for many solid–solid phase transitions could be extended to much lower temperatures than would be possible if no shear stresses were present. Since densification is a structural change, the results of this study are in concordance with these conclusions.

Inherent in the above explanation is the question of whether there is a true metastable equilibrium structure for the glass at any given temperature and pressure. The most important criterion of equilibrium is reversibility. In order to prove that there is indeed a metastable equilibrium volume for glass which is a function of pressure, it must be shown that the purported metastable equilibrium density can be approached by glasses whose densities are respectively greater and less than the purported equilibrium density. This reversibility was demonstrated for the $Na_2O.Al_2O_3.4SiO_2$ glass but not for SiO_2 glass. Apparently the activation energy necessary to cause densified samples of SiO_2 glass to revert to a less dense phase is greater than the thermal energy available at 600° C.

The work of Douglas & Jones(20) and Douglas & Isard(21) strongly supported the view that at a given temperature at atmospheric pressure a glass structure does approach a true metastable equilibrium and the data from the present study (Figures 1–6) firmly suggest that this conclusion can be extended to include the pressure variable.

Structural aspects of densification

Figure 8 and the data of Cohen & Roy(17) show that the relationship between the index of refraction and the density of progressively densified silica glass, alkali silicate glasses, and the sodium aluminosilicate glasses which were studied is virtually linear. The molar refraction for the densified phases was calculated, and as expected from the linear relationship between the index of refraction and density, the molar refraction remains almost constant. Dachille & Roy(22) have shown that a change in the primary co-ordination number of the silicon ions would require a change of 10–15% in the molar refractivity, whereas the largest change observed was 3·5% for silica glass and less for the other glasses. It is interesting to note that the molar refractivities of the normal silica glass (density, 2·203 g/cm^3) and the most dense silica glass (2·624 g/cm^3) are equal to the respective molar refractivities of cristobalite and α-quartz. This calculation indicates that densification involves a change in the packing of tetrahedra rather than a major structural rearrangement of the first co-ordination sphere of the ions.

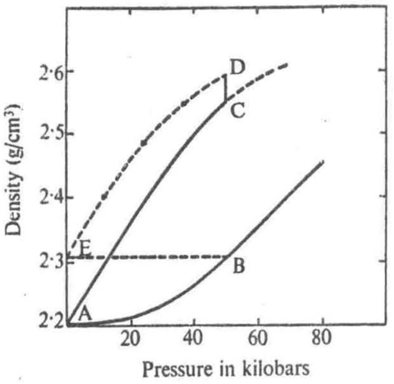

Figure 13. ***The relationship between the densification and compressibility of glass (Previously published(5))***

A significant feature of the data on the densification of glass is that each glass composition which was studied apparently attained a maximum density. Attempts to densify a glass beyond this maximum density by increasing the temperature and pressure either proved abortive or resulted in the devitrification of the glass. This maximum density strongly suggested a special structural significance. The maximum density phase for silica glass was attained near the pressure and temperature limits of the apparatus; however, the maximum density phases for all other glasses were attained well below this limit. The silica glass, which is difficult to devitrify when 'dry' (preheated to 800° C for half an hour and desiccated prior to being subjected to pressure), would invariably begin to devitrify at 650° C (within two to three minutes) at pressures which cause the glass to attain its apparent maximum density; it appears therefore that the attainment of a maximum density for the silica glass is structurally significant.

Lacy(23) pointed out some interesting relationships in the atomic packing in silicate glasses. On the assumption that the region of influence of each ion is spherical and by using values of the ionic radii found in crystalline substances, he was able to calculate approximately the fraction of the molar volume which the ions in a glass occupied. It was shown that 43% of the total space in silica glass is occupied, which is considerably less than that theoretically possible for spheres of uniform size (74%). It was also pointed out that the closest overall packing that has been found is 52% for lithium metasilicate glass.

The fraction of the molar volume which the ions occupy in the progressively densified glasses studied was calculated using Goldschmidt's values of ionic radii and the measured densities of the densified glasses. The results of the calculations for silica glass, the alkali silicate glasses, and the sodium aluminosilicate glasses studied are shown in Figures 14 and 15. In Table 4 the per cent molar volume occupied by the ions in a given glass before it was subjected to pressure is compared to the value for the most dense glass which can be produced. It is seen from Figures 14 and 15 that the value of per cent molar volume occupied by the ions tends toward an asymptotic maximum as the

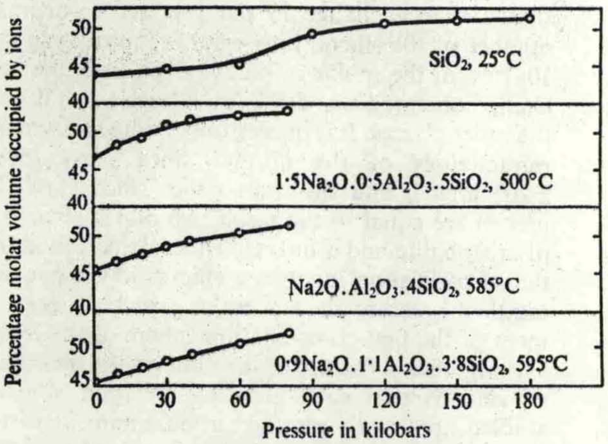

Figure 14. *The pressure dependence of the per cent molar volume occupied by the ions for SiO_2 glass and glasses in the series $(2-X)Na_2O.XAl_2O_3.(6-2X)SiO_2$*

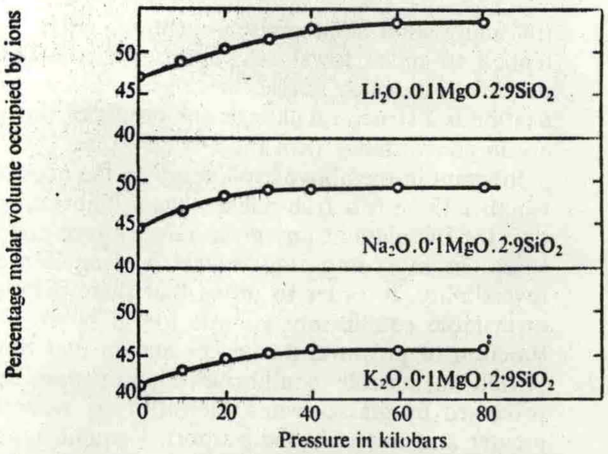

Figure 15. *The pressure dependence at 500° C of the per cent molar volume occupied by the ions for glasses in the series $R_2O.0{\cdot}1MgO.2{\cdot}9SiO_2(R=Li, Na, K)$*

glasses are progressively densified. It is also seen from Table 4 that the value for the most dense glasses is approximately 52% in most cases, irrespective of the value for the starting glasses. The notable exception is the potassium silicate glass. There is an interesting coincidence between this maximum figure of 52% with the figure of 52% for lithium metasilicate glass quoted by Lacy(19) as the highest packing found in any glass investigated. Indeed, attempts to densify a lithium metasilicate glass were unsuccessful.

As the density of silica may be increased by 20%, it is somewhat surprising to realise that the most dense phase of silica glass has a very open structure; in fact, it is just as spacious as α-quartz, for its density is nearly the same. Why, then, is it not possible to produce a denser glass phase? Before attempting to answer this, it is necessary to review some experiments and proposals made by Bernal.(24)

Bernal proposed a theory of the structure of simple monoatomic liquids based on a geometrical approach. He has recently given a more complete discourse on his theory,* but the substance of this has not been published. The portion of Professor Bernal's discourse which is of most interest to this paper is his description of an experiment he made to determine how closely similar sized spheres could be irregularly packed. This was determined by filling a container with steel balls and shaking the container until the balls no longer rattled, i.e. had achieved the closest possible irregular packing. The volume which the balls occupied could be measured; hence the packing density could be calculated. The balls could occupy approximately 68% of the total volume compared to 74% for cubic closest packing of the same size spheres.

The fact that irregularly closest packed balls of the same size can fill up 68% of the available volume shows that the structure of even the most dense silica glass does not correspond to an irregular closest packed oxygen network.

It is now possible to return to the question: Why is it not possible to produce denser glass phases than found in this study? If the answer is related to a geometrical limitation of the packing of ions in the glass, the structure of the maximum density phases must consist, to a first approximation, of irregularly oriented close packed or closest packed structural units. The obvious structural unit to consider in silicate glasses is the SiO_4 tetrahedron. The Si–O bond is several times stronger than the alkali– or alkaline earth–oxygen bonds, and it is not unreasonable to suggest that the Si–O tetrahedra will remain inviolate. To test this idea an experiment along similar lines to the experiment of Professor Bernal was performed. A large number of ¼-in dia. plastic balls (6000) were glued together to form 1500 individual tetrahedra. The tetrahedra were placed in

Table 4. *The per cent molar volume occupied by the ions*

Composition	*% Volume occupied before densification*	*% Volume occupied for maximum density phase*
SiO_2	44	52
GeO_2	42	49
$Li_2O.0{\cdot}1MgO.2{\cdot}9SiO_2$	47	52
$Na_2O.0{\cdot}1MgO.2{\cdot}9SiO_2$	44	50
$K_2O.0{\cdot}1MgO.2{\cdot}9SiO_2$	41	46
$1{\cdot}5Na_2O.0{\cdot}5Al_2O_3.5SiO_2$	46	52
$Na_2O.Al_2O_3.4SiO_2$	46	52
$0{\cdot}9Na_2O.1{\cdot}1Al_2O_3.3{\cdot}8SiO_2$	46	52
$1{\cdot}2Li_2O.SiO_2$	52	52
$LiRb(PO_3)_2$	50	50
$Li_2Rb_2(P_2O_7)$	50	50
$NaPO_3$	51	51

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*Symposium on Crystal Synthesis and Structure in Solid State Research, State College, Pennsylvania, 27–28 April 1962.