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Atomic structure and chemical order in Ge-As selenide and sulfoselenide glasses: An x-ray absorption fine structure spectroscopic study

S. Sen and B. G. Aitken
Glass Research Division, Corning Incorporated, Corning, New York 14831

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The nearest-neighbor coordination environments of Ge and As atoms in $Ge_xAs_ySe_{1-x-y}$ glasses with $x:y=1:2$ and 1:1 and in $Ge_{0.154}As_{0.308}$ $(S,Se)_{0.538}$ sulfoselenide glasses with wide-ranging Se contents have been studied with Ge and As *K*-edge extended x-ray absorption time spectra spectroscopy. The average coordination numbers of Ge and As atoms are found to be 4 and 3, respectively, in all glasses. The compositional makeup of the first coordination shells of Ge and As atoms indicate that chemical order is largely preserved in stoichiometric and Se-excess $Ge_xAs_ySe_{1-x-y}$ glasses. On the other hand, chemical order is found to be strongly violated in the case of Se-deficient $Ge_xAs_ySe_{1-x-y}$ glasses where the chalcogen deficiency is entirely taken up by the formation of As-As homopolar bonds at low and intermediate levels of Se deficiency. The Ge atoms take part in homopolar bonding only in strongly Se-deficient glasses indicating clustering of As atoms. In the case of sulfoselenide glasses the distribution of S and Se atoms in the first coordination shells of Ge and As atoms is found to be random, signifying a chemically ordered chalcogen ''sublattice.'' It is shown that the intermediate-range structural and topological aspects of such compositional variation of chemical order may play a central role in controlling properties such as the molar volume of chalcogenide glasses.

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I. INTRODUCTION

The structure-property relationships in Ge-As chalcogenide glasses have received a great deal of research attention in recent years.[1,2] The nonlinear variation in physical properties with composition in these glasses has been variously ascribed to rigidity percolation, topological phase transition, and chemical bonding effects.[3–6] According to the topological models the physical properties of chalcogenide glasses are expected to be controlled by the average coordination number $\langle r\rangle$ rather than the actual chemical composition of the glass.[4,7,8] Phillips was the first to suggest, on the basis of the counting of bond length and bond angle constraints, that the glass-forming tendency of covalently bonded glasses such as chalcogenides would be maximized when $\langle r\rangle=2.4$.[7] Subsequently, it was shown by Thorpe that a system of 3-dimensionally connected atoms would undergo a rigidity percolation type of transition at the same average coordination number.[8] Such a transition can be manifested through a maximum in properties such as bulk modulus of binary or multicomponent glasses when the condition $\langle r\rangle=2.4$ is satisfied by the glass composition. Previous studies have shown that the compositional dependence of elastic, thermodynamic, transport, and electronic properties in binary and multicomponent Ge-As-S, Se glasses indeed shows signatures of a transition at $\langle r\rangle\sim2.4$.[4,6] However, the existence of another extremum at $\langle r\rangle\sim2.67$ in the compositional variation of a number of physical properties of Ge-As-S, Se glasses has often been observed.[4] Tanaka recently speculated that such an extremum at $\langle r\rangle\sim2.67$ corresponds to a transition in the topological dimensionality D of the glass structure with $D\leqslant2$ for $\langle r\rangle<2.7$ and $D=3$ for $\langle r\rangle>2.7$.[4] On the other hand, structural models based on chemical ordering have correlated physical property variations with the formation of Ge/As-Ge/As (S/Se-S/Se) homopolar bonds in chalcogen-deficient (-excess) nonstoichiometric glasses, especially in binary Ge-S, Se, or As-S, Se systems.[9,10] Recent structural studies with Raman spectroscopy and Ge and As *K*-edge extended x-ray absorption fine-structure spectroscopy (EXAFS) have indicated a more complex picture of structure-property relationships in ternary Ge-As-S glasses.[5,11] These studies have shown that the covalent network structure of stoichiometric and S-excess Ge-As-S glasses is chemically ordered and consists of corner-sharing GeS_4 tetrahedra and AsS_3 trigonal pyramids with S-S homopolar bonds in the S-excess glasses. However, the structure of S-deficient glasses with low and intermediate levels of S-deficiency show a violation of chemical order where the deficiency of S is entirely taken up by the formation of As-As homopolar bonds.[5] The Ge atoms participate in homopolar bonding only after all As atoms are exhausted in homopolar bond formation. Such a strong clustering of As atoms may result in low-dimensional intermediate-range structural units such as sheets of $AsAs_3$ trigonal pyramids similar to that characteristic of crystalline As. In fact, Raman spectroscopic results have shown conclusively that such As-As homopolar bonding results in the formation of molecular As_4S_3 units in S-deficient Ge-As-S glasses, especially in As-rich compositions.[5] It was also shown in that study that the formation of such molecular units rather than the rigidity percolation phenomenon is responsible for observed maxima in physical properties, particularly that of the thermal expansion. It should be noted in this regard that the degree of chemical ordering in chalcogenide glass structure also depends critically on the nature of the chalcogen atom. For example, Ge and As *K*-edge EXAFS studies have shown that, in Ge-As-Te glasses, Ge/As-Ge/As homopolar bonds exist even in excess Te-containing compositions, whereas such bonds in Ge-As-S glasses are observable only in S-deficient compositions.[12] One may argue that the topology or average coordination number of a glass rather than its actual chemical composition can in fact become more important for glasses in the Ge-As-Se system due to the similarity in the electronic structures and bonding of Ge, As, and Se atoms. However, to the best of our knowledge, there has been no report in the literature of any detailed study of the short-range structure and chemical ordering in ternary Ge-As-Se glasses. In this paper we report the results of such a study, based on Ge and As *K*-edge EXAFS spectroscopy, of the local coordination environments of Ge and As and chemical ordering in ternary Ge-As-Se and quaternary Ge-As-S-Se glasses. The ternary glasses are from two compositional series of the type $Ge_xAs_ySe_{1-x-y}$ with $x:y = 1:1$ and 1:2, which were selected so as to be able to directly compare these results with our recently published EXAFS data on the analogous Ge-As-S glasses.[5] The compositions of the quaternary glasses can be represented by the formula $Ge_{0.154}As_{0.308}(S+Se)_{0.538}$, with Se/(Se+S) atomic ratios ranging from 0.2 to 0.8. As the corresponding sulfide glass $Ge_{0.154}As_{0.308}S_{0.538}$ was previously shown to contain a high concentration of molecular As_4S_3 groups, an additional objective of the present study was to determine whether analogous $As_4(S,Se)_3$ species were present in the corresponding sulfoselenide glasses as well as in the selenide endmember. In addition, a quaternary sulfoselenide glass of composition $Ge_{0.100}As_{0.200}S_{0.560}Se_{0.140}$ was made in order to study the ordering behavior, if any, of S and Se atoms in a chalcogen-excess composition.

II. EXPERIMENT

A. Sample preparation

The Ge-As-Se and Ge-As-S-Se glasses investigated in this study were prepared by melting mixtures of the constituent elements (⩾99.9995% purity, metals basis). These mixtures were flame sealed in evacuated (10^{-6}-Torr) fused silica ampoules and subsequently melted in a rocking furnace at ~900 K for at least 24 h. Cylindrical glass rods were formed by quenching the ampoules in water, followed by annealing for 1 h at the respective glass transition temperatures. The nominal compositions of the glasses studied here are listed in Tables I–III. The compositions of these glasses have also been denoted in this paper in terms of "%Se (or, Se+S) in excess of stoichiometry" which corresponds to the percentage amount of Se (or, Se+S) in a glass in excess of the stoichiometric composition, i.e., $Ge_xAs_y(Se,S)_{2x+1.5y}$ (see Tables I–III).

B. EXAFS spectroscopy

1. Data collection

All Ge and As *K*-edge (11103 and 11867 eV, respectively) EXAFS spectra were collected at beam line *X*18*B* at the National Synchrotron Light Source at Brookhaven National Laboratory. The stored electron-beam energy was 2.58 GeV and typical beam currents were between 150 and 300 mA. A weak link channel-cut Si(111) crystal was used as the monochromator. The second crystal was bent to detune the incident beam by 25% at 10 keV in order to reject higher harmonics. All samples were finely ground to powders and were uniformly spread on mylar tapes on the sample holder of a liquid-nitrogen-cooled cryostat. Sample temperatures were maintained within a range of 80–90 K in order to lower the effect of thermal Debye-Waller factor on the signal. The EXAFS data were collected in the transmission mode with an energy resolution of 2 eV. Ionization chambers filled with mixtures of nitrogen and argon gases were used as detectors for measuring the incident and transmitted x-ray beam intensities.

2. Data Analysis

The Ge and As *K*-edge EXAFS data have been analyzed using the standard software packages EXBROOK and EXCURV92 developed by the Daresbury Laboratory.[13] The EXBROOK package has been used to subtract a linear background in the pre-edge region and a quadratic background in the post-edge region from the raw absorption spectra. The EXAFS oscillations are subsequently k^3 weighted and fitted using the nonlinear least-squares fitting routine in EXCURV92, based on the curved-wave theory of EXAFS.[14] The electron-scattering phase shifts for As-Se, Ge-Se, As-S, Ge-S, and Ge/As-Ge/As atom pairs, as calculated by EXCURV92, were tested by fitting the Ge and As EXAFS spectra of the As_2Se_3, As_2S_3, AsS, GeS, GeS_2, and $GeSe_2$ crystals, and proved to be adequate without further refinement. It should be noted in this regard that the similar atomic numbers of Ge, As, and Se make their backscattering amplitudes and phase shifts similar. Thus these atoms are practically indistinguishable from one another as backscatterers in EXAFS spectroscopy. Furthermore, the similar atomic sizes of Ge, As, and Se result in similar heteropolar Ge-Se, As-Se, and homopolar Ge/As-Ge/As bond lengths, which in turn makes the distinction on the basis of bond lengths rather difficult. However, detailed Ge and Se *K*-edge EXAFS spectroscopy of Ge_xSe_{1-x} glasses by Zhou, Paesler and Sayers has shown that Ge-Se and Ge-Ge bond lengths are indeed distinguishable and remain fairly constant (2.365 ± 0.005 and 2.425 ± 0.020 Å, respectively) over a wide range of x values.[15] Such a difference in Ge-Se and Ge-Ge bond lengths was also observed by Choi, Gurman and Davis in amorphous Ge_xSe_{1-x} thin films by Ge and Se *K*-edge EXAFS spectroscopy, where the Ge-Se and Ge-Ge bond lengths are ~2.37 and 2.45 (±0.03) Å respectively.[16] Usually the three structural parameters that are varied in EXCURV92 in order to obtain the best fit are (i) the radial distance R of the neighboring atoms around the central photoexcited Ge or As atom, (ii) the number N of the neighboring atoms around the central atom within a shell of radius R, and (iii) the Debye-Waller factor $2\sigma^2$. The nonstructural fitting parameters include the amplitude factor which corrects for amplitude reduction resulting from events such as multiple excitations and the imaginary part of the potential which is a measure of the mean free path of the photoelectron.[17] These nonstructural parameters have been optimized by fitting the EXAFS spectra of the model crystalline compounds and have been treated as transferable constants for analysis of the glass spectra. Moreover, in light of the above discussion, the Ge-Se and Ge-Ge/As distances for all glasses have been kept constant to

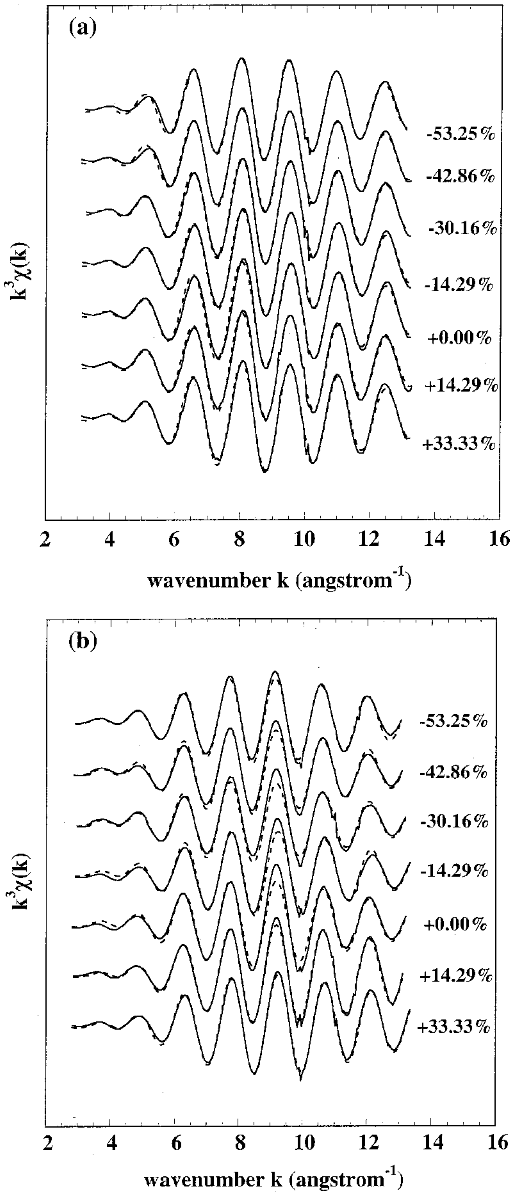


FIG. 1. k^3-weighted (a) Ge and (b) As K-edge EXAFS spectra of $Ge_xAs_ySe_{1-x-y}$ glasses with $x:y=1:1$. The %Se in excess of stoichiometry for each glass composition is indicated alongside each spectrum. Solid lines represent experimental data, and dashed lines correspond to least-squares fits obtained using EXCURV92.

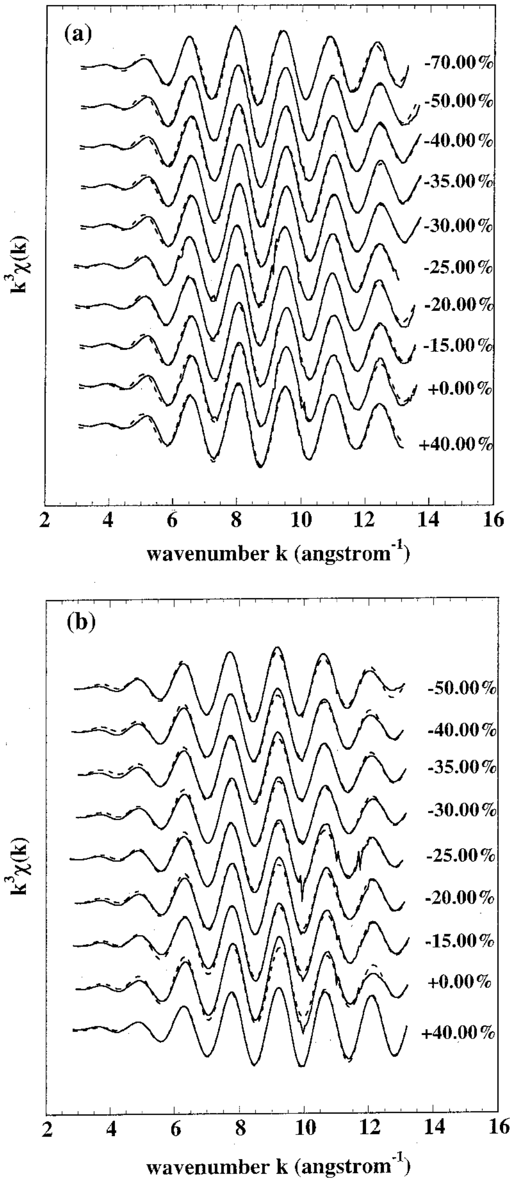
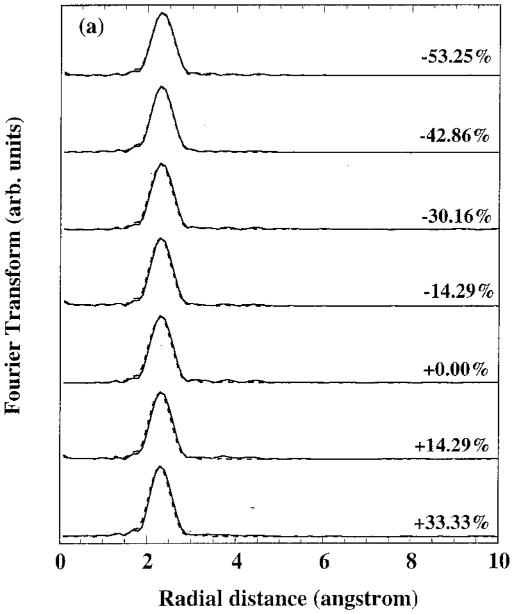


FIG. 2. k^3-weighted (a) Ge and (b) As K-edge EXAFS spectra of $Ge_xAs_ySe_{1-x-y}$ glasses with $x:y=1:2$. The %Se in excess of stoichiometry for each glass composition is indicated alongside each spectrum. Solid lines represent experimental data, and dashed lines correspond to least-squares fits obtained using EXCURV92.

their observed values in binary Ge_xSe_{1-x} glasses (i.e., 2.365 and 2.425 Å, respectively) in our analyses of the Ge EXAFS data. This procedure has allowed us to determine the number of Se and Ge/As atoms in the first coordination shell of the Ge atoms in a self-consistent fashion. In contrast with the case for Ge no such systematic study of the variation of As-Se and As-As/Ge bond lengths has been reported in the literature for binary As_xSe_{1-x} glasses. Neutron-diffraction studies as As_2Se_3 glass show that the average As-Se bond length is ~2.43 Å.[18] This bond length is similar to the typical As-As/Ge bond lengths observed in chalcogenide glasses. Strongly overlapping ranges of As-Se and As-As bond lengths have also been observed in the case of As_4Se_4 and As_2Se_3 crystals, although the mean As-Se distances in these crystals (2.38–2.40 Å) turn out to be slightly shorter than the mean As-As distance (2.44 Å).[19] Therefore, it is practically impossible to distinguish between As and Se backscatterers in the first coordination shell of the As atoms and only the average nearest-neighbor distances have been extracted for As from the fitting of the As EXAFS data. It is important to note that the Debye-Waller factor and the coordination number are correlated quantities in EXAFS data analysis and the quality of the fit can be kept unchanged by varying both the quantities simultaneously over a limited range. The related uncertainties in the coordination numbers of Ge and As atoms in these glasses are found to be of the order of ±0.15 or less.



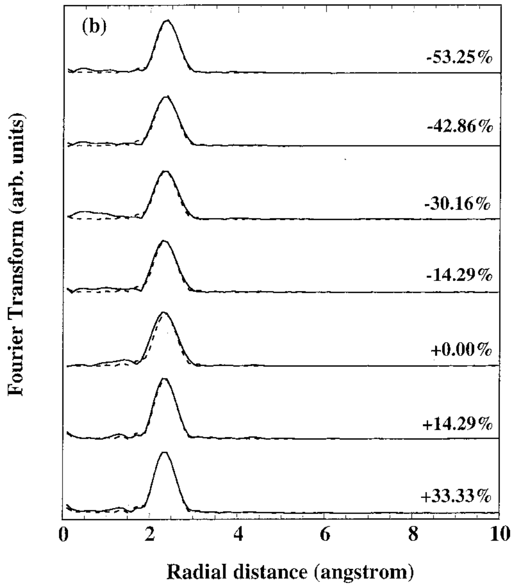
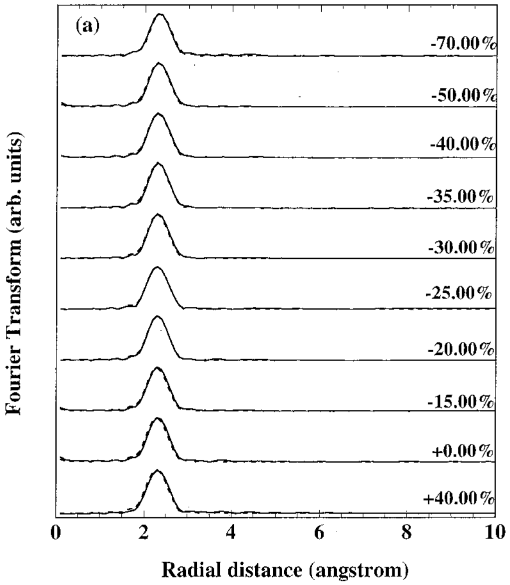


FIG. 3. Magnitudes of the Fourier transform of the k^3-weighted (a) Ge and (b) As K-edge EXAFS spectra of $Ge_xAs_ySe_{1-x-y}$ glasses with $x{:}y=1{:}1$ with various levels of Se in excess of stoichiometry. Solid lines represent experimental data, and dashed lines correspond to least-squares fits obtained using EXCURV92.



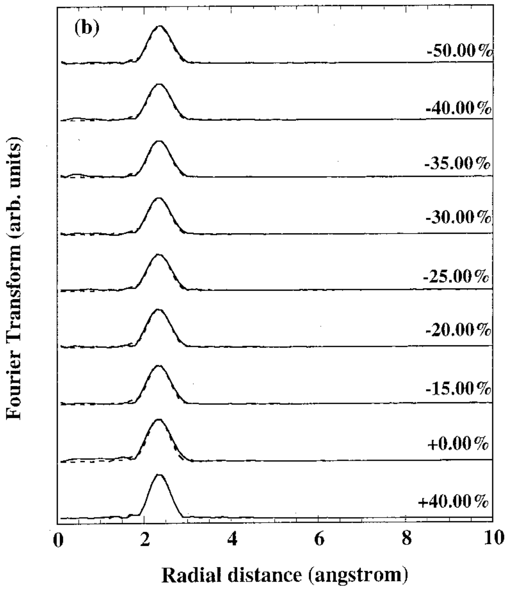


FIG. 4. Magnitudes of the Fourier transform of the k^3-weighted (a) Ge and (b) As K-edge EXAFS spectra of $Ge_xAs_ySe_{1-x-y}$ glasses with $x{:}y=1{:}2$ with various levels of Se in excess of stoichiometry. Solid lines represent experimental data, and dashed lines correspond to least-squares fits obtained using EXCURV92.

III. RESULTS

A. $Ge_xAs_ySe_{1-x-y}$ ($x{:}y=1{:}1$ and $1{:}2$) glasses

The k^3-weighted experimental Ge and As K-edge EXAFS spectra and the theoretical fits for the two series of $Ge_xAs_ySe_{1-x-y}$ glasses with $x{:}y=1{:}1$ and $x{:}y=1{:}2$ are shown in Figs. 1 and 2. The corresponding Fourier transforms are shown in Figs. 3 and 4. The Ge EXAFS spectra were fitted following the procedure described in Sec. II, where the nearest-neighbor Ge-Se and Ge-Ge/As distances for all glasses were kept constant at 2.365 and 2.425 Å, respectively. This fitting yields an average first shell coordination number of 4.0 ± 0.1 for Ge atoms in all glasses (Tables I and II). This result is consistent with a tetrahedral configuration for the coordination polyhedra of Ge atoms. More interestingly, the nearest-neighbor coordination shell of the Ge atoms in all glasses is found to consist solely of Se atoms except for the most Se deficient glasses in each series where it consists of a mixture of Se and X ($X=$Ge,As) atoms (Tables I and II and Fig. 5).

The coordination number and average nearest-neighbor distance for As atoms in these glasses, as obtained from fitting the As EXAFS spectra, are found to be insensitive to whether the nearest-neighbor atoms in the fitting process are

TABLE I. (a) Ge K-edge EXAFS structural parameters for $Ge_xAs_ySe_{1-x-y}$ $(x{:}y=1{:}1)$ glasses. (b) As K-edge EXAFS structural parameters for $Ge_xAs_ySe_{1-x-y}$ $(x{:}y=1{:}1)$ glasses.

(a)

Composition	First coordination shell[a]						%Se in excess of stoichiometry
	N_{Se}	R_{Se} (Å)	$2\sigma^2_{Se}$ (Å^2)	N_x	R_x (Å)	$2\sigma^2_x$ (Å^2)	
$Ge_{0.150}As_{0.150}Se_{0.700}$	4.1	2.36(5)	0.012	0.0	– – –	– – –	+33.33
$Ge_{0.167}As_{0.167}Se_{0.666}$	4.0	2.36(5)	0.012	0.0	– – –	– – –	+14.29
$Ge_{0.182}As_{0.182}Se_{0.636}$	4.1	2.36(5)	0.012	0.0	– – –	– – –	0.0
$Ge_{0.200}As_{0.200}Se_{0.600}$	4.1	2.36(5)	0.012	0.0	– – –	– – –	−14.29
$Ge_{0.225}As_{0.225}Se_{0.550}$	4.0	2.36(5)	0.012	0.0	– – –	– – –	−30.16
$Ge_{0.250}As_{0.250}Se_{0.500}$	4.0	2.36(5)	0.012	0.0	– – –	– – –	−42.86
$Ge_{0.275}As_{0.275}Se_{0.450}$	3.5	2.36(5)	0.012	0.6	2.42(5)	0.012	−53.25

(b)

Composition	First coordination shell (Se/Ge/As)[b]			%Se in excess of stoichiometry
	N	R (Å)	$2\sigma^2$ (Å^2)	
$Ge_{0.150}As_{0.150}Se_{0.700}$	3.0	2.41(0)	0.010	+33.33
$Ge_{0.167}As_{0.167}Se_{0.666}$	3.0	2.41(7)	0.010	+14.29
$Ge_{0.182}As_{0.182}Se_{0.636}$	3.1	2.41(8)	0.013	0.0
$Ge_{0.200}As_{0.200}Se_{0.600}$	3.0	2.41(0)	0.013	−14.29
$Ge_{0.225}As_{0.225}Se_{0.550}$	3.0	2.42(0)	0.014	−30.16
$Ge_{0.250}As_{0.250}Se_{0.500}$	3.0	2.43(0)	0.014	−42.86
$Ge_{0.275}As_{0.275}Se_{0.450}$	3.1	2.44(0)	0.011	−53.25

[a] The subscripts Se and x denote structural parameters corresponding to Se and Ge/As nearest neighbors, respectively.

[b] These structural fit parameters are independent of the nature of the nearest neighbors of As atoms, within the limits of statistical significance.

chosen to be either Se or X $(X=\mathrm{Ge,As})$, or any combination of the two. The fitting yields a first shell coordination number of 3.0±0.1 for As in all glasses, consistent with a trigonal pyramidal configuration for the coordination polyhedra of As atoms (Tables I and II). On the other hand, the average nearest-neighbor distance for As atoms within each glass series remains nearly constant at 2.40–2.41 Å for glasses with excess and stoichiometric Se contents but starts increasing progressively in Se-deficient glasses to up to 2.43–2.44 Å with decreasing Se content (Fig. 6). As mentioned previously, the average As-Se nearest-neighbor distances (2.38–2.40 Å) in As-selenide crystals tend to be slightly shorter than the As-As nearest-neighbor distances (2.44 Å).[19] Therefore, the increase in the average nearest-neighbor distances for As atoms in Se-deficient $Ge_xAs_ySe_{1-x-y}$ glasses is consistent with the formation of As-X bonds in glasses with even the lowest levels of Se deficiency (Tables I and II).

B. $\mathbf{Ge_{0.154}As_{0.308}(S,Se)_{0.538}}$ glasses

The k^3-weighted experimental Ge and As K-edge EXAFS spectra and the theoretical fits for the four chalcogen-deficient sulfoselenide glasses in this series with S/(S+Se) ratios of 0.2, 0.4, 0.6, and 0.8 are shown in Fig. 7. The corresponding Fourier transforms are shown in Fig. 8. The Ge EXAFS spectra were fitted with a mixed shell of S and Se nearest neighbors around Ge atoms, where the Ge-Se and Ge-S distances were allowed to vary freely. Such a fitting procedure results in a coordination number of 4.0±0.1 for Ge atoms in these glasses (Table III). Furthermore, the Ge-S and Ge-Se bond lengths are found to be independent of the S/(S+Se) ratio of the glass and have values of 2.21 and 2.36 Å, respectively, except for the glass with the highest S/(S+Se) ratio which has a slightly longer (~2.38 Å) Ge-Se bond (Table III). This result may imply the presence of some Ge-X bonds in the highest S-containing glass, consistent with the finding in a previous study that nearly 10% of the nearest neighbors of Ge atoms in the pure sulfide end member $Ge_{0.154}As_{0.308}S_{0.538}$ glass of this series are in fact X atoms.[5] The average number of nearest-neighbor S atoms around each Ge in this series of sulfoselenide glasses follows a trend similar to that expected from a random substitution of Se by S (or vice versa) around Ge atoms (Fig. 9). Since the Ge atoms in these glasses show predominantly heteropolar bonding to S and Se nearest neighbors, the chemical compositions of these glasses mandate that, on average, each As atom be coordinated to ~1.5 As atoms and 1.5 S and/or Se atoms. Such a constraint has been used to fit the As EXAFS spectra of these glasses which yields remarkably consistent As-S, As-Se, and As-As bond lengths of 2.23–2.25, 2.33–2.35 and 2.44–2.45 Å, respectively (Table III). Moreover, the average number of S nearest neighbors around each As atom in these glasses, when plotted as a function of the S/(S+Se) ratio, clearly indicate a random substitution of Se by S in the coordination polyhedra of As atoms (Fig. 9). Similar random substitution of Se by S in the glass structure

TABLE II. (a) Ge K-edge EXAFS structural parameters for $Ge_xAs_ySe_{1-x-y}$ ($x{:}y=1{:}2$) glasses. (b) As K-edge EXAFS structural paramaters for $Ge_xAs_ySe_{1-x-y}$ ($x{:}y=1{:}2$) glasses.

Composition	(a) First coordination shell[a]						%Se in excess of stoichiometry
	N_{Se}	R_{Se} (Å)	$2\sigma^2_{Se}$ (Å^2)	N_x	R_x (Å)	$2\sigma^2_x$ (Å^2)	
$Ge_{0.100}As_{0.200}Se_{0.700}$	4.0	2.36(5)	0.012	0.0	− − −	− − −	+40.0
$Ge_{0.125}As_{0.250}Se_{0.625}$	4.1	2.36(5)	0.012	0.0	− − −	− − −	0.0
$Ge_{0.138}As_{0.276}Se_{0.586}$	4.1	2.36(5)	0.012	0.0	− − −	− − −	−15.0
$Ge_{0.143}As_{0.286}Se_{0.571}$	4.0	2.36(5)	0.012	0.0	− − −	− − −	−20.0
$Ge_{0.148}As_{0.296}Se_{0.555}$	4.0	2.36(5)	0.012	0.0	− − −	− − −	−25.0
$Ge_{0.154}As_{0.308}Se_{0.538}$	4.0	2.36(5)	0.012	0.0	− − −	− − −	−30.0
$Ge_{0.160}As_{0.320}Se_{0.520}$	4.1	2.36(5)	0.012	0.0	− − −	− − −	−35.0
$Ge_{0.167}As_{0.334}Se_{0.500}$	4.0	2.36(5)	0.012	0.0	− − −	− − −	−40.0
$Ge_{0.182}As_{0.364}Se_{0.454}$	4.0	2.36(5)	0.012	0.0	− − −	− − −	−50.0
$Ge_{0.200}As_{0.400}Se_{0.400}$	3.6	2.36(5)	0.012	0.5	2.42(5)	0.012	−60.0
$Ge_{0.222}As_{0.444}Se_{0.333}$	2.1	2.36(5)	0.012	1.9	2.42(5)	0.012	−70.0

Composition	(b) First coordination shell (Se/Ge/As)[b]			%Se in excess of stoichiometry
	N	R (Å)	$2\sigma^2$ (Å)	
$Ge_{0.100}As_{0.200}Se_{0.700}$	3.0	2.40(4)	0.010	+40.0
$Ge_{0.125}As_{0.250}Se_{0.625}$	3.1	2.40(6)	0.010	0.0
$Ge_{0.138}As_{0.276}Se_{0.586}$	3.0	2.40(6)	0.014	−15.0
$Ge_{0.143}As_{0.286}Se_{0.571}$	3.0	2.40(6)	0.014	−20.0
$Ge_{0.148}As_{0.296}Se_{0.555}$	3.0	2.41(2)	0.014	−25.0
$Ge_{0.154}As_{0.308}Se_{0.538}$	3.1	2.41(4)	0.014	−30.0
$Ge_{0.160}As_{0.320}Se_{0.520}$	3.0	2.41(6)	0.014	−35.0
$Ge_{0.167}As_{0.334}Se_{0.500}$	3.0	2.41(8)	0.014	−40.0
$Ge_{0.182}As_{0.364}Se_{0.454}$	3.0	2.42(9)	0.014	−50.0

[a] The subscripts Se and x denote structural parameters corresponding to Se and Ge/As nearest neighbors, respectively.

[b] These structural fit parameters are independent of the nature of the nearest neighbors of As atoms, within the limits of statistical significance.

has also been observed in the chalcogen-excess $Ge_{0.100}As_{0.200}S_{0.560}Se_{0.140}$ glass. In this glass the average nearest-neighbor coordination environment of the Ge (As) atoms consists of 3.2 (2.4) S and 0.8 (0.6) Se nearest neighbors, thus maintaining the S:Se ratio of 4:1 of the bulk composition. The corresponding Ge(As)-S and Ge(As)-Se bond lengths are found to be 2.22 (2.24) and 2.36 (2.41) Å, respectively.

IV. DISCUSSION

The analyses of the Ge and As K-edge EXAFS spectra of the GeAs selenide and sulfoselenide glasses reported here indicate that Ge and As atoms are always four- and three-coordinated, respectively, in all glasses regardless of composition. The atomic makeup of the nearest-neighbor shells of Ge and As atoms, however, changes with composition. The Ge atoms in the stoichiometric and excess Se containing $Ge_xAs_ySe_{1-x-y}$ glasses in both compositional series are found to be bonded only to Se atoms forming $GeSe_4$ polyhedra. The lack of variation in the nearest-neighbor distances for As atoms in the stoichiometric and excess Se-containing glasses also indicate predominantly heteropolar bonding with the formation of $AsSe_3$ polyhedra. Such chemical ordering automatically requires the formation of Se-Se homopolar bonds in the excess Se containing glasses. In fact the formation of Se-Se homopolar bonds has indeed been observed in previous Raman spectroscopic studies on binary Ge-Se glasses with excess Se.[20]

On the other hand, in the case of Se-deficient glasses, the progressive increase in the average nearest-neighbor distances for As atoms suggests that the structural response to Se deficiency in Ge-As-Se glasses is the formation of As-X homopolar bonds (Tables I and II and Fig. 6). In contrast, the Ge EXAFS spectra do not show any evidence of the formation of Ge-X homopolar bonds in glasses with low or intermediate levels ($>-50\%$) of Se deficiency (Tables I and II and Fig. 5). This result implies that As-As bonds are always the first metal-metal bonds to appear at low Se-deficiency levels in these glasses. Ge-X bonds begin to form only at high levels of Se deficiency (Tables I and II and Fig. 5). In fact, the corresponding compositions of the Se-deficient glasses in each series where the Ge-X bonds first becomes detectable by EXAFS imply that these bonds begin to form only when all As atoms are exhausted in As-As homopolar bonding (Tables I and II). This result provides strong evidence in favor of an inhomogeneous distribution or cluster-

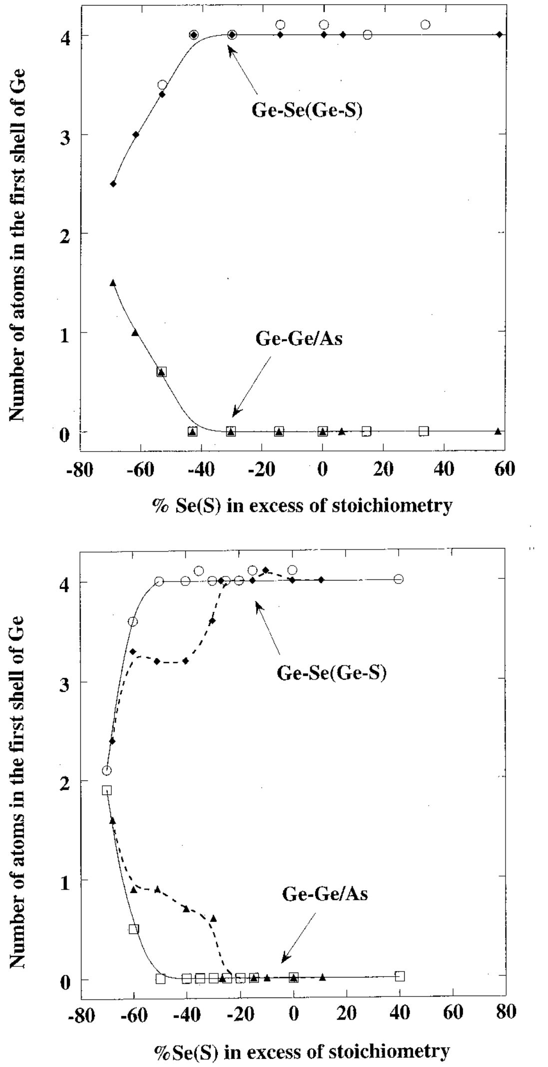


FIG. 5. (a) Compositional variation in the atomic makeup of the first coordination shell of Ge atoms in $Ge_xAs_ySe_{1-x-y}$ (open symbols) and $Ge_xAs_yS_{1-x-y}$ glasses (filled symbols) with $x{:}y = 1{:}1$, as derived from fitting the Ge *K*-edge EXAFS data. The data for sulfide glasses are taken from Ref. 5. Solid lines through the data points are guides to the eye only. (b) Compositional variation in the atomic makeup of the first coordination shell of Ge atoms in $Ge_xAs_ySe_{1-x-y}$ (open symbols) and $Ge_xAs_yS_{1-x-y}$ glasses (filled symbols) with $x{:}y = 1{:}2$, as derived from fitting the Ge *K*-edge EXAFS data. The data for sulfide glasses are taken from Ref. 5. Solid and dashed lines through the data points are guides to the eye only.

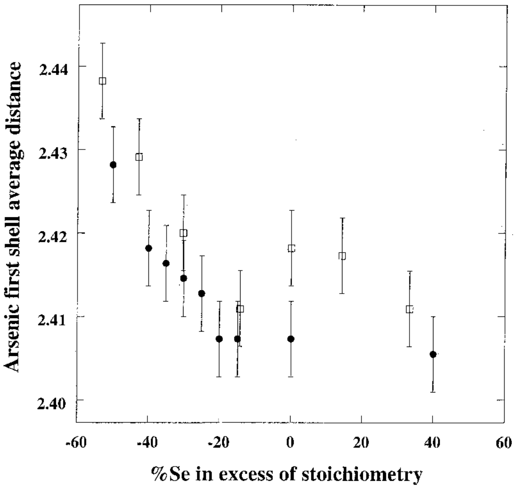


FIG. 6. Compositional variation in the average distances between As and its nearest-neighbor atoms in $Ge_xAs_ySe_{1-x-y}$ glasses with $x{:}y = 1{:}1$ (squares) and 1:2 (circles), as derived from fitting the As *K*-edge EXAFS data.

ing of As atoms and violation of chemical order in Se-deficient Ge-As-Se glasses. Such a preference of formation of As-As bonds over Ge-As or Ge-Ge bonds in Se-deficient glasses is completely consistent with recent calculations of enthalpies of bonds between Ge, As, and Se atoms.[21] These calculations indicate that Ge-Se, As-Se, and Se-Se bonds have similar enthalpies of 234.0, 227.2, and 227.0 kJ/mol respectively, and will have no significant energetic preference of formation over one another. On the other hand, the enthalpies of Ge-Ge and Ge-As bonds are 186.0 and 196.3 kJ/mol and their formation will be less preferred with respect to that of As-As bonds with an enthalpy of 201.0 kJ/mol. It must be noted in this regard that the bond enthalpies have been defined to be positive in this study and therefore, bonds form in the sequence of decreasing enthalpy.[21] Similar phenomena such as As clustering and the avoidance of Ge-*X* bond formation until all As atoms are exhausted in As-As homopolar bonding have also been observed in previous Ge and As EXAFS studies of $Ge_xAs_yS_{1-x-y}$ glasses with $x{:}y = 1{:}1$ and 2:5:1 (Ref. 5) (Fig. 5). However, these studies have also shown that the Ge atoms in S-deficient $Ge_xAs_yS_{1-x-y}$ glasses with $x{:}y = 1{:}2$ behave differently from glasses with $x{:}y = 1{:}1$ and 2.5:1. Homopolar Ge-*X* bonds in $Ge_xAs_yS_{1-x-y}$ glasses with $x{:}y = 1{:}2$ become detectable at intermediate levels of S deficiency as a result of thermodynamic stabilization of a mixed average coordination environment of 1.5 As and 1.5 S atoms around each As atom[5] (Fig. 5). Previous studies based on Raman spectroscopy have shown that such a coordination environment for As atoms can be attributed to the formation of As_4S_3 molecules in these glasses.[5] The present results on Se-deficient $Ge_xAs_ySe_{1-x-y}$ glasses with $x{:}y = 1{:}1$ and 1:2 do not reveal any such peculiarity in the clustering behavior of chalcogen atoms or any indication of the formation of molecular As_4Se_3 species (Fig. 5). The latter result is consistent with the observed rapid decrease of the thermal expansion coefficient of the $Ge_{0.154}As_{0.308}(S+Se)_{0.538}$ sulfoselenide glasses with increasing Se concentration, indicating the progressive replacement of molecular As_4S_3 species in S-rich glasses by structural elements with higher connectivity in their Se-rich analogs.[22] The apparent lack or low concentration of molecular As_4Se_3 species is also consistent with the fact that the pronounced local maximum near a chalcogen deficiency of 30% in the magnitude of the thermal-expansion coefficient of Ge-As-S glasses is only weakly expressed in the corresponding selenide glasses.[22] Our results also indicate that, in contrast with the case of clustering of As atoms in Se-

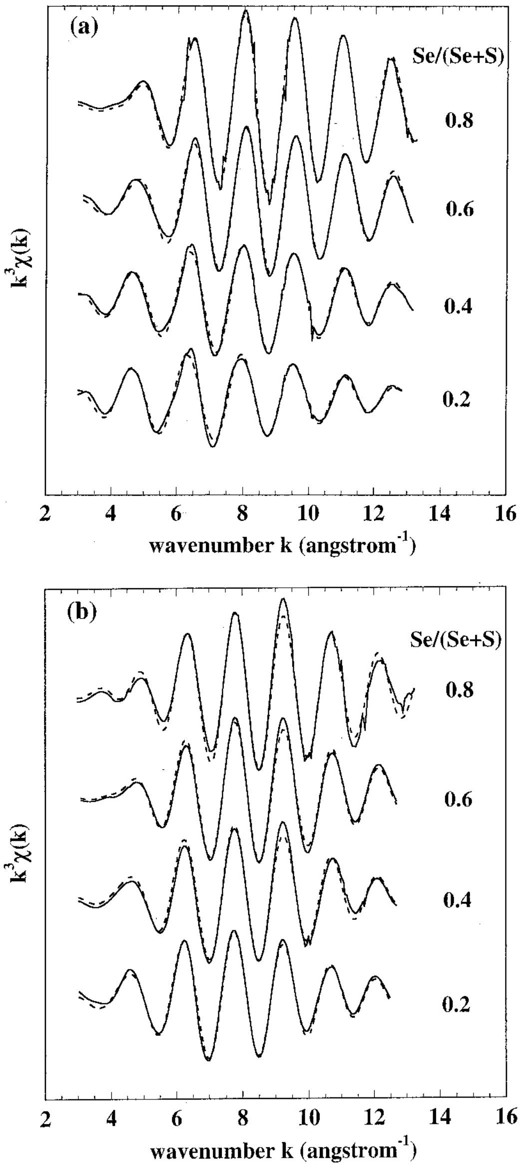


FIG. 7. k^3-weighted (a) Ge and (b) As *K*-edge EXAFS spectra of $Ge_{0.154}As_{0.308}(S,Se)_{0.538}$ glasses with varying Se/(Se+S) ratios indicated alongside each spectrum. Solid lines represent experimental data and dashed lines correspond to least-squares fits obtained using EXCURV92.

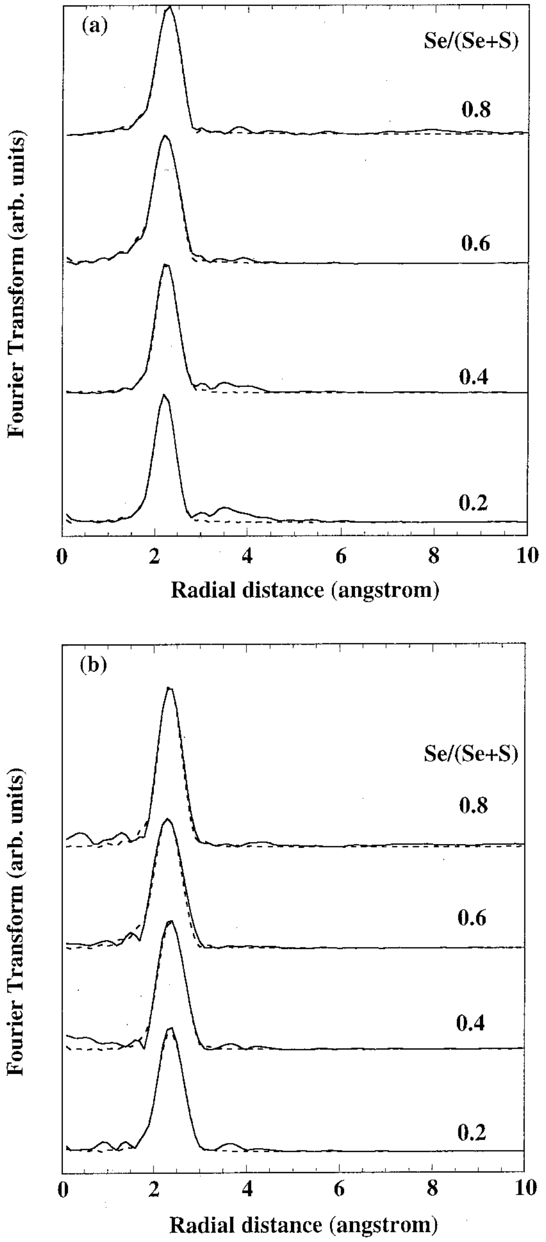


FIG. 8. Magnitudes of the Fourier-transform of the k^3-weighted (a) Ge and (b) As *K*-edge EXAFS spectra of $Ge_{0.154}As_{0.308}(S,Se)_{0.538}$ glasses with varying Se/(Se+S) ratios indicated alongside each transform. Solid lines represent experimental data and dashed lines correspond to least-squares fits obtained using EXCURV92.

deficient $Ge_xAs_ySe_{1-x-y}$ glasses, the distribution of S and Se in the first coordination shell of Ge and As atoms is random in both S,Se-excess and -deficient sulfoselenides (Fig. 9). It should be noted in this regard that previous studies based on Ge *K*-edge EXAFS spectroscopy indicate that chemical order is largely preserved in binary Ge-Se/S glasses.[15] However, a recent neutron-diffraction study has claimed violation of chemical order and presence of homopolar Ge-Ge and Se-Se bonds in the stoichiometric $GeSe_2$ glass.[23]

The strongly constrained local coordination environments of Ge, As, and S/Se atoms in these glasses allow one to extrapolate the structural aspects to the intermediate range in spite of the short-range nature of EXAFS spectroscopy as a structural probe. Thus it can be argued that the presence of Se-Se bonds in excess Se containing glasses and that of As-As bonds in glasses with low and intermediate Se deficiency levels as evidenced in this study can have important topological effects on the intermediate-range structure of these glasses. For example, within the experimental resolution, the Ge and As EXAFS spectra of the stoichiometric $Ge_xAs_ySe_{1-x-y}$ glasses in both series do not show any evidence of Ge/As-Ge/As homopolar bonding. Therefore the atomic structure of these glasses is likely to consist predominantly of a fully three-dimensional network of corner-sharing

TABLE III. (a) Ge *K*-edge EXAFS structural parameters for $Ge_{0.154}As_{0.308}(S+Se)_{0.538}$ glasses. (b) As *K*-edge EXAFS structural parameters for $Ge_{0.154}As_{0.308}(S+Se)_{0.538}$ glasses.

Composition (Se/Se+S) atomic ratio	(a) First coordination shell[a]					
	N_{Se}	R_{Se} (Å)	$2\sigma^2_{Se}$ (Å^2)	N_S	R_S (Å)	$2\sigma^2_S$ (Å^2)
0.8	3.2	2.36(1)	0.010	0.8	2.20(7)	0.010
0.6	2.5	2.36(1)	0.010	1.5	2.20(7)	0.010
0.4	1.5	2.36(7)	0.010	2.5	2.20(9)	0.010
0.2	0.8	2.38(5)	0.012	3.2	2.21(5)	0.010

Composition (Se/Se+S) atomic ratio	(b) First coordination shell[b]								
	N_{Se}	R_{Se} (Å)	$2\sigma^2_{Se}$ (Å)	N_S	R_S (Å)	$2\sigma^2_S$ (Å^2)	N_x	R_x (Å)	$2\sigma^2_x$ (Å^2)
0.8	1.5	2.35(1)	0.010	— — —	— — —	— — —	1.5	2.44(6)	0.010
0.6	1.0	2.35(1)	0.010	0.5	2.25(0)	0.010	1.5	2.45(0)	0.010
0.4	0.6	2.33(7)	0.010	1.0	2.24(9)	0.010	1.5	2.45(1)	0.010
0.2	0.3	2.34(5)	0.012	1.2	2.23(5)	0.010	1.5	2.45(0)	0.010

[a] The subscripts Se and S denote structural parameters corresponding to Se and S nearest neighbors, respectively.

[b] The subscripts Se, S, and *x* denote structural parameters corresponding to Se, S, and Ge/As nearest neighbors, respectively.

$GeSe_4$ tetrahedra and $AsSe_3$ trigonal pyramids. However, in glasses with excess Se, the formation of Se-Se bonds may result in low-dimensional structural units such as chains or rings of Se atoms embedded in a three-dimensional network of $GeSe_4$ and $AsSe_3$ polyhedra. Similarly, in the Se-deficient $Ge_xAs_ySe_{1-x-y}$ glasses the clustering of As atoms may eventually lead to the formation of corner-sharing $AsAs_3$ trigonal pyramids, possibly forming low-dimensional sheet-like intermediate-range structural units resembling the structure of crystalline As.[24] Such structural units will be interspersed with three-dimensional domains of corner-sharing Ge coordination tetrahedra in these glasses. The nature and relative abundance of such intermediate-range structural units in chalcogenide glasses may exert an important control on their physical properties, especially those that are strongly dependent on the topological aspects of atomic packing such as molar volume. For example, the presence of low-dimensional intermediate-range structural units such as chains or rings of Se atoms in Se-excess glasses and ‘‘sheets’’ of As atoms in Se-deficient glasses would be expected to lead to an increase in molar volume of these glasses with respect to that of a stoichiometric glass. In this scenario one can expect a local minimum in the molar volume of binary As-S/Se or ternary Ge_xAs_yS/Se_{1-x-y} glasses at the stoichiometric composition to be superimposed on the main trend of decreasing volume with increasing average coordination number or decreasing Se concentration. The existence of such a local minimum in molar volume near the stoichiometric composition has indeed been observed experimentally in binary As-S/Se glasses, ternary $Ge_xAs_ySe_{1-x-y}$ glasses with $x:y=1:1$ and 1:2, and ternary $Ge_xAs_yS_{1-x-y}$ glasses with $x:y=1:1$, 1:2, and 2.5:1.[5,11,22,25] Such a topological argument can not be extended directly to As-free glasses such as binary Ge-S/Se compositions since, in contrast with As-As bonds, the formation of Ge-Ge bonds in the S/Se-deficient $Ge_x(S/Se)_y$ glasses is not likely to result in low-dimensional structural units. In fact the experimental molar volume of $Ge_x(S/Se)_y$ glasses show a local maximum at the stoichiometric $Ge(S/Se)_2$ composition.[25] This behavior can be related to the presence of a significant concentration of edge-shared $Ge(S/Se)_4$ tetrahedra in this glass as has been shown in a recent Ge *K*-edge EXAFS spectroscopic study.[26] The concentration of these structural units is maximized in the stoichiometric composition and may lead to low-dimensional intermediate-range structural units with less efficient packing compared to corner-shared tetrahedra. How-

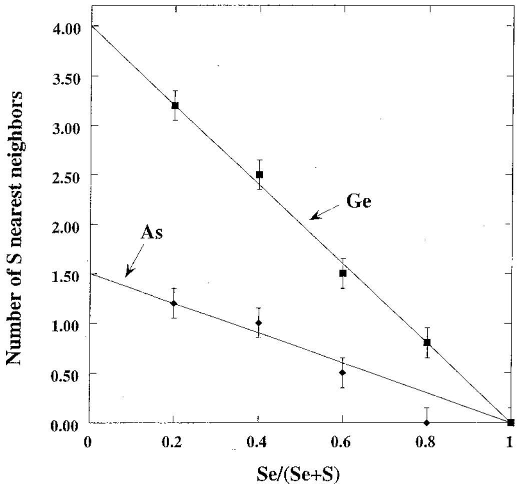


FIG. 9. Compositional variation in the number of S nearest neighbors in the first coordination shell of Ge and As atoms in $Ge_{0.154}As_{0.308}(S,Se)_{0.538}$ glasses with varying Se/(Se+S) ratios, as derived from fitting the Ge and As *K*-edge EXAFS data. Solid lines correspond to the expected number of S nearest neighbors around Ge and As in the case of a random distribution of S and Se atoms in these glasses.

ever, such topological arguments can become inadequate in explaining the compositional trends for elastic and thermal properties of chalcogenide glasses that are not directly related to the topology but depend more on the bond strength and connectivity or average coordination number.

V. SUMMARY

The present Ge and As EXAFS results indicate that, irrespective of glass composition, Ge and As atoms are invariably four and three-coordinated, respectively, in ternary $Ge_xAs_ySe_{1-x-y}$ and quaternary $Ge_{0.154}As_{0.308}$ $(S,Se)_{0.538}$ glasses. Chemical order is preserved in stoichiometric and Se-excess glasses where Ge and As atoms predominantly form heteropolar bonds with Se atoms. On the other hand, metal-metal homopolar bonds are formed almost exclusively between As atoms in glasses with low and intermediate levels of Se deficiency indicating violation of chemical order and clustering of As atoms. The Ge atoms take part in homopolar bonding at high levels of Se deficiency only when all As atoms are exhausted in the formation of As-As bonds. These structural aspects of Ge-As selenide glasses are similar to those observed in their sulfide analogs in previous studies. However, no evidence of the stabilization of molecular As_4Se_3 species is observed in selenide glasses at or near a Se deficiency level of −30% in contrast with their sulfide analogs which show the formation of As_4S_3 molecules, especially in glasses with Ge:As=1:2. The Ge and As EXAFS results also show that chemical order is preserved in the chalcogen ''sublattice'' of the $Ge_{0.154}As_{0.308}$ $(S,Se)_{0.538}$ sulfoselenide glasses where the average numbers of S and Se atoms in the coordination shells of Ge and As atoms follow a random distribution. The formation of chalcogen-chalcogen bonds in chalcogen-excess glasses and that of As-As bonds in chalcogen-deficient glasses with low and intermediate levels of chalcogen deficiency are expected to result in low-dimensional intermediate-range structural units. The topological consequences of such structural units can be important in explaining the compositional variation of properties such as molar volume in these glasses.

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[1] A. B. Seddon, J. Non-Cryst. Solids **184**, 44 (1995).

[2] U. Senapati, K. Firstenberg, and A. K. Varshneya, J. Non-Cryst. Solids **222**, 153 (1997).

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

[4] K. Tanaka, Phys. Rev. B **39**, 1270 (1989).

[5] S. Sen, B. G. Aitken, and C. W. Ponader, Phys. Rev. B **64**, 104202 (2001); B. G. Aitken and C. W. Ponader, J. Non-Cryst. Solids **274**, 124 (2000).

[6] A. K. Varshneya, J. Non-Cryst. Solids **273**, 1 (2000); W. A. Kamitakahara, R. L. Cappelletti, P. Boolchand, B. L. Halfpap, F. Gompf, D. A. Neumann, and H. Mutka, Phys. Rev. B **44**, 94 (1991); M. Tatsumisago, B. L. Halfpap, J. L. Green, S. M. Lindsay, and C. A. Angell, Phys. Rev. Lett. **64**, 1549 (1990); B. L. Halfpap and S. M. Lindsay, *ibid.* **57**, 847 (1986); R. Aravinda Narayanan, S. Asokan, and A. Kumar, Phys. Rev. B **54**, 4413 (1996).

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

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

[9] W. Zhou, M. A. Paesler, and D. E. Sayers, Phys. Rev. B **46**, 3817 (1992).

[10] R. A. Street and D. K. Biegelsen, J. Non-Cryst. Solids **32**, 339 (1979).

[11] B. G. Aitken and C. W. Ponader, J. Non-Cryst. Solids **256&257**, 143 (1999).

[12] P. E. Lippens, J. C. Jumas, J. Olivier-Fourcade, and L. Aldon, J. Non-Cryst. Solids **271**, 119 (2000).

[13] N. Binsted, S. J. Gurman, and J. C. Campbell, SERC Daresbury Lab. EXCURV092 Program (1992).

[14] S. J. Gurman, N. Binsted, and I. Ross, J. Phys. C **17**, 143 (1984).

[15] W. Zhou, M. A. Paesler, and D. E. Sayers, Phys. Rev. B **43**, 2315 (1991).

[16] J. Choi, S. J. Gurman, and E. A. Davis, J. Non-Cryst. Solids **297**, 156 (2002).

[17] A. M. Edwards, M. C. Fairbanks, R. J. Newport, S. J. Gurman, and E. A. Davis, J. Non-Cryst. Solids **113**, 41 (1989).

[18] W. A. King, A. G. Clare, W. C. LaCourse, K. Volin, A. C. Wright, and A. J. Wanless, Phys. Chem. Glasses **38**, 269 (1997).

[19] A. L. Renninger and B. L. Averbach, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. **29**, 1583 (1973).

[20] S. Sugai, Phys. Rev. B **35**, 1345 (1987).

[21] M. H. R. Lankhorst, J. Non-Cryst. Solids **297**, 210 (2002).

[22] B. G. Aitken, XIX Int. Congr. Glass, Invited Papers (2001), p. 135 (unpublished).

[23] I. Petri, P. S. Salmon, and H. E. Fischer, Phys. Rev. Lett. **84**, 2413 (2000).

[24] P. M. Smith, A. J. Leadbetter, and A. J. Apling, Philos. Mag. **31**, 57 (1975); D. Schiferl and C. S. Barrett, J. Appl. Crystallgr. **2**, 30 (1969).

[25] A. Feltz, *Amorphous and Liquid Semiconductors* (VCH, New York, 1993).

[26] P. Armand, A. Ibanez, H. Dexpert, and E. Philippot, J. Non-Cryst. Solids **139**, 137 (1992).