Nuclear Quadrupole Resonance in Amorphous Semiconductors *

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Nuclear quadrupole resonance (NQR) has provided a valuable tool for investigating the local structural order in semiconducting glasses. Measurements of NQR lineshapes and spin-lattice relaxation times help elucidate the local structural order and the unusual vibrational properties, respectively, of these glasses. In addition, NQR lineshape measurements on samples that are made under conditions that produce solids whose structures are far from equilibrium, such as fast-evaporated films or rapidly-drawn fibers, provide detailed information on the changes in the local structural order from that which occurs in the well-annealed amorphous semiconductors.

Key words: NQR, chalcogenide glasses, amorphous semiconductors, structure, vibrational properties.

Introduction

The interpretation of the usual scattering experiments, such as x-ray, neutron or electron scattering, is in the case of amorphous semiconductors greatly complicated by the absence of long range periodic order. Therefore information concerning the static and dynamic properties of these solids must be gathered from many different experimental techniques. In the chalcogenide (group IV) and pnictide (group V) amorphous semiconductors nuclear quadrupole resonance (NQR) is a particularly useful technique. This usefulness results from the fact that NQR provides information on interatomic spacings and thus local structural order. In the case of ^{75}As, analyses of the NQR lineshapes yield detailed information on the local bonding at the arsenic sites in the glasses, and in some cases also about the so-called "intermediate range order" that occurs on a scale of several interatomic spacings. Of particular importance is the fact that ^{75}As NQR measurements can distinguish between As-chalcogen and As–As bonds in a wide range of chalcogenide glass systems. One can also examine the detailed local structural rearrangements that accompany the well-known photo-induced polymerization that occurs in some of these semiconducting glasses. ^{75}As NQR measurements also probe some dynamic processes in these amorphous semiconductors, processes such as highly anharmonic "tunneling" or "disorder" modes that are supposed to exist in all of these materials.

We will discuss local bonding information obtained primarily from ^{75}As NQR in chalcogenide and pnictide amorphous semiconductors. The use of spin-lattice relaxation measurements to probe disorder modes in these materials will also be discussed. The As-containing amorphous semiconductors of most interest include amorphous arsenic, simple binary arsenic-chalcogenide glasses, such as As_2Se_3 and As_2S_3, and more complicated chalcogenide glasses, such as the metal chalcogenide systems including Cu–As–Se and Cu–As–S.

Nuclear Quadrupole Resonance

The theoretical foundations of NQR can be found in many reviews [1]. We summarize here only the elements essential for an understanding of the data presented below. The NQR Hamiltonian can be written in the form

$$\mathcal{H} = \mathbf{I} \cdot \mathbf{Q} \cdot \mathbf{I}, \tag{1}$$

where $\mathbf{I}$ is the nuclear spin operator and $\mathbf{Q}$ is the quadrupolar tensor. This tensor contains the gradient of the electric field (EFG) at the nuclear site and the quadrupole moment of the nucleus, Q. In the principal axis system one can use the maximum component of the tensor, V_{zz}, and the asymmetry in the remaining two components, $(V_{xx} - V_{yy})/V_{zz}$, to define two independent parameters, eq and η, respectively, (e is the electronic charge). In the case of ^{75}As, $I = 3/2$ and there

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are two doubly degenerate energy levels whose separation yields a resonant frequency given by

$$v = \left(\frac{e^2 q Q}{2 h}\right)\left(1 + \frac{\eta^2}{3}\right)^{1/2}. \tag{2}$$

Because there is only one resonant transition one cannot independently determine the two independent parameters q and η from the NQR absorption.

Experimental Details

The experiments described in this review all involve use of a standard pulsed spectrometer whose features have been described in [2, 3]. The pulse sequence employed was usually a $90° - \tau - 180°$ sequence, after which the spin echo was observed. The glassy samples used were made by methods described in [4].

Binary Chalcogenide Glasses

In the binary chalcogenide glasses we shall use as examples the prototype glasses, As_2Se_3, As_2S_3, and As_2O_3. In these stoichiometric glasses the arsenic atoms are bonded to three chalcogens and the NQR spectra of the glasses are essentially centered about the NQR line (or lines) observed in the layered, crystalline modifications [2, 5]. This fact is illustrated for the glasses As_2Se_3 and As_2S_3 in Figure 1. In this figure the open squares and circles represent the ^{75}As NQR echo intensities as functions of frequency. Solid and dashed vertical lines indicate the positions of ^{75}As NQR absorptions in several crystalline modifications in these two binary systems. The linewidths of the crystalline NQR spectra are so narrow on the scale of Fig. 1 that they cannot be accurately represented [6]. In the As–Se and As–S systems, the stoichiometric compositions (A_2B_3) exhibit similar nearest neighbor order in both the amorphous and crystalline phases. In particular, each arsenic is bonded to three chalcogen atoms, and each chalcogen to two arsenics. The much broader lines in the glasses are due to small distortions in the apex bond angles of the AsS_3 or $AsSe_3$ pyramidal units. Estimates of the distortions in the apex pyramidal bonding angles for the As sites in these glasses yield distributions whose half widths are only a few degrees [2, 7]. Note in particular that one specific crystalline modification in the As–S system, namely orpiment or As_4S_4 which is a molecular crys-
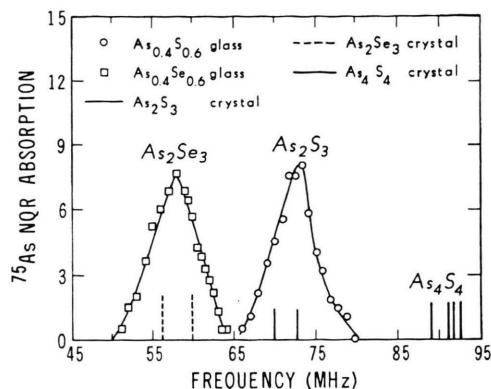

Fig. 1. ^{75}As NQR spectra in selected crystalline and glassy chalcogenides. The spectra for the crystals are indicated schematically because they are too narrow to be displayed accurately on the scale of this figure.

tal that contains As–As bonds, exhibits ^{75}As NQR frequencies well outside of those observed in the stoichiometric binary glass. We will demonstrate below that one can use this separation to probe the presence of As–As bonds in the arsenic chalcogenide glasses. One can also infer from the positions of these NQR lineshapes and other details of the NQR data that vestiges of the ring structures (intermediate range order) of the crystalline compounds are maintained in the glasses [2]. An example of this ring structure is shown for a particular crystalline modification in the As–O system (claudetite) in Figure 2. Note in Fig. 2 that the basic conclusions drawn for the sulfur and selenium systems also hold for the oxide system. In particular, the ^{75}As lineshape in glassy As_2O_3 is much broader than those that occur in the crystalline compounds, and this lineshape is centered about the layered crystalline modification (claudetite) as opposed to the molecular form (arsenolite). Similar conclusions can be drawn in the oxide system with regard to distortions in the pyramidal AsO_3 apex bond angles.

In mixed systems, such as glassy $As_2S_xSe_{3-x}$, the ^{75}As NQR lineshapes exhibit peaks that scale essentially linearly with x. Results such as this suggest that the mixed As–Se pyramidal structures occur essentially randomly [8] with no evidence for segregation of the chalcogen elements suggested in some models [9].

Arsenic-Arsenic Bonds

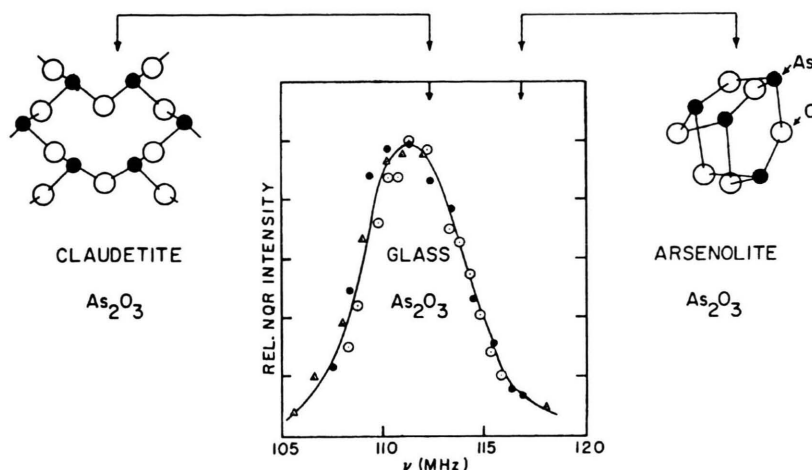In non-stoichiometric binary chalcogenide glasses and in metal-chalcogenide glassy systems, such as

Fig. 2. ^{75}As NQR spectrum in glassy As_2O_3. The NQR frequencies for two crystalline modifications of As_2O_3, claudetite and arsenolite, are indicated by arrows at the top of the figure. Also shown are the local ring structure of claudetite and the local molecular structure of arsenolite.

Cu–As–S and Cu–As–Se, ^{75}As NQR measurements have recently been employed to study the occurrence of As–As bonds in the non-stoichiometric compositions [4, 10]. An example of this use of ^{75}As NQR is shown in Fig. 3, which compares the spectrum for an As_2Se_3 fiber, whose ^{75}As NQR lineshape differs only subtly from that of the well-annealed bulk glass (see discussion below), with that of glassy AsSe, where essentially all As sites have at least one As–As bond. (If one assumes that the nearest-neighbor coordination numbers for As and Se do not change from the stoichiometric composition and that each As site has
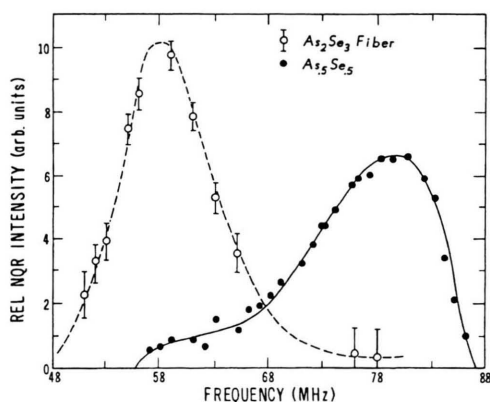
at most one As–As bond, then one can easily calculate that all As sites have one As–As bond for the composition AsSe.) The ^{75}As NQR spectrum for glassy AsSe is peaked at the position of the NQR resonances in crystalline As_4Se_4, in which each arsenic site has one As–As bond. We take this correspondence as evidence that the ^{75}As NQR is sensitive to the presence of As–As bonds in the chalcogenide glasses. In fact, one can use this identification to "count" As–As bonds in other non-stoichiometric chalcogenide compositions. We use as an example the metal chalcogenide glass system, Cu–As–Se, as shown in Figure 4. It can be shown that along the pseudo binary line Cu_2Se–As_2Se_3 there exist no As–As bonds, but along the line Cu–As_2Se_3 the fraction of As sites that contains one As–As bond increases with the copper concentration [4]. The presence of the peak near 78 MHz for 15 at.% Cu in Fig. 4 is a qualitative indication of this fact. In fact, more detailed measurements on both Se and S metal chalcogenide systems have shown that the ^{75}As NQR spectra can be employed to measure with reasonable quantitative accuracy the fraction of As sites that contain one As–As bond [4].

Fig. 3. ^{75}As NQR spectra of a glassy As_2Se_3 fiber (dashed line and open circles) and a bulk samples of glassy $As_{0.5}Se_{0.5}$. In glassy $As_{0.5}Se_{0.5}$, essentially all of the arsenic atoms are bonded to at least one other arsenic. See text for details.

Glasses Far From Equilibrium

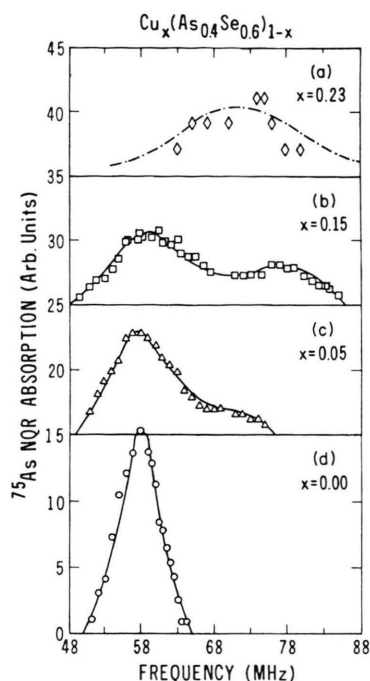The NQR spectra observed in fast evaporated films of amorphous As_2S_3 and As_2Se_3 and in rapidly drawn fibers of As_2Se_3 are very different from those observed

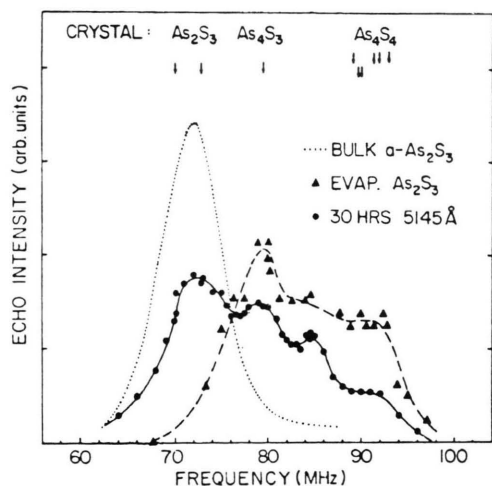Fig. 4. ^{75}As NQR spectra in copper-containing chalcogenide glasses of composition $Cu_x(As_{0.4}Se_{0.6})_{1-x}$.

Fig. 5. ^{75}As NQR spectra in bulk glassy As_2S_3 (dotted line) and in a rapidly-evaporated film of glassy As_2S_3 (dashed line and filled triangles). The structure of the film can be altered by optical excitation as shown for excitation with 5145 Å light from an Ar$^+$ laser (solid line and filled circles). The irradiation time was 30 hours. Indicated by arrows at the top of the figure are positions of the ^{75}As NQR resonance in selected crystals in the As–S system.

in the bulk, well annealed glasses [10, 11]. In these materials there is substantial NQR intensity in the region where several molecular crystalline phases exhibit NQR lines. As discussed above, one important molecular crystal structure is that which contains either As_4S_4 or As_4Se_4 "molecules" held together by van der Waals forces. Several ^{75}As NQR studies have shown that the fast evaporated films and the rapidly drawn fibers exhibit much greater molecular structure, as well as the presence of As–As and Se–Se or S–S bonds. An example of this situation is shown in Fig. 5, where the ^{75}As NQR spectrum is shown (triangles) for a rapidly-evaporated film of glassy As_2S_3. The NQR spectrum for the well-annealed bulk glass is shown by a dotted line in this figure. Note the NQR intensity in the region near 94 MHz in the spectrum for the fast-evaporated film. In this region are the ^{75}As NQR resonances for crystalline As_4S_4 and As_4S_3. [The As_4S_3 molecule also exhibits As–As bonds at three of the four As sites.]

Upon the application of light of band gap energies these fast evaporated films can be irreversibly photopolymerized into materials that more closely resemble the polymeric bulk glasses [11]. This situation is illustrated in Fig. 5 by the NQR spectrum shown with solid circles (solid line). For this spectrum the sample was irradiated for 30 hours using light of wavelength 5145 Å. At least qualitatively, the spectrum is approaching that of the bulk glass after optical excitation, although the spectrum of the well-annealed bulk glass is not duplicated until annealing is performed above the glass transition temperature. In the well annealed, bulk glasses there is no such irreversible, photostructural effect [5, 11, 12].

In the As_2Se_3 system the situation is not as dramatic, but local bonding distortions can be observed. Figure 6 shows the differences between the ^{75}As NQR spectra observed for the bulk glass (solid line and open squares) and a fast-evaporated film on a 300 K substrate (dashed line). Also shown for comparison is the fiber spectrum of Fig. 3 (dashed line and open circles). In the case of glassy As_2Se_3 the NQR spectrum of the rapidly-evaporated film shows no evidence for the presence of As–As bonds, but the asymmety to higher frequency has been interpreted as due to greater distortions in the $AsSe_3$ pyramidal units in the film.

A second method for producing glassy As_2Se_3 under highly non-equilibrium conditions is to draw fibers of the material at rapid rates [10]. Figure 7 displays the same spectrum as Figs. 3 and 6 (dashed

line) of a fiber, which was drawn at 40 m/min and was annealed at 300 K for one year. As seen from Fig. 6, this spectrum is very close to that of the well-annealed bulk glass. If the draw rate is increased to 75 m/min and the fiber is placed immediately in liquid nitrogen to stall the annealing process, then the ^{75}As NQR spectrum in Fig. 7 shown by the solid line (and open squares) is observed. Annealing at 200 °C for several hours produces the spectrum indicated by the dashed line (and solid circles) in Figure 7. In analogy with the case for the rapidly-evaporated films, the spectrum approaches that of the well-annealed bulk glass, but the glass spectrum is not duplicated unless the annealing is performed above the glass transition temperature. In the case of the rapidly-drawn fibers these results are corroborated by differential scanning calorimetry [12].

Influence of Defects

In glassy As_2Se_3 and As_2S_3 one may introduce significant densities (10^{17} spins/cm^3) of paramagnetic defects ("dangling" Se and As bonds) by optical excitation with light of energy greater than or equal to the optical band gap energies. It is not surprising that the presence of these defects does not alter the ^{75}As NQR spectra of the well-annealed chalcogenide glasses [5]. This fact is illustrated for glassy As_2Se_3 in Figure 8. In this figure the solid triangles represent data taken on

the well-annealed glass, and the open circles represent data taken after optical excitation. The excitation was performed, and the NQR spectra were recorded, at 77 K. Although the NQR lineshape is unchanged, there are better signal-to-noise ratios for the data taken after optical excitation because the spin-lattice
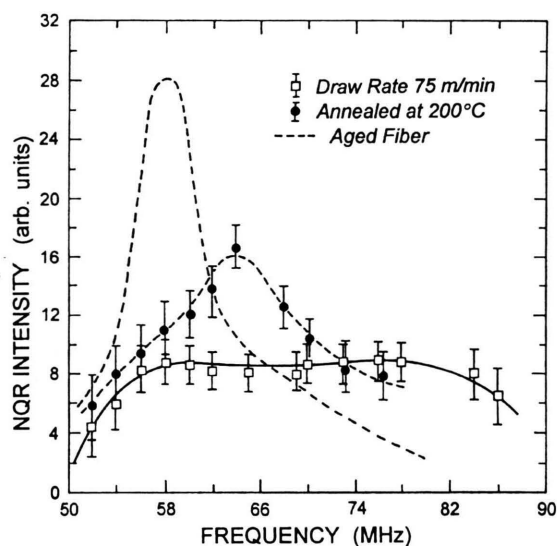

Fig. 7. ^{75}As NQR spectra in an As_2Se_3 fiber pulled at 40 m/min and annealed at 300 K for about one year (dashed line), in a rapidly drawn fiber pulled at 75 m/min and immediately stored at 77 K (solid line and open squares), and in the same fiber annealed at 200 °C (dashed line and solid circles).
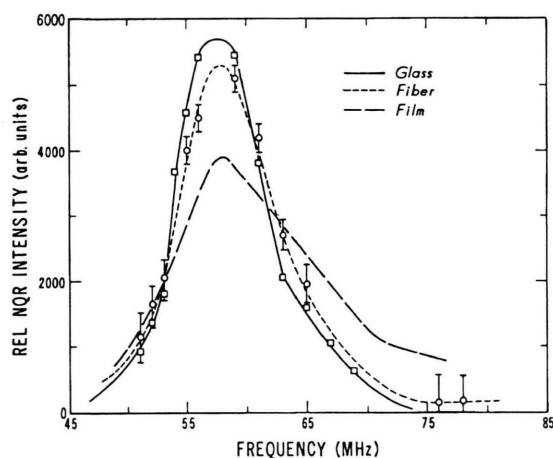

Fig. 6. ^{75}As NQR spectra in bulk glassy As_2Se_3 (solid line and open squares), in a rapidly evaporated film (dashed line), and in a fiber pulled at 40 m/min and annealed at 300 K for about one year (short dashed line and open circles).
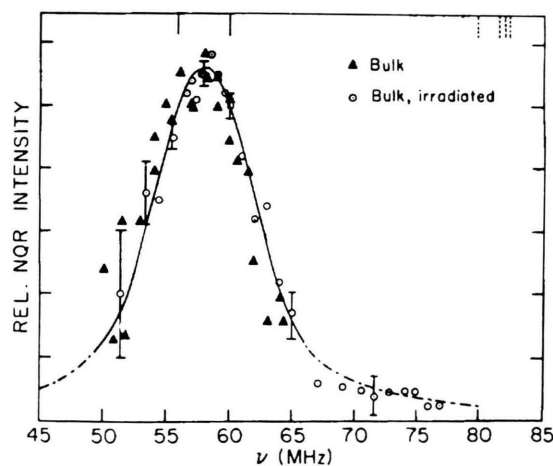

Fig. 8. ^{75}As NQR spectra in bulk glassy As_2Se_3 (solid triangles) and in bulk glassy As_2Se_3 after optical excitation at 77 K (open circles). See text for details.
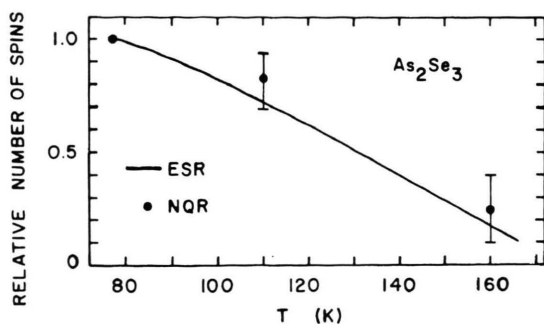
Fig. 9. Temperature dependence of the relative number of paramagnetic states in glassy As_2Se_3 after optical excitation at 77 K. The solid line shows the data measured using electron spin resonance, and the three data points are extracted from the spin-lattice relaxation times observed in ^{75}As NQR. See text for details.

Fig. 10. (a) ^{75}As NQR in orthorhombic As (dashed line) and amorphous arsenic (solid line and filled circles). (b) calculated NQR spectrum using a simple tight-binding model and a model for amorphous As with the dihedral angle distribution, $P(\delta)$, shown in the inset. See text for details.

relaxation rate has increased dramatically. This increase is due to the presence of the paramagnetic centers produced by the irradiation. The proof of this assertion is shown in Fig. 9, where the relative number of electron spin resonance (ESR) centers is plotted as a function of annealing temperature after optical excitation at 77 K. The solid line represents data obtained by direct measurement of these centers using ESR, and the solid points represent data obtained from measurements of the T_1 values in the NQR experiments. It is evident from this figure that the decrease in T_1 in the ^{75}As NQR measurements is due to the increase in the paramagnetic Se and As dangling bonds.

Amorphous Arsenic

In addition to the chalcogenide glasses, an ^{75}As NQR lineshape has also been observed for amorphous arsenic (a-As). Unlike the largely symmetric lineshapes observed in the chalcogenide glasses, the lineshape in a-As is highly asymmetric and is not centered about either of the two crystalline modifications. At 4 K the lineshape observed in semiconducting, orthorhombic arsenic is centered near 46 MHz (dashed line in Fig. 10a), and the lineshape of the semi-metallic, rhombohedral arsenic is centered near 23.5 MHz. (The difference between the structures of these two crystalline forms of As is subtle. They are both layered compounds, but the orthorhombic form has six-membered rings where the As appears in a
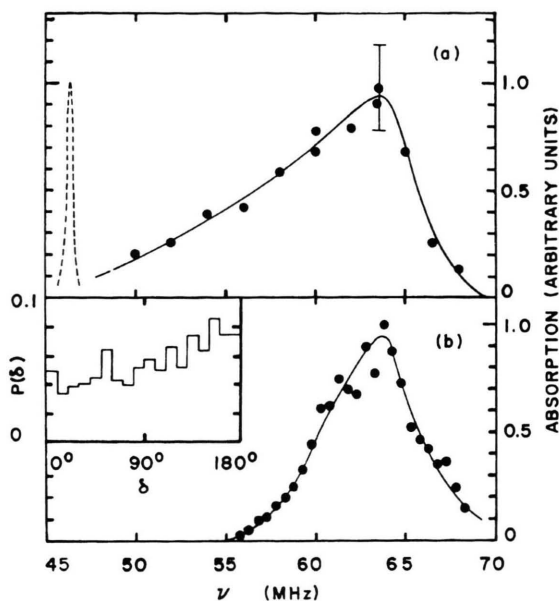
staggered configuration while the rhombohedral modification has six-membered rings in the chair configuration.) On the other hand, the NQR lineshape in a-As is highly asymmetric and peaked near 65 MHz (solid line and filled circles in Figure 10a). Calculations based on a very simple tight-binding model suggest that the bonding in these three forms of As is essentially p-type and that the s admixtures of the bonding wave functions are approximately 3, 7, and 10% in rhombohedral, orthorhombic, and amorphous arsenic, respectively [14, 15]. The asymmetry in the ^{75}As NQR spectrum for a-As has been shown to be due to the distribution in dihedral bonding angles (angular rotation between adjacent pyramids connected by a given As–As bond) in the amorphous phase. A simple calculation based on a molecular model of a-As is shown in Figure 10b. The inset to Fig. 10b shows the dihedral angle distribution for this model. Although, in this simple model calculation, the calculated spectrum does not match the observed spectrum in any quantitative way, the qualitative trend is obtained.
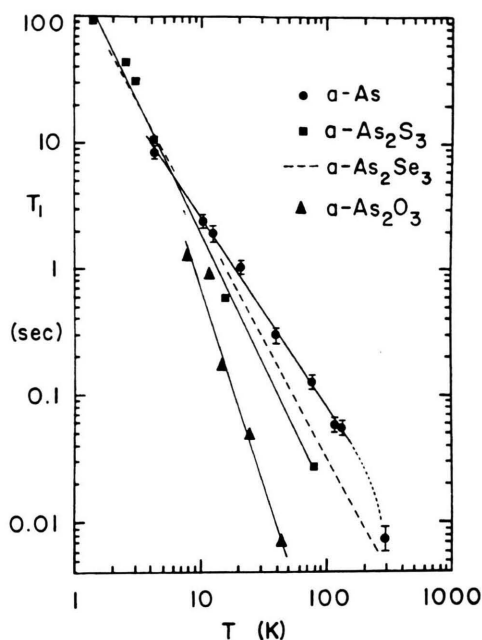
Fig. 11. Temperature dependences of the spin-lattice relaxation times for ^{75}As NQR in several amorphous semiconductors.
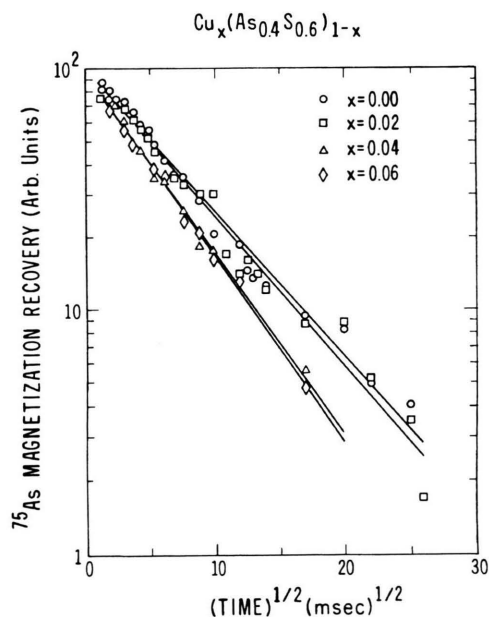

Fig. 12. Recovery of the magnetization following a 90°–180°-echo pulse sequence in a series of $Cu_x(As_{0.4}Se_{0.6})_{1-x}$ glasses. Note that the data are plotted as functions of the square root of the time. See text for details.

Spin-Lattice Relaxation and "Disorder Modes"

Spin-lattice relaxation is the process by which the ensemble of nuclear spins transfers energy to the lattice after rf excitation. For nuclei with spin greater than $\frac{1}{2}$, such as ^{75}As, this relaxation often results from a modulation of the electric field gradient by a Raman process involving either phonons or some other lattice modes. In crystalline solids the low-temperature behavior exhibits a very rapid temperature dependence (exponential or power law with the power law exponent -7 or -9). In amorphous solids the spin lattice relaxation times T_1 usually obey a power law whose exponent is approximately -2. Typical curves for ^{75}As NQR are shown in Fig. 11 for two chalcogenide glasses, one pnictide amorphous semiconductor (a-As) and one oxide glass. The interpretation of this behavior is that the relaxation involves a Raman process where highly anharmonic two-level systems, often called "disorder modes," substitute for at least one of the phonons. Measurements of T_1 in a wide range of semiconducting and insulating glasses using a wide range of nuclei show that this relaxation mechanism is important in essentially all glasses [16].

One final feature of the spin-lattice relaxation in glassy solids should be mentioned. Usually this relaxation does not exhibit a well-defined rate (exponential decay of the magnetization), but rather a distribution of rates is observed. This distribution is often well-approximated by an exponential in the square root of the time as shown for a series of $Cu_x(As_{0.4}Se_{0.6})_{1-x}$ glasses in Figure 12. This particular behavior is probably due to slow spin diffusion in the magnetically excited ^{75}As system coupled with the existence of an inhomogeneous distribution of relaxation centers [4].

Summary

The prototype chalcogenide glasses, As_2Se_3, As_2S_3, and As_2O_3, provide examples to illustrate the use of ^{75}As NQR as a probe of the local structural order and of some of the vibrational properties. In these stoichiometric glasses the arsenic atoms are three-fold coordinated to the two-fold coordinated chalcogen atoms, and the NQR spectra are centered about the NQR lines observed in corresponding layered crystalline modifications. Although the ^{75}As NQR lines are broad in the glasses, crude estimates of the distortions

in the arsenic pyramidal units that are necessary to produce these broadenings yield half widths of only a few degrees. Further interpretations of the NQR spectra suggest that the ring structures present in the crystals are at least partially preserved in the glasses.

In chalcogenide glasses for which As–As bonds occur, such as glasses made with excess arsenic, rapidly evaporated films, or rapidly drawn fibers, the ^{75}As NQR spectra can be used to estimate the numbers of such bonds. In glasses made under conditions that produce structures far from equilibrium, the NQR spectra are also useful in probing the changes in these structures produced by annealing or by optical excitation. A standard photo-polymerization process that occurs in rapidly deposited As_2Se_3 and As_2S_3 glassy films is the optically induced break-up of As–As (and also presumably of Se–Se or S–S) bonds that are replaced by As–Se or As–S bonds.

Amorphous arsenic exhibits an asymmetric ^{75}As lineshape that occurs at higher frequencies than either of the related, layered crystalline modifications. This lineshape can be explained by the local bonding distortions introduced by the orientational disorder between adjacent As_3 pyramidal units that make up the amorphous phase. Even though these distortions are significant, the bonding remains predominantly p-type in amorphous arsenic.

In amorphous semiconductors that contain arsenic, the ^{75}As spin lattice relaxation is almost always due to a Raman process where at least one highly anharmonic two-level system (disorder mode) replaces one of the phonons. In general the decays of magnetization are not exponential in time but rather exponential in the square-root of the time. This unusual behavior is attributed to the existence of an inhomogeneous distribution of relaxation centers possessing different relaxation rates. In cases where the ^{75}As nuclear spin diffusion is not rapid enough, such a distribution can produce the observed square-root-of-time behavior.

Acknowledgements

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