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Nuclear quadrupole resonance in the glassy Cu-As-S and Cu-As-Se systems

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Nuclear quadrupole resonance (NQR) of ^{75}As has been used to study bonding arrangements in the metal chalcogenide glass systems, Cu-As-S and Cu-As-Se. In the compositions $Cu_x(As_{2/5}Z_{3/5})_{1-x}$, where $Z=S$ or Se, the ^{75}As NQR spin-echo measurements are consistent with the appearance of As—As bonds whose density increases with x. For the compositions $(Cu_{2/3}Z_{1/3})_y(As_{2/5}Z_{3/5})_{1-y}$ the NQR measurements yield no evidence for the presence of As—As bonds. Both of these results are consistent with a recent structural model proposed to explain the local structural order in metal chalcogenide glasses.

I. INTRODUCTION

Chalcogenide glasses containing metal atoms (atoms from columns I, II, or III of the Periodic Table) form an interesting class of amorphous semiconductors for several reasons. First there is experimental evidence from several model systems[1-5] that the metal atoms in these glasses are tetrahedrally coordinated. The coordination suggests that covalent forces are at least partially responsible for the local structural order. Second, a general structural model[6,7] has recently been proposed which is consistent with the basic properties of glass formation in these systems. In the model, the average coordination number n_{av} approaches 4 (tetrahedral structure) as metal atoms are added to the glasses. Finally, these glasses are convenient systems in which to follow continuously the evolution from materials of low average coordination number $n_{av} \leq 2$, to materials which are nearly tetrahedral ($n_{av} \rightarrow 4$).

This evolution is of great interest because the typical chalcogenide glasses ($n_{av} \leq 3$) are "soft" structures where the electronic defects are dominated by a strong electron-lattice interaction. In fact, this interaction is so strong in general that the electronic defects possess negative effective electron-electron correlation energies (negative U). On the other hand, the tetrahedrally coordinated amorphous semiconductors, such as amorphous silicon (a-Si), are thought to be dominated by electronic states which possess $U>0$. Being able to follow this trend continuously and systematically in one material system should be of real importance in quantifying the differences in electronic properties between glasses where the dominant defects possess a negative U and glasses where the dominant defects possess a positive U.

The two prototype metal chalcogenide systems which perhaps have been studied the most thoroughly are $Cu_xAs_uZ_{1-x-u}$ where $Z=S$ or Se. The formal-valence-shell model[6,7] predicts that $n_{av}=8-\bar{N}$, where $\bar{N}$ is the average number of s and p valence electrons ("average column number") for a specific glass composition. In the $Cu_xAs_uZ_{1-x-u}$ system one obtains

$$n_{av}=2+2x+u \ . \tag{1}$$

In addition, if one requires that the anion sublattice is made up exclusively of S or Se atoms (i.e., only Cu—Z and As—Z bonds are allowed), then the allowed compositions are restricted to line (AB) in the ternary phase diagrams (Fig. 1) given by[6,7]

$$(Cu_{2/3}Z_{1/3})_y(As_{2/5}Z_{3/5})_{1-y} \ . \tag{2}$$

At low Cu concentration (≤ 30 at. % Cu) departures from this line are accommodated by the introduction of Z—Z or As—As bonds depending upon whether the

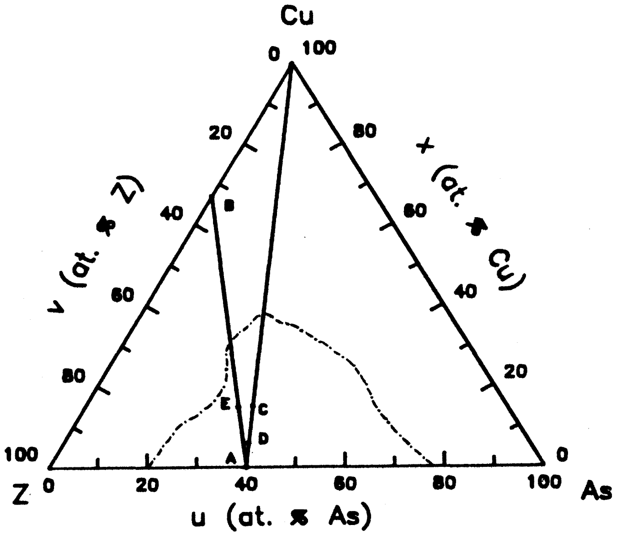

FIG. 1. Phase diagram for the Cu-As-Se and Cu-As-S systems. The points shown represent compositions of interest in the text: A, $As_{0.4}Z_{0.6}$; B, $Cu_{2/3}Z_{1/3}$; C, $Cu_{0.15}(As_{0.4}Se_{0.6})_{0.85}$; D, $Cu_{0.6}(As_{0.4}S_{0.6})_{0.94}$; E, $Cu_{0.15}As_{0.31}Se_{0.54}$, where Z represents S or Se. The glass-forming region for Cu-As-Se as determined in Ref. 28 is shown as the dashed curve. The glass-forming region for Cu-As-S is not as extensive and is known not to exceed about 6 at. % Cu along the line $Cu_x(As_{0.4}S_{0.6})_{1-x}$ and 43 at. % As along the binary As_uS_{1-u} line.

composition is Z or As rich.[6,7] Further details of the model are discussed below in Section III.

Previous NQR work on the chalcogenide glasses focused on binaries[8,9,10] such as $As_{0.4}Se_{0.6}$ and $As_{0.4}S_{0.6}$ and ternaries[11] such as $As_{0.4}Se_{0.6x}S_{0.6(1-x)}$. In glassy $As_{0.4}S_{0.6}$ and $As_{0.4}Se_{0.6}$ broad NQR absorption peaks are found which are centered between the two peaks observed in the layered crystalline modifications. The AsS_3 and $AsSe_3$ pyramidal sites in the glasses are very similar to those occurring in the crystals. In the ternary system the NQR peak shifts continuously from $As_{0.4}S_{0.6}$ to $As_{0.4}Se_{0.6}$ with increasing x.

In the following discussion we will show that one expects As—As bonds for glass in the system $Cu_x(As_{0.4}Se_{0.6})_{1-x}$. The presence of As—As bonds in As-S and As-Se binary glasses has been known for some time. The earliest experiments involved Raman scattering measurements in As-rich As_uS_{1-u} glasses where the presence of As—As bonds is, of course, expected.[12–15] Even in the stoichiometric composition $As_{0.4}S_{0.6}$ some As—As bonds occur, although only at defect concentrations. In resonance Raman scattering experiments Ewen and Owen[13] have shown that in bulk glasses of the As_uS_{1-u} system the As—As bonds exist as isolated entities and not as a part of As_4S_4 molecules.

Rapid quenching from the melt is known to increase the As—As homopolar bond density[16,17] as well as rapid evaporation of films onto room-temperature substrates.[18,14] In the case of rapidly evaporated films of $As_{0.4}S_{0.6}$ one can get As_4S_4 molecules embedded in the structure. In fact the earliest NQR measurements[18] of an NQR peak near 90 MHz in rapidly evaporated $As_{0.4}S_{0.6}$ were interpreted in terms of isolated As_4S_4 molecules, but the results of the present work suggest that one may only infer the presence of As—As bonds from these measurements. No As—As bonds are observed[11] by NQR in the stoichiometric ternary system $As_2S_xSe_{3-x}$. In this system only mixed AsS_nSe_{3-n} (where $n=0,1,2,3$) pyramidal units are observed, as one would expect.

Magnetic resonance experiments[19,20] have also looked at ^{77}Se in glassy $As_{0.4}Se_{0.6}$ and $Cu_x(As_{0.4}Se_{0.6})_{1-x}$, but the results are not as definitive as the ^{75}As measurements because of the lack of a quadrupolar interaction for the selenium which has nuclear spin $I=\frac{1}{2}$. The ^{77}Se line shapes in glassy $As_{0.4}Se_{0.6}$, where the selenium sites each have two Se—As bonds, and in glassy Se, where the selenium sites each have two Se—Se bonds, are very similar. More sophisticated experiments, such as those involving sample spinning, will be required to differentiate between these two selenium local environments.

Section II describes the experimental procedures employed in making and measuring the glassy samples. In Sec. III we summarize the basic results of the formal-valence-shell model which are necessary to understand the ^{75}As NQR measurements. Section IV presents some essential features of NQR which are useful in the context of the present study. Results of the NQR line shape are presented in Sec. V and discussed in Sec. VI. A summary of the most important conclusions is contained in Sec. VII.

II. EXPERIMENTAL PROCEDURE

Glassy samples were synthesized by melting pure (99.9999%) elemental starting materials in an evacuated quartz ampoule which was rocked at 575 °C (binary glasses) or at 950 °C (ternary glasses) for 24 hours. Mixtures were then cooled slowly to temperatures slightly higher than the respective glass transition temperatures and quenched in ice water. Glasses with high copper concentrations ($\geq 15\%$) were prepared in smaller ampoules to allow for faster quenching rates. Samples were then crushed into small chunks and placed in pyrex tubes to fit inside the NQR coils.

A standard pulsed NMR spectrometer as described previously[21] was employed. 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 linewidths in these glasses are all considerably greater than 1 MHz, the line shapes were determined by measuring the echo amplitude as a function of frequency. Typical 90° pulse widths of ~ 5 μsec were employed so that the spectral coverage for a given measurement was on the order of 100 kHz. The NQR line shapes in these glasses are all slowly varying on the scale of 100 kHz.

Care was taken to insure that the resulting line shapes were not distorted by variations in spin-spin relaxation times (T_2) as a function of resonant frequency. Values of T_2 were determined by measuring the echo amplitude as a function of pulse separation, and in all cases these values were found to be independent of frequency. Spin-lattice-relaxation times (T_1) were measured using the repetition-rate technique.[22]

III. FORMAL VALENCE SHELL MODEL

A recently developed model[6,7] has been employed to explain both local coordination numbers and the fractions of like-atom bonds as function of composition in ternary amorphous semiconductors which contain metal atoms (groups I, II, or III of the Periodic Table). This formal valence shell (FVS) model employs the concept of covalent bonding and the constraint that all atoms obtain a closed shell of eight valence electrons which are shared between nearest neighbors in pairs (bonds). These assumptions lead to a generalized rule where the average number of bonds per atom (B) (one half of the average coordination number) is related to the average number of valence electrons per atom $\bar{N}$ by the equation

$$2B=8-\bar{N} . \quad (3)$$

Consider the ternary system $Cu_xAs_uZ_v$ where Z is a chalcogen atom and $x+u+v=1$. For this system $N_x=1$, $N_u=5$, and $N_v=6$, so that

$$\bar{N}=x+5u+6v . \quad (4)$$

One can think of $\bar{N}$ as the average column number of a given composition. In the FVS model the atoms with the greatest number of valence electrons (greatest N) form the anion sublattice in most cases. Thus in the $Cu_xAs_uZ_v$ system the preferred bonds are Cu—Z and As—Z. When only these bonds are present one obtains the specific line[6,7] in the phase diagram which is given by expression (2) and shown in Fig. 1 (line AB). Off this line the glass formation is accomplished by introducing As—As or Z—Z bonds.[6,7] In the $Cu_xAs_uZ_v$ system the total number of bonds (which is the average number of bonds per atom because of the normalization condition $x+v+v=1$) is

$$B=4x+3u-a\ , \qquad (5)$$

where a is the number of As—As bonds. Note that this description only works for compositions which are As rich with respect to the pseudobinary line mentioned above. Using Eqs. (3), (4), and (5) and the normalization condition one obtains

$$a=(3x+5u-2)/2\ . \qquad (6)$$

We now define a parameter b which is the number of As atoms bonded to other As atoms normalized to the total As concentration:

$$b=2a/u\ . \qquad (7)$$

From Eq. (6) this parameter is

$$b=(3x+5u-2)/u\ . \qquad (8)$$

The parameter b is useful because it relates directly to experiments which measure the fraction of As sites which contain one As—As homobond. Implicit in the derivation of b is the assumption that there is at most one As—As bond per As site. This assumption will undoubtedly break down for large arsenic concentrations ($u \rightarrow 1$).

Thus for the compositions given by expression (2) the value of b is zero for all $x \leq 0.28$. However, for other compositions, as for example for the compositions given by $Cu_x(As_{0.4}Se_{0.6})_{1-x}$, the value of b is greater than zero for $x>0$ (see Fig. 1). The value of b is also greater than zero for the binary As-Se or As-S compositions for which $x=0$ and $u>\frac{2}{5}$ in Eq. (8).

IV. ^{75}As NQR DETERMINATIONS OF As—As BONDS

A nucleus with spin I greater than $\frac{1}{2}$ possesses a nuclear quadrupole moment Q. For such a nucleus there is an interaction with the gradient of the electric field at the nuclear site. The electric field is predominantly determined by the bonding electrons. In highly symmetric environments, such as perfect tetrahedral or cubic symmetries, this field gradient at the nuclear site can be zero, but in most cases the gradient is nonzero and the quadrupolar interaction is important in determining NMR or NQR resonant frequencies and linewidths. For ^{75}As with $I=\frac{3}{2}$, the quadrupolar interaction often provides a very sensitive probe of the local environment.

For the experiments performed in this study, the Hamiltonian can be written as

$$H=\mathbf{I}\cdot\overleftrightarrow{\mathbf{Q}}\cdot\mathbf{I}\ , \qquad (9)$$

where $\mathbf{I}$ is the nuclear spin operator, and $\overleftrightarrow{\mathbf{Q}}$ is the quadrupole coupling tensor. This Hamiltonian is usually written in terms of parameters which are derived from the principal components of the electric field gradient (EFG) tensor.

$$H=\frac{e^2qQ}{4I(2I-1)}[3I_z^2-I(I+1)+\tfrac{1}{2}\eta(I_+^2+I_-^2)]\ , \qquad (10)$$

where γ is the nuclear gyromagnetic ratio, e is the electronic charge, I_+, I_- are the usual raising and lowering operators, $eq=eq_{zz}$ is the maximum principal component of the EFG tensor, and $\eta=(q_{xx}-q_{yy})/q_{zz}$ is the asymmetry parameter which is a measure of the departure of the EFG tensor from axial symmetry.

For the case of $I=\frac{3}{2}$ Eq. (10) yields a single resonant absorption where

$$\nu=\frac{1}{2}\left[\frac{e^2qQ}{h}\right](1+\tfrac{1}{3}\eta^2)^{1/2}\ . \qquad (11)$$

The quantity e^2qQ/h is called the quadrupolar coupling constant which depends on the nucleus through Q and the local environment through q.

It will be shown that the NQR measurements in Cu-As-Se and Cu-As-S glasses are sensitive to As—As bonds because of changes in q (and/or η) between As sites which are bonded to one As resonant neighbor and those As sites which have three sulfur neighbors. If the number of As sites with one As—As bond (area under NQR absorption associated with these sites) is given by A_t and the total number of sites (total NQR absorption) is given by A, then

$$b=\frac{A_t}{A}\ , \qquad (12)$$

where b is defined in Eq. (7) above.

V. RESULTS

Samples of glasses in the system $Cu_x(As_{2/5}Se_{3/5})_{1-x}$ and $Cu_x(As_{2/5}S_{3/5})_{1-x}$ are expected by Eq. (8) to possess As—As bonds. When Eq. (8) is applied to these systems, then the number of As atoms which are bonded to one other As atom normalized to the total As concentration is

$$b=\frac{5}{2}\frac{x}{(1-x)}\ . \qquad (13)$$

NQR data for ^{75}As are shown in Fig. 2 for the $Cu_x(As_{2/5}S_{3/5})_{1-x}$ system at 77 K. Note that for pure $As_{0.4}S_{0.6}$ glass (curve f) the ^{75}As NQR line is centered near 72 MHz and has a full width at half height of approximately 6 MHz. This line is centered about the two NQR lines which occur in crystalline $As_{0.4}S_{0.6}$ at 70.38 and 72.86 MHz at 77 K. (There are two inequivalent arsenic sites in the unit cell of crystalline $As_{0.4}S_{0.6}$). Thus the ^{75}As NQR line in glassy $As_{0.4}S_{0.6}$ is representative of the distorted AsS_3 pyramidal units which occur in the glassy solid.

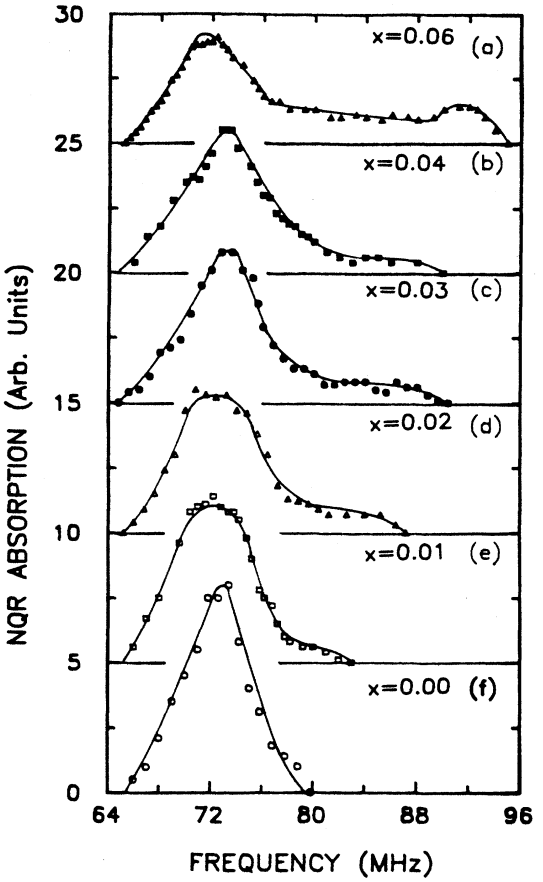

FIG. 2. ^{75}As NQR line shapes for various copper concentrations x in $Cu_x(As_{0.4}S_{0.6})_{1-x}$ normalized to the same area. The labels (a), (b), (c), (d), (e), and (f) correspond to the x values 0.06, 0.04, 0.03, 0.02, 0.01, and 0.00, respectively. Lines are aids to the eye.

As copper is added to $As_{0.4}S_{0.6}$ according to the formula $Cu_x(As_{0.4}S_{0.6})_{1-x}$, the ^{75}As NQR line shape changes as shown in Fig. 2. Only 6 at. % Cu can be added in the system before the samples become crystalline. As copper concentration is increased a "tail" begins to appear on the high-frequency side of the line shape. The growth of this tail as a function of x is attributed to the presence of AsS_3 pyramidal sites which are distorted with respect to those which occur in $As_{0.4}S_{0.6}$. The absence of such a tail on the lower-frequency side of the line shape indicates that specific distortions are probably occurring. The larger resonant frequencies associated with the distorted sites are probably due to an increase in the apex angles of the distorted (AsS_3) pyramids.[9] At about 6 at. % Cu [curve (a) in Fig. 2] there appears in the ^{75}As NQR spectrum a peak near 90 MHz which we will argue can be attributed to arsenic pyramidal sites at which there is one As—As bond.

The attribution of the NQR peak centered near 90 MHz to arsenic pyramidal units with one As—As bond and two As—S bonds comes from a comparison with the NQR spectrum observed in crystalline As_4S_4. In this molecular crystal each As site has one As—As bond and the NQR lines for the four inequivalent sites in the crystal are all centered near 90 MHz (89.27, 91.48, 92.09, and 92.92 at 77 K).[10] We take these results to indicate that the peak in the glass near 90 MHz is due to the presence of As sites at which there is one As—As bond.

This hypothesis can be tested by examining the binary system As_uS_{1-u} where the presence of As—As bonds can again be estimated by Eq. (8). For this system the fraction of As sites which contain one As—As bond relative to the total number of As sites is given by

$$b=\frac{5u-2}{u} . \tag{14}$$

Glasses in this system can only be made for $u \leq 0.43$, but for $u=0.43$ the value of b in Eq. (14) is 0.35.

Figure 3 shows the ^{75}As NQR spectrum for glassy $As_{0.43}S_{0.57}$. If our interpretation is correct, then the ratio of the area under the peak at 90 MHz to the total area in the NQR spectrum for this glass should be $b=0.35$. The experimental value of this ratio is $b_{ex}=0.40\pm0.05$. The error estimate on this value for b_{ex} is determined crudely by attributing all the area between the two peaks at 72 and 90 MHz to one peak or the other. Also shown in this figure for comparison is the curve of Fig. 2(a) for glassy $Cu_{0.06}(As_{0.4}S_{0.6})_{0.94}$. These results (Fig. 3) support the interpretation that the peak near 90 MHz in the Cu-As-S system is due to arsenic sites at which there is one As—As bond.

The difficulty with the Cu-As-S glass system is the fact that these glasses can only be prepared for copper concentrations less than about 6 at. %. In the Cu-As-Se glasses, on the other hand, one can make glasses with copper concentrations approaching 30 at. % and thus test the procedure developed above more completely.

In Fig. 4 are shown ^{75}As NQR line shapes for glasses in the system $Cu_x(As_{0.4}Se_{0.6})_{1-x}$ for $0 \leq x \leq 0.23$. The NQR line shape for $As_{0.4}Se_{0.6}$ is centered about 58 MHz as shown in Fig. 4(d). Like the sulfur system, this peak is centered about the two NQR lines which occur[9] in crystalline $As_{0.4}Se_{0.6}$. As Cu is added to the composition

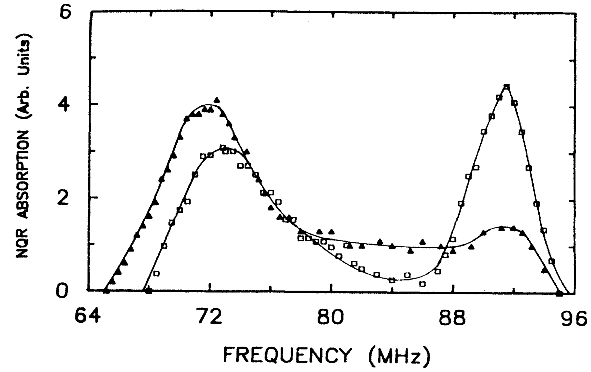

FIG. 3. ^{75}As NQR line shapes for $x=0.06$ in $Cu_x(As_{0.4}S_{0.6})_{1-x}$ and the binary glass $As_{0.43}S_{0.57}$ (open squares) normalized to the same area. Lines are aids to the eye.

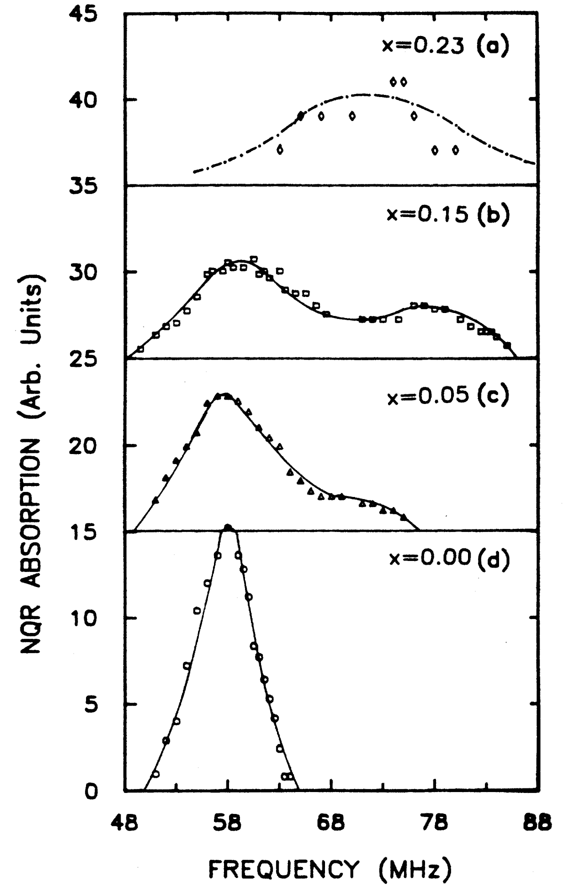

FIG. 4. ^{75}As NQR line shapes for various cooper concentrations x in $Cu_x(As_{0.4}Se_{0.6})_{1-x}$ normalized to the same area. The labels (a), (b), (c), and (d) correspond to the x values 0.23, 0.15, 0.05, and 0.00, respectively. Lines are aids to the eye.

there appears a well-defined peak near 78 MHz for $x \simeq 0.15$ [Fig. 4(b)]. By arguments similar to those presented above for the sulfur system we attribute the peak near 78 MHz as due to arsenic pyramidal sites where there is one As—As bond. An estimate of the error under this peak for $x = 0.15$ [Fig. 4(b)] compared to the total area yields a value of $b_{\text{ex}} = 0.37 \pm 0.05$ while the model calculation [Eq. (13)] yields $b = 0.44$.

The NQR curve for $x = 0.15$ of Fig. 4(b) is reproduced in Fig. 5 (open squares). Also shown in this figure are data suitably normalized for a fast-evaporated film of $As_{0.4}Se_{0.6}$ (solid squares).[18] It can be seen from this figure that rapid evaporation of $As_{0.4}Se_{0.6}$ onto a room-temperature substrate leads to departures from the ideal stoichiometry locally and to the presence of As—As bonds. (One also presumably gets Se—Se bonds for this situation.)

The third curve shown in Fig. 5 is that for the $As_{0.5}Se_{0.5}$ binary glassy alloy. At this composition Eq. (14) yields a value of $b = 1$ for the fraction of As sites which have one As—As bond. Although the derivation of Eq. (14) breaks down near this point because there is a significant probability that there will be two As—As bonds at a given As site, nonetheless the value should be close to unity. Experimentally, the data of Fig. 5 (solid circles) yield a value of $b_{\text{ex}} = 0.95 \pm 0.05$. When the copper concentration is increased to 23.1% the glass becomes highly conductive and the Q factor of the probe is reduced. As is evident from Fig. 4(a) there is a marked decrease in the signal-to-noise ratio. Although the scatter in the data is considerable, it appears that most of the intensity has shifted to the higher-frequency range. This conclusion is at least qualitatively consistent with the predictions of the model.

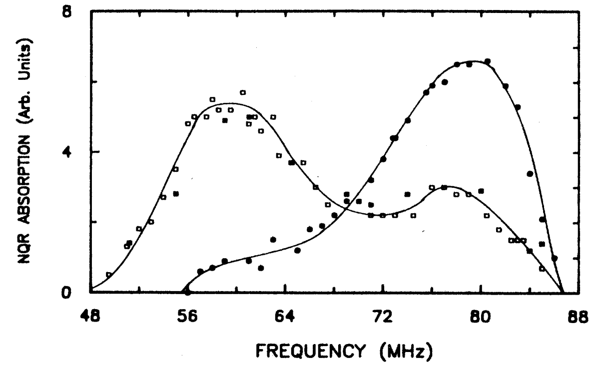

FIG. 5. ^{75}As NQR line shapes for $x = 0.15$ in $Cu_x(As_{0.4}Se_{0.6})_{1-x}$ (open squares), the binary glass $As_{0.5}Se_{0.5}$ (solid circles) and an optically irradiated thin film of $As_{0.4}Se_{0.6}$ (solid squares), all normalized to the same area.

A final major test of our interpretation of the NQR data in the Cu-As-S and Cu-As-Se glassy systems is shown in Fig. 6. This figure shows two glasses with 15 at. % Cu which occur very close to one another in the ternary phase diagram (points C and E in the phase diagram of Fig. 1). One sample lies along the stoichiometric line given by expression (2) (with $\frac{2}{3}y = 0.15$) where no As—As bonds are expected. The data for this sample are shown as solid circles in Fig. 6. Note that for this sample

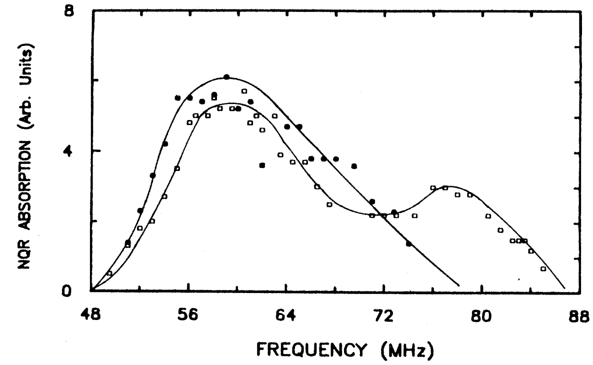

FIG. 6. ^{75}As NQR line shapes of 15 at. % copper in $Cu_{0.15}(As_{0.4}Se_{0.6})_{0.85}$ (open squares) and $(Cu_{2/3}Se_{1/3})_{0.225}(As_{0.4}Se_{0.6})_{0.775}$ (solid circles). Lines are aids to the eye.

there is essentially no intensity near 80 MHz and hence no NQR evidence for the existence of As—As bonds ($b_{ex} \leq 0.1$).

For comparison in Fig. 6 the data for a sample along the line $Cu_x(As_{0.4}Se_{0.6})_{1-x}$ is also shown ($x=0.15$). These are the same data as those of Fig. 4(b) where the experimental and calculated values of the parameter b are $b_{ex}=0.37$ and $b=0.44$, respectively. The comparison shown in Fig. 6 is striking considering that this comparison provides a very stringent test for both the NQR interpretation and the predictions based on the FVS model. The two glass compositions in Fig. 6 differ from one another by only 3 at. % in Se concentration (and 3 at. % in As concentration).

VI. DISCUSSION

For the $Cu_x(As_{0.4}S_{0.6})_{1-x}$ and $Cu_x(As_{0.4}Se_{0.6})_{1-x}$ compositions the number of As sites which have one As—As bond is given by Eq. (13). A comparison of this equation with the observed NQR results in these systems is presented in Fig. 7. The circles in Fig. 7 represent data from the selenium system and the squares data from the sulfur system. Within the limits set by the uncertainties discussed in the previous section, the agreement with the model calculation is generally good.

Fast-evaporated films of $As_{0.4}S_{0.6}$ are known from infrared absorption[23] and ^{75}As NQR studies[18] to contain As_4S_4 molecules. The manifestation of these As_4S_4 molecules in the ^{75}As NQR spectrum is the appearance of a broad, structured peak at higher frequencies. In the As_4S_4 molecule each arsenic site is bonded to one arsenic and two sulfur atoms. There are thus two As—As bonds in each As_4S_4 molecule.

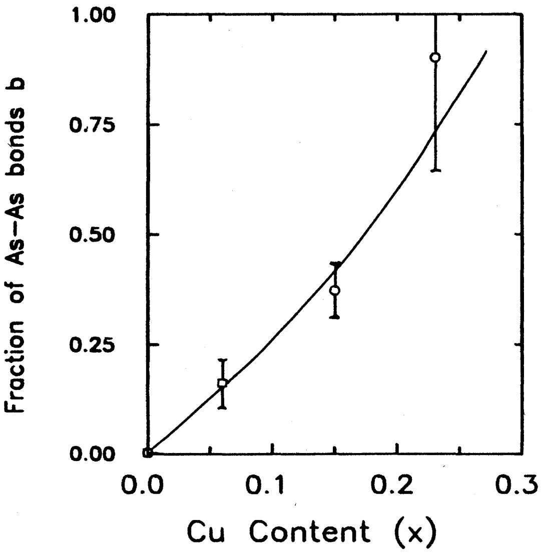

FIG. 7. Fraction of arsenic sites which contain one As—As bond, b, as a function of copper concentration in $Cu_x(As_{0.4}S_{0.6})_{1-x}$ (open squares) and in $Cu_x(As_{0.4}Se_{0.6})_{1-x}$ (open circles). Solid line shows the prediction of Eq. (13).

Recent extended x-ray-absorption fine-structure (EXAFS) measurements on As_uS_{1-u} films have also detected As—As homopolar bonds.[24–26] It appears that these bonds may play a role in the photodarkening effect which occurs in these glasses.[6] There is also some evidence, albeit circumstantial, that the presence of As—As bonds in stoichiometric $As_{0.4}S_{0.6}$ and $As_{0.4}Se_{0.6}$ leads to less regular intermediate range order[16,24] such as the presence of well-defined ring structures[18,24] in these glasses. All of these intermediate range features are outside of the context of both the present NQR measurements and the FVS model.

The presence of homopolar bonds has been studied in one other metal chalcogenide glass system, namely the $Ag_x(Ge_{1/3}Se_{2/3})_{1-x}$ system.[27] In this system Fischer-Colbrie *et al.*[27] have investigated Ge—Ge bonds which occur because these compositions are germanium rich with respect to the pseudobinary line for which, according to the FVS model, there are only Ag—Se and Ge—Se bonds $[(Ag_{2/3}Se_{1/3})_y(Ge_{1/3}Se_{2/3})_{1-y})]$. These authors have developed an expression similar to that shown above for the Cu-As-Se or Cu-As-S systems [Eq. (13)]. For the system where the normalized compositions are given by $Ag_xGe_uSe_{1-x-u}$ the number of Ge atoms which are bonded to one other Ge atom normalized to the total Ge concentration is

$$a'=(3x+6u-2)/2 \ . \qquad (15)$$

Equation (15) for the $Ag_xGe_uSe_{1-x-u}$ system is the analog of Eq. (6) for the $Cu_xAs_uSe_{1-x-u}$ systems.

Measurements of x-ray radial distribution functions, grazing incidence x-ray scattering and differential anomalous x-ray scattering techniques allowed these authors[27] to measure the fraction of Ge—Ge bonds and obtain good agreement with the predictions of Eq. (15). One would anticipate that most other metal chalcogenide glass systems would follow this same pattern.

Considering the success of the FVS model in explaining the presence of homopolar bonds in three metal chalcogenide glass systems (Cu-As-Se, Cu-As-S, and Ag-Ge-Se), one might be tempted to draw further conclusions concerning structural arrangements beyond nearest-neighbor order. Unfortunately, the simplicity of the FVS model does not support further conclusions. For example, one could imagine in the Cu-As-Se system a compositional separation of the compositions $Cu_x(As_{2/5}Se_{3/5})_{1-x}$ into regions of $(Cu_{2/3}Se_{1/3})_y(As_{2/5}Se_{3/5})_{1-y}$ and regions of As_uSe_{1-u}, but the model does not predict unique values of y or u because all allowed values yield identical results for all the nearest-neighbor parameters such as the fraction of As—As bonds and the average coordination number of Cu, As, and Se. Arguments based on local charge neutrality would suggest that the threefold- or fourfold-coordinated chalcogen atoms reside near the tetrahedrally coordinated copper atoms,[7] but details concerning intermediate range order, such as ring structures, require knowledge which is beyond the scope of either the FVS model or the present NQR results.

VII. SUMMARY

We have used the nuclear quadrupole resonance (NQR) technique to investigate the local structural order in two metal chalcogenide glass systems, Cu-As-S and Cu-As-Se. The most dramatic change in the local bonding arrangement as a function of composition is the formation of As—As bonds with the addition of metal atoms to the glasses. Except along a specific tie line given by $(\mathrm{Cu}_{2/3}Z_{1/3})_y(\mathrm{As}_{2/5}Z_{3/5})_{1-y}$ where $Z=\mathrm{S}$ or Se, the fraction of arsenic sites which contain at least one As—As bond increases with increasing metal concentration. A recently proposed model[6,7] has been employed to calculate the density of these As—As bonds as a function of glass composition. Using this model the fraction (b) of As sites with one As—As bond normalized to the total As concentration was calculated for compositions along three different lines of the phase diagram, As_uZ_{1-u}, $\mathrm{Cu}_x(\mathrm{As}_{0.4}Z_{0.6})_{1-x}$, and $(\mathrm{Cu}_{2/3}Z_{1/3})_y(\mathrm{As}_{2/5}Z_{3/5})_{1-y}$. The functional dependences of b for these three compositions are given by $b=(5u-2)/u$, $b=\frac{5}{2}(x/1-x)$, and $b=0$, respectively. From the NQR line-shape measurements we have associated the high-frequency peak with the presence of one As—As bond at an arsenic site. Comparisons between the model predictions and the NQR measurements are consistent with this assignment.

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