Structural phase transitions in chalcogenide glasses

Keiji Tanaka

Department of Applied Physics, Faculty of Engineering, Hokkaido University, Sapporo 060, Japan

The composition dependence of the structural and electronic properties in chalcogenide glasses suggests that there exists a structural phase transition at the average coordination number of 2.67. Materials having smaller coordination numbers are characterized by molecular structures, and otherwise three-dimensional networks govern the properties. The result is discussed in light of topological and percolative arguments.

I. INTRODUCTION

Since Zachariasen's pioneering work[1] one of the long-standing problems in condensed-matter physics has been how to grasp the structure of disordered solids. For crystalline materials, Bragg's equation gives, in principle, a method for uniquely determining periodic lattices, and understanding of relationships between microscopic structures and macroscopic properties has been a subject in solid-state physics. Amorphous solids, as opposed to crystals, possess no long-range order, and since we have no established techniques capable of identifying non-periodic configurations, physics on amorphous materials is far behind that of the crystalline science.

A lack of the translational regularity, however, makes it possible to change continuously the elemental ratios in glassy compounds. Hence, compositional studies seem to be vitally important for amorphous materials. It is a purpose of this paper to emphasize such an approach, in which the dependence of various properties on compositions for series of glassy chalcogenide semiconductors is exploited to draw a structural picture in a coherent fashion.

Upon examining the amorphous structure of covalent glasses, we may classify building elements into two components;[2] one is normal bonding structure consisting of covalent bonds of densities on orders of 10^{22}–10^{23} cm^{-3}, which can be specified by chemical and topological natures, and the other is defects, e.g., impurities, dangling bonds, valence-alternation pairs, and wrong bonds (homopolar bonds in stoichiometric alloys). The density of defective bonds is, in general, less than 10^{-2} of that for the covalent bonds, and therefore structural behaviors are determined mostly by the normal configurations. Further, these are primarily responsible for such electronic properties as the band-gap energy, in contrast to gap states originating from defects. Thus, consideration of glassy characters using topological concepts may give fruitful ideas similar to those obtained through the unified understanding of crystalline properties based on periodic lattices. We will discuss in the present work physical characteristics seemingly governed by the topological bonding structure, which involves a hierarchy of correlation ranges, from short to medium.

Regarding the short-range configuration extending to ~ 5 Å in scale, the present status of understanding is more or less substantial.[3,4] X-ray diffraction and extended x-ray absorption fine-structure (EXAFS) studies give information on radial distributions, and Raman-scattering spectra are feasible to examine molecular clusters. These investigations manifest that the short-range orders in amorphous materials are nearly the same as those in crystalline counterparts. The coordination number is preserved in covalent glasses, obeying the so-called $8-N$ rule, where N is the valency of an atom. The rule suggests that the numbers of nearest-neighbor atoms for S(Se), As, and Si(Ge) are, respectively, 2, 3, and 4. The average coordination number Z of covalent bonds is a good measure representing characters of atomic units.[5] If a sample has a composition of Ge(Si)$_x$As$_y$S(Se)$_{1-x-y}$, then

$$Z = 4x + 3y + 2(1 - x - y) . \tag{1}$$

It should be kept in mind that an implicit assumption made on using the average coordination number is indiscriminate in species of valence bonds. The chemical property is obscured, and instead the topological nature will emerge.

To characterize the medium-range structure over distances of ~ 20 Å,[6] the network dimensionality D seems to be a useful quantity, which is defined as the number of dimensions where covalently bonded clusters can be extended. Zallen[4] has argued that $D = 1$, 2, and 3, respectively, for amorphous Se, As$_2$S(Se)$_3$, and Si(Ge). For instance, $D = 1$ for Se corresponds to a chainlike morphology, in which entangled chain molecules are held together with weak intermolecular forces mostly consisting of the van der Waals type, and $D = 3$ means three-dimensional continuous-random networks.[7]

We have at present, however, no experimental techniques available to define the medium-range structure with confidence, and proposed ideas, specifically for chalcogenide glassy alloys, appear to be controversial in a qualitative sense. For glassy As$_2$S$_3$, as an example, helical $(D \simeq 1)$,[8] layerlike $(D \simeq 2)$,[9] and cross-linked $(D \simeq 3)$ (Ref. 10) structural models have been inferred, depending on different kinds of structural studies. Further, for ternary alloys such as Ge-As-S(Se), structural dimensions have not been suggested. Nomenclature denoting classes of structures is also a source of the problem, since any clearcut lattices cannot be envisaged for disordered materials. Each word may embody some aspect of a material, but it would not necessarily visualize the overall features.

In the present paper, I will attempt to obtain conceptu-

al ideas representing the amorphous structure through examining compositional changes in several properties. The study focuses on properties of materials having high covalency[4] and, hence, discussion of glassy compounds containing heavy elements, e.g., Te, Sb, Sn, and Bi, is hardly given, since physical properties of such glasses may be influenced substantially by metallic characters which render the coordination numbers changeable.[11,12] Further, bulk glasses are inspected as far as possible because some evaporated films seem to have structures different from bulk glasses and/or to contain a large number of defects and voids[13-16] which make them unsuitable for the present purpose. Even for bulk glasses, properties vary resting on preparation procedures and so forth,[17] whereas the variations may be neglected in comparison to compositional dependencies.

Ge-As-S glasses are systematically studied, and Sec. II deals with the experimental details. Section III provides results together with comparative data on other Ge- and As-chalcogenide alloys. We will see various signatures suggesting a structural phase transition at $Z = 2.67$, in addition to that at 2.4 predicted by Phillips[5] and others[18-21] and demonstrated experimentally.[22] It is shown that the transition at $Z = 2.67$ can be accounted for on the basis of a constraint model for two-dimensional materials. Si-S(Se) glasses may be exceptions to the present argument and, therefore, the composition dependence is discussed separately in the last part. Section IV contains a summary. A preliminary result of the present work was published elsewhere.[23]

II. EXPERIMENTS

Glassy $Ge_x As_y S_{1-x-y}$ ingots having various compositions in a glass-forming region[24] shown in Fig. 1 were prepared by the melt-quenching method. Chemical mixtures of Ge, As, and S chunks of 99.9999% purity were vacuum-sealed in silica glass tubes, which were heated at 1000 °C for 12 h. The glass tubes were rocked continuously during heating in order to ensure homogeneity. The melts were quenched in air. The composition richest in S content, $Ge_{10}As_{10}S_{80}$, was very explosive, and could not be prepared despite several trials. By contrast, two samples deficient in S atoms were crystallized, even when quenched into water. Accordingly, these were excluded from further measurements. The chemical compositions of prepared glasses were ascertained by electron-microprobe x-ray analysis. The ingots were polished to wafers 20–50 μm thick for x-ray and optical experiments.

The density was measured using the Archimedean method along with methylalcohol as a reference medium. The atomic volume was calculated from the density and an atomic weight for a given composition. X-ray diffraction patterns for polished samples were monitored in a transmission geometry using copper radiation (40 kV, 40 mA) and a position-sensitive proportional counter. The exposure time was about 10 min. Details of elastic and optical experiments were described in previous papers.[25,26] In brief, the bulk modulus was evaluated from velocities of acoustic waves of 10 MHz and/or by measuring deformation of samples under hydrostatic pressure.[25] There were no meaningful differences be-
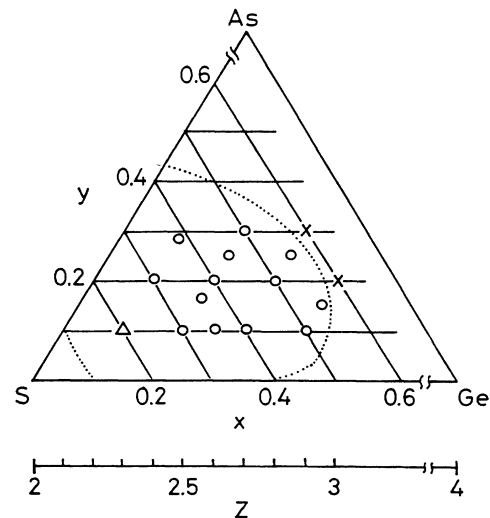

FIG. 1. Chemical compositions of prepared $Ge_x As_y S_{1-x-y}$ glasses (O), crystallized samples (×), and an exploded sample (△). The triangular diagram contains only the S-rich portion, in which the glass-forming region is shown by a dotted line. The average coordination number Z of a sample is given by projecting the compositional point onto the bottom scale.

tween the acoustic and the static values. The reversible photodarkening phenomenon was evaluated from shifts of the optical-absorption edge.[26]

III. RESULTS AND DISCUSSION

A. Atomic volume and microscopic structure

Figure 2 shows the atomic volume v_a as a function of the average coordination number Z for As-S,[27,28] As-Se,[29,30] Ge-S,[31] Ge-Se,[29] and Ge-As-S systems. The result for Ge is calculated from the thin-film density,[32] and the value for S at room temperature is obtained through interpolating the data of the melt and of the glassy form, which is stable only at lower temperatures than -30 °C.[33] Not surprisingly, small quantitative variations exist among some data reported by different authors, but inconsistency in the composition dependence is not marked. (Similar observations are confirmed for other dependencies discussed in the present paper.)

Several features are worth pointing out in Fig. 2. It may be startling that, even for the ternary glasses fixed by two compositional quantities x and y, the average coordination number Z appears to be determinative of the atomic volume. Further, for all systems depicted in the figure, we see that a gross composition dependence is a decrease in the atomic volume with an increase in Z. In addition, there seem to exist minima at $Z = 2.4$ and maxima at $Z = 2.67$,[34] except for the peak in As-S having a limited glassy-forming region of $Z \lesssim 2.45$. The existence of the extrema in the ternary alloys may be vague, probably because of different atomic sizes. The maxima at 2.67 and minima at 2.4, however, can be disclosed also in the data for Ge-As-Se (Ref. 35) and Ge-Sb-Se (Ref. 36) ternary systems, and for Ge-As-S glasses reported by Myuller et al.[24]
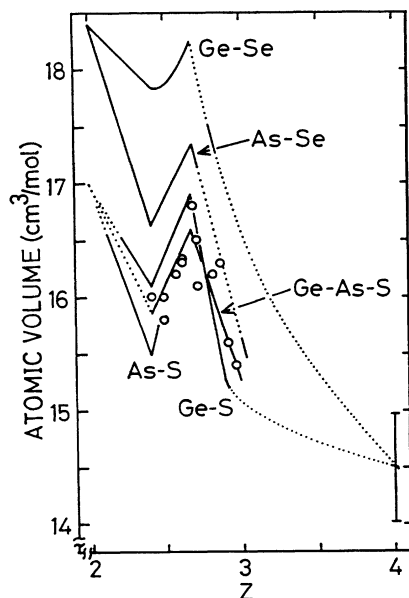
FIG. 2. The atomic volumes for various chacogenide glasses as a function of the average coordination number Z. The present results for Ge-As-S glasses are plotted by circles. Solid lines for binary alloys show representative tendencies with an accuracy of ± 0.1 cm^3/mol. Dotted lines depict estimated behaviors.

It can be argued with the following two reasons that the Z dependence of the atomic volume originates from changes in bonding topology. First, for the binary alloys the figure shows the minima occurring at GeS(Se)$_4$ and As$_2$S(Se)$_3$, and the maxima at GeS(Se)$_2$ and As$_2$Se. Among these compounds, As$_2$S(Se)$_3$ as well as GeS(Se)$_2$ are stoichiometric samples constructed totally with heteropolar bonds,[3,4] whereas the extrema are situated
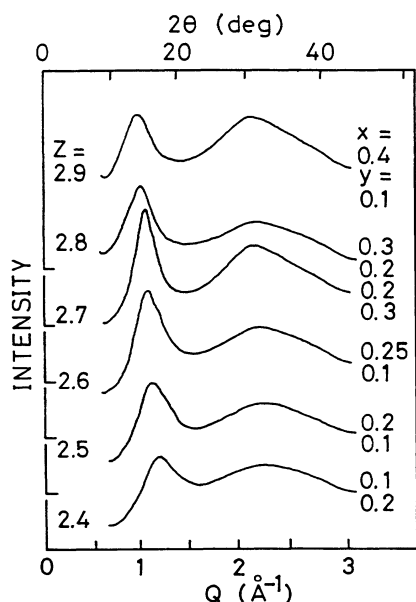
FIG. 3. X-ray diffraction patterns for several Ge$_x$As$_y$S$_{1-x-y}$ glasses. The average coordination number Z is given in the left-hand panel.
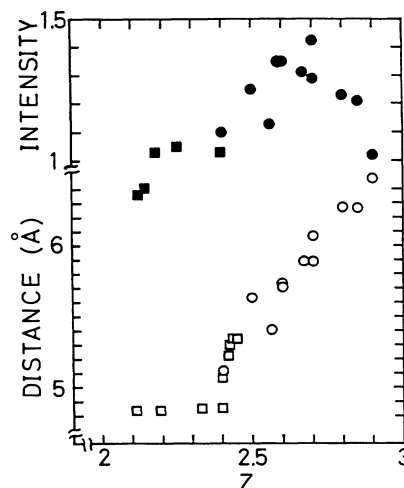
FIG. 4. FSDP characteristics in Ge-As-S (circles) and As-S (squares) glasses as a function of the average coordination number Z. Open and solid symbols show the distance $(=2\pi/Q)$ and the intensity normalized with that of the second peak at $Q \simeq 2.2$ Å^{-1} (see Fig. 3).

also at the nonstoichiometric materials GeS(Se)$_4$ and As$_2$Se. This fact indicates without a doubt that the dependence has no connection with chemical ordering. Second, the variations of the atomic volume in Ge(As)-Se and Ge-As-Se systems can be attributed mainly to some change in bonding structures, since Ge, As, and Se atoms are located closely in the same rank on the Periodic Table, so that the atomic radii are nearly the same. The observations that sulfide systems exhibit similar trends to those of the selenide imply preponderance of a topological rule over the composition dependences.

It is known that chalcogenide glassy alloys show a diffraction peak at Q $(=4\pi \sin\theta/\lambda) \simeq 1$ Å^{-1}, often termed the first sharp diffraction peak (FSDP).[3,6] The peak position suggests periodic structures separated by ~ 5 Å, and the half-width implies correlation lengths of ~ 20 Å, on medium-range scales. Figure 3 shows a selection of x-ray diffraction patterns for Ge-As-S glasses. We see that both the intensity and the position of the FSDP change with the compositional variation.

Figure 4 presents the Z dependencies of the intensity and the distance d $(=2\pi/Q)$ calculated from the FSDP for the Ge-As-S system together with those for As-S glasses.[9,27] The intensities are normalized with those of the second peak at $Q \simeq 2.2$ Å^{-1}; nonetheless, the overall features are unaffected by the normalization procedure. We emphasize again that the compositional changes are governed by the one parameter Z in both systems. For Ge-As-S alloys, with increasing Z from ~ 2.4, the intensity increases, peaks at around $Z = 2.67$, and then decreases. A continuous strengthening in the peak intensity for As-S glasses with Z in a region of $Z \leq 2.43$ seems to be along this line. The fact that glassy Se exhibits no FSDP is also in accord with the compositional trend.[37] In contrast, the distance increases monotonically with Z for both systems when $Z \gtrsim 2.4$. Similar characteristics for the FSDP intensity and position can be pointed out in other compounds, e.g., As-Se,[38,39] Ge-Se,[40] and Ge-S.[41,42]

Therefore, it may be argued that the composition variations are universal among covalent chalcogenide glasses.

In order to grasp the Z dependencies of the atomic volume and the FSDP characteristics, we tentatively assume a variation scheme of medium-range glassy structures with Z as follows.

(i) In glassy Se(S) of $Z = 2$, the network dimension is approximately unity.

(ii) Upon introducing As and/or Ge atoms to these chalcogen glasses, the one-dimensional molecules are cross linked, and gradual structural transformations from $D = 1$ to 2 take place. At $Z = 2.67$, layer structures are fully evolved, namely $D = 2$ when $Z = 2.67$. The layer structures may be considered to be segmental, not fragmental,[43] since the fragmental clusters would be surrounded by a number of dangling bonds having unpaired electrons. Experiments reveal, however, that the spin density is at most 10^{19} cm^{-3}.[2,13] In the present context, it may be helpful to imagine a pile of crumpled papers, which typify covalent layer clusters.

(iii) When Z increases further, the structures undergo the transition to three-dimensional networks, progressively multiplying cross-linked sites. Finally, at $Z = 4$ three-dimensional continuous-random networks appear.

This model for the structural variation underlies discussion throughout the present work, and will be examined in some respects.

The above assertion is mostly consistent with previous arguments, specifically with the Zallen's view.[4] It has been accepted widely that $D = 1$ in twofold-coordinated glassy materials. (Zallen assigns $D = 0$ for orthorhombic S with the reasoning that the crystal consists of S$_8$ rings.[4] Nonetheless, for glassy S there is ample evidence suggesting polymeric structures.[33]) The idea that $D = 3$ when $Z = 4$ is in current use.[3,4] Thus, a priori, that D increases with Z seems plausible. The assumption that $D = 2$ for materials of $Z \simeq 2.5$ has been proposed previously with structural models based on some kind of layer configuration, e.g., the distorted layer structure[9,39] and the raft geometry.[6] Further, almost all present pressure studies useful in obtaining insights into amorphous structures support the low-dimensional nature.[4,23] In the following, we see that under the present hypothesis the Z dependencies of the atomic-volume and FSDP characteristics can be understood coherently.

The atomic volume is one of most fundamental properties, given through normalizing the compositionally averaged atomic weight with the density. By dividing the atomic volume with Avogadro's number, N_a, we can evaluate the mean volume occupied by an atom included in a material of interest. Thus the quantity for a D-dimensional solid can be estimated approximately as

$$v_a(D) \simeq N_a r^D R^{3-D} , \qquad (2)$$

where R and r denote the van der Waals and the covalent bond lengths. Here, the filling factor[4] of atoms in space is neglected in order to clarify the argument. (The introduction seems to improve quantitative agreement between the estimated volumes and the experimental re-

sults.) Since $R \simeq 4$ and $r \simeq 2$ Å, we expect $v_a(1) > v_a(2) > v_a(3)$, inequalities in harmony with the gross experimental tendency. The increase in the atomic volume from $Z = 2.4$ to 2.67, however, appears puzzling.

The increase in the atomic volume can be connected with the FSDP characteristics, in case the structure is two dimensional. In light of the layer model, the FSDP is interpreted as the peak diffracted from stacks of layers held together by intermolecular bonds mostly consisting of van der Waals forces.[3,6,9,23] Since the layer separation d calculated from the peak position seems to correlate with R, the monotonic increase in v_a ($= N_a r^2 R$) from $Z = 2.4$ to $Z = 2.67$ can be related to the expansion of the interlayer distance. In the present context, therefore, the compositional change in this region might be regarded as an application of "negative pressure."[44]

The correspondence of the changes in the atomic volume and the FSDP position is also supported quantitatively. Fractional changes in the atomic volume in the compositional region of interest are, as shown in Fig. 2, about 5% which is approximately $\frac{1}{5}$ as large as those of the distance d shown in Fig. 4. The difference is understandable, provided that the layers are not completely flat but have corrugated finite thicknesses, as those included in layer crystals such as As$_2$S(Se)$_3$ and GeS(Se)$_2$.[4,6,9,27] The change in d would be partitioned by atoms located at bordering and in internal regions of the layers, i.e., $\Delta v_a \simeq \Delta d(N_b/N)$, where the ratio represents the fractional number of the layer-bordering atoms. For the layer structures in the chalcogenide crystals, the fraction can roughly be estimated at $\frac{1}{5}$.

The atomic volume starts to decrease again at $Z = 2.67$, since the structure is transformed from two- to three-dimensional networks. Below the critical composition, As and/or Ge atoms can be incorporated into the layers, enhancing the layer rigidity. At $Z - 2.67$ the number of atoms included in unit area of the layers becomes ultimate. In higher-Z materials, the excess coordination $Z - 2.67$ promotes three-dimensional crosslinking. We may envisage that the cross linking proceeds, accompanying intercalated atoms, because as shown in Fig. 4 the increase in the distance still remains in this compositional region.

The assumption of the structural transition at $Z = 2.67$ gives a plausible explanation for the composition dependence of the FSDP intensity shown in Fig. 4. According to the present picture, the intensity increases, reflecting degrees of the two-dimensional correlation. Therefore, the FSDP intensity grows continuously from $Z = 2$ to $Z = 2.67$ with the layer evolution. At $Z = 2.67$, the layer structure is fully developed, exhibiting the maximal FSDP intensity. The structural transition causes the turn of the peak intensity, which decreases further with increasing number of cross-linked sites.

It seems worthwhile to consider here experimental evidence indicating that the atomic volume does not necessarily correlate with the FSDP position. Chalcogenide glasses exhibit the reversible photostructural transformation and, for instance, in As$_2$S$_3$ at room temperature it has been demonstrated that the photostructural transformation accompanies an increase in the volume, in con-

trast to an increase in the FSDP angle, suggesting shrinkage in the interlayer distance.[13] It has been reported, however, that the photoinduced change in the peak position is not reproducible.[45] In addition, the fractional changes in the volume and the peak position for the photostructural phenomenon are at most 1.5%, much smaller than the observed compositional changes, $\sim 10\%$, in the region of $2.4 \leq Z \leq 2.67$. We can assume, therefore, that the atomic volume is primarily governed by the layer separation, while it may be modified by secondary effects, such as changes in structural randomness,[13] which are neglected in the present speculation.

B. Topological considerations

It may be valuable to consider the transitions at $Z = 2.4$ and 2.67 in light of the constraint-counting argument originally proposed by Phillips for amorphous covalent materials.[5] Taking the short-range structure into account, he has asserted that in the glasses having the highest stability the number of topological constraints N_{co}, evaluated for an atom is equal to the number of the flexibility, namely the spatial dimension $N_d = 3$:

$$N_{co} = N_d \ . \tag{3}$$

For a material having the coordination number of Z, $N_{co}(Z)$ can be expressed as a sum of radial and angular valence-force constraints:[5,18−20]

$$N_{co}(Z) = Z/2 + (2Z - 3) \ , \tag{4}$$

where 2 in the angular term corresponds to the two freedoms θ and φ in a polar-coordinate representation (r, θ, φ) of an atom bonded to another atom located at the origin, and 3 can be related to the system rotation around x, y, and z axes. Combining Eqs. (3) and (4), we obtain $Z = 2.4$, i.e., the coordination number of the most stable glass is 2.4. The same conclusions are also drawn by percolative arguments[20,21] and counting the number of zero-frequency modes.[19]

In order to understand the transition at $Z = 2.67$, consideration for medium-range structures may be indispensable. Following the Phillips's prediction,[5,18−20] we can express the constraint for an atom included in a planar cluster extending in, e.g., the x-y plane as

$$N_{co}(Z) = Z/2 + (Z - 1) \ , \tag{5}$$

where the angular term is calculated as excess degrees of Z variables in θ over a rotation freedom around the z axis. Note that the number of the angular constraints is reduced to $Z - 1$ because of the presumption of the planar medium-range configurations. If the cluster is laid in a three-dimensional space, each atom must have three independent freedoms for stable existence. Therefore, the constraint-balancing condition (3), unified with Eq. (5), gives $Z = 2.67$. That is, a two-dimensional glass appears to be fixed stably in a three-dimensional space, if the coordination number is 2.67.

The above notion developed for ideal planar clusters seems applicable to real materials. As was mentioned in Sec. III A, layer clusters included in chalcogenide glasses may have corrugated structures with finite
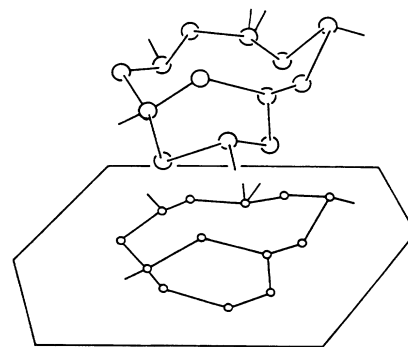

FIG. 5. A structural model for glassy Ge-As-S(Se), and the projected lattice onto a segmental plane. Ge, As, and S(Se) atoms are represented, respectively, by fourfold-, threefold-, and twofold- coordinated circles.

thicknesses.[3,6,9,23] However, if the clusters are inherently two dimensional as illustrated in Fig. 5, they can be projected to segmental planes, which may extend in restricted scales corresponding to the medium-range order. Hence, the present idea can be adopted to real layer structures through the hypothetical planar lattices. Note that homological projection of three-dimensional networks onto planes is impossible, inevitably creating crossed bonds.

The experimental observations seem to be consistent with these constraint ideas. Since the FSDP is influenced mainly by intermediate structures, the intensity has only one peak at $Z = 2.67$. By contrast, both the short- and medium-range orders reflect upon the atomic volume, and therefore it has the extrema at $Z = 2.4$ as well as $Z = 2.67$. The existence of the minima of the atomic volume [and the band-gap energy (see Fig. 6)] at $Z = 2.4$ may be in accord with the Phillips's argument, because with respect to microscopic structures the stability can be associated with tight bonds having short bond lengths. Thus it is conceivable that a stable glass has a small atomic volume.

However, the reasons why the interlayer separation increases with Z at around 2.5 and the maximal volume appears at $Z = 2.67$ are still vague. Probably concomitant with these dependencies is that, as is suggested by a pressure study,[23] the interlayer interaction sustained through lone-pair electrons in Ge-chalcogenide glasses appears to be weaker than that in As-chalcogenide alloys. A few possible explanations can be offered for these observations. As for a topological reason, evolution of medium-range order may accompany areal extensions of rigid-layer segments,[25] requiring more free space between the layers. As a consequence, the separation and the volume would increase, accompanying weaker interlayer interaction. Regarding this speculation, it is mentioned that a lattice model for a crystalline $GeS(Se)_2$ layer consisting of balls and sticks is more rigid than that for an $As_2S(Se)_3$ layer.[25] This fact may imply that folding of a single layer into segmental structures becomes more and more difficult with increasing Z, and the separation between the segments is enlarged. Alternatively, the features could be ascribed to a chemical nature. We note that even in crystalline compounds similar structural trends

are observed, i.e., GeS(Se)$_2$ layer crystals have wider layer separations and greater atomic volumes than those of As$_2$S(Se)$_2$ crystals.[23] This characteristic may have some connection with the increases in the layer separation and in the atomic volume in glassy samples.

A more fundamental problem is that no theoretical explanations are given for the experimental observations, implying two-dimensional structures in chalcogenide glasses of $Z \simeq 2.5$. In this context, it may be worth mentioning that oxide glasses Si(Ge)O$_2$ of $Z = 2.67$ are three dimensional.[46] The problem is open for future studies.

C. Electronic properties

It may be quite startling that the Z dependence resembling that of the atomic volume is discernible for the optical band-gap energy Eg. Figure 6 shows some examples for As-S,[16,47] As-Se,[47] Ge-S,[14,16,31,48] and Ge-Se (Refs. 47 and 49–51) systems. For Ge-S(Se) glasses, the maxima at $Z = 2.67$ can clearly be marked, and for the As-Se system we can envisage the peak at around $Z = 2.67$. For the As-S system the critical composition is out of the glass-forming region. In contrast, minima or inflections seem to exist at $Z = 2.4$ in all binary systems. It is mentioned further that the extrema at $Z = 2.4$ and 2.67 are also seen in the composition dependencies of dielectric constants in Ge-Se and As-Se glasses.[29,44]

For the compositional behavior of the band-gap energy, we try to delineate an elemental picture, extracting essences from rigorous theoretical calculations.[52] To evaluate the band-gap energy E_g, consideration of three quantities is required. Namely, E_0, the average energy splitting between the conduction and the valence band; E_V, the valence-band width; and E_C, the conduction-band width, which are all combined to give an expression
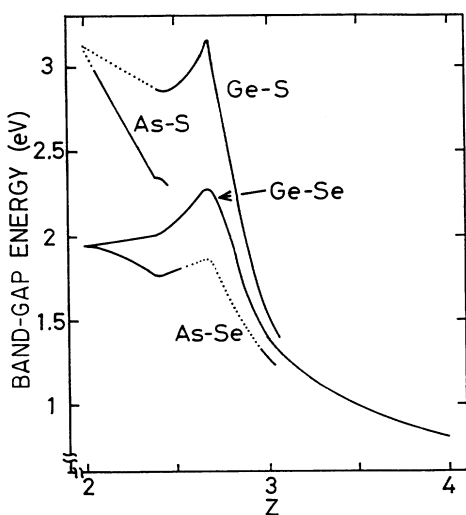
$$E_g = E_0 - E_V/2 - E_C/2 . \tag{6}$$

FIG. 6. The optical band-gap energies for Ge(As)-S(Se) glasses as a function of the average coordination number Z. The accuracy of the representative lines is about ±0.1 eV. The data of S, Ge, and Ge-Se of $3 \le Z \le 4$ are obtained for amorphous films.

E_0 remains constant, or at least is modified monotonically if inherent band characters are not changed throughout the compositional regions of interest. The conduction band in chalcogenide glasses arises from antibonding states and, hence, we expect in terms of a simple tight-binding theory[52] that the band broadens with the coordination number Z,

$$E_C \propto \langle H \rangle Z , \tag{7}$$

where $\langle H \rangle$ denotes the transfer integral. The broadening is a consequence of short-range effects, accompanying the contraction of the atomic volume, and it is effective in decreasing the band-gap energy. The fact that the covalent-bond length is modified slightly, 2.2–2.4 Å, for all investigated systems implies a nearly constant contribution from the transfer integral.[52] In contrast, it is known that the width E_V of the valence band is substantially influenced by the intermolecular interaction, since the valence band originates from the lone-pair–electron states, wave functions of which protrude into the intermolecular space. A pressure study[16] for chalcogenide glasses suggests that the width E_V changes approximately as

$$E_V \propto \exp(-d'/\xi) . \tag{8}$$

where ξ is assumed to be a constant representing a degree of spatial extension of lone-pair electrons and d' is the intermolecular distance changing as a function of Z. In the present context, d' is proportional to d for the materials exhibiting FSDP's. Of course, expressions other than Eq. (8) may be available; nonetheless, it seems universal that the width becomes wider with decreasing d'.

On the basis of the above analysis, a scenario can be written for the composition dependence of the band-gap energy shown in Fig. 6. When Z increases from 2, the band-gap energy decreases predominantly through the short-range effect. [A slight increase for the Ge-Se system may be upset by the intermolecular effect expressed in Eq. (8) through the interlayer expansion: i.e., as shown in Fig. 2 the decrease in the atomic volume for glassy Ge-Se in this region is relatively small. The presumed contraction of the valence-band width with Z is also in accord with electronic structures examined using ellipsometry.[50]] In the region $2.4 \le Z \le 2.67$ the band gap broadens mainly reflecting the increase in the layer separation. When $Z \ge 2.67$ the coordination number becomes a dominant factor again in decreasing the band gap, because the degree of cross linking is successively enhanced with increasing Z.

D. Elastic properties

The Z dependence of the bulk modulus exhibits a threshold at $Z = 2.67$, which is exemplified in Fig. 7 for the Ge-As-S (Ref. 25) and Ge-Sb-S (Ref. 36) systems. Ge-As-Se glasses manifest a dependence quantitatively similar to that in Ge-As-S,[35] and the data are excluded from the figure. We see that the bulk moduli of these ternary glasses are nearly constant when $Z \lesssim 2.67$; otherwise the rigidity increases dramatically with Z.

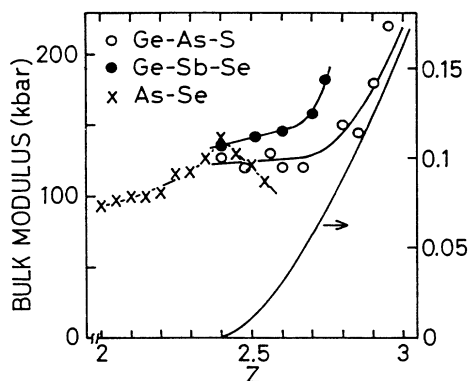It should be mentioned here that the composition

FIG. 7. The bulk moduli for As-Se, Ge-As-S, and Ge-Sb-Se glasses as a function of the average coordination number Z. A theoretical curve obtained through numerical simulation is also shown, for which the scale is given on the right-hand side (see the text).

dependencies of elastic properties in binary systems do not necessarily show the threshold at $Z = 2.67$. An example is seen in Fig. 7 for the bulk modulus in the As-Ge system,[30] which reveals a prominent peak at As_2Se_3, the stoichiometric composition of $Z = 2.4$. This dependence is attributable to a chemical effect,[23,53] namely the strength difference between homopolar and heteropolar bonds, and, accordingly, it is eliminated from the present argument.

Comparison of the observed threshold at $Z = 2.67$ with a theoretical prediction may be valuable. He and Thorpe[21] have shown through numerical simulation, taking only the valence forces into account, that an elastic phase transition occurs at $Z = 2.4$. They found that, for the networks generated by random removal of covalent bonds from the diamond lattice, the bulk moduli were zero when $Z \leq 2.4$; otherwise these increased in proportion to $(Z - 2.4)^{1.5}$ along with the rigidity percolation. The threshold composition 2.4 is different from the experimental value 2.67.

There may be a possibility that consideration for the intermolecular effect leads to an increase in the theoretical threshold. In typical chalcogenide glasses, the intermolecular force constant is about 5% of the covalent-bond-stretching constant.[16] With respect to the scale used by He and Thorpe, plotted on the right-hand side of Fig. 7, the intermolecular effect may add ~0.05 to the calculated modulus. The contribution seems to be greatest at $Z = 2$, and decreases to zero at $Z = 4$, since there is no intermolecular interaction in tetrahedrally connected networks. Therefore, the theoretical curve would be biased, showing a threshold at $Z = 2.67$. This possibility appears, however, too coincidental.

Alternatively, it is tempting to speculate that in all chalcogenide glasses the topological rigidity thresholds are located at $Z = 2.67$ in light of the following two ways. The first is based on the medium-range constraint argument given in Sec. III B, which predicts that $D \leq 2$ if $Z \leq 2.67$ and $D \simeq 3$ otherwise. Thus elastic properties are governed by weak intermolecular forces in low-Z materials, and, by contrast, when $Z \geq 2.67$ these are gradually

dominated by stronger covalent bonds with increasing Z.[25] The threshold at 2.67 can, therefore, be connected to the transition between the two kinds of distinct structures.

The second approach follows the ring-correction idea given by Thorpe.[19] He has demonstrated that, while a simple rigidity-percolation analysis predicts the elastic transition at $Z = 2.4$, the existence of ring structures consisting of atoms fewer than six is effective to increase the threshold. Since layer structures are favorable in creating small rings,[54] we can expect shifts of the threshold to greater Z values in low-dimensional materials. The fact that the bonding angle for chalcogen atoms is nearly 90° can contribute to multiplying small rings. As examples for these speculations, we see, on the basis of the Thorpe's idea on the ring correction, that crystalline forms of $GeS(Se)_2$ layers and $SiSe(S)_2$ chains, both of which have the 2.67 coordination, are just rigid. This means that, in the corresponding glassy systems, the threshold may exist at $Z = 2.67$. In real glasses, however, various distributions of ring sizes can be envisaged, so that if an intimate correspondence between the two speculations exists, it is vague.

It is known that the composition dependencies of ultrasonic propagation characteristics at low temperatures also show thresholds at around $Z = 2.67$. Gilroy and Phillips[55] examined acoustic attenuation at 550 kHz in Ge-Se(S) glasses and found that the attenuation normalized with respect to that in Se decreased with increasing Z to zero at $GeSe_2$, $Z = 2.67$. Duquesne and Bellessa[56] measured the acoustic attenuation in amorphous Ge-Se in the 100-MHz range at temperatures between 0.1 and 10 K, and evaluated the density of the two-level tunneling systems. The composition dependence in their publication[56] reveals that the density decreases when Ge atoms are added to the Se matrix, and is nearly constant between $GeSe_2$ and pure Ge. In short, both data indicate the threshold at $Z = 2.67$, while the concentration is estimated to be roughly 10^{19} cm^{-3}, comparable to defect densities.[2]

Gilroy and Phillips have asserted, following Phillips's idea, that the threshold shifts to $Z = 2.67$ provided the bond-bending constraint for Se atoms is neglected.[55] That is, for Ge_xSe_{1-x} glasses the total number of constraints per atom can be expressed as

$$N_{co} = 2x + (1-x) + 5x , \qquad (9)$$

where the first two terms represent the stretching constraints for Ge and Se atoms and the last term denotes the bending constraint for Ge atoms. Combining this expression with Eq. (3) gives $x = \frac{1}{3}$, or $Z = 2.67$.

Neglect of the angular constraint for Se(S) atoms, however, seems dubious, since the configuration between pairs of Ge atoms bonded through Se(S) is preserved fairly well in these glasses.[5,42] In contrast, the present model assuming low-dimensional structures bearing out the flexibility in materials of $Z \leq 2.67$ may give more plausible explanations employable to these acoustic behaviors.

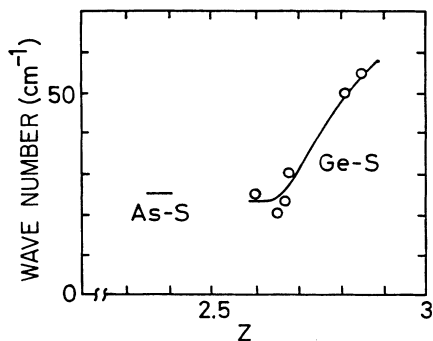A brief examination into Raman-scattering spectra reinforces the present argument. Figure 8 shows the

FIG. 8. The peak wave numbers of the low-frequency Raman-scattering peak as a function of the average coordination number Z in As-S and Ge-S glasses. The accuracy of the results for As-S shown by a line is within ± 5 cm^{-1}.

peak wave number of the so-called "low-frequency peak"[6] as a function of Z for As-S (Refs. 17 and 57) and Ge-S (Ref. 58) glasses. We see that the peak wave number is nearly constant, 20–30 cm^{-1}, when $Z \lesssim 2.67$, and otherwise it increases with Z, exhibiting a threshold at around $Z = 2.67$. The origin of the low-frequency peak is still a subject of considerable debate, whereas in any models the peak frequency is related in a qualitative way with the medium-range structures.[6,17] Accordingly, the present model based on the structural transition at $Z = 2.67$ is in harmony with this Z dependence.

E. Photodarkening

The reversible photodarkening phenomenon observed in chalcogenide glasses shows an interesting composition dependence. Figure 9 displays the magnitudes evaluated at room temperature for As-S,[59] As-Se,[60] Ge-S,[26] Ge-Se,[26] and Ge-As-S (Ref. 26) glasses. The photodarkening strongly peaks at around $Z = 2.67$ in all systems except As-S, which in the glass-forming region exhibits a tendency to increase with Z, similar to the characteristics in the
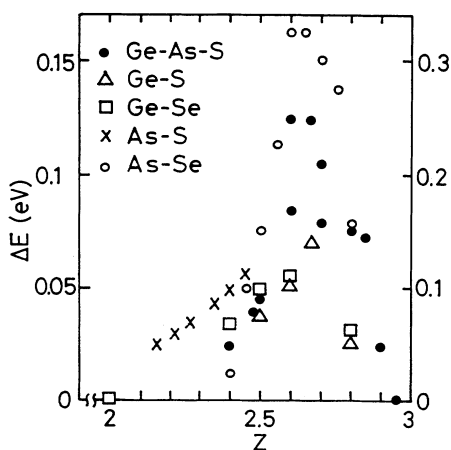
other materials.

The composition dependence can be understood, provided the structural transition occurs at $Z = 2.67$. The photodarkening has been supposed to result from structural transformations which are triggered by photoexcitation of electron systems.[13,16,26] A part of the transformed atomic structures seems to be relaxed thermally at room temperature, and therefore materials having higher glass-transition temperatures exhibit greater photodarkening effects. Since the glass-transition temperature becomes higher with Z when $Z \lesssim 2.67$,[43] the enhancement of the photodarkening in this compositional region can mainly be ascribed to the increase in the glass-transition temperature. In contrast, it is speculated that cross-linked rigid structures are unfavorable to the phenomenon, since no free space is available to photoinduced atomic motions. Hence the magnitude seems to decrease with increasing Z above the critical composition.

F. Si-S(Se) systems

Si-S(Se) glassy systems may have unique characteristics, whereas experimental studies are limited because of hygroscopic and volatile properties. Figure 10 shows the Z dependencies of the atomic volume, the position and the intensity of the FSDP,[61] and the band-gap energy[51] for Si-Se glasses. The composition dependencies of the structural and electron properties resemble those in Ge- and As-chalcogenide systems shown in Figs. 2, 4, and 6, namely the atomic volume, the FSDP intensity, and the band-gap energy exhibit maxima at $Z = 2.67$, and the FSDP position changes monotonically. (The band-gap energy for Si-S glasses may follow a similar dependence, while the feature in samples of $Z \geq 2.67$ has not been known because the band gaps are in excess of 3.6 eV.[51] No other data relevant to the present purpose seem available in this system.) Thus we would apply the dimension-
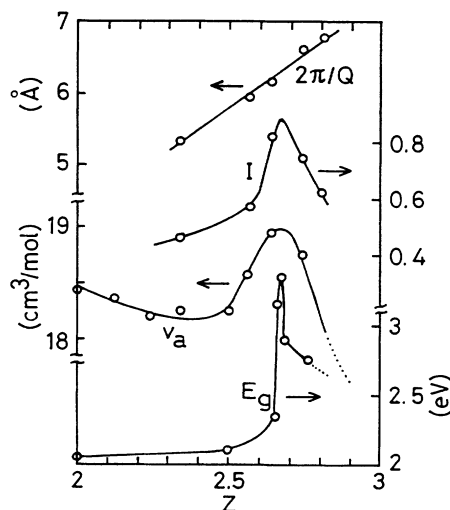

FIG. 9. Dependence of the reversible photodarkening effect evaluated by the shift ΔE of the optical-absorption edge on the average coordination number Z for Ge-As-S and Ge(As)-S(Se) systems. The data for Ge-Se, As-S, and As-Se are obtained using thin-film samples, and for As-Se a scale plotted on the right-hand side is employed.

FIG. 10. The atomic volume v_a, the optical band-gap energy E_g, the FSDP position $2\pi/Q$, and the normalized FSDP intensity I for Si-Se glasses as a function of the average coordination number Z.

al idea developed for Ge(As) alloys to the Si-Se system also.

Nevertheless, the structure of Si-chalcogenide glasses is supposed to be one dimensional. Johnson et al.[61] have suggested that glassy $SiSe_2$ with $Z = 2.67$ is constructed by entangled chains consisting of edge-sharing $Si(Se_{1/2})_4$ tetrahedra. Griffiths et al.[62] and Gladden and Elliott[63] have proposed for $SiSe_2$ glass a cross-linked chain-cluster structure, which on a scale of ~ 20 Å may be viewed as one dimensional. Since glassy Se has polymeric chain molecules, all Si-Se glasses with $Z \leq 2.67$ appear to be essentially one dimensional.

Amorphous Si has three-dimensional networks, and therefore it is conceivable that in the Si-Se system $D \simeq 1$ when $Z \leq 2.67$ and $D \simeq 3$ otherwise. If this assertion is justified, the FSDP can be ascribed to the interchain correlation. Then, the continuous intensity increase in the region of $Z \leq 2.67$ can be related to its evolution and, in contrast, the decrease in the remaining part seems to indicate structural changes to more cross-linked networks.

The composition dependencies of the other properties shown in Fig. 10 can be sketched out in the framework of this structural model. An equality $v_a(1) > v_a(3)$ derived from Eq. (2) can be employed to grasp the gross tendency of the atomic volume decreasing with Z. The correlation between the atomic volume and the FSDP position in $2.4 \leq Z \leq 2.67$ similar to that in Ge- and As-chalcogenide materials implies that the argument given in Sec. III A, i.e., the increase in the atomic volume can be associated with the expanding intermolecular distance, is applicable here. Since the natures of the conduction and valence band in these materials are assumed to be the same as those in Ge- (As-) chalcogenide glasses,[51] the correspondence between the band-gap energy and the atomic volume can be interpreted, as was done in Sec. III C.

In light of the constraint argument, the short-range constraint represented by Eq. (4) may be responsible for the existence of the minimum for the atomic volume at $Z = 2.4$. (The minimum of the band gap at $Z = 2.4$ may be obscured by the expanding interchain distance, essentially with the same reasoning as that for Ge-Se glasses.) On the other hand, however, it may be dubious to apply the layer-constraint model described in Sec. III B for interpreting the maxima at $Z = 2.67$ in Si-alloy glasses. Detailed discussion of this problem should be based on more versatile experimental data, and it is beyond the scope of the present paper.

IV. FINAL REMARKS

At present, we have no conclusive experimental evidence indicating low-dimensional structures in chalcogenide glasses. However, there exists much circumstantial evidence. Among the evidence, the composition dependence seems worth noting, for which the present study gives a plausible and unified explanation.

Investigations on the composition dependencies of structural, elastic, and electronic properties have revealed the existence of the extrema or the thresholds at $Z = 2.67$, which can be understood provided that chalcogenide glasses undergo a structural phase transition at this critical coordination number. Specifically, in As- and Ge-chalcogenide glasses the signatures can be explained as originating from the topological change from two-dimensional structures in materials of $Z \leq 2.67$ to three-dimensional networks in materials having greater Z values. In Si-chalcogenide systems, it appears that $D = 1$ when $Z \leq 2.67$ and $D = 3$ otherwise. The nature of these Z dependencies has been discussed in light of the topological constraint arguments, which emphasize the importance of short- and medium-range structural orders.

The network-dimensionality approach may also be valuable in dealing with amorphous tetrahedral materials. For instance, we can prepare one-dimensional polysilane, two-dimensional siloxene, and three-dimensionally networked Si films.[64] Studies on these materials will be interesting for examining the universality of the dimensional concept in amorphous semiconductors. It also seems interesting to examine the Z dependence of defect characters in glassy samples which were prepared under fixed and reproducible conditions.

[1]W. H. Zachariasen, J. Am. Chem. Soc. 54, 3841 (1932).

[2]S. R. Ovshinsky and D. Adler, Contemp. Phys. 19, 109 (1978).

[3]S. R. Elliott, Physics of Amorphous Materials (Longmans, London, 1984).

[4]R. Zallen, The Physics of Amorphous Solids (Wiley, New York, 1983).

[5]J. C. Phillips, J. Non-Cryst. Solids 34, 153 (1979).

[6]J. C. Phillips, J. Non-Cryst. Solids 43, 37 (1981).

[7]A more accurate description for D seems to be given by fractions. For instance, for Se, D is assigned to a number less than unity, since the chain lengths are not infinite and ring molecules may be contained.

[8]G. Pfeiffer, M. A. Paesler, and J. M. Lee, J. Non-Cryst. Solids 97&98, 379 (1987).

[9]L. E. Busse, Phys. Rev. B 29, 3639 (1984).

[10]T. G. Fowler and S. R. Elliot, J. Non-Cryst. Solids 92, 31 (1987).

[11]M. Stevens, P. Boolchand, and J. H. Hernandez, Phys. Rev. B 31, 981 (1985).

[12]K. Murase, T. Fukunaga, K. Yakushiji, T. Yoshimi, and I. Yunoki, J. Non-Cryst. Solids 59&60, 883 (1983); J. C. Phillips, Phys. Rev. B 36, 4265 (1987).

[13]K. Tanaka, in Fundamental Physics of Amorphous Semiconductors, edited by F. Yonezawa (Springer-Verlag, Berlin,

1981), p. 104.

[14]K. Tanaka, Y. Kasanuki, and A. Odajima, Thin Solid Films 117, 251 (1984).

[15]L. Tichy, A. Triska, H. Ticha, and M. Frumar, Philos. Mag. B 54, 219 (1986).

[16]K. Tanaka, Jpn. J. Appl. Phys. 25, 779 (1986).

[17]K. Tanaka, Phys. Rev. B 36, 9746 (1987).

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

[19]M. F. Thorpe, J. Non-Cryst. Solids 57, 355 (1983).

[20]J. C. Phillips and M. F. Thorpe, Solid State Commun. 53, 699 (1985).

[21]H. He and M. F. Thorpe, Phys. Rev. Lett. 54, 2107 (1985).

[22]J. C. Phillips, Phys. Rev. B 31, 8157 (1985).

[23]K. Tanaka, J. Non-Cryst. Solids 97&98, 391 (1987).

[24]R. L. Myuller, V. N. Timofeeva, and Z. U. Brisova, in Solid State Chemistry, edited by Z. U. Brisova (Consultants Bureau, New York, 1966), p. 46.

[25]K. Tanaka, Solid State Commun. 60, 295 (1986).

[26]K. Tanaka, T. Nakagawa, and A. Odajima, Philos. Mag. B 54, L3 (1986).

[27]S. Tsuchihashi and Y. Kawamoto, J. Non-Cryst. Solids 5, 286 (1971).

[28]S. Maruno and M. Noda, J. Non-Cryst. Solids 7, 1 (1972).

[29]A. Feltz, H. Aust, and A. Blayer, J. Non-Cryst. Solids 55, 179 (1983).

[30]R. Ota, N. Soga, and M. Kunugi, Yogyo-Kyokai-Shi 81, 36 (1973).

[31]Y. Kawamoto and S. Tsuchihashi, J. Am. Ceram. Soc. 54, 131 (1971).

[32]W. Paul, G. A. N. Connell, and R. J. Temkin, Adv. Phys. 22, 531 (1973).

[33]W. J. MacKnight and A. V. Tobolsky, in Elemental Sulfur, edited by B. Meyer (Wiley, New York, 1965), p. 95.

[34]A preliminary experiment for Ge-S systems shows that the maximum at $Z=2.67$ disappears when the atomic volume at 20 kbar is plotted as a function of Z.

[35]U. Tille, G. H. Frischat, and K. L. Leers, in Proceedings of the 4th International Conference on the Physics of Non-Crystalline Solids, edited by G. H. Frischat (Trans-Tech, New York, 1977), p. 631.

[36]S. Mahadevan, A. Giridhar, and A. K. Singh, J. Non-Cryst. Solids 57, 423 (1983).

[37]W. Wei, B. W. Corb, and B. L. Averbach, J. Non-Cryst. Solids 53, 19 (1982).

[38]A. L. Renninger and B. L. Averbach, Phys. Rev. B 8, 1507 (1973); K. S. Liang, J. Non-Cryst. Solids 18, 197 (1975).

[39]A. J. Leadbetter and A. J. Apling, J. Non-Cryst. Solids 15, 250 (1974).

[40]O. Uemura, Y. Sagara, and T. Satow, Phys. Status Solidi A 26, 99 (1974); J. C. Malaurent and J. Dixmier, J. Non-Cryst. Solids 35&36, 1227 (1980).

[41]S. C. Rowland, S. Narasimhan, and A. Bienenstock, J. Appl. Phys. 43, 2741 (1972).

[42]L. Cervinka and A. Hruby, in Proceedings of the 5th International Conference on Amorphous and Liquid Semiconductors, edited by J. Stuke and W. Brenig (Taylor and Francis, London, 1974), p. 431.

[43]K. Tanaka, Solid State Commun. 54, 867 (1985).

[44]G. Lucovsky, Phys. Rev. B 15, 5762 (1977).

[45]H. Hamanaka, K. Tanaka, K. Tsuji, and S. Minomura, J. Phys. (Paris) Colloq. 42, CA 399 (1981).

[46]K. Tanaka, Philos. Mag. Lett. 7, 183 (1988).

[47]R. A. Street, R. J. Nemanich, and G. A. N. Connell, Phys. Rev. B 18, 6915 (1978).

[48]L. Tichy, A. Triska, and C. Barta, Philos. Mag. B 46, 365 (1982).

[49]V. A. Vassilyev, M. Koos, and I. Kosa Somogyi, Philos. Mag. B 39, 333 (1979); H. Oheda, Jpn. J. Appl. Phys. 18, 1973 (1979).

[50]H. J. Trodahl and L. Vina, Phys. Rev. B 27, 6498 (1983).

[51]J. H. Harris and M. A. Tenhover, J. Non-Cryst. Solids 83, 272 (1986).

[52]J. Robertson, Adv. Phys. 32, 361 (1983); R. M. White, J. Non-Cryst. Solids 16, 387 (1974); M. Lannoo and M. Bensoussan, Phys. Rev. B 16, 3546 (1977); T. T. Nang, M. Okuda, and T. Matsushita, ibid. 19, 947 (1979).

[53]P. Boolchand, Phys. Rev. Lett. 57, 3233 (1986).

[54]This assertion is supported by two facts. First, according to a percolation theory, the percolative threshold for a square lattice is greater than that for a diamond lattice, even though $Z=4$ for both structures (Ref. 4). Second, the result that the threshold is located at $Z=2.4$ in numerically generated lattices by He and Thorpe (Ref. 21) seems to imply ineffective ring correction in three-dimensional networks. The number of small rings consisting of six atoms is assumed to be few at $Z\simeq2.5$, since the origin of the networks is a diamond lattice in which all rings are six membered.

[55]K. S. Gilroy and W. A. Phillips, Philos. Mag. B 47, 655 (1983); W. A. Phillips, J. Non-Cryst. Solids 77&78, 1329 (1985).

[56]J. Y. Duquesne and G. Bellessa, Philos. Mag. B 52, 821 (1985).

[57]P. J. S. Ewen, M. J. Sik, and A. E. Owen, in The Structure of Non-Crystalline Materials, edited by P. H. Gaskell (Taylor and Francis, London, 1974), p. 231.

[58]G. Lucovsky, J. P. deNeufville, and F. L. Galeener, Phys. Rev. B 9, 1591 (1974); K. Arai, N. Koshizuka, and H. Namikawa, in Raman Studies on Glassy Structure in Ge-S and Ge-S-As Glasses, Proceedings of the Conference on Structure and Excitations of Amorphous Solids, AIP Conf. Proc. No. 31, edited by G. Lucovsky and F. L. Galeener (AIP, New York, 1976), p. 217.

[59]K. Tanaka, Thin Solids Films 66, 271 (1980); V. M. Malinovsky, A. P. Sokolov, and V. G. Zhdanov, Solid State Commun. 51, 647 (1984).

[60]J. Teteris, Phys. Status Solidi A 83, K47 (1984); V. L. Averianov, A. V. Kolobov, B. T. Kolomiets, and V. M. Lyubin, ibid. 57, 81 (1980).

[61]R. W. Johnson, D. L. Price, S. Susman, M. Arai, T. I. Morrison, and G. K. Shenoy, J. Non-Cryst. Solids 83, 251 (1986).

[62]J. E. Griffiths, M. Malyj, G. P. Espinosa, and J. P. Remeika, Phys. Rev. B 30, 6978 (1984).

[63]L. F. Gladdeen and S. R. Elliott, Phys. Rev. Lett. 59, 908 (1987).

[64]S. Nitta, M. Kawai, M. Sakaido, I. Murase, and A. Hatano, in Tetrahedrally-Bonded Amorphous Semiconductors, edited by D. Adler and H. Fritzsche (Plenum, New York, 1986), p. 501.