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Crystalline-like ordering in melt-quenched network glasses?☆

Adrian C. Wright

J.J. Thomson Physical Laboratory, University of Reading, Whiteknights, Reading RG6 6AF, UK

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ABSTRACT

The existence of crystalline-like ordering in melt-quenched glasses is still a subject of debate in the literature, although it is not such an emotive issue as it was during the almost 50 years of the great crystallite *vs.* random network controversy. However, whereas the latter is now relegated to history, arguments concerning the extent (if any) of crystalline-like ordering in glasses still arise, especially in connection with newly discovered glass-forming systems. The objective of the present paper, therefore, is to present a rational discussion of the present perception of the relationship between the structures of vitreous and crystalline phases and that of the melt from which they are formed. The limitations of the various experimental techniques for studying the intermediate-range order in glasses are assessed, together with the role of chemistry in determining both the short- and intermediate-range order. It is concluded that, whilst there are no unambiguous data that uniquely establish the presence of crystalline-like ordering in glasses, there is strong circumstantial evidence for its existence, *e.g.* in respect of their devitrification behaviour, and especially of that for glasses having more than one component.

1. Introduction

> "One question more than any other has focused the efforts of those working on the structure of glasses. This is the extent to which the atomic structure can be considered to be uniform, continuous, with randomness at the heart. Alternatively, is the structure essentially inhomogeneous, granular, with some close relationship to the structure of a neighbouring crystalline phase?"
>
> [Philip Hedley Gaskell (1998) [1]]

The relationship between the structure of glasses and that of related crystalline phases has long been a subject of considerable debate in the scientific literature, as evidenced by the great (Russian) crystallite *vs.* (Western) random network controversy [2], which dominated glass research for over 40 years. Even today the extent to which there is crystalline-like ordering in glasses remains controversial, although it is now more than 40 years since the final conference [2,3] that effectively marked the demise of the (early) crystallite theory. Hence the time has come for a rational and unbiased consideration of the evidence for and against the presence of crystalline-like ordering in melt-quenched network glasses and, in particular, to try to answer the long-standing question.

Just how non-crystalline are non-crystalline solids?

The present paper will review the evidence for the extent of any crystalline-like ordering in melt-quenched network glasses in the light of the data provided by modern experimental and modelling techniques, all of which have been developed and/or greatly improved since the crystallite and random network theories were actively proposed during the 1920s and 1930s. Only melt-quenched network glasses, as defined in Ref. [4], will be considered here, but much will also apply to amorphous network solids prepared by methods other than melt-quenching (*e.g.* vapour-deposited thin films), and to both glasses (*e.g.* metallic, invert and molecular) and related amorphous solids having structures for which a random packing model is more appropriate. Similarly, discussion will mainly be limited to chemically-ordered single-component glasses such as vitreous silica, together with a few binary systems.

2. Crystalline concepts

One of the problems associated with the controversy between supporters of the crystallite and random network theories [2] is that the concept of a crystallite, and hence that of crystalline-like ordering, has evolved over time. This is further compounded by the fact that the meaning associated with the Russian word "kristallit" is not easily translated into English [2,3]. Thus, before examining the experimental evidence for and against crystalline-like ordering in melt-quenched network glasses, it will be helpful to briefly summarise the various theories, concepts and models that have been proposed concerning

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E-mail address: a.c.wright@reading.ac.uk.

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the structure of network glasses. However, the present paper will not include a detailed history of their development, since this is addressed elsewhere [2,3,5].

2.1. (Early) Crystallite theory

The very first concept concerning glass structure [6], which subsequently became known as the (early) ***crystallite theory***, was proposed by Frankenheim [7] in 1835, and later invoked by Lebedev [8] in his famous paper of 1921. The structure is envisaged as comprising an agglomeration of discrete crystallites, with a distribution of crystallite sizes and discontinuous bonding across the interface between crystallites; *i.e.* the crystallites are separated by some form of "grain boundary". The early crystallite theory was supported by the X-ray diffraction data of Randall et al. [9–11], the estimated crystallite volume fraction being ~0.8 [12]. The word ***crystallite*** was first used in connection with glasses by Rosenhain [13] in 1927.

That a clear, transparent glass can contain a large volume fraction of small crystallites is clearly demonstrated by Vogel's [14] electron micrograph of a binary magnesium phosphate glass. However, this is very much an exception, and crystallites of this size would be easily detectable by X-ray or neutron diffraction.

2.2. Colloidal theory

Before the advent of X-ray diffraction, ***amorphous solids*** were identified *via* their isotropic properties, rounded shape (minerals), lack of cleavage planes and etch pits with circular boundaries, the minimum size of any detectable crystallites being limited by the resolving power of contemporary optical microscopes. Thus amorphous solids included colloidally-derived minerals, *etc.*, and some authors (*e.g.* von Weimarn [15–17]) proposed a continuous gradation from glasses, through colloidally-based, to polycrystalline and eventually to single-crystalline materials, a concept that was supported by Randall et al. [11] as late as 1930.

2.3. Random network theory

Diametrically opposed to the crystallite theory is the idea that, within the confines of stereochemistry, glass structure is entirely random in nature. The hypothesis that glasses comprise a random array of atoms linked by directional bonding was first proposed by Rosenhain [13], and later taken up by Zachariasen [18] in his well-known paper of 1932. The term ***random network*** was, however, first introduced by Warren [19] in 1933.

2.4. Cybotactic theory

Although sometimes referred to as the ***modern crystallite theory*** [20], to avoid confusion, this approach is better named the ***cybotactic theory***, since it extends Stewart's [21,22] concept of cybotactic groupings to the vitreous state. It was introduced by Valenkov & Porai-Koshits [23] in 1936 and further defined by Lebedev [24] in a paper of 1940, and proposes that, in the vitreous state, there are fluctuations in the degree of order, with more ordered regions (frozen-in cybotactic groupings), having a structure approaching that of related crystalline phases, being inter-connected by those of lower order, but with continuous bonding throughout.

2.5. Layer structures

In early diffraction studies of chalcogenide glasses, it was observed that the first peak in the diffraction pattern was very sharp, and at approximately the same relatively low scattering vector magnitude, Q, as a Bragg peak for a related crystalline phase with a layer-structure, the Bragg peak being that corresponding to the inter-layer spacing. Hence it was suggested (*cf.* Refs [25,26]) that the glasses also have a layer structure. However, many of the problems associated with crystallites also apply to extreme layer models, as discussed in Section 11.

2.6. Pseudo-lattice planes

The concept of ***quasi-lattice planes*** in network glasses is discussed in papers by Gaskell [1,27], as an explanation of the origin of the first peak in the diffraction pattern for a network glass. Alternatively [28], the "walls" of the network cages can act as pseudo-planes for "Bragg" diffraction. The most important question concerns the relationship between the atomic arrangement in such "planes" and that in the corresponding planes of related crystalline phases that give-rise to the equivalent Bragg peak.

2.7. Crystalline-like ordering

Crystalline-like ordering in glasses can occur at two different levels, depending on the network distortion. If the network distortion is negligible, the atomic co-ordinates should map directly onto those of the crystalline phase, as defined by the crystalline unit cell. This will be termed ***atomic crystalline ordering***. However, if there is significant network strain, the atomic co-ordinates will deviate from those defined by the crystal but, nevertheless, the network topology may still map onto that of the crystalline phase, thus retaining ***topological crystalline ordering***.

3. Experimental evidence

Modern experimental techniques for studying glass structure have improved greatly in both accuracy and resolution, compared to the time (1930s) of the initial objections to the (early) crystallite theory, and hence should provide a much more stringent test of theories invoking crystalline-like ordering in glasses. However, useful information can only be obtained from those techniques that can probe structure beyond the basic structural units, or network-modifying-cation first co-ordination shells, and especially from those that are direct (*i.e.* do not rely on "finger-printing" by comparison with related crystalline materials) and can probe the intermediate-range order over ranges of inter-atomic distance, r, up to and beyond 10 Å. In this respect, the most important techniques are X-ray and neutron diffraction and so, for this reason, it is necessary to clearly establish the form of the diffraction pattern, $I(Q)$ and the real-space correlation function, $T(r)$,[1] for a single-phase network glass.

The real-space total correlation function, $T(r)$, for a network glass comprises a series of peaks that become broader with increasing r, due to the inherent disorder characterising the amorphous solid state. The highest frequency Fourier components in reciprocal space, therefore, decay more rapidly, since they arise from the broadest features at the longest distances in real space. Hence the resulting interference function, $Qi(Q)$, and diffraction pattern, $I(Q)$, similarly have peaks that increase in width with increasing scattering vector magnitude, Q. The rapid decay of the highest frequency Fourier components means that the first peak in the diffraction pattern of an amorphous solid is usually the sharpest and, as such, it has attracted a great deal of attention in the literature. The structural origins of this often-named ***first sharp diffraction peak*** (FSDP) will be discussed in Section 11 but, at this point, it is perhaps worth making a few general comments to dispel some of the mysticism and misunderstanding with which this feature has been associated. First, and this seems to be completely lost on many authors who claim special importance for the first diffraction peak, any diffraction pattern with peaks must by definition have a first peak, and the fact that this is usually the sharpest means that it is also

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[1] For a more detailed definition of the functions used in this paper, see Ref. [29].