Nuclear Quadrupole Resonance in the Chalcogenide and Pnictide Amorphous Semiconductors

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**Abstract:**
NQR, Chalcogenide glasses, Pnictides, Amorphous semiconductors

(See next page.)
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The NQR technique provides information on a scale of the interatomic spacings and is thus a sensitive probe of the local environments of the major constituent atoms in an amorphous semiconductor. In the specific case of $^{75}$As, analyses of the NQR lineshapes and of nuclear spin-spin phenomena yield detailed structural information concerning not only the local bonding at an arsenic site but also the presence of intermediate range order in some chalcogenide glasses. The lineshapes also provide a very sensitive probe of photo-induced polymerization in films of amorphous chalcogenides.

Studies of $^{75}$As spin-lattice relaxation processes in amorphous semiconductors provide a probe of certain dynamical properties. In particular, low temperature measurements of spin-lattice relaxation rates can be explained by the presence of highly anharmonic "tunneling" or "disorder" modes which are present in most amorphous semiconductors.
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INTRODUCTION

The absence of long range periodic order in amorphous semiconductors makes the interpretation of the usual scattering experiments, such as x-ray, neutron or electron scattering, both difficult and model dependent. For this reason information concerning the static and dynamic properties of these solids must be gathered using many different experimental techniques. In the chalcogenide (group VI) and pnictide (group V) amorphous semiconductors nuclear quadrupole resonance (NQR) spectroscopy has proved to be one of the important techniques.

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Local bonding information obtained from studies of $^{75}$As NQR in chalcogenide and pnictide amorphous semiconductors is discussed in the following section. A second section describes the use of dipolar effects between $^{75}$As nuclei to draw conclusions concerning order beyond the nearest neighbors. The use of spin-lattice relaxation measurements to probe disorder modes is presented in a third section. A final section summarizes the major conclusions.
NQR LINESHAPES AND LOCAL BONDING

The Hamiltonian which is appropriate for nuclear quadrupole resonance is given by

\[ H_Q = I \cdot Q' \cdot I. \]  

(1)

where \( I \) is the nuclear spin operator. The quadrupolar tensor \( Q' \) can be expressed in terms of two independent parameters which relate to the gradient of the electric field at the nuclear site (\( q \) and \( n \)) and to a third parameter (\( Q \)) which is the quadrupole moment of the nucleus. Since \( Q \) is an atomic parameter, it does not depend on the local configuration of the atoms in the solid. For this reason, the local structural information is contained in the parameters \( q \) and \( n \). These parameters are given by

\[ eq = V_{ez} \]  

(2)

and

\[ n = \frac{(V_{xx} - V_{yy})}{V_{zz}} \]  

(3)

where \( e \) is the electronic charge. The quantities \( V_{ij} \) (\( V_{xx} < V_{yy} < V_{zz} \)) are the three principal components of the electric field gradient tensor at the nuclear site and are determined predominantly by the wave functions of the bonding electrons.

For the case of \( ^{75} \)As where \( I = 3/2 \) there are two doubly degenerate energy levels whose separation yields a resonant frequency of

\[ \nu = \frac{1}{2} \frac{e^2 Q a}{\hbar} \left( 1 + \frac{3}{2} \right)^{1/2}. \]  

(4)

Because there is only one resonant transition between these two doubly degenerate energy levels, one cannot uniquely determine the two independent parameters \( q \) and \( n \). If a magnetic field \( H \) is applied to the sample then the degeneracy is lifted by the nuclear Zeeman interaction which is of the form

\[ H_z = - \gamma H \cdot H. \]  

(5)

where \( \gamma \) is the nuclear gyromagnetic ratio. In this case one can in principle determine \( q \) and \( n \) independently.

NQR has been investigated in several of the chalcogenide glasses which contain arsenic.\(^1\)\(^-\)\(^3\) In all cases the NQR lineshape is very broad in comparison to the lines observed in the crystalline forms. The linewidths (full width at half height) in glasses \( \text{As}_2\text{S}_3 \) and \( \text{As}_2\text{Se}_3 \) are listed in Table 1, and the lineshapes are shown in Fig. 1. Even though these lineshapes are very broad, the quadrupolar interaction of Eq. (1) is so sensitive to small changes in local bonding configurations that the As sites are still very well defined in these glasses.
Table 1. Parameters for $^{75}$As NQR in several amorphous semiconductors

<table>
<thead>
<tr>
<th>Amorphous Semiconductor</th>
<th>Peak Frequency (MHz)</th>
<th>Linewidth (MHz)</th>
<th>a</th>
<th>b</th>
<th>$T_2$ (µsec)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>As$_2$Se$_3$</td>
<td>58</td>
<td>10</td>
<td>1.8</td>
<td>600</td>
<td></td>
<td>1, 7</td>
</tr>
<tr>
<td>As$_2$S$_3$</td>
<td>71</td>
<td>5</td>
<td>2.0</td>
<td>600</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>As$_2$O$_3$</td>
<td>111</td>
<td>6</td>
<td>3.1</td>
<td>500$^\circ$</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>64</td>
<td>10$^d$</td>
<td>1.5</td>
<td>200</td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>As$_2$Se$_2$.5Se$_0.5$</td>
<td>68</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>As$_2$S$_2$.Se$_2$</td>
<td>63</td>
<td>8</td>
<td></td>
<td></td>
<td></td>
<td>3</td>
</tr>
</tbody>
</table>

$^a$full width of half maximum

$^b_{T_1} = T^{-B}$

$^c$4.2K

$^d$asymmetric line

Fig. 1. Relative $^{75}$As NQR absorption at 4.2K in glassy As$_2$Se$_3$ and As$_2$S$_3$ as a function of frequency. The resonant frequencies of crystalline As$_2$Se$_3$ and As$_2$S$_3$ at 4.2K are shown as vertical lines. Data are those from ref. 1.
In As$_2$S$_3$, As$_2$Se$_3$ and As$_2$O$_3$ the arsenic atoms are bonded to three chalcogens and the NQR spectrum of the glass is essentially centered about the NQR line (or lines) observed in the layered crystalline modifications. The situation for As$_2$O$_3$ is shown in Fig. 2. Crude estimates of the distortions in the pyramidal apex bond angles for the As sites in these glasses yield half widths of at most a few degrees. In addition the fact that the lineshapes are centered about lines occurring only in the layered crystalline compounds suggests that the ring structure characteristic of these crystalline modifications is preserved in the glasses. In the case of As$_2$O$_3$ shown in Fig. 2, there is both a layered and a molecular crystalline form, and the NQR spectrum for the glass is centered about that for the layered crystalline form (claudetite 1).

Fig. 2. Relative $^{75}$As NQR absorption at 77K in glassy As$_2$O$_3$. Different symbols represent data on samples stored at 77K for various lengths of time. The solid and dotted vertical lines represent the resonant frequencies of the claudetite and arsenolite crystalline modifications of As$_2$O$_3$, respectively. Data are those from ref. 2.
The mixed system $As_{x}Se_{3-x}$ exhibits $^{75}As$ NQR lineshapes whose peaks scale linearly with $x$. Although the lineshapes are sometimes asymmetric, the widths are similar to those in pure $As_{2}S_{3}$ and $As_{2}Se_{3}$ (see Table 1). These results are interpreted as suggesting that mixed S-Se pyramidal structures occur in these glasses roughly in proportion to the S and Se content. In particular, there is no evidence for segregation of S and Se in separate rings as suggested in some models.

Since these NQR experiments do not determine $q$ and $n$ independently, experiments have also been performed on glassy $As_{2}S_{3}$ and $As_{2}Se_{3}$ in the presence of a magnetic field. The experiments in a magnetic field suggest that there are at least two inequivalent sites for the As atoms in glassy $As_{2}S_{3}$ and $As_{2}Se_{3}$. Values of $n$ vary from 0 to 0.4, but the exact distribution of values of $n$ is still controversial. There appear, however, to be real differences between the glassy and crystalline sites as far as the asymmetry parameter is concerned.

In addition to the chalcogenide glasses just discussed, an $^{75}As$ NQR lineshape has also been observed in amorphous arsenic (a-As). This lineshape is essentially independent of the temperature as is also the case for the chalcogenide glasses. Unlike the largely symmetric lineshapes observed in the chalcogenide glasses, the lineshape in a-As is highly asymmetric as shown in Fig. 3.

The second main difference between the NQR spectra in a-As and the chalcogenide glasses is the fact that there is no crystalline spectrum which is close in frequency to the a-As line. The lineshape observed in semiconducting, orthorhombic As is shown schematically in Fig. 3. The common form of semimetallic rhombohedral As exhibits an $^{75}As$ NQR line which occurs well below the frequency range shown in Fig. 3 (~ 23.5 MHz at 4.2K).
Although the three forms of arsenic occur at very different frequencies, the bonding is still very similar. This situation results from the fact that very small admixtures of s-character to the electronic bonding wave functions have a dramatic effect on the resonant frequency. For precisely zero s-character the resonant frequency is zero by symmetry. Calculations based on a very simple tight-binding model suggest that the bonding involves essentially p wave functions in all three forms of arsenic and that the s admixture is approximately 3%, 7% and 10% in rhombohedral, orthorhombic and amorphous As, respectively.

The broad asymmetric NQR lineshape in a-As can also be understood, at least qualitatively, with the help of simple model calculations. If the individual As pyramidal units are well defined but there is a distribution of dihedral angles (angle of rotation along a common As-As bond), then the asymmetric low-frequency tail on the NQR lineshape can be reproduced, although the linewidth is underestimated by about a factor of two. The distribution of dihedral angles used to test this approach was that determined from a hand-built or a computer-generated model. The degree of asymmetry of the calculated NQR lineshape depends on the degree of asymmetry in the dihedral angle distribution. This explanation also explains why there is no parallel effect in the chalcogenide glasses.

The NQR spectra of fast evaporated films of amorphous As$_2$S$_3$ and As$_2$Se$_3$ are very different from those observed in the bulk glasses. An example of these differences is shown in Fig. 4 for As$_2$S$_3$. It is apparent from Fig. 4 that there is substantial NQR intensity in the region where the molecular As$_4$S$_4$ and As$_4$S$_3$ crystalline forms occur. Thus the fast evaporated amorphous film has a much greater molecular character than the bulk glass. Upon the application of light at band gap energies the As$_4$S$_4$ molecules are irreversibly photopolymerized into sites resembling those in the layered crystalline form of As$_2$S$_3$. Under the application of light the structure of the film approaches that of the bulk glass. In well-annealed bulk glasses there is no photostructural effect observed by NQR.

SPIN-SPIN RELAXATION AND DIPOLAR EFFECTS

In a solid the spin-spin relaxation time $T_2$ is determined by the dipolar interaction between nuclear spins of the form

$$H_D = \frac{1}{2} \sum_{j \neq k} \left[ \frac{\mu_j^* \mu_k}{r_{jk}^3} - \frac{3(\mu_j^* \cdot r_{jk})(\mu_k^* \cdot r_{jk})}{r_{jk}^5} \right]$$

where the prime denotes $j \neq k$, $r_{jk}$ is the radius vector from $\mu_j$ to $\mu_k$, and the magnetic moments $\mu_j$, $\mu_k$ are given by $\mu_j = g_j \hbar \sigma_j$.

The dipolar Hamiltonian $H_D$ is usually too complicated to evaluate exactly, and approximate methods are often employed. In particular, one often calculates the second moment of the broadening due to the dipolar terms. In spin-echo experiments, such as those described in this paper, the important terms in the dipolar interaction only involve those between mutually resonant spins. The magnitude of $T_2$ is, within certain approximations, inversely proportional to the square root of the second moment.
In the As-containing chalcogenide glasses the spin-spin relaxation times $T_2$ are on the order of ~500 µsec (see Table I) independent of the temperature. Similar results are obtained for crystalline As$_2$S$_3$ (orpiment) where second-moment calculations based on the known crystal structure yield agreement within experimental uncertainty. One may thus conclude that the temperature-independent $T_2$ values for glassy As$_2$S$_3$ and As$_2$Se$_3$ in Table I are dipolar in origin. Because these dipolar interactions involve only mutually-resonant spins, the nearly identical values of $T_2$ between the crystalline and glassy phases have been cited as evidence for the existence of intermediate range order in the glasses.

The value of $T_2$ in a-As is less than those observed in the chalcogenide glasses because the mutually resonant As nuclei are closer together.
in this amorphous solid. Calculations based on orthorhombic arsenic, where
T₂ is similar, are in agreement with experiment. Once again one may con-
clude that the origin of the spin-spin relaxation rates in a-As is the
dipolar interaction.

The situation is different in glassy As₂O₃ where T₂ depends on the
temperature at temperatures above ~ 10K. (At temperatures below ~ 10K T₂
is essentially independent of temperature and results from dipolar inter-
actions as in arsenic sulfide and selenide.) Above 10K the temperature
dependence of T₂ parallels that of T₁ to be discussed in the next section.
This parallel suggests that there exists "spectral diffusion" of the ex-
cited magnetization.₁³

SPIN-LATTICE RELAXATION AND DISORDER MODES

In NQR spin-lattice relaxation is the process by which the ensemble
of nuclear spins transfers energy to the lattice after rf excitation. The
process is often exponential and hence can be characterized by a rate T⁻¹
where T₁ is called the spin-lattice relaxation time. For nuclei with
I > 1/2, such as 75As, T₁ usually results from a modulation of the electric
field gradient by a Raman process involving either phonons or some other
lattice modes.

The low temperature behavior of T₁ in crystalline solids often results
from first-order Raman phonon processes which yield a rapid temperature de-
pendence (T₁ ~ T⁻⁴ or T⁻⁶). In amorphous solids the temperature dependences
are much weaker as shown in Fig. 5, and the rates at any given temperature
are much faster than in the corresponding crystalline solids. With the
exception of glassy As₂O₃ which we discuss below, all the amorphous semi-
conductors containing As exhibit a power law behavior for T₁ of the form
T₁ ~ T⁻β where β < 2. The values of β are shown in Table 1 for As₂S₃,
As₂Se₃, As₂O₃, and As. These results are more general than just NQR
measurements of 75As and they are thought to be a rather universal proper-
ty of spin-lattice relaxation in amorphous solids.₁⁴

The model interpretations ¹,15,16,17 of these T₁ data all involve a
coupling to anharmonic "tunneling" or "disorder" modes in the amorphous
solids. The elementary excitations in the amorphous solids are assumed to
consist of ordinary phonons and a series of essentially two-level, highly
anharmonic systems called tunneling or disorder modes.₁₈,₁₉ The ensemble
of disorder modes exhibits a continuous distribution of energy splittings
with the two levels separated by a potential barrier. The physical origin
of these modes in amorphous solids is thought to be the tunneling (or at
higher temperatures hopping) of atoms or groups of atoms between two meta-
stable equilibrium positions which are nearly equal in energy.

The process by which the nuclear spins are relaxed is not entirely
clear¹⁴-¹⁷ and the exact mechanism remains a matter of some debate.
Szeftel and Alloul¹⁶ suggest a Raman process involving a phonon and a
tunneling mode while Reinecke and Ngai¹⁷ prefer a Raman process involving
two tunneling modes. To lowest order in perturbation theory the Reinecke
and Ngai process can be written as

\[ T_{1}^{-1} = \frac{\hbar m}{2\pi^{2} \sigma} \int \frac{E_{m} f_{m}^{2}(E) dE}{1 + \cosh(E/kT)} \]  

(7)
where $H$ is the matrix element coupling the disorder modes to the nucleus, $r(E)$ is the density of disorder modes which is assumed to be nearly constant in $V$, and $E_\text{max}$ is a maximum energy difference between two disorder modes. Equation (7) yields a temperature dependence of $T_1^{-1} = T$ for $r(E)$ constant and $T_1^{-1} = T^{1/2}$ for $r(E) = E^{1/2}$. In this model departures of $\beta$ from unity in Table I are explained by the energy dependences of the densities of tunneling modes which vary from material to material.

Glassy $\text{As}_2\text{O}_3$ is an exception to this general picture in two ways. First, the temperature dependence of $T_1$ is more rapid ($\beta = 3$ while $\beta < 2$ in all other amorphous solids studied to date\textsuperscript{14}). Second, above approximately 10 K $T_2$ varies rapidly with temperature in a manner which parallels $T_1$ ($T_2 \propto T^{1/3}$ with $\beta = 3$). As mentioned in the previous section, the parallel behavior of $T_1$ and $T_2$ suggests the possibility of spectral diffusion in the nuclear spin system on the time scale of the experiment, and the greater value of $\beta$ for glassy $\text{As}_2\text{O}_3$ may result from this diffusion process.

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**Fig. 5.** Temperature dependence of $T_1$ for $^{75}\text{As}$ NQR in glassy $\text{As}_2\text{S}_3$ (squares), $\text{As}_2\text{Se}_3$ (dashed line), $\text{As}_2\text{O}_3$ (triangles) and $\alpha$-$\text{As}$ (circles). Data are from references 1, 7 and 13.
Fig. 6. Relative number of paramagnetic spins measured at 4.2K as a function of annealing temperature. Circles represent data extracted from the $^{75}\text{As}$ spin-lattice relaxation data at 4.2K after annealing at temperature of 77, 110 and 160K. The solid line represents the data obtained from previous (see ref. 21) ESR intensity measurements. The ESR and NQR results have been normalized at 77K for comparison. Data are those of ref. 2.

When light of energy near the band gap is incident on glassy As$_2$Se$_3$ (or As$_2$S$_3$) at low temperatures, an additional mechanism contributes to the spin-lattice relaxation.\textsuperscript{2} Irradiation at 77K with 6764 Å light produces an optically induced paramagnetism which was first observed by electron spin resonance (ESR) techniques.\textsuperscript{20} The ESR sites provide an enhanced nuclear spin lattice relaxation at low temperatures. From the magnitude of $T_1$ at 4.2K following irradiation with 6764 Å light at 77K, one can estimate using a standard NMR procedure\textsuperscript{2} the number of paramagnetic impurities which contribute to the relaxation rate. This number ($< 10^{17}$ cm$^{-3}$) is consistent with that deduced from earlier ESR measurements.\textsuperscript{20} In addition, Fig. 6 shows that the annealing of the paramagnetism is identical with the annealing of the increased spin-lattice relaxation rates measured at 4.2K. Thus one can in favorable circumstances probe, at least indirectly, paramagnetic states via measurements of $T_1$ in amorphous semiconductors.

**SUMMARY**

Symmetric $^{75}\text{As}$ NQR lineshapes are observed in the chalcogenide glasses As$_2$S$_3$, As$_2$Se$_3$ and As$_2$O$_3$. These NQR lines are centered about lines which occur in the layered, crystalline modifications. Analyses of the NQR lines indicate that the local bonding at an As site is somewhat distorted, but the ring structure of the crystals tends to be preserved in these
glasses. In a-As the NQR lineshape is asymmetric, and this asymmetry can be associated with a distribution of As-As dihedral bond angles. This distribution is consistent with the ones found in models of the a-As structure. NQR lineshapes can also be used effectively to monitor photo-induced structural changes from a molecular to a polymeric structure in fast evaporated films of As$_2$S$_3$ and As$_2$Se$_3$.

The spin-spin relaxation rates from $^{75}$As are similar in crystalline and amorphous chalcogenides and pnictides. Several present calculations indicate that these rates originate from dipolar effects, and the similarities between the crystalline and amorphous forms are an additional indication of the presentation of some intermediate range order in the amorphous semiconductor.

Spin-lattice relaxation rates for $^{75}$As are always more rapid in the amorphous semiconductors than in their crystalline counterparts. The temperature dependences of these rates are best described as power laws with exponents $\beta \approx 2$. The increased spin-lattice relaxation rates in the amorphous materials are attributed to the presence of anharmonic tunneling modes, and the values of $\beta$ are thought to provide estimates of the energy dependences of the densities of these low frequency tunneling modes.

ACKNOWLEDGEMENTS

Portions of the research described in this paper were supported by the National Science Foundation under grant number DMR-83-04471 and by the Office of Naval Research.

REFERENCES


