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Transformations in amorphous solids under high pressures

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Phase polymorphism at high pressure has been much studied for many crystalline solids [1]. With an increase in pressure, in crystals there occur phase transitions (primarily of the first order) to a closer packing of atoms in accordance with the Le Chatelier principle. Recently, indications have emerged that the first-order phase transitions are possible in many melts too, even though these transitions can supposedly be realized only in the supercooled liquid domain, well below the melting temperature [2, 3].

In a series of papers, most often using water as an example, a parallel is drawn between the phase transitions in a supercooled liquid and the transformations in the corresponding amorphous solid phases [4–6]. However, analogies of this sort are not fully justified because amorphous substances are nonergodic systems and have no domain of thermodynamic stability in the phase diagram at all, whereas the notion of ‘phase’ itself can be applied to amorphous modifications only rather conventionally. Amorphous substances exist in the metastable state only at sufficiently low temperatures, when diffusion is frozen. At the same time, the relaxation processes in amorphous phases can proceed even at low temperatures [7].

Nevertheless, a distinct short-range (local) order does exist in amorphous and vitreous substances [7]. This brings up the natural question: are jump-like changes of the volume, the local-order structure, and of other properties in the amorphous phase possible on compression? It is well known that several tetrahedral amorphous semiconductors and chalcogenide glasses crystallize under pressure (see paper [8] and references cited therein).

At the same time, the existence of reversible transformations between amorphous modifications involving changes of the local-order structure and the density (in the subsequent discussion also referred to as structural or coordination transitions) has been firmly established by different experimental techniques for SiO_2 and GeO_2 oxide glasses and amorphous H_2O ice [9–17]. Moreover, there is experimental evidence for the structural transitions under pressure in other amorphous materials, too. The case in point are amorphous modifications of carbon [18, 19].

Most intriguing is elucidation of the mechanism of the like transformations. The phase transitions in crystals occur through nucleation and diffusive growth of the new phase (diffusive transformations) or as coherent atomic displacements in the lattice (martensite transformations). Neither of the two possibilities can be realized in the case of transformations between amorphous phases. In this connection, the question of not only the mechanism, but the very possibility

of abrupt structural transitions in amorphous materials under compression has until recently remained an open question.

The results of precision measurements on the density of SiO_2 and GeO_2 oxide glasses under pressure are given below. The transformation between low- and high-density amorphous modifications ($lda \leftrightarrow hda$) of H_2O ice was studied by an ultrasonic technique. The study of the transformation kinetics and the dynamics of amorphous networks in the neighborhood of transition points received primary emphasis. Conceptual approaches to the description of transformations between amorphous phases are considered.

The densities of $a\text{-SiO}_2$ and $a\text{-GeO}_2$ were measured by a tensometric method in hydrostatic conditions up to 9 GPa [20]. One of the main advantages of this procedure is the high precision of measurements on absolute (about 0.3%) and relative (of the order of 10^{-3} %) volume changes alike, the latter being particularly important for studying relaxation processes. Some results of the measurements are given in Figs 1 and 2. Experimentally, $a\text{-GeO}_2$ proved to be the most convenient object, where the coordination transition was observed in the 4–13 GPa range [13–15]. Along with the investigation of the equation of state under continuous

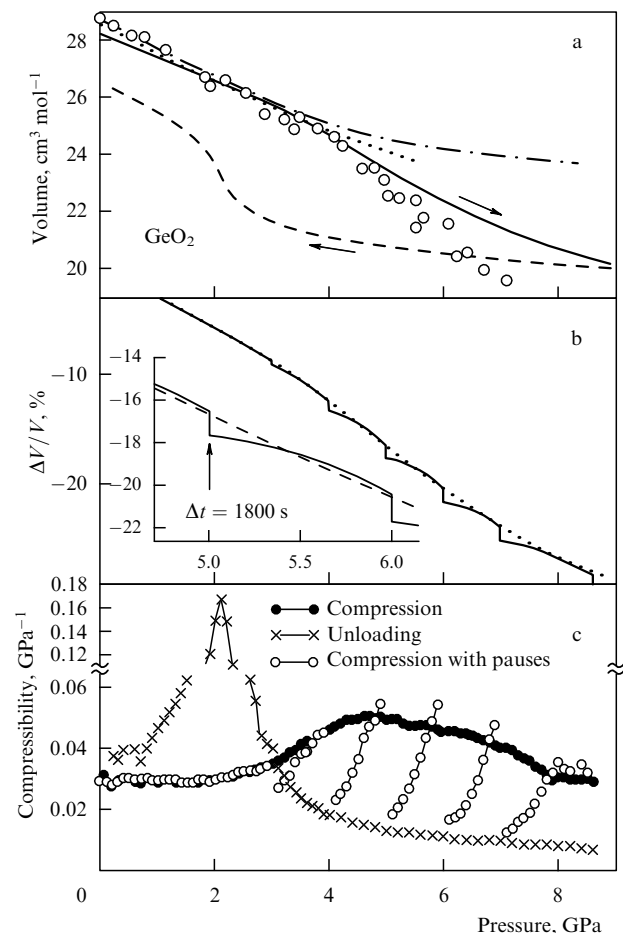


Figure 1. (a) Quasi-static equation of state of $a\text{-GeO}_2$ as compared with the data of Ref. [15] (circles) and with the equations of state obtained from ultrasonic (the dashed line) [19] and Brillouin (the dot-and-dash line) [20] experiments; (b) volume change in the experiment with a continuous variation of the pressure (the dashed line) compared with that in the experiment with a fixed pressure (the solid line); (c) change of compressibility under different experimental conditions.

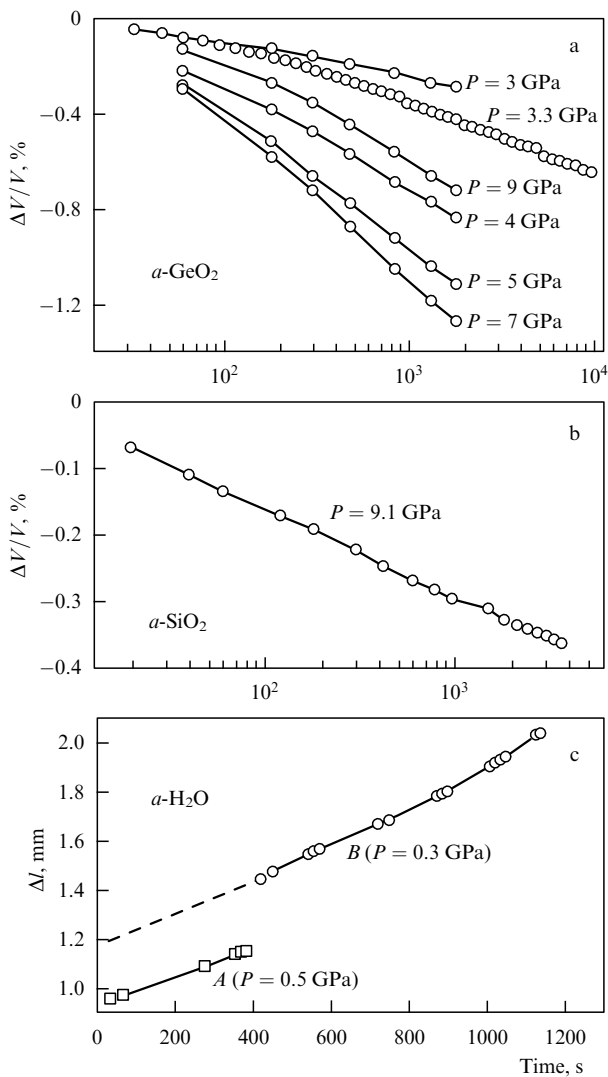


Figure 2. Time dependence of the volume changes of $a\text{-GeO}_2$ (a) and $a\text{-SiO}_2$ (b), and of the reduction in linear dimension (proportional to the volume) of a sample of amorphous H_2O ice (c) under fixed pressures.

changes of pressure (Fig. 1a, b), series of measurements were conducted in which the pressure was fixed for a long time, 30–160 min (Figs 1 and 2).

The following four major features of the transformation stand out.

(i) The anomaly corresponding to the coordination compaction of the amorphous GeO_2 network was recorded over a broad pressure range (Fig. 1a).

(ii) For a fixed pressure, a change of volume (which is a logarithmic function of time) is observed in the transition range (Fig. 2a). The typical amplitude of the relaxation depends only slightly on the pressure.

(iii) On prolonged exposure to a fixed pressure, in response to the relaxation, the quasi-static compressibility decreases sharply (Fig. 1c) to the values resulting from ultrasonic and Brillouin experiments at these pressures [21, 22]. However, on further pressure increase, the compressibility re-increases, i.e. the amorphous network ‘forgets’ about the preceding relaxation. As a consequence, the $\Delta V(P)$ dependence follows the curve obtained with increasing density continuously (Fig. 1b).

(iv) A ‘negative’ hysteresis is observed for the coordination transition in $a\text{-GeO}_2$, i.e. the inverse transformation commences at $P \approx 4$ GPa in the pressure range of the direct transition, the onset of which was recorded at $P \approx 3$ GPa (Fig. 2a).

The intense coordination compaction of $a\text{-SiO}_2$ proceeds in the 10–25 GPa range [9–12]. However, the use of the precision tensometric technique made it possible to establish that the behavior of compressibility of the SiO_2 glass becomes inelastic even at $P \approx 6\text{--}7$ GPa [23, 24], while a tangible logarithmic volume relaxation is observed at $P = 9.1$ GPa (Fig. 2b). Therefore, the $a\text{-SiO}_2$ transformation kinetics are supposedly similar to the kinetics of the coordination transition in $a\text{-GeO}_2$. The above-specified features of the transformation in $a\text{-GeO}_2$ and the relaxation in $a\text{-SiO}_2$ at the onset of the coordination transition differ radically from the features of conventional first-order phase transitions.

The reversible transformation between the *lda* and *hda* phases of amorphous ice also exhibits unusual features (Figs 3 and 4). The experimental setup and procedure in the ultrasonic study of ice is described thoroughly in Ref. [25]. The direct and inverse *lda* \leftrightarrow *hda* transformations are preceded by a softening of the shear modulus of amorphous ice networks. A similar elastic softening is observed in the compression of $a\text{-SiO}_2$ and $a\text{-GeO}_2$, too [21]. The time kinetics of the *lda* \rightarrow *hda* transformation prove to be unusual and different from the logarithmic kinetics (Fig. 2c). This transformation has a broad (compared with the transitions between crystal phases) ‘tail’ in which density relaxation changes are observed (Fig. 4).

To summarize, it may be concluded that the structural transformations in amorphous phases of SiO_2 , GeO_2 , and H_2O are unusual in nature and kinetics, which differ

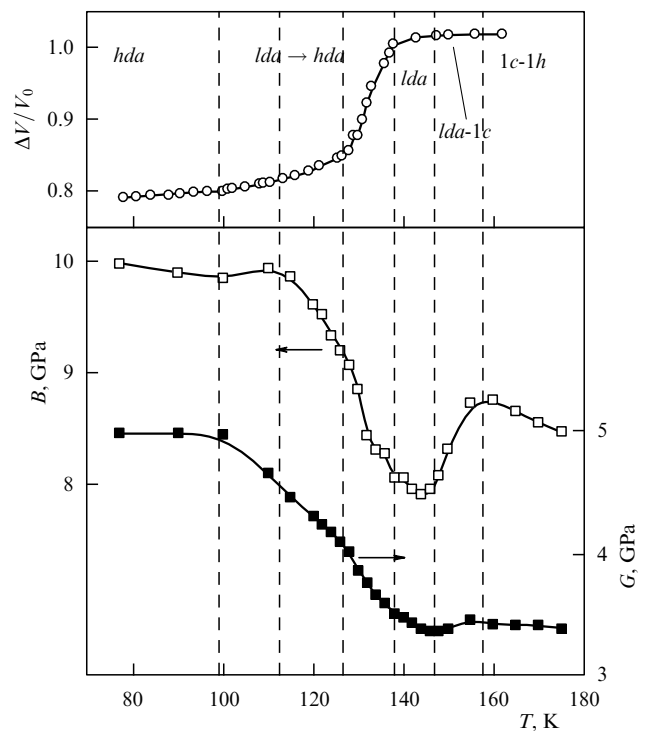


Figure 3. Relative volume $\Delta V/V_0$, bulk modulus B , and shear modulus G as functions of the temperature T , the increase of which induces the *hda* \rightarrow *lda* transition.

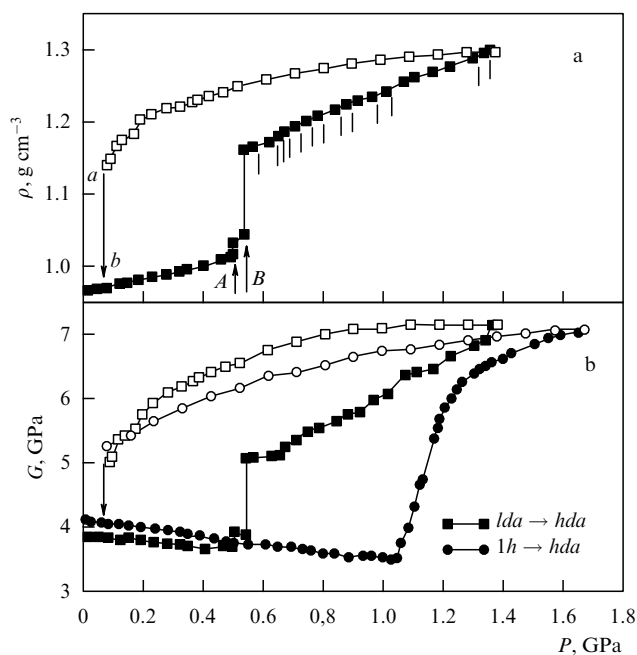


Figure 4. (a) Dependence of the density ρ on the pressure P for $T = 110$ K for the direct and inverse $lda \leftrightarrow hda$ transitions. The $a-b$ portion of the inverse transition corresponds to the temperatures 120–130 K. The vertical lines in the $\rho(P)$ curve mark off the points at which the pressure was fixed for a short time to observe volume changes. At points A and B , the pressure was fixed respectively for 9 and 20 min to perform the time measurements presented in Fig. 2c. (b) Comparison of the $\rho(P)$ and $G(P)$ dependences for the $lda \rightarrow hda$ and $1h \rightarrow hda$ transitions. Empty marks correspond to decreasing pressure.

significantly from the kinetics of first-order phase transitions. In this case, a complex pattern of the variation of elastic characteristics may be observed in the range of coordination transition (Figs 1 and 3) as well as prior to the transformation (Figs 3 and 4).

Notice that the conception of different amorphous phases (the polymorphism of amorphous phases) actually rests on the fact that quite specific types of short-range order prevail in disordered structures. These types are determined by the chemical nature and the character of the bonds in the solid state of a given substance. Being energy-disadvantageous, other types are normally present as defects of amorphous networks and are statistically insignificant. In the transition region between two amorphous structures, a two-phase (or two-domain) model can predict some of the features of intermediate states [15], but on the whole it fails to describe the transformation [23, 24]. First and foremost it is not clear what determines the pressure dependence of the concentrations of amorphous phases of different types.

Evidently, consideration of the behavior of glasses and amorphous phases under pressure calls for the introduction of new approaches and concepts. A fundamental distinction between the amorphous state of a substance from the crystalline one is the existence of a wide scatter in the geometrical parameters of the environment of individual atoms (the bond lengths and the angles between them). That is, an adequate language for the description of amorphous networks should deal with the distributions of geometric (lengths and angles) and topological (3-, 4-, 5- nominal, etc. rings of bonds and so forth) characteristics. The evolution of an amorphous network under pressure can be described in

terms of changes of the corresponding distributions (see the calculations for a -SiO₂ in Ref. [26]). The distribution of the geometric parameters is also responsible for the scatter in the local energy and dynamic characteristics of amorphous networks (see examples in Refs [27, 28]).

The structural transformations in crystals at sufficiently low temperatures (the martensite transitions to the crystal phase or solid-phase amorphization) are associated, as a rule, with the appearance of soft modes in the phonon spectrum, i.e. with the approach to the lattice instability line (spinodal) [29]. The softening of the shear modulus of the amorphous phases prior to the transformation is indicative of analogous dynamic mechanisms. However, the scatter in local (on an atomic-size scale) geometric and dynamic characteristics should give birth to the scatter in the pressure (or the temperature) of local spinodals for local-order rearrangement, the localized nature of soft phonon modes also being caused by the disordered structure.

As is easy to see, the features of transitions between amorphous phases in SiO₂, GeO₂, and H₂O can be described when the distribution of local spinodals and the corresponding pressures for local coordination rearrangements are taken into account. In particular, by analogy with spin glasses, the logarithmic relaxation (Fig. 2c) should be associated with the uniform spectrum of activation energies of local rearrangements [30]. We believe [24] that the distribution of local spinodals of the amorphous phase is determined primarily by the atomic-scale stress tensor [31]. The question of the number of atoms involved in soft modes remains a question of crucial importance. Computer simulations [32] show that the structural compaction of the a -SiO₂ network proceeds as a series of discrete rearrangements involving about 10 atoms.

The distinctions between the $lda \rightarrow hda$, $hda \rightarrow lda$ transitions and the transformations in oxide glasses are naturally related to the local-order specificity of the corresponding phases and the salient features of the distribution of local dynamic characteristics. One would expect the existence of an interrelation between the features of the phonon spectrum of amorphous phases and their behavior under pressure. In particular, under compression the lda phase of ice behaves (prior to the coordination transition) similarly to the $1h$ crystal modification, i.e. like a topologically rigid tetrahedral network. This corresponds to the virtual absence of low-energy excitations (two-level states) in the spectrum of lda ice [33]. That is, being geometrically rigid at standard pressures, the tetrahedral network of lda ice remains topologically stable up to the onset of transformation. The a -SiO₂, a -GeO₂ glasses and the hda phase of ice, on the contrary, respond to pressure like soft networks, which conforms with a tangible density of low-energy two-level states [33].

For the description of coordination transitions in amorphous networks, primarily of the soft type, the conception of percolation of soft phonon modes is highly fruitful. Consider, for instance, the temperature-induced $hda \rightarrow lda$ transition. There occur successively a softening of the shear modulus early in the process, then a softening of the bulk modulus, and only then the onset of significant volume variation (Fig. 3). This behavior should be observed if the structure rearrangement is governed by the softening of an angular interaction between pairs of adjacent bonds.

Indeed, an isolated soft mode (a 'soft angle' contained by two bonds) directly contributes to a decrease of the shear modulus, whereas increasing compressibility necessitates the formation of three-dimensionally organized groups of 'soft

angles' in the vicinity of certain atoms, i.e. an increase in the density of soft modes. In order for the transformation (i.e. volume variation) to commence, a still higher density of soft modes is required, when soft clusters are formed of several atoms.

Therefore, consideration of the distributions of geometric and dynamic atomic characteristics is an adequate way to describe the nature of amorphous solids and their response to pressure. Taking into consideration the local nature of soft phonon modes and spinodals in disordered networks makes it possible to account for the specific features of coordination transformations in amorphous phases under pressure. At the same time, the general rules which associate the geometry of an amorphous network and the bond type with the character of the transformation (including crystallization) have hardly been formulated thus far.

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