PHYSICAL REVIEW B VOLUME 60, NUMBER 17 1 NOVEMBER 1999-I

Unified approach to the constraint counting theory of glasses

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(Received 8 April 1999)

An approach to the constraint counting theory of glasses is applied to many glass systems which include an oxide, chalcohalide, and chalcogenides. In this, shifting of the percolation threshold due to noncovalent bonding interactions in a basically covalent network and other recent extensions of the theory appear natural. This is particularly insightful and reveals that the chemical threshold signifies another structural transition along with the rigidity percolation threshold, thus unifying these two seemingly disparate toplogical concepts. [S0163-1829(99)11441-3]

Phillips, who pioneered the constraint counting theory[1] (CCT), formulated the optimum condition for glass formation,

$$n_{co}=n_d\,, \tag{1}$$

where n_{co} includes the bond stretching and bond bending constraints acting on an atom and n_d the degrees of freedom available to it. Cast in the language of the percolation theory[2], the above condition is achieved for a covalently bonded random network at a mean coordination number of atoms, $\langle r\rangle_c=2.4$, known as the rigidity percolation threshold (RPT): the rigidity of the network sharply increases at this juncture and continues the trend for higher $\langle r\rangle$. Recently, these ideas have been further extended to understand the glass formation of chalcohalides[3,4] which contain one fold coordinated atoms and oxides in which the chalcogen bond angle constraints are broken.[5] Prior to these developments, a threshold had been predicted at $\langle r\rangle=2.67$ based on the chemically ordered covalent network (COCN) model, called the chemical threshold[6] (CT). At the CT, the system achieves maximum chemical ordering as the bonding becomes completely heteropolar. Tanaka, based on the dimensionality arguments of Zallen,[7] considered the CT as nothing but another structural transition from two dimensions (2D) to (3D) and $\langle r\rangle=2.4$ as the transition from 1D to 2D structure.[8] These thresholds have been discerned by experiments on many glass systems especially those which contain chalcogens[9,10] (S,Se,Te) and are of contemporary interest.[11]

In this article, through numerous examples, we show that all the above ideas can be understood in a single, elegant, framework and are unified. The main features of this framework are derived from the version of Döhler *et al.*[12] of CCT and initially we show that all the subsequent extensions[4,5] of Phillip's CCT, to understand the shifting of $\langle r\rangle_c$ to higher and lower values of the mean-field result of 2.4, are simple applications of the approach enunciated thereof. Recently, electrical switching studies were performed on Te-based glasses mostly containing aluminum (Al-Te,[13] Al-As-Te,[14] Al-Ge-Te,[15] Ge-As-Te[10]) and topological thresholds discerned. The attempt here to understand the thresholds in these systems has yielded some very remarkable results. By considering the Al-Te system first, we reiterate the way to consider ionic interactions in a basically covalent network. In Al-Ge-Te and Al-As-Te perhaps for the first time it is shown that a chemical threshold can be described by CCT. The chemical thresholds in these systems are confirmed by a simple chemical bond approach. The success of CCT is reflected when the compositional pathways belonging to the optimal glass forming tendency pass right through the separated, low- and high-arsenic content glass forming regions in the Ge-As-Te glass system. Finally, the parameters on which the RPT in a glass system would depend on are identified.

The philosophy of Eq. (1) is that a ''good'' glass should be rigid mechanically and at the same time strain free: less than $\langle r\rangle_c$ the network is under constrained (floppy) and greater than $\langle r\rangle_c$ it is over constrained (rigid). A shift in $\langle r\rangle_c$ to higher values occurs when the constraints are not enough to match the degrees of freedom at the mean-field value of $\langle r\rangle_c=2.4$. In simple terms, the approach of Döhler *et al.* views the nonobservance of the mean-field result as due to the modification of the embedding dimension (n_d) whereas others consider this as due to the changes in the constraints (n_{co}) acting on the atoms. An important assumption of CCT is that the covalent bonds network the atoms. This breaks down as the covalent interactions are marred by the presence of electronegative chalcogen Te atoms and the electropositive Al, Na atoms in the systems of interest here. Ionic interactions between atoms, since they are not directional, reduce the angular constraints on them. In other words, the polarizing ability of the atoms acts as additional internal degrees of freedom which modify the embedding dimension to $n_\delta=n_d+n_i$, where n_i represents the internal degrees of freedom.

Döhler *et al.* modified Philip's CCT by considering the fact that (n_d+1) angles in the n_d dimensions are not linearly independent[12] and gave the following formulas for counting the number of constraints (n_{co}) which depends on coordination number (r) and degrees of freedom (n_d):

$$n_{co}(r,n_d)=(r/2)+(1/2)r(r-1),\quad r<n_d-1, \tag{2a}$$

$$n_{co}(r,n_d)=(r/2)+(1/2)(n_d-1)(2r-n_d),\quad r>n_d-1. \tag{2b}$$

The mean coordination number of a two-component system A_xB_{1-x} is given by

$$\langle r\rangle=xr_A+(1-x)r_B\,, \tag{3}$$

and the number of constraints per atom in it is

$$n_{co}(A_xB_{1-x}) = xn_{co}(r_A) + (1-x)n_{co}(r_B). \quad (4)$$

Equations (3) and (4) can be generalized for systems with a greater number of components. To illustrate the efficacy of this approach, we consider a chalcohalide ($Ge_xS_{1-x-y}I_y$) ternary system[4] and an oxide[5] [$(Na_2O)_x(TeO_2)_{1-x}$], in which optimum glass forming compositions were recently predicted using the equation $\langle r\rangle_c = 2.4 - 0.4(n_1 - m_2)/N$. The above equation, which is based on the vector percolation model, includes correction terms to account for the additional constraints due to the presence of one fold-coordinated iodine atoms ($-0.4n_1/N$) and reduced constraints on the two fold-coordinated oxygen atoms ($+0.4m_2/N$).

In the $Ge_xS_{1-x-y}I_y$ system, r and n_{co} [Eq. (2)] for Ge, S, and I, when n_d is 3, are (4 and 7), (2 and 2), and (1 and 1/2), respectively. Using Eq. (4), n_{co} $(Ge_xS_{1-x-y}I_y) = 7x + 2(1 - x - y_c) + (1/2)y_c$. Based on condition (1), $y_c = (10x - 2)/3$. The optimum glass forming composition pathway (y_c) is obtained thus, which is as predicted.[4]

We now calculate the optimum glass composition in the oxide $(Na_2O)_x(TeO_2)_{1-x}$. The r and n_{co} for Na, O, and Te, when n_d is 3, are (1 and 1/2), (2 and 2), and (4 and 7), respectively:

$$n_{co}[(Na_2O)_x(TeO_2)_{1-x}] = (1/2)2(x_c/3) + 2(2-x_c)/3 + 7(1-x_c)/3. \quad (5)$$

Using Eq. (1), we get $x_c = 0.25$ which is higher than the expected value[5] of 0.20. The following arguments will set the trend for all future discussions in this article. Sodium, which is electropositive, with its polarizing ability enables the bond angle between Te-O$^-$-Na$^+$ to relax. The polarizability of Na is hence here considered as another degree of freedom and the total degrees of freedom for a Na atom increases to 4 from 3. Consequently, the embedding dimension is modified to $n_\delta = (3+1)(2x_c/3) + 3(2-x_c)/3 + 3(1-x_c)/3$. Condition (1) now becomes

$$n_{co} = n_\delta, \quad (6)$$

and the result $x_c = 0.20$ is arrived at using Eqs. (5) and (6) which again exactly reproduces the result obtained earlier.[5]

Attention is now drawn towards some chalcogenide glass systems. Electrical switching studies undertaken on them have yielded very interesting results which include composition dependent crossover from memory to threshold switching behavior[14] and modified percolation thresholds. In this work we are mainly concerned with tackling the latter. The electrical switching phenomenon observed in chalcogenide glasses had been successfully used as a tool to characterize the topological thresholds in them: the switching field (E_c) sharply varies around these thresholds. E_c for a glass is the critical field at which it switches from a lower conducting state to a higher conducting state. The switching field is modulated by the atomic network topology and the arrows in Fig. 1 indicate the thresholds. The variation of E_c with composition for chalcogenide glass systems is discussed in Refs. 10 and 16. Presently, the thresholds observed in Al-based chalcogenide glasses are understood, with the help of CCT. Subsequent discussions in this article involve the elements Al, Ge, As, and Te whose r's are assumed to be 4, 4, 3, and 2, respectively. The constraints acting on them are 7, 7, 9/2, and 2, respectively, with n_d as 3 [Eq. (2)]. Initially, we consider the binary Al_xTe_{1-x}, for which percolation threshold was observed[13] at $x = 0.23$ ($\langle r\rangle = 2.46$). The total number of constraints $n_{co}(Al_xTe_{1-x}) = 7x + 2(1-x)$ and $n_\delta = (3+1)x + 3(1-x)$, assuming an extra degree of freedom for the polarizability[17] of aluminum. Applying Eq. (6), we get $x = 0.25$ ($\langle r\rangle = 2.50$).

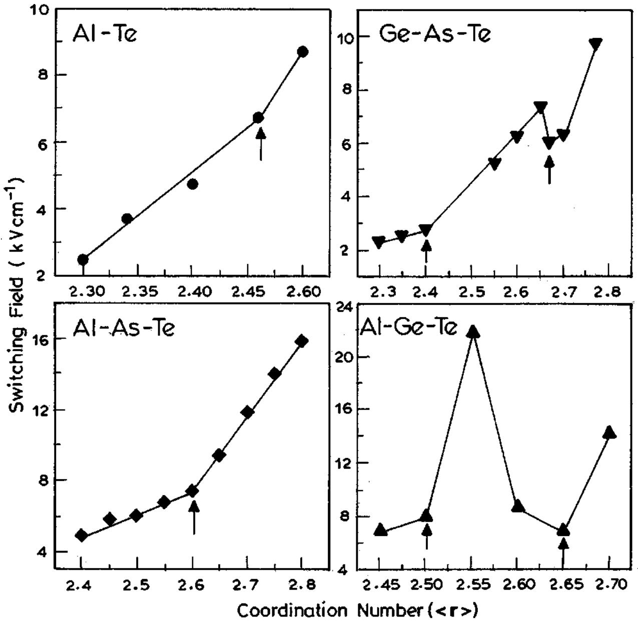

FIG. 1. Dependence of E_c with $\langle r\rangle$ in some glass systems discussed in the text.

In $Al_{0.2}Ge_xTe_{0.8-x}$, E_c registers sharp changes at $\langle r\rangle = 2.5$ and 2.65 (Fig. 1). The total constraint acting on this system is

$$n_{co}(Al_{0.2}Ge_xTe_{0.8-x}) = 7(0.2) + 7x_c + 2(0.8-x_c). \quad (7)$$

The embedding dimension is modified as before by associating an internal degree of freedom with aluminum, to account for its polarizability. Thus, $n_\delta = (4)0.2 + 3x_c + 3(0.8-x_c)$. When Eq. (7) and n_δ are plugged into Eq. (6), we get $x_c = 0.04$ ($Al_{0.20}Ge_{0.04}Te_{0.76}$) or $\langle r\rangle_c = 2.48$, which is quite close to the experimental value. The bond angle between Ge-Te-Al relaxes due to the dipolar distortion brought about by the electropositive Al which results in the shift in the RPT to 2.48.

The threshold around $\langle r\rangle = 2.67$ has long been recognized as the chemical threshold at which the bonds in the glass system are completely heteropolar.[6] Through a simple calculation, we will confirm this, following a chemical bond approach. In the Al-Ge-Te system, the bond strengths of Ge-Te $>$ Al-Te $>$ Te-Te,[18] which is also the order in which the bonds are formed. Heteropolar bonds alone would be present when the valence requirements of Te are exactly met by Ge and Al. The composition x_c at which this would occur is given by the following equation: $2(0.8-x_c) = 4(0.2) + 4x_c$ which gives $x_c = 0.13$ ($Al_{0.2}Ge_{0.13}Te_{0.67}$) or $\langle r\rangle_c = 2.67$.

The same result is obtained using CCT by assuming an internal degree of freedom for Te. For $\langle r\rangle<2.67$ it is clear from the above calculation that Te homopolar bonds are prevalent. Te-Te bonds, owing to their lesser bond strength, also because of their lone pair interactions, are easily excitable and hence the bond angles between them are not rigidly positioned, justifying the additional degree of freedom for Te. Thus the modified $n_\delta=3(0.2)+3x_c+(4)(0.8-x_c)$. Substituting n_δ and n_{co} from Eq. (7) in (6), we get $x_c=0.13$ or $\langle r\rangle=2.67$. This result is a significant one because for the first time CCT has been used to describe the chemical threshold and, hence, this transition can also be considered as another RPT in the system. This gives credence to Tanaka's contention[8] that $\langle r\rangle=2.67$ signifies a structural phase transition at which the network dimensionality (D) changes from 2 to 3, whereas at $\langle r\rangle=2.4$, it is a structural change from $D=1$ to 2. The dimensionality of the network is the number of dimensions in which the covalently bonded molecular unit is macroscopically extended.[7]

Focus now shifts to the $Al_{0.2}As_xTe_{0.8-x}$ system in which only one threshold is observed contrary to ''expectations,'' at $\langle r\rangle=2.60$ (Fig. 1). This belies our expectations because systems with more than two components are specifically chosen to realize the two thresholds.[10] What do we assosciate this threshold with, the RPT or CT? The clue is provided by the binary As_xTe_{1-x} system[16] in which the RPT and CT are supposed to coincide[19] at $x=0.4$.

In the $Al_{0.2}As_xTe_{0.8-x}$, the bond strengths are interesting, with As-As>As-Te>Al-Te and so on.[18] As before we check for chemical ordering, with crucial adjustments which take into account the formation of As homopolar bonds ahead of others. Of the $3x$ bonds involving As, x of them would form As-As bonds and the remaining $2x$ along with Al bonds form heteropolar bonds with Te at x_c given by the following equation: $2(0.8-x_c)=4(0.2)+(3x_c-x_c)$. That is, $x_c=0.2$ ($Al_{0.2}As_{0.2}Te_{0.6}$) or $\langle r\rangle_c=2.60$, a stunningly accurate result. The knowledge gained from applying CCT to understand the chemical threshold in $Al_{0.2}Ge_xTe_{0.8-x}$ suggests that perhaps again assuming Te to possess an additional degree of freedom would lead us to the result n_{co} ($Al_{0.2}As_xTe_{0.8-x}$) $=7(0.2)+(9/2)x_c+2(0.8-x_c)$ and $n_\delta=3(0.2)+3(x_c)+(4)(0.8-x_c)$. Condition (6) yields $x_c=0.23$ ($Al_{0.2}As_{0.23}Te_{0.57}$) or $\langle r\rangle_c=2.63$.

A pattern has emerged. In the literature there are many instances when chalcogenide glasses containing Ge (e.g., Ge-Se, Ge-As-Se) show both thresholds clearly[20] and chalcogenide glasses containing As (e.g, As-Se,[19] As-Te[16]) only one. This fact seems to be much more universal than the actual coordination number at which these thresholds occur: one threshold occurs at $\langle r\rangle=2.4\pm0.1$ and another at $\langle r\rangle=2.7\pm0.1$. As mentioned earlier, the first threshold signifies a transition from $D=1$ to a $D=2$ layered structure and the second threshold represents a transition from $D=2$ to $D=3$. This means that in As_xTe_{1-x} and $Al_{0.2}As_xTe_{0.8-x}$ systems, say, a layered structure is acheived but a 3D structure is not evolved yet. This probably is because the homopolar bond concentration increases with As which rather leads to fragmentation.

These ideas could be put on a firmer footing when we consider the glass system in which both Ge and As are present and that is the $Ge_{0.075}As_xTe_{0.925-x}$ glass system, in which thresholds were observed at $\langle r\rangle=2.4$ and 2.67 through electrical switching studies (Fig. 1). As before we apply CCT to this system:

$$n_{co}(Ge_{0.075}As_xTe_{0.925-x})=7(0.075)+(9/2)x_c+2(0.925-x_c). \qquad (8)$$

When the embedding dimension is 3, condition (1) yields $x_c=0.25$ ($Ge_{0.075}As_{0.25}Te_{0.675}$) or $\langle r\rangle_c=2.4$. Although As is a component, the bond strength of Ge-Te, which is 456 $\mathrm{kJ\,mol^{-1}}$, is greater than the As-As bond strength of 382 $\mathrm{kJ\,mol^{-1}}$ and hence, heteropolar bonds are formed first. This helps in polymerization (contrary to the situation when homopolar bonds are more probable) and the second structural phase transition is made possible, which will be confirmed by CCT soon. As before we calculate the composition at which the Te valence requirements are satisfied by Ge and As, giving leeway to the formation of As-As bonds as follows. That is, $2(0.925-x_c)=(3x_c-x_c)+4(0.075)$ and hence $x_c=0.39$ ($Ge_{0.075}As_{0.39}Te_{0.535}$) or $\langle r\rangle_c=2.54$. No sharp changes in the switching fields occur about this composition. It may be recalled that in the Al-based glasses considered above, chemical ordering coincided with one of the percolation thresholds. Perhaps chemical ordering on its own does not dramatically influence the switching field.

Presently, we will compute the composition at which a second threshold would be observed. Experimentally, it is found to occur at $\langle r\rangle=2.67$. Among the constituents Te is the biggest and the most electronegative. Consequently, the electronic distribution around Te would lead to a dipolar distortion of the network and a van der Waals interaction between the layers would result. So we assosciate two internal degrees of freedom with Te atoms, one for electronic polarization and another for the van der Waals bond.[12] The modified dimension is thus $n_\delta=3(0.075)+3x_c+(5)(0.925-x_c)$. Now again by condition (6) and using Eq. (8) we arrive at $x_c=0.55$ or $\langle r\rangle_c=2.70$. Figure 2 shows the compositional pathways in $Ge_yAs_xTe_{1-x-y}$ obtained by generaliz-

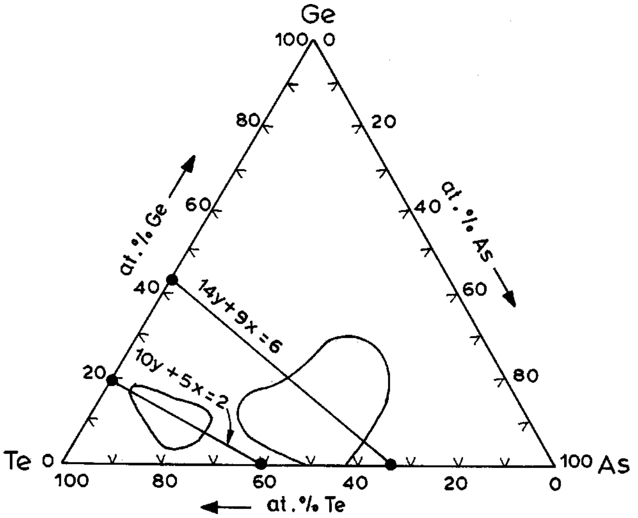

FIG. 2. The ternary phase diagram of the Ge-As-Te glass system with the compositional pathways corresponding to the first and second thresholds, passing through the center of the well-separated glass forming regions.

ing the above arguments. *The description of both the thresholds by CCT brings about a qualitative improvement in the description of ternary glass phase diagrams* which is being discussed in a forthcoming article. In Al-based glasses, we did not consider the electronic polarization and van der Waals bonding, engendered by Te atoms, as effects due to the presence of electropositive Al atoms, it is believed would ‘‘shield’’ or overwhelm them.

Before we conclude, some general remarks on the calculations are in order, as they are based on some heuristic arguments. The RPT is a function of the coordination number of the constituent atoms and the extra internal degree of freedom of the constituents (e.g., polarizability). CCT as proposed by Phillips considers only short-range interactions.[1] But it is clear from the present study that the long-range interaction influences the D and will have to be included. Thus, RPT $=\mathrm{RPT}(r,n_i,D)$. This equation gives physically meaningful results only for unique values of the variables. For example, in the present context when Al is assumed to have a coordination different from 4 and or when As is associated with an internal degree of freedom, physically meaningless results are obtained. Assuming an r of 4 and n_i of 1 for aluminum, in the $\mathrm{Al_{0.2}As}_x\mathrm{Te}_{0.8-x}$ and $\mathrm{Al_{0.2}Ge}_x\mathrm{Te}_{0.8-x}$ systems, $\langle r\rangle_c=2.48$ is obtained, theoretically. This threshold is experimentally confirmed only in the latter and that is because the D in the two systems are different which is due to the contrasting bonding arrangements, as discussed earlier. Further, there are other interesting features such as the maximum at $\langle r\rangle=2.55$ in Al-Ge-Te (Fig. 1), apart from the topological thresholds which we were seized off up until now. Naively speaking, at $\langle r\rangle=2.55$ the reign of the rigidity effect ends and that of chemical ordering begins and, mathematically, it is possible to show that the network is optimized, using the present approach, by suitably modifying the embedding dimension. But better physical insights are necessary to understand them more.

Another important feature in this article is that the ‘‘contributions’’ to a threshold are considered as solely due to a particular element. Al, which has a fixed concentration throughout mainly bonds with Te and hence, their contributions to the first threshold are linked, whereas the constraints on Te, since it bonds with both Ge and Al, is matched only at the second threshold in the Al-Ge-Te glass system. So the Al atoms are rigidly positioned in relation to the other atoms beyond $\langle r\rangle=2.50$, after which only the constraints on Te matter.

To summarize, in the present approach some of the recent extensions of CCT are naturally absorbed and the chemical threshold is described using CCT. This greatly improves our understanding of the glass forming regions in chalcogenide glasses.

It is a pleasure to acknowledge the helpful suggestions of E. S. R. Gopal and P. K. Thiruvikraman. We thank the Department of Science and Technology, Government of India, for financial support.

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