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The Diffraction of X-Rays in Glass

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X-ray diffraction patterns of vitreous SiO_2 and GeO_2 have been made in an evacuated camera using $\text{Cu } K\alpha$ radiation monochromatized by crystal reflection. Intensity curves are obtained from the microphotometer records in the usual way. A method is developed for calculating the scattering of x-rays in an amorphous solid and is applied to the diffraction patterns of glass. In vitreous SiO_2 each Si is tetrahedrally surrounded by 4 oxygens at a distance

$\text{Si}-\text{O}=1.60\text{\AA}$, and each oxygen is shared between two such tetrahedral groups. The resulting network which is built up is a random network, it does not repeat at regular intervals, and is accordingly non-crystalline. From this picture of the glassy state, scattering curves are calculated for vitreous SiO_2 and GeO_2 which are in good agreement with the experimental curves.

INTRODUCTION

A MONOCHROMATIC pencil of x-rays, passed through a thin sample of glass, gives rise to a diffraction pattern consisting of one or more broad diffuse rings, very similar in appearance to the rings obtained by the diffraction of x-rays in liquids. Although these rings have been observed by a number of workers,¹⁻⁵ there has been very little done in the way of a serious attempt to interpret the x-ray diffraction patterns of glass.

In a preliminary publication,⁶ it has been shown that the diffraction pattern of vitreous SiO_2 can be interpreted in terms of scattering

from a non-crystalline, random network, and that from such a model of the vitreous state, a scattering curve could be calculated which is in fairly good agreement with the observed intensity curve. A more careful comparison of the curves was, however, impossible because of the uncertainties in the experimental curve caused by background correction. In the present paper, the work has been repeated with sufficiently improved experimental conditions to completely eliminate this troublesome correction. The work has been extended to include both vitreous SiO_2 and GeO_2 , and in addition the experimental scattering curve for SiO_2 has been put upon an absolute basis by calibration against rocksalt.

EXPERIMENTAL

In the previous work the radiation used was $\text{Cu } K\alpha$ filtered with a nickel sheet. This does not give a strictly monochromatic beam and hence gives rise to a background. In addition there is scattering of the primary beam in the air path between the sample and the film. Both of these

¹ Debye and Scherrer, *Abh. Gött Ges.* 16 (1916).

² Wyckoff and Morey, *J. Soc. Glass Tech.* 9, 265 (1925).

³ Seljakow, Strutinski and Krasnikow, *Zeits. f. Physik* 33, 53 (1925).

⁴ Parmelee, Clark and Badger, *J. Soc. Glass Tech.* 13, 285 (1929). Clark and Amberg, *J. Soc. Glass Tech.* 13, 290 (1929).

⁵ Randall, Rooksby and Cooper, *Zeits. f. Krist.* 75, 196 (1930).

⁶ B. E. Warren, *Zeits. f. Krist.* 86, 349 (1933).

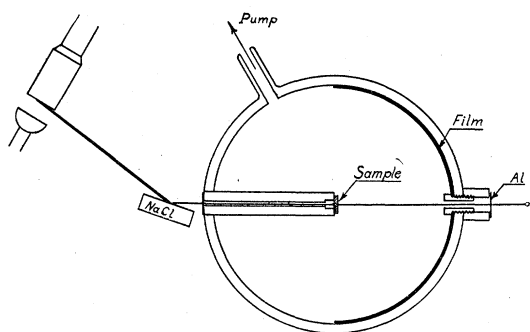


FIG. 1. Vacuum camera with monochromator.

troublesome factors are eliminated in the new experimental arrangement shown in Fig. 1. The radiation from a copper target Philips tube is monochromatized by reflection from a rocksalt crystal set to reflect the $K\alpha$ line. The reflected beam passes through a thin slip of the material of about $3/4$ the optimum thickness. The cylindrical camera is of radius 4.40 cm and is evacuated to eliminate air scattering. 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. With the tube running at 20 m.a. and 30 kv peak, exposures of 30 hours were found to be sufficient. The microphotometer curves were changed to intensity curves by the usual method of making calibration blackening steps on the film.

CALCULATION OF X-RAY SCATTERING IN AN AMORPHOUS SOLID

The method of calculating the intensity of x-ray scattering in an amorphous solid, which is developed here, is essentially a modification of the method used by Zernicke and Prins⁷ in treating diffraction in liquids. The intensity of scattering from an array of atoms which is allowed to take all possible orientations in space is given as a function of the angle of scattering by the expression⁸

$$I = \sum_m \sum_n f_m f_n (\sin sr_{mn}) / sr_{mn}, \quad (1)$$

⁷ Zernicke and Prins, *Zeits. f. Physik* **41**, 184 (1927).

⁸ P. Debye, *Ann. d. Physik* **46**, 809 (1915).

where $s = (4\pi \sin \theta) / \lambda$, r_{mn} is the distance from atom m to atom n , and f_n is the scattering factor for atom n . The summation is taken with respect to any one atom over all the other atoms including the one singled out, and then the one singled out is in turn allowed to be each of the atoms in the array. Considering now the case of SiO_2 and making the reasonable assumption that on the average each silicon is surrounded in the same way as every other silicon, and similarly for oxygen, Eq. (1) becomes

$$I = N \left\{ f_{\text{Si}} \sum_n f_n \frac{\sin sr_{\text{Si}n}}{sr_{\text{Si}n}} + 2f_0 \sum_n f_n \frac{\sin sr_{\text{O}n}}{sr_{\text{O}n}} \right\}, \quad (2)$$

where N is the effective number of SiO_2 molecules in the sample.

It was shown⁶ that in vitreous SiO_2 each Si is tetrahedrally surrounded by four oxygens with an Si-O distance of 1.60Å, and that each oxygen is shared between two tetrahedral groups exactly as in the crystalline modifications of SiO_2 . The bonds from an oxygen to the two tetrahedral groups which it joins, are presumed to be roughly diametrically opposite, but the relative orientation of the two groups about their common line of bonding is wholly random, so that it is a random non-repeating network* which is built up.

We now proceed 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 1.60Å, 4 Si at 3.20Å, 12 oxygens at 4.00Å, and 12 Si at 5.20Å. Out so 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 but varies from 5.0Å to 6.6Å, depending on the orientations of the groups. Beyond this the distances become quite indefinite, and one can assume a continuous distribution of scattering matter and carry out the summation by direct integration. Beginning with the 12 Si at 5.20Å, it is a considerable simplification to replace the discreet array of atoms by spherical SiO_2 scattering units comprising one Si at the center and two oxygens spread uniformly over the surface

* W. H. Zachariasen, *J. Am. Chem. Soc.* **54**, 3841 (1932).

of a sphere of radius Si-O=1.60Å. For such a unit, the appropriate scattering factor is

$$f = f_{\text{Si}} + 2f_{\text{O}}(\sin 1.60s)/1.60s. \quad (3)$$

While this introduction of spherical scattering units is a rough approximation, it is nevertheless a sufficiently good one at the small angles of scattering to be considered. The final distributions are listed in Table I.

TABLE I. *Distribution of surrounding atoms.*

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

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.

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

where ρ is the density in SiO₂ molecules per cc and

$$\Phi(x) = (3/x^2) \{(\sin x)/x - \cos x\}.$$

$(4/3)\pi R^3 \rho$ is the number of SiO₂ molecules which would be contained in the spherical hole⁹ which has been cut in the continuous distribution and is hence equal to the number of molecules which have been summed discreetly. The value of R to be used is taken roughly as the radius of this hole. For SiO₂, R_1 is taken equal to 6.05Å, and R_2 equal to 4.55Å. The exact values of R_1 and R_2 have but little effect upon the positions of the peaks and hence are not very critical. If an inconsistent value of R is chosen, this fact will show up by producing negative intensities at small angle.

Eq. (2) now takes the form

$$\begin{aligned} \frac{I_C}{N} = f_{\text{Si}} \left\{ f_{\text{Si}} + 4f_{\text{O}} \frac{\sin 1.60s}{1.60s} + 4f_{\text{Si}} \frac{\sin 3.20s}{3.20s} + 6f_{\text{O}} \frac{\sin 4.00s}{4.00s} + 12f_{\text{Si}} \frac{\sin 5.20s}{5.20s} - 17f\Phi(6.05s) \right\} \\ + 2f_{\text{O}} \left\{ f_{\text{O}} + 2f_{\text{Si}} \frac{\sin 1.60s}{1.60s} + 3f_{\text{O}} \frac{\sin 2.62s}{2.62s} + 6f_{\text{Si}} \frac{\sin 4.00s}{4.00s} - 8f\Phi(4.55s) \right\}. \quad (5) \end{aligned}$$

With the atomic scattering factors from James and Brindley¹⁰ the intensity is calculated as a function of $(\sin \theta)/\lambda$. From Eq. (5) one obtains the coherent scattering and to this must be added the incoherent scattering.

$$I_{\text{inc}} = N \{ I_{\text{Si}} + 2I_{\text{O}} \}, \quad (6)$$

where the intensity of incoherent scattering per atom is given by Wentzel's theory as¹¹

$$I = Z - \sum_1^Z (f_n)^2. \quad (7)$$

⁹ Actually it is of course incorrect to assume a sharp cut-off for the continuous distribution, but as this has only a small effect upon the final curve due to the fact that $\Phi(sR)$ decreases very fast with angle, there seems to be no point in trying to refine this part of the calculation.

¹⁰ James and Brindley, *Phil. Mag.* **12**, 81 (1931).

¹¹ E. O. Wollan, *Rev. Mod. Phys.* **4**, 233 (1932).

The scattering factors for the different electron groups are taken from the table of James and Brindley. The total intensity, coherent plus incoherent is plotted as a function of $(\sin \theta)/\lambda$ in Fig. 2a and compared with the experimental curve derived from the microphotometer records. The intensity as calculated from Eqs. (5) and (6) is expressed in electron units per SiO₂ molecule. Since the intensity from the microphotometer records is in arbitrary units, the scale of ordinates for the experimental curve is so chosen that the heights of the two peaks coincide. Except for this choice of ordinate scale for the experimental curve there is nothing arbitrary in the comparison. The agreement is quite satisfactory in both the position and the shape of the peak, in fact the agreement over the whole curve is as good as could be expected in view of the experimental error and the necessary approximations

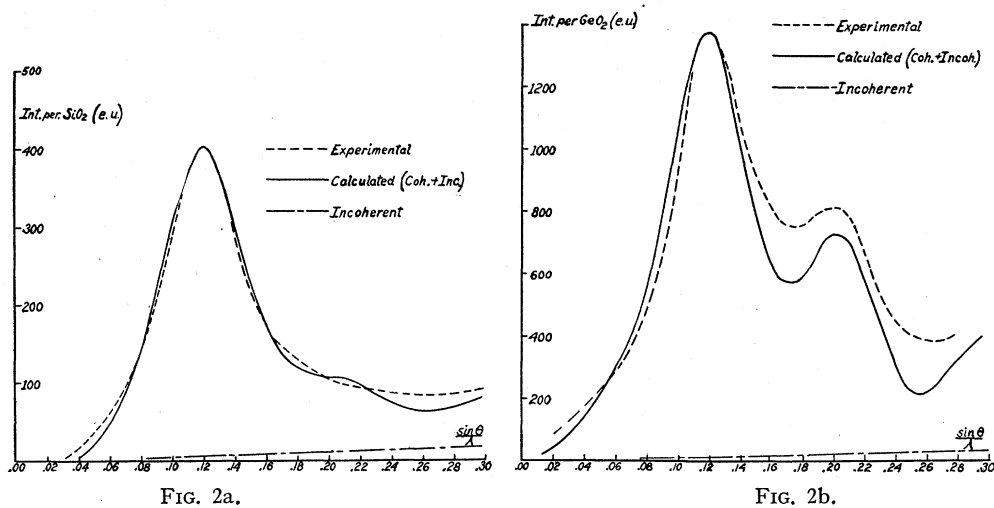


FIG. 2a. Comparison of calculated and experimental scattering curves for vitreous SiO₂.
 FIG. 2b. Comparison of calculated and experimental scattering curves for vitreous GeO₂.

in the calculated curve. It is of further interest to note that if the Si—O distance of 1.60Å is changed by as much as 5 percent there is definite disagreement between the positions of the peaks, and hence a fairly definite Si—O interatomic distance is determined by the curve. The distance 1.60Å which gives the best agreement between calculated and observed intensity curves is the same value as found in crystalline forms of SiO₂.

From similarities 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 vitreous SiO₂, and this turns out to be the case. The intensity of coherent and incoherent scattering for GeO₂ is given by equations of the same form as (5) and (6) with appropriate scattering factors and a slightly larger interatomic distance Ge—O=1.65Å. The intensity curve calculated in this way shows two peaks similar to the experimental curve, but with the second peak in the calculated curve somewhat too strong and at too large an angle. This discrepancy is due to the second order maximum of the strong term

$$12 f_{\text{Ge}} f(\sin 5.35s)/5.35s.$$

The only conclusion which we can draw is that the distance from any one Ge out to the 12 next nearest Ge neighbors is not the perfectly definite value of 5.35Å 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 that this distance should vary a little. If we assume this distance to be $5.35 \pm 0.60\text{Å}$ a fairly satisfactory agreement is obtained as seen on Fig. 2b. 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 the glass, but also the degree of regularity in the grouping. While a similar variation in interatomic distances must also be present in vitreous SiO₂, the effect does not show up so markedly in the diffraction pattern due to the smaller scattering of silicon relative to oxygen. That SiO₂ and GeO₂ give quite different scattering patterns is due to the *relative difference* in the scattering power of the atoms.

ABSOLUTE DETERMINATION OF SCATTERING IN AN AMORPHOUS SOLID

As a further check on the correctness of the theory which has been developed here for the scattering of x-rays in an amorphous solid, an absolute determination of the scattering curve was made. Powdered SiO₂ glass and rocksalt were mixed together in proportions 8 : 1 by weight and bound together with dilute collodion into a thin slip 39 mg per cm². The diffraction

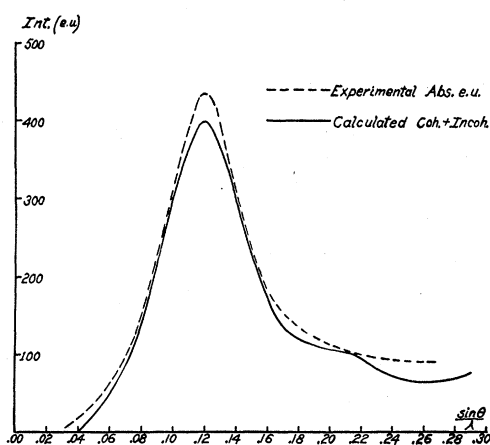


FIG. 3. Comparison of calculated scattering curve for vitreous SiO_2 with absolute determination of experimental scattering curve.

pattern of the slip shows the broad diffuse ring of silica and superimposed upon it the sharp rings of rocksalt. From the microphotometer record an intensity curve in arbitrary units is constructed in the usual way.

Let y be the ordinate of the intensity curve measured directly in cm. The quantity desired is the intensity per SiO_2 molecule expressed in electron units. If we denote this by I' , then $I' = ky$. It is easy to show that k is given by the expression

$$I' = \frac{mF^2(\lambda^3/v)(N_{\text{NaCl}}/N_{\text{SiO}_2})R}{32\pi \sin \theta \sin 2\theta A}, \quad (8)$$

where m = multiplicity, F = structure factor, v = volume of unit cell, N = number of molecules in sample, R = radius of camera, θ = glancing angle, and A the area under the peak in sq. cm, all referred to some one of the rocksalt peaks. Correcting also for the absorption of the beam passing through the sample in different directions, the intensity curve for SiO_2 is obtained directly in electron units. In Fig. 3 the calculated intensity curve is compared with the experimental curve. Both curves give the intensity per SiO_2 molecule expressed in electron units. It might be pointed out that in this comparison no arbitrary parameter is involved in either curve.

CONCLUSIONS

Glass is a definite example of an amorphous solid. For thermodynamic reasons it is customary to refer to glass as an "under cooled 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 would appear on the whole preferable to classify glass as an amorphous solid, although obviously the two terms "amorphous solid" and "under-cooled liquid" mean the same thing.