PHYSICAL REVIEW B **74**, 174206 (2006)

Nuclear quadrupole resonance study of local bonding in glassy As_xSe_{1-x}

Eungho Ahn
Research Institute of the Global Environment, Sookmyung Women's University, Seoul, Korea 140-742

G. A. Williams
Department of Physics, University of Utah, Salt Lake City, Utah 84112, USA

P. C. Taylor
Department of Physics, Colorado School of Mines, Golden, Colorado 80401, USA

(Received 3 February 2006; revised manuscript received 25 August 2006; published 29 November 2006)

Nuclear quadrupole resonance (NQR) experiments were performed on glassy As_xSe_{1-x} to study the local structural order. The bonding in As_xSe_{1-x} is governed by preferential bonding (chemical ordering) between arsenic and selenium at arsenic concentrations $x \leqslant 0.40$; however, the bonding for higher arsenic concentrations is governed mostly by statistical considerations. At concentrations $x \geqslant 0.45$ the glasses are inhomogeneous with the presence of local regions of different composition. Measurements of the NQR spin echo intensity identify regions formed by arsenic atoms bonded to zero, one, two, or three selenium atoms. The NQR spectral line shapes and the longitudinal relaxation times suggest that these regions have a more ordered structure as compared to the homogeneous samples with low arsenic content. The existence of a small concentration of crystalline inclusions in amorphous $As_{0.60}Se_{0.40}$ is also suggested.

DOI: 10.1103/PhysRevB.74.174206 PACS number(s): 61.18.Fs, 61.43.Dq, 61.43.Fs

I. INTRODUCTION

Some of the best-studied chalcogenide glasses are those in the binary system As_xSe_{1-x}. Most of the studies have concentrated on the stoichiometric composition where $x=0.4$ or on selenium-rich compositions where $x<0.4$. Glasses in this range of compositions exhibit high photosensitivity and low electrical conductivity. Films made with small x have been used as photoreceptors in electrophotographic applications. These materials also have potential use in digital radiography. One of the important physical properties of glasses in the system As_xSe_{1-x} is the high degree of infrared transparency, which makes them useful for infrared optical devices. Fibers made from As_xSe_{1-x} exhibit very low optical losses in the infrared part of the electromagnetic spectrum.

Several scattering techniques have been applied to glasses in the As_xSe_{1-x} system to determine the dependence of the glassy structure on composition. For $x<0.4$ the bulk properties of glassy As_xSe_{1-x} are similar to many other chalcogenide systems when one compares samples with the same average coordination number. Glasses whose bulk properties depend only on the average coordination number $\langle r \rangle$, and not on the specific chemical composition, are said to obey the isocoordination rule.[1] There are many indications that this rule does not apply to As_xSe_{1-x} near where stoichiometric crystalline compounds exist at $x=0.4$ and $x=0.5$. Near these compositions the glass properties can be strongly influenced by the chemical nature of the bonds and less strongly influenced by $\langle r \rangle$.

A second interesting property of the glassy chalcogenides is the concept of rigidity percolation.[2] In the simplest mean field approximation, rigidity percolation occurs when the number of constraints per atom equals the number of degrees of freedom per atom. For fewer constraints than the number of degrees of freedom per atom, the system is under constrained and therefore "floppy." For more constraints than degrees of freedom per atom the system is overconstrained and therefore "rigid." In the As_xSe_{1-x} system this transition occurs exactly at the stoichiometric composition where $x=0.4$. This transition depends only on $\langle r \rangle$ and is therefore independent of the specific chemical bonds. Unfortunately, when the predicted rigidity percolation transition occurs right at a stoichiometric composition, as it does in the As_xSe_{1-x} system, it is difficult to separate the role of $\langle r \rangle$ from the role played by the specific nature of the chemical bonds.

Nonetheless, several authors have attacked this problem. Hayashi *et al.* observed changes in the electronic spectra of a-As_xSe_{1-x} at $x=0.40$, and suggested that these changes correspond to the predicted rigidity percolation in this system.[3] Kasap *et al.*[4] performed temperature-modulated differential scanning calorimetry on amorphous As_xSe_{1-x} and observed a structural transition at $\langle r \rangle \approx 2.2$, which is lower than $\langle r \rangle = 2.4$ as predicted by the mean field theory and observed in their own earlier experiments.[5] Brand *et al.*[6] used specific heat measurements to study glasses in the As_xSe_{1-x} system and claimed to observe rigidity percolation at $\langle r \rangle = 2.7$.

Since both the isocoordination rule and rigidity percolation depend only on $\langle r \rangle$, it is important to understand the local bonding arrangements of glasses in the As_xSe_{1-x} system. Usuki *et al.*[7] used neutron diffraction measurements to conclude that the $AsSe_{3/2}$ pyramidal unit, which is the basic structural element in $As_{0.40}Se_{0.60}$, is formed over a wide composition range in the As-Se alloys, but bonds between like atoms, specifically As-As, are present only in a limited composition range ($x \geqslant 0.40$). Also, Georgiev *et al.* have recently suggested[8] that arsenic may be fourfold coordinated in a-As_xSe_{1-x}, with three single bonds and one double bond allowing the lone pair orbital of arsenic to make a double bond with selenium at low concentrations of arsenic. Mastelaro *et al.*[9] used EXAFS to observe the formation of arsenic-

arsenic (As-As) and selenium-selenium (Se-Se) bonds in the arsenic and selenium rich compositions, $x > 0.40$ and $x < 0.40$, respectively.

Nuclear quadrupole resonance (NQR) is a powerful method to study amorphous systems where it is used to probe the local bonding arrangements. In addition, NQR is sometimes more sensitive than x-ray diffraction for finding crystalline inclusions in an amorphous sample. Finally, longitudinal relaxation times T_1, as measured in NQR, are also sometimes useful probes of local structural order.

II. EXPERIMENTAL DETAILS

The ^{75}As NQR measurements employed a Hahn echo pulse sequence. The nuclear spin of ^{75}As is $I = 3/2$. All measurements were performed at 77 K.

The NQR experiments used a standard NQR pulsed spectrometer consisting of a Wavetek Model 3100 wave form generator to drive a Matec Gating Modulator, Model 5100. The transient response of the nuclei was recorded with Matec model 501 rf preamplifier and receiver followed by a LeCroy 900 A signal averager. Each plotted point is an average of 500 individual traces. This experimental setup is similar to that published previously.[10] The experiments utilized a 90°–180° spin echo pulse sequence, where the pulses are separated by a time, τ, and the spin echo appears at time 2τ.

T_1 measurements were performed on samples of glassy As_xSe_{1-x} with $x = 0.08$, 0.15, 0.20, 0.27, 0.32, 0.36, 0.40, 0.45, 0.50, 0.55, and 0.60. For $0.08 \leqslant x \leqslant 0.36$ (except $x = 0.20$) the samples were obtained from D. G. Georgiev and P. Boolchand, University of Cincinnati. For $x = 0.60$ the sample was obtained from R. L. Cappelletti of the National Institute of Standards and Technology. The remaining samples were prepared by M. C. DeLong at the University of Utah. Details on all of these samples are described elsewhere.[11] The samples prepared at the University of Utah were produced by combining elemental arsenic and selenium in the necessary proportions in a quartz tube and heating up to 900 °C. The melt was mixed by rocking for 90 h and then quenched in air from 700 °C.

III. RESULTS

The ^{75}As NQR spin-echo spectra from samples of glassy As_xSe_{1-x} for $x \leqslant 0.4$ are shown in Fig. 1. All of these spectra consist of a single broad line that corresponds to one type of arsenic site, which we will argue consists of an arsenic atom bonded to three selenium atoms. Figure 2 shows the spin-echo spectra for $x > 0.4$. These spectra are qualitatively different from the spectra for $0.08 \leqslant x \leqslant 0.40$. In particular, three peaks are clearly resolved in the case of $x = 0.60$ [Fig. 2(d)]. For $x \leqslant 0.4$ there is no intensity near 80 MHz.

T_1 was measured for all samples at the peak frequencies of the NQR spectra. In samples with $x \geqslant 0.45$, the NQR spin-echo spectra exhibit more than one peak. In these cases the T_1 values were measured for each peak. A plot of T_1 as a function of x is shown in Fig. 3. This plot shows a nearly linear increase of T_1 over the composition range $0.08 \leqslant x \leqslant 0.36$. For $x > 0.4$, T_1 decreases rapidly and then levels off.

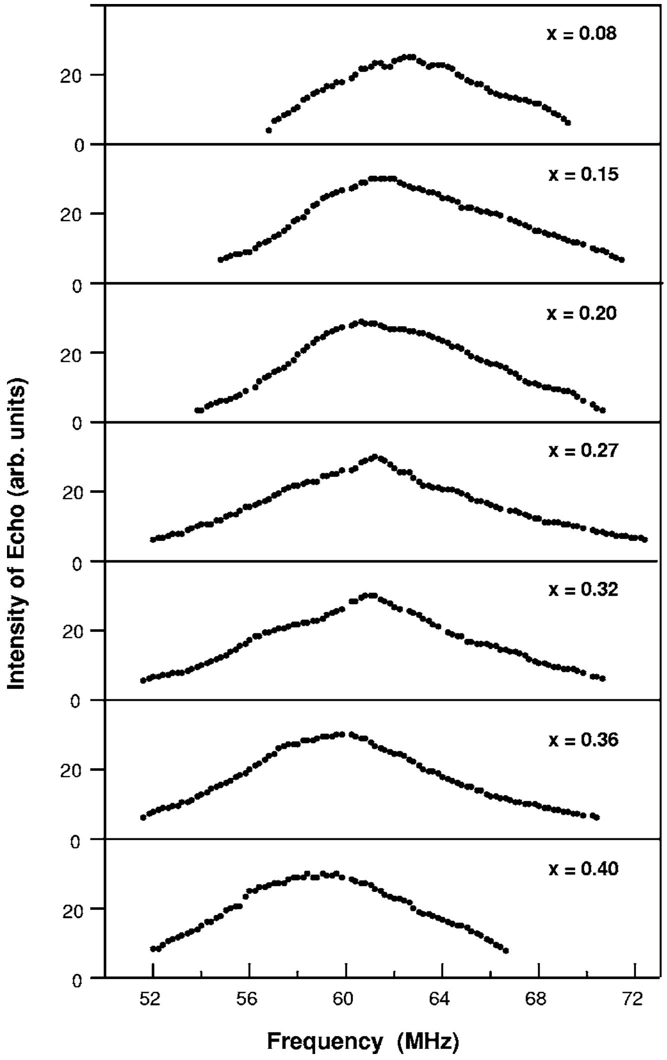

FIG. 1. The ^{75}As NQR spin-echo spectra at 77 K in a-As_xSe_{1-x} for x=0.08, 0.15, 0.20, 0.27, 0.32, 0.36, and 0.40. Each spectrum consists of a single broad line. The spectra are offset for clarity. As the concentration of arsenic increases, the positions of the peaks decrease approximately linearly from 63 MHz at $x = 0.08$ to 59 MHz at $x = 0.40$.

There are specific frequencies at which the decay of the longitudinal magnetization in glassy $As_{0.60}Se_{0.40}$ exhibits a two-component behavior that cannot be explained by either an amorphous or crystalline structure alone. Figure 4 shows that in general the decay is nonexponential. Below we will show that the slow diffusion model describing the spin relaxation in amorphous solids[12] produces a good fit to the experimental data (60.40 MHz and 61.00 MHz in the figure). A noticeable exception is the decay at 60.70 MHz in Fig. 4. At this frequency, the log of decay is linear in $\sqrt{t}$ for values less than about 0.30 s1/2. For longer times, the log of the decay deviates from linear behavior. Figure 4(b) shows that the log of the decay at longer times is linear with t (i.e., the standard exponential relaxation process).

IV. DISCUSSION

Much can be inferred about the local structural order in As_xSe_{1-x} glasses from the results presented in the previous

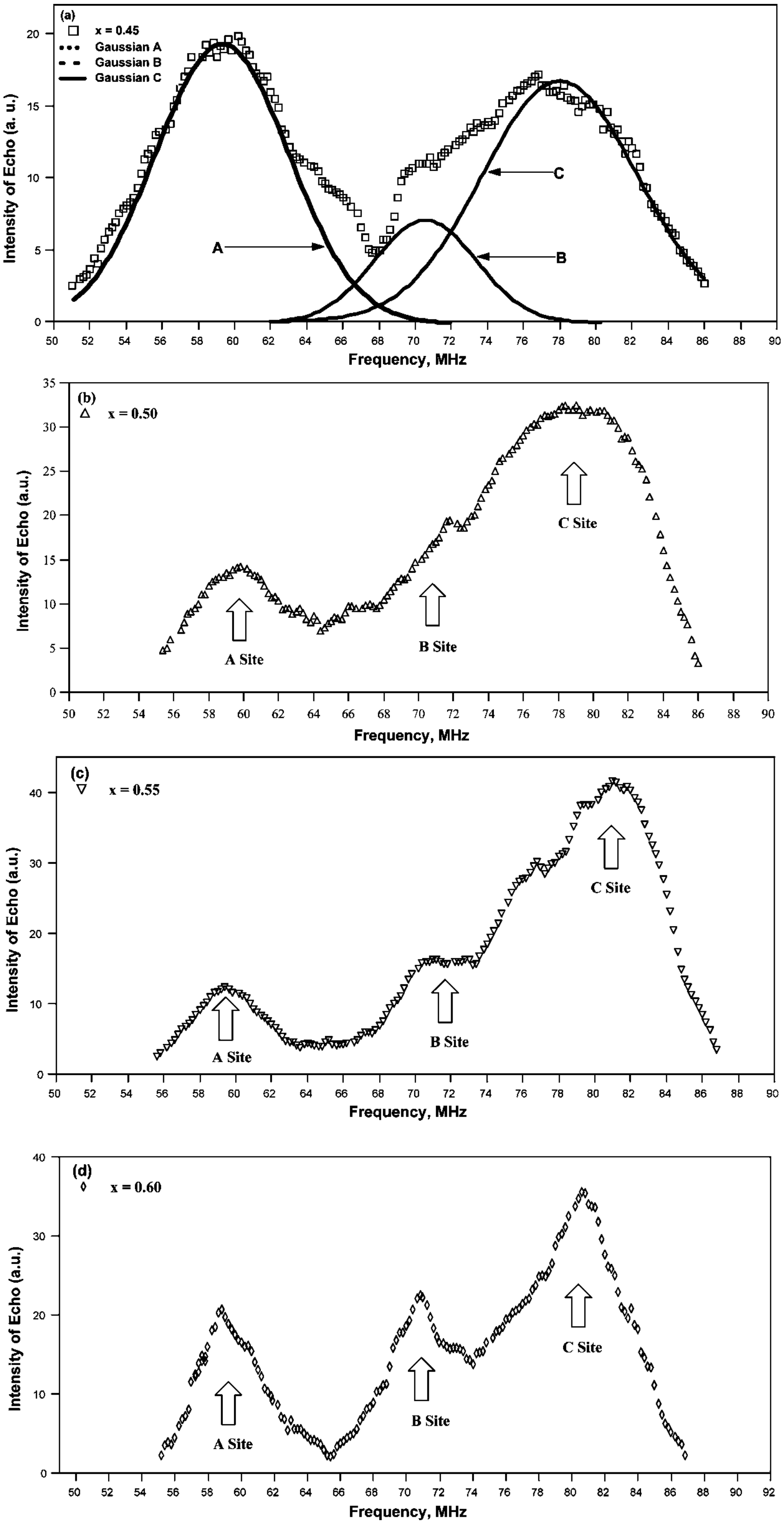

FIG. 2. NQR spin-echo spectrum of (a) a-$As_{0.45}Se_{0.55}$, (b) a-$As_{0.50}Se_{0.50}$, (c) a-$As_{0.55}Se_{0.45}$, and (d) a-$As_{0.60}Se_{0.40}$. The spectra can be deconvolved into three Gaussian peaks (*A*, *B*, and *C* as indicated by the solid lines).

section. By comparison with ^{75}As NQR spectra observed in crystalline As-Se compounds, one can infer the nearest neighbor order surrounding an arsenic site in the glasses. The crystalline structures of $As_{0.40}Se_{0.60}$ (Ref. 13) and $As_{0.50}Se_{0.50}$ (Ref. 14) have been published. In crystalline $As_{0.40}Se_{0.60}$ each arsenic atom is bonded to three selenium atoms in a pyramidal arrangement that is very nearly axially symmetric,[13] and in crystalline $As_{0.50}Se_{0.50}$ each arsenic atom is bonded to two selenium atoms and one arsenic atom in a pyramidal arrangement that is far from axial symmetry.[14] Our analysis of the atomic bonding in the glassy samples is based on comparisons with previously reported NQR spin-echo spectra of glassy[15] and crystalline[16] $As_{0.40}Se_{0.60}$, glassy[10] and crystalline[17] $As_{0.50}Se_{0.50}$,[16] and amorphous As (a-As)

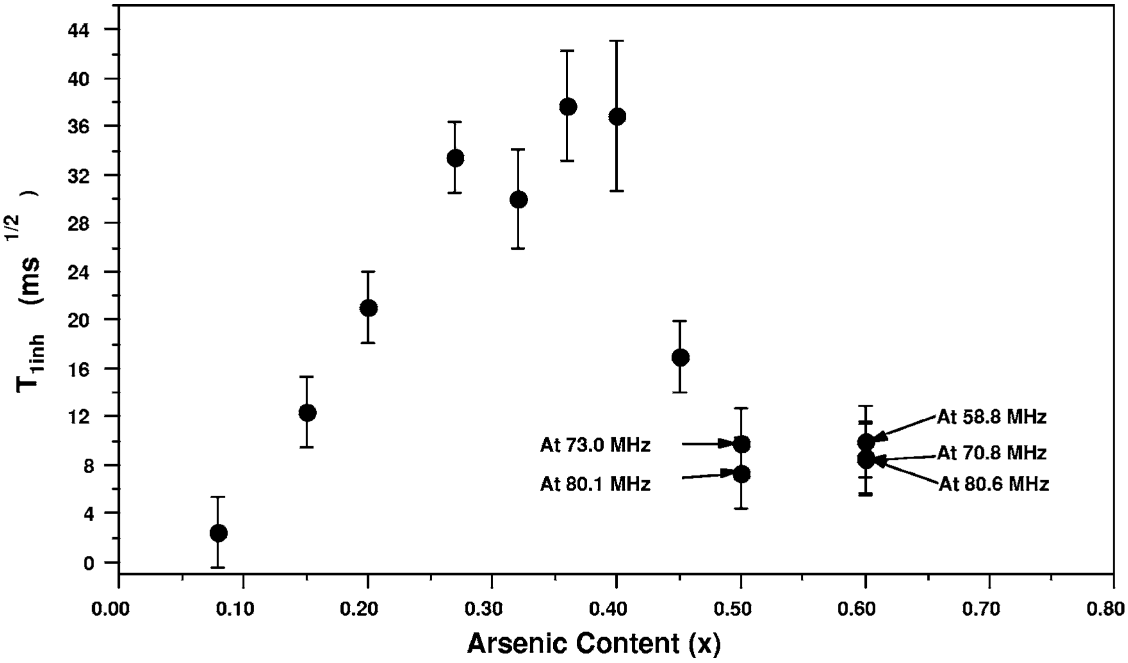

FIG. 3. Spin-lattice relaxation times, T_1, as a function of arsenic concentration, x, in a-As_xSe_{1-x} glasses.

(Ref. 18) as shown in Fig. 5. The frequency range of the NQR spin-echo spectrum for a-$As_{0.40}Se_{0.60}$ overlaps with that of a-As (see Fig. 5). This accidental overlap, in general, precludes a unique assignment of this NQR spin-echo spectrum to a specific bonding arrangement.

Recent tight binding calculations of the NQR frequencies in crystalline As_2Se_3, As_4Se_4, and the two crystalline forms of As match the observed frequencies shown in Fig. 5 within approximately 15%.[19] These calculations confirm that the presence of As–As bonds in crystalline As_4Se_4 produces resonances near 80 MHz, and the presence of only As–Se bonds in As_2Se_3 produces resonances near 60 MHz.

Except for a-As, the NQR spin-echo spectra of these glasses are essentially centered about the NQR spin-echo spectra observed in the crystalline materials. Therefore, one may infer that the glassy NQR peak near 58 MHz corresponds to arsenic sites where the arsenic is bonded to three selenium atoms (or perhaps bonded to three arsenic atoms in the arsenic-rich samples). Because of this ambiguity and the fact that one expects fewer arsenic atoms bonded to three other arsenic atoms at the compositions studied, we will assume in what follows that all of the intensity around 58 MHz corresponds to arsenic atoms bonded to three selenium atoms. Following the same logic, one may infer that the glassy NQR peak near 80 MHz corresponds to arsenic sites where the arsenic atom is bonded to two selenium atoms and one arsenic atom.

This analysis ignores the possibility that has recently been suggested[8] that in these glasses at low arsenic concentrations arsenic atoms may be fourfold coordinated with three single bonds and one double bond with a selenium atom involving the lone pair of the arsenic. Although this possibility cannot be excluded, there is no direct evidence for its existence and there are no NQR data with which to make meaningful comparisons. For this reason, we ignore the possibility of distorted, tetrahedral arsenic sites in the following discussion.

The NQR spin-echo spectra for different samples of As_xSe_{1-x} can be analyzed to estimate the distributions of the apex bond angles of the local $AsSe_3$ pyramidal units.[15] Crystalline solids, which are characterized by unique As sites, exhibit narrow NQR spin-echo line shapes whose widths are less than about 200 kHz. In comparison, glassy solids exhibit much broader spectra due to the small distortions in the apex bond angles in the $AsSe_3$ pyramidal units. In general, the narrower the spectral width, the more ordered the local structure.

Since there is no evidence for As–As bonds in the NQR spectra for $x \leqslant 0.4$, we conclude that the local bonding arrangement is chemically ordered such that the probability of having As–As bonds in the network is near zero even at $x = 0.40$. As the concentration of arsenic increases for $x \leqslant 0.4$, the positions of the peaks decrease approximately linearly from 63 MHz at $x=0.08$ to 59 MHz at $x=0.40$ as shown in Fig. 6. The underlying mechanism for this shift is not understood but may be related to the development of intermediate range order, which manifests itself as 12-membered As-Se "rings" as x increases toward 0.40. These rings occur in the crystalline phase at $x=0.40$.[20]

For $x \geqslant 0.45$ a three-peak structure is observed. As described above, the two peaks near 58 and 80 MHz can be ascribed to arsenic pyramidal sites with zero As–As bonds and one As–As bond, respectively. In glassy $As_{0.5}Se_{0.5}$ each arsenic site would have one As–As bond if the material were perfectly chemically ordered. The fact that there are sites with no As–As bonds implies that there must be sites with two As–As bonds. Therefore, we attribute the peak near 70 MHz in Figs. 2(c) and 2(d) for glassy $As_{0.55}Se_{0.45}$ and $As_{0.6}Se_{0.4}$, respectively, to this bonding arrangement.

For $x=0.45$ [Fig. 2(a)], the line shape consists of a very broad asymmetric peak around 58 MHz, and a peak centered

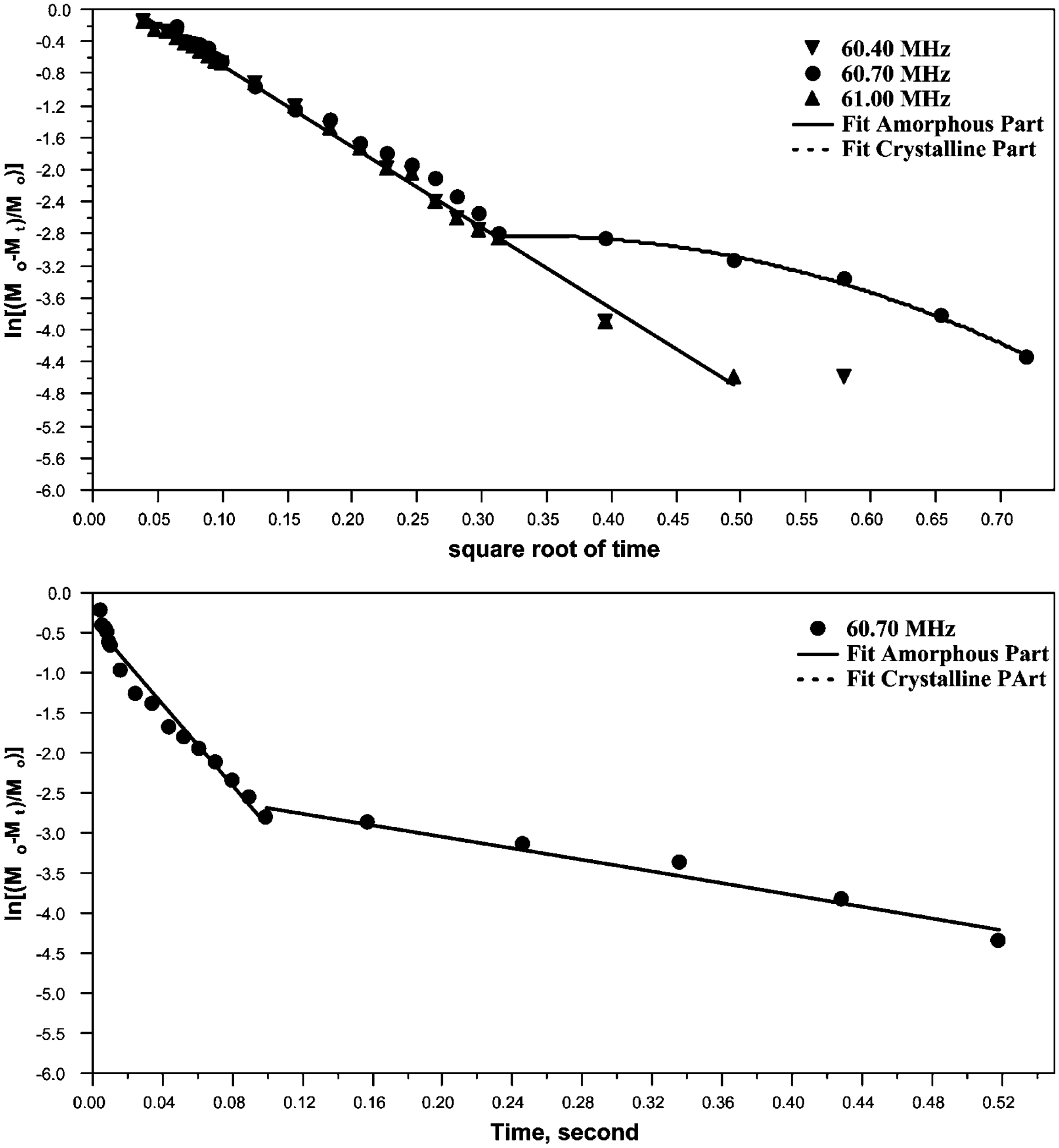

FIG. 4. The function $\ln\{(M_0 - M_z)/M_0\}$ as a function of (a) square root of time, $\sqrt{t}$ and (b) time, t, at 60.40 (inverted triangles), 60.70 (circles), and 61.00 (triangles) MHz for glassy $As_{0.60}Se_{0.40}$.

near 80 MHz. Assuming that the three resolved peaks that contribute to the NQR spectra for glassy $As_{0.55}Se_{0.45}$ and $As_{0.6}Se_{0.4}$ also occur for glassy $As_{0.45}Se_{0.55}$, we deconvolve this spectrum into three Gaussian contributions labeled A, B, and C in Fig. 2(a). Therefore, the Gaussian curves C, B, and A in Fig. 2(a) represent arsenic sites with one As–As bond, two As–As bonds and no As–As bonds (i.e., three As–Se bonds), respectively. With a further increase of the arsenic concentration the contribution of three separate components becomes more evident. At $x=0.55$ a well-defined shoulder corresponding to the B site in Fig. 2(c) becomes apparent. At $x=0.60$ all three component are completely resolved.

Figure 7(a) shows that the spectral width of the three resolved peaks in the NQR spin-echo spectrum of a-$As_{0.60}Se_{0.40}$ is considerably narrower than those in the other glassy samples, such as glassy $As_{0.40}Se_{0.60}$. The NQR spin-echo spectrum of a-$As_{0.60}Se_{0.40}$ corresponds to a significantly more ordered structure in spite of the fact that the average coordination number, $\langle r \rangle$, is the largest of any of the glasses measured. The same narrowing of the peak occurs, albeit to a lesser extent, in a-$As_{0.50}Se_{0.50}$ as shown in Fig. 7(b). The peak begins to narrow at $x \cong 0.5$ [Fig. 7(b)], and this tendency increases as the concentration of arsenic increases. We speculate that this local ordering occurs because the local structural order inhomogeneously separates into quasi one-dimensional regions similar to the small molecules that occur in crystalline As_4Se_4 ($As_{0.5}Se_{0.5}$).[14] Although there is no evidence in infrared absorption for the presence of isolated molecules in the glasses, there could exist “nodules” connected to the network which contain As–As bonds. The lower di-

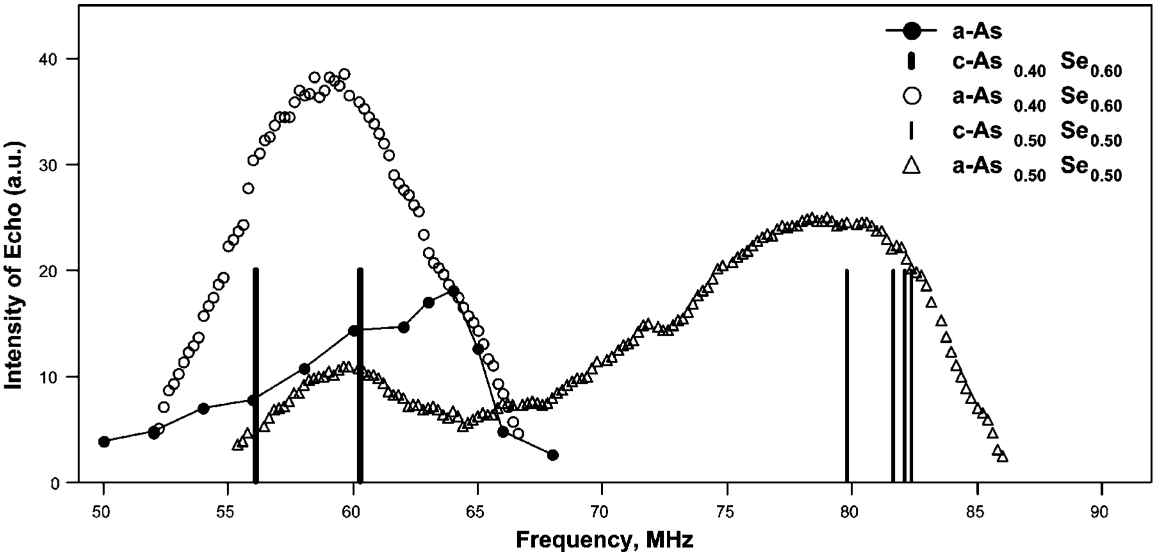

FIG. 5. NQR spin-echo spectra of crystalline (thick solid lines) and glassy (open circles) $As_{0.40}Se_{0.60}$, and crystalline (thin solid lines) and glassy (open triangles) $As_{0.50}Se_{0.50}$, and a-As (solid circles). The lines in the spectra of c-$As_{0.40}Se_{0.60}$ and c-$As_{0.50}Se_{0.50}$ correspond to inequivalent arsenic sites in the corresponding unit cells.

mensionality of these regions allows the local bonding configurations to relax, which explains why the structure is more ordered locally even though the average nearest-neighbor coordination number is large.

All samples with $x \leqslant 0.40$ (Fig. 1) show spectra that are similar to each other. These spectra have only one broad peak corresponding to a structure that consists of $AsSe_3$ pyramidal units. In contrast, the numbers and the widths of the peaks in the spectra for $x \geqslant 0.45$ clearly show that different arsenic sites with less distorted environments coexist in these samples. The complex composition of these spectra suggests that at high arsenic content the glass network may separate into smaller arsenic-rich molecularlike domains that can relieve the stress building up as the average coordination number increases. This is indirectly confirmed by the decrease of both the glass transition temperature (T_g) (Refs. 21 and 22) and the nonreversing heat flow (ΔH_{nr}).[8] The ΔH_{nr} provides a measure of network stress. Measurement of ΔH_{nr} at $x = 0.45$ reveals that the glass is rigid but stress free. Since $\langle r\rangle > \langle r_p\rangle$, where $\langle r_p\rangle$ is the average coordination number at the onset of rigidity (2.4 in this system where $x=0.4$), the glassy network should be rigid; however, in order to be stress free, Georgiev *et al.* speculated that the glass network separates into smaller arsenic-rich molecularlike domains.[8] A similar conclusion was inferred from neutron inelastic scattering experiments[1] in a-$As_{0.60}Se_{0.40}$ that show very sharp peaks in the range between 0 and 20 meV. This observation supports our conclusion that arsenic-rich molecularlike domains may form in glassy As_xSe_{1-x} at high arsenic concentrations.

Whether the compositions of the local structural units are determined randomly (statistically) or by preferential bonding between As and Se atoms can be tested using statistical modeling. We label the probabilities of an arsenic site with no As–As bonds, one As–As bond, two As–As bonds and three As–As bonds as P_0, P_1, P_2, and P_3, respectively. For the composition As_xSe_{1-x} one can easily determine that the probabilities P_0, P_1, P_2, and P_3, normalized to the total arsenic concentration x, are $(1-x)^3$, $3x(1-x)^2$, $3x^2(1-x)$, and x^3, respectively. We have already discussed the fact that the data for $x \leqslant 0.4$ indicate no evidence for anything other than As–Se bonds. Therefore the predicted behavior of P_0 over this range is not observed experimentally. This discrepancy

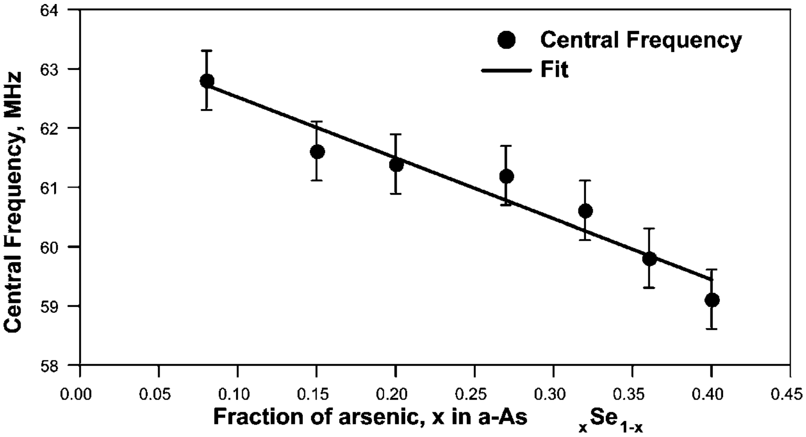

FIG. 6. The dependence of the central peak frequency of the NQR spin-echo spectrum (solid circles) on the atomic fraction of arsenic, x, in a-As_xSe_{1-x}. The line is an aid to the eye.

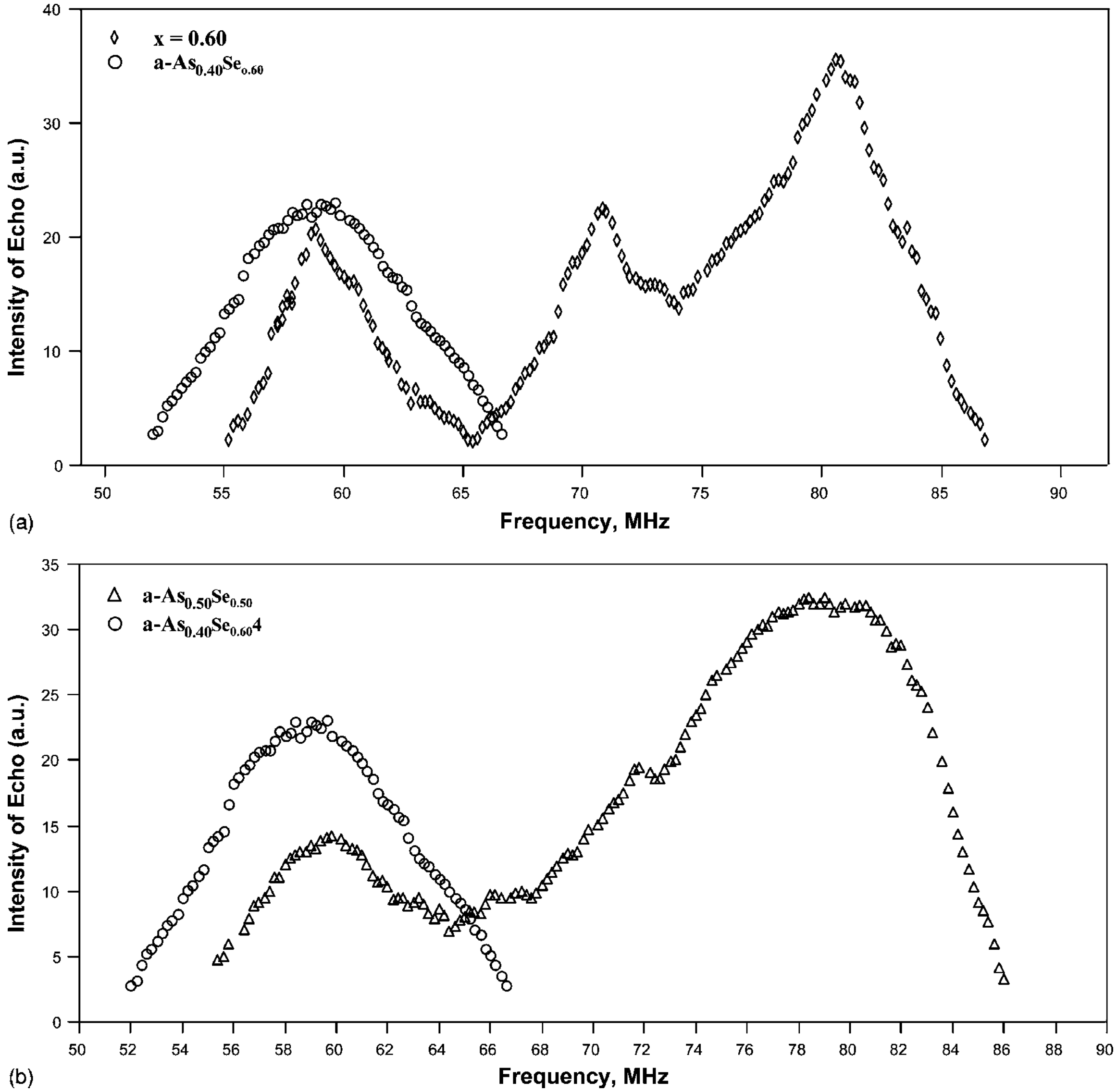

FIG. 7. (a) NQR spin-echo spectrum of a-$As_{0.60}Se_{0.40}$ (open diamonds) compared to a-$As_{0.40}Se_{0.60}$ (open circles). All three peaks in a-$As_{0.60}Se_{0.40}$ are narrower than the peak in a-$As_{0.40}Se_{0.60}$. (b) NQR spin-echo spectrum of a-$As_{0.50}Se_{0.50}$ (open triangles) compared to a-$As_{0.40}Se_{0.60}$ (open circles).

is, of course, the result of preferential bonding between As and Se in a-As_xSe_{1-x} for $x \leqslant 0.40$. The existence of only one peak for arsenic concentrations $x \leqslant 0.40$ suggests that all arsenic atoms have more or less structurally similar environments corresponding to $AsSe_3$ pyramidal units.

At $x \geqslant 0.45$ (Fig. 2) and above, As–As bonds appear, and bonding between arsenic and selenium and arsenic and arsenic becomes more random. Figure 8 shows a comparison of the measured values of P_0, P_1, and P_2 obtained from the relative areas under the respective NQR peaks with those predicted statistically. Although there is considerable scatter in the data, the relative intensities (areas) of the three peaks in the ^{75}As NQR spin-echo spectra of a-As_xSe_{1-x} for $0.45 \leqslant x \leqslant 0.60$ are in qualitative agreement with a model that assumes the random occurrence of arsenic sites with no As–As, one As–As, and two As–As bonds. [We have ignored the possible presence of As sites with three As–As bonds in the analysis of the NQR data because of the ambiguity mentioned above. The inclusion of these sites will not significantly alter the conclusions.] The statistical analysis is based on the assumption that there are no Se–Se bonds for $x > 0.4$.

For glassy As_xSe_{1-x} with $x \geqslant 0.4$ the average number of arsenic-arsenic bonds per arsenic pyramidal unit is given by [23]

$$b = \frac{5x - 2}{x}. \tag{1}$$

Therefore if complete chemical ordering were to persist for $x > 0.4$, then every arsenic pyramidal site would have exactly one As–As bond at $x = 0.5$. This prediction is clearly not in accord with the data shown in Fig. 8 for $x \geqslant 0.45$.

As mentioned above the spin-lattice relaxation in these glasses is nonexponential. This behavior is known to occur in materials where spin-diffusion limits the relaxation rates. In

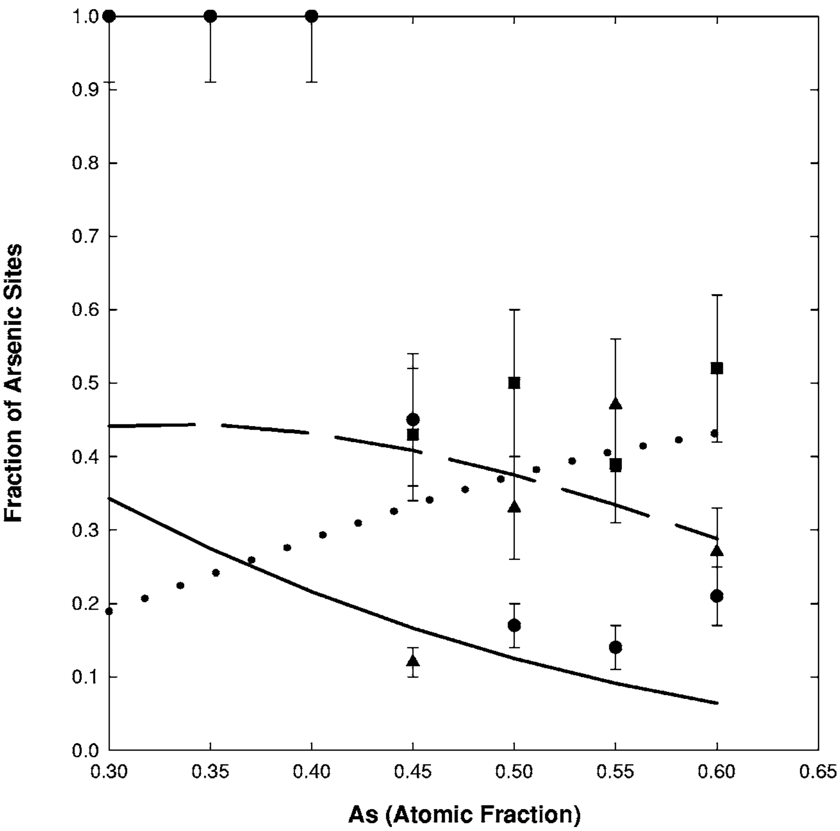

FIG. 8. Statistical modeling (lines) and experimental data for a-As$_x$Se$_{1-x}$ for $x \geqslant 0.30$. Lines represent statistical (random) probability for finding an As site with zero (P_0, solid line), one (P_1, dashed line), and two (P_2, dotted line) As-As bonds. Solid circles, solid squares, and solid triangles represent the experimentally determined values corresponding to P_0, P_1, and P_2, respectively. See text for details.

this case it can be shown[12] that the spin-lattice relaxation depends exponentially on $t^{1/2}$. Physically, this dependence occurs because As sites far away from the relaxation centers take progressively longer to diffuse their magnetic polarization to As sites close to these centers.

The measurements of the spin-lattice relaxation times in As$_x$Se$_{1-x}$ glasses with low arsenic content exhibit an increase in T_1 with increasing As content up to $x=0.40$, where $\langle r \rangle = \langle r_p \rangle = 2.4$. Glasses are known to possess a higher density of low frequency modes compared to the crystalline substances of the same composition, and the spin-lattice relaxation for quadrupolar nuclei is often governed by a Raman process involving these modes.[24] Therefore, one may speculate that the increase in T_1 with x may be due to the reduction in the number of low frequency modes in the network as it becomes more rigid.

For $x \geqslant 0.40$, however, T_1 decreases dramatically, and the widths of the NQR spin-echo spectra also decrease. The reasons for these anomalous behaviors are not entirely clear, but such behaviors may be due to inhomogeneities in the structure, such as the appearance of arsenic-rich molecular clusters that are loosely connected to the rest of the network.

There is evidence for a small fraction of a crystalline phase in the highest arsenic concentration, a-As$_{0.60}$Se$_{0.40}$. Confirmation of this occurrence comes from the differences in the decay of the magnetization at different resonant frequencies. The fact that only one frequency exhibits an exponential decay for T_1 at long times indicates that the sample may have inclusions of the crystalline phase. Indeed, the frequency that exhibits this anomalous behavior is 60.70 MHz, which closely corresponds to one resonant frequency of c-As$_{0.40}$Se$_{0.60}$, 60.25 MHz. The T_1 at this frequency at long times [Fig. 4(b)] is 0.276 sec, which also corresponds to the value obtained in c-As$_{0.40}$Se$_{0.60}$.[15]

Crystalline As$_{0.40}$Se$_{0.60}$ exhibits two peaks, at 56.07 MHz and at 60.25 MHz. Therefore, the same behavior is expected for T_1 plots around 56 MHz. We have been unable to observe this behavior at 56 MHz probably due to a lower signal-to-noise ratio. At 60.40 MHz and 61.00 MHz no crystalline component exists. The crystalline component at 60.70 MHz is about 10% of the total signal at this frequency, and is less than 0.05% over the whole range of the a-As$_{0.60}$Se$_{0.40}$ line shape. Therefore, NQR measurements of T_1 are significantly more sensitive than x-ray diffraction in terms of finding crystalline inclusions in an amorphous material. To observe crystalline inclusions in an amorphous material using standard x-ray diffraction techniques the concentration must be, in general, at least 1 at. %.

V. SUMMARY

We have studied the glassy system As$_x$Se$_{1-x}$ with x varying from 0.08 to 0.60 using ^{75}As NQR spin-echo spectra at 77 K. For the compositions with $0.08 \leqslant x \leqslant 0.40$ the spectra consist of a single broad line whose central frequency decreases approximately linearly from 63 MHz at $x=0.08$ to 58 MHz at $x=0.40$. Over this composition region there are only As–Se bonds and no As–As bonds.

The spectra for $0.45 \leqslant x \leqslant 0.60$ show contributions from several different local bonding arrangements. We have interpreted these contributions as arising from a threefold-coordinated arsenic site with varying numbers of As–Se and

As–As bonds. In particular, these spectra can be deconvolved into three peaks. By comparison with NQR spin-echo spectra that occur in crystalline arsenic-selenium compounds, these three peaks have been interpreted as due to threefold coordinated, pyramidal arsenic sites with varying numbers of As–As bonds. For $x > 0.40$, the relative numbers of sites with different numbers of As–As bonds appear to follow a random distribution, so chemical effects do not dominate the formation of the As–Se network. As $\langle r \rangle$ increases, the network connectivity increases, and becomes more constrained. The network cannot sustain a large number of constraints per atom homogeneously. Therefore, as the arsenic concentration increases, small arsenic-rich clusters form in the network to release the local strains.

ACKNOWLEDGMENTS

The authors gratefully acknowledge D. G. Georgiev, P. Boolchand, R. L. Cappelletti, and M. C. DeLong for supplying the samples used in this study. We also thank P. Boolchand, R. L. Cappelletti, and M. F. Thorpe for several helpful discussions. Research at the University of Utah was supported by the National Science Foundation under Grant No. DMR-0073004.

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