increases, this peak diminishes in intensity, and at the same time a new peak at about twice the angle gradually increases in intensity, the change in the patterns being perfectly continuous.

Representing the composition as $(\text{SiO}_2)_{1-x}(\text{Na}_2\text{O})_x$, the ratio of oxygen to silicon atoms becomes $\text{O}:\text{Si} = \frac{2-x}{1-x}$. Since x is less than unity, this ratio is necessarily greater than 2. Each silicon will still be tetrahedrally surrounded

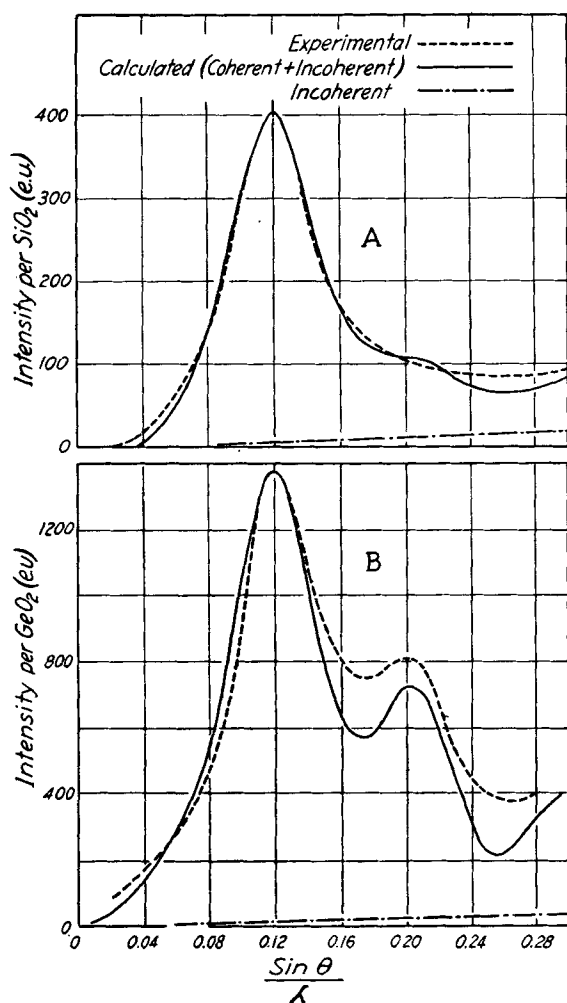


FIG. 3.—Comparison of calculated and experimental scattering curves: (a) vitreous SiO_2 , (b) vitreous GeO_2 .

the twelve next nearest Ge neighbors is not the perfectly definite value 5.35 Å which has been assumed, but varies slightly. Since there is no reason why the two bonds to any oxygen should be exactly diametrically opposite, it is quite reasonable to expect that this distance should vary a little. If the distance is assumed to be 5.35 ± 0.60 Å, a fairly satisfactory agreement is

⁵ In this work, the author is indebted to G. W. Morey for his kind cooperation in preparing the various samples.

by 4 oxygens, but with the O:Si ratio greater than 2, it is necessary that only part of the oxygens be shared between two silicons. The other oxygens, which are bonded to only one silicon, will be the ones which are bonded to the Na-atoms. Hence the original set of inter-neighbor distances which determined the silica pattern become progressively of less importance and the first peak diminishes in intensity. At the same time a new set of distances, depending on the atoms surrounding any Na-atom, become more and more important. It is probably this

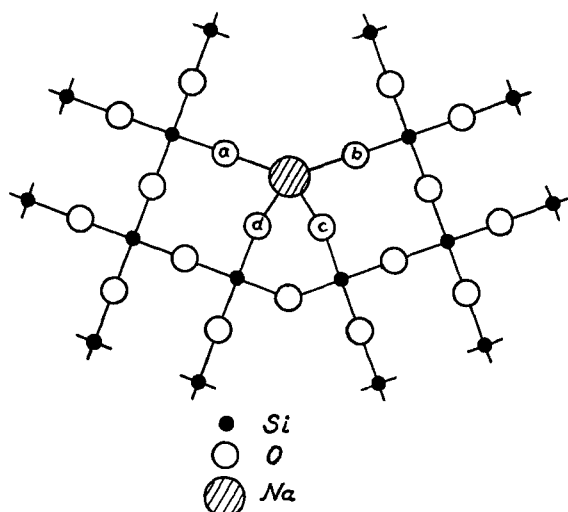


FIG. 4.—Schematic illustration of the atomic arrangement in a soda-silica glass.

new set of distances which is responsible for the peak at larger angle which grows in intensity with increasing soda content.

Figure 4 illustrates schematically the probable arrangement in a soda-silica glass. Each silicon is bonded to 4 oxygens (in 3 dimensions a tetrahedral arrangement, of course) and some of the oxygens are shared between 2 silicons. The other oxygens, such as *a*, *b*, and *c*, are joined to one silicon and 2 or 3 sodium atoms. It will probably be some time before the analysis of the soda-silica patterns is completed, but the results will certainly be of the greatest interest, for the atomic arrangement which is found will be essentially that of a typical glass.

IV. General Discussion

The agreement between the calculated and experimental X-ray scattering curves for the simple glasses is sufficiently satisfactory to allow one to consider the random network hypothesis of the glassy state as completely substantiated. The atomic arrangement and interatomic distances in a glass are practically the same as in the corresponding crystalline modifications, the essential difference being that the random network which is built up in a vitreous substance does not repeat at regular intervals, and hence the material is noncrystalline. It is just this point which differentiates the glassy from the crystalline state. The random network picture of the vitreous state, which has been deduced here from X-ray scattering results, is in complete agreement with the conclusions reached by Zachariasen⁶ from other considerations.

There is no evidence for the existence of compounds in glass from any of the X-ray diffraction patterns so far analyzed. As long as the sample is a true glass, containing no devitrification products, the diffraction pattern consists solely of one or more diffuse rings, which are readily interpreted in terms of a random network.

Glass is a definite example of an amorphous solid. For thermodynamic reasons it is customary to refer to glass as an "undercooled liquid," the point being that this term implies the absence of a definite melting point. However, the term "amorphous solid" also implies just this, and since, in addition, the atoms in a glass do have permanent neighbors, which is a characteristic of the solid state, it might be preferable to classify glass as an "amorphous solid," although obviously in the sense in which the two terms are used here, "amorphous solid" and "undercooled liquid" mean exactly the same thing.

EASTMAN LABORATORY OF PHYSICS
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASS.

⁶ W. H. Zachariasen, *Jour. Amer. Chem. Soc.*, **54**, 3841 (1932).