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Ge and As x-ray absorption fine structure spectroscopic study of homopolar bonding, chemical order, and topology in Ge-As-S chalcogenide glasses

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The coordination environments of Ge and As atoms in $Ge_xAs_yS_{1-x-y}$ glasses with $x:y=1:2$, 1:1, and 2.5:1 and with wide-ranging S contents have been studied with Ge and As *K*-edge x-ray absorption fine structure spectroscopy. The coordination numbers of Ge and As atoms are found to be 4 and 3, respectively, in all glasses. The first coordination shells of Ge and As atoms in the stoichiometric and S-excess glasses consist of S atoms only, implying the preservation of chemical order at least over the length scale of the first coordination shell. As-As homopolar bonds are found to appear at low and intermediate levels of S deficiency, whereas Ge-Ge bonds are formed only in strongly S-deficient glasses indicating clustering of metal atoms and violation of chemical order in S-deficient glasses. The composition-dependent variation in chemical order in chalcogenide glasses has been hypothesized to result in topological changes in the intermediate-range structural units. The role of such topological transitions in controlling the structure-property relationships in chalcogenide glasses is discussed.

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I. INTRODUCTION

The physicochemical properties of chalcogenide glasses in the system Ge-As-S,Se have been studied intensively in the last 20 years because of their technological importance in the field of optical devices.[1,2] The chalcogenide glasses have also been used as model systems for studying the influence of topological constraints on the compositional variation of various physical properties in covalently bonded amorphous materials.[3,4] It has been argued on the basis of the theory of constraint counting that the physical properties of these glasses would be predominantly controlled by the average coordination number $\langle r\rangle$, irrespective of their actual chemical compositions.[3,4] The Ge, As, and S(Se) atoms in a $Ge_xAs_y(S,Se)_{1-x-y}$ glass are 4, 3, and 2 coordinated, respectively. Therefore the average coordination number $\langle r\rangle$ for such a glass can be written as $\langle r\rangle=4x+3y+2(1-x-y)$. A simple counting of the bond length and angle constraints on the total number of degrees of freedom available to a mole of three-dimensionally connected atoms shows that the system of atoms would undergo a rigidity percolation type of transition at $\langle r\rangle=2.4$.[3,4] Detailed studies of the compositional dependence of elastic, thermodynamic, transport, and electronic properties in chalcogenide glasses indicate that some properties indeed show such a transition at $\langle r\rangle\approx2.4$, although another important transition or extremum is almost always present at $\langle r\rangle\approx2.67$.[5,6] The latter transition has recently been speculated to be a manifestation of a topological phase transition in the chalcogenide glass structure. According to this model, for $\langle r\rangle\leqslant2.7$, the topological dimensionality D of the glass structure is $\leqslant2$ whereas for $\langle r\rangle>2.7$ the glasses are characterized by a three-dimensionally connected structure, i.e., $D=3$.[6]

However, these topological arguments do not take into account the differences between the characters of various homopolar and heteropolar bonds and the degree of chemical order in the chalcogenide glass structure. Recent spectroscopic studies have clearly indicated the presence of homopolar bonds in the atomic structure of nonstoichiometric chalcogenide glasses.[7–9] Homopolar bonding may result in a violation of the chemical order in the structure with clustering of the constituent atoms.[9] Such clustering of constituent atoms would have important influences on the nature and dimensionality of the intermediate-range structural units in the glass. A systematic study of the bonding environment and chemical order in chalcogenide glasses over a wide composition range and $\langle r\rangle$ values is therefore needed in order to test these hypotheses. We report here the results of a detailed Ge and As *K*-edge x-ray absorption fine structure (EXAFS) spectroscopic study of the local coordination environments of Ge and As atoms in Ge-As-S glasses. Three series of $Ge_xAs_yS_{1-x-y}$ glass compositions with $x:y=1:1$, 2.5:1, and 1:2 and with $\langle r\rangle$ values ranging between 2.351 and 2.975 have been studied. We also report the Ge EXAFS results for a number of S-deficient binary Ge-sulfide glasses in order to make a structural comparison between these and the S-deficient ternary glasses.

II. EXPERIMENT

A. Sample preparation

The Ge-As-sulfide glasses were prepared by melting mixtures of the constituent elements (⩾99.9995% purity, metals basis). These mixtures were contained in evacuated (10^{-6} Torr) flame-sealed fused-silica ampoules and were melted in a rocking furnace at ~1200 K for at least 24 h. Cylindrical glass rods were obtained by quenching the ampoules in water followed by annealing for 1 h at the respective glass-transition temperatures. The nominal compositions of the GeAsS glasses studied here are shown in Fig. 1 and are also listed in Tables I, II, and III. The compositions of these glasses have also been denoted in this paper in terms of ‘‘% S in excess of stoichiometry’’ which corresponds to the

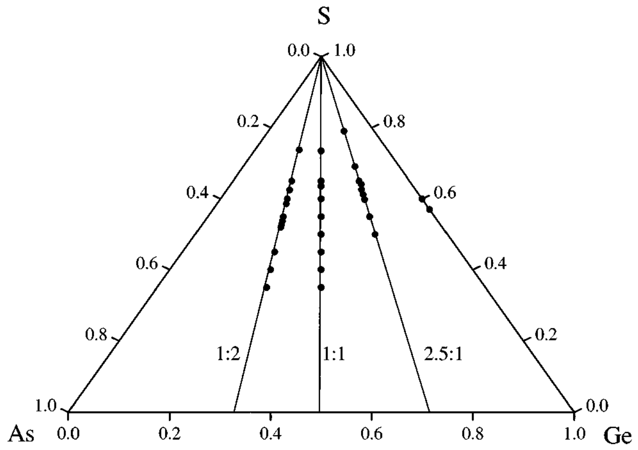

FIG. 1. Ternary plot of the $Ge_xAs_yS_{1-x-y}$ glass compositions investigated in this study.

percentage amount of S in a glass in excess of the stoichiometric composition, i.e., $Ge_xAs_yS_{2x+1.5y}$ (see Tables I, II, III, and IV).

B. EXAFS spectroscopy

1. Data collection

All Ge and As *K*-edge (11 103 and 11 867 eV, respectively) EXAFS spectra were collected at beam line X10C at the National Synchrotron Light Source at Brookhaven National Laboratory with electron-beam energy of 2.5 GeV and beam currents between 150 and 300 mA. A Si(220) monochromator was used with the focusing mirror tuned to reject higher harmonics. All samples were finely ground to powders and were mounted 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 the thermal Debye-Waller factor on the signal. The EXAFS data were collected in the transmission mode in energy steps 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. Synthetic As_2S_3, AsS, GeS, and GeS_2 crystals were used as model compounds.

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.[10] The EXBROOK package has been used to subtract a linear background in the preedge region and a quadratic background in the postedge 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.[11] The three structural parameters that are varied 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 $2\sigma^2$.

TABLE I. Ge and As *K*-edge EXAFS structural parameters for $Ge_xAs_yS_{1-x-y}$ $(x{:}y=1{:}1)$ glasses.

	First coordination shell[a]						%S in excess of stoichiometry
Composition	N_S	R_S (Å)	$2\sigma_S^2$ (Å^2)	N_x	R_x (Å)	$2\sigma_x^2$ (Å^2)	
Ge *K*-edge							
$Ge_{0.133}As_{0.133}S_{0.734}$	4.0	2.21	0.012	0.0			+57.7
$Ge_{0.175}As_{0.175}S_{0.650}$	4.0	2.20	0.012	0.0			+6.1
$Ge_{0.182}As_{0.182}S_{0.636}$	4.0	2.20	0.014	0.0			0.0
$Ge_{0.200}As_{0.200}S_{0.600}$	4.0	2.20	0.015	0.0			−14.3
$Ge_{0.225}As_{0.225}S_{0.550}$	4.0	2.22	0.012	0.0			−30.2
$Ge_{0.250}As_{0.250}S_{0.500}$	4.0	2.22	0.009	0.0			−42.9
$Ge_{0.275}As_{0.275}S_{0.450}$	3.4	2.22	0.010	0.6	2.46	0.005	−53.3
$Ge_{0.300}As_{0.300}S_{0.400}$	3.0	2.23	0.006	1.0	2.47	0.004	−61.9
$Ge_{0.325}As_{0.325}S_{0.350}$	2.5	2.23	0.012	1.5	2.47	0.004	−69.2
As *K*-edge							
$Ge_{0.133}As_{0.133}S_{0.734}$	3.0	2.25	0.014	0.0			+57.7
$Ge_{0.715}As_{0.175}S_{0.650}$	3.0	2.25	0.015	0.0			+6.1
$Ge_{0.182}As_{0.182}S_{0.636}$	3.0	2.27	0.009	0.0			0.0
$Ge_{0.200}As_{0.200}S_{0.600}$	2.5	2.23	0.010	0.5	2.46	0.005	−14.3
$Ge_{0.225}As_{0.225}S_{0.550}$	1.8	2.26	0.005	1.2	2.46	0.005	−30.2
$Ge_{0.250}As_{0.250}S_{0.500}$	1.2	2.22	0.005	1.9	2.45	0.005	−42.9
$Ge_{0.275}As_{0.275}S_{0.450}$	0.0			3.0	2.43	0.011	−53.3
$Ge_{0.300}As_{0.300}S_{0.400}$	0.0			3.1	2.44	0.012	−61.9
$Ge_{0.325}As_{0.325}S_{0.350}$	0.0			3.1	2.43	0.008	−69.2

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

TABLE II. Ge and As K-edge EXAFS structural parameters for $Ge_xAs_yS_{1-x-y}$ (x:y=2.5:1) glasses.

	First coordination shell[a]						%S in excess of stoichiometry
Composition	N_S	R_S (Å)	$2\sigma_S^2$ (Å^2)	N_x	R_x (Å)	$2\sigma_x^2$ (Å^2)	
Ge K-edge							
$Ge_{0.150}As_{0.060}S_{0.790}$	4.0	2.20	0.007	0.0			+102.6
$Ge_{0.222}As_{0.088}S_{0.690}$	4.0	2.20	0.008	0.0			+20.0
$Ge_{0.250}As_{0.100}S_{0.650}$	4.0	2.20	0.009	0.0			0.0
$Ge_{0.258}As_{0.103}S_{0.638}$	4.0	2.20	0.007	0.0			−5.0
$Ge_{0.267}As_{0.107}S_{0.626}$	4.0	2.21	0.009	0.0			−10.0
$Ge_{0.277}As_{0.111}S_{0.612}$	4.0	2.21	0.009	0.0			−15.0
$Ge_{0.287}As_{0.115}S_{0.598}$	4.0	2.21	0.010	0.0			−20.0
$Ge_{0.321}As_{0.129}S_{0.550}$	3.2	2.22	0.009	0.9	2.44	0.013	−34.4
$Ge_{0.357}As_{0.143}S_{0.500}$	2.6	2.22	0.007	1.5	2.46	0.011	−46.2
As K-edge							
$Ge_{0.150}As_{0.060}S_{0.790}$	3.0	2.26	0.007	0.0			+102.6
$Ge_{0.222}As_{0.088}S_{0.690}$	3.0	2.25	0.014	0.0			+20.0
$Ge_{0.250}As_{0.100}S_{0.650}$	3.0	2.24	0.013	0.0			0.0
$Ge_{0.258}As_{0.103}S_{0.638}$	2.7	2.25	0.007	0.3	2.48	0.012	−5.0
$Ge_{0.267}As_{0.107}S_{0.626}$	1.7	2.23	0.008	1.3	2.46	0.012	−10.0
$Ge_{0.277}As_{0.111}S_{0.612}$	1.3	2.24	0.009	1.7	2.46	0.011	−15.0
$Ge_{0.287}As_{0.115}S_{0.598}$	0.9	2.23	0.007	2.1	2.45	0.013	−20.0
$Ge_{0.321}As_{0.129}S_{0.550}$	0.0			3.0	2.43	0.014	−34.4
$Ge_{0.357}As_{0.143}S_{0.500}$	0.0			3.0	2.43	0.014	−46.2

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

The calculated electron scattering phase shifts for As-S, Ge-S, and Ge-As atom pairs were tested by fitting the Ge and As EXAFS spectra of the model compounds and proved to be adequate without further refinement. It should be noted in this regard that Ge and As backscatterers cannot be distinguished by EXAFS due to the similarity in their electronic structures. The nonstructural fitting parameters include the amplitude factor that corrects for amplitude reduction resulting from events such as multiple excitations and the imaginary part of the potential that is a measure of the mean free path of the photoelectron.[12] These parameters have been optimized by fitting the EXAFS spectra of the model compounds and have been treated as transferable constants for analysis of the glass spectra. 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 ± 0.2 or less.

III. RESULTS

A. $Ge_xAs_yS_{1-x-y}$ (x:y=1:1 and 2.5:1) glasses

The k^3-weighted experimental Ge and As K-edge EXAFS spectra and the theoretical fits for the two series of $Ge_xAs_yS_{1-x-y}$ glasses with x:y=1:1 and x:y=2.5:1 are shown in Figs. 2 and 3. These spectra show clear signs of progressive change in the local coordination environment of Ge and As atoms in these glasses as a function of increasing S deficiency (Figs. 2 and 3). The corresponding Fourier transforms are shown in Figs. 4 and 5. The fitting of the Ge and As EXAFS spectra yields first-shell coordination numbers of 4 and 3 for Ge and As atoms, respectively, in these glasses (Tables I and II). This result is consistent with tetrahedral and trigonal pyramidal configuration for the coordination polyhedra of Ge and As atoms, respectively. However, more interestingly, the first shell of both Ge and As atoms is found to change from one consisting solely of S atoms in excess-S-containing glasses to one consisting of an increasing fraction of X atoms (X=Ge, As) in S-deficient glasses. The Ge-S and Ge-X bond lengths in these glasses vary over a narrow range of 2.20–2.23 and 2.46–2.47 Å, respectively (Tables I and II). The As-S and As-X bond lengths are found to range between 2.23–2.26 and 2.43–2.47 Å, respectively. These bond lengths do not show any significant compositional variation and are fairly typical of the Ge-sulfide and As-sulfide binary crystalline phases.[13] It must be noted that similar electronic structures of Ge and As backscattering atoms do not allow them to be distinguished directly by EXAFS. However, with increasing S deficiency the As-X bonds are always the first metal-metal bonds to appear at the lowest S deficiency level in these glasses (Tables I and II). On the other hand, Ge-X bonds begin to form at a much higher S deficiency level only when the first coordination shell of As atoms consists solely of X atoms. This result clearly implies that the As-X and Ge-X bonds in these glasses are exclusively between the same atom types, i.e., they are As-As and Ge-Ge bonds. This compositional varia-

TABLE III. Ge and As K-edge EXAFS structural parameters for $Ge_xAs_yS_{1-x-y}$ $(x:y=1:2)$ glasses.

	First coordination shell[a]						%S in excess of stoichiometry
Composition	N_S	R_S (Å)	$2\sigma_S^2$ (Å^2)	N_x	R_x (Å)	$2\sigma_x^2$ (Å^2)	
Ge K-edge							
$Ge_{0.117}As_{0.233}S_{0.650}$	4.0	2.20	0.011	0.0			+11.0
$Ge_{0.125}As_{0.250}S_{0.625}$	4.0	2.21	0.011	0.0			0.0
$Ge_{0.133}As_{0.267}S_{0.600}$	4.1	2.20	0.010	0.0			−10.0
$Ge_{0.138}As_{0.276}S_{0.586}$	4.0	2.20	0.008	0.0			−15.0
$Ge_{0.150}As_{0.300}S_{0.550}$	4.0	2.20	0.009	0.0			−26.7
$Ge_{0.154}As_{0.308}S_{0.538}$	3.6	2.20	0.007	0.6	2.46	0.013	−30.0
$Ge_{0.167}As_{0.333}S_{0.500}$	3.2	2.21	0.008	0.7	2.44	0.013	−40.0
$Ge_{0.183}As_{0.367}S_{0.450}$	3.2	2.20	0.010	0.9	2.43	0.012	−50.9
$Ge_{0.200}As_{0.400}S_{0.400}$	3.3	2.21	0.009	0.9	2.44	0.008	−60.0
$Ge_{0.217}As_{0.433}S_{0.350}$	2.4	2.21	0.008	1.6	2.45	0.013	−67.9
As K-edge							
$Ge_{0.088}As_{0.175}S_{0.737}$	3.0	2.26	0.006	0.0			+68.1
$Ge_{0.117}As_{0.233}S_{0.650}$	3.0	2.26	0.009	0.0			+11.0
$Ge_{0.125}As_{0.250}S_{0.625}$	3.0	2.25	0.007	0.0			0.0
$Ge_{0.133}As_{0.267}S_{0.600}$	2.3	2.23	0.008	0.6	2.48	0.008	−10.0
$Ge_{0.138}As_{0.276}S_{0.586}$	2.4	2.24	0.010	0.8	2.48	0.010	−15.0
$Ge_{0.150}As_{0.300}S_{0.550}$	1.5	2.23	0.011	1.4	2.47	0.013	−26.7
$Ge_{0.154}As_{0.308}S_{0.538}$	1.5	2.22	0.010	1.5	2.46	0.012	−30.0
$Ge_{0.160}As_{0.320}S_{0.520}$	1.1	2.23	0.012	2.0	2.45	0.013	−35.0
$Ge_{0.167}As_{0.333}S_{0.500}$	0.8	2.21	0.005	2.2	2.46	0.010	−40.0
$Ge_{0.183}As_{0.367}S_{0.450}$	0.0			3.0	2.43	0.014	−50.9
$Ge_{0.200}As_{0.400}S_{0.400}$	0.0			3.0	2.43	0.011	−60.0
$Ge_{0.217}As_{0.433}S_{0.350}$	0.0			3.0	2.45	0.010	−67.9

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

tion of the atomic makeup of the first coordination shell of Ge and As atoms in these two series of glasses is shown in Figs. 6 and 7.

A second shell of Ge/As next-nearest neighbors has been fitted to the Ge and As EXAFS spectra of some ternary glasses only when it is found to have at least 95% probability of being statistically significant, according to the criterion of Joyner, Martin, and Meehan.[14] The fitting of this second shell yields metal-metal next-nearest-neighbor distances of ~3.41±0.03 Å and is found to have no significant effect on the fit parameters of the first coordination shell. These metal-metal distances are consistent with the Ge-Ge and As-As distances in crystalline Ge and As sulfides.[13] However, the second-shell coordination numbers derived from this fitting are found to vary between 0.70 and 2.30 and are therefore substantially underestimated. This discrepancy may arise from a large distribution of interatomic distances in the second shell that is consistent with the associated relatively large Debye-Waller factors of $\sim 0.020 \pm 0.005$ Å^2 for this shell. As the structural data corresponding to the second shell are not available for all glasses and, moreover, are only semiquantitative at best, these will not be discussed in any further detail in this paper.

B. $Ge_xAs_yS_{1-x-y}$ $(x:y=1:2)$ glasses

The k^3-weighted experimental Ge and As K-edge EXAFS spectra and the theoretical fits for the $Ge_xAs_yS_{1-x-y}$ glasses with $x:y=1:2$ are shown in Fig. 8. The corresponding Fourier transforms are shown in Fig. 9. The fitting of the EXAFS spectra shows that the first-shell coordination numbers and Ge(As)-S and Ge(As)-X distances in these glasses are similar

TABLE IV. Ge K-edge EXAFS structural parameters for Ge_xS_{1-x} binary glasses.

	First coordination shell[a]						%S in excess of stoichiometry
Composition	N_S	R_S (Å)	$2\sigma_S^2$ (Å^2)	N_{Ge}	R_{Ge} (Å)	$2\sigma_{Ge}^2$ (Å^2)	
$Ge_{0.40}S_{0.60}$	2.7	2.20(0)	0.010	1.3	2.45(0)	0.011	−25.0
$Ge_{0.43}S_{0.57}$	2.8	2.21(3)	0.011	1.4	2.43(4)	0.013	−33.7

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

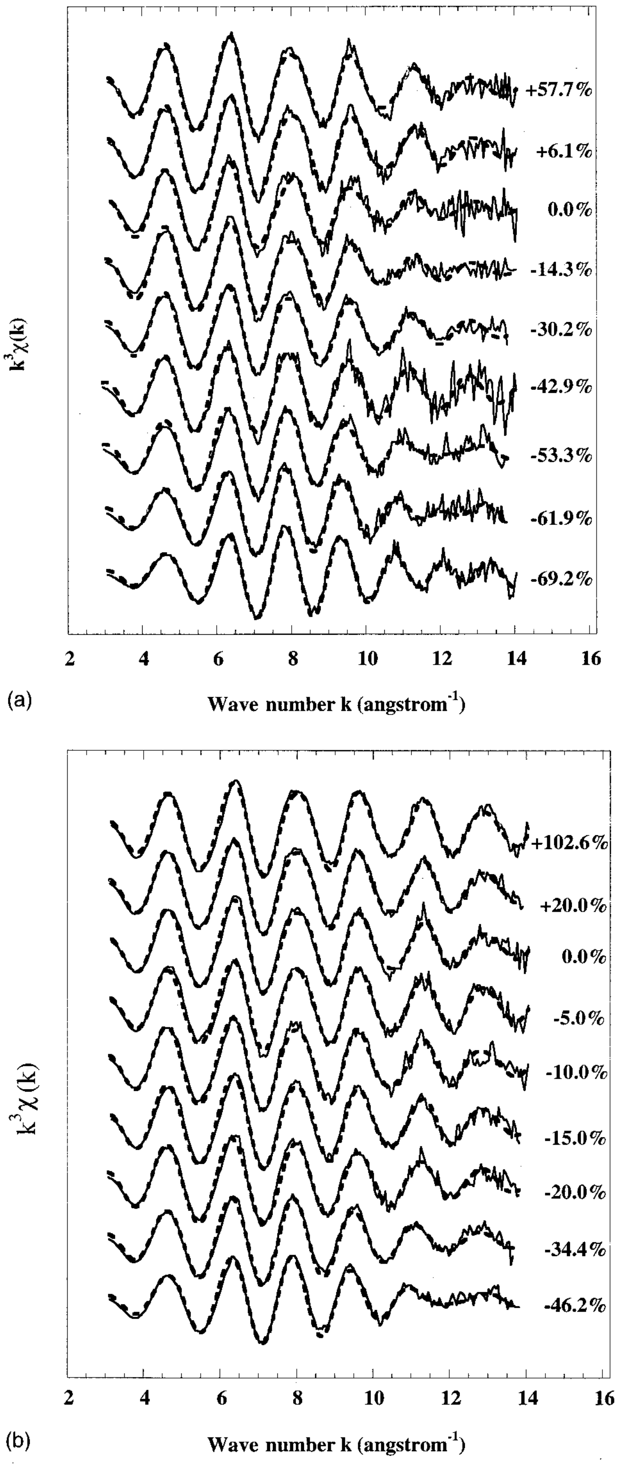

FIG. 2. k^3-weighted Ge K-edge EXAFS spectra of $Ge_xAs_yS_{1-x-y}$ glasses with (a) $x{:}y=1{:}1$ and (b) $x{:}y=2.5{:}1$. The %S in excess of stoichiometry for each glass composition is indicated alongside each spectrum. Solid lines represent experimental data and dashed lines correspond to least-squares fits obtained using EXCURV92.

to those in the previous two series of glasses discussed above (Table III). However, there are important differences in the compositional variation of the first-shell coordination environments of Ge and As atoms in these relatively As-rich

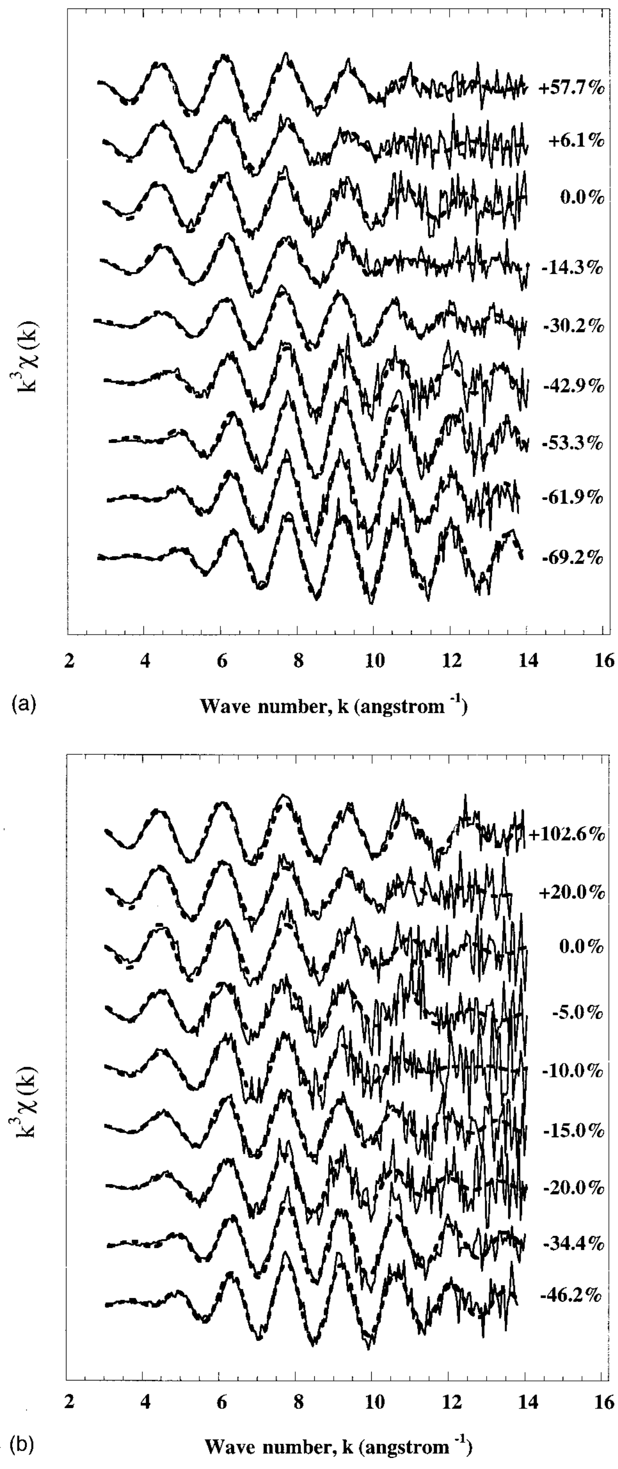

FIG. 3. k^3-weighted As K-edge EXAFS spectra of $Ge_xAs_yS_{1-x-y}$ glasses with (a) $x{:}y=1{:}1$ and (b) $x{:}y=2.5{:}1$. The %S in excess of stoichiometry for each glass composition is indicated alongside each spectrum. Solid lines represent experimental data and dashed lines correspond to least-squares fits obtained using EXCURV92.

glasses compared to that in the $Ge_xAs_yS_{1-x-y}$ glasses with $x{:}y=1{:}1$ and 2.5:1. Although the initial S deficiency in this series of glasses leads to the formation of As-As bonds, the Ge-X bonds begin to form at a S-deficiency level where the

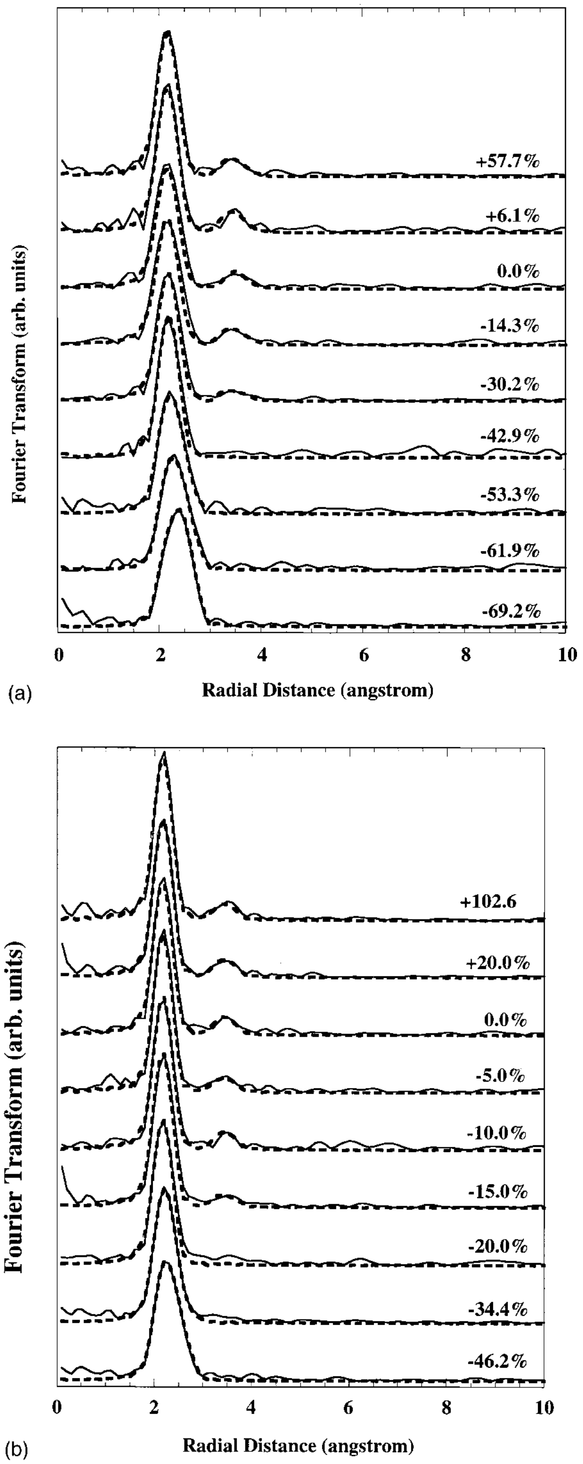

FIG. 4. Magnitudes of the Fourier-transform of the k^3-weighted Ge K-edge EXAFS spectra of $Ge_xAs_yS_{1-x-y}$ glasses with (a) $x{:}y=1{:}1$ and (b) $x{:}y=2.5{:}1$ with various levels of S in excess of stoichiometry. Solid lines represent experimental data and dashed lines correspond to least-squares fits obtained using EXCURV92.

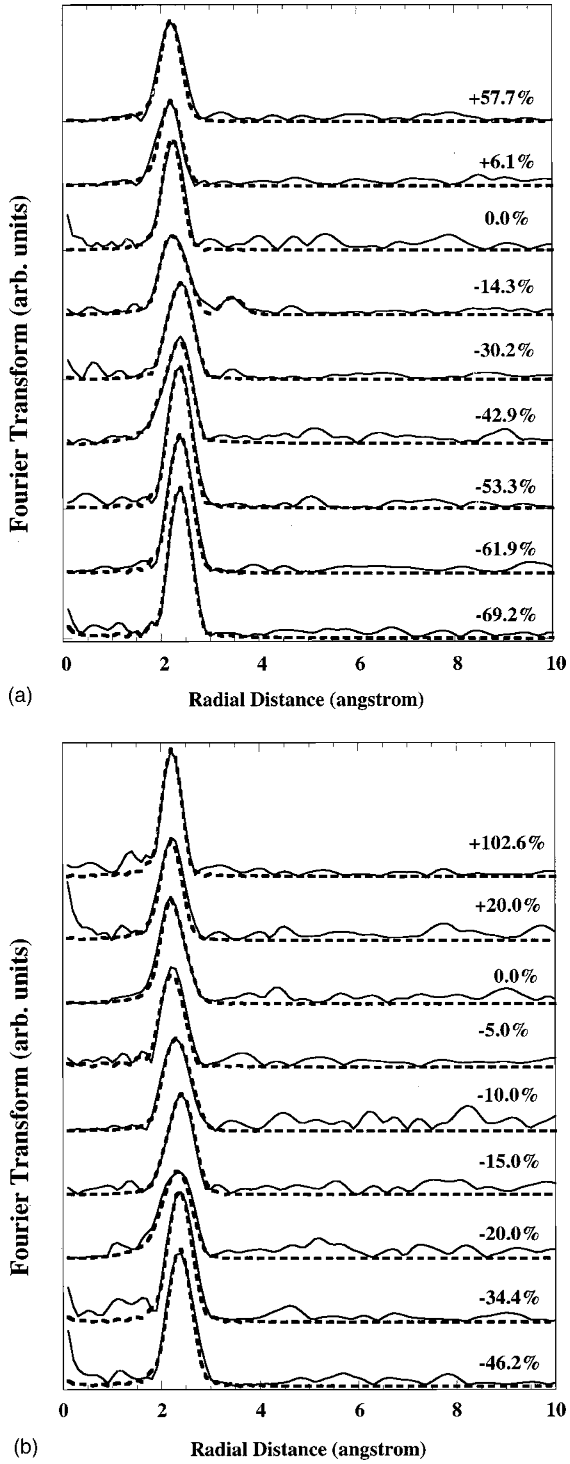

FIG. 5. Magnitudes of the Fourier-transform of the k^3-weighted As K-edge EXAFS spectra of $Ge_xAs_yS_{1-x-y}$ glasses with (a) $x{:}y=1{:}1$ and (b) $x{:}y=2.5{:}1$ with various levels of S in excess of stoichiometry. Solid lines represent experimental data and dashed lines correspond to least-squares fits obtained using EXCURV92.

average first-shell environment of As atoms consists of ~1.5 As and ~1.5 S atoms. This is in contrast with the case of the previous two series of glasses where Ge-X bonds appear only when each As atom is bonded to three other As atoms. This result possibly implies the stabilization of a mixed first-shell coordination environment of S and As around As atoms in the As-rich glasses. Any further increase in S deficiency in these As-rich glasses results in the progressive increase in concentration of both the Ge-X and As-X bonds in the first coordination shells of Ge and As atoms. This compositional

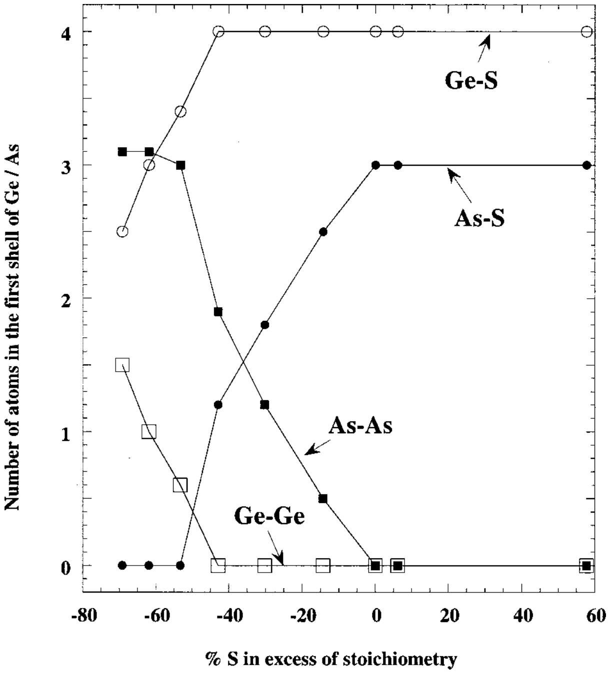

FIG. 6. Compositional variation in the atomic make-up of the first coordination shell of Ge and As atoms in $Ge_xAs_yS_{1-x-y}$ glasses with x:y = 1:1, as derived from fitting the Ge and As K-edge EXAFS data. Solid lines through the data points are guides to the eye only.

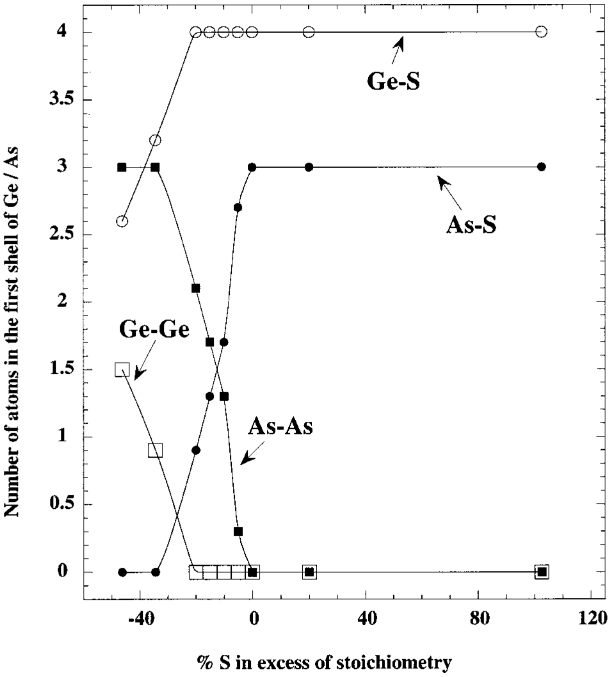

FIG. 7. Compositional variation in the atomic make-up of the first coordination shell of Ge and As atoms in $Ge_xAs_yS_{1-x-y}$ glasses with x:y = 2.5:1, as derived from fitting the Ge and As K-edge EXAFS data. Solid lines through the data points are guides to the eye only.

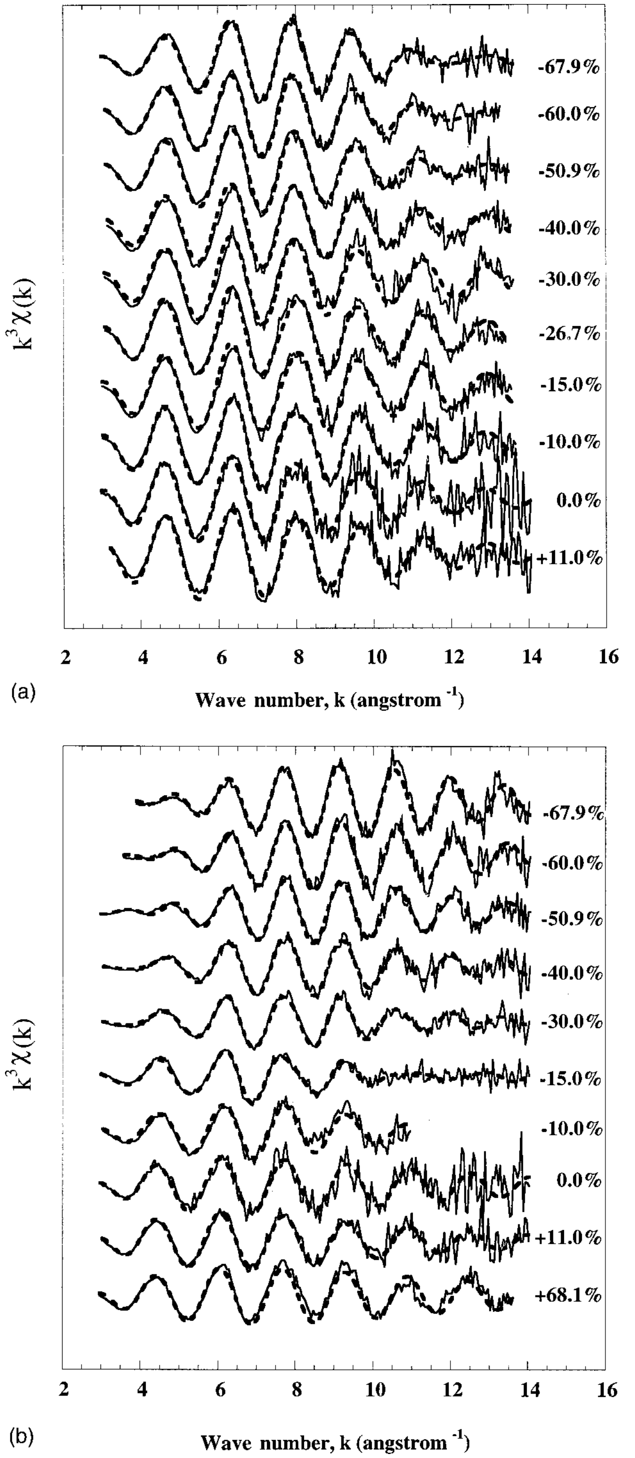

FIG. 8. k^3-weighted (a) Ge and (b) As K-edge EXAFS spectra of $Ge_xAs_yS_{1-x-y}$ glasses with x:y = 1:2. The %S in excess of stoichiometry for each glass composition is indicated alongside each spectrum. Solid lines represent experimental data and dashed lines correspond to least-squares fits obtained using EXCURV92.

variation of the local coordination environments of Ge and As atoms is shown in Fig. 10. In this regard it is interesting to compare the effect of S deficiency on the coordination environment of Ge atoms in these ternary Ge-As-S glasses with that in the S-deficient binary Ge-S glasses. The k^3-weighted experimental Ge EXAFS spectra and the theo-

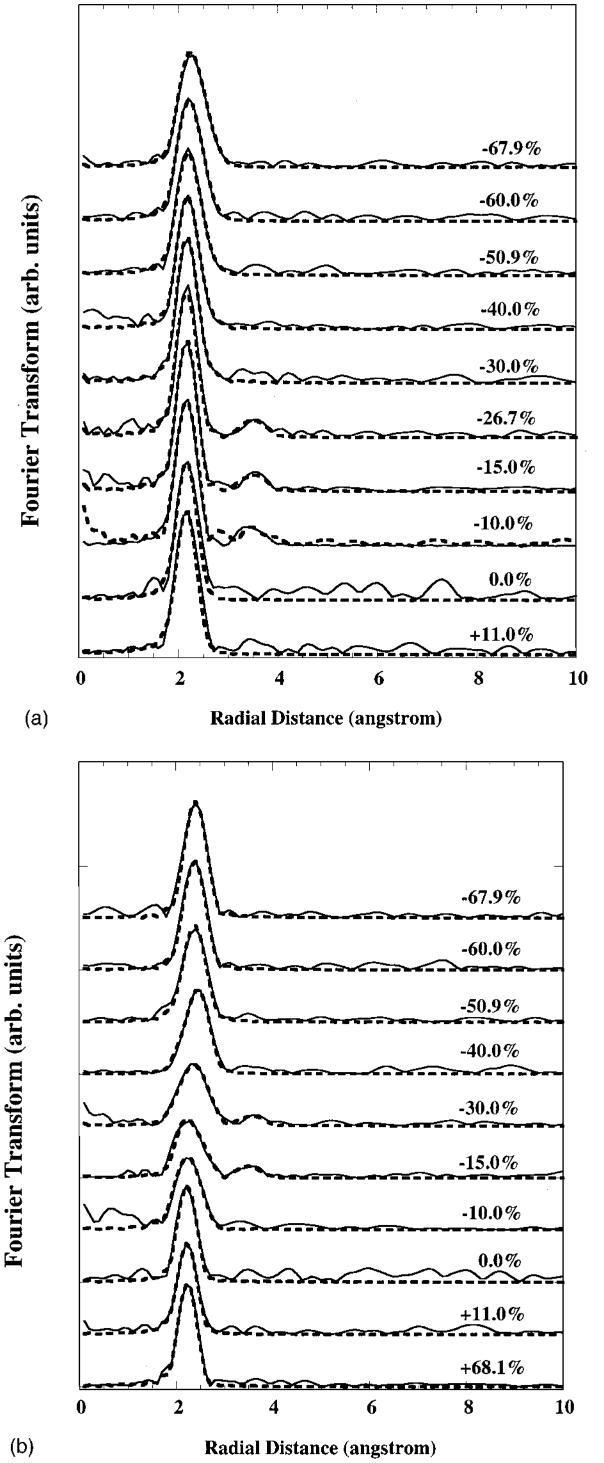

FIG. 9. Magnitudes of the Fourier-transform of the k^3-weighted (a) Ge and (b) As K-edge EXAFS spectra of $Ge_xAs_yS_{1-x-y}$ glasses with $x{:}y = 1{:}2$ with various levels of S in excess of stoichiometry. Solid lines represent experimental data and dashed lines correspond to least-squares fits obtained using EXCURV92..

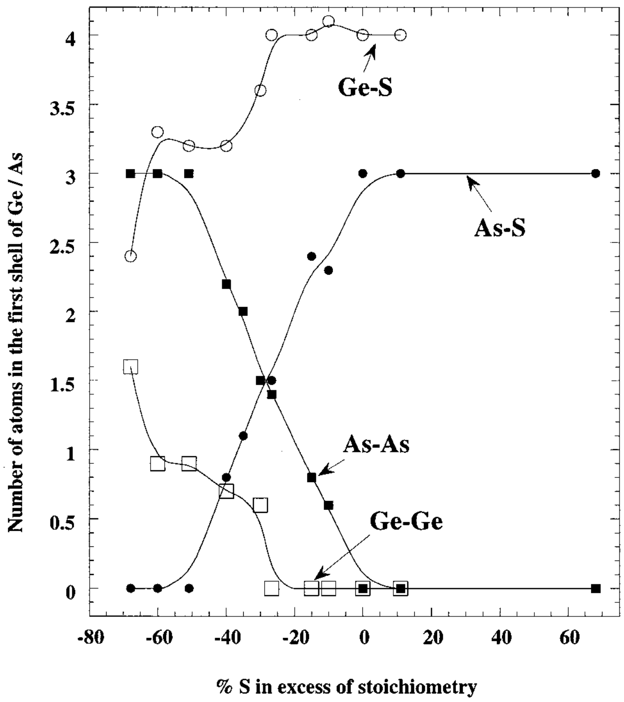

FIG. 10. Compositional variation in the atomic make-up of the first coordination shell of Ge and As atoms in $Ge_xAs_yS_{1-x-y}$ glasses with $x{:}y = 1{:}2$, as derived from fitting the Ge and As K-edge EXAFS data. Solid lines through the data points are guides to the eye only.

retical fits for two S-deficient Ge-sulfide glasses are shown in Fig. 11. The corresponding Fourier transforms are shown in Fig. 12. The fitting of the Ge EXAFS spectra yields a first-shell coordination number of 4 for the Ge atoms in these binary glasses (Table IV). Moreover, the average Ge coordination environment is found to consist of a mixture of S and Ge atoms in the right proportion as demanded by the chemical composition indicating the preservation of chemical order in these glasses (Table IV).

IV. DISCUSSION

The Ge and As K-edge EXAFS results reported here indicate that the first-shell coordination numbers of Ge and As are 4 and 3, respectively, in all glasses irrespective of composition. However, the coordination environments of Ge and As atoms show gradual and systematic changes as a function of glass composition. The Ge and As atoms in the stoichiometric and excess-S-containing $Ge_xAs_yS_{1-x-y}$ glasses in all three compositional series are found to be bonded only to S atoms forming GeS_4 and AsS_3 polyhedra. This result automatically implies the presence of S-S homopolar bonds in excess S-containing glasses. This hypothesis is corroborated by the results of a previous study based on Raman spectroscopy that showed the appearance of a vibrational band at $\sim 490\ cm^{-1}$ corresponding to S-S stretching vibration in Ge-As-S glasses with excess S.[8] On the other hand, the initial structural response to S deficiency in all Ge-As-S glasses is found to be the formation of As-As homopolar bonds. The first-shell coordination environment of Ge atoms in the two series of $Ge_xAs_yS_{1-x-y}$ glasses with $x{:}y = 2.5{:}1$ and 1:1 do not show any evidence of metal-metal homopolar bonding until all the As-As bonds are exhausted in the structure (Figs. 6 and 7). Such a structural scenario leaves Ge atoms with the possibility of the formation of Ge-Ge homopolar bonds only in the highly S-deficient glasses in these two series. This

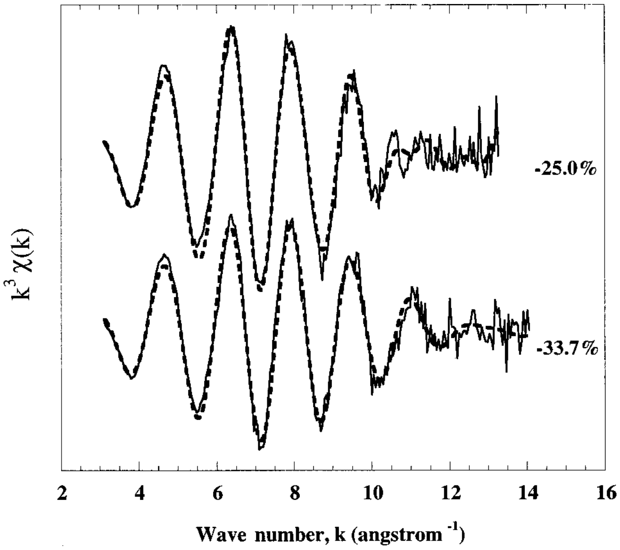

FIG. 11. k^3-weighted Ge *K*-edge EXAFS spectra of binary Ge_xS_{1-x} glasses. The %S in excess of stoichiometry for each glass composition is indicated alongside each spectrum. Solid lines represent experimental data and dashed lines correspond to least-squares fits obtained using EXCURV92.

result, to our knowledge, provides the first direct evidence in favor of an inhomogeneous distribution or clustering of network-forming atoms and violation of chemical order in chalcogenide glasses. This should be contrasted with the case of binary S-deficient Ge-sulfide glasses where chemical order is clearly preserved over a length scale corresponding to at least the nearest-neighbor distances around Ge atoms.

Formation of bonds between like atoms imposed by chemical order as evidenced in the formation of S-S bonds in excess-S-containing glasses or imposed by thermodynamic constraints, as seen in the avoidance of As-Ge bonds and in the formation of As-As and Ge-Ge bonds in S-deficient glasses, may have strong topological consequences. For example, within the experimental resolution, the Ge and As EXAFS spectra of the stoichiometric $Ge_xAs_yS_{1-x-y}$ glasses in all three series do not show any evidence of metal-metal distances corresponding to homopolar bonding or edge-shared GeS_4 tetrahedra. Therefore the atomic structure of these glasses is likely to consist predominantly of a fully three-dimensional network of corner-sharing GeS_4 tetrahedra and AsS_3 trigonal pyramids. However, in glasses with excess S, the formation of S-S bonds may eventually stabilize low-dimensional rings of S atoms in spatial association with the interconnected three-dimensional network of GeS_4 and AsS_3 polyhedra.[15] On the other hand, in the two series of $Ge_xAs_yS_{1-x-y}$ glasses with $x{:}y=2.5{:}1$ and 1:1 glasses each As is found to be bonded to three other As atoms at high-enough S deficiency whereas each Ge may still be bonded to nearly all S atoms. This result implies a clustering of As atoms in the form of corner-sharing $AsAs_3$ trigonal pyramids, possibly arranged in corrugated sheets much like in crystalline As.[16] Such quasi-two-dimensional sheets of As atoms will be interspersed with three-dimensional networks of corner-sharing $Ge(S_xGe_{4-x})$ tetrahedra in these glasses. At low and intermediate levels of S deficiency the As atom clusters in these glasses can mimic the topological changes that are observed in the atomic structures of various S-deficient crystalline phases of As sulfide. For example, the stoichiometric As_2S_3 crystal has a two-dimensional sheetlike structure of cross-linked AsS_3 pyramids that changes into molecular As_4S_4 and As_4S_3 structures with a moderate increase in S deficiency. By the same token one could expect that for $Ge_xAs_yS_{1-x-y}$ glasses with intermediate S deficiency, where the As atoms are coordinated to a combination of S and other As atoms, the molecular As_4S_4 and/or As_4S_3 units can be energetically stabilized in the glass structure. The present As EXAFS results cannot distinguish between discrete molecules and a continuous network on the basis of the local coordination environment of As alone. However, the thermodynamic stabilization of a mixed average coordination environment of 1.5 As and 1.5 S atoms around each As atom as has been observed in the As-rich $Ge_xAs_yS_{1-x-y}$ glasses with $x{:}y=1{:}2$ at intermediate levels of S deficiency is completely consistent with the formation of As_4S_3 molecular clusters. In fact, a recent Raman spectroscopic study has clearly shown that As-As homopolar bonding indeed results in the formation of discrete As_4S_3-based molecular clusters especially in As-rich Ge-As-S glasses at intermediate levels of S deficiency corresponding to $\langle r\rangle\sim 2.6$.[15]

Thus, the physical properties of chalcogenide glasses will be strongly dependent on the nature and relative abundance of these molecular, two-dimensional sheetlike, or three-dimensional network-based intermediate-range structural units in the glass. In this scenario the percolation of rigidity in a chalcogenide glass structure may not be described solely on the basis a single value of the average coordination number $\langle r\rangle$. For example, if a two-dimensional atomic cluster is embedded in a three dimensional space then the constraint-counting formalism yields a value of $\langle r\rangle\sim 2.67$ for rigidity transition.[6] This value of $\langle r\rangle$ should be contrasted with that of

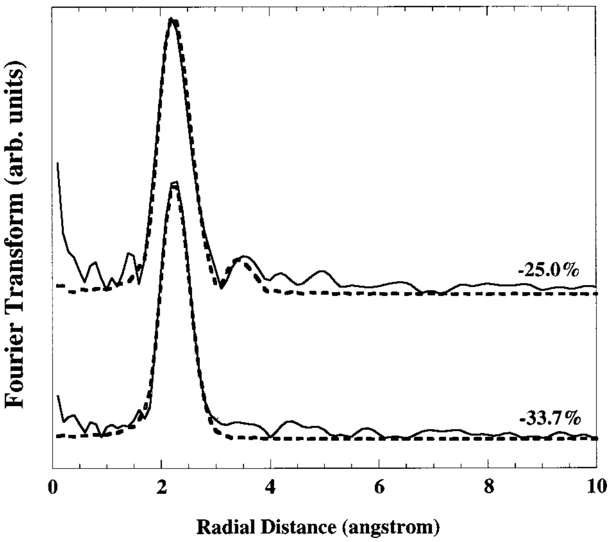

FIG. 12. Magnitudes of the Fourier-transform of the k^3-weighted Ge *K*-edge EXAFS spectra of Ge_xS_{1-x} glasses with various levels of S in excess of stoichiometry. Solid lines represent experimental data and dashed lines correspond to least-squares fits obtained using EXCURV92.

2.40 corresponding to the case when the embedded atomic cluster is three-dimensional. Therefore, instead of a single transition one could expect the presence of multiple extrema in the compositional variation of the physical properties of chalcogenide glasses, governed by the structure and topology or the effective dimensionality of the percolating structural unit(s) in question. It should also be noted that the degree of homopolar bonding and chemical order in a chalcogenide glass structure are likely to depend significantly on the nature of the constituent elements themselves. For example, a recent Ge and As EXAFS study of Ge-As-Te glasses has shown the existence of Ge/As-Ge/As homopolar bonds even in excess Te-containing glasses with $\langle r\rangle \sim 2.4$ whereas this study shows the presence of only Ge-S and As-S heteropolar bonds in the Ge-As-S glasses with similar $\langle r\rangle$ values.[10] Thus, the nature of the chalcogen atom plays a key role in controlling the chemical order and the concept of a universality in $\langle r\rangle$ values associated with structural and/or topological transitions loses its meaning. On the other hand, the observed differences between Ge and As in the propensity of homopolar bond formation in Ge-As-S glasses as a function of the Ge:As ratio indicate that chemical composition would also be a critical factor in determining the onset of these structural and topological transitions.

V. SUMMARY

The Ge and As EXAFS results show that Ge and As atoms in ternary $Ge_xAs_yS_{1-x-y}$ glasses are always 4 and 3 coordinated, respectively. Ge and As atoms are found to be bonded only to S atoms in the stoichiometric and S-excess glasses, indicating preservation of chemical order. The S-deficient Ge-As-S glasses on the other hand, show formation of metal-metal homopolar bonds that are exclusively between As atoms, especially at low and intermediate S deficiencies. Ge atoms take part in metal-metal bonding only at intermediate to high levels of S deficiency. Such clustering of like atoms and violation of chemical order has been argued to result in topological changes of the intermediate-range structural units in ternary Ge-As-S glasses as a function of composition. These structural and topological changes are likely to result in extrema in the compositional variation of the relevant physical properties of these materials at nonunique composition-dependent $\langle r\rangle$ values. This scenario renders the concept of a universal, single $\langle r\rangle$ value ($\langle r\rangle = 2.4$)-based rigidity transition untenable, at least in the case of chalcogenide glasses in the ternary Ge-As-S system.

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