LETTERS TO THE EDITORS

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Colour of Heavy Lead Silicate Glass

IT has been generally accepted in the optical industry that heavy lead flint glasses are yellow in colour. The Schott catalogue[1] on Jena optical glasses marks most of the heavy flints they produce as being yellow, and it is further pointed out that noticeable yellow colour would result even by using chemically pure materials. The question whether the yellow colour is intrinsic to the composition or is due to the presence of colouring oxides as impurities has been the concern of many ceramists and glass technologists[2,3]. Based on the fact that for heavy lead glasses the colour of the glass becomes browner as the temperature is raised, it was considered p obable that the yellow tinge at room temperature might be due to the residual effect of thermal broadening and shifting of the characteristic ultra-violet absorption band towards the longer wave-lengths of the spectrum. Thus it has been suggested by several workers as being due to the thermal dissociation of lead silicate into unbonded lead oxide[2]. W. Weyl[3] further suggested, on the modern view, that the deepening in colour might be due to the influence of the PbO bond in the glassy structure. On the other hand, it is also well known that colouring oxides such as iron, copper, etc., all produce more intense colours in heavy lead glasses than in ordinary lead-free glasses. In fact, it is not impossible that the thermal deepening in colour is partly due to the presence of such oxides.

In relation to this problem, particular mention should be made of the work carried out by Sir Herbert Jackson[4] and his colleagues Smith and Cooke[5] of the British Scientific Instrument Research Association early in 1924, who not only stressed the heavy colouring effect of iron oxide in heavy lead glasses, but also, by using raw materials containing less than 0·00005 per cent iron oxide, succeeded in producing a glass of refractive index 1·83, density 5·05, completely free from colour. But for glasses melted in platinum, of densities varying from 6·06 to 7·05 (corresponding to indices of refraction from 1·924 to 2·09), the colour deepened progressively from faint yellow to orange, when viewed through 1 cm. thickness. They also mentioned that chromium oxide coloured the glass intensely.

Recently, we have reinvestigated the colouring effect of iron oxide, as well as chromium oxide and copper oxide, in heavy lead silicate glasses. For glass of refractive index 1·915, iron oxide contributed a yellow colour, copper oxide green, and chromium oxide yellow, when viewed through 2 cm. thickness at concentrations of 0·01, 0·005 and 0·0005 per cent respectively. Spectrophotometric measurements indicated that the colouring effect of each oxide was proportional to its concentration over the range studied. Comparatively, the colouring power for iron oxide, copper oxide and chromium oxide was approximately in the ratio 1 : 2 : 40 respectively. Chromium oxide thus appeared by far the most powerful agent which could render a noticeable tint at a concentration so low as 0·00002 per cent at 2 cm. thickness.

We were naturally interested in producing a glass as free from colour as possible. For raw materials pure lead nitrate was prepared by dissolving spectrum pure lead in nitric acid, and precipitated silica was obtained by distillation from sodium silicofluoride and sulphuric acid. By sintering the batch and melting in a pure thoria crucible, a glass was obtained free from any noticeable tint through 5 cm. thickness, the refractive index being 1·90. It thus appeared that up to the index 1·90, heavy lead silicate glass could still be colourless. We found also that by melting in platinum, the attack—though not detrimental to the crucible—contributed appreciable colour to the glass. Details of the present results are to be published elsewhere.

We wish to acknowledge the courtesy of the British Scientific Instrument Research Association in allowing us to mention the results quoted above. The experiments were carried out by the staff of these laboratories working as a team.

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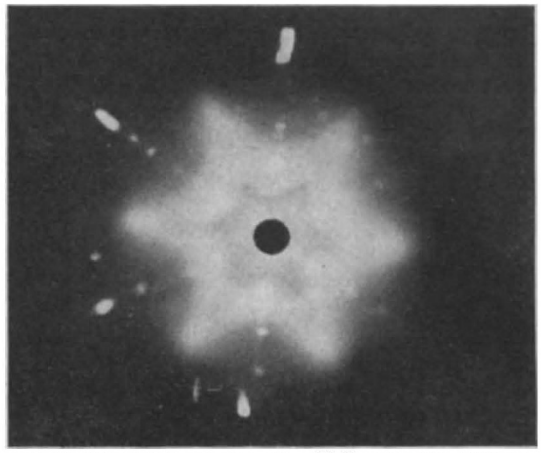
[1] "Jaener Glas für die Optik", No. 5858, p. 15, p. 4. Catalogue of Schott and Genossen, Jena.
[2] Möhl, H., and Lehmann, N., *Sprechsaal*, **62**, 463 (1929).
[3] Weyl, W., *J. Soc. Glass Tech.*, **27**, 289 (1943).
[4] Jackson, Sir Herbert, *Nature*, **120**, 264 and 301 (1927).
[5] Report 27, British Scientific Instrument Research Association, 1924, Report to Members.

Statistical Structure of Ice and of Ammonium Fluoride

BOOTH[1] has pointed out that if a strong diffuse streak of X-ray scattering connects two regions in the reciprocal lattice of a centro-symmetrical crystal, then the structure factors corresponding to those two regions must have the same sign; and he has suggested that this may be helpful in overcoming the X-ray crystallographer's bugbear: determination of phase. This argument is quite sound, it seems to me, if the diffuse scattering is due to displacement or vibration of those atoms the diffraction of which is mainly responsible for the reinforcing scattered waves which give the Bragg reflexions; and in crystals where this is the case, the method should be very useful.

In ice, however, where the contribution of the centro-symmetrically arranged oxygen atoms certainly decides the phase of the scattered waves, strong diffuse streaks do connect regions where the structure factors are *not* of the same sign; moreover, the diffuse pattern is more symmetrical than could possibly be the case if Booth's rule were satisfied. The diffuse pattern is very strong near 0° C., but it has almost disappeared at − 183° C., although it is still easily visible



LAUE PHOTOGRAPH OF ICE AT − 2° C., SHOWING STRONG DIFFUSE PATTERN

on the Laue photograph (published by Barnes in 1929[2]) of ice at − 78·5° C. It is, therefore, of thermal origin; but comparison with theory shows that it cannot, in the main, be due to acoustical vibrations, because no combination of any elastic constants whatever could give the star-shaped pattern found.

Since the diffuse streaks cannot be due to the oxygen atoms in ice, they must presumably be due to strong vibratory movements of the hydrogen nuclei, which may still, according to Bernal and Fowler[3], retain about 0·5 electrons each.

Bernal and Fowler have also pointed out that if ice is molecular (and its Raman and infra-red spectra prove that it is) then the unit cell cannot be so small as that given by X-rays. It must be at least three times as large. But Pauling[4] has shown from the experimental value of the residual entropy that the water molecules in ice cannot have the definite orientations which would permit a unique crystalline configuration such as that suggested by Bernal and Fowler. In fact, there are $(3/2)^N$ permitted molecular configurations (N is Avogadro's number) of a mole of ice. The change from one configuration to another, Pauling suggests, would take place by group movements of hydrogen nuclei, each of which would move from the neighbourhood of one oxygen to that of its next oxygen neighbour (or possibly by a rotation of the water molecules).

The diffuse X-ray scattering indicates that this is so; in which case, the small unit cell found by X-ray structure analysis would indeed be the true *statistical* unit cell, although the instantaneous configuration would be more complex and might not even be strictly periodic. It might well be that even at very low temperatures indeed the apparent unit cell would still be small because different molecular configurations would be frozen in, in different parts of a single crystal. Such time- or space-averaged statistical structures are becoming increasingly familiar to X-ray crystallographers.

A similar star-shaped diffuse pattern is observed for ammonium fluoride (isomorphous with ordinary ice), in which, therefore, similar strong vibratory movements of the hydrogen atoms must be taking place. Although, undoubtedly, the H—F bond is much more ionic in character than the N—H bond, yet even in this case a resonance between the structures N : H F−, N− H+ F− and N− H : F seems probable.

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[1] Booth, A. D., *Nature*, **158**, 380 (1946).
[2] Barnes, W. H., *Proc. Roy. Soc.*, A, **125**, 670 (1929).
[3] Bernal, J. D., and Fowler, R. H., *J. Chem. Phys.*, **1**, 515 (1933).
[4] Pauling, L., "The Nature of the Chemical Bond" (Cornell University Press, 1945), 302.

Spiral Cracks in Glass Tubes*

ANYONE dropping very hot glass tubing into cold water expects it to shatter. However, one does not expect it to shatter in a simple geometric pattern such as a spiral. I was surprised to observe such fracture, and to find that the spiral pattern is a preferred one. (The experiments were limited to 'Pyrex' glass, since soda glass was not available.)

A method of making these spiral cracks in 'Pyrex' tubing is the following: one lays one end of a stick of thick-walled capillary tubing on a hot plate. (A tube 7 mm. in diameter with a 1·5 mm. hole is a suitable size. A suitable hot plate is one having 1 kW. rating and a flat metal top 8 in. in diameter. The temperature of the hot plate was probably between 500° and 600° C., which is well below the 'strain-point' of 'Pyrex'. Heating the glass essentially from one side seems to promote spiral fracture.) A rubber blow-tube is slipped over the cool end of the glass tube, and then, while blowing air through the glass tube to keep water out of the capillary, one plunges the hot glass endwise into a bucket of water. The spiral fracture shown in the photograph results.

It was noticed that quenching from a high temperature gives rise