Pressure-driven transformation of the ordering in amorphous network-forming materials

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The pressure-induced changes to the structure of disordered oxide and chalcogenide network-forming materials are investigated on the length scales associated with the first three peaks in measured diffraction patterns. The density dependence of a given peak position does not yield the network dimensionality, in contrast to metallic glasses where the results indicate a fractal geometry with a local dimensionality of $\simeq 5/2$. For oxides, a common relation is found between the intermediate-range ordering, as described by the position of the first sharp diffraction peak, and the oxygen-packing fraction, a parameter that plays a key role in driving changes to the coordination number of local motifs. The first sharp diffraction peak can therefore be used to gauge when topological changes are likely to occur, events that transform network structures and their related physical properties.

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I. INTRODUCTION

Network structures govern the physicochemical characteristics of a broad class of glassy and liquid materials, and can be altered profoundly by changing the state conditions [1–5]. Here, essential information on the structure is provided by diffraction, and it is therefore desirable to link generic features in the structure factor $S(k)$ measured by experiment, where $k$ denotes the magnitude of the scattering vector, to the character of network-forming motifs, and to the way in which these motifs are organized [6–16]. In this quest, the bulk number density $\rho$ is a key parameter that depends on the nature of the interatomic interactions, is a prerequisite for building accurate atomic-scale models, and can be manipulated by changing the pressure. There has not, however, been a systematic investigation of the density dependence of the rudimentary features in $S(k)$ for network-forming materials.

At ambient conditions, the open network structures of oxide and chalcogenide glass-forming materials often lead to $S(k)$ functions that are characterized by three peaks with positions $k_i$ ($i = 1, 2, 3$) that scale roughly with the interatomic distance $d$ such that $ki d \simeq 2–3$, $k2 d \simeq 4.6–4.9$, and $k3 d \simeq 7.7–8.9$ [6–10,15] (Fig. 1). According to Fourier transform theory, each feature corresponds to real-space ordering with a periodicity of $2\pi/k_i$ and a correlation length of $2\pi/\Delta k_i$, where $\Delta k_i$ is the peak width [10]. The peaks are associated with ordering on length scales that are commensurate with the nearest-neighbor separations ($k_3$), with the size of the local network-forming motifs ($k_2$), and with the arrangement of these motifs on an intermediate range ($k_1$). The features at $k_2$ and $k_1$ are commonly referred to as the principal peak and first sharp diffraction peak (FSDP), respectively, and the real-space periodicity associated with these features is directly observable for several network-forming materials [10,12,15,17]. The finding $k_3 d \simeq 7.7–8.9$ is roughly in keeping with the Ehrenfest relation $k_3 d = 7.725$ [10].

In contrast to their network-forming counterparts, the local motifs in metallic glasses are closely packed to favor an efficient filling of space [11,13,18]. In this case, $S(k)$ is dominated by a first peak at a scaled peak position $k1 d \simeq 7–8$ [7] (Fig. 1), and the associated real-space periodicity is directly observable for many of these materials [14,19]. Recent experiments in which pressure was used as a parameter to tune the density found a “universal” fractional power-law relation $k_3 \propto \rho^{1/D_3}$ with $D_3 \simeq 5/2$ [16], similar to the value of $D_3 \simeq 2.31$ found from an investigation in which composition was used as a tuning parameter [14]. These findings are at odds with an often assumed $D_3 = 3$ dependence, i.e., with an expectation that the density under compression should vary in inverse proportion to the cube of the one-dimensional interatomic distance, and it is proposed that the motifs pack to give a fractal geometry with a local dimensionality of $\simeq 5/2$ [14,16,20]. As pointed out by Zeng *et al.* [16], it is unknown whether this type of behavior is also observed for other classes of amorphous material. We have therefore been motivated to examine the density dependence of the peak positions in $S(k)$ for network glass-forming oxide and chalcogenide systems at high pressures. Under ambient conditions, these systems cover a range in network dimensionality from, e.g., 1-D for amorphous Se to 3-D for amorphous SiO$_2$ [21].

The paper is organized as follows. In Sec. II, we consider the reduced density dependence of the peak positions in $S(k)$ for network-forming versus metallic glasses, where the peak positions are categorized as according to Fig. 1. In general, a given peak position $k_i$ is not found to share a common density dependence for a given class of network-forming materials, and does not provide a direct measure of the network dimensionality. In Sec. III, we investigate whether the oxygen-packing fraction $\eta_0$ provides an alternative parameter for rationalizing the high-pressure diffraction results for amorphous oxides. This parameter is chosen because it plays a key role in facilitating the pressure-driven changes to the connectivity of network-forming motifs [4]. Here, a relationship is found between $\eta_0$ and the intermediate-range ordering as described by $k_1$, which also holds for the available data for molten oxides at high-pressure and high-temperature conditions. The implications of this relationship are discussed in terms of predicting when network transformations are likely to occur. Conclusions are drawn in Sec. IV.

II. NETWORK DIMENSIONALITY

Figure 2(a) shows the reduced density $\rho/\rho^0$ dependence of the scaled peak position $k3/k1^0$, where superscripts refer to ambient pressure parameters, as obtained from *in situ* high-pressure x-ray and neutron diffraction experiments on
different amorphous materials under compression at ambient temperature. In these experiments the structure factor is defined by [22]

\[ S(k) = \sum_{\alpha} \sum_{\beta} w_{\alpha \beta}(k) S_{\alpha \beta}(k), \]

i.e., there is a weighted overlap of partial structure factors \( S_{\alpha \beta}(k) \) where \( w_{\alpha \beta}(k) = c_{\alpha} c_{\beta} f_{\alpha}(k) f_{\beta}^{*}(k) |\langle f(k) \rangle|^{2} \). \( c_{\alpha} \) and \( f_{\alpha}(k) \) are the atomic fraction and x-ray form factor (or coherent neutron scattering length) for chemical species \( \alpha \), respectively, and \( \langle f(k) \rangle = \sum_{\alpha} c_{\alpha} f_{\alpha}(k) \) is the mean form factor. The data sets correspond to the bulk metallic glasses \( \text{La}_{62}\text{Al}_{14}\text{Cu}_{11.7}\text{Ag}_{2.3}(\text{Ni}_{3}\text{Co}_{5}) \), \( \text{La}_{62}\text{Al}_{14}\text{Co}_{10.83}\text{Ni}_{10.83}\text{Ag}_{2.34}, \text{Cu}_{7}\text{Ti}_{13}\text{Zr}_{11}\text{Ni}_{9}\text{Nb}_{1} \), and \( \text{Ce}_{68}\text{Al}_{10}\text{Cu}_{20}\text{Co}_{2} \) [16,23], the network-forming oxide glasses \( \text{B}_{2}\text{O}_{3} [24,25], \text{Si}_{2} \) [26–29], and \( \text{GeO}_{2} [30–35] \), the modified oxide glasses \( \text{CaSiO}_{3} [36] \) and \( \text{MgO}_{0.62}\text{SiO}_{2}_{0.38} [37] \), the network-forming chalcogenide glasses \( \text{GeSe}_{2} [38,39], \text{GeSe}_{4} [40–42] \), and \( \text{As}_{2}\text{Se}_{3} [36] \), and elemental glassy Se [43–46]. For each chalcogenide glass, the measured x-ray and neutron \( S(k) \) functions are comparable because of a similarity in the relative weighting factors \( w_{\alpha \beta}(k) [5,15] \).

In Fig. 2(a), the data sets for the metallic glasses sit on a common curve given by \( k_{3}/k_{0}^{3} = \left( \rho/\rho_{0} \right)^{1/D_{3}} \) with \( D_{3} = 5/2 \) [16] which provides a bound on the reduced density dependence of \( k_{3}/k_{0}^{3} \) for most of the other materials.

FIG. 1. Representative structure factors \( S(k) \), as measured at ambient pressure by neutron diffraction (ND) [solid curves] or x-ray diffraction (XRD) [broken (red) curves] and plotted in terms of the scaled scattering vector \( kd \), for a bulk-metallic glass \( \text{Pd}_{2.5}\text{Ni}_{7.5}\text{Cu}_{30}\text{P}_{20} \) \( (d = 2.656 \text{ Å} \text{ (ND)} \) or \( d = 2.739 \text{ Å} \text{ (XRD)} \), for a network-forming chalcogenide glass \( \text{GeSe}_{2} (d = 2.363 \text{ Å}) \), for a network-forming oxide glass \( \text{SiO}_{2} (d = 1.599 \text{ Å}) \), and for elemental glassy Se \( (d = 2.349 \text{ Å}) \). The ND and XRD \( S(k) \) functions for \( \text{GeSe}_{2} \) and the ND \( S(k) \) function for \( \text{SiO}_{2} \) show a “three-peak” structure that is typical of network-forming materials, where the approximate positions of these peaks as labeled by \( k_{1}, k_{2} \), and \( k_{3} \) are indicated by the vertical broken lines. A principal peak at \( k_{3} \) is absent in the XRD \( S(k) \) function for \( \text{SiO}_{2} \) (see the text). For the metallic glass, ordering does not appear on a length scale associated with either \( k_{1} \) or \( k_{2} \) and the magnitude of \( S(k) \) has been halved for clarity of presentation. For Se, ordering does not appear on a length scale associated with \( k_{1} \).

FIG. 2. The reduced density \( \rho/\rho_{0} \) dependence of the scaled (a) peak position \( k_{3}/k_{0}^{3} \), (b) principal peak position \( k_{2}/k_{0}^{2} \), and (c) FSDP position \( k_{3}/k_{0}^{3} \) as measured by using in situ high-pressure x-ray or neutron diffraction for materials under compression. In (a) the solid curve corresponds to \( D_{3} = 5/2 \) and accounts for the metallic glass data taken from Refs. [16,23], and the chained and broken curves correspond to \( D_{3} \) values of 6 and \( \sim 10 \), respectively. In (b) the solid curve corresponds to \( D_{3} = 1.82 \), and the broken curve corresponds to \( D_{3} = 5 \). The vertical arrows indicate (from left to right) the reduced densities at which the coordination number \( \bar{n}_{\alpha \beta} \) of the local motifs in glassy \( \text{GeO}_{2}, \text{B}_{2}\text{O}_{3}, \) and \( \text{SiO}_{2} \) starts to exceed its ambient pressure value of 4, 3, or 4, respectively. In (c) the solid and broken curves correspond to \( D_{3} \) values of 10/9 and 5/3, respectively, and bracket most of the measured data points. The horizontal and vertical error bars on several of the data points give representative uncertainties.
a principal peak is not always present in the $S(k)$ function measured by both x-ray and neutron diffraction, even when this feature is prominent in the partial structure factors $S_{\alpha\beta}(k)$, on account of the weighting factors $w_{\alpha\beta}(k)$ in Eq. (1). For instance, a principal peak is present in the neutron diffraction $S(k)$ but not in the x-ray diffraction $S(k)$ for glassy SiO$_2$ (Fig. 1) because there is a cancellation in the latter of the principal peaks in $S_{\text{SiO2}}(k)$ and $S_{\text{GeO2}}(k)$ with a principal trough in $S_{\text{GeO2}}(k)$ [47]. The data sets for SiO$_2$ [29] and B$_2$O$_3$ [24] are therefore taken from neutron and x-ray diffraction, respectively. The other data sets in Fig. 2(b) correspond to GeO$_2$ [31–34], CaSiO$_3$ [36], (MgO)$_0$ [37], GeSe$_2$ [38,39], GeSe$_4$ [40–42], and As$_2$Se$_3$ [36].

In Fig. 2(b), the data sets for the chalcogenide glasses indicate a power-law dependence $k_2/k_1^2 = (\rho/\rho^0)^{1/D_2}$ with $D_2$ values of 1.82(8), 3.13(5), 3.65(6), and 4.42(2) for Se, GeSe$_4$, As$_2$Se$_3$, and GeSe$_2$, respectively. Here, the ambient-pressure network dimensionality is 1-D for Se, where the structure is formed from Se$_n$ chains ($n$ is an integer $\geq 2$); increases in the order from GeSe$_4$ to GeSe$_2$, as the added Ge atoms form more cross-links between Se$_n$ chains, to give a dimensionality $\leq 3$ for GeSe$_2$; and is 2-D for As$_2$Se$_3$, where As$_2$Se$_3$ pyramids link to form layer-like arrangements [21,48]. There may therefore be a relation between $D_2$ and the network dimensionality, although the $D_2$ values do not give a direct measure of that dimensionality. In comparison, the data sets for the oxide glasses do not appear to show any systematic dependence of $D_2$ on the network dimensionality. For example, B$_2$O$_3$ and SiO$_2$ have 2-D and 3-D structures, respectively, but the $k_2/k_1^2$ ratio remains approximately invariant for both of these materials when they are initially compressed, which corresponds to a densification mechanism where the integrity of the local motifs remains unchanged as they pack more efficiently on an intermediate length scale [5]. The $k_2/k_1^2$ ratio then increases more rapidly as the A-O (A = B or Si) coordination number $n_{AO}$ of these motifs starts to exceed its ambient pressure value [Fig. 2(b)].

Figure 2(c) shows the reduced-density dependence of the scaled FSDP position $k_1/k_1^0$ for the network-forming oxide glasses B$_2$O$_3$ [24,25], SiO$_2$ [26–29], and GeO$_2$ [30–33,35,49,50], the modified silicate glasses CaSiO$_3$ [36] and (MgO)$_0$[SiO$_2$)$_0$ [37], and the network-forming chalcogenide glasses GeSe$_2$ [38,39] and GeSe$_4$ [40,41], all under compression at ambient temperature. Also shown are the results obtained from x-ray diffraction experiments on liquid MgSiO$_3$ and CaSiO$_3$ at temperatures in the range $\approx 1873–2390$ K and pressures up to 6 GPa [51], and on molten basalt (an aluminosilicate) at temperatures in the range 2273–3273 K and pressures up to 60 GPa [52] where an estimate of $k_1^0$ was taken from Ref. [53]. The results for most of these materials are bracketed by curves of the form $k_1/k_1^0 = (\rho/\rho^0)^{1/D_1}$ with minimum and maximum $D_1$ values of 10/9 and 5/3, respectively. There appears to be no systematic dependence of $D_1$ on the network dimensionality. Indeed, the $k_1/k_1^0$ ratio can be used to give a rough estimate of $\rho/\rho^0$ for a wide range of materials.

**III. FSDP versus Oxygen Packing Fraction**

The results of Sec. II invite the question as to whether there is a means for rationalizing the behavior of the peak positions in $S(k)$ for disordered network-forming systems under high-pressure conditions. In particular, is there any generic feature that can be used as a fingerprint for structural change? In the case of oxides, the oxygen-packing fraction $n_O$ is found to play a key role in determining when changes will occur to the coordination number $n_{AO}$ of local motifs [4]. These transformations transform the network connectivity, and thereby trigger changes to physical properties such as the network compressibility [52] and viscosity [3]. In glassy SiO$_2$ and GeO$_2$, for example, the pressure-driven departure from a tetrahedral network starts to occur when $n_O \approx 0.58$, which falls within the range of values found for a random loose-packing of hard spheres, and the transformation to an octahedral network is largely completed for a compression at which $n_O \approx 0.64$, the value found for a random close-packed arrangement of hard spheres [4]. In glassy B$_2$O$_3$, the ambient pressure value $n_{BO} = 3$ is first exceeded for a compression at which $n_{BO} \approx 0.44$ [4]. The oxygen-packing fraction is therefore a likely candidate for identifying markers of structural change.

The FSDP is a robust feature in the $S(k)$ functions measured by both x-ray and neutron diffraction, and $k_1/k_1^0$ shows a greater change with $\rho/\rho^0$ than either $k_2/k_1^2$ or $k_3/k_3^2$ (Fig. 2). But, as shown in Fig. 3(a), a plot of $n_O$ versus $k_1/k_1^0$ does not show communal behavior. In this figure, the neutron and x-ray diffraction data sets correspond to the network-forming oxide glasses B$_2$O$_3$ [24,25], SiO$_2$ [27–29], and GeO$_2$ [30–33,35,49,50], to the modified silicate glasses (MgO)$_0$[SiO$_2$)$_0$ [37] and CaSiO$_3$ [36], and to molten MgSiO$_3$ and CaSiO$_3$ [51] under high-pressure and high-temperature conditions. For a network former such as AO$_2$ or AO$_3$, the $n_O$ values were calculated by assuming that atoms of type A fit into the interstitial vacancies formed by spherical oxygen atoms. Then, for a system of volume $V$ containing $N_O$ oxygen atoms of volume $V_O$, $n_O = N_O V_O / V = \rho O V$ where $\rho O \equiv N_O / V = c O \rho$ is the number density of oxygen atoms [4]. For a modified material, the $n_O$ values were calculated by assuming that the space occupied by the modifier atoms $M$ is not available to oxygen. Then, for a system containing $N_M$ modifier atoms of volume $V_M$, $n_O = N_O V_O (V - \sum N_M V_M) = \rho O (1 - \sum N_M \rho M V_M)$ where $\rho M \equiv N_M / V = c M \rho$ is the number density of modifier atoms [4]. The $n_O$ values then follow from the measured densities and modifier radii, and from oxygen radii that were taken from Ref. [4], except for the pressure range corresponding to $4 < \bar{n}_{SiO} < 6$ for the data sets from Refs. [27,28] where the pressure dependence of the oxygen radius was taken from Ref. [5]. The $n_O$ values from Ref. [35] were taken directly from that paper.

The data sets describing the intermediate-range order do, however, fall into a distribution about a common curve if they are plotted as $n_O H_{AO}^0$ versus $k_1/k_1^0$ [Fig. 3(b)], provided that $H_{AO}^0$ for a given material spans a range for which $n_{AO}$ retains its ambient pressure value. The inset to this figure focuses on the data sets corresponding to these ambient-pressure $n_{AO}$ values, and shows a communality that is insensitive to the ambient-pressure network dimensionality, e.g., 2-D for B$_2$O$_3$ versus 3-D for SiO$_2$ and GeO$_2$. Thus, the position of the FSDP in a measured diffraction pattern can be used to gauge the likely starting point at which a network’s topology will start its pressure-driven transformation. For example, in the case of
tetrahedral networks, $\tilde{n}_{\text{MO}}$ will start to exceed four when $\eta_O \simeq 0.58$ [4] and the corresponding $k_1$ value can be estimated from Fig. 3(b) via knowledge of the ambient-pressure parameters $\eta_O^0$ and $k_1^0$. We note that $\eta_O$ will increase with decreasing free volume; i.e., $k_1/k_1^0$ will be sensitive to the reduction in this volume with increasing pressure.

The sensitivity of $\eta_O$ to structural change most likely originates from an ability of the $\text{O}^{2-}$ ion to change its size and shape in response to the coordination environment in which it is confined. For example, in molecular dynamics simulations of the structure of $\text{B}_2\text{O}_3$ under compression it is necessary to incorporate both of these features into an ionic interaction model [25], and in the limit when a confining potential is removed the isolated $\text{O}^{2-}$ ion is unstable [54,55]. The chalcogen packing fraction did not provide a basis for rationalizing the pressure-dependent behavior of the peak positions in $S(k)$ from the experiments on chalcogenide glasses reported in Sec. II.

**IV. CONCLUSIONS**

In summary, the density-driven structural changes to disordered network-forming materials have a profound effect on their physical properties. Here, we investigated the use of pressure as a parameter to tune the density and, by analyzing the information available from *in situ* high-pressure x-ray and neutron diffraction experiments, we find that the more-open structures of network-forming materials lead to a richer variety of behavior as compared to their amorphous metallic counterparts [16]. For glassy and liquid oxides, we find that $\eta_O$ provides a link between the ordering that occurs on an intermediate length scale, as described by the position of the FSDP, and the structural changes that occur on a local length scale. Thus, the FSDP provides a marker for the associated transformation of the material properties, which will prove valuable when exploring the structure-property relationships for this important class of materials, e.g., under the extreme conditions found in planetary interiors, or when preparing new glassy materials with the desired characteristics via a high-pressure processing route [4,52,56,57].

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