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Nuclear-quadrupole-resonance studies of As_2Se_3 fibers

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Pulsed nuclear-quadrupole-resonance (NQR) experiments have been performed at 77 K on rapidly drawn fibers of As_2Se_3. The NQR line shape at 77 K was compared to the line shape of bulk glassy As_2Se_3 and to thin-film As_2Se_3. The fiber was found to have a line shape that is intermediate between the glassy and thin-film line shapes. The line shape of the fiber was also compared to the line shapes of glassy $As_{0.5}Se_{0.5}$ at 77 K. The absence of a peak near 78 MHz in the fiber spectrum indicates that there are no As-As bonds in this sample.

I. INTRODUCTION

Studies of ^{75}As nuclear-quadrupole-resonance (NQR) line shapes[1–5] provide information regarding the local bonding at an arsenic site. It is well known that NQR line shapes are very sensitive to small changes in local structural order. Previous studies[2,3] of ^{75}As NQR line shapes in bulk glassy As_2Se_3 reveal that even small deviations in local structural order can generate a substantial NQR linewidth. In this paper we compare the NQR line shape of a rapidly drawn As_2Se_3 fiber to previously studied line shapes of well aged, bulk glass, rapidly evaporated thin films and nonstoichiometric glassy arsenic selenides that contain arsenic-arsenic bonds. The deviation of the fiber line shape from that observed in the well-annealed bulk glass is used to deduce structural information about the bonding of arsenic atoms in these fibers.

The variation in physical (thermal, mechanical, and optical) properties of As_2Se_3 fibers as compared to bulk glass samples has been studied extensively[6–8] and has been shown to be related to a modification in the structure due to the fiber processing conditions. Variations in drawing and aging conditions affect local structural order and hence, should lead to a similar variation in observed ^{75}As NQR line shapes. The full widths at half maxima of the ^{75}As NQR line shapes in As_2Se_3 bulk glass, thin film, and fibers are compared to draw conclusions regarding the $AsSe_3$ pyramidal units in the fiber.

Section II describes the details of sample preparation and the pulsed NQR experimental setup. Results are presented in Sec. III and discussed in Sec. IV.

II. EXPERIMENTAL PROCEDURE

As_2Se_3 fibers were prepared from 99.999% pure As and Se by weighing the elements in an inert atmosphere glove box, placing them in a 1.3-cm-i.d. fused silica ampoule and sealing the ampoule under vacuum ($\sim 10^{-3}$ Torr). Approximately 10 g of material were prepared for each sample. Samples were melted in a rocking furnace at a maximum temperature of 900 °C for a minimum of 5 h. The sample was then cooled to 400 °C, removed from the furnace, and allowed to air cool to room temperature. The ingot of glass was removed from the fused silica ampoule, and a portion (~ 5 g) was placed in a fused silica fiber drawing bushing with a 3-mm-diameter orifice. Fibers were drawn from the melt by heating the bushing to a temperature such that the orifice temperature was approximately 250 °C. (The glass temperature was slightly higher.) Fibers were drawn at a rate of 5 m/min in air. Samples examined in this study were well aged, having hung at room temperature in air for approximately 18 months prior to examination.

NQR measurements were made using a Matec Model 5100 (which employed a Matec Model 525 gated amplifier for frequencies between 20 and 200 MHz) and a Matec Model 625 broadband receiver with the appropriate auxiliary equipment arranged in a single-coil phase detection system. The output of the detection system was linear and flat over the frequency range covered in these experiments. The signal was enhanced using a LeCroy 9400 signal averaging digital oscilloscope. The ^{75}As NQR spectrum was recorded at 77 K using phase sensitive detection of the spin echo following a 90-τ-180 pulse sequence. Since the ^{75}As NQR linewidth in the fiber was greater than 7 MHz, the line shapes were measured by recording the echo amplitude as a function of frequency. Typical 90° pulse widths of ~ 2.5 μs were employed. Care was taken to ensure that the lineshapes were not distorted by variations in the spin-spin relaxation times (T_2). For each frequency, the receiver phase was optimized to obtain a maximum echo height.

Approximately 3-cm lengths of fiber were tightly packed into a 120-mm-diameter quartz tube to maximize sample volume. Freshly prepared fibers (at draw rate 40.7 m/min) were kept in liquid nitrogen before measurements were made. Tubes were then fitted tightly into the NQR coil. The whole system was immersed in a dewar of liquid nitrogen. The signal was typically averaged over 5000 pulse sequences.

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III. RESULTS

The ^{75}As NQR line shape of the As_2Se_3 fiber is compared to the bulk glass and to a rapidly evaporated film deposited on a room-temperature substrate in Fig. 1. In Fig. 2 the same fiber spectrum is compared to two samples in the Cu-As-Se ternary glass system.

The spectrum for bulk As_2Se_3 is essentially fit by a single Gaussian line shape whereas all of the other samples have asymmetric line shapes. In one case $[Cu_{0.15}(As_{0.4}Se_{0.6})_{0.85}]$, there are two peaks in the ^{75}As NQR spectrum. In Fig. 3, the NQR line shape of the fiber is compared to the line shape of glassy $As_{0.5}Se_{0.5}$. All the line shapes are normalized to the same area so that the intensity comparison is absolute for samples of the same at. % As.

In Fig. 1, we see a subtle deviation of the fiber line shape from the bulk line shape. The fiber line shape in Fig. 1 is slightly asymmetric and shows a full width at half maximum (FWHM = 8.8 MHz), which is intermediate between those of the film (13.8 MHz) and bulk (8.4 MHz). In Fig. 2, we compare the line shapes of the two copper arsenic selenide samples to the fiber. The 15-at. % copper in As_2Se_3 sample has a peak near 76 MHz, which is due to the presence of As-As bonds in this sample[9] and which will be discussed in greater detail below. The fiber line shape shows no such peak near 76 MHz. The other (solid circles) copper arsenic selenium glass shown in Fig. 2 is known[9] not to possess any As-As bonds.

In Fig. 3, we compare the line shape of glassy $As_{0.5}Se_{0.5}$ to the fiber spectrum. $As_{0.5}Se_{0.5}$ has a strong peak near 78 MHz, which has been attributed[9] to the presence of As-As bonds in the binary glassy alloy. The absence of a peak at this frequency for the fiber suggests that no such bonding exists in rapidly drawn, aged As_2Se_3 fibers.

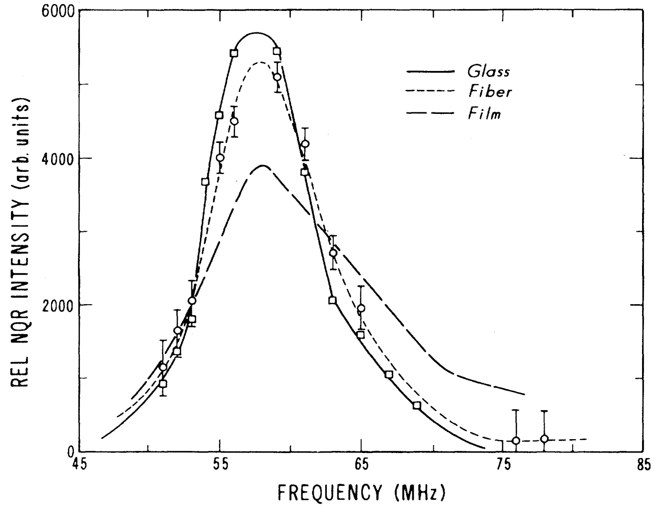

FIG. 1. The ^{75}As NQR line shape of glassy As_2Se_3 fibers (short-dashed line) is compared to that of the bulk As_2Se_3 glass (solid line) and to that of a rapidly evaporated thin film of As_2Se_3 (long-dashed line). All line shapes are normalized to the same area. The FWHM's were found to be 8.8, 8.4, and 13.8 MHz, respectively, for the fiber, bulk glass, and film. The line shape of the fiber exhibits an asymmetry toward higher frequencies that is similar to, but not as pronounced as, that observed in a film deposited on a 300-K substrate. Data for the film are taken from Ref. 3.

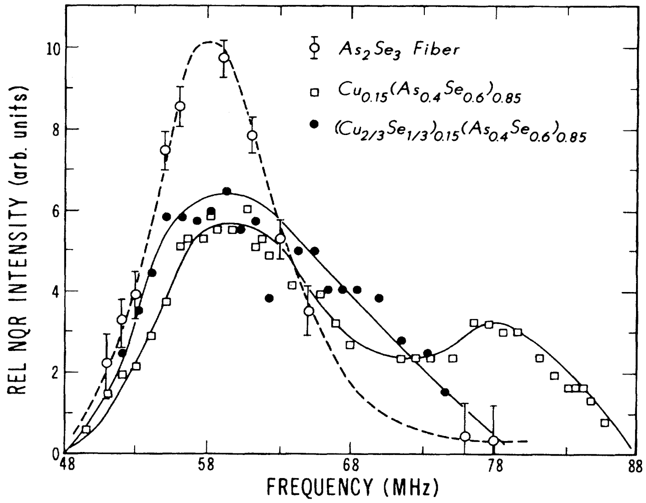

FIG. 2. The ^{75}As NQR line shape of glassy As_2Se_3 fiber is compared to that of two glassy copper arsenic selenide samples, $Cu_{0.15}(As_{0.4}Se_{0.6})_{0.85}$ and $(Cu_{2/3}Se_{1/3})_{0.15}(As_{0.4}Se_{0.6})_{0.85}$ at 77 K. The 15-at. % copper-doped As_2Se_3 sample shows a peak near 78 MHz, which is attributed to the presence of As-As bonds in the system. The fiber line shape has no peak near 78 MHz, indicating the absence of such bonding. The other copper arsenic selenium glass contains no As-As bonds. Data for the glassy copper arsenic selenide samples are taken from Ref. 9. See text for details.

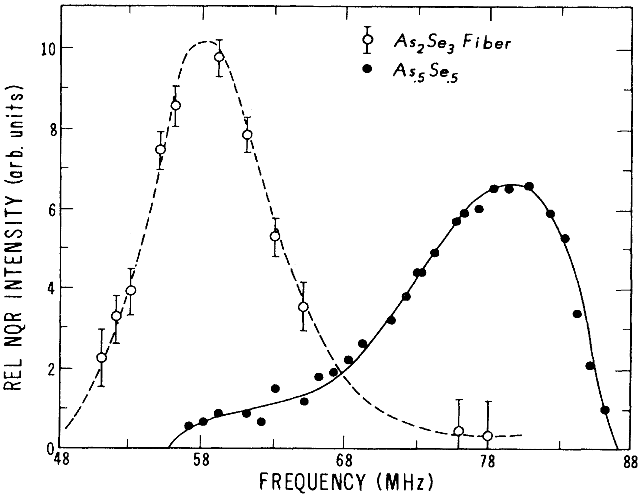

FIG. 3. The NQR line shape of $As_{0.5}Se_{0.5}$ binary glassy alloy is compared to the As_2Se_3 fiber line shape. The peak near 78 MHz for the $As_{0.5}Se_{0.5}$ is due to the presence of As-As bonds in this sample (Ref. 9). The fiber line shape shows no such peak indicating the absence of As-As bonds in As_2Se_3 fibers. Data for the $As_{0.5}Se_{0.5}$ binary glass were taken from Ref. 9. See text for details.

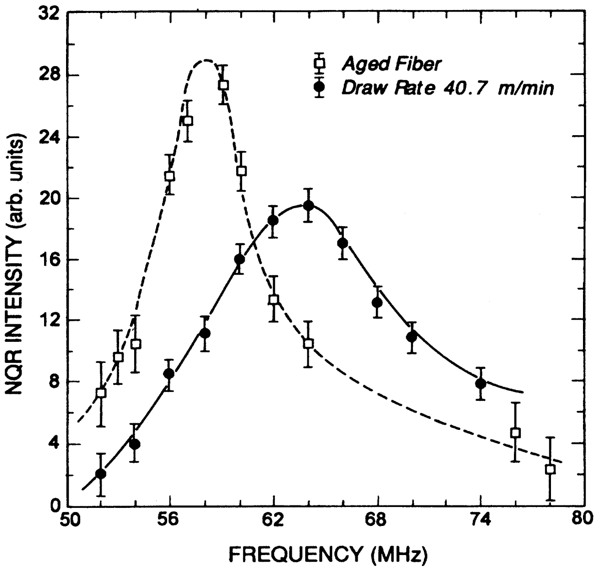

FIG. 4. Comparison of the NQR line shape of an As_2Se_3 fiber (draw rate 5 m/min, and aged for more than 18 months) to that of a freshly prepared fiber (draw rate 40.7 m/min). The changes in the asymmetries in the NQR line shapes and the changes in the FWHM (from 8.8 MHz in the aged fiber to 12 MHz in the freshly prepared fiber) indicate the greater distortions in the $AsSe_3$ pyramidal units and the possible presence of As-As bonds in the freshly drawn fiber. Details are discussed in the text.

Figure 4 shows the NQR line shape of the freshly prepared fiber (draw rate 40.7 m/min) compared to the aged fiber (denoted as As_2Se_3 fiber). The changes in line shapes are exhibited in both the asymmetry and also in the shift of the peak from 58 to 64 MHz. Also, the FWHM for the freshly prepared fiber is 12 MHz compared to the FWHM of 8.8 MHz for the aged fiber. The NQR intensity near 78 MHz is approximately a factor of 2 higher for the freshly drawn fiber compared to the aged fiber. This line shape indicates the possible presence of As-As bonds in the freshly prepared fiber.

In Fig. 4, we have used a freshly drawn fiber at a draw rate of 40.7 m/min in order to enhance the comparison with the annealed bulk sample. In addition, fibers drawn at a rate of 5 m/min anneal much more rapidly than those drawn at greater rates, and therefore make the NQR experiments much more difficult to perform in the as-drawn condition. Experiments on freshly drawn fibers as a function of draw rate will be published elsewhere.

IV. DISCUSSION

The analysis of ^{75}As NQR line shapes in arsenic selenide glasses can provide detailed information concerning the local structural order surrounding the As sites in these glasses. On the other hand, this probe is applicable to the bulk of the As sites (approximately 99% of the As sites with 1% error bars) but is insensitive to distortions of the local structural order on the level of defects. With this caveat in mind, we can nonetheless learn a significant amount concerning local distortions in the As bonding sites by careful examination of the ^{75}As NQR line shapes in As_2Se_3 fibers by comparison with bulk glasses and amorphous thin films.

As mentioned in the previous section, the three important features of the ^{75}As NQR spectrum in As_2Se_3 fibers are the slight increase in the linewidth over that which is observed in well-annealed, bulk glassy As_2Se_3, the slight asymmetry to higher frequencies, and the lack of any significant intensity near 78 MHz where there is a bump in the spectra for the $As_{0.5}Se_{0.5}$ and $Cu_{0.15}(As_{0.4}Se_{0.6})_{0.85}$ glasses. These three features have important implications for the local structural order in the fibers.

In both the $As_{0.5}Se_{0.5}$ and $Cu_{0.15}(As_{0.4}Se_{0.6})_{0.85}$ glasses, there exist As-As bonds. This fact can be appreciated by consideration of a simple structural model that represents a generalization of the "8-N" rule originally proposed by Mott[10] where for covalent bonding the number of bonds (nearest neighbors) for atoms from groups IV, V, VI, or VII of the Periodic Table is equal to eight minus the valence (column number) of the atom. The generalization is called the formal valence shell model, and the basic assumption of this model is that in order to maintain covalency (eight electrons surrounding each atom obtained by electrons formally "shared" between nearest neighbors in bonds) for metals (atoms from groups I, II, or III of the Periodic Table), the number of bonds must be equal to four and the electrons required to produce this coordination must be "formally" donated by over coordinating other atoms in the glass (chalcogenide atoms in the case of the chalcogenide glasses).[11,12] Within the context of this model, it is easy to calculate that the glass $(Cu_{2/3}Se_{1/3})_{0.15}(As_{0.4}Se_{0.6})_{0.85}$ has no As-As bonds but that the glass $Cu_{0.15}(As_{0.4}Se_{0.6})_{0.85}$ has 44% of the As sites containing one As-As bond. The normal 8-N rule can be used to establish that $As_{0.5}Se_{0.5}$ has $\sim 100\%$ of the As sites with one As-As bond.[13]

From this reasoning it is clear that the peak near 78 MHz in the ^{75}As spectra is the result of As-As bonds.[4] This interpretation is supported by the occurrence of ^{75}As NQR peaks around 78 MHz in some crystalline solids where it is known that every As site contains one As-As bond.[4] It is also clear from the ^{75}As NQR spectrum for the aged fibers that there is no appreciable contribution from As-As bonds to the structure.

There is, however, a slight asymmetry in the spectrum for the aged fibers, and this asymmetry is also observed in a much more pronounced fashion in rapidly deposited films of As_2Se_3 and in $(Cu_{2/3}Se_{1/3})_{0.15}(As_{0.4}Se_{0.6})_{0.85}$ glass. In previous papers[4,9,13] this asymmetry has been attributed to specific distortions in the apex angles of the $AsSe_3$ local pyramidal units. In particular the distortions are probably not symmetric in all three apex angles but rather asymmetric distortions where one angle is distorted to a greater extent than the other two. It therefore appears that in the aged fibers there remain slight distortions in the local $AsSe_3$ pyramidal units, distortions that are not nearly as great as those observed in rapidly evaporated films deposited on room-temperature substrates or in certain metal containing bulk As-Se glasses.

These conclusions are consistent with a model proposed to explain time-dependent changes seen in fresh and aged fibers.[8] The observation of a low level of distortion to the $AsSe_3$ pyramidal units in well-aged fiber is expected to accompany the release that occurs during aging, of stored energy imparted to the structure during drawing. During fiberization, the sheet or layerlike structure of the glass is believed to align closely to the axial direction of the draw stress, and a nonequilibrium structure is quickly frozen in. One might expect the corresponding distortion of pyramidal units in this case to be similar to that seen in rapidly evaporated films. As the fiber ages, the stored energy (and pyramidal distortion) is gradually released as the structure undergoes relaxation, and the fiber structure becomes more "bulklike." The change with time in the $AsSe_3$ units, and hence overall fiber structure, gives rise to the macroscopic changes in physical (mechanical, thermal, and optical) and possibly electrical properties. These changes have been quantified for As_2Se_3 samples and shown to be related to changes in draw-induced defect concentrations, which are dependent on age and draw (temperature, stress) conditions.[8] Defect concentrations were obtained using electron spin resonance, which are reported separately.[14]

The present results lead to the obvious suggestion that ^{75}As NQR will be a very useful probe of freshly drawn fibers that have not aged and are therefore more strained.[8] NQR measurements of the rapidly drawn and freshly prepared fibers (draw rate 40.7 m/min) clearly illustrate distortions of the pyramidal units that are similar to the rapidly evaporated films. Detailed studies are in progress to investigate the strain-relief process in rapidly drawn fibers at different draw rates using NQR and neutron scattering.

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