



Nuclear quadrupole resonance study of the glassy $\text{As}_x\text{Se}_{1-x}$ system

Eungho Ahn ^{a,*}, G.A. Williams ^a, P.C. Taylor ^a, D.G. Georgiev ^b, P. Boolchand ^b,
B.E. Schwickert ^c, R.L. Cappelletti ^d

^a Department of Physics, University of Utah, Salt Lake City, UT 84112-0830, USA

^b Department of Electrical, Computer Engineering and Computer Science, Cincinnati, OH 45221-0030, USA

^c IBM Almaden, M/S E1, 650 Harry Road, San Jose, CA 95120, USA

^d National Institute of Standards and Technology, Gaithersburg, MD 20899-8562, USA

Abstract

Nuclear quadrupole resonance (NQR) of ^{75}As has been used to study the local bonding structure of glassy arsenic–selenium systems. We have studied the glassy system $\text{As}_x\text{Se}_{1-x}$ with $x = 0.08, 0.15, 0.27, 0.32, 0.36, 0.40, 0.50,$ and 0.60 using ^{75}As NQR at liquid nitrogen temperature (77 K). The ^{75}As NQR spin-echo spectra from $x = 0.08$ up to $x = 0.40$ each consist of a single broad line. As the concentration of arsenic increases, the positions of the peaks decrease approximately linearly from 63 MHz at $x = 0.08$ to 58 MHz at $x = 0.40$. For $x = 0.50$, the spectrum, consists of a very broad asymmetric peak near 81 MHz. The spectrum for $x = 0.60$ consists of three well-resolved, narrow peaks, but otherwise extends over a similar frequency range as that of $x = 0.50$. By comparison with NQR spectra that occur in crystalline arsenic–selenium compounds, these three peaks have been interpreted as due to three fold co-ordinated, pyramidal arsenic sites with, varying numbers of arsenic–arsenic bonds. © 2002 Elsevier Science B.V. All rights reserved.

PACS: 61.43.Dq; 61.82.Fk; 71.23.Cq

1. Introduction

Amorphous semiconductors have very wide applications in modern technologies, for instance, solar cells, thin film transistors, light sensors, optical memory devices, electrophotography, and so on. These applications require an understanding of the physical properties of amorphous materials. Nuclear quadrupole resonance (NQR) is a powerful method to understand, amorphous systems,

and it is used to probe local bonding and the distributions of bond angles. In addition, the structure of arsenic-rich compounds in the binary As–Se system is not as well understood, as it is in $\text{a-As}_2\text{Se}_3$ and $\text{a-As}_4\text{Se}_4$. In this study we examine glassy As–Se systems with different concentrations of arsenic using the NQR technique to investigate the local bonding structure at arsenic sites with different numbers of As–As bonds.

2. Experimental

The NQR setup employs a high power, variable frequency, pulsed rf generator. The generator is

* Corresponding author.

E-mail address: moztart@physics.utah.edu (E. Ahn).

gated using a Matec Gating Modulator Model 5100, The rf source is a Wavetec Model 3001 waveform generator. The experiments utilize the spin-echo method; the transient response of nuclei is recorded with a LeCroy 900 A signal averager. The $a\text{-As}_x\text{Se}_{1-x}$ ($0.08 \leq x \leq 0.36$) samples came from Georgiev and Boolchand of the University of Cincinnati [1] and the sample with $x = 0.60$ is from Schwickert [2] and Cappelletti [3]. The samples with $x = 0.40$ and 0.50 were grown at the University of Utah [4]. NQR spectra were recorded at liquid nitrogen temperature (77 K) using the spin-echo following a $90^\circ\text{-}\tau\text{-}180^\circ$ pulse sequence. The spectrum was determined by measuring the echo amplitude as a function of the frequency. The 90° pulse widths were $5 \mu\text{s}$. Other experimental details are available elsewhere [5].

3. Theoretical background

NQR measures transitions between nuclear energy levels that are split by an electric field gradient at the nuclear site. Such an interaction requires a nucleus with spin I larger than $1/2$ (^{75}As has $I = 3/2$). For $I = 3/2$ the single NQR resonant frequency is given by $\nu_{\text{NQR}} = \nu_Q(1 + \eta^2/3)^{1/2}$, where $\nu_Q = e^2q_{zz}Q/2h$ and e is the electronic charge, q_{zz} the maximum component of the electric field gradient at the nuclear site, Q the nuclear quadrupole moment, and h the Planck's constant. The parameter η , which varies between 0 and 1, is a measure of the departure of the electric field gradient from axial symmetry. Since the electric field gradient is predominantly determined by bonding electrons, the NQR technique allows the study of local bonding or local structural order in the solid.

4. Experimental results

The ^{75}As NQR spin-echo spectra from samples of glassy $\text{As}_x\text{Se}_{1-x}$ with $x = 0.08, 0.15, 0.27, 0.32, 0.36,$ and 0.40 are shown in Fig. 1. All of these spin-echo spectra consist of a single broad line. As the concentration of arsenic increases, the positions of the peaks decrease approximately linearly

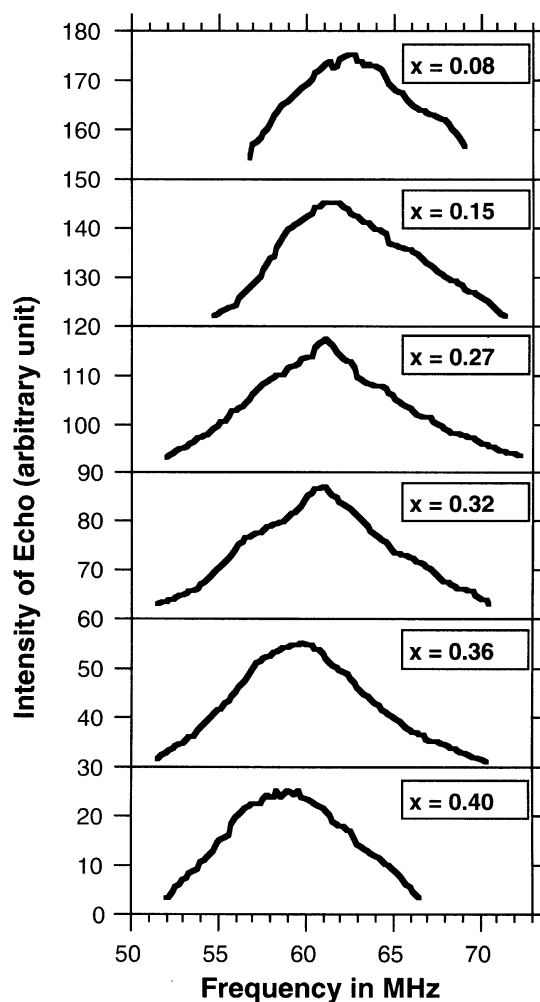


Fig. 1. The ^{75}As NQR spin-echo spectra at 77 K in $a\text{-As}_x\text{Se}_{1-x}$ for $x = 0.08, 0.15, 0.27, 0.32, 0.36,$ and 0.40 each consist of a single broad line. The spectra are offset for clarity. As the concentration of arsenic increases, the positions of the peaks decrease approximately linearly from 63 MHz at $x = 0.08$ to 58 MHz at $x = 0.40$.

from 63 MHz at $x = 0.08$ to 58 MHz at $x = 0.40$. This dependence is shown in Fig. 2.

Figs. 3 and 4 show the spin-echo spectra for $x = 0.50$ and 0.60 , respectively. These spectra are qualitatively different from the spectra for lower x . Three peaks are clearly resolved in the case of $x = 0.60$ (Fig. 4). For $x = 0.50$ the three peak structure is inferred from a fit to three Gaussian functions (Fig. 3).

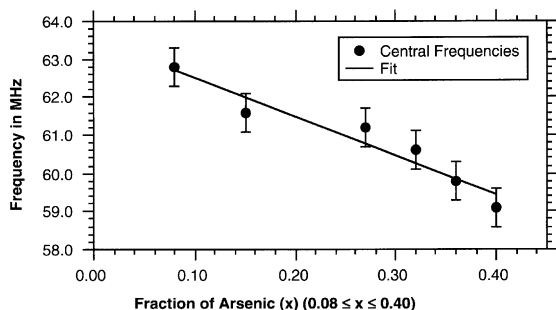


Fig. 2. The dependence of the peak frequency of the NQR spin-echo spectrum on the atomic fraction of arsenic in $a\text{-As}_x\text{Se}_{1-x}$.

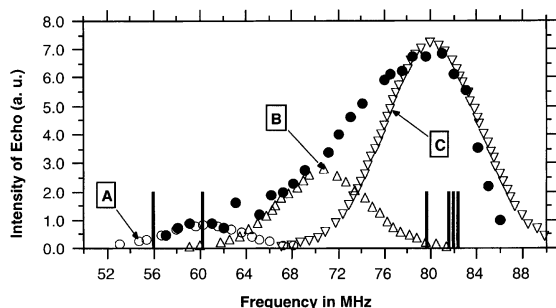


Fig. 3. NQR spin-echo spectrum in $a\text{-As}_x\text{Se}_{1-x}$ for $x = 0.50$ ($a\text{-As}_{0.50}\text{Se}_{0.50}$ [6], solid circles) has a broad peak, which extends from approximately 56 to 87 MHz at 77 K. The vertical lines (at 56.07 and 60.25 MHz) indicate the positions of the resonances in $c\text{-As}_{0.40}\text{Se}_{0.60}$ [8]. These two lines result from the two inequivalent arsenic sites in the unit cell. The $c\text{-As}_{0.50}\text{Se}_{0.50}$ [9] spectrum has four narrow lines (at 79.79, 81.63, 82.08, and 82.38 MHz). The curves A (circles), B (triangles), and C (inverted triangles) are Gaussian functions that represent arsenic sites with either zero or three, two, and one As–As bond, respectively.

5. Discussion

The ^{75}As NQR spin-echo spectra (Fig. 1) of glassy $\text{As}_x\text{Se}_{1-x}$ with $0.08 \leq x \leq 0.40$ each consist of a single broad line. With increasing x the positions of the peaks decrease approximately linearly from 63 MHz at $x = 0.08$ to 58 MHz at $x = 0.40$ (Fig. 2). The underlying mechanism for this shift is not understood. We note that the frequency range of the NQR spectrum for $x = 0.40$ overlaps with that of pure $a\text{-As}$ (see Fig. 4). This accidental overlap

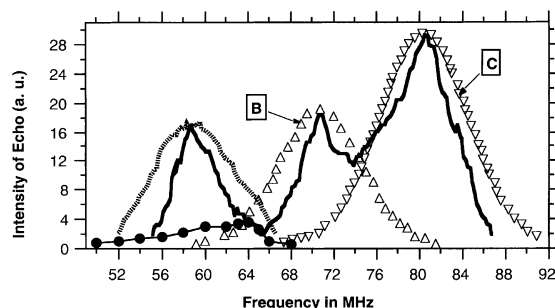


Fig. 4. The ^{75}As NQR spin-echo spectrum in $a\text{-As}_x\text{Se}_{1-x}$ for $x = 0.60$ ($a\text{-As}_{0.60}\text{Se}_{0.40}$, solid line) has three resolved peaks which extend from approximately 54 to 88 MHz at 77 K. The spectrum for $a\text{-As}_{0.40}\text{Se}_{0.60}$ [5] is shown as solid squares. The NQR resonance of pure $a\text{-As}$ [7] (three As–As bonds, solid circles with line) is located between approximately 50 and 68 MHz. The fitted Gaussian functions B (triangles) and C (inverted triangles), taken from Fig. 3, are also shown.

precludes a unique assignment of NQR peaks to specific bonding sites.

In the following we will analyze the three peak structure found for the NQR spectra for high arsenic concentrations, namely $x = 0.50$ and $x = 0.60$. Our analysis of the $a\text{-As}_{0.50}\text{Se}_{0.50}$ and $a\text{-As}_{0.60}\text{Se}_{0.40}$ structures is based on comparisons with the previously reported NQR spectra of the binary glassy As–Se systems, $a\text{-As}_{0.40}\text{Se}_{0.60}$ [5], $a\text{-As}_{0.50}\text{Se}_{0.50}$ [6], pure $a\text{-As}$ [7] (Fig. 4) and crystalline As–Se systems, namely $c\text{-As}_{0.40}\text{Se}_{0.60}$ [8] and $c\text{-As}_{0.50}\text{Se}_{0.50}$ [9] (Fig. 3). The NQR spectra of these glasses are essentially centered about NQR lines observed in the crystalline materials. This analysis ignores the possibility, which has recently been suggested [10], that in these glasses arsenic may be four fold co-ordinated with three single bonds and one double bond at low concentration of arsenic. Although this possibility cannot be excluded, 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 spectrum for $x = 0.60$ consists of three well-resolved, narrow peaks shown in Fig. 4. We suggest that the lowest frequency peak is due to arsenic sites with either zero (or three As–Se bonds) or three As–As bonds. This assignment is based on three comparisons: first, the peak is

similar to that which occurs in a-As_{0.40}Se_{0.60} (solid squares in Fig. 4); second, the peak is similar to that which occurs in pure a-As (three As–As bonds, solid circles with line in Fig. 4); and third, the peak occurs in the same frequency range as the two NQR lines in c-As_{0.40}Se_{0.60} (see Fig. 3). The highest frequency peak in the a-As_{0.60}Se_{0.40} spectrum is suggested to be due to arsenic sites at which there are two As–Se bonds and one As–As bond. Again two comparisons suggest this assignment. First, this peak is similar to that of a-As_{0.50}Se_{0.50}, and second, the peak occurs in the same frequency range as the four lines that occur in c-As_{0.50}Se_{0.50} (Fig. 4). Based on the above assignments we may speculate that the middle frequency peak is due to the remaining possible coordination, namely arsenic with two As–As bonds with one As–Se bond.

For $x = 0.50$, the spectrum (Fig. 3) consists of a very broad but asymmetric single peak at 81 MHz. This spectrum suggests that a large portion of the arsenic sites has an NQR frequency similar to those in c-As_{0.50}Se_{0.50}. Fig. 3 also contains a tail that extends to lower frequencies (approximately to 60 MHz), which is suggestive of the presence of arsenic sites with either zero, two or three As–As bonds. This interpretation, is inferred from the same considerations discussed above for a-As_{0.60}Se_{0.40}. Therefore, the spectrum can be decomposed into three Gaussian peaks (A, B, and C) as shown in Fig. 3. Here Gaussian A models the contribution from arsenic sites with either zero (or all three As–Se bonds) or three As–As bonds, and

Gaussian C models arsenic sites with one As–As bond. There must however also exist arsenic sites with two As–As bonds, which manifest themselves at intermediate frequencies, and their contribution is modeled by Gaussian B.

Fig. 4 also shows that the spectral widths of the three resolved peaks in the NQR echo spectrum of a-As_{0.60}Se_{0.40} are considerably narrower than those in the other glassy samples measured here. Specifically, Fig. 4 compares the spectral width of a-As_{0.60}Se_{0.40} to the fitted spectral widths of Gaussians B and C mentioned above in the discussion of a-As_{0.50}Se_{0.50}. In general, the narrower the spectral width, the more ordered the local structure. This can, for example, be seen from the very narrow echo spectra of the crystalline samples (maximum; 200 kHz). Compared with the broad NQR spectra we found for $x \leq 0.40$, for which all the arsenic sites have a similar bonding structure, the spectra for $x = 0.50$ and 0.60 clearly show that different arsenic sites with distinct bonding structures co-exist in these samples. Because of the relatively narrower peaks in, the NQR spectrum for $x = 0.60$, the sites are probably more ordered. This suggests that at high arsenic content $x > 0.50$, the glass network progressively dissociates into arsenic-rich smaller molecular clusters, as reflected in the reduction [11,12] of both glass transition temperature (T_g) as well as the non-reversing heat flow. A similar conclusion was inferred from neutron inelastic scattering experiments [13]. However, further experiments are necessary, especially those on, samples with $0.50 < x < 0.60$.

Table 1

Comparison of the intensities of the NQR peaks of a-As_{0.60}Se_{0.40} with a binomial distribution

Intensity	No As–As and three As–As bond sites	Two As–As bond sites	One As–As bond sites
NQR	21 ± 5%	27 ± 5%	52 ± 5%
Binomial distribution	26%	33%	41%

See text for details.

Table 2

Comparison of the intensities of the NQR peaks of a-As_{0.50}Se_{0.50} with a binomial distribution

Intensity	No As–As and three As–As bond sites	Two As–As bond sites	One As–As bond sites
NQR	6 ± 5%	25 ± 5%	69 ± 5%
Binomial distribution	34%	22%	44%

See text for details.

The relative intensities of the three peaks in the ^{75}As NQR spin-echo spectrum of $\text{a-As}_{0.60}\text{Se}_{0.40}$ can be reproduced by a model of the random occurrence [14] of As sites with no As–As, one As–As, two As–As, and three As–As bonds (binomial distribution, Table 1). However the same kind of statistical modeling [14] does not appear to reproduce the distribution found in the ^{75}As NQR spin-echo spectrum of $\text{a-As}_{0.50}\text{Se}_{0.50}$ (Table 2).

6. Summary

We have studied the glassy system $\text{As}_x\text{Se}_{1-x}$ with $x = 0.08, 0.15, 0.27, 0.32, 0.36, 0.40, 0.50,$ and 0.60 using ^{75}As NQR at 77 K. For the compositions with $0.08 \leq x \leq 0.40$ 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 $x = 0.40$. The spectra, for $x = 0.50$ and $x = 0.60$, however, show several contributions. We have interpreted these contributions as arising from three fold co-ordinated arsenic sites with varying numbers of As–Se and As–As bonds. In particular, the spectra for $x = 0.50$ and $x = 0.60$ have been analyzed to contain three peaks. By comparison with NQR spectra that occur in crystalline arsenic–selenium compounds, these three peaks have been interpreted as due to three fold co-ordinated, pyramidal arsenic sites with varying numbers of arsenic–arsenic bonds. The spectrum for $x = 0.60$ consists of three peaks. The three peaks have been assigned to

contributions from, arsenic sites with: (1) either zero or three As–As bonds, (2) one As–As bond, and (3) two As–As bonds.

Acknowledgements

The research at the University of Utah is partially supported by NSF under grant No. DMR 0073004. The work at University of Cincinnati is supported by NSF grant No. DMR-01-01808.

References

- [1] Department of Electrical and Computer Science, University of Cincinnati, Cincinnati, OH 45221-0030, USA.
- [2] IBM Almaden, M/S El, 650 Harry Road, San Jose, CA 95120, USA.
- [3] National Institute of Standards and Technology, Gaithersburg, MD 20899-8562, USA.
- [4] The Crystal Growth Laboratory, Department of Physics, University of Utah, USA.
- [5] M. Rubinstein, P.C. Taylor, Phys. Rev. B 9 (1973) 4248.
- [6] Z.M. Saleh, G.A. Williams, P.C. Taylor, Phys. Rev. B 47 (1993) 4990.
- [7] P. Craig Taylor, Z. Naturforsch. 51a (1996) 603.
- [8] S.A. Dembovskii, A.A. Vaipolin, Tverd. Fiz. Tela 6 (1964) 1796.
- [9] E.A. Kravchenko, S.A. Dembovskii, A.P. Chernov, G.K. Semin, Phys. Stat. Sol. 31 (1969) K19.
- [10] D.G. Georgiev, P. Boolchand, M. Micoulaut, Phys. Rev. B 62 (2000) R9228.
- [11] P. Boolchand, Asian J. Phys. 9 (2000) 709.
- [12] P. Boolchand, W.J. Bresser, Philos. Mag. B 80 (2000) 1757.
- [13] B. Effey, R.L. Cappelletti, Phys. Rev. B 59 (1999) 4119.
- [14] M.F. Thorpe, private communication.