Structural Organization of Arsenic Selenide Liquids:
New Results from Liquid State NMR

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Abstract

Insights into the structure and dynamics of the binary As-Se glass system have been obtained from high-temperature ^{77}Se NMR studies of molten samples. In materials having As contents < 20 at.%, dynamic exchange averaging processes are detected and analysed quantitatively by detailed lineshape simulations. At high temperatures (1.5·melting Temperature), only a single averaged ^{77}Se NMR signal is observed, whose chemical shift arises from the quantitative distribution of As-Se and Se-Se bonds. A detailed analysis of the compositional dependence reveals a strong tendency towards chemical ordering, based on the structurally dominant $AsSe_{3/2}$ groups. Furthermore, the experimental data serve to differentiate between various intermediate-range ordering scenarios and favor a structural description in terms of a network in which $AsSe_{3/2}$ and $Se_{2/2}$ groups are randomly linked.

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Introduction

During the past few years, there has been a resurgence of the interest in non-oxide chalcogenide glasses for optical fiber applications. This renewed interest stems in particular from their potential usage as low-phonon energy host materials for rare-earth dopants. Driven by this materials science application, more detailed fundamental concepts concerning the local structure and intermediate range order of these materials are being developed, and solid state nuclear magnetic resonance (NMR) spectroscopic techniques have played an important role in this endeavour. In particular, the favorable NMR properties of the ^{31}P isotope have been exploited to advantage for a structural determination of binary and ternary phosphorus sulfide, selenide, and telluride materials [1]. In the solid state, magic angle spinning NMR spectra have provided information about the microstructural units present, while dipolar spin echo decay methods have given information about the extent of P-P bonding. Complementary high-temperature liquid state NMR studies of the glassforming compositions have provided important insights into the chemical equilibria and the kinetics leading to glass formation [2-4].

While phosphorus chalcogenide glasses are important model systems, their practical importance is rather limited owing to their instability in ambient atmosphere. For the systems of larger application interest, unfortunately, NMR investigations of similar detail have not been possible because of insufficient NMR sensitivity of the nuclear isotopes (^{77}Se, ^{75}As, ^{73}Ge) involved. While ^{73}Ge and ^{75}As possess large nuclear electric quadrupole moments, the main problems associated with the spin-1/2 isotope ^{77}Se include its natural abundance (7.6 %), signal broadening by chemical shift anisotropy effects, and spin-lattice relaxation times (>100 s). Owing to these unfavorable circumstances, the amount of structural information obtained by solid state ^{77}Se NMR of chalcogenide glasses has been limited. In the molten state, however, rapid bond breaking/bond making dynamics on the NMR timescale produce isotropic signals with smaller widths, whose chemical shifts are due to the average selenium coordination in the liquid. Furthermore spin-lattice relaxation times on the order of 10 to 100 ms allow rapid signal averaging, yielding larger signal to noise ratios in a short amount of time. Detailed ^{77}Se-NMR studies of the binary P-Se melts have appeared recently [4,5], indicating the power of this method to reveal new information on structure and dynamics. In particular, detailed insights into the chemical bond distribution and the intermediate range order in P-Se glasses has been obtained. In the present study, we have extended our investigations to binary As-Se glasses, whose structural organization has been considered in many previous studies [6-10]. There is unequivocal agreement that the structure of these glasses primarily constructed by pyramidal AsSe$_{3/2}$ groups,

however, the extent of As-As bond formation below the corresponding composition of 40 at.% As has been subject to some discussion. Likewise, such chemical disordering would imply the existence of Se-Se bonding at larger As contents. Furthermore, the open question remains as to whether the various structural building blocks are randomly linked or if any clustering exists. While it has been demonstrated previously that high-temperature ^{77}Se NMR is able to differentiate between Se- and As bonded selenium in arsenic-selenium liquids [11], in the present contribution we will illustrate how the effect can be used to reveal new information on short- and intermediate range order in this system.

Experimental

Glasses of composition from As_xSe_{1-x} ($0 \leq x \leq 0.50$) were prepared within evacuated silica ampules, heated above 900°C for at least 24 h, and quenched rapidly in ice-water. The glassy state was verified on the basis of x-ray powder diffraction patterns and differential scanning calorimetry. For all of the NMR measurements General Electric GN-300 and Bruker CXP-200 spectrometers were used, operating at ^{77}Se resonance frequencies of 57.3 MHz and 38.1 MHz, respectively. At the GN-300 spectrometer, high-temperature liquid state ^{77}Se NMR spectra were obtained in the temperature region 480 °C $\geq$ T $\geq$ 140 °C using a commercial high-temperature probe from Doty Scientific. At the CXP-300 spectrometer, the temperature range 600°C $\geq$ T $\geq$ 200 °C was covered with a homebuilt probe. In both probes, these temperature ranges were attained by resistive heating and measured with thermocouples in the immediate vicinity of the sample. All of the chemical shifts are reported with respect to a sample of solid CdSe, using liquid selenium at 300°C as a secondary reference (δ=1381 ppm).

Results

Figure 1 shows a typical temperature dependent set of ^{77}Se NMR spectra of binary As_xSe_{1-x} melts containing 12.5 mole% As. At low temperature (<200°C), we observe three well-resolved resonances in this sample, which we assign to three different types of selenium species. The good resolution indicates that narrowing by rapid molecular motion is sufficiently complete to produce isotropic spectra, while, on the other hand, averaging by chemical exchange is still slower on the

NMR timescale. The peak near 1361 ppm (species 1) coincides with the spectrum of pure amorphous selenium and is therefore assigned to Se atoms that are part of selenium chains only. The peak near 1114 ppm (species 2) is found in all of those samples containing 20 mole% As or less. Since its fractional area increases with increasing As content (data not shown), this resonance must signify selenium involved in bonding with arsenic. Based on arguments presented below, we assign it to a selenium species bonded to one arsenic and one selenium atom, i.e. the selenium atom in the midst of a As-Se-Se fragment. The assignment of the resonance at 1289 ppm (species 1`) is the most tentative one. Based on the fact that in samples with different arsenic contents, the area of this peak remains in a fixed relation to that at 1114 ppm, we assign this resonance to a selenium with a second-nearest As neighbor, i.e. to the selenium atom at the end of that As-Se-Se- fragment. A third, smaller feature near 980 ppm (species 3) becomes also evident at temperatures > 180 °C. We attribute this feature to selenium atoms bridging between two As species. Unlike for species 1, 1´ and 2, the temperature windows separating motional narrowing from chemical exchange averaging are not sufficiently distinct for species 3. Therefore, it is difficult to quantify its spectral contribution.

As illustrated in Figure 1, signal coalescence owing to the onset of chemical exchange is observed above T = 180 °C, indicating that bond breaking and re-forming is occurring on the NMR timescale. At a sufficiently high temperature (>280°C) only a single resonance remains, whose frequency approximately corresponds to the weighted average of the individual peak positions. In glasses containing more than 20 % arsenic, the spectra in the slow-exchange limit are not observable, most likely because molecular motion is slowed down by increased network rigidity, making it impossible to identify separate temperature regimes for motional narrowing and exchange narrowing. At appropriate temperatures >300 °C, these spectra show the lineshapes typical of the fast-exchange limit [12].

Figure 2 illustrates that the average peak position depends on arsenic content and temperature. In the sample containing 12.5 mole% As, the chemical exchange process is revealed in the chemical shift trend shown (see above), while at larger As contents only the exchange-averaged spectra are observable. The intrinsic temperature dependence observed for each composition is probably an effect of the unpaired electron spin concentration in the liquid, which is expected to rise because of thermal depolymerization [13]. As a result, an increasing paramagnetic contribution to the chemical shift is expected (and observed) as the temperature is increased; the contribution is approximately linear as shown in Fig 2.

The dependence of chemical shift on As content is also evident from Figure 3, which compiles data measured at a uniform temperature of 400 °C. As the As content is increased, the

chemical shift decreases in a linear fashion up to a limiting value measured near 40 at.% As. Within the concentration interval extending from 40 to 50 mole% arsenic, the [77]Se chemical shift remains approximately constant, which we suggest is due to the selenium atoms attaining a constant chemical environment.

Discussion

Chemical Exchange Dynamics. Using standard chemical exchange theory [12], we have attempted to simulate the temperature dependent spectra of Figure 1. These simulations are based on a simplified model assuming that species 1 is in exchange with species 2 and 1`, but that there is no exchange between 1` and 2. Furthermore, species 3 was not included in the simulations, because its quantitative spectral contribution is not well-known (due to incomplete motional narrowing as mentioned above). In spite of these simplifications, Figure 4 reveals that qualitatively, the simulation can reproduce the basic features of this temperature dependent. Detailed comparisons between model and experiment (Figure 5) reveal some discrepancies, particularly in the line widths, which arise from the simplifying assumptions made, particularly the neglect of species 3. Figure 6 shows a plot of the chemical exchange rate constant. An Arrhenius function is fitted to the data with a correlation coefficient R=0.99 resulting in an activation energy of 48 kJ/mole.

Chemical Bond Distribution. The nearly linear dependence of the average chemical shift within the composition region $0 \leq x \leq 40$ at % As, and its approximate invariance at larger As concentrations are consistent with a chemically ordered network structure composed mostly of $AsSe_{3/2}$ groups. Thus, the change in chemical shift with x is due to the progressive conversion of Se-Se-Se- to As-Se-Se to As-Se-As fragments. As predicted by such a chemically ordered model, above 40% As, the chemical environment of Se remains constant, and further introduction of As results in the formation of additional As-As bonds only. Thus, the nearly constant [77]Se chemical shift at As contents exceeding 40 at.% is an indication of the degree of chemical order in this glass system.

Beyond this information concerning short-range order, the detailed composition dependence of [77]Se chemical shifts enables a discussion of various intermediate range-order scenarios, relating to the linking of the As- and Se-bearing units in the network. Four basic scenarios are considered, from which different predictions with respect to the fraction of Se-only bonded selenium species

are made. First of all, a *molecular clustering model*, based on the formation of As_4Se_4 molecules dispersed in a selenium-rich matrix can be considered. This model is of certain interest, because a similar proposal was previously made for P-Se glasses [14]. A second scenario (*domain model*) envisions the $AsSe_{3/2}$ units congregating into domains, implying that the majority of the arsenic-bonded selenium species are bridging between two As atoms. The remaining two scenarios are based on a random dispersal of $AsSe_{3/2}$ and $Se_{2/2}$ groups, simulated in two different ways. In the *random-linkage model* the fraction of Se-only bonded Se species is calculated analytically based on the statistical probability as discussed in a previous publication [4]. Finally, in the *random shot model*, a graph theoretical approach has been taken. $AsSe_{3/2}$ groups are placed onto a two-dimensional triangular grid at random (according to the respective As concentration of the glass considered), and the number of Se-only bonded Se atoms are determined by a simple counting algorithm. The Random Shot Model Simulation was implemented in C++ and used the gcc-2.95.2 compiler. To simulate the hexagonal grid of the possible Arsen locations, two 2D-arrays were used and interpreted as even or odd triagonal subgrids of the hexagonal grid. The transformation of the 2D arrays in the triagonal subgrids is simply described by the following transformation matrices

$$\begin{vmatrix} a & \dfrac{a}{2} \\ 0 & \dfrac{\sqrt{3}a}{2} \end{vmatrix} \text{ and } \begin{vmatrix} a & \dfrac{a}{2} \\ 0 & \dfrac{\sqrt{3}a}{2} + const \end{vmatrix}.$$

For each 60x60 grid simulation, we needed on a Sparc Ultra 10 workstation less than 30 ms, including all file I/O operations.

No As-As bonds are allowed. Figure 7 illustrates the principle, and Figure 8 shows simulations for three different As concentrations. The construction of the network from these units produces four distinct next-nearest neighbor (NNN) environments for each arsenic site, being linked via selenium to zero, one, two or three $AsSe_{3/2}$ groups. The populations of these NNN environments are plotted in Figure 9 as a function of composition. Repeated simulations (10.000) of these model have shown that the maximum As content that can be incorporated into the glass without producing As-As links is near 37 mole%, which is less than the chemical limit (40%). This discrepancy arises from the rigidity of the random shot modelling approach used. Since, no further relaxation (i.e. re-positioning of the As atom is considered, the placement of As atoms in excess of 37% without forming As-As bonds becomes statistically improbable. In all of the other respects, the analytical random linkage and the numerical random shot models make essentially identical predictions as expected.

Figure 10 indicates that the four intermediate-range order scenarios make different predictions concerning the fraction 'f_1' of Se atoms that are exclusively bonded to Se. Experimentally, this number is available in principle, from the chemical shift data measured in the fast exchange region. In principle, the experimental shift 'δ_{exp}' corresponds to the weighted average of the three basic types of selenium species:

$$\delta_{exp} = f_1 \delta_1(Se\text{-}\mathbf{Se}\text{-}Se) + f_2 \delta_2(Se\text{-}\mathbf{Se}\text{-}As) + f_3 \delta_3(As\text{-}\mathbf{Se}\text{-}As),$$

where the f_i are fractional contributions with $f_1 + f_2 + f_3 = 1$.

Each one of the three selenium species has a characteristic shift δ_i. In the present study, we have analyzed the chemical shift data measured at 400 °C, since this temperature lies in the middle of the experimental range investigated. However, like in Figure 2 the slopes of all $\delta(T)$ curves are identical within experimental error (the temperature dependent chemical shift curves lie essentially parallel to each other for different samples), the speciation can be extracted in principle at any temperature. For species 1, the chemical shift of molten Se (near 1400 ppm) is a good approximation, while for species 3, the chemical shift of 1000 ppm observed at 400 °C in liquid As_2Se_3 (40 at.% As) can be taken as a reference. For the chemical shift of species 2 we assume that it lies close to the average (1200 ppm) of the two other species. The principal difficulty in extracting f_1 from the average chemical shift, then, lies in the lack of knowledge of the relative contributions f_2 and f_3 of the singly and doubly As - bonded selenium atoms. We are able to address this question quantitatively only in glasses containing 12.5 mole% As and 17.5 mole% As, where we know the ratio f_1/f_2 independently from the low-temperature data (Figure 1). Figure 10 reveals that the f_1 extracted from this additional information for the 12.5% As and the 17.5% As glasses wich are close to the f_1 - predicted from a statistical linking scenario.

For the other glasses in our study, only upper and lower limits for f_1 can be specified. To obtain the lowest limiting estimate of f_1, we assume $f_3 = 0$, i.e. all of the As- bonded Se atoms are of the type As-Se-Se. Naturally, the limiting composition for such a scenario is 25 mole% As, above which As-Se-As links have to be present. On the other hand, the δ_{exp}-s can also be used to estimate an upper limit f_1 if we assume $f_2 = 0$, i.e. all of the As- bonded Se atoms are bridging between two As sites. The region of possible f_1-s consistent with the experimental data is represented by the vertical bars displayed in Figure 10. Clearly, the experimental data eliminate both the molecular and the domain scenarios from consideration, and show best consistency with the random linkage model. As such the results are in agreement with a continuous network structure of arsenic selenide glasses and are not in agreement with any scenarios involving

clustering and phase separation processes, at least within the concentration region extending from zero to 40 mole% arsenic. On the other hand, the situation at larger As concentrations is less evident from ^{77}Se NMR data. For such As-rich glasses, the formation of As-As bonds has been most clearly detected from [75]As NQR spectroscopy [15] carried out on the glasses themselves. We anticipate that the combination of liquid state ^{77}Se NMR with solid state [75]As NQR spectroscopy offers new prospects for discussing chalcogenide glass chemical order and intermediate range order in future applications.

Acknowledgments

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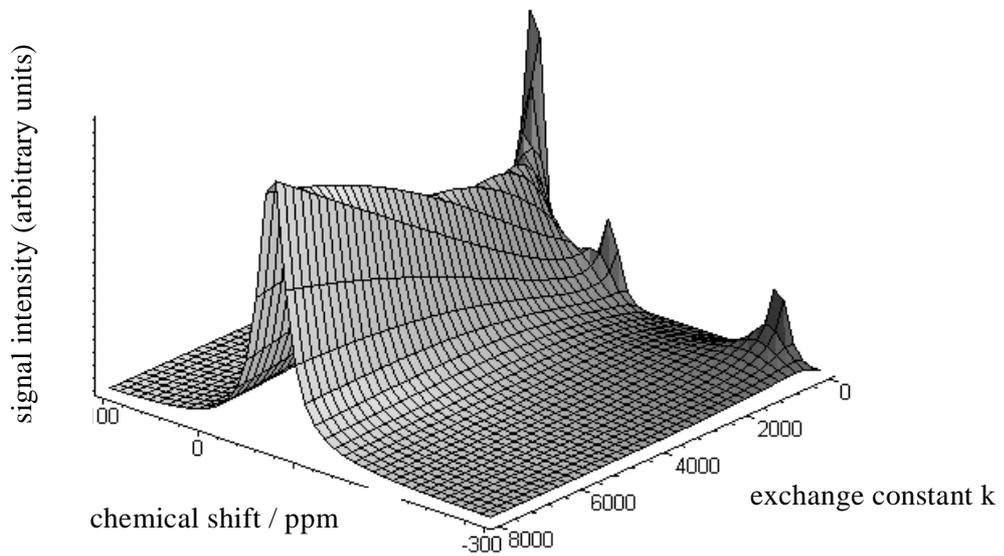15. Z. M. Saleh, G. A. Williams, P. C. Taylor, Phys. Rev. B 40 (1989) 10557
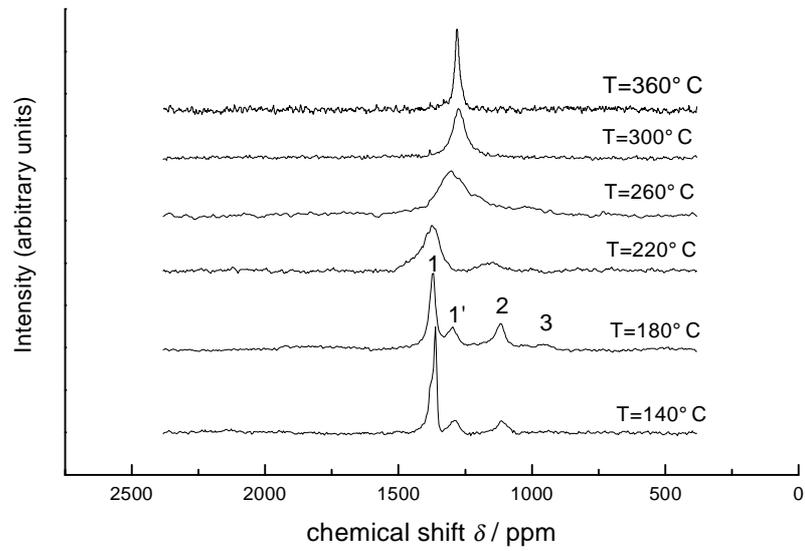
Figure 1: Experimental temperature dependent ^{77}Se NMR spectra of As$_{12.5}$Se$_{87.5}$ melt
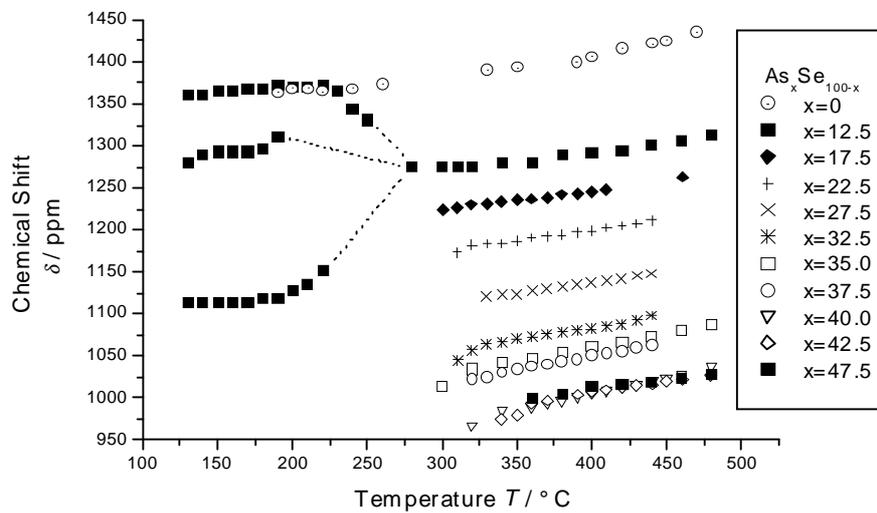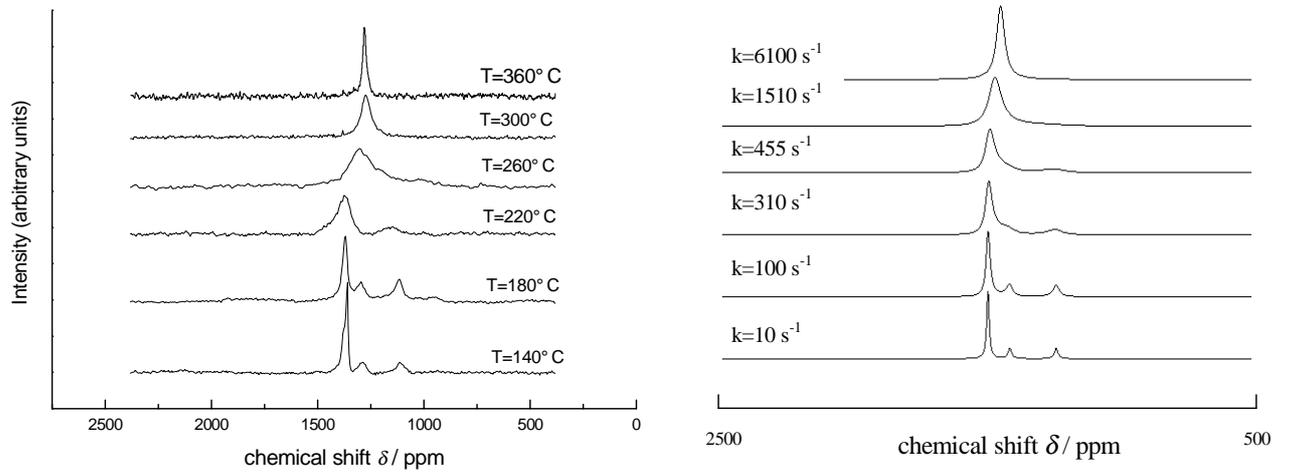

Figure 2: Dependence of ^{77}Se chemical shift on Composition and Temperature in As-Se glasses.
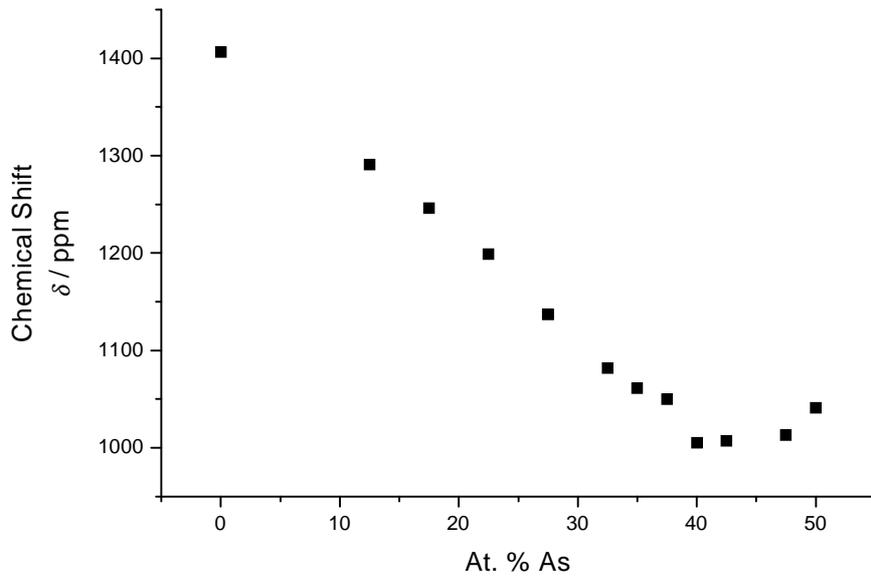
**Figure 3:** ^{77}Se NMR chemical shifts of As$_x$Se$_{100-x}$ glasses at 400°C

Figure 4: Chemical Exchange Simulation of ^{77}Se NMR-Spectra: Lineshapes are shown as a function of exchange rate constant k. For further discussion , see text.

Figure 5: Temperature dependence of the ^{77}Se NMR-spectra of As-Se melt containing 12.5 mole%As. Left: experimental spectra; right: simulations using a three-site exchange model (see text). In the simulation plots, the chemical exchange rates assigned to the respective temperatures are indicated.
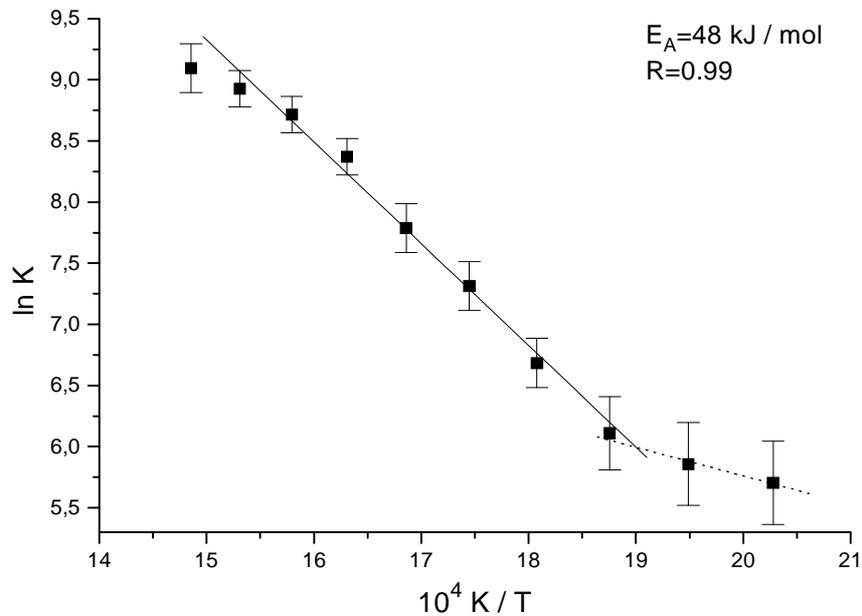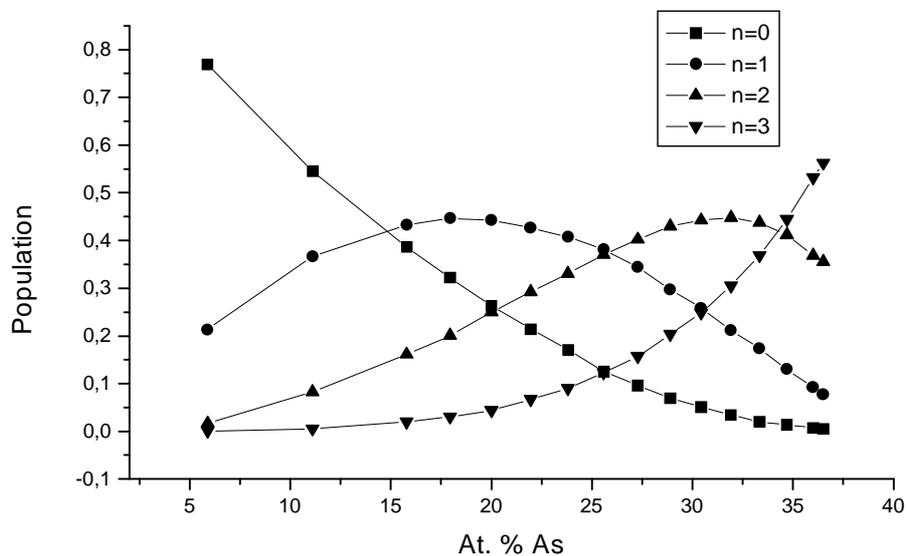

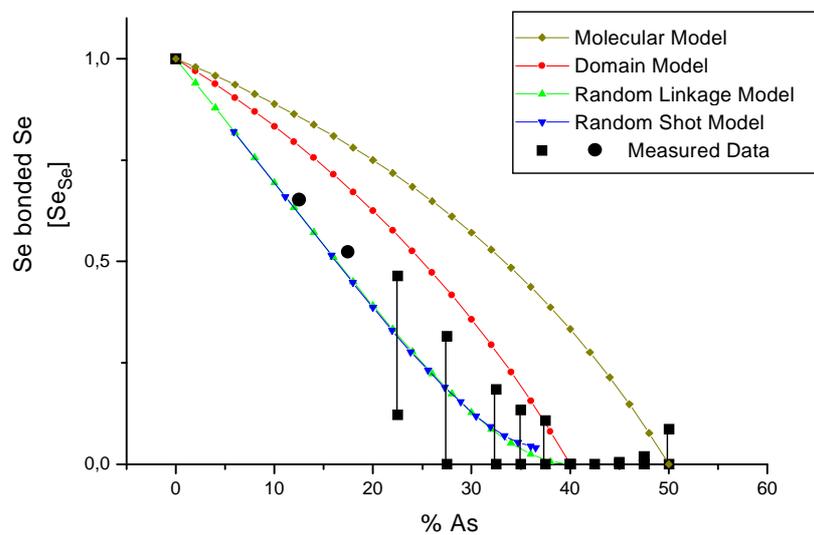**Figure 6:** Kinetic Analysis of Chemical Exchange in As$_{12.5}$Se$_{87.5}$ Melt (Arrhenius Plot)
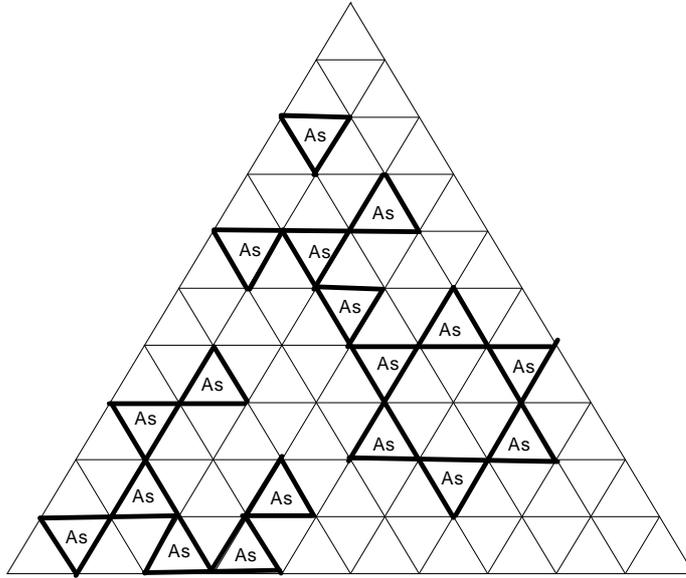
Figure 7: Random Shot Model (Graph Theory) Example

10% As   20% As   Percolation Limit
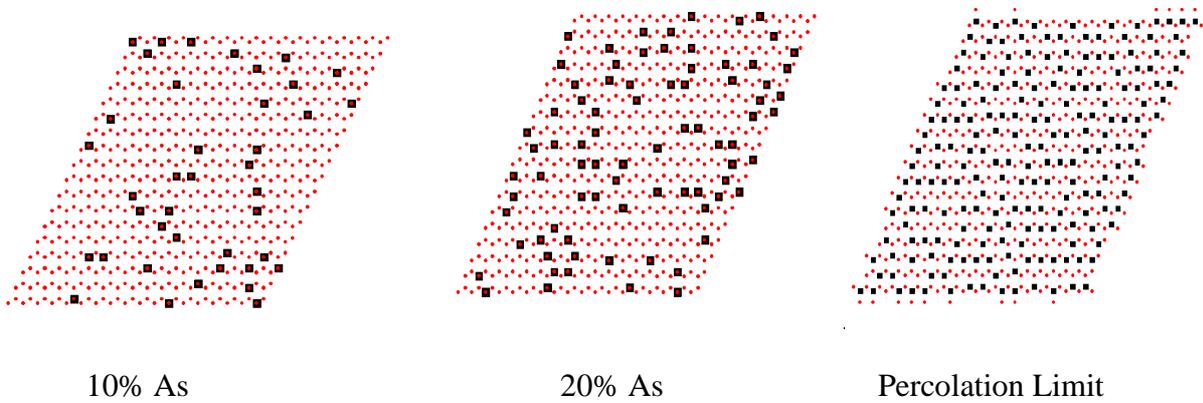
Figure 8: Typical Random Shot simulations of As-Se glasses having different As contents

Figure 9: Compositional Dependence of NNN Enviroments as generated by the *random shot model*

Figure 10: Comparison of the different scenarios with respect to the fraction f_1 of the Se-only bonded Se atoms. Possible ranges of f_1 deduced from the analyis of the experimental [77]Se chemical shifts are indicated (see text).