RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 50, NUMBER 14 1 OCTOBER 1994-II

Glass-forming tendency, percolation of rigidity, and onefold-coordinated atoms in covalent networks

P. Boolchand
Department of Electrical and Computer Engineering, University of Cincinnati, Cincinnati, Ohio 45221-0030

M. F. Thorpe
Physics and Astronomy Department, and Center for Fundamental Materials Research,
Michigan State University, East Lansing, Michigan 48824-1116

(Received 22 February 1994)

A three-dimensional covalent network of N atoms possessing a fraction (n_r/N) of r-fold-coordinated atoms will, in general, display percolation of rigidity at an average coordination number $\langle r\rangle = 2.4 - 0.4(n_1/N)$, where n_1/N represents the fraction of onefold-coordinated atoms. As an example, we show how these ideas can elucidate the glass-forming region in the Ge-S-I ternary system.

For a covalent network constrained by bond-stretching (α) and bond-bending (β) forces, a mechanical critical point exists when the number of constraints per atom (n_c) equals the dimensionality or degrees of freedom (n_d) of the space in which it is embedded.

$$n_c = n_d . \tag{1}$$

This general condition, enunciated by Phillips[1] nearly fourteen years back, has stimulated considerable interest in glass science. This condition is satisfied exactly in some of the best glass formers in nature such as As_2Se_3 and SiO_2. In SiO_2 the β constraint associated with O atoms is apparently broken as revealed by experiments[2] and this ensures $n_c = n_d$. Equation (1) is thought to describe the formation of optimally polymerized networks.[1] One of us recognized that the glass condition (1) can be cast in the language of percolation theory. Specifically, it was shown that for covalent networks in which the N atoms chemically bond with coordination numbers greater than or equal to 2, the number of zero frequency modes $F = N(n_d - n_c)$ vanishes when the average coordination number $\langle r\rangle$ increases to 2.40.

$$\langle r\rangle = 2.40. \tag{2}$$

The character of a covalent network undergoes a qualitative change[3] from being easily deformable at $\langle r\rangle < 2.40$ to being rigid at $\langle r\rangle > 2.40$. The predictive power of these basic ideas has stimulated experimental work to look for such a threshold in a variety of physical properties in glasses. Discontinuities in floppy modes[4] detected by inelastic neutron scattering[5] and Lamb-Mössbauer factors,[6] further discontinuities in other observables such as Mössbauer site-intensity ratios,[6] activation energies[7] for viscosity and enthalpy relaxation near T_g, specific heat[7] jumps at T_g and Raman A_1 vibrational mode frequencies[8] in ternary Ge-As-Se glasses and liquids, all have been observed to occur close to $\langle r\rangle \simeq 2.40$. In covalent glassy networks indicated above which do not contain onefold-coordinated atoms (OFC atoms), the experimental evidence is in general agreement with the prediction of Eq. (2), although not without some exceptions.[9]

Within the context of network glasses which represent a metastable system in structural arrest, vector percolation has been used to describe elastic behavior[3] of glasses in terms of rigidity. Specifically, networks possessing twofold- and higher-fold-coordinated atoms are successfully[3] handled by Eq. (2). However, OFC atoms which interrupt network connectivity are specifically excluded in Eq. (2). Such atoms in a glassy network have been considered to be ineffective[3,10] percolatively and therefore unimportant. For this reason, one can remove onefold-coordinated atoms to form a "plucked network" as in previous discussions of H in a-Si networks,[10] H in a-C networks[11] and recently H in a-Ge-Si alloys.[12] For example, presence of H in a-Si network degrades the mechanical properties of the network (e.g., elastic moduli, hardness). Dangling bonds can be systematically eliminated[3,10–12] from the complete network and then standard counting procedures applied to the plucked network. However, we have found it more instructive to consider the complete network and explicitly treat onefold-coordinated atoms in the counting of constraints. This leads to a result with a correction term explicitly due to OFC atoms. In this paper, we look at the effect of such atoms on the glass-forming tendency.

Let us consider a three-dimensional-covalent network consisting of N atoms with n_r of these possessing a coordination number of r. For an atom having $r \geq 2$, one has $r/2$ α constraints and $2r-3$ β constraints (as discussed earlier[3]), while for an atom possessing $r=1$, there is $\frac{1}{2}$ of an α constraint but no β constraints. The total number of constraints can then simply be enumerated as

$$n_c = \left[n_1(1/2) + \sum_{r \geq 2} n_r(r/2 + 2r - 3) \right] \bigg/ N . \tag{3}$$

The number of zero frequency modes per atom F/N is given by

$$F/N=n_d-n_c=3-\left[(1/2)(n_1/N)+\sum_{r\geq 2}(5r/2)(n_r/N)-\sum_{r\geq 2}3(n_r/N)\right] \qquad (4)$$

$$=3-\left[(1/2)(n_1/N)+\sum_{r\geq 1}(5/2)(rn_r/N)-(5/2)(n_1/N)-\sum_{r\geq 1}3(n_r/N)+3(n_1/N)\right] \qquad (5)$$

$$=6-(5/2)\langle r\rangle-n_1/N \qquad (6)$$

where $\langle r\rangle=\Sigma_{r\geq 1}rn_r/N$ and $\Sigma_{r\geq 1}n_r/N=1$. The general condition for onset of rigidity occurs at

$$\langle r\rangle=2.4-0.4(n_1/N) \qquad (7)$$

when one requires F to vanish. This brings us to the central result of the present work. This exact result is also obtained in the plucked network upon requiring $\langle r\rangle'=2.40$, where $\langle r\rangle'=[\langle r\rangle-2(n_1/N)]/(1-n_1/N)$ is the average coordination number of the plucked network. The plucked network thus also incorporates the effect of OFC atoms in the complete network but only close to the rigidity percolation threshold.

At the outset we observe that the present result of Eq. (7) goes over to the familiar result of Eq. (2) due to He and Thorpe[3] when a covalent network does *not* contain OFC atoms ($n_1=0$). More significantly, the present result highlights the role played by such atoms in contributing to the rigidity of a network. Specifically, the additional term $-0.4(n_1/N)$ suggests that, in general, the rigidity percolation threshold depends explicitly on the concentration of the onefold-coordinated atoms in a network. These ideas can be put to a quantitative test in real glasses as we comment next.

Bulk glasses in the Ge-S-I ternary system can be formed by a fast quench over a wide composition (region II) as shown in the phase diagram of Fig. 1, taken from the work of Dembovskii, Krilenko, and Buslaev.[13] Noteworthy in the phase diagram is region I, where glass formation occurs even upon slow cooling the melts at a rate of 2 °C/min. The general shape of region I, where glass formation is apparently optimized, can be understood in terms of ideas developed above where OFC atoms are considered explicitly. Let us consider a $\mathrm{Ge}_x\mathrm{S}_{1-x-y}\mathrm{I}_y$ ternary, in which Ge, S, and I atoms bond in conformity to the $8\text{-}\mathcal{N}$ rule and possess a coordination number r of 4, 2, and 1, respectively. For a given Ge concentration x, one can obtain the critical iodine concentration $y=y_c$, at which the glass condition (1) in this ternary is satisfied exactly. This requires the average coordination number $\langle r\rangle$ of the network to satisfy Eq. (7), i.e.,

$$\langle r\rangle=4x+2(1-x-y_c)+y_c=2.4-0.4y_c$$

$$\text{or } y_c=(10x-2)/3. \qquad (8)$$

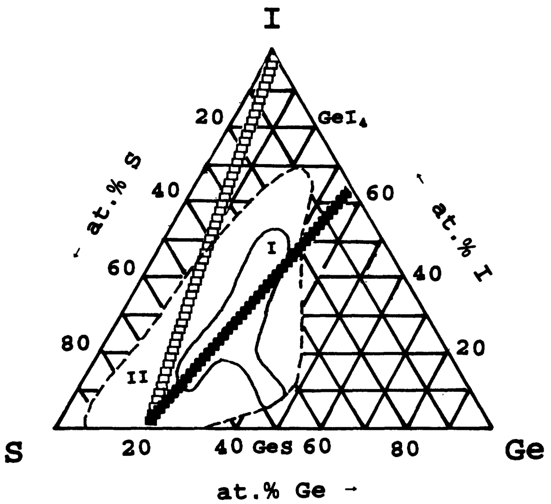

FIG. 1. Glass formation in the Ge-S-I ternary as determined by Dembovskii, Kirilenko, and Buslaev (Ref. 13). Region I: glasses formed by slow (2 °C/min) cooling. Region II: glasses formed by fast (water-quench) cooling. The optimum glass-forming compositions including corrections for the onefold-coordinated I atoms using Eq. (8) is shown by filled squares and incorrectly using Eq. (9) by open squares.

In Fig. 1, the filled square pathway represents a plot of Eq. (8). It is remarkable that this calculated trend, which has *no adjustable parameters*, reproduces the principal features of glass formation in region I. Specifically in the center of the phase diagram (Fig. 1), note that the filled square pathway nicely overlaps with the glass forming tendency in region I. We also observe that the filled square pathway extends outside the glass-forming region towards higher Ge and I concentration. At higher ($y_c>0.40$) iodine concentrations, Raman scattering results[14] provide signature of monomeric GeI_4 units appearing in these glasses. Such units do not contribute to network formation. Their appearance most likely provides the reason for the deviation in the maximum iodine concentration to which glass formation can occur between the predicted ($y_c=0.62$) value, based strictly on mechanical effects [Eq. (8)] and the observed value ($y_c\simeq 0.55$), which clearly includes chemical (or enthalpic) effects as well. Refinements to the theory to include such effects and further investigations of the phase diagram (Fig. 1) region I near the composition GeS are ongoing. Glass formation in this ternary appears to be qualitatively promoted along the filled square pathway because the network is optimally constrained and can polymerize with minimal accumulation of strain.

On the other hand, if we completely exclude OFC atoms (I atoms) in the count of constraints to determine the composition of a $\mathrm{Ge}_x\mathrm{S}_{1-x-y}\mathrm{I}_y$ glass network at which the glass-forming tendency is optimized, then we must require Eq. (2) to be fulfilled as follows:

$$\langle r\rangle=[4x+2(1-x-y_c)]/(1-y_c)=2.4$$

$$\text{or } y_c+5x=1. \qquad (9)$$

The open square pathway (Fig. 1) is a plot of Eq. (9). This pathway exhibits *no overlap* with region I. Thus, the lack of any overlap between region I and the prediction of Eq. (9) which explicitly *excludes* OFC atoms on the one hand, and the clear overlap between region I and the prediction of Eq.

(8) which explicitly *includes* the effect of OFC atoms on the other, underscores in no uncertain terms the qualitative importance of including constraints due to I atoms in describing the glass-forming tendency in the Ge-S-I ternary. The prediction of Eq. (8) would apply directly to many other ternaries such as Ge-Se-I, Si-S-I, etc. in the IV-VI-VII family of glasses. The present ideas can also be extended to include other ternaries like As-S-I, Sb-S-I in the V-VI-VII family of glasses.

The constraints counting arguments developed to include OFC atoms [Eq. (6)] yield a result, which will stimulate an understanding of the mechanical behavior of covalent networks containing such atoms. Specifically, one can use present ideas to understand vibrational density of states, mechanical hardness, elastic constants and Lamb-Mössbauer factors, in hydrogenated or fluorinated group IV semiconductors (such as Si and diamond), and IR transmitting glasses based on Te-chalcohalides (Te_3Br_2). These represent some examples of covalent networks containing a significant fraction of OFC atoms.

In conclusion, we have examined the role of OFC atoms in determining the mechanical equilibrium of covalent networks using constraint theory. The rigidity percolation threshold is shown to occur generally at $\langle r\rangle = 2.40 - 0.4(n_1/N)$, where n_1/N represent the fraction of onefold-coordinated sites. This exact result should be of broad interest in understanding the role of alloying monovalent atoms on physical properties of network glasses.

It is a pleasure to acknowledge discussions with several colleagues including A. Angell, B. Goodman, D. McDaniel, J. C. Phillips, M. Tamor, and M. Zhang. This work was supported by NSF Grants Nos. DMR 90-24955, DMR 92-07166, and CHE 92-24102.

---

[1] J. C. Phillips, J. Non Cryst. Solids **34**, 153 (1979); **43**, 37 (1981).

[2] Richard Zallen, *The Physics of Amorphous Solids* (Wiley, New York, 1983), p. 72; also see R. L. Mozzi and B. E. Warren, J. Appl. Cryst **2**, 164 (1969); P. J. Bray and M. L. Lui, in *Structure and Bonding in Noncrystalline Solids*, edited by G. E. Walrafen and A. G. Revesz (Plenum, New York, 1983), p. 285.

[3] M. F. Thorpe, J. Non Cryst. Solids **57**, 355 (1983); H. He and M. F. Thorpe, Phys. Rev. Lett. **54**, 2107 (1985).

[4] Y. Cai and M. F. Thorpe, Phys. Rev. B **40**, 10 535 (1989).

[5] W. A. Kamitakahara, R. L. Cappelletti, P. Boolchand, B. Halfpap, F. Gompf, D. A. Neumann, and H. Mutka, Phys. Rev. B **44**, 94 (1991).

[6] P. Boolchand, R. N. Enzweiler, R. L. Cappelletti, W. A. Kamitakahara, Y. Cai, and M. F. Thorpe, Solid State Ionics **39**, 81 (1990); W. Bresser, P. Boolchand, and P. Suranyi, Phys. Rev. Lett. **56**, 2493 (1986).

[7] M. Tatsumisago, B. L. Halfpap, J. L. Green, S. M. Lindsay, and C. A. Angell, Phys. Rev. Lett. **64**, 1549 (1990).

[8] K. Murase and T. Fukunaga, in *Defects in Glasses*, edited by F. L. Galeener, D. L. Griscom, and M. J. Weber, MRS Symposia Proceedings No. 61 (Material Research Society, Pittsburgh, 1986), and references therein.

[9] K. Tanaka, Phys. Rev. B **39**, 1270 (1988).

[10] G. H. Dohler, R. Dandoloff, and H. Bilz, J. Non. Cryst. Solids **42**, 87 (1980).

[11] J. C. Angus and F. Jansen, J. Vac. Sci. Tech. A **6**, 1778 (1988); M. A. Tamor, W. C. Vassell, and K. R. Kertner, Appl. Phys. Lett. **58**, 592 (1991).

[12] N. Mousseau and M. F. Thorpe, Phys. Rev. B **48**, 5172 (1993).

[13] S. A. Dembovskii, V. V. Kirilenko, and Ju A. Buslaev, Izv, Akad. Nauk USSR, Neorg, Mat. **7**, 328 (1971).

[14] L. Koudelka and M. Pisarcik, J. Non. Cryst. Solids **113**, 239 (1989).