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Invited Lecture

Intermediate phases in binary and ternary alloys. How far can we go with a semi-empirical bond-constraint theory?

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This paper extends the scope of semi-empirical bond constraint theory, SE BCT, and uses it provide quantitative information relative the two transitions that bracket intermediate phases in binary and ternary alloys. Reversibility windows have generally been defined in terms of the average bonding coordination, r_c (N_{av}, <r>), and show considerable *scatter* between different systems when displayed in this way. This paper designates these transitions in terms of the average number of bonding constraints/atom, n_c (C_{av}), and provides important insights into the extent to which SE BCT can be augmented and improved by considering i) broken bond-bending constraints, as well as ii) longer range forces beyond 2-body bond-stretching and 3-bond-bending valence forces of the original formulation.

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1. Introduction

A significant number of important research results over the past 20-25 years have established important connections between i) local and atom-specific chemical bonding bond-constraints and ii) the formation of ideal defect free]bulk glasses and non-crystalline thin films. Significant newl ideas were introduced more than 25 years ago by Jim Phillips in two articles published in the Journal of Non-Crystalline Solids [1,2]. These papers proposed a semi-empirical bond constraint theory, SE BCT, that attempted to explain the ease of glass formation in several well-known and technologically important materials including As_2S_3 and SiO_2. SE BCT demonstrated that descriptions of non-crystalline solids using the mean-field atomic coordination or average number of bonds/atom, r_c ($N_{av,}$<r>), and the average number of valence bonding stretching and bending constraints/atom, n_c (C_{av}) provided a simple way to classify non-crystalline solids into good, and marginal or poor glass formers.

The mean-atomic coordination, r_c is simply obtained from the chemical formula, and the coordination of the constituent atoms in the covalent limit, and has been extended to ionic systems as well [3]. The bonding constraints in this mean-field description are 2-body bond-stretching forces, and the 3-body bond-bending forces [1], and are *counted* in the context of a conventional valence force field model [4]. If m is the atomic coordination, then the number of two-body bond-stretching constraints/atom is m/2, so that any given atom-pair has one bond-stretching constraint. The number of bond-bending constraints/atom is 2m-3 [1]. This applies exactly to 2-fold coordinated atoms such as O, S, Se and Te in predominantly covalent bonds. It also applies to 3-fold and 4-fold coordinated atoms in non-planar arrangements; e.g., P, As and Sb, and Si and Ge, in pyramidal and tetrahedral arrangements, respectively. For planar bonding such as N in Si nitride, Si_3N_4, and B in boroxol rings in B_2O_3, the number of bond-bending constraints is reduced from 2m-3 = 3, to m-1 = 2 [1].

For non-planar bonding of 3- and 4-fold coordinated atoms, an important relationship exists between n_c and r_c: n_c= 2.5 r_c - 3, however, this applies only in the limit of the *limited* 2- and 3-body force field identified above. None-the-less, this provides a simple criterion for identification of ideal glasses and thin films. An ideal glass or thin film covalent network, e.g., an As or Ge chalcogenide, is defined by the condition that n_c = 3, the number of degrees of freedom/atom in a 3-dimensional network, or equivalently, r_c = 2.4. However, it is not immediately obvious what *ideal* means in terms of other electronic, optical, or structural properties, properties other than glass formation by quenching from a melt.

This mean-field approach is also important in understanding the basis for different concentrations of bonding defects in chalcogenide and oxide glasses and thin films that show significant departures from SE BCT idealicity. *Ideal behavior* is defined with respect to low densities of intrinsic bonding defects, ~10^{10} cm^{-2} or 10^{15} cm^3, and stability with respect to property changes, such as the glass transition temperature, at ambient or elevated temperatures [4,5]. A value of r_c equal to the network dimensionality provides a criterion for ideal and relatively easy glass formation, e.g., for compounds such as

$As_2S(Se)_3$, as well as alloys such as $GeSe_4$. In this context, chalcogenide glasses, and thin films have bee organized into three different groups: i) *flexible (*also designated as *floppy* or under-coordinated with $r_c < 2.4$ and $n_c < 3$, ii) *ideal*, or optimally-coordinated with $r_c = 2.4$ and $n_c = 3$, and finally iii) *stressed rigid* or over-coordinated with $r_c > 2.4$ and $n_c > 3$. Glasses and thin films with n_c either << 3, or >> 3, generally contain significant concentrations of intrinsic bonding defects, which in many instances are in too high for device applications.

Intrinsic defect concentrations in stressed rigid regimes, $r_c > 2.4$, are expected to be proportional to $a+ b(r_c - 2.4)^2$, where the scaling parameters, a and b are empirically-determined [4,5]. This relationship is based on an assumption that bond-angle strain, , is directly proportional to $r_c - r_c$(ideal network) = $r_c - 2.4$, and that strain energy was therefore proportional to $(\quad)^2$ [4,5]. This assumes that bond-bending forces are substantially weaker than bond-stretching forces, so that strain build-up will result in bond angle changes or distortions. Since ideal glasses are still expected to have small densities of intrinsic bonding defects, this leads to the empirical relationship defined above, $D(r_c) = D_o + D_1(r_c - 2.4)^2$, where $D(r_c)$ is the density of intrinsic bonding defects, D_o is the residual density of defects in an ideal glass or thin film, and D_1 is the scaling parameter. In binary alloy systems such A_xB_{1-x}, e.g, A = As, P, Si, Ge, and B = O, S, Se and Te, D_o and D_1 are expected to be different for different bonding chemistries, different bonding coordination, and different bond-ionicities. Defects are also expected to be greater in under-coordinated or flexible glasses and films show the same general scaling properties, but the values of D_1 differ. There is another issue with respect to defect scaling that involves the rc scaling. It will demonstrated that n_c or C_{av} is a more appropriate metric for ideal behavior, and it is therefore desirable to recast defect scaling in terms of nc = 3, i.e., $D(r_c) = D_o + D_1(n_c - 3.0)^2$.

The transition between flexible (often, also designated as floppy) and stressed rigid glasses, e.g., Ge_xSe_{1-x}, which is expected to occur at $r_c = 2.4$ (x = 0.2), or equivalently, $n_c = 3$ was initially assumed to be abrupt based on Maxwellian theory [6], but this was shown generally not to be the case [7]. This extraordinary and unexpected result was based on the experiments of Boolchand and co-workers [8,9,10], but was first predicted by theory that went beyond the limits of a mean-field approximation [7].

This important extension of SE BCT has been studied experimentally by Boolchand and his co-workers [8,9,10] using two complementary techniques, Raman scattering spectroscopy, and reversibility of heat flow. Changes in the Raman scattering have been interpreted in terms of a transition between floppy and stressed rigid glass alloys in the Ge_xSe_{1-x} system that was not abrupt, but displayed a finite range of compositions in what has been designated as an *intermediate phase* or IP; i.e., intermediate between the floppy and stressed rigid compositional regimes that bracket the the IP with two separated transitions: floppy or flexible to rigid but not stress with IP, and rigid, but not stressed with the IP to stressed rigid. IP's was first identified by discontinuities in the frequencies of Raman active modes as a function of alloy composition and in the Ge_xSe_{1-x} system, these occurred between x ~ 0.18 to 0.2, or equivalently, the $GeSe_4$ alloy composition at which $r_c \sim 2.4$ and $n_c \sim 3$, and x ~ 0.26, at which $r_c \sim 2.5$ and $n_c \sim 3.4$.

Subsequent measurements have identified two other unanticipated and significant properties of these alloys with the IP regime; i) whereas many of the properties of glasses in both the floppy and stressed rigid regimes, e.g., the glass transition temperature, T_g, change or *age* with time, the same properties did not change over the same time periods for compositions within the IP [6,7], and ii) alloy compositions within the floppy and stressed rigid regimes displayed irreversible heat flow, or equivalently, energy dissipation, while alloys compositions with the IP exhibited reversible heat flow, or no energy dissipation. However, there was never an experimental demonstration that the compositions in the regime designated as flexible, indeed display *floppy* vibrations.

Most of the studies of the Boolchand group were directed toward chalcogenide alloy glasses, and many of the materials studied displayed significant differences in the compositional extent of the IP's when displayed as a function of the mean-coordination or r_c metric. This paper will provide a new way of addressing these differences that is qualitatively different, and more accord with the chemical bonding [8,9,10]. Before addressing this new perspective for defining the onset and extent of IP regimes, it is important to introduce the concept of symmetry determined broken bond-bending constraints as they apply to one of the IP regimes to be discussed. This is important because it puts the rc value of 2.4 in a more proper perspective; it losses its significance if i) bend-constraints are broken, the start of IPs that occur at values of $r_c > 2.4$, and ii) longer range additional forces are operative, e.g., forces related to repulsions associated both non-bonding lone pairs on both chemical constituents of an alloy, e.g,, As_xSe_{1-x}, where the first IP transition takes place close at ~2.9.

Broken constraints were first introduced to explain the glass forming properties of SiO_2. Based on bond, and bond constraint counting alone, values of $r_c = 2.67$, and $n_c = 3.67$ for SiO_2 are significantly different than the respective ideal network values of 2.4 and 3.0. This was explained by observing that the Si-O-Si bond bending force is unusually weak due to a large dispersion in the Si bond angle from approximately 120 to 170 degrees with a shallow minimum at ~150 degrees. As a result of this one bond-bending constraint/O-atom is effectively removed or *broken*, and even though r_c remains at 2.67, n_c is reduced to exactly 3, and relationship between n_c and r_c presented above, $n_c = 2.5\ r_c = 3$ no longer apples. In many thin film and bulk glasses and thin of technological important there is a close association between chemical bonding self-organizations (CBSOs) that reduce local site symmetry at Ge and Si four-fold coordinated bonding sites, thereby break bond-bending constraints, reducing bond-strain through reductions in n_c. The first example to be addressed later on this paper is a second glass forming regime, and IP in the $Ge_xSe(S)_{1-x}$ alloy systems that occurs at x~0.4; this

IP regime was first identified in Ge_xS_{1-x} alloys by a symmetric Raman vibration [11].

The chemically ordered alloy that defines the *average* composition of the second glass-forming regime of the Ge_xSe_{1-x} alloy system is Ge_2Se_3. The local-bonding arrangement at this alloy composition was initially identified from a structural interpretation of the Raman scattering [11], and involves pairs $GeSe_3$ pyramidal groups connected through homopolar Ge-Ge bonds. This is a second example of a chemically ordered composition in this alloy system. In this case, as for the compound composition, $GeSe_2$, the *microscopic mechanism* by which this ordering occurs during glass formation, or thin film deposition and annealing at a temperature that is about 70 to 75% of T_g, has been designated as a chemical bonding self-organization, or CBSO; it does not herald an IP at $GeSe_2$, but does compositions near Ge_2Se_3. The driving force for this self-organization is a generally a reduction of macroscopic bond-strain energy when it occurs at an IP transition, or within the IP regime. To be energetically favorable, this departure from random alloy bonding must reduce the strain energy contribution to the electronic structure to more than balance the loss of configurational, or alloy mixing entropy associated with chemically order, rather than random statistical bonding.

The formation of homopolar Ge-Ge bonds reduces the symmetry of the local Ge bonding symmetry from *ideal tetrahedral* with four *equivalent* Se nearest neighbors to *distorted tetrahedral* with three Se and one Ge nearest neighbors, i.e., from T_d to C_{3v} symmetry. The Se atom bonding remains 2-fold coordinated to Ge nearest neighbor atoms.

The reduction in symmetry for the Ge atoms, changes the symmetry of the bond-bending vibrations [12], and reduces their vibration frequencies through force constant reductions; this removes some of these bending-modes from the constraint counting arena; they are effectively broken constraints. There are two bond-stretching, and five bond-bending constraints for 4-fold coordinated Ge with full tetrahedral symmetry [1,2]. The atomic motions of these motions are essentially the same as the bond-stretching and bond-bending normal-mode motions for tetrahedral molecules that described in text books/monographs that address vibrational spectroscopy, e.g., [12]. There are three triply degenerate (F) and two doubly degenerate (E) bond-bending mode motions in the T_d symmetry group. The reduction in bond-bending constraints is based on a quantum mechanics foundation that underpins the classical description of empirical force constants, as applied to covalent, two electron pair bonded molecules; the *local molecular groups* in chalcogenide glasses and thin films. There is significantly larger bond-bending force constant for the bending mode of a Se-Ge-Se group, than for a Ge-Ge-Se, simply because the energies of the localized electronic states for the two Se-Ge segments of the Se-Ge-Se molecular are the same, while the corresponding energies for the two constituent segments of the Ge-Ge-Se group are different. Applying the Pauli exclusion principle to these bending motions demonstrates the force constant is inherently greater for the symmetric group, Se-Ge-Se, than for the asymmetric group, Ge-Ge-Se. Proceeding in this way, the number of effective or un-broken bond-bending constraints for the C_{3v} Ge tetrahedral molecular environment in Ge_2Se_3 is reduced from 5 to ~2.3 [13]. In contrast, the bond-stretching force constraints involve only nearest-neighbor pairs; there are 2/Ge atom in a 4-fold coordinated bonding environment independent of the symmetry, and the particular neighbors. The total number of constraints/Ge atom is thereby reduced from 7, or 5 bending + 2 stretching for a Td symmetry to ~4.3 or ~2.3 bending + 2 stretching for a *distorted* tetrahedral arrangement in which one of the four Ge neighbors is different from the other three, as in the Ge_2Se_3 molecular fragment.

In the absence of broken bond-bending constraint n_c for the Ge_2Se_3 composition is 4; however, when broken bending constraints are taken into account this is reduced to value of ~3 for consistent with the observation of relatively easy glass formation. The value of r_c for this composition is 2.8, and is unchanged by constraint counting. This means that the quantitative relationship between n_c and r_c that applies for 2-body stretching and 3-bond bending is changed when broken bond-bending constraints are taken into account, and the significance of $r_c = 2.4$ is reduced. Stated differently, this type of reduction in bond-bending constraints depends on deviations from completely symmetric bonding that are specific to the molecular bonding environment under consideration, and the changes n_c cannot be generalized.

This discussion so far has identified two new properties of alloy systems that go beyond the originally proposed mean-field approach of Phillips in Refs. 1 and 2. First, when constraint counting based on mean-field theory yields values greater than 3, or less than 3, this results in the percolation, or atomic scale inter-connection of bond-strain or *floppiness*, leading to the formation of defects. Second, even when $r_c > 2.4$, there can be CBSO's that reduce n_o to a value of 3, and thereby lead to good glass formation. Implicit also in the identification of IP phases is that the relationship between intrinsic defects and deviations from $r_c = 2.4$ is no longer applicable. This is essentially the driving force for re-examination of IP boundaries, and more importantly CBSO's that take place within the IP regime [14].

In summary, the mean-field description of Refs. 1 and 2 applies reasonably well in the so-called floppy and stressed rigid alloy regimes that bracket an IP, but is not applicable in the IP region itself. Additionally, the mean-field approach can fail to give the composition of the first transition that marks the beginning of the IP, if the 2- and 3-body force field is too *simple*, and does not give a good description of the local and shorter-range aspects of the intermediate range order as in $As_3S(Se)_3$. This will be addressed below, where the IP regimes in Ge_xSe_{1-x} and As_xSe_{1-x} are compared, and contrasted. Even though the mean-field theory approach is not applicable, it can in effect be modified by including strain-reducing CBSOs that change the local bonding from random to distinctly non-random!

2. Revisiting the intermediate phase in Ge_xSe_{1-x} alloys

Boochand and coworkers [15] have demonstrated that an IP initially identified in a-Ge_xSe_{1-x} alloys, extends from i) the onset of local rigidity in the context of a mean-field description at x ~0.20 with r_c ~2.4, and n_c ~3.0, to a composition that ii) defines the beginning of a stressed rigid alloy regime at x ~0.26 with r_c ~2.52 and n_c ~3.3. This IP window was based primarily on a width estimated from Raman scattering. A better and more accurate estimate of the positions of the two transitions that bracket the IP can be obtained form the experiments that have addressed reversible heat flow. These experiments indicate that the transition is closer to x = 0.2. This suggests that the compositions at threshold and within IP regime include a small fraction of edge-shared (ES) and well as corner shared (CS) tetrahedral, and these must be taken into account in a modification of the valence force field. Using x = 0.18 value. the IP regime then extends from:

(1) a transition from floppy to rigid and unstressed at x = 0.18, with $r_c(1) = 2.36$ and $n_c(1) = 3.0$; to
(2) a transition from rigid and unstressed to a stressed rigid regime at x = 0.25, with $r_c(2) = 2.52$ and $n_c(2) = 3.39$.

The total number of bonding constraints/Se is taken directly from SE BCT and is one stretching and one bending constraint, so that $n_c(Se) = 2$. There is question regarding the leading edge of the IP regime, the first transition, but even if this were due surface oxidation of the GeSe alloy, the importance of ES arrangements would not change, and would still determined the composition that applies at the rigid to stressed rigid transition that occurs at the end of the IP region.

The total number of bonding constraints for Ge was refined to include an additional constraint from the ES groups that increased the number from 7 to 9, and increased the total for a 28% fraction of these groups to 7.56. The specific force in this case is associated with repulsion between the lone pair orbitals on the two Se atoms that define the edge. This represents an important refinement of SE BCT that is important whenever atoms with non-bonding pairs are close enough to be exposed to repulsive forces between their non-bonding lone pair electrons. A second example will be addressed later on in the paper and is present in As_xSe_{1-x} alloys where there are lone--pairs on first neighbor As and Se atoms, as well as second-neighbor As-As and Se-Se pairs as well..

Several papers have addressed the width of this IP regime from modeling perspective, but not have addressed it in the context of the changes in bonding that occur within the IP that give rise to the most remarkable properties within that regime: i) the absence of aging, i.e., changes in time with properties such as T_g, and ii) the reversibility of heat flow. Since a mean-field description is not applicable in this IP regime, a fresh perspective is presented for addressing the microscopic and macroscopic aspects of bonding within the IP regime that can be directly correlated with these properties. The foundation for these new ideas was developed during the development of graduate courses that addressed differences in the length scales of order between non-crystalline and nano-crystalline (grain size ~ 2 to >4 nm) thin film solids, and in particular i) qualitative and quantitative differences in factors contributing to defect and defect precursor concentrations, e.g., the scaling with over-coordination with respect to an ideal r_c value of 2.4, and the increased defect densities in both the floppy and stressed rigid alloy regimes that bracket this value, and ii) the inherent connections between not only local bond-strain, but for what I shall designate as *percolated macroscopic strain* as the driving force for the formation of defects and defect precursors as well. A recent paper by the Thorpe group addresses these issue [28], but the forces involved are alloy system, bonding-chemistry specific, so that the first author (GL) believes a unified theoretical approach is not possible. The model and/or argument presented below provides important insights into the underlying microscopic bonding chemistry changes that explain these interesting, and technologically important properties of an IP regime.

The atomistic way that this will be addressed the IP regime in this is based on augmenting the mean-field concepts of r_c and n_c, with a microscopic description of bonding, and bonding changes that define the balance between the idealized random bonding in a particular non-crystalline network, and strain-reducing CMSO's that sustain the IP regime in that alloy system.

Returning to the Ge_xSe_{1-x} system, at the IP onset at x = 0.18, the mean-field, or average bonding arrangement consists of 4-fold coordinated Ge atoms, CS or ES connected through pairs of Se atoms; for purposes of simply the argument, CS and ES connections are treated in the same way with the *effective-medium* number of bonds/Ge atom, 7.56 instead of 7.

At the onset of the IP regime, for transition from floppy to rigid, but not stressed, we assume a random number of Se atoms separating pairs of Ge atoms, and this distribution is reasonably described by considering a *truncated statistical distribution with one, two or three Se atoms,* that includes a mixture of heteropolar bonding, Ge-Se, and homopolar Se-Se bonding, and does not include Ge-Ge bond formation:

$$N_{n=1,2,3}(\text{Ge-Se}_n\text{-Ge}) = 1\text{Ge-Se-Ge} + 2\text{Ge-Se-Se-Ge} + 1\text{Ge-Se-Se-Se-Ge}.$$

The truncated distribution is consistent with all spectroscopic studies to date employing infrared and/or Raman spectroscopy. Interconnected Ge-Se-Ge bonds are take as the local arrangement that eventually *stiffens and constrains* the bonding of the network; these bonds are the dominant species, in CS and ES configurations at the compound composition $GeSe_2$ and are interconnected throughout the film or glass. The Ge-Se-Ge linkages provide the local bonding group that percolates or extends bond strain, and eventually generates a stressed rigid network. In contrast, the local arrangements with 2 and 3 Se-atoms between two Ge-atoms do not present a stiffening constraint. There are two issues that can be addressed in the context of SE BCT:

i) what is the concentration of n=1 groups that is necessary to percolate bond-strain throughout a this Ge-Se (4-2) network and generate a stressed rigid network ?, and
ii) how is the concentration of n=1 groups minimized in the IP regime ?.

The answers to these queries is turns out to be a good representation of what the many-body interactions in the IP range, and provides a perspective for applying a similar approach to other alloys, e.g., As_xSe_{1-x}, where IP extends from ~2.29 to ~2.38.

The answer to first question has already been addressed [16]; the bonding in the alloy for n_c between ~2.36 and 2.52 is characterized by non-statistical (equivalently, non-random) bonding arrangements which increase chemical ordering. These are strain-driven, both local and globally, and represent a more favorable total energy (electronic, including strain), that more than compensates for the reduction of configurational entropy, which is an important factor in the stability of meta-stable non-crystalline glasses and thin films.

Consider first the onset of the IP phase at which two conditions must be met. First, in the mean-field Maxwellian llimit, a value of r_c ~2.4 represents a *boundary* between bonding which is *floppy* on one side, r_c<2.4, and *stressed rigid* on the other, r_c>2.4, the so-called Maxwellian transition. However, equally important for the random bonding at this composition in truncated model with n=3, the relative concentration of local stressed groups, Ge-Se-Ge, is well below a percolation limit, that falls between about, 0.44 to 0.5 for the interconnection of tetrahedrally-bond atoms, and ~0.5 for a Bethe Lattice construction, extended from 2 to 3-dimensions [17]. If n=3 the [Ge-Se-Ge] fraction is 0.25, well below the percolation limit in three dimensions. Moreover, if n were increased to 4 or 5, then the [Ge-Se-Ge] fraction would be reduced further, to ~0.12, and ~0.06, respectively. Stated otherwise, the respective concentration of *strain-percolation inhibiting* groups is high, ranging from 0.75, to as much as 0.88 and 0.94 respectively.

Since defect and defect precursor concentrations are strain-related, both local and what shall be referred to as *percolated macroscopic strain* are important. It is this confluence, the combination of a low relative low concentration of locally-strained bonding, and incomplete percolation of macroscopic strain is responsible for the remarkable IP properties: i) the reversible heat flow with low densities of as-formed defects, and ii) non-detectable aging with the conversion of defect precursors to defects\. Translated to semiconductor device physics, these two special properties are called initial performance limited by *pre-existing defects*, and reliability determined by the rate of conversion of *pre-existing defect precursors* to electronically-active defects under an electric field stress.

The issue is then
"are these mean-field theory arguments consistent with the value of r_c ~2.52 that marks the end of IP regime" ?

This can be determined from a local bonding model, and the result will be shown to be independent of the value n, 1, 2, or 3 that is assumed for the random bonding statistics at the begining of the IP regime. This approach is not under-pinned by a general theory, and as stated above, because of force-field differences, each alloy system addressed will generally require a different set of bonding issues. This will be evident in comparisons between the first and second IP regimes in the Ge_xSe_{1-x} alloy system. The strain-reducing/limiting CBSO's generate non-statistical bonding distributions with increased chemical ordering. In the random bonding model with n=1, 2, and 3, the number of n = 3 linkages is reduced as the Ge content is increased above 0.18, while the concentratioons of n=1 to n = 2 two linkages change according.ly. This process continues until all of the n = 3 linkages are removed and equal number of n=1 and n=2 linkages are eventually obtained. This 50% concentration of strained groups is at the limit for the percolation of local bond strain to macroscopic strain. This value of x that this corresponds to is determined by setting Ge_xSe_{1-x} equal to a mixture of $GeSe_4$ (the Ge-Se-Se-Ge linkage) and $GeSe_2$ (the Ge-Se-Ge linkage). Proceeding in this way:

$$GeSe_4 + GeSe_2 = Ge_2Se_6\text{, so that } x = 0.25 \text{ and } 1-x = 0.75,$$

yielding a value for r_c equal to 2.5, very close experimentally determined value of 2.52.

This relatively simple model provides an insight into the two requirements of an IP, relatively low mean-field values of n_c, in this case 3.0 at the initiation of the IP, and 3.39 at the termination, and continuously responsive CBSO's that suppress percolation of bond-strain until the concentration of locally rigid sites exceeds the percolation limit. In this case the CBL limit provides a good estimate of where this occurs. It is important to note this confluence of minimal local bond strain, and suppression of macroscopic strain is the basis for both the low defect, and defect precursor concentrations that are the hallmark of an IP phase.

One final comment is in order. Mean-field theory applies in the floppy and stressed rigid regimes, as such the transition compositions, and therefore the effective width of the IP region can be obtained from mean-field considerations. For the first transition, one simply determines the alloy composition, $r_c(1)$ at which $n_c(1)$ = 3.0. For Ge_xSe_{1-x}, this must include the bonding constraints that a result from repulsions between non-bonding electrons in the Se atoms in the EC arrangements. This yields a value of $r_c(1)$ = 0.18 in excellent agreement with a our re-assessment of the Hnr plots for the Ge_xSe_{1-x} alloys. In complementary way, values of $n_c(2)$ and $r_c(2)$ are obtained by looking into IP from the stressed rigid regime and using a mean-field model to identify where this transition occurs. This gives the values of 2.5 and 3.39, respectively for $n_c(2)$ and $r_c(2)$.

3. Intermediate phases in $As_xSe(S)_{1-x}$ alloys

The next important issue to be resolved: is the argument and model presented above unique to Ge_xSe_{1-x}, and other 4-2 systems such as Si_xSe_{1-x}, which exhibits a quantitatively similar bracketed IP phase, or does it apply to other systems in which the IP windows are markedly different, e.g., $As_xSe(S)_{1-x}$ [18]. For these 3-2 alloys, the onset of the IP phase occurs at a significantly reduced value of r_c, ~2.3 in the so-called floppy regime, instead of 2.4, at the transition point between flexible/floppy and stressed rigid bonding in the Maxwellian limit; however, the value of 2.4 is based on the two component valence force field and restricted to 2- and 3-body bond-bending and bond-stretching forces. In each these alloy systems (S and Se), the termination of the IP regime occurs at concentration of As of about 35-37%, also below the mean-field value for the onset of stressed rigid bonding. The question is why, and the answer is simple. The model proposed in the last Section is correct; namely, IP phases require a *confluence of two effects*: i) values of mean-field n_c, ≤3, and even extending into the floppy regime, and ii) suppression of the percolation of local bond strain into macroscopic strain. Stated differently, the demonstration of the reversibility of heat-flow captures the essence of this remarkable phase!! The issue is then: i) what is different in 3-2 chalcogenide alloys than 4-2?, and ii) the answer is obvious, the difference in *network connectivity*, or local topology. An this has two different components -- the first is qualitative and based on connectivity, and the second quantitative and based on the restricted force field which does not include constraints that are due to forces associated with repulsions arising from lone pairs on both the As and chalcogenide atoms.

In order to prevent the percolation of local bond strain, e.g., As-Se-As linkages from reaching the percolation limit for network connectivity, and there must be at least two As-Se-Se-As linkages/As atom pair. This is the analog of the two Ge-Se-Se-Ge linkages that occur at mean-field value bonding at x = 0.2 in the Ge_xSe_{1-x} alloy. But, more importantly, the 3-fold coordination, and the associated non-bonding lone pair on the As-atom, as well as those on the Se-atoms introduces additional constraining forces that play a significant role determine the onset as well as the termination of the IO. These are in effect many-body forces a since they not only involve repulsive interactions between non-bonding pairs on both As and Se atoms, but also involve interactions between non-bonding pairs on each of these atoms, and electrons in bonding orbitals as well. A similar situation prevails in As_2O_3, and this has been addressed in Ref. 19. Fig. 1(a) contains a plot of the normalized energy for As_2S_3 as a function the As-S-As bond angle. This plot demonstrates the strong dependence of energy on the relative orientation of the $As\text{-}S_{2/2}$ groups that bridge the S atom in the As-S-As bond. It is obvious from this plot that there are strong, collective many body forces that are important in this 3-2 chalcogenide. Figure 1(b) illustrates a similar plot for As_2O_3. These strong, many-body forces are not readily addressed in the spirit of a mean-field model, but it will shown that implicitly taking them into account in empirical manner validates the use of the Ge_xSe_{1-x} threshold condition as a qualitative template for As_xSe_{1-x} requires that there be at least two As-Se-Se-As linkages/As atom pair.

This template threshold approach suggests that the transition between floppy and rigid bonding in As-S and As-Se alloys should occur at the composition $As_2Se(S)_5$, or equivalently in $As_xSe(S)_{1-x}$ notation, for x=2/7, or 0.286. This corresponds very closely to the experimentally determined onset of IP behavior of r_c=2.29, as determined by reversibility of heat-flow, for As-Se and As-S, and for P-Se alloys, as well [18]. However, based on the 2- and 3-body force field, the value of r_c at threshold would be less than 3 and not be consistent the rigid character of the IP phase.

This is disparity is easily resolved by adding an additional constraint to each of the As-atoms and associating the non-bonding lone-pair of that atom with repulsive interactions. These repulsive contributions to the total energy are consistent with ab-initio calculations for As_2O_3 and As_2S_3 that indicate an energy difference between i) up-up and down-down and ii) up-down orientations of the As-atom lone-pairs asi indicated by the plots in Figs. 1(a) and 1(b) [22]. The addition of these forces increases the constraints/As atom from 4.5 (1.5 stretching and 3 bending) to 5.5. Proceeding in this way the concentration of As that corresponds to n_c = 3 corresponds to r_c = 2.29, which is the composition, As_2S_5, that is suggested by the template model based on the onset of the IP phase in Ge_xSe_{1-x} alloys.

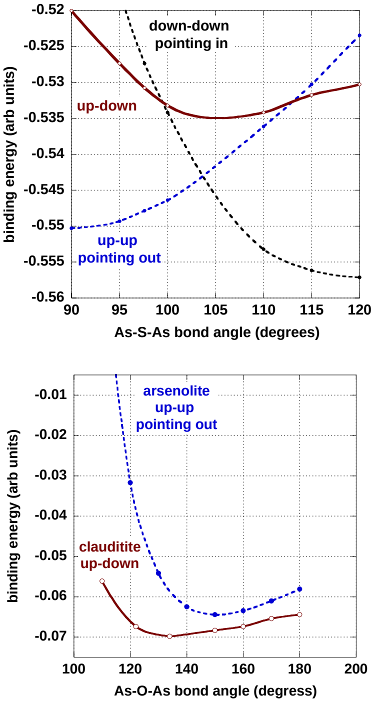

Fig. 1. (a) Normalized energy for As_2S_3 as a function the As-S-As bond angle. (b) Normalized energy for As_2O_3 as a function the As-O-As bond angle.

When does the IP phase terminate?; by analogy with the model for Ge_xSe_{1-x}, the percolation of As-Se-As occurs at a mean-field concentration corresponding to

$$1As_2Se(S)_3 + 1As_2Se_5\text{, or equivalently, } x = 3/8 \text{ or } 0.375,$$

a condition at which there equal numbers of strain blocking As-Se-Se-As and strain percolating As-Se-As bonding arrangements. This corresponds to $r_c = 2.38$, again close to the experimentally determined value of 2.37, and with $n_c = 3.24$. More importantly, this value is below the threshold for mean-field value of 2.4 for a locally stressed rigid phase. Fig. 2 compares the IP regimes for the two IP regimes in the Ge_xSe_{1-x} alloys system with the IP in the As_xSe_{1-x} alloy system, plotted as a function of n_c (C_{av}). Both IP's beginning at a value of 3.0, consistent with theory. The IP range smaller in the As_xSe_{1-x} system, and this is clearly related to the intrinsic difference between 4-2 and 3-2 alloys; there are lone-pairs on both atoms in the 3-2 alloys, and only on one of the atoms in the 4-2 alloys, and this is reflected in the modified force field constraint counting that has been addressed above.

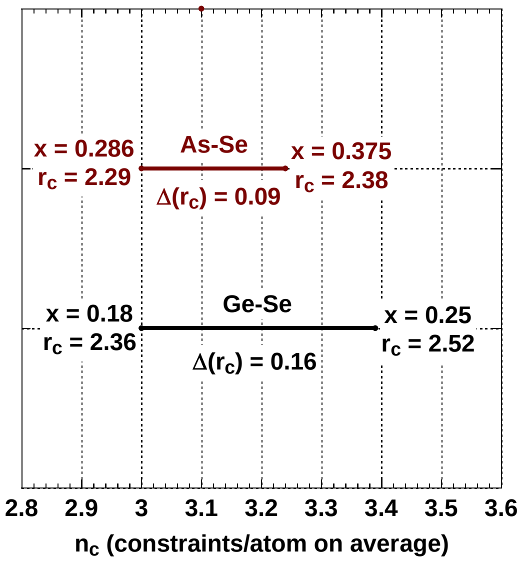

Fig. 2. Schematic representation of the IP regimes in the Ge_xSe_{1-x} alloy system. Displayed as function of n_c, rather than r_c, this schematic captures the essence of the IPs, and their dependence on the constraint changes that occur in these two different alloy regimes.

The As_xSe_{1-x} alloy system displays glass formation to x~0.7, and this is presumably associated with a diphasic material in which the As_2Se_3 network is mixed with small molecules such as As_4Se_4 and As_4Se_3 which reduced macroscopic strain percolation through the creation of a hard-soft material system [18]. In contrast glass formation is limited in the As_xS_{1-x} system to a regime that extends to x~0.5 by macroscopic chemical phase separation.

4. Other IPs

This section addressed other chemically related systems and the question of IP formation/termination limits. In these systems, the mean-field approach for estimating the these limits works equally good as well, and the same limitations as discussed above apply. The first such system is the second glass-forming regime in the Ge_xSe_{1-x} alloy system centered at x~0.4. This regimes is detached with respect to good glass formation at lower Ge concentrations by a range of very poor glass formation centered on the compound composition x = 0.33, i.e., $GeSe_2$. Does this second composition also reside within an IP? The existence of good glass formation at the composition Ge_2Se_3, x = 0.4, demonstrates that homopolar Ge-Ge bond in this chemically does not introduce an additional and significant bonding constraint. Stated differently it provides a free/unhindered rotation about the axis of the σ-bond between the two Ge-atoms. It is possible to use the same analysis as presented above to estimate the bracketing concentrations for an IP regime. Since $GeSe_2$ is stressed rigid, and Ge_2Se_3 is not, then a 50-50 mix of $Se_{3/2}$-Ge-Ge-$Se_{3/2}$ and 2Ge-$Se_{4/2}$ would then be expected to suppress percolation of rigidity at the alloy composition associated with this mean-field mix. This type of chemical ordering has been previously proposed in Ref 20.

It is then a simple matter to determine x solving the *bond-counting equation* given by $Ge_xSe_{1-x} = GeSe_2 + Ge_2Se_3$ to determine the position of the first or rigid transition: x is equal to 3/8 or ~0.38.. In the spirit of the same chemical self-organization model, the second boundary of the IP would then be determined by a 50-50 mix of Ge_2Se_3 and Ge_3Se_4, so that x = 5/12 or 0.42. The range of good glass formation in this system is from ~0.38 to ~0.42 so that the bond counting model works for this IP as well as the first IP in the same Ge_xSe_{1-x} alloy system. This question of an IP is of course better resolved by determining if there is a reversible heat-flow regime in the alloy composition range between $GeSe_2$ (x = 0.38) and Ge_3Se_4 (x = 0.42). The IP range for this alloy is also included in Fig. 2.

A second issue relates to the P_xSe_{1-x} alloy that is isoelectronic to As_xSe_{1-x} [18,21]. This alloy system shows an IP regime from ~2.28 to 2.4, with a width of 0.12, which is ~50% larger than for As_xSe_{1-x}. There are two important differences between P-Se(S) and As-Se(S) bonding chemistry. The P-containing alloys have a significant number of small molecules in the composition range about x = 0.286 (P_4S_{10}). and extended to higher concentrations, to 0.57 (P_4S_7), and also include P_4S_4 and P_4S_3 in the P-S alloys system However are only only P_4Se_4 and P_4Se_3 molecules in the P-Se alloy system. Several of the P-S molecular compositions, and a proposed P-Se network contribution also involve 4-fold coordinated P=S(Se) bonds where three of the bonds are associated with 2-fold coordinated S(Se) and the fourth with a terminal P=S(Se) donor acceptor pair bond which has -bond character as well. Boolchand and coworkers have suggested that the small molecule, P_4Se_4, as well as the Se-

Se, $PSe_{3/2}$ and $Se{=}PSe_{3/2}$ bonding arrangements are important in defining the IP regime boundaries [22]. In the light of the new model described above, and based on IP boundaries that quite similar for P_xSe_{1-x} and As_xSe_{1-x}, the P-Se and also P-S systems need additional study with the identification of specific experiments that could resolve this question.

Finally, when plotted with r_c as the scaling variable, the $As_xGe_xSe_{1-2x}$ alloys have an IP range that begins at approximately the same concentration as the As_xSe_{1-x} alloys and overlaps a portion of the Ge_xSe_{1-x}, but terminates at value that is smaller than the end of the range. Since any bonding model analysis would then require clustering of the As- and Ge-atom local bonding groups, and the transferability of binary alloy constraints to the ternary system. This consists of using the experimentally determined values of the boundaries of the IP to determine, the corresponding values of x, in this case the concentrations of the As and Ge alloy concentrations which are the same, and the determining the values of n_c and r_c at the floppy to rigid, but not stressed first transition, and the values of n_c and r_c at the rigid to stressed rigid transition as well. The determination of the r_c values is determined simply by the composition and the bonding coordinations, but the determination of the n_c has requires the inclusion additional forces beyond the 2-body and 3-body stretching and bending forces of the original formulation of the SE BCT [1,2]. These adjustments are made to take into account:

i) EC for Ge, so that the number of constraints/Ge is increased from 7 to 7.5, and

ii) repulsions involving the lone pairs on both the As and Se atoms, and as for As_2Se_3 alloys these have been incorporated into by increasing the number of constraints/As by one, from 4.5 to 5.5.

A value of x = 0.11 has been obtained from heat flow measurements for the first transition from floppy to rigid; this corresponds to a value for $r_c = 2.33$, that is in between the values of 2.29 and 2,36, respectively for As_2Se_{1-x} and Ge_xSe_{1-x} alloys. The value of n_c is uses the modified constraints per atom for As and Ge as indicated below:

$$n_c = 0.11(7.5) + 0.11(5.5) + 0.78(2) = 2.99.$$

Consistent with the nature of the IP and in particular with the first transition corresponding to the onset of rigidity, n_c is very nearly equal to 3.

Similarly, a value of x = 0.15 is obtained from heat flow measurements for the first transition from rigid to stressed rigid; this corresponds to a value for $r_c = 2.45$, that is intermediate to the values of 2.38 and 2.52, respectively for As_2Se_{1-x} and Ge_xSe_{1-x} alloys. The value of n_c is once more uses the modified constraints per atom for As and Ge as indicated below:

$$n_c = 0.15(7.5) + 0.15(5.5) + 0.70(2) = 3.35.$$

There is a consistency with the nature of the IP's, for the ternary $As_xGe_xSe_{1-2x}$ alloys, and the *parent* pseudo-binary As_2Se_{1-x} and Ge_xSe_{1-x} alloys; the values of x, n_c, and r_c, for the two transitions, as well as the IP width, $\Delta(r_c)$, are each arithmetic averages of the corresponding values for the *parent* pseudo-binary alloys. This relationship is evident in Fig. 3(a). Fig. 3(b) is more inclusive and includes the second IP centered at x~0.4 as well.

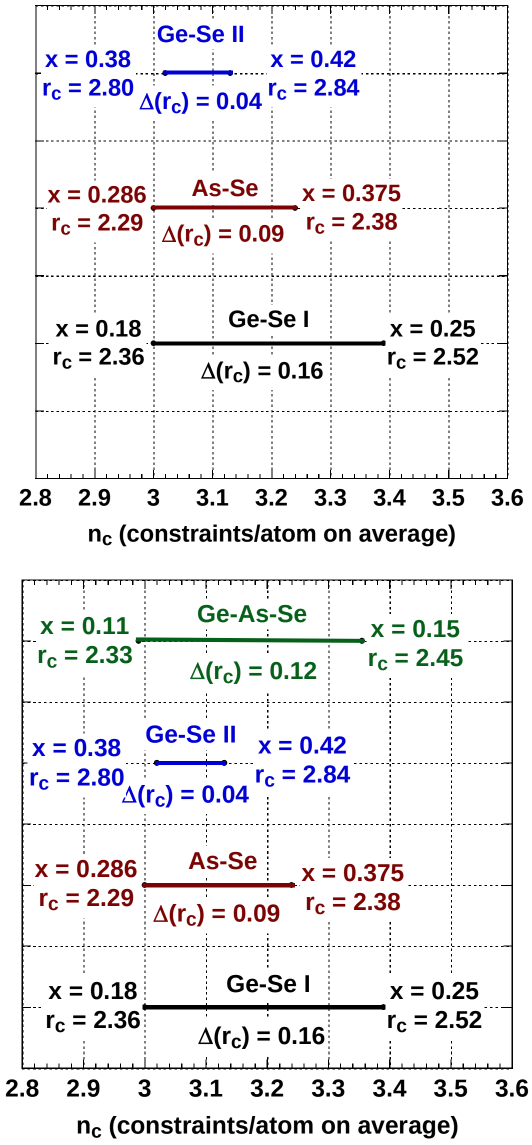

Fig. 3. (a) Schematic representation of the IP regimes in the Ge_xSe_{1-x} and As_xSe_{1-x} alloy systems. (c) Schematic representation of the IP regimes in the Ge_xSe_{1-x}, As_xSe_{1-x} and $As_xGe_xSe_{1-2x}$ alloy systems.

5. Discussion

The arguments and examples presented above for the local atomic bonding, and the associated percolation of macroscopic stress require a reexamination of some the approximations and assumptions presented in Refs. 1 and 2. This has been done and the assumptions in these seminal papers \have been modified for this application of SE BST in this paper for quantification of the LP boundaries using the mean-field metric. In addition and most importantly n_c, instead of the traditional approach of Boolchand using r_c., has been used for the re-plotting the results originally obtained by Boolchand et al., and modified above. This is demonstrated in Figs. 2, and 3(a) and 3(b), which capture of the universal character of the IPs as discussed in a recent paper of the Thorpe group [28];

i) the first transition occurs at the onset of rigidity, and can be obtained by including a more complete set of forces for constraint counting than the original SE BCT from *looking into the IP* from the flexible or floppy regime, and ii) the extent of the IP is determined by strain-relieving CBSOs that ward off a stress-rigid phase can be calculated by *looking into the IP* from the stressed rigid regime.

Since the CBSOs are determined by the coordinations and local site symmetries of the constituent atoms. Both of these aspects of the IPs are clearly evident in Fig. 2(b).

The bonding constraints addressed in SE BST were restricted to 2-body and 3-body bond-stretching and bond-bending forces, respectively; however, the forces that contribute the development of local and global rigidity generally involve more than 3-atoms. In the two systems that are addressed in this paper, they are specifically forces that represent the interactions that take into account repulsions between the non-bonding lone pair electrons of the chalcogenide and As atoms. These interactions have been incorporated into modified force constants and the total number constraints for these atoms. For example, electronic structure calculations have demonstrated that total energy is essentially independent of this angle for the 4-2 alloys GeS_2 SiO_2 and GeO_2, whereas in the 3-2 alloys in the As-O and systems, constraints, and bond-strain derived from repulsions involving lone pair electrons on each of constituent atoms favors \trans- or staggered orientation of non-bonding pairs on the As-atoms rather than either the cis- or eclipsed orientations [19]. This result has been found in ab-initio calculations of optimized bond-angles, IR effective charges, and relaxation after optical excitation that gives rise to photo-darkening and photo-structural changes in As_2S_3 and GeS_2 [23,24,25]. Representative results from these electronic structure calculations have been displayed in Fig. 1. In addition, there are differences in the orientation of these As-groups in relaxed, and photo-darkened states that play a role in stabilizing the photo-structural change that accompanies the photo-darkening. This is not the case for photo-structural change that accompanies light-soaking and photo-darkening in GeS_2. The electronic structural calculations of Ref. 23, and the extension of these calculations to photo-darkening in Refs. 24 and 25 are consistent with this new perspective on the combined contributions of local bond-strain, and percolated local bond-strain that give the IPs their unique and special properties with respect to the reversibility of heat-flow, low pre-existing defects, and aging, the conversion of defect precursors into defect states. More importantly, they explain why intermediate phases are important in device applications. These include i) a-Si(H) in solar cells and thin film transistors, ii) the SiO interfacial transition region between crystalline Si and a-SiO_2 in field effect transistors, iii) a-Si,N,H alloys in thin film transistor gate dielectrics, and finally, iv) a newly discovered medium-k gate dielectric that is allowing the continuance of Moore's law scaling for at least 2 more generations of complementary metal oxide semiconductor CMOS, circuits and systems [16,26].

Finally, the observation noted above that ternary alloy metrics in the As-Ge-Se system are simple averages of constituent of those of the relevant binary alloys systems, As-Se and Ge-Se. This suggests that CBSOs may take place in parallel and that in effect double percolation may apply. Double percolation, a well-established phenomenon in polymer blend-carbon black composites [27], then has the potential to provide another more general framework to cast the results of the chemical bonding oriented approach of this paper. Double percolation may also explains the ranges of the IP observed in the 3-4-2 ternary chalcogenide alloy, as noted immediately above, but may also be applicable to other ternary alloys such as Ge-Se-I, in which the IP phase has markedly different width [22].

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