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THE STRUCTURE OF AMORPHOUS SOLIDS - A PERSPECTIVE VIEW

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Resumé - On passe en revue des données sur la structure d'un certain nombre de solides amorphes représentatifs - métaux purs et semiconducteurs, alliages amorphes et verres d'oxydes - et on se propose de suggérer quels sont les modèles les plus adéquats. Historiquement, les empilements denses aléatoires ou les réseaux aléatoires ont été considérés comme les modèles les mieux adaptés, surtout pour les solides amorphes de composition chimique simple - métaux purs et semiconducteurs, oxydes stoechiométriques. Pour des matériaux plus complexes, différentes informations indiquent que les modèles aléatoires ne sont viables qu'au prix de certaines complications comme par exemple, l'existence d'un ordre chimique, l'existence d'unités structurales locales ou peut être à moyenne distance. On discute l'exemple particulier des verres de métasilicates alcalins et on montre qu'il est difficile de construire un modèle aléatoire avec les contraintes idoines qui rende compte de l'ensemble des résultats expérimentaux - polyèdres de coordination définis aussi bien pour les cations alcalins que pour les atomes de silicium, tendance à la formation de chaînes d'unités SiO_3^- , densité mesurée et en même temps fonctions de distribution de paires expérimentales. La question se pose alors de savoir si les modèles, basés sur des empilements périodiques ou non et dont l'ordre est brisé par des défauts, ne seraient pas plus appropriés. On suggère une stratégie pour répondre à cette question.

Abstract - Structural data for a number of typical amorphous solids - elemental metals and semiconductors, amorphous alloys and oxide glasses - are surveyed and an attempt made to suggest the most appropriate models. Historically, random close-packed structures or random networks have been considered to be the most appropriate, especially for chemically simple amorphous solids - elemental metals and semiconductors, stoichiometric oxides. For more complex materials, there are a number of indications that random models are only tenable with some qualification - to allow chemical ordering, local and perhaps medium-range structural units, for instance. The particular example of alkali metasilicate glasses is discussed and it is shown that it is difficult to devise a suitably constrained random model which incorporates all the known experimental facts - defined coordination polyhedra for the alkali cations as well as the silicon atoms, a preference for SiO_3^- units connected in chains, the measured density, as well as the experimental pair distribution functions. Questions are therefore raised: do random models represent the most general paradigm for the structure of amorphous materials, or are defective ordered models based on periodic or aperiodic packing more appropriate? An attempt is made to suggest a strategy to answer such questions.

I - INTRODUCTION

The invitation to present the opening talk of the third conference on the Structure of Non-Crystalline Materials represents a great honour, for which I am grateful. There are definite responsibilities involved in giving an introductory lecture, however: a requirement to maintain a degree of balance and to give a statesmanlike account of the several positions occupied by the proponents of various 'theories' of the structure of glasses. Secondly, a need to extract a coherent view of the results of a number of structural techniques and, thirdly, to present an account which allows each of us working over a wide range of material types to feel that his/her contribution may be included in an overall scheme of structural organisation. For these reasons I include both the backwards look and an attempt to see over the parapet a little way into the future - in what I describe as a perspective view - trying to picture reality in all its dimensions - not necessarily three, as we shall see later in the conference.

To begin with a digression. In 1974, when the first conference in this series was being planned under the auspices of the Society of Glass Technology one felt that 'our approach to an understanding of the structure of these solids is evolving more rapidly now than at any earlier period in the history of the subject' /1/. In fact evolution was so rapid that one wondered whether the structure of glasses might be solved before the conference was held in 1976. There was no need to worry: whole new families of glasses have been developed or extended since then. The subject has continued to grow at such a rate that fragmentation is now a more worrying feature: three international conferences in the space of five weeks, glassy metals, amorphous semiconductors, halide glasses have largely gone their separate ways. The frequency of this meeting has been doubled and the large number of papers offered to the conference represents an eloquent testimony to the interest in the subject.

What are the reasons for this interest? Firstly, the materials we study are important with new industries evolving and old industries relishing in a history reaching back to the dawn of civilization. Secondly, the subject encapsulates a crucial, largely unsolved mystery. Thirdly, the answer to the mystery lies at the heart of any understanding of the nature of the transformations between liquids, glasses and crystals.

II - APPROACHES TO THE STRUCTURE OF GLASSES (AND AMORPHOUS SOLIDS)

Initially, we limit discussion to glasses quenched from the melt, rather than from the vapour. (It is not a serious restriction since ultrarapid quenching by Q-switched laser techniques allows a-Si to be produced from the melt whereas it had hitherto been prepared by vacuum deposition). With this restriction, we are forced to recognize the centrality of the glass transition between the supercooled liquid and glassy states. The importance of Turnbull's criteria /2/ relating to the avoidance of crystallization, developed further by Davies /3/ and Uhlmann /4/, becomes evident. Moreover, the apparently continuous, homogeneous nature of the transformation between the super-cooled liquid and glassy states suggests a need to relate the structure of the glass at room temperature to a series of liquid state structures and, by implication, a similarity between the structures of glasses and liquids.

This then leads naturally to our first concepts of the structure of glasses as being a disordered arrangement of atoms - in accord with the simplest views of liquids - but with the possibility of interatomic bonding at local level leading to networks which may have a high viscosity or a large temperature coefficient ($-\partial\eta/\partial T$) leading to inhibition of nucleation.

In simple stoichiometric glasses like SiO_2 , the concept of the (continuous) random network /5/ seems the most appropriate realization of these notions. For less open structures - the alkali silicates, for example - alkali ions are inserted into suitable spaces in the network with local charge neutrality maintained by 'non-bridging' singly-charged oxygen ions.

In close-packed systems such as the metallic alloys, a similar conceptual rationalization is possible: close-packing of metal atoms leads to local tetrahedral ordering - as opposed to tetrahedral-octahedral ordering in cubic close packing and the view of the random close-packed structure, associated with ideas exposed by Bernal /6/, emerges as the model for liquid and glassy monoatomic metals. Binary, ternary alloys etc are accommodated either by 'stuffing' the additional components in interstitial cavities, as in the model proposed by Polk /7/, or as random mixtures of the two elements.

Disorder or randomness appears in another guise in that it is assumed that the structure corresponds not only to the mean chemical composition but also includes fluctuations around that mean. A particular example - a glass of disilicate composition might therefore be represented by a network containing disilicate groups $\equiv\text{Si}-\text{O}^-$ with one non-bridging oxygen ion (NBO) and significant fractions of Si atoms with two or more NBO's, and those with none (fig. 1).

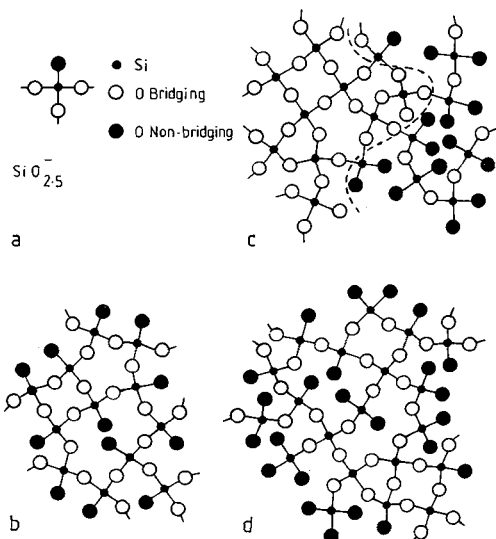


Fig. 1 - Schematic representation of 'chemical' and 'compositional' order in a glass of disilicate composition. a) The disilicate anion with 3 bridging oxygens (Q_3 in NMR terminology). b) A positionally-disordered but compositionally-ordered network. Positionally and compositionally-disordered networks are shown in c) and d): c) shows segregated Q^4 and Q^2 regions whereas d) represents a random mixture of Q^4 - Q^1 anions.

These two viewpoints thus lead to the notion of disordered positional and compositional correlations as expressed, for instance, in the separate Bhatia-Thornton structure factors /8/ or, what is easier to visualize, the fourier transform - the reduced radial compositional and positional correlation functions /9/.

In any logical development of the subject, this simple - simplistic, even - set of concepts, represents the correct starting point: Occam's razor, after all - explanatory principles should not be needlessly multiplied. Certainly, for simple glasses, the successes of the random models are based ultimately on observation not dogma - the ideas do represent and explain a large proportion of experimental findings. As the subject has evolved however, an increasing number of facts have emerged which fit into the existing framework only after modification and refinement and even then uncomfortably. It is perhaps time to review the situation at least, and present the alternatives for examination and to suggest a strategy for further progress.

In the following section, I set out a series of experimental facts representing an attempt to encapsulate within the confines of limited space (and more importantly, limited vision) a perspective view of the structural knowledge of certain amorphous metals, glassy oxides, and amorphous semiconductors. Chalcogenides are omitted

deliberately and the important investigations of Phillips, Boolchand and others are described, by the latter, elsewhere in this volume.

III - THE EXTENT OF ORDER IN SELECTED AMORPHOUS SOLIDS

III.1 Elemental amorphous tetrahedral semiconductors One of the more important characteristics of this group of materials is the availability of good experimental radial distribution functions - derived from X-ray /10/,/11/ and neutron /12/ structure factors in the case of a-Ge. This latter material has been extensively investigated and several CRN models, and some amorphous cluster models have been devised. Perhaps the fairest summary of the situation has been given by Etherington et al. /12/ who compared experimental data with predicted rdfs for most models and concluded that no model adequately reproduces experimental data to within experimental accuracy. Nonetheless CRN models are usually regarded as giving the most informative representation of structural properties and they also provide a successful basis for the calculation of electronic properties and vibrational spectra. A recent addition to the literature is the computer-generated model reported by Wooten, Winer and Weaire /13/ in which a periodic 216-atom cell with the diamond cubic structure is modified by interchanging atoms followed by some relaxation (with changes in topology allowed). The process is stopped when the fit to the experimental rdf is judged to be satisfactory. The fit obtained is good but as yet only a limited description has been given of the details of the more successful structures: the presence of 7-fold rings appears to be a crucial ingredient.

It is also worth noting that no adequate model exists for a-C. Indeed the relative importance of trigonally- and tetrahedrally-bonded carbon has yet to be unambiguously established. One of the major obstacles to progress is the variability of the structure of a-C as a function of preparation conditions - the 'ideal' amorphous state of this system has yet to be established.

III.2 Elemental amorphous metals Data exists for amorphous Fe, Co and Cr /14/ prepared by condensation on He-cooled substrates and examined below their crystallization temperatures (~ 100 K). A more recent study has been made by Lauriat /15/ of the structure of a-Fe prepared by decomposition of $\text{Fe}(\text{CO})_5$. The resulting powder has some carbon-containing impurities - it is suggested that less than 1% carbon is contained in the bulk a-Fe, the remainder (~ 7%) being a surface impurity. The X-ray and neutron-derived pair functions are essentially identical and the peaks are consistent with a polytetrahedral structure (fig. 2). Note in particular the absence of a $\sqrt{2}$ distance which would correspond to the diagonal of an octahedron.

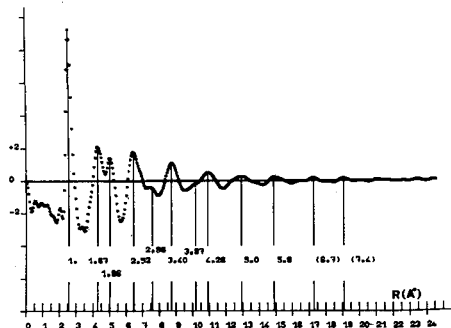


Fig. 2 - X-ray rdf for a-Fe after Lauriat /15/.

III.3 Stoichiometric oxides Excellent experimental data exists for SiO_2 both from X-ray, neutron scattering and indirect techniques. As with the amorphous elemental semiconductors, the local structure has been established beyond dispute (except that the oxygen bond angle distribution is still controversial) but it is still not possible to establish details of the medium-range structure. Thus while CRN models

can be shown to give an adequate representation of experimental data, none are exact and the differences do not allow preferred ring statistics etc to be established. Amorphous cluster models are about equally successful. In 1982 it was possible to write '... our knowledge of the structure of vitreous silica, a material first studied extensively over 50 years ago, is essentially incomplete.' /16/.

For B_2O_3 , the weight of evidence has shifted so that it now seems that the local structure contains a high proportion of boroxol rings - as originally suggested on the basis of I.R and Raman data by Krogh-Moe /17/. Apart from several modelling studies /18/, the ^{11}B NMR data of Jellison et al /19/ indicates the presence of two different oxygen sites which are consistent with bridging oxygens within the boroxol ring and to external BO_3 triangles. (There might be some discussion over the extent to which the boroxol ring represents local or medium-range ordering.)

In amorphous alumina, like a-C, questions arise over the coordination state of Al - tetrahedral or octahedral or a mixture. EXAFS and EELS near edge studies yield the Al-O bond length from which the relative proportion of 4- and 6-coordinated Al can be estimated /20/.

III.4 Binary amorphous alloys The extent of positional and compositional order in these materials appears to be very variable. For many alloys Bhatia-Thornton partial structure factors have been obtained and indicate chemical ordering of the atomic species - for others the ordering is relatively insignificant. Positional order may be diagnosed in an approximate manner by measuring the breadth, ΔQ , of the first diffraction peak and, as with line-broadening in crystals, an effective correlation length $\xi = 2\pi/\Delta Q$ may be obtained. Values range from about 8 Å in the liquid to 12 Å in glassy $Ni_{81}B_{19}$ /21/ (which, as shown below, appears to be well-ordered on the basis of partial structure factors) to about 18 Å for several magnesium-based alloys (Mg-Cu, MgNi and MgCa). In some alloys of this type, an effective "ordering potential" can be calculated /22/, and this is particularly important as the degree of chemical order can then be quantified.

Accurate partials are available for the transition metal-metalloid glasses and the greater information content of these data allows more refined interpretation. Broadly the evidence available from neutron scattering and NMR data indicates almost complete chemical ordering: B is surrounded preferentially by Ni in a- $Ni_{81}B_{19}$ with a first neighbour shell of 9 atoms and approximately trigonal prismatic coordination (6 at the vertices and a further 3 atoms capping square faces)/23/.

Elsewhere, I have argued that this apparently secure experimental fact - a well-defined local structure for the metalloid presents considerable difficulties /24/. It has not yet been established that there are any cogent reasons for the stability of an individual trigonal prismatic unit - on chemical grounds (i.e. strong directional bonding as in oxides) or from space-filling considerations (using a central force field). The most plausible reason for this particular local structural arrangement may be that it is a part of a much larger organizational scheme which extends to 10 Å at least and thus can be considered to be a medium-range structural effect. Briefly, the argument is that for a well-defined trigonal prism to exist at all in the 'normal' glass-forming range, it is necessary to organise 9 nearest-neighbour metal atoms which are themselves constituents of other capped prisms so that the possible arrangement of neighbouring prisms also becomes constrained. These then constrain their neighbours and so on - fig. 3. Thus in structures based either on periodic (crystallographic) or aperiodic (non-crystallographic) medium-range ordering, a definite local structure emerges: for example, the octahedral environment of Na in NaCl is a result of a (periodic) long-range packing of atoms rather than particular short-range, directional, forces. (This argument is relevant in the next section: the Na-O shell in alkali silicates appears to be ordered - and this may also be the result of a medium-range organizational scheme - it cannot arise from directional Na-O bonds!)

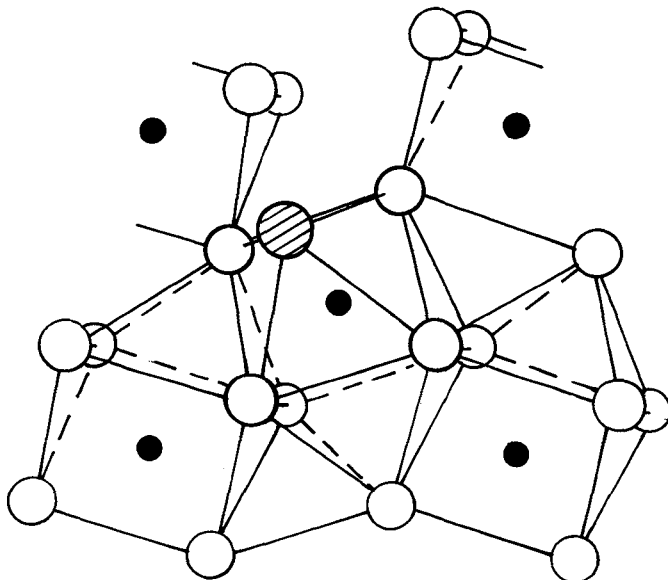


Fig. 3 - A trigonal prismatic unit consisting of 9 metal atoms (large circles) surrounding a metalloids (small filled circles) must be extensively connected to other prisms by edge and vertex-sharing in typical metallic glasses with about 20 at. % of the metalloids. If the neighbouring trigonal prisms are packed efficiently, only tetrahedral and half octahedral interstices exist. The possible positions of neighbouring local structural units are severely constrained - as the sheet of prisms indicates. Note that a similar sheet of prism exists above and below the plane linked by capping atoms such as the one shaded. The result is that for a well-defined trigonal prism to exist at all, the medium-range structure is also defined within relatively narrow limits.

This essentially speculative argument is (more securely) supported by the oscillations in the B-B partial pair distribution function (representing the correlations between the centres of trigonal prismatic clusters) which extend to at least 12 Å. This and other experimental data, and the fact that a random sphere packing model of Lamparter et al. /21/ does not reproduce that data, have prompted the examination by Dubois, Gaskell and Le Cœur of a domain model for TM-M alloys based on packed domains of positionally-correlated atoms with carefully prescribed interfacial structures /25/. Briefly the argument is that an acceptable ideal structure should be based on local structural principles which are maintained for all atoms - even in the boundaries between domains. The results of this model are in good agreement with experiment.

Another successful model is the, ostensibly random, molecular dynamics simulation of Beyer and Hoheisel /26/. Experimental rdfs are well represented - what is not so clear is what the final structure looks like. A preliminary examination (J.-M. Dubois and the author) suggests that trigonal prisms exist but with no evidence as yet of a discernable medium-range order /24/.

III.5 Alkali silicate glasses A random model for these glasses suggests the following characteristics.

- a) Positional disorder - absence of geometrically-ordered medium-range units but with the possibility of local organization as in other glasses.
- b) Random spatial arrangement of the two species - in particular, a statistical

distribution of alkali cations.

c) Chemical disorder - especially the presence of a variety of anionic groups. Recent evidence has thrown some light on the assumptions which underly these characteristics.

III.5.1 The local structure of network-modifying ions In common parlance, the silicon-oxygen groups form 1-, 2- or 3-dimensional networks, depending on composition, and the other atoms 'modify' the connectivity by breaks in the chain of Si-O-Si bonds. The Si-O bond is often regarded as the strongest interaction - largely covalent, perhaps - whereas the modifier, M-O link is considered to be weak - often ionic. The silicon environment is, in fact, found to be largely undistorted but the environment of many modifier atoms has remained a matter for speculation until recently. EXAFS and neutron-scattering (with isotopic substitution) now allows a much less ambiguous interpretation of the experimental data.

The results are interesting. Greaves et al /27/ have shown that the environment of Na in $\text{Na}_2\text{Si}_2\text{O}_5$ glass is relatively well-defined with a coordination number of 5 as in the disilicate crystal. Examination of the Ca edges of a number of glasses and crystals again shows a quantitative similarity between the distributions for crystals and glasses - even with subsidiary shoulders on the first peak - equivalent to those in crystals. The coordination number is 7 and the static breadth only a little larger than that of the crystal. The X-ray absorption near edge structure (XANES) of Ca-containing glasses reported by Geere et al /28/ shows that the symmetry of the first-neighbour shell is largely insensitive to the concentration and to the occurrence of phase-separation.

More recent studies of the environment of Ti in $\text{K}_2\text{O} \cdot \text{TiO}_2 \cdot 2\text{SiO}_2$ glasses have been reported by Yarker et al /29/ using a combination of neutron scattering (with isotopic substitution of Ti) EXAFS and XANES. The results confirm 5-fold coordination for Ti with a well-defined environment. The Ti-O peak has two components at 1.65 and 1.96 Å with weights 0.75 and 4.1 and with breadths given by $\sigma = 0.006$ Å and 0.102 Å respectively. The environment of Ti is thus extremely well-defined - σ values have been corrected for termination broadening - an equivalent figure for the Si-O first peak is $\sigma = 0.05$ Å). There is evidence for a square planar configuration of oxygen atoms with one short bond perpendicular to the plane, similar to the local organization observed in $\text{c-Na}_2\text{TiSiO}_5$.

III.5.2 Spatial distribution of modifier atoms In a number of glasses, the modifier atoms appear to be randomly distributed. There are also a number of cases where direct and indirect methods suggest some degree of clustering. The most recent result by a direct method is contained by the work of Yarker et al /29/ on $\text{a-K}_2\text{O} \cdot \text{TiO}_2 \cdot 2\text{SiO}_2$. By using a double difference method the Ti-Ti distribution can be obtained and, although inevitably noisy, a first-neighbour Ti-Ti peak is observed at 3.4 Å (fig. 4).

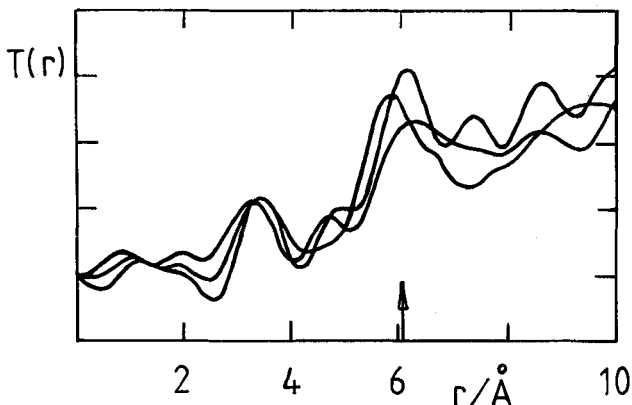


Fig. 4 - Three different estimates of the Ti-Ti distribution, $T(r)$, for vitreous $\text{K}_2\text{O} \cdot \text{TiO}_2 \cdot 2\text{SiO}_2$ (after Yarker et al /29/). Note the position of the first peak at about 3.4 Å suggesting Ti-Ti clustering at smaller distances than the mean value calculated for a spatially random distribution, shown by an arrow at 6.1 Å.

Calculations (by this author) suggest that a purely random distribution of Tl atoms in a glass of this composition and density would lead to a mean Ti-Ti distance of 6.1 Å (which corresponds to the position of a second Ti-Ti peak in the experimental data). This result is consistent with early X-ray work by Milberg and Peters /30/ who observed a composition-independent peak at 3.8 - 3.9 Å in thallium-silicate glasses which they ascribe to Tl-Tl pairs clustering at a preferred distance. Later work on Tl-containing glass confirmed the presence of a defined environment for the Tl⁺ ion. Panek and Bray /31/ have used ²⁰⁵Tl NMR to show Tl-Tl pairing even in Tl-dilute glasses. Recent EPR data of Kawazoe and Takagi /32/ gave evidence for the presence of two types of Tl⁺ site, the proportions of each being composition-dependent. These investigations are important since it is considered that Tl can probe the alkali sites in glasses which are otherwise difficult to examine.

III.5.3 Variability in anion type The extent of chemical ordering in silicates is a matter of some debate. Recent Magic Angle ²⁹Si NMR results on glassy sodium silicates /33/ suggests that at stoichiometric compositions - SiO₂, Na₂Si₂O₅, Na₂SiO₃ - only one Si site is observable (fig. 5). Intermediate composition can be represented by a composition-dependent weighted sum of contributions ascribed to Si atoms with 4,3 or 2 bridging oxygens (Q₄, Q₃, Q₂ atoms). The individual species exist only within appropriate ranges: thus for compositions between SiO₂ and Na₂SiO₅, only the Q₄ and Q₃ species are observed and Q₃ and Q₂ from disilicate to metasilicate compositions.

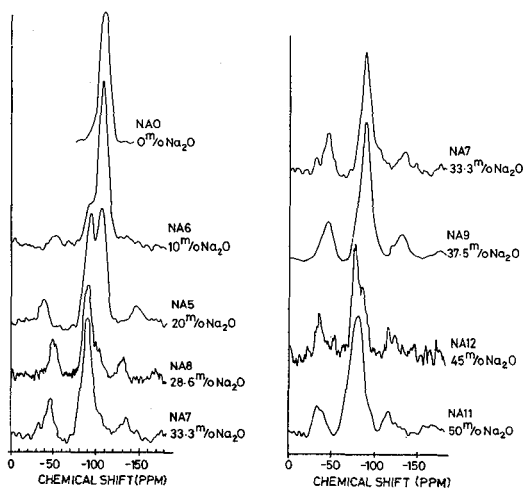


Fig. 5 - ²⁹Si spectra obtained by Magic Angle NMR for a series of sodium silicate glasses:

- a) 0-33 mol % Na₂O;
- b) 33-50 mol % Na₂O after Dupree et al /33/.

This evidence implies a degree of chemical ordering in the glass - a result which is not anticipated from the usual pictures of the Zachariasen random network and is at variance with the 'complex anion' models proposed by a number of authors /34/.

III.5.4 Constrained randomness in a model for alkali silicates The discussion above has indicated that random models for alkali silicates may need to incorporate additional constraints associated with the packing pattern of atoms which produce an identifiable M⁺ environment. Furthermore, the nature of the anionic species may be more closely defined and related to the species present in the crystal than had been imagined previously.

In an attempt to see whether randomness, packing and chemical constraints may be mutually consistent, a model for the alkali metasilicates has been constructed. The starting point is a further constraint on possible models: the density of the glass and crystal are found to agree to about 5% - the glass having the lower density.

This fact suggests that the packing of oxygen atoms is similar in the amorphous and crystalline metasilicate phases. In $c\text{-Li}_2\text{SiO}_3$, /35/ the oxygen sublattice is a dilated hcp structure with Si and Li atoms occupying half of the tetrahedral interstices and Si-O, Li-O chains running parallel to the hexad axis - each Si-O-Si chain being surrounded by six Li-O-Li chains (fig. 6). In a model for the glass, the hcp oxygen sub-lattice is retained but the choice of tetrahedral interstices is more random. It cannot be completely random since chains must predominate to be consistent with the ^{29}Si NMR data, hence constraints are built in to preserve two-fold connectivity where possible (three-fold connectivity is excluded). Further, each Si-O chain is surrounded by six Li-O chains as in the crystal. Finally, the ratio of Si and Li atoms is controlled: the type of atom is selected by a random number generator, sites being chosen in order, working from the bottom of the model along each {001} plane and then to the next plane above. Where a Si atom is selected but cannot be placed in a given location (to preserve Si-Si avoidance, say) it is then stored and placed in the next available site.

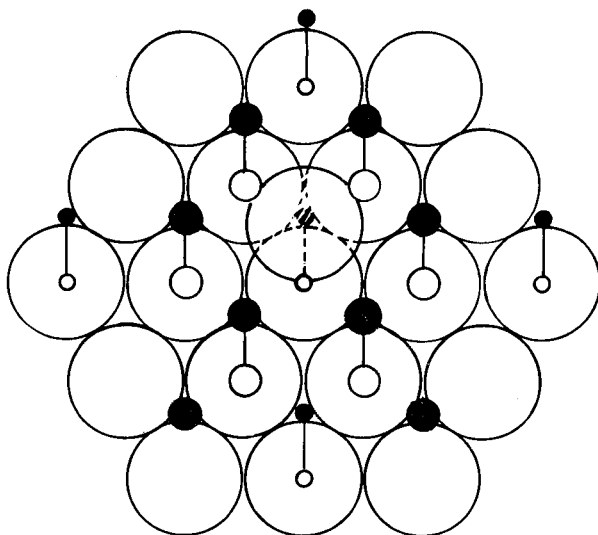


Fig. 6 - The hexagonally close packed oxygen sub-lattice corresponding to an idealised metasilicate structure. Silicon atoms are shown by the small circles occupying tetrahedral interstices (at two levels) forming chains running parallel to the hexad axis. Each Si-O chain is surrounded by six parallel Li-O chains (medium-sized circles).

-avoiding random Si-O and Li-O chains. Inevitably Si-O chains terminate and new ones must therefore originate. A majority of Si atoms however have the Q^2 configuration. The model is then relaxed using a modified Keating potential with stretching, V_s , and bending terms V_b :

$$V = \sum_i V_s + \sum_j V_b \quad V_s = \frac{3}{16} \frac{\alpha}{d^2} \sum_{l,i} (r_{li} \cdot r_{li} - d^2)^2$$

$$V_b = \frac{3}{8} \frac{\beta}{d^2} \sum_{\substack{l\{i,i'\} \\ i \neq i'}} (r_{li} \cdot r_{li'} - d^2 \cos^2\theta)^2$$

The sum is over the i stretching and j bending coordinates; α and β are stretching and bending force constants, r_{li} is the vector connecting atoms l and i , d and θ are the equilibrium bond length and bond angle respectively. Some sophistication is introduced into the choice of the Si-O parameters d and θ by taking different values corresponding to bridging and non-bridging bonds. Polyhedra centred on the metal atom are treated similarly with distances to four equivalent oxygens having the same bond length with a larger value for a fifth atom. Interactions between non-bridging oxygen atoms are also modelled by a Keating stretching term.

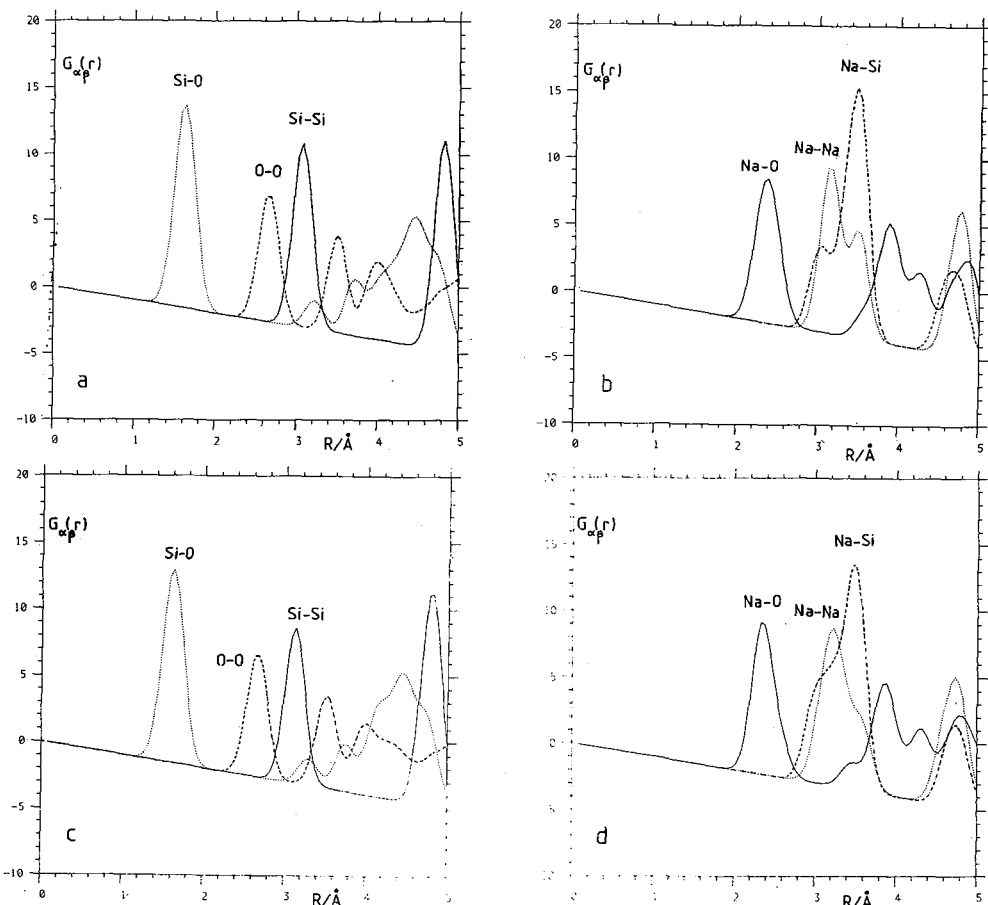


Fig. 7 - a), b) Experimental partial pair distribution functions, ppdfs, for $c\text{-Na}_2\text{SiO}_3$. c), d) Computed ppdfs for a model of $c\text{-Na}_2\text{SiO}_3$ obtained by energy-minimization of a starting structure based on the hcp lattice shown in fig. 5. Parameters in the Keating potential energy function were varied to produce the quality of fit shown here.

Choice of accurate parameters α , β etc is vital for success and to ensure consistency with the crystalline structure, at least, an hcp oxygen sublattice was 'stuffed' with an ordered array of Si, Li (Na) atoms and the resulting crystal structure relaxed and compared with X-ray data for $c\text{-Li}_2\text{SiO}_3$ and Na_2SiO_3 . Constants were then adjusted to give an optimal fit. This by no means guarantees that the constants are appropriate even to a crystalline material of different symmetry, still less to a glass but it is difficult to see how a better choice can be made. Experimental and calculated partial pair distribution functions for crystalline Na_2SiO_3 are shown in fig. 7.

With this choice of parameters for the interatomic potential, partial distribution functions have been calculated for the random model and are given in fig. 8. Experimental partial distribution functions are not yet available and the total X-ray interference function (fig. 9) provides a relatively insensitive test. However, the density, ρ , is known accurately and values of the volume per oxygen atom, V_{O} , obtained from ρ , are plotted in fig. 10 as a function of the non-bridging oxygen stretch parameter ($\alpha_{\text{O-O}}$) in the potential energy function (this is the quantity over which there is most doubt).

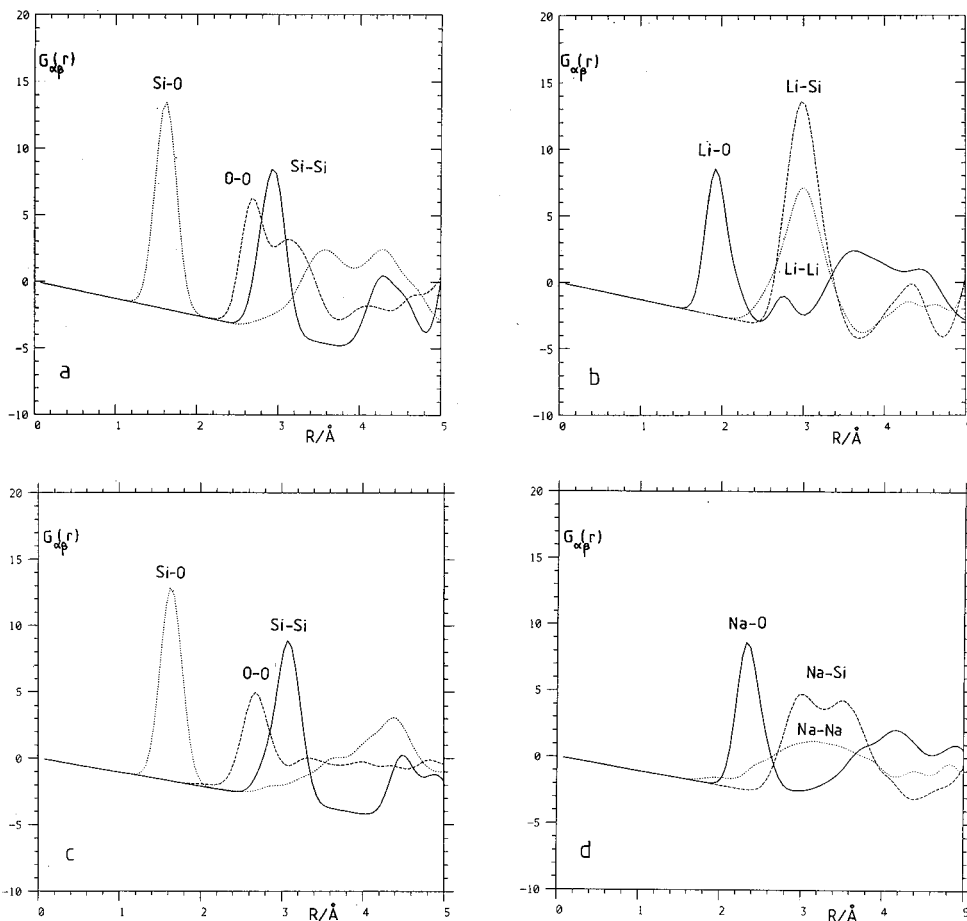


Fig. 8 - Computed ppdfs for random chain models of a), b) vitreous Li_2SiO_3 c), d) Na_2SiO_3 . Parameters in the potential energy function are identical to those used in calculating the ppdfs for the crystalline silicates.

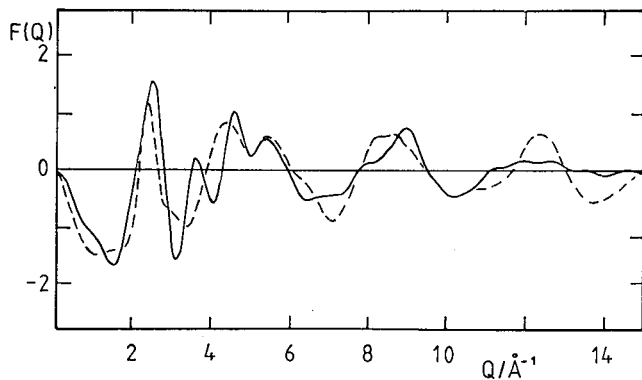


Fig. 9 - Calculated total reduced X-ray interference function, $F(Q)$ for the random chain model of $\alpha\text{-Na}_2\text{SiO}_3$ (full line) compared with the experimental data of Yasui et al /36/.

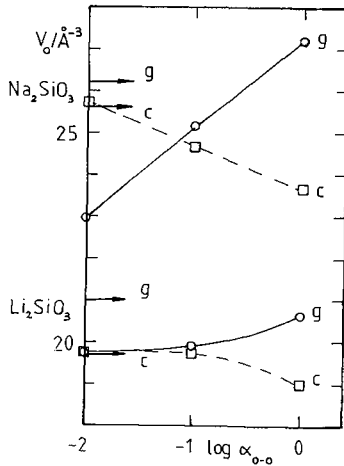


Fig. 10 - Volume per oxygen atom, V_O , computed for crystalline (c) and glassy (g) models for Li_2SiO_3 and Na_2SiO_3 as a function of the non-bridging O-O stretching constant α_{O-O} in the Keating potential energy function. For values of α_{O-O} which produce good agreement with experimental data (arrows), the computed value for V_O for the glass are seriously in error.

For values of α_{O-O} which produce good agreement between experimental and calculated V_O values for c- Li_2SiO_3 and c- Na_2SiO_3 , the best agreement with the corresponding partial pair distribution functions and the lowest strain energy, the values calculated for V_O for the random model do not agree with experimental data for the glass. The extent of disagreement is relatively large; for Na_2SiO_3 the experimental value of V_O is 26.2 \AA^{-3} whereas the value of V_O obtained from the model is 23.0 \AA^{-3} , an error of about 13%. For Li_2SiO_3 , $V_O(\text{exp}) \approx 21 \text{ \AA}^{-3}$, the calculated value of $V_O = 19.6 \text{ \AA}^{-3}$ an error of about 8%. Note that in both cases the calculated value of V_O is smaller than the experimental data (the density is higher). The density is also equal to or higher than that of the crystalline form.

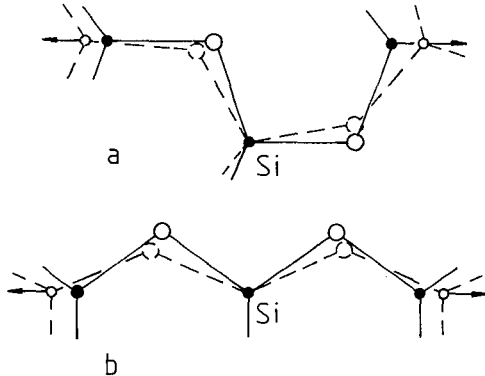


Fig. 11 - a) Expansion of Si-Si distances parallel to the hexad axis is easy: bending at the oxygen atom (large circles) only is required and this force constant is small. Cooperative rotation of the silicon oxygen tetrahedron is possible so that the stiffer Si bond angle is not distorted. b) Where the chain runs in a direction normal to the hexad axis, in a random model, cooperative motion is no longer possible and bending of the (stiffer) Si angle becomes necessary to allow elongation.

The reason for the errors in the calculated values of ρ or V_O are easily established and may be related to the degree of randomness as characterized by the degree of convolution of the silicate chain - measured, perhaps, by a fractal dimension. In a crystalline metasilicate the volume is determined by the unit length of the chain and the distance between chains - both being affected by the size of the M^+ cation. However the dilatation which a large cation implies can, within limits, be obtained without any constraint, except (possibly) that encountered in bending at the oxygen atom - and this force is weak. If Si-O-Si bonds run normal to the c-axis - as they must at times in a random chain model, then it becomes more difficult to expand the lattice without strain as fig. 10 indicates. Consequently, the topology of the random chain model, while meeting the coordination requirements, does not lead to satisfactory packing - as measured by the density.

This does not mean that a random model cannot be constructed. An alternative model could, for example, be constructed in the same spirit starting from a dense random-packed cluster of oxygen atoms with Si, Li atoms inserted into tetrahedral interstices. Since the packing fraction of random sphere models is lower than hcp (0.63 compared to 0.73), the values of V_0 would be expected to be somewhat higher than observed above. However, until it can be proved otherwise, there must be doubts about the ability of this model to satisfy the constraints representing coordination, anionic composition (and packing density). For this discussion, the point is that randomness is not necessarily the hallmark of an acceptable model. A personal view would be that a successful model would probably require more order rather than less and tests are being done on a domain model similar to that for the a-transition metal-metalloid alloys. A model for the glass based on the metasilicate crystal has already shown some success /36/.

IV - ALTERNATIVES TO RANDOMNESS

The illustrations given in the previous section indicate that for many amorphous materials it may be most appropriate to represent the structure of the 'ideal' glass by a random model. For others, departures from randomness are such that, operationally at least - more ordered models may be preferable.

Before proceeding further, two points should be examined.

IV.1 - The 'ideal glass' The low temperature state of a glass is usually characterized by its effective glass temperature, or fictive temperature, T_f . If we choose to define an ideal glass as the closest approach to a totally disordered solid then, by definition, the ideal glass corresponds to quenching at the highest cooling rates, evaporation at high rates onto liquid He substrates etc. - conditions which lead to the highest values of T_f . A definition more consistent with the normal understanding of perfect defect-free solids is that state representing the lowest energy configuration available to that phase. This definition is adopted here and corresponds to the ground state of amorphous packing represented by the lowest extrapolated value of T_f corresponding to infinitely slow quenching rates. Thus $T_f = T_0$, where T_0 is the characteristic temperature entering into the Fulcher-Vogel equation for viscosity, $\eta = A \exp(B/(T - T_0))$ leading to infinite viscosity (solid-like properties) for $T \leq T_0$.

IV.2 - Structural implications of randomness The concept of randomness - although occasionally elevated to the status of a positive quantity - is nonetheless a negative definition implying the absence of any preference for a particular configuration. A random model is thus entirely consistent with the usual negative description of the glassy state - dis-ordered, amorphous, non-crystalline etc).

This description is most appropriate for structures having many alternative configurations with little or no bias imposed by chemical bonding, energy, space filling etc. Materials in which the inter-atomic potential energy is dominated by terms involving local structural parameters (and which thus have a well-defined local structure) but with weak interactions with other units clearly fit this description. An example would be silica with an open structure of highly stable SiO_4 units, strong Si-O bonds but only a small energy penalty associated with distortions of intertetrahedral bridging oxygen angles and with no obvious preference for 5, 6 or 7-membered rings. In modelling terms there will be many different limited size models which equally well represent the known properties of the material. Extensions to other open structures, Si, Ge, As, appear almost equally valid. The stability of these structures to crystal nucleation resides firstly in the structural degeneracy - a large number of disordered structures are available to the system at high temperatures thus the entropy term in the free energy function dominates. Furthermore, although each local configuration contains elements of the crystal structure - a 6-fold ring passing through each Si atom, say, there are also elements (5- and 7-membered rings) which are inconsistent with crystallinity so that bonds must be broken and reformed, at the level of the local unit, before crystal nucleation is possible.

IV.3 - Constrained randomness It is important, if obvious, to recognize that the essential logical criterion for choosing a random, no preference, model is that experimental facts do not indicate any preference. Where experimental facts suggest otherwise - local chemical ordering, correlated domains - then absolute randomness is untenable. There are then two alternatives; one is to refine random models to implicitly or explicitly include the non-random elements, or to abandon the principle and examine defective but intrinsically ordered models.

Extension of the concept of the random structure - what might be called constrained randomness - has already been included implicitly in all successful models of glasses: models built without constraints rarely, if ever, represent real glasses. First-neighbour bond lengths are normally closely constrained and certain bond angles may be also. Chemical short range order is included in models for transition metal-metalloid alloys. Longer-range organization leading to medium-range domains can be incorporated, in principle, by adjustment of the length scale corresponding to the onset of randomness - as for example, in models for α - B_2O_3 based on boroxol units connected randomly, or a model for transition metal-metalloid glasses with randomly packed trigonal prisms.

Increasingly, it would seem, as more complex, close-packed systems are investigated - especially those near an edge of a glass-forming region, the constraints become more dominant and the principle of randomness more tenuous.

IV.4 - Defective ordered structures "'Disorder' is not mere chaos: it implies defective order. To think about a disordered state we must have in mind an ideal of order from which it falls short. It is much easier to characterize disordered systems in terms of their deviations from this ideal than it is to define a perfectly disordered system on which some partial degree of order is to be imposed. The concept of disorder is primitive and intuitive; it belongs with statistical terms such as 'random', 'stochastic', 'unpredictable' which can only be defined within a specific context of what is already known or can be taken for granted." The quotation is the opening paragraph of Ziman's "Models of Disorder" /37/ and serves to illustrate the philosophy underlying models for an amorphous material which may have a 'clearly-expressed preference' for a particular perfectly ordered configuration but which nevertheless fail to achieve it. Failure to reach the ordered state may be the result of kinetic and/or topological constraints. In such cases it may be more profitable to discuss the state of the disordered material in terms of defects in the ordered state. In the following two sections the principles underlying topologically- and kinetically-'frustrated' structures are discussed (although it may be difficult to disentangle the two types of constraints - elements of each are always present).

IV.5 - Topological constraints Formation of the structure of an amorphous tetrahedral semiconductor by sequential addition of atoms necessarily leads to a pentagonal ring as the lowest energy configuration of 5 connected atoms. One bond energy is saved and the ring contains only a small angular mismatch (7.5°). Similarly, sequential close-packing of atoms leads to a minimum energy configuration of four atoms as a tetrahedron and further low energy structures by continuation of this polytetrahedral packing. Five tetrahedra almost complete a loop around a common axis with again only a 7.5° angular mismatch.

Continuation of such structures to give space-filling structures without breaks of symmetry is impossible. The structure may, however, tend towards it and it is profitable to examine the actual structure from the view point of the perfect structure - in this case the fully ordered polytope in a higher-dimensional space /38/. Mapping this structure into ordinary 3-space necessarily involves defective regions.

Models of this type need not be limited to atoms in polytetrahedral arrays. Other models have been devised for covalent solids in which tetrahedral units contain a number of atoms in an ordered array /39/ and others are certainly possible for

amorphous alloys based on a decoration of pentagonal rings to give 5-fold rings of trigonal prisms (fig 12) /24/.

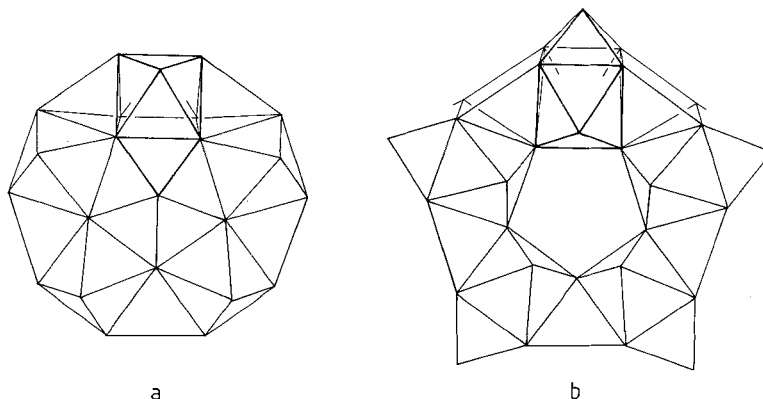


Fig. 12 - Pentagonal rings based on a packing of capped trigonal prisms linked a) with tetrahedra b) half octahedra.

The stability of such models to crystal nucleation derives both from the relatively low energy penalty compared to the crystal: for small particles, polytetrahedral structures are, both energetically and entropically stabilized and the energy penalty with respect to crystals may only be significant for almost macroscopic particles.

IV.6 Kinetic constraints Amorphous structures also have a distinct preference a tendency to form the ordered, crystalline lattice. In this case, we can assume that the necessary frustration must be essentially kinetic in origin (even if topological features are involved in the specification of kinetic parameters). The result may be a material which, at one extreme, might be a quenched liquid with crystalline inclusions and could not therefore be described as a glass. At the other extreme might be a paracrystalline or highly microcrystalline material with a domain size comparable to a small number of interatomic distances. Often, in the past, this type of model has been considered only in terms of a series of microcrystallites, arbitrarily orientated, with unspecified interfaces - possibly involving some more disordered 'connecting tissue'. Such models have been rightly dismissed - on experimental grounds, because some interfaces must be highly energetic thus leading to initiation of grain growth - but principally because the particles must be so small that the interfacial structure and the resulting strain spreading throughout the model must be specified and quantified. "Until a protagonist of these models produces an actual three-dimensional structure that conforms to the assumptions he makes we must be doubtful whether it can be done at all, nohow." /40/.

Nevertheless there is extensive experimental evidence of similarity between the structures of the glass and the compositionally-equivalent crystal - a similarity which may not necessarily end at the local structural level. This point has been made eloquently by the NMR work on borates by Bray /41/; Moreover similarities in physical and chemical properties often lead to explanations involving equilibrium phase diagrams as shown by Babcock /42/ and Goodman /43/. The problem is how the periodic structure of the crystal can be compatible with the amorphousness of the glass - a problem which requires that crystal-like regions shall be undetectable by diffraction and EM imaging. A reason must also be offered for the fact that the super-cooled liquid containing such nuclei may, nonetheless, be kinetically prevented from developing those nuclei to give a polycrystalline aggregate.

Relatively few attempts have been made to tackle these problems in the manner advocated by Ziman /40/. A personal view is that success must depend on a low energy interface so that models based on twinning, stacking faults (possibly) seem likely contenders. A model based on multiple twinning originally designed for a-Ge /39/ and then extended to SiO₂ /16/ provides close fits to both sets of rdfs and interference functions - arguably not as good as a CRN model for Ge and better than most CRN models for SiO₂. A more recent approach is that of Dubois et al /25/, whose model is based on domains separated by interfaces where 'chemical twinning' planes change orientation. Strain is generated by interfacial mismatch but since each interface atom is completely bonded, the strain is small and spreads throughout the structure. Formation of a domain structure on a sufficiently small scale is thought to be the result of either intrinsic compositional fluctuations in the supercooled liquid or fluctuations generated by exsolution from growing domains. The essential point is that the local composition at the interface between two clusters will be different from that in the interior of a domain. A composition fluctuation can thus be incorporated into the structure by a local variation in orientation of the chemical twinning plane see also /44/. Examples of multiple twinned crystal growth are seen in the precipitation of Si from a hyper-eutectic Al-Si alloy /45/.

V - SUMMARY

The evidence presented in this paper suggests that the existence of a unique structural description for all glasses may be a mirage. Almost certainly there are materials - the good glass-formers with open structures, elemental amorphous metals and semiconductors where a random network or dense random-packed model may be the most appropriate model. Equally there are others, close-packed alloys with dissimilar elements, glass-forming materials at the edge of their stability range, for which the concept of randomness introduces difficulty and artificiality. It may be preferable, therefore, to abandon randomness as a paradigm in favour of defective ordered models. Intermediate cases will occur where "constrained randomness" may represent an appropriate description.

For the future, it seems important that the concept of variability in glass structures should be recognized and developed.

The constraints on randomness should be investigated further with the accent on the specification of the nature and magnitude of those constraints.

It should no longer be assumed that a random model consistent with the known constraints is even possible, as the discussion of the alkali silicates illustrates.

Further experimental work is needed to define the local structure. It has been shown how an adequate quantitative definition of local structural parameters - which are often all we can quantify - may also lead to bounds being placed on acceptable medium-range structures. For many glasses, such local parameters either do not exist or are incomplete - even in simple glasses like the alkali silicates and borates - hence the importance of experimental studies of partials by EXAFS, neutron scattering etc.

Finally, it is necessary to evaluate the similarities and differences between the three types of model - random, kinetically- and topologically-constrained structures. It is not clear, for example, to what extent curved space models are distinguishable from random models. In both, defects are intrinsic, but is it possible to distinguish characteristic features such as the amplitude of energy or density fluctuations, the spatial distribution of defective regions? "And what does it mean physically that a three-dimensional structure should be the (bounded) projection of a structure of higher dimensionality, or even the result of the flattening of a structure curved out of normal space?" /46/ Real glasses which may be represented by these models could be examined to identify differences in, say, the temperature/time evolution of the structure in the annealing range. Setting aside the possibility of nucleation of a macroscopic crystalline phase by an

essentially discontinuous, heterogeneous (in the most general sense of the word) nucleation process we might imagine that under conditions which favour an evolutionary progression towards the ideal glass, the energy of a constrained random model would decrease as would fluctuations in bond length and angles - the material becomes more ordered. Topologically-frustrated models also become more ordered but perhaps with a redistribution of the pentagonal domains and defect regions. Kinetically-frustrated models must, by definition, progress to a more ordered structure, but here, surely, the changes should be seen by high resolution electron microscopy - the structure should ripen as the domains grow leading eventually to a microcrystalline structure with characteristic changes in properties. To date, only a start has been made in answering most of these questions.

A final quotation (on evolution). "Natural selection through random mutation must have played an important part in those processes, but to regard that as the sole explanation of evolutionary change is improbable, unprovable and dogmatic, the fact is that matter has an innate tendency to assemble itself into more and more complex forms" /47/.

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