Acta Cryst. (1954). **7**, 122

An Electron-Optical Study on the Surface of Glass

By John J. Antal* and A. H. Weber
Saint Louis University, St. Louis 3, *Mo.*, *U.S.A.*

(*Received* 23 *January* 1953 *and in revised form* 27 *May* 1953)

Electron-diffraction patterns have been obtained from the surface of glass after deposition of a thin film of bismuth (thickness < 10 Å) to reduce electrostatic charging. The bismuth film is made up of preferentially oriented aggregates which contribute in a recognizable manner to the diffracted intensity. In order to compute radial distribution functions an approximate method was used which combined microphotometer and visual methods for obtaining the dependent coherent scattering. The results indicate that the surface structure of water-washed soda-lime-silica glass is essentially that of the bulk material with a deficiency of alkali atoms in the topmost atom layers.

1. Introduction

The surface structure of glass has been investigated by Preston (1942) to aid in understanding the nature of glass fracture, by Kamogawa (1940, 1943*a*, *b*), who employed electron-diffraction methods, and by Weyl (1950), who studied the surface chemistry of silica. Electron diffraction is indicated for this type of study but involves electrostatic charging of the glass surface and apparently is characterized by a lack of precision in intensity measurements. Kamogawa used an auxiliary low-voltage electron gun to eliminate the charging by secondary electron emission. In the present studies it was found possible to obtain a good diffraction pattern from glass surfaces after depositing a very thin film (thickness < 10 Å) of bismuth on the surface to reduce charging. Some characteristics of thin bismuth films were thus determined and also are discussed.

2. Preliminary studies

In preparation for the electron-optical studies a standard glass-surface cleaning procedure was developed. Several glass-washing techniques (Oliver, 1942; Thomson, Murison & Stuart, 1933; Hoag, 1948) were investigated. Electron-microscope pictures of collodion replicas taken before and after the various washings indicated that a detergent†–distilled water–alcohol–distilled water wash was most suitable for cleanliness without chemical damage. Several of the electron micrographs are shown in Fig. 1. In washing the specimens were handled with forceps and swabbed with cotton lightly.

It was originally considered that a metal film deposited on glass might through its structure be indicative of the supporting glass surface structure. To investigate this possibility, several low-melting-point metals (Pb, Sn, Sb and Bi) were deposited by evaporation within the electron-diffraction camera on microscope-slide glass surfaces. Of these Bi alone showed a preferred orientation. The occurrence of a preferred orientation of the condensed Bi could be influenced by (1) the temperature of the furnace during evaporation, (2) the temperature of the substrate during evaporation, (3) the physical structure of the substrate, (4) the chemical composition of the surface, (5) the thickness of the deposited film. Each of these factors was investigated separately to determine its contribution to the preferred orientation of the Bi. (Since all films were condensed in an evacuated chamber the effect of gas pressure was not studied in the present investigation.)

No change in the Bi orientation was noted in the ranges 300–700° C. furnace temperature and 16–50° C. specimen temperature (the usual operating ranges). Various portions of a glass specimen surface containing sleeks and small scratches were examined but no change in the Bi diffraction pattern was found. Again no change of orientation was obtained for Bi deposited on glasses of different chemical compositions: Pyrex, soda-lime-silica (boron-free), borosilicate and glass from photographic plates.

A variation in the diffraction pattern with thickness of the deposited film was observed but could not be studied quantitatively because the film-thickness measurements were inaccurate. Hence it was decided to develop a reliable method of film-thickness measurement. Originally kinetic theory was used to calculate the average film thickness (Platenberg & Weber, 1946). However, in this method the amount of Bi evaporated depends on the condition of the surface of the molten Bi in the evaporating furnace. It is found that a film of the oxide of the metal is present on the molten surface even when it has been scraped clean in the vacuum (Jenkins, 1935). This oxide film inhibits the evaporation of Bi to an extent depending on the the amount of oxide present. The necessary

---

* Now at Watertown Arsenal, Watertown, Massachusetts, U.S.A.

† Several suggested detergents (William & Backus, 1949; Strong, 1938) and others were tried. The synthetic detergent 'Surf' was found to be quite suitable since it was most easily rinsed from the glass surfaces.

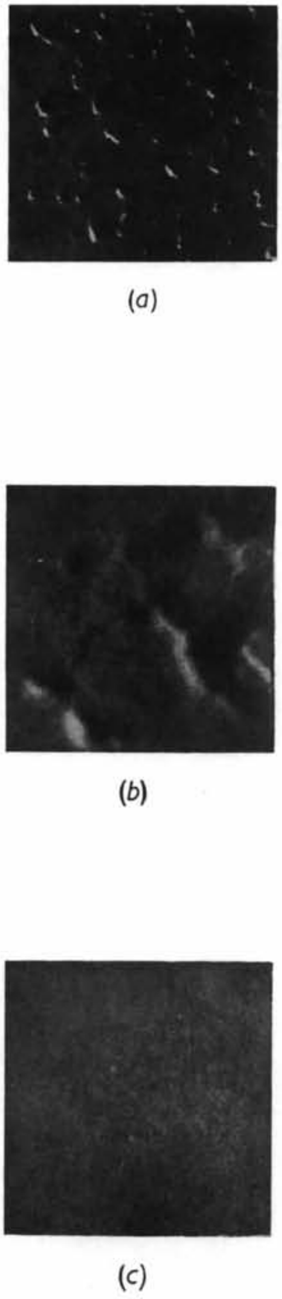

Fig. 1.

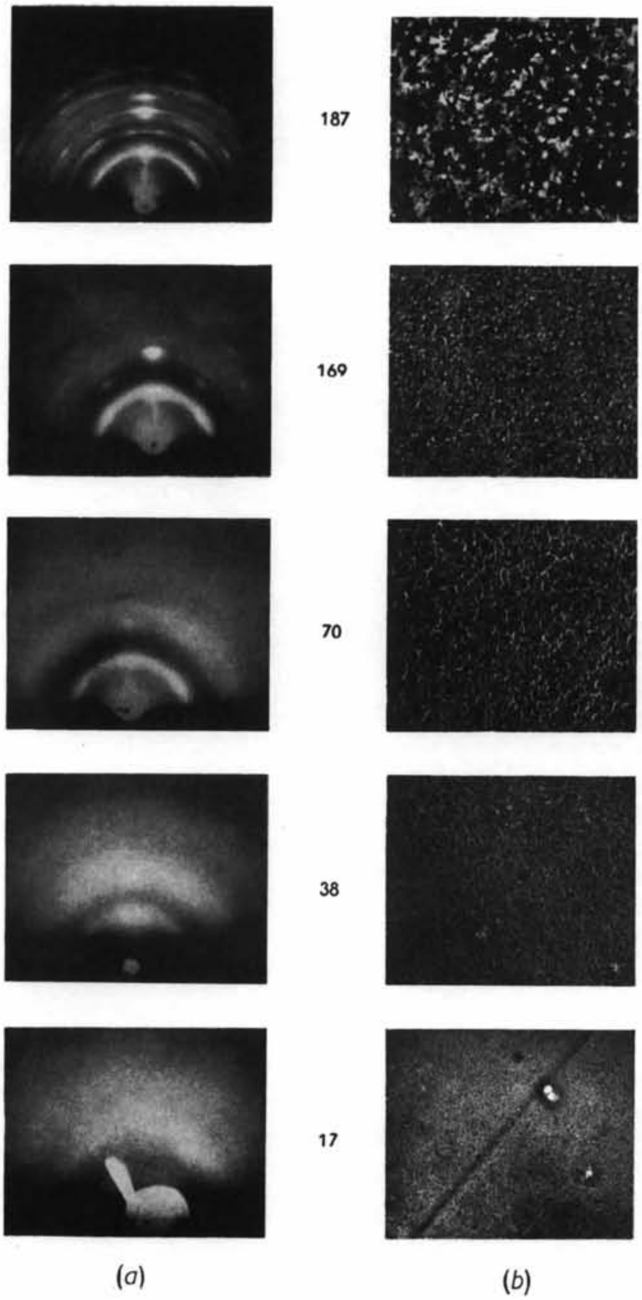

Fig. 2.

Fig. 1. Electron micrographs showing the effect of various washing techniques on the condition of the surface of the glass. (*a*) KOH–HCl–H_2O wash; excessive etching. (*b*) Aqua regia–H_2O wash; excessive etching. (*c*) Recommended detergent–alcohol–H_2O wash; cleanliness without chemical attack.

Fig. 2. Several of a series of electron-diffraction patterns and electron micrographs for various thicknesses of Bi on the glass surface. (*a*) Electron diffraction patterns; (*b*) electron micrographs (11,000 ×). Numbers between each pair are Bi thicknesses in Ångström units.

alternate exposure of the Bi in the furnace to high temperature and to air admitted to the evaporation chamber varies considerably the amount of oxide present.

A radioactive-tracer method employing Bi^{210} ultimately was developed (Antal & Weber, 1952) and this method yielded reliable film-thickness measurements. The method was especially convenient for thicknesses below 10 Å, the region of interest in the diffraction studies.

A series of specimens was prepared, containing respectively thirty Bi film thicknesses between 1·5 and 300 Å on glass, from spectroscopic plates of the chemical composition (within about 3%) stated in § 5 below. These samples were examined by both electron diffraction and electron microscopy* and a number of the patterns and micrographs are shown in Fig. 2. The results of the electron-optical examinations are conveniently discussed as follows with respect to diffraction by the glass surface (§ 3) and the structure of the Bi films (§ 4).

3. Diffraction by the glass surface

The diffraction pictures of Fig. 2 show a composite pattern in most cases. For films thicker than 200 Å the electron-diffraction patterns showed the presence of preferentially oriented Bi only.

Thicknesses ranging from 200 to about 10 Å showed a composite pattern of diffuse halos and spotty Debye–Scherrer rings. Since the diffuse halos become more intense relative to the spots the thinner the films, it is concluded that the glass surface was increasingly more responsible for the halo intensity the thinner were the Bi films. Measurement of the scattering parameters for the maxima of these halos yielded

$$s = (\sin\theta)/\lambda = 1{\cdot}6,\ 2{\cdot}6,\ 3{\cdot}4,\ 4{\cdot}6\ \text{Å}^{-1}.$$

These values agree well with those of Kamogawa (1940, 1943*a*, *b*) and Maxwell & Mosely (1935) for glass.

Diffraction patterns were obtained for Bi films 1·8 Å thick, in which case so little Bi is presented to the electron beam that it is difficult to explain the intensity of the diffraction as due to Bi alone. The most intense spots from the preferentially oriented Bi were on the Bi Debye–Scherrer ring of smallest radius and persisted to the thinnest films examined, even though all complete rings disappeared. For the thinner films it is assumed that, ignoring the spots, the diffraction pattern is that of the glass alone. When densitometer traces were taken later of the diffraction patterns, a radius of traverse was chosen at approximately 45° to the shadow edge so that no part of the spots would be recorded.

As further evidence that the diffraction patterns were those of glass, a pattern from the surface of highly crystalline quartz was obtained which exhibited strong Kikuchi lines and a superimposed diffuse scattering, exactly as found by Kamogawa (1940, 1943*a*, *b*).

4. Bi film structure

The diffraction and microscopy results provide also some information on the structure of thin Bi films deposited on glass by evaporation in a vacuum. Germer & White (1941) have shown that for the metal films they studied (Bi was not included) agglomeration was prominent, resulting in a film of profile features much larger than the average film thickness. This irregular profile picture for Bi was established by photoconductance and electron-diffraction transmission experiments (Weber & Friedrich, 1944; Weber & O'Brien, 1941; Weber & Keogh, 1948). The electron micrographs of Fig. 2 gave direct confirmation of the aggregation process. Below 160 Å thickness Bi was definitely formed of aggregates separated by spaces of various widths. At extremely small thicknesses, the state of aggregation was irregular. When so little Bi is present there is much free surface for movement and the conditions under which such films age probably have an important bearing on their final arrangement.

The orientation of the Bi on the glass surface was random about an axis perpendicular to the surface, but the predominant orientation was for planes of the 200 type parallel to the surface.

It is surprising that the charging of the glass specimens was reduced so considerably by the presence of such a small, discontinuous amount of Bi on the surface. Apparently conduction through the films was not the only factor involved. Secondary emission from the Bi may have been partly responsible for the decrease in charging. The experiments of Weber & Friedrich (1944) showed that the conductance of very thin Bi films on glass was increased considerably by illuminating them with mercury radiation and so it is possible that the bluish fluorescence of the glass under impact of the electron beam increases the conductance in the same way. A small amount of charging occurred for the thinnest films, leaving a small smear around the central beam in the photographs.

5. Analysis of patterns from glass surfaces

The resulting electron-diffraction patterns from a soda-lime-silica boron-free glass were studied quantitatively by determining their radial distribution function by approximation methods. The densitometer used to determine the intensity distributions employed a Welch Densichron as detector. The resultant amplified

---

* The surface of the Bi-on-glass specimens was first examined with electron diffraction; the Bi was then stripped off with collodion to yield an electron microscope specimen. The radioactivity of the films provided a convenient check on the amount of Bi actually removed, and this aided the evaluation of micrographs when strong adherence of the Bi to the glass was suspected.

output was passed through a non-linear d.c. amplifier which expanded the scale of recorded densities and so aided in covering the extreme range of intensities encountered in electron diffraction. The densitometer was calibrated by a step wedge made on the type of photographic plate (Eastman Spectroscopic Plate type IV-O) used in the electron diffraction experiments. The plate was exposed in the diffraction camera to diffuse electron radiation transmitted by a very thin glass film. The exposure time was varied 88-fold (the reciprocity law should hold within this range for the 35 ke.V. electrons used (Becker & Kipphan, 1931)). The densitometer trace for a soda-lime-silica glass, adjusted to relative intensities, is shown in Fig. 3, trace *A*.

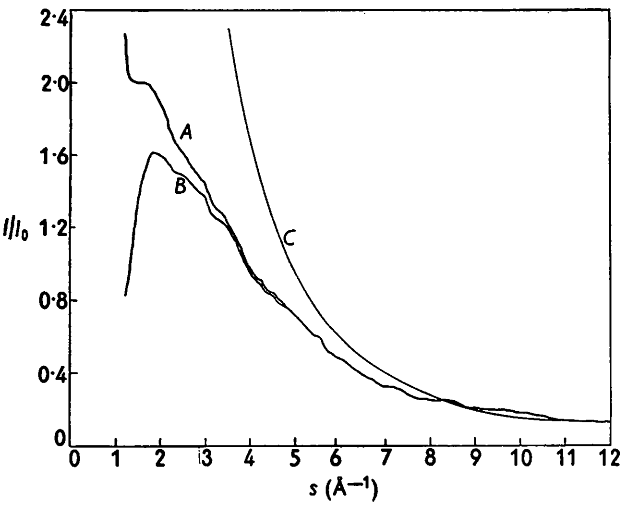

Fig. 3. (*A*) Densitometer trace of diffraction pattern of the surface of soda-lime-silica glass corrected to relative intensities. (*B*) Trace *A* with incoherent scattering intensity subtracted. (*C*) Independent coherent scattering, illustrating serious misfit with trace *B*.

An attempt was made to analyze the diffraction patterns rigorously, as has been done with X-ray diffraction data from glass (Warren & Biscoe, 1938). The chemical composition of the glass was

SiO_2	72·3%	SO_3	0·4%	K_2O	Nil
Na_2O	13·6%	R_2O_3	0·35%	F_2	*ND*
CaO	11·3%	Fe_2O_3	0·099%	Sb_2O_3	*ND*
MgO	2·1%	BaO	Nil		

which determined the 'formula' for the glass 'molecule' as

$$Si_{0\cdot723}Na_{0\cdot272}Ca_{0\cdot113}Mg_{0\cdot021}S_{0\cdot004}R_{0.007}Fe_{0\cdot002}O_{1\cdot745} \qquad (1)$$

The incoherent and independent coherent (atomic) scattering were calculated by the last two terms in the following expression (Brockway, 1936) for the total scattered intensity $I(\theta)$

$$I(\theta) = I_0\left(\frac{8\pi^2me^2}{h^2}\right)^2\left[i\Sigma j\Sigma\frac{(Z-f)_i(Z-f)_j}{s^4}\frac{\sin sr_{ij}}{sr_{ij}} + i\Sigma\frac{(Z-f)^2}{s^4} + i\Sigma\frac{S_i}{s^4}\right]. \qquad (2)$$

Values for the incoherent scattering function S_i were taken from the tables of Bewilogua (1931) for the four most abundant constituents of the glass, divided by s^4, and each multiplied by the appropriate subscript in (1). This result was subtracted from the corrected densitometer trace (*A*, Fig. 3). The independent coherent scattering function was determined by evaluating $(Z-f)^2/s^4$ for the 'molecule' of glass for a series of points along the s axis. Although this curve should have followed *B*, Fig. 3, after normalization at $s = 11$ Å^{-1}, where no dependent coherent scattering should be present, it did not do so. Apart from the factors of multiple scattering and scattering by the residual gas in the diffraction camera (mentioned by Pauling & Brockway, 1935), which might contribute to a non-uniform background, the added factor of specular reflection from these extremely smooth glass surfaces was undoubtedly prominent.

Hence, in order to analyze the intensity distribution, it was necessary to resort to an approximate method for determining the dependent coherent scattering function. The use of a rotating sector in the diffraction camera was thought not feasible for the reflection patterns. The visual method of Pauling & Brockway (1935) is sufficient for determination of interatomic distances, but too few halos (five at most) were obtained in the diffraction patterns to attain satisfactory accuracy. A combination of the microphoto-

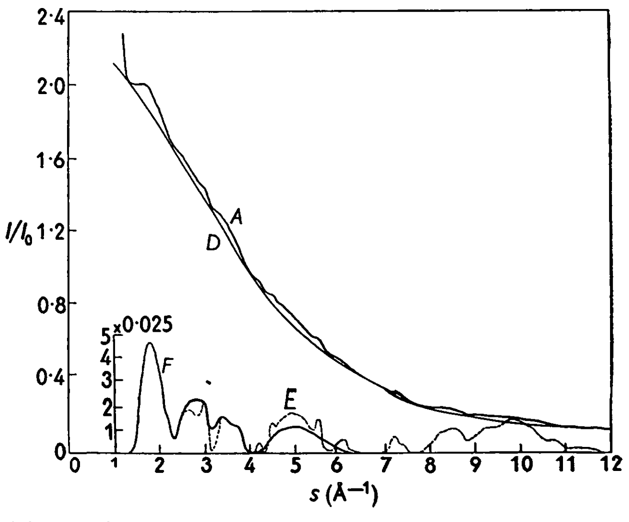

Fig. 4. (*A*) Total scattered intensity, as obtained from the photographic plate of an electron-diffraction pattern of the surface of soda-lime-silica glass. (*D*) Smooth curve drawn to touch minima of trace *A*. (*E*) Rough dependent coherent scattering curve obtained by subtracting trace *D* from *A*. (*F*) Final dependent coherent scattering curve obtained by smoothing trace *E* from visual examination of the original photographic record.

meter and visual methods was used finally which supplied some reliable information. The method was as follows: (1) the original corrected densitometer trace, converted to relative intensities, was plotted and a smooth curve approximating the uniform background was drawn in tangent to its minima (*A* and *D*, Fig. 4); (2) the difference of these two curves was obtained, yielding trace *E* of Fig. 4; (3) curve *E* was then modified by visual examination of the photographic plate (because of the small area between the original intensity curve and the approximated background, sharp maxima and minima were developed which were not observed visually and so were smoothed over). The resulting final curve *F*, Fig. 4, was used as the dependent coherent scattering function from which a radial distribution function was computed. It was found that the procedure was quite invariable to personal errors; the microphotometer curve formed a confining frame and thus limited the amount of guesswork involved in the visual estimations.

6. Radial distribution functions

A radial distribution function for the surface of the soda-lime-silica glass was computed using the approximate dependent coherent scattering curve *F* of Fig. 4 plus a fifth halo of low intensity and larger radius which was not recorded by the densitometer but observed visually. This function was inserted as $s^4I(s)$ in the integral

$$D(r) = K(1/r) \int s^5 I(s) \sin(sr) ds \qquad (3)$$

used by Pauling & Brockway (1935). The integration was carried out according to the 32-point Fourier synthesis scheme of Danielson & Lanczos (1942); the resultant radial distribution curve is shown by Fig. 5. Included on Fig. 5 are the radial distribution curve of Warren & Biscoe (1938) determined for a similar glass from X-ray diffraction data and the peak locations on the radial distribution curve of Weber & Breen (private communication, to be published) determined for this same glass from neutron-diffraction data. Comparing these radial distribution functions, it is seen that all peaks indicating distances between Si and O atoms coincide. Not resolved in the electron-diffraction curve, however, are distances to the alkali atoms. (Na and Ca have almost identical radii and both would be expected to contribute to the Na peaks of Warren & Biscoe.) Several explanations of this result will be considered. The first is that the alkali atom distances are masked by the prominence of nearby peaks. Actually a few points only determine the shape of the first three peaks, and so a shoulder on the slope of a peak might exist but remain undetected. More halos would be necessary to disclose such structure in the radial distribution curve.

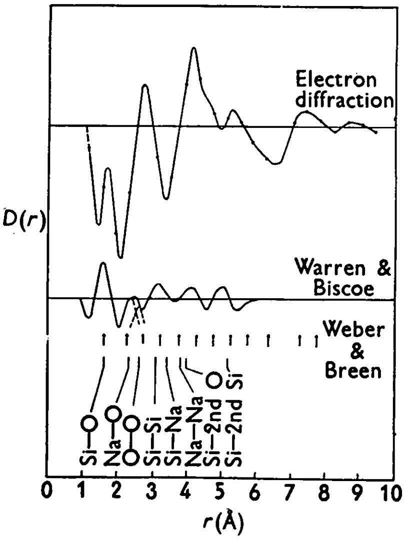

Fig. 5. Radial distribution functions for soda-lime-silica glass. The electron-diffraction curve was determined from the dependent coherent scattering curve *F* of Fig. 4 plus a fifth halo determined from visual examination of the photographic plate having a low intensity peak at $s = 6{\cdot}65$ Å^{-1}. The radial distribution curve of Warren & Biscoe is for a soda-silica glass containing 26·9 % soda content. This curve was taken from their paper and plotted on a linear background by subtracting $K_m 4\pi r^2 \varrho_0$ from all ordinates. The location of the peaks by Weber & Breen are for a neutron transmission radial density distribution determination for the same glass used in the present electron diffraction studies. The interatomic distances expected in soda-silica glass listed at the bottom of the figure were given by a model of Warren & Loring (1935).

Another possibility is that very few alkali atoms actually were located in the glass surface. A knowledge of the depth of penetration of the electron beam would aid in deciding upon a reason for this. For 36 ke.V. electrons incident at an angle of 30′ to the glass surface, the velocity perpendicular to the surface is $V' = V \sin 30' = 9{\cdot}75 \times 10^7$ cm.sec^{-1} or 30 e.V. Extrapolating the absorption curve of Bethe & Livingston (1937) a value of 2000 me.V. g.$^{-1}$ cm.$^{-2}$ is obtained for the specific energy loss of these electrons. Assuming a value of 2·5 g.cm.$^{-3}$ for the density of glass, and considering that inelastically scattered electrons constitute 75 % of the total intensity (Thomson & Cochrane, 1939), the elastically scattered electrons would penetrate a depth perpendicular to the surface of $(30 \times 10^{-6})/(2000 \times 0{\cdot}75 \times 2{\cdot}5) = 0{\cdot}8$ Å.

This value represents the minimum depth of penetration since surface roughness has not been included. Sheet glass manufactured by modern machinery is known to be quite smooth, albeit wavy (*Photographic Plates* ...). The waviness would contribute a negligibly small angle of incidence (estimated as $\sin^{-1} 0{\cdot}000015 = 3{\cdot}1'$) and can be neglected. Hence it may be assumed that the electron beam actually did not penetrate more than about ten times this minimum calculated value or about 10 Å perpendicular to the surface. Thus the top few atom layers only of the glass were being studied. In such a small effective depth a deficit of alkali atoms is not improbable.

Since the specimens were cleaned immediately before examination it is likely that the replacement of Na^+ ions with H^+ ions during the water washing was responsible for the alkali deficiency. Volatilization of the Na atoms under electron bombardment in the diffraction camera ($Na^+ + e^- \rightarrow Na$) might account for some of the removal of surface alkali, but indications are that this reaction proceeds slowly, if at all, with the electron intensities used. Again, tempering of the glass surface was not specially controlled during manufacture and a compression in the surface might eliminate alkali atoms from the topmost atom layers. Examination of the specimen between crossed polaroids under a light microscope revealed no visible strain, however. Hence, the results indicate that the true picture of the topmost glass surface is one in which the Si and O atoms form a random network enclosing fewer alkali atoms than are found in the bulk structure.

7. Conclusions

In summary, the present investigation led to these conclusions:

(1) It is possible to obtain true electron-diffraction patterns from the surface of glass by depositing an extremely thin film of Bi on the surface, although the aggregated metal is quite discontinuous.

(2) Bi deposits with an orientation of the (200) planes parallel to the glass surface and a random orientation about an axis perpendicular to the surface, and agglomerates into groups of crystallites whose size increases with increasing film thickness. The preferred orientation is not a direct function of the substrate, except perhaps of its smoothness.

(3) An approximate method for obtaining a dependent coherent scattering curve for the surface of glass was developed which combines the features of the microphotometer and visual methods, offering a larger amount of information for radial-distribution-function calculations than is possible with the same diffraction pattern and either method separately.

(4) A calculation of the radial distribution function for a soda-lime-silica glass surface indicated a deficiency of alkali atoms in the topmost atom layers which is attributed primarily to water washing of the surface prior to examination.

The authors are considerably indebted to Prof. W. A. Weyl of the Pennsylvania State College for valuable comments and suggestions and to Mr H. U. Rhoads of Saint Louis University for the electron micrographs. A grant from the Research Corporation which made possible this investigation is acknowledged with gratitude.

References

Antal, J. J. & Weber, A. H. (1952). *Rev. Sci. Instrum.* **23**, 424.

Becker, A. & Kipphan, E. (1931). *Ann. Phys., Lpz.* **10**, 15.

Bethe, H. A. & Livingston, M. S. (1937). *Rev. Mod. Phys.* **9**, 245.

Bewilogua, L. (1931). *Phys. Z.* **32**, 740.

Brockway, L. O. (1936). *Rev. Mod. Phys.* **8**, 231.

Danielson, G. C. & Lanczos, C. (1942). *J. Franklin Inst.* **233**, 435.

Germer, L. H. & White, A. H. (1941). *Phys. Rev.* **60**, 447.

Hoag, J. B. (1948). *Electron and Nuclear Physics*, 3rd ed., p. 461. New York: Van Nostrand.

Jenkins, R. O. (1935). *Proc. Phys. Soc.* **47**, 109.

Kamogawa, H. (1940). *Phys. Rev.* **58**, 660.

Kamogawa, H. (1943*a*). *Proc. Phys.-Math. Soc. Japan*, **17**, 384.

Kamogawa, H. (1943*b*). *Proc. Phys.-Math. Soc. Japan*, **17**, 396.

Maxwell, L. R. & Mosely, V. M. (1935). *Phys. Rev.* **47**, 330.

Oliver, A. R. (1942). *Phys. Rev.* **61**, 313.

Pauling, L. & Brockway, L. O. (1935). *J. Amer. Chem. Soc.* **57**, 2684.

Photographic Plates for Spectroscopy and Astronomy Rochester, N. Y.: Eastman Kodak.

Platenberg, M. G. & Weber, A. H. (1946). *Phys. Rev.* **69**, 649.

Preston, F. W. (1942). *J. Appl. Phys.* **13**, 629.

Strong, J. (1938). *Procedures in Experimental Physics.* New York: Prentice-Hall.

Thomson, G. P. & Cochrane, W. (1939). *Theory and Practice of Electron Diffraction*, p. 186. London: Macmillan.

Thomson, G. P., Murison, C. A. & Stuart, N. (1933). *Proc. Roy Soc.* A, **45**, 381.

Warren, B. E. & Biscoe, J. (1938). *J. Amer. Ceram. Soc.* **21**, 259.

Warren, B. E. & Loring, A. (1935). *J. Amer. Ceram. Soc.* **18**, 269.

Weyl, W. A. (1950). *Research*, **3**, 230.

Weber, A. H. & Friedrich, L. W. (1944). *Phys. Rev.* **66**, 248.

Weber, A. H. & Keogh, C. T. (1948). *J. Appl. Phys.* **19**, 1077.

Weber, A. H. & O'Brien, D. F. (1941). *Phys. Rev.* **60**, 574.

William, R. & Backus, R. (1949). *J. Appl. Phys.* **20**, 98.