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Nuclear-magnetic-resonance relaxation in glassy Cu-As-Se and Cu-As-S

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Nuclear magnetic resonance (NMR) of ^{63}Cu and nuclear quadrupole resonance (NQR) of ^{75}As have been used to study relaxation effects and the possibility of local atomic diffusion in the Cu-As-S and Cu-As-Se glassy systems. The frequency and temperature dependences of the spin-lattice and spin-spin relaxation times have been measured. The NMR spin-lattice relaxation measurements for ^{63}Cu in the Cu-As-Se and Cu-As-S glassy systems suggest that the spin-lattice relaxation rate T_1^{-1} is probably dominated by two relaxation mechanisms depending on the temperature. For $T < 300$ K, T_1^{-1} for ^{63}Cu and ^{75}As exhibits a weak temperature dependence, which has been frequently observed for ^{75}As in the chalcogenide glasses and many other nuclei in the oxide glasses. For $T > 300$ K, on the other hand, a much more efficient relaxation mechanism takes over where both T_1^{-1} and T_2^{-1} increase rapidly with temperature. We suggest that this sudden decrease in the relaxation times is probably due to the local diffusion of Cu. The dramatic decrease of T_2 with temperature for $T > 300$ K is anomalous and may be related to clustering of copper atoms in these glasses.

I. INTRODUCTION

In addition to their potential applications as switching and memory devices, chalcogenide glasses containing metal atoms from groups I,II,III of the Periodic Table have become an important class of amorphous semiconductors with a special academic interest. In these glasses there is experimental evidence that the metal atoms are fourfold coordinated which suggests that covalent bonding is at least partially responsible for the local structural order. The importance of metal chalcogenide glasses is their ability to evolve from materials with low average coordination number (soft structure) to materials which are nearly tetrahedral. Furthermore, a general structural model,[1] the formal-valence-shell model, has been recently proposed which is consistent with the basic properties of glass formation. According to this model, the average coordination number n_{av} increases from $n_{\text{av}} = 2.4$ for zero metal concentration to $n_{\text{av}} \rightarrow 4$ at high metal concentrations. Nuclear-quadrupole-resonance (NQR) measurements obtained previously[2] on several metal-chalcogenide glasses are consistent with the general predictions of this model. As inferred from the NQR measurements[2] and the formal-valence-shell model,[1] dramatic changes occur in the local structural order of $\text{Cu}_x(\text{As}_{0.4}\text{Se}_{0.6})_{1-x}$ and $\text{Cu}_x(\text{As}_{0.4}\text{S}_{0.6})_{1-x}$ when copper atoms are added. One important change is the formation of As-As bonds which are absent in the binary ($x = 0$) glass.

Recently, considerable attention has been focused on the study of atomic diffusion in amorphous semiconductors. The importance of diffusion lies in its impact on the various metastable changes in electrical conductivity and other transport properties. The spin-lattice and spin-spin relaxation times T_1 and T_2, respectively, can be very important quantities for probing local atomic diffusion, thermal conductivity, and specific heat. At low temperatures there are profound differences between the glassy and crystalline solids when the temperature dependences of the thermal conductivity, specific heat, and ultrasonic attenuation are considered. These differences have been successfully explained in terms of an ensemble of two-level systems (TLS) which appears to be a characteristic of the glassy state.[3-6] At higher temperatures (10–300 K) the temperature dependences of these properties have been linked to a thermally activated structural relaxation within the glassy network. The thermal conductivity, specific heat, and ultrasonic attenuation measurements provide only macroscopic information about the dynamics of the glassy state. The nuclear relaxation measurements, on the other hand, provide information about the origins of some of these properties on a microscopic scale. Major differences between the crystalline and glassy states as identified by the NMR and NQR relaxation measurements are the following: (1) Glassy materials exhibit significantly larger spin-lattice relaxation rates T_1^{-1} (shorter T_1) than their crystalline counterparts.[7] For example, in the As_2S_3 composition, the glassy phase has a T_1^{-1} which is about 20 times larger than that of the crystalline phase at room temperature. (2) At low temperatures, the glassy state usually exhibits a characteristic temperature dependence of T_1^{-1} which is proportional to T^{α} where $1 \leq \alpha \leq 2$ depending on the glass.[3] This temperature dependence is considerably weaker in glasses than in their crystalline counterparts ($7 \leq \alpha \leq 9$).[7] (3) A distinct frequency dependence is frequently observed in glasses which, as we shall see below, is not what one would observe in crystals. (4) The NMR magnetization recovery curves in most glassy materials exhibit a nonexponential behavior which is rarely observed in crystals. The nonexponential behavior is related to the inhomogeneous environment of the spin ensemble in glasses where there is a distribution of relaxation rates. In glasses, the interactions between some of the individual spins and the lattice can be strong enough at high temperatures so that the rapid components of T_1 become comparable to T_2. The efficient relaxation has been linked to the greater density of low-frequency TLS and phonons in glasses. The two-level systems, also known as disorder modes, are believed to arise when a group of atoms occupy two metastable equilibrium states separated by a small energy barrier.[5]

Several previous models,[3,5,6] based on Raman-like processes involving disorder modes and phonons, have succeeded in explaining the temperature dependence and the higher relaxation rates in glasses. All these models predict frequency independent relaxation rates in agreement with the available experimental data. Recently, however, there have been several studies[8] where a frequency dependent T_1^{-1} is clearly observed in glasses. The frequency dependence of the spin-lattice relaxation rate cannot be explained by Raman-like processes.

In chalcogenide glasses that contain metal atoms such as Ag and Cu, there is experimental evidence for the motion of Ag atoms[9] in glassy Ag-As-S and more recently of Cu atoms[10] in glassy Cu-As-Se-Te. This evidence comes from ionic conductivity measurements. In this study the temperature, frequency, and compositional dependences of the relaxation rates T_1^{-1} and T_2^{-1} of ^{75}As NQR and ^{63}Cu NMR are measured. These relaxation rates are interpreted in terms of Raman-like processes at lower temperatures (T_1^{-1}) and local motion of Cu at higher temperatures (T_1^{-1} and T_2^{-1}) in the Cu-As-S and Cu-As-Se glasses.

The local-field fluctuations responsible for nuclear relaxation involve several interactions, two of which are more likely to be dominant in our case: (1) Magnetic dipole-dipole interactions where the local magnetic field produced by one dipole moment at the site of another fluctuates in time in response to changes in the angle between the dipolar axis and the applied magnetic field (molecular vibrations and reorientations). This interaction, while affecting both relaxation rates, is mainly responsible for the diffusion of energy within the spin system (spin diffusion). As we shall see below, spin diffusion can be either rapid or slow, a characterization which differentiates between homogeneous and inhomogeneous relaxation processes, respectively. And (2) electric quadrupole interactions (in cases where the spin of the nucleus $I > 1/2$) where the local electric field gradients fluctuate in time due to the diffusive and vibrational motions of ions. These fluctuations are triggered either by phonons modulating the positions of nearby atoms or by neighboring atoms making "jumps" from one position to another such as occurs in a disorder mode.[6] The local field fluctuations produced by the motion of a given atom serve as links between the spin system and the lattice. Since the energy of the spin system is transferred to the lattice through these local field fluctuations, we shall refer to them as "relaxation centers."

When present, quadrupolar interactions between the nuclear quadrupole moments and electric field gradients are almost always a dominating mechanism for spin-lattice relaxation.[11] The link between the spin system and the lattice can be supplied by other agents such as the anisotropic component of the chemical shift interaction or a magnetic interaction due to paramagnetic impurities. These interactions can, in principle, become efficient relaxation mechanisms. It is evident from our previous NMR measurements,[12] however, that the anisotropic components of the chemical shift in all the glasses studied, are very small in comparison with the quadrupolar interaction. This conclusion is supported by the fact that the broadening of the NMR spectra[12] is in all cases inversely proportional to the applied magnetic field. Therefore, the relaxation mechanism due to the chemical shift anisotropy is probably not a dominating mechanism in these glasses at any temperature. Adding Cu to the Cu-As-S and Cu-As-Se glasses is known to produce some S or Se dangling bonds which act as paramagnetic centers. Since T_1 is independent of Cu concentration over the range of 1 to about 23 at. % where the densities of paramagnetic centers vary by several orders of magnitude, the paramagnetic impurity interaction can also be eliminated as a dominant relaxation mechanism. Therefore, the local fluctuations of the electric-field gradients are probably the most likely agents for spin-lattice relaxation. Since atomic diffusion is known to produce large field fluctuations, we are led to suggest that this atomic diffusion is probably the most likely candidate for the spin-lattice-relaxation mechanism for $T > 300$ K.

Any one of the above processes that produces electric- or magnetic-field fluctuations can produce relaxation. These fluctuations interact differently with the individual spins depending on the coupling and the separation between the spins and the relaxation center. The spin-lattice relaxation rate of one nuclear spin coupled to one relaxation center can, in general, be written as[13]

$$T_1^{-1} = a(\mathbf{r})\tau_c \ , \tag{1}$$

where $a(\mathbf{r})$ represents the magnitude of the coupling between the spin and the relaxation center and τ_c is the correlation time that is a characteristic of the molecular reorientations or atomic motion. This correlation time is defined as the average time spent by the nuclear spin in a given environment. In Eq. (1), it is assumed that atomic motion is described by one single correlation time. As we shall see below, a single correlation time is not sufficient to describe atomic motion in glasses and a distribution of correlation times must instead be assumed.

One aim of this study is to use the relaxation time measurements to investigate the possibility of Cu diffusion in the glassy state. The experimental details regarding the relaxation-time measurements are discussed in Sec. II. The effects of atomic motions on T_1^{-1} and T_2^{-1} are summarized in Sec. III. A brief summary of the basic results of a model that has been commonly employed to explain the relaxation effects in glasses is outlined in Sec. IV. In Sec. V, the temperature, frequency, and compositional dependences of both relaxation rates T_1^{-1} and T_2^{-1} of ^{63}Cu NMR are discussed. In Sec. VI we discuss the ^{75}As NQR relaxation effects in glassy Cu-As-Se. Relaxation effects in glassy Cu-As-S are compared with those in Cu-As-Se and reviewed in Sec. VII. In Sec. VIII, we present a general discussion of the relaxation effects of the ^{75}As NQR and ^{63}Cu NMR in the glassy Cu-As-S and Cu-As-Se systems.

II. EXPERIMENTAL PROCEDURE

The glassy samples used in this study were prepared by the method of quenching from the melt as described previously.[2] In this method pure (99.9999%) elemental materials were mixed in evacuated quartz ampoules which were rocked at 575 and 950 °C for the binary and ternary glasses, respectively. Mixtures were then cooled slowly to temperatures slightly higher than the respective glass transition temperatures and then quenched in ice water. Samples then were crushed into small chunks and placed in pyrex tubes to fit inside the NQR or NMR coils.

A standard pulsed NMR spectrometer as described previously[14] was used. The ^{75}As NQR and ^{63}Cu NMR signals were obtained at various temperatures using phase-sensitive detection of the spin echo following the pulse sequence. The general experimental procedure used to obtain the relaxation-time measurements for the As NQR and Cu NMR is outlined in many texts.[15] The spin-spin relaxation time T_2 was determined by measuring the echo amplitude as a function of twice the pulse separation 2τ. The spin-lattice relaxation time T_1 was determined using the standard repetition rate technique where the echo amplitude is measured as a function of repetition time t. Both T_1 and T_2 values were then obtained at different temperatures and NMR frequencies.

A few points concerning the relaxation-time measurements must be addressed before the results are discussed. Due to the large widths of the resonance lines involved in the ^{75}As NQR measurements, only a small fraction of the resonant frequencies contained in the inhomogeneously broadened line is simultaneously excited by the rf pulse. This means that not all nuclei in the vicinity of a "resonant" nucleus are necessarily at resonance. Therefore, the observed dipolar distance between neighboring "resonant" nuclei can be substantially greater than the actual distance between nuclei in the sample. Since the spin-spin interaction is intimately related to this distance, the magnitude of T_2 can be dramatically altered. There is only one broad line in the ^{75}As NQR resonance and the frequency dependence of the relaxation times was investigated by measuring the relaxation times at different frequencies within the same line.

For the NQR measurements, where no external magnetic field is applied, only one transition $[(m=\pm\frac{1}{2})\leftrightarrow(m=\pm\frac{3}{2})]$ exists and the spin echo following a 90°-τ-180° pulse sequence is recorded. For NMR, with a quadrupole perturbation, on the other hand, the $\pm$ degeneracy is removed by the external magnetic field and, for nuclei with spin $I=\frac{3}{2}$ such as Cu, three transitions are allowed. Accordingly, there are three components of the resonance line $[(m=-\frac{1}{2})\leftrightarrow(m=\frac{3}{2})$, $(m=-\frac{1}{2})\leftrightarrow(m=\frac{1}{2}),(m=\frac{1}{2})\leftrightarrow(m=\frac{3}{2})]$ all of which can contribute to the relaxation curves. When there are simultaneous contributions from all three transitions, the relaxation process becomes very complex and it is difficult to determine a meaningful T_1^{-1}. The maximum spectral width imposed by a typical 90° pulse in our experiments was comparable to the width of the central component $(m=-\frac{1}{2}\leftrightarrow m=\frac{1}{2})$ and therefore the satellite contributions to the NMR signal are negligible. Therefore, only the central transition contributes to the measurement. Also, because the entire central component is excited, essentially all nuclei can be considered "resonant" in a given experiment. Two values of the external magnetic field were used to examine the frequency dependence of the relaxation times.

Some of the samples have exhibited partial crystallization during high-temperature measurements. To avoid this problem care was taken by using a fresh piece of the sample after a high-temperature measurement was recorded. For ^{63}Cu NMR, the spin-spin relaxation time T_2 becomes extremely short at higher temperatures and measurements beyond 480 K were not practical. In most of the glasses the ^{75}As NQR signals are already small due to the broad lines involved because only a small fraction of the spin ensemble is excited in a given experiment. The NQR signals were hard to obtain for temperatures above 200 K.

III. TEMPERATURE DEPENDENCE AND ATOMIC MOTION

The temperature dependence of the spin-lattice relaxation rate T_1^{-1} is a useful experimental quantity that can be used to distinguish relaxation mechanisms. An important temperature dependence is the one that results from thermally activated atomic motions. These motions are usually described as instantaneous transitions (jumps) between sites. Such transitions, if thermally activated, are characterized by a correlation frequency $\omega_c=2\pi/\tau_c$ where τ_c is the temperature-dependent correlation time defined as the time spent by the atoms in a given environment.

In nonviscous liquids and many crystalline solids, atomic motion is homogeneous and can be described by a single correlation time τ_c. Nuclear relaxation caused by this type of atomic motion (Debye relaxation) is described by the classic Bloembergen, Purcell, and Pound (BPP) model.[16,17] According to this model, the effectiveness of this relaxation mechanism is determined by the magnitude of the correlation frequency ω_c of the atomic motion with respect to the Larmor frequency ω_L. At low temperatures, the jump frequency ω_c is much smaller than ω_L and the contribution to the spin-lattice relaxation rate by the atomic motion mechanism is negligible. When the temperature is increased so that ω_c and ω_L are comparable, the spin-lattice relaxation mechanism due to atomic motion becomes more effective and reaches a maximum when $\omega_c=\omega_L$. As the temperature increases further so that $\omega_c\gg\omega_L$ (extreme narrowing condition), the effectiveness of this relaxation mechanism decreases with increasing temperature. In this case, the spin-lattice relaxation rate is described by a single BPP spectral density function of the form $j(\omega,\tau)=2\tau/(1+\omega^2\tau^2)$ and the resulting magnetization recovery curves are characterized by a single exponential. In relaxation measurements, this process is described by a plot of $\ln(T_1^{-1})$ versus inverse temperature, where a symmetric characteristic maximum occurs at a temperature where $\omega_L=\omega_c$. When the frequency (or magnetic field) is decreased, the condition

$\omega_c = \omega_L$ is satisfied at a lower correlation frequency (longer correlation time) shifting the peak to a lower temperature (Fig. 1). For this case, the spin-spin relaxation time is well defined because the spin ensemble reaches thermal equilibrium (spin temperature) on a time scale which is very short in comparison with the time involved in transferring the spin energy to the lattice ($T_2^{-1} \gg T_1^{-1}$). The spin-spin relaxation rate also has a simple temperature dependence in which T_2^{-1} remains constant at low temperature ($\omega_c > \omega_L$) and begins to decrease only when $\omega_c = \omega_L$ (motional narrowing). T_2^{-1} is usually several orders of magnitude larger than T_1^{-1} and, when motional narrowing occurs, T_2^{-1} decreases and approaches T_1^{-1} when the temperature is high enough for the extreme narrowing condition to occur.

In a contrasting case, in viscous liquids, glasses,[18-20] and some superionic compounds[21] atomic motion is highly inhomogeneous and cannot be described by a single correlation time τ_c (non-Debye type). In this case, the motion is described by a distribution of correlation times τ_i and the spectral density function is written for each τ_i as $j(\omega,\tau_i) = 2\tau_i/(1+\omega^2\tau_i^2)$. Since the spin-lattice relaxation rate T_1^{-1} is proportional to the ensemble average of $j(\omega,\tau_i)$, there will be a distribution of relaxation rates and the magnetization recovery curves become nonexponential. The nonexponential behavior is related to the inhomogeneities of the spin environment and to the relative values of the individual rates T_{1i}^{-1} and T_2^{-1}. Due to the distribution of correlation times, there will remain inhomogeneities in the spin environment that result in a distribution of relaxation rates. The measured T_1^{-1} will be an inhomogeneous average of this distribution. Since this relaxation process cannot be described by a single BBP spectral density function, the BPP model must be modified to incorporate this fact.

The effects of the distribution of the correlation times are manifested in the shape of the BPP peak. For a homogeneous spin ensemble, the BPP peak occurs at a well-defined correlation time which corresponds to a well-defined temperature. For the inhomogeneous case, the condition $\omega_c = \omega_L$ is satisfied over a wide range of temperatures and the peak in the $\ln(T_1^{-1})$ versus inverse temperature plot is broadened. On the high temperature side of the peak, the correlation time is unique at a given temperature (extreme narrowing condition). Therefore, the distribution in the correlation times is limited to the low-temperature side of the BBP peak, which becomes highly asymmetric. Since this peak is an extension of the simple BPP peak to the inhomogeneous case, it is sometimes called the "modified BPP peak." Since atomic motion is usually thermally activated, the temperature dependence of T_1^{-1} is expected to be proportional to the dependence of the spectral density function on the correlation times. Various spectral distribution functions[16,21] have been introduced to fit the non-BPP type temperature dependences.

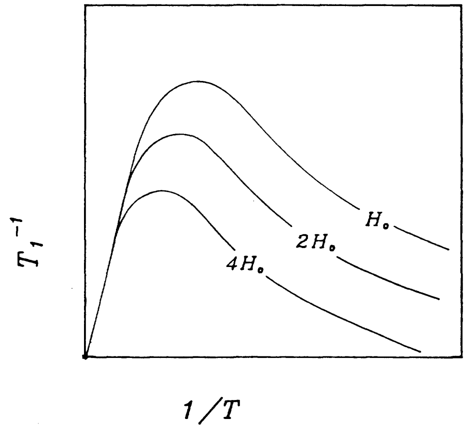

FIG. 1. The temperature and magnetic field dependences of the spin-lattice relaxation rate T_1^{-1} and the shift of the relaxation peak at $\omega_c\tau_c = 1$ with the field.

So far, we have discussed the effects of the distribution of correlation times due to the inhomogeneous ensemble on the spin-lattice relaxation rate T_1^{-1}. If T_2^{-1} remains significantly greater than the largest component of the spin-lattice relaxation rate distribution, the behavior of T_2^{-1} remains well described by the BPP model with simple modifications such as the broadening and asymmetry of the peak. If, on the other hand, some of the T_1^{-1} components become comparable to T_2^{-1} the situation becomes more complicated. The measured decay of the transverse component of the magnetization no longer represents the dephasing time T_2^{-1} but rather a time constant which is driven by the T_1^{-1} process.

IV. PROPOSED MODELS OF RELAXATION IN GLASSES

In the Introduction it was stated that relaxation occurs by means of "local-field fluctuations" of different types. These field fluctuations act as "heat sinks" and transfer energy from the spin system to the lattice until thermal equilibrium is achieved. In most cases, the situation is homogeneous and can be described by a single correlation time. When this occurs, the magnetization recovery curves obey a single exponential decay which defines the measured T_1. The measurements of the relaxation rates in the glassy Cu-As-S and Cu-As-Se systems reveal a decay behavior which cannot be fit by a single exponential curve. This behavior is a characteristic of relaxation in the glassy state and is exhibited by most glasses. According to the previous section, the nonexponential behavior is related to an inhomogeneous environment of the spin ensemble which results in a distribution of the relaxation rates.

Several models that are based on a distribution of relaxation rates have been proposed to explain this behavior. A model, recently proposed by Stöckman and Heitjans,[13] assumes that the increase in the relaxation rates in glasses is due to internal field fluctuations produced by a random distribution of defects called relaxation centers. According to this model, the individual atomic jumps are described by a distribution of correlation times τ_i and the spectral density function is written as $j = j(\omega,\tau_i)$. Furthermore, the individual spins interact directly and independently with a relaxation center which results in a distribution of relaxation rates. Assuming now that each spin interacts with a number of noninteracting, randomly distributed, relaxation centers, the measured spin-lattice relaxation rate of a spin coupled to a number of these relaxation centers is written as[13]

$$T_1^{-1}=\sum a(\mathbf{r}_i)j(\omega,\tau_i)\ , \tag{2}$$

where $a(\mathbf{r}_i)$ is a function representing the coupling of the nuclear spin to a relaxation center i, and $j(\omega,\tau_i)$ is the conventional BPP spectral density function[16,21] which describes the field fluctuations due to that relaxation center. In the BPP formulation (Sec. III), this function is given by the formula

$$j(\omega,\tau)=\frac{2\tau}{1+(\omega\tau)^2}\ . \tag{3}$$

The model then assumes that the spin system reaches thermal equilibrium through *spin diffusion* and distinguishes two limiting cases. The first limiting case is *rapid spin diffusion* where T_1^{-1} is homogeneously averaged over the whole sample, and a single exponential decay of the magnetization is obtained. In other words, the nuclear spins achieve thermal equilibrium among themselves on a time scale which is very short compared with the times involved in transferring the energy of the spin system to the lattice. This average is written as

$$M_{\text{hom}}=M_0\exp[-\langle 1/T_1\rangle t]\ . \tag{4}$$

In this case, the decay of the spin system is described by one time constant and a single spin-lattice relaxation rate T_1^{-1} is defined. This situation corresponds to the simple BPP theory discussed in the previous section. The second limiting case is *slow spin diffusion* where the inhomogeneities of the spin system are not removed and T_1^{-1} is inhomogeneously averaged over the whole sample. In this case, a spin close in distance to a relaxation center (or having a stronger coupling with the relaxation center due to its correlation frequency) may interact significantly with the lattice before thermal equilibrium with the rest of the spins is achieved. Each individual spin relaxes according to a specific rate $\tau_{1_c}^{-1}$ and the measured spin-lattice relaxation of the sample is an inhomogeneous average of these individual relaxation times. This inhomogeneous average is written as[13]

$$M_{\text{inh}}=M_0\langle\exp[-t/T_{1_{\text{inh}}}]\rangle\ . \tag{5}$$

The average in Eq. (5) has been calculated elsewhere[13] for the case of a power-law dependence of the coupling between a spin and a relaxation center of the form $a(\mathbf{r})=a_0(\mathbf{r}_0/\mathbf{r})^6$ where r_0 is the distance between the relaxing nucleus which is the closest distance possible to a relaxation center and a_0 is the corresponding coupling strength. This dependence is appropriate for the dipole-dipole or the quadrupolar interactions which are the important processes for the spin-lattice relaxation measurements described in this work. The result is[13]

$$M_{\text{inh}}=M_0\exp[-(t/T_{1_{\text{inh}}})^{1/2}]\ , \tag{6a}$$

with

$$T_{1_{\text{inh}}}=\{(\tfrac{4}{3})\pi^{3/2}r_0^3a_0^{1/2}\int[j(\omega,\tau)]^{1/2}n_\tau(\tau)d\tau\}^{-1/2}\ . \tag{6b}$$

The function $j(\omega,\tau)$ is the spectral density function defined above and n_τ is the density of relaxation centers. In the case of a thermally activated relaxation process, the correlation time τ_c has an Arhenius-type temperature dependence of the form

$$\tau_c=\tau_0\exp[\Delta E/kT]\ , \tag{7}$$

where τ_0 is the prefactor and ΔE is the activation energy. τ_0 is the correlation time due to phonons which is typically about 10^{-12} sec (phonon frequency 10^{12} Hz).

V. ^{63}Cu NMR RELAXATION EFFECTS IN THE Cu-As-Se GLASSY SYSTEM

The effects of glass composition, temperature, and resonant frequency on the relaxation rates of ^{63}Cu NMR are now considered. The frequency dependences were studied by measuring the relaxation time constants T_1 and T_2 at different magnetic fields that correspond to different ^{63}Cu resonant frequencies. As we have mentioned earlier, out of the three components of the NMR spectra with quadrupole perturbation essentially only the central one is observed. This central transition has a linewidth which is on the order of the spectral width provided by the 90° pulse. Contrary to the NQR measurements, all copper nuclei in the glassy samples are simultaneously resonant in a given NMR experiment and the measured T_2 will, therefore, reflect the actual separation between Cu nuclei. The transverse relaxation time measurements are considered first.

The ^{63}Cu NMR magnetization, as measured experimentally by the echo amplitude as a function of 2τ following a 90°-τ-180° pulse sequence, has a well-defined exponential decay at all times. This behavior is maintained at all temperatures. In Fig. 2, a sample of these tran-

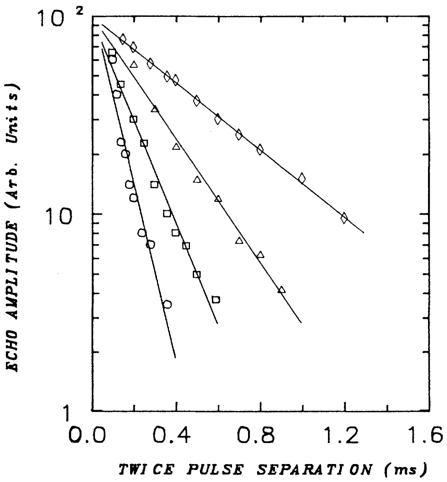

FIG. 2. ^{63}Cu NMR echo amplitude (arbitrary units) vs twice pulse separation (2τ) of $Cu_{0.15}(As_{0.4}Se_{0.6})_{0.85}$ for different temperatures: diamonds, 250 K; triangles, 300 K; squares, 320 K; circles, 350 K. Contrary to ^{75}As NQR, these curves consist of a simple exponential decay.

sients obtained at different temperatures is shown for glassy $Cu_{0.15}(As_{0.4}Se_{0.6})_{0.85}$. A characteristic time constant can easily be extracted by measuring the time which corresponds to the $1/e$ value of the maximum amplitude (extrapolation to $2\tau=0$) of these curves. The temperature dependence of T_2 is obtained by plotting these values as a function of temperature. Figure 3 shows the compositional dependence of the spin-spin relaxation time T_2. In this figure is shown a sample of decay curves obtained at 77 K for several compositions in the glassy Cu-As-Se system. In $Cu_x(As_{0.4}Se_{0.6})_{1-x}$, the decay becomes less rapid (longer T_2) as x is decreased. This result is qualitatively consistent with the fact that the effective distance between copper atoms increases as their concentration in the sample is decreased (more dilute). An increase in T_2 can, in principle, be accompanied by a decrease in the linewidth, but in this case the quadrupolar interaction makes the dipolar contribution to the linewidth negligible.

To examine the T_2 dependence on the copper concentration and consequently on the average Cu-Cu distance we calculate the second moment of the linewidth. The second moment is intimately related to T_2. In these calculations we assume a random distribution of copper atoms in the glass. For a system of spin $\frac{3}{2}$ nuclei (Cu and As), the second moment M_2 due to the dipole-dipole interaction is given by[21,22] (SI units).

$$M_2=(\tfrac{3}{5})I(I+1)(\mu_0/4\pi)^2\gamma^4\hbar^2\sum r_{ij}^{-6} , \tag{8}$$

where I is the nuclear spin, $\mu_0/4\pi=10^{-7}$ is the permeability of free space, γ is the gyromagnetic ratio, $\hbar$ is the Planck's constant divided by 2π, and r_{ij} is the separation between the ith and jth copper atoms. For Gaussian lines, the dipolar linewidth is related to the second moment by the relation[22]

$$\Delta\nu(\mathrm{FWHM})=(8\ln 2M_2)^{1/2} , \tag{9}$$

where $\Delta\nu$(FWHM) is the full width at half maximum measured in Hz. Equation (9) is derived for Gaussian lines but since we are interested in a crude estimate of the linewidth, this formula can be applied to Lorentzian lines with an error of about ±20%. The dipolar linewidth assuming a random distribution of copper atoms is calculated elsewhere[22] and is given by (SI units)

$$\Delta\nu(\mathrm{FWHM})=\left[\frac{4\sqrt{5}}{3\sqrt{3}}\right]\pi^2\left[\frac{\mu_0}{4\pi}\right]\gamma^2 hn , \tag{10}$$

where n is the nuclear spin density in spins per cubic meter. The spin-spin relaxation time T_2 is related to the dipolar linewidth by

$$T_2=1/[\pi\Delta\nu(\mathrm{FWHM})] . \tag{11}$$

Using these equations we calculate T_2^{-1} as a function of copper concentration x and compare the results with the experimental data in Fig. 4. Although only three points are available in this figure, these data suggest that the experimental results appear to depend linearly on x or on r^{-3} which is what one would expect for the dipole-dipole interactions that are responsible for T_2. It is also apparent from Fig. 4 that the experimental results are significantly less than the calculated values. This discrepancy appears to be larger than the 20% error due to the Gaussian approximation used in the linewidth calculations. Therefore, the smaller values of T_2 observed experimentally may be due to a clustering effect where the actual Cu-Cu separation r within a cluster is smaller than the one predicted by assuming a random distribution of copper atoms. Using Fig. 4, one could estimate roughly the average Cu-Cu separation within the clusters if information were available about the cluster sizes.

To determine the temperature and frequency dependences, the spin-spin relaxation time T_2 is plotted as a function of temperature for each glassy composition. These measurements are then obtained at different magnetic fields (or Larmor frequencies). Plots of the relaxa-

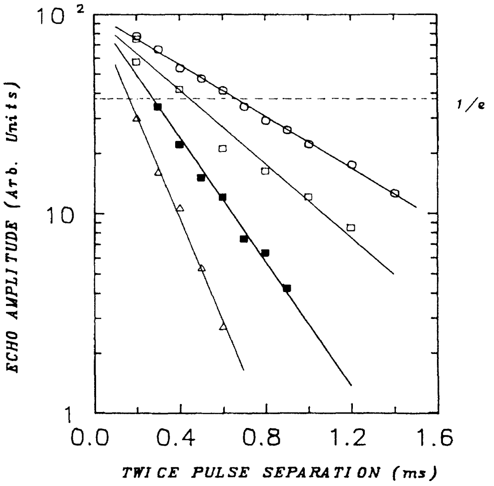

FIG. 3. ^{63}Cu NMR echo amplitude vs twice pulse separation (2τ) obtained at 77 K for the $Cu_x(As_{0.4}Se_{0.6})_{1-x}$ system with various copper concentrations x: circles, $x=0.05$; squares, $x=0.15$; triangles, $x=0.23$. The solid squares denote the composition $(Cu_{2/3}Se_{1/3})_y(As_{0.4}Se_{0.6})_{1-y}$, where $x=(2/3)y=0.15$.

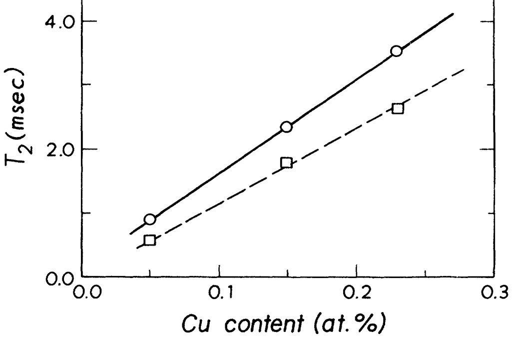

FIG. 4. Experimental (squares and dashed line) and calculated (circles and solid line) spin-spin relaxation time T_2 of ^{63}Cu NMR vs copper concentration x. See text for details.

tion rates T_2^{-1} versus inverse temperature $(1000/T)$ for $x=0.053$, 0.15, and 0.23 in glassy $Cu_x(As_{0.4}Se_{0.6})_{1-x}$ are shown in Fig. 5. These data were obtained at a magnetic field $H_0=8.45$ T. Also shown in Fig. 5 are similar data obtained at a lower magnetic field $H_0=4.45$ T for one of these glasses $(x=0.15)$. For $T<300$ K, T_2^{-1} is essentially unchanged with temperature. As T approaches room temperature (300 K), a sharp increase of T_2^{-1} is observed which is anomalous for a dipole-dipole relaxation without atomic motion.

More information about the dynamics of the system can generally be obtained by examining the spin-lattice relaxation rate T_1^{-1}. As was stated in the Introduction, the most probable relaxation mechanism for ^{63}Cu in these glasses at high temperatures is the one due to the diffusive motion of copper and concomitant fluctuations in the local-electric-field gradients. We now consider the effect of these fluctuations on the spin-lattice relaxation time T_1.

To obtain T_1 the magnetization recovery is monitored as a function of the time between two successive pulse sequences (repetition rate technique). A set of such plots obtained at different temperatures for $Cu_{0.15}(As_{0.4}Se_{0.6})_{0.85}$ is shown in Fig. 6. Ordinarily, the plot of this magnetization recovery should yield an exponential decay. The curves in this figure clearly show nonexponential decays. As was discussed in Sec. III, based on the model proposed by Stöckman,[13] this behavior is characteristic of dilute systems and also of the glassy state in many cases. Such nonexponential behavior is somewhat surprising for systems in which the nuclear spins are not dilute. Further implications will be discussed in Sec. VIII.

The curves in Fig. 6 do not have constant slopes and therefore do not define a characteristic time constant. Instead, these curves represent a continuous distribution of relaxation rates so that only an inhomogeneous average of the time constant $T_{1_{\rm inh}}$ can be obtained from the experimental data. This inhomogeneous average can be extracted using the arguments of Sec. III. In Fig. 7 we replot the data of Fig. 6 using the square root of time $t^{1/2}$ instead of t itself. The experimental data exhibit an excellent fit to the stretched exponential in Eq. (6a) which was derived for the case of *slow spin diffusion.*

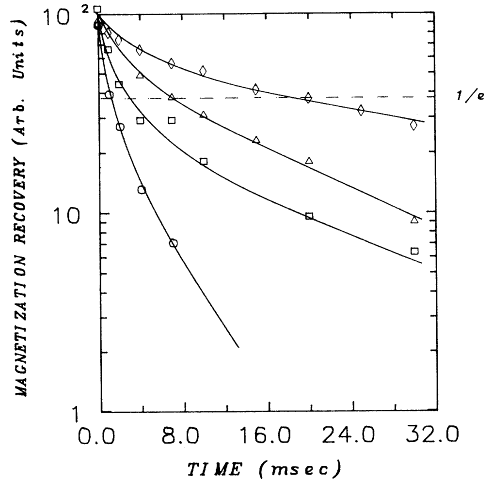

FIG. 6. ^{63}Cu magnetization recovery vs time for $Cu_{0.15}(As_{0.4}Se_{0.6})_{0.85}$ obtained at different temperatures: circles, 380 K; squares, 330 K; triangles, 300 K; diamonds, 200 K.

The temperature dependences of the ^{63}Cu NMR spin-lattice relaxation time T_1, obtained at a magnetic field $H_0=8.45$ T, are summarized in Fig. 8. There are three glassy samples represented in this figure. Two of these samples are glasses made with $x=0.05$ and $x=0.15$ along the $Cu_x(As_{0.4}Se_{0.6})_{1-x}$ composition line. The third sample is a glass made with $x=(\frac{2}{3})y=0.15$ along the

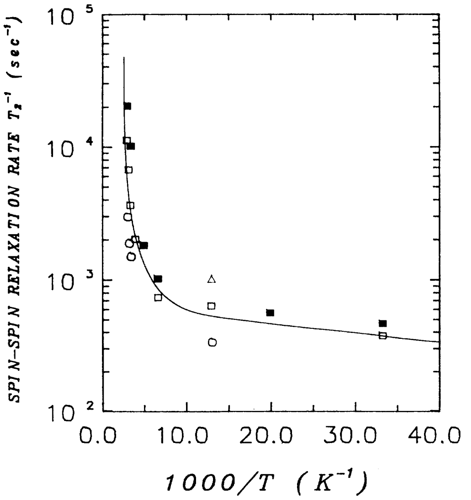

FIG. 5. Temperature dependences of the spin-spin relaxation rate T_2^{-1} of ^{63}Cu NMR obtained at (open symbols) $H_0=8.45$ T; (Solid symbols) $H_0=4.25$ T in $Cu_x(As_{0.4}Se_{0.6})_{1-x}$: (circles) $x=0.053$, (squares) $x=0.15$, (triangles) $x=0.23$.

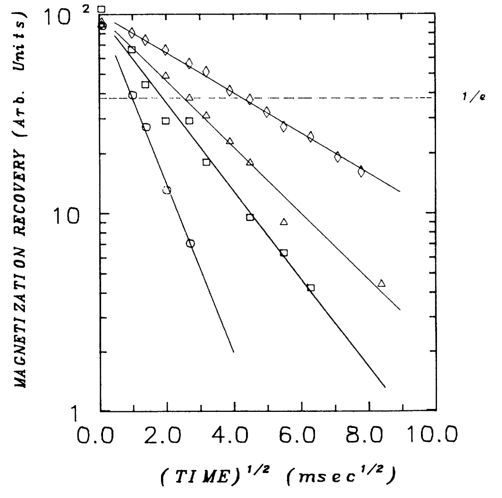

FIG. 7. ^{63}Cu NMR magnetization recovery vs square root of repetition period $(t^{1/2})$ for $Cu_{0.15}(As_{0.4}Se_{0.6})_{0.85}$ obtained at different temperatures: circles, 380 K; squares, 330 K; triangles, 300 K; diamonds, 200 K. See text for details.

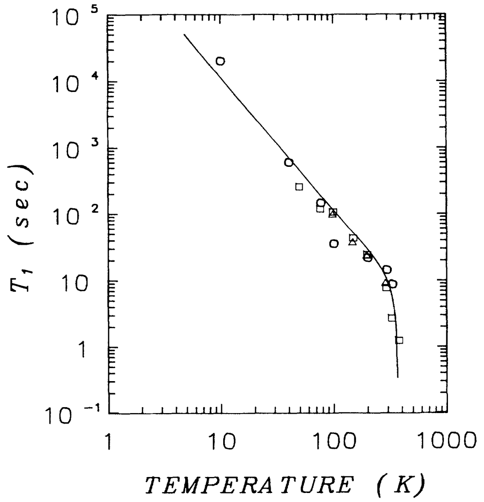

FIG. 8. ^{63}Cu NMR relaxation time T_1 vs temperature T for different glassy compositions: (circles) $Cu_{0.15}(As_{0.4}Se_{0.6})_{0.85}$, (squares) $Cu_{0.05}(As_{0.4}Se_{0.6})_{0.95}$, and (triangles) $(Cu_{2/3}Se_{1/3})_y(As_{0.4}Se_{0.6})_{1-y}$, with $x=(2/3)y=0.15$.

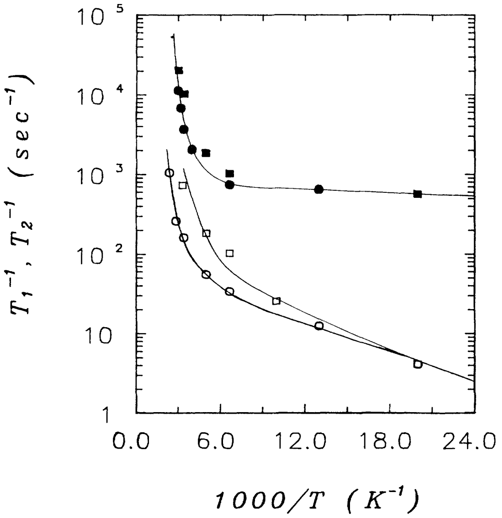

FIG. 9. ^{63}Cu NMR measurements of T_1^{-1} (open symbols) and T_2^{-1} (solid symbols) vs temperature (for $T>300$ K) in $Cu_{0.15}(As_{0.4}Se_{0.6})_{0.85}$. Data were obtained at two different fields: (circles) $H_0=8.45$ T and (squares) $H_0=4.25$ T.

$(Cu_{2/3}Se_{1/3})_y(As_{0.4}Se_{0.6})_{1-y}$ composition. As shown in Fig. 8, there is essentially no dependence of T_1 on composition within experimental error. Two temperature regimes are clearly distinguished in Fig. 8. For $T<300$ K, there is a weak power-law temperature dependence of T_1 ($T_1 \propto T^{\alpha}$ with $\alpha=2\pm0.2$) which is similar to those observed for the ^{75}As, ^{11}B, ^{23}Na, and other NMR and NQR results in both chalcogenide and oxide glasses.[7,8,23–25] (The ^{75}As NQR measurements of T_1 and T_2 for the Cu-As-Se glass are discussed in Sec. VI.) The T_1 data in this temperature region ($T<300$ K) are consistent with the power-law dependences commonly observed in glasses. These similarities between the previously published data[7,8,23–25] and the Cu NMR suggest that Raman-like processes are probably responsible for the relaxation of the copper nuclei in the lower temperature region ($T<300$ K).

As T approaches 300 K, T_1 of the copper resonance begins to decrease rapidly with increasing temperature. The temperature scale displayed in Fig. 8 is not suitable for clear analysis of the dramatic change in the temperature dependence of T_1. Therefore, the data shown in Fig. 5 (T_2 data) and Fig. 8 (T_1 data) are displayed in Fig. 9 on an expanded scale. The relaxation rates T_1^{-1} (open symbols) and T_2^{-1} (solid symbols) are plotted versus inverse temperature (1000/T) in this figure. The circles and squares in this figure denote the data obtained at high field ($H_0=8.45$ T) and low field ($H_0=4.25$ T), respectively. As clearly shown in Fig. 9, there is a sharp increase with temperature in both relaxation rates which begins to occur at about the same temperature (300 K).

In light of the discussion presented in the Introduction a maximum relaxation rate occurs when the correlation frequencies of the diffusive motions of the copper nuclei are on the order of the Larmor frequency, i.e., $\omega_c=\omega_L$. Assuming that $\omega_c(=2\pi/\tau_c)$ is thermally activated, the condition $\omega_c=\omega_L$ can, in principle, be satisfied by changing the temperature of the sample. The sharp increase of T_1^{-1} is an indication that the correlation frequency ω_c of the diffusive movements of the copper atoms is beginning to approach the Larmor frequency ($\omega_c \rightarrow \omega_L$). Of course, the inhomogeneous nature of the spin-lattice relaxation processes strongly suggests that there is no unique correlation time at temperatures below the maximum in T_1^{-1}. In fact, this dramatic increase of T_1^{-1} represents the low-temperature side of the modified BPP peak which is expected to occur at a higher temperature where the condition $\omega_L=\omega_c$ is satisfied. Other evidence which supports this interpretation is the observed frequency dependence of T_1^{-1} shown in Fig. 9 (c.f., Fig. 1). We were unable to reach the modified BPP peak in the temperature range available.

VI. ^{75}As NQR RELAXATION EFFECTS IN THE Cu-As-Se GLASSY SYSTEM

In the previous section we discussed the relaxation effects in the NMR measurements on the copper nuclei in the Cu-As-Se glassy system. In this section the effects of copper concentration x, NQR frequency, and temperature on the ^{75}As NQR relaxation rates are discussed. Contrary to the ^{63}Cu NMR measurements, the ^{75}As NQR measurements cannot be extended over the same temperature range. The ^{75}As NQR signals are considerably weaker in general than those of copper due to the much broader ^{75}As NQR linewidths.[2] The ^{75}As relaxation effects have been investigated previously[7,26] in amorphous As and the binary glasses As_2Se_3 and A_2S_3.

The effect of copper concentration x on the magnetization decay curves (T_2) is shown in Fig. 10. The magnetization decay versus twice the time delay between the two pulses (2τ) is shown for different copper concentrations x in the glassy $Cu_x(As_{0.4}S_{0.6})_{1-x}$ and $Cu_x(As_{0.4}Se_{0.6})_{1-x}$.

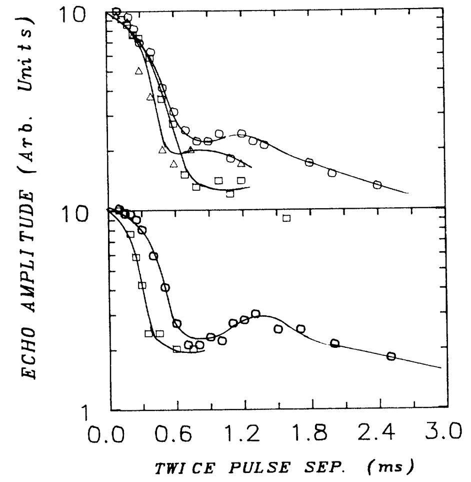

FIG. 10. ^{75}As NQR echo intensity vs twice pulse separation (2τ) for various glassy compositions. (Upper) $Cu_x(As_{0.4}S_{0.6})_{1-x}$: circles, $x=0.00$; squares, $x=0.04$; triangles, $x=0.06$. (Lower) $Cu_x(As_{0.4}Se_{0.6})_{1-x}$: circles, $x=0.00$; squares, $x=0.15$. All curves are normalized to the same amplitude at $2\tau=0$.

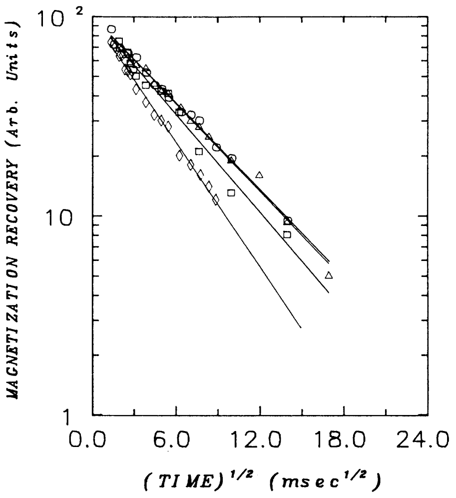

FIG. 11. ^{75}As NQR magnetization recovery vs square root of time ($t^{1/2}$) for different copper concentrations x in $Cu_x(As_{0.4}Se_{0.6})_{1-x}$: (triangles) $x=0.00$ obtained at 58 MHz, (squares and circles) $x=0.15$ obtained at 58 and 78 MHz, respectively. Diamond symbols denote data for the $As_{0.50}Se_{0.50}$ glass obtained at 78 MHz.

The data for $x=0.0$ are in agreement with the results observed previously.[23] In these curves there is an obvious nonexponential, and even nonmonotonic, time dependence of the magnetization decay in both glassy systems.

The magnetization begins with a Gaussian decay, followed by a slight increase and finally an exponential decay thereafter. The reason for the nonmonotonic behavior, which occurs in both glasses at about $2\tau=0.7$ msec, and has been observed previously,[8,23] is not yet known. As copper concentration x increases the initial decay, which remains Gaussian, becomes more rapid in both systems.

As in the ^{63}Cu NMR measurements, the spin-lattice relaxation time of ^{75}As NQR is obtained by plotting the ^{75}As NQR magnetization recovery amplitude as a function of time. These plots indicate relaxation recovery curves which are not exponential but seem to fit a stretched exponential of the form obtained in Eq. (6a) for the inhomogeneous average. A set of these ^{75}As NQR magnetization recovery amplitudes, plotted as a function of the square root of time ($t^{1/2}$), is shown in Fig. 11. The symbols in this figure denote the NQR experimental data while the straight lines denote the stretched exponential fits. As clearly shown in Fig. 11, the stretched exponential lines fit the data fairly well. We take this result to suggest that the spin-diffusion process which dominates the interactions among the As nuclear spins is slow. The open triangles in Fig. 11 denote data for the binary glass As_2Se_3 which agree with the data obtained previously.[23] The circles and squares denote data for the samples with $x=0.15$ in the $Cu_x(As_{0.4}Se_{0.6})_{1-x}$ system obtained at 78 MHz and 58 MHz, respectively. These two NQR frequencies have been attributed[2] to a local structural environment which contains one As-As bond per As site (78 MHz) and one with no As-As bonds (58 MHz). The diamond symbols denote data for an As-rich glass ($As_{0.5}Se_{0.5}$) obtained at 78 MHz where, according to Ref. 2, there is one As-As bond per As site. The triangles, circles, and squares show essentially no dependence of T_1 on the composition or frequency within experimental error.

In other chalcogenide glasses previous authors[8,24,26] have reported a temperature dependence for the ^{75}As NQR spin-lattice relaxation rate T_1^{-1} which is proportional to $T^{-\alpha}$ where $1 \leq \alpha \leq 2$, depending on the glass composition. When copper is added to these glasses the As NQR lines become even broader. The widths of the NQR lines of the ^{75}As resonance, which are greater than 20 MHz in some glasses,[2] reduce the signal intensities substantially. This reduction in the NQR signals limits the ^{75}As relaxation measurements to temperatures below 200 K in most copper containing glasses. Consequently, it is much more difficult to study the high-temperature effects in T_1 of the ^{75}As resonance.

The T_1 temperature dependences of the ^{75}As NQR for glasses with copper concentrations $x=0.00$ (dashed line) and $x=0.15$ (solid squares) in the $Cu_x(As_{0.4}Se_{0.6})_{1-x}$ system are shown in Fig. 12. The data for $x=0.00$ (glassy As_2Se_3) were obtained previously.[23] As clearly shown in Fig. 12, T_1 for the sample with $x=0.15$ seems to follow a weaker temperature dependence in comparison with the sample with $x=0.00$ in the $Cu_x(As_{0.4}Se_{0.6})_{1-x}$ system. In the As_2Se_3($x=0.00$), Jellison, Peterson, and Taylor[23] reported a $T^{-1.8}$ dependence compared with a $T^{-1.3}$ dependence which we observe for the sample with $x=0.15$. The weaker temperature dependence of As NQR for the copper containing glass can be interpreted in terms of the existence of a nonconstant distribution of the energy barriers which separate the two metastable equilibrium states of the disorder modes.

Also shown in Fig. 12 are the T_1 data for the ^{63}Cu NMR, reproduced from Fig. 8, for $x=0.05$ (open circles)

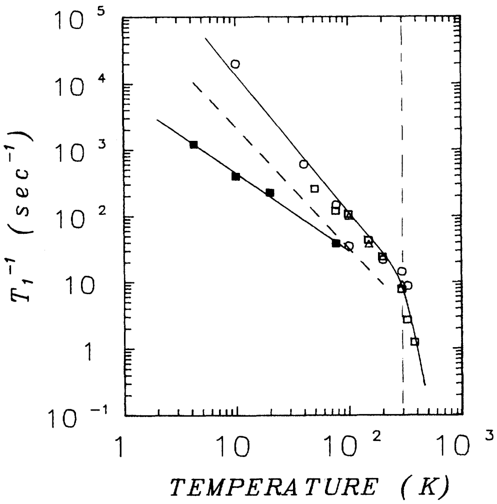

FIG. 12. ^{75}As NQR spin-lattice relaxation time T_1 vs temperature for $T < 300$ K: (Dashed line) As_2Se_3 at 58 MHz (after Taylor, Ref. 26); (solid squares) $Cu_{0.15}(As_{0.4}Se_{0.6})_{0.85}$ at 58 MHz. Also shown are the low temperature ($T < 300$ K) data for T_1^{-1} of ^{63}Cu NMR vs temperature for $Cu_{0.15}(As_{0.4}Se_{0.6})_{0.85}$ replotted for comparison from Fig. 8 using the same symbols.

and for $x = 0.15$ (open squares) in the $Cu_x(As_{0.4}Se_{0.6})_{1-x}$ glassy system. The open triangles in Fig. 12 denote ^{63}Cu T_1 data for a glass with $x = (\frac{2}{3})y = 0.15$ along the $(Cu_{2/3}Se_{1/3})_y(As_{2/5}Se_{3/5})_{1-y}$ system. In the low-temperature region ($T < 300$ K) the ^{63}Cu NMR data of Fig. 12 follow a power-law temperature dependence similar to the one obtained for ^{75}As NQR for most glasses ($T^{-\alpha}$ with $\alpha = 2 \pm 0.2$). These results strongly support the "universality" of the weak temperature dependence for all nuclei studied to date in the chalcogenide and a large number of nuclei in the oxide glasses.[4,23–25]

VII. RELAXATION EFFECTS IN THE Cu-As-S GLASSY SYSTEM

The small glass-forming region in the Cu-As-S system makes it difficult to study the relatively weak dependence of the spin-lattice relaxation rates on Cu concentration. In addition, since this glass forming region is limited to small copper concentrations ($x = 0$ to 0.06), the ^{63}Cu NMR signals are severely diminished and the temperature dependences for $T > 300$ K are not accessible. Preliminary Cu NMR measurements in this system suggest, however, that the relaxation times are similar to those obtained above for the Cu-As-Se glasses. Therefore, it can be argued that these similarities in the behaviors of the relaxation times are indications that the relaxation mechanisms are probably similar in both glasses, at least in the low temperature range ($T < 300$ K). The stretched exponential T_1^{-1} decay curves of ^{75}As NQR obtained at 77 K are shown in Fig. 13, for glassy $Cu_x(As_{0.4}S_{0.6})_{1-x}$ with $x = 0.00$, $x = 0.02$, $x = 0.04$, and $x = 0.06$. In this figure, the magnetization recovery is plotted as a function of $t^{1/2}$. The various symbols denote the experimental data while the straight lines denote the stretched exponential fits derived from Eq. (6a). In contrast to the Cu-As-Se system, the data in Fig. 13 show a slight dependence of T_1 on the copper concentration x. This compositional dependence is too weak, however, to draw any meaningful conclusions.

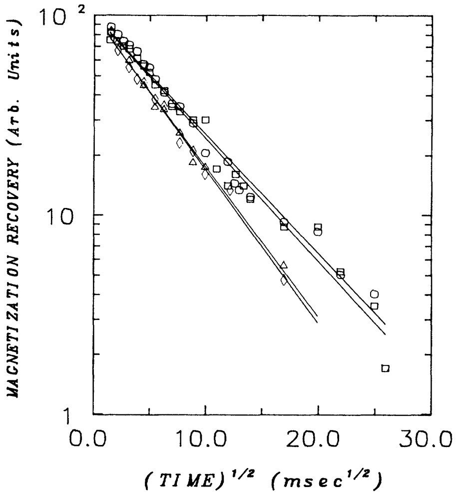

FIG. 13. ^{75}As NQR relaxation recovery vs the square root of time ($t^{1/2}$) obtained at 77 K in $Cu_x(As_{0.4}S_{0.6})_{1-x}$ for different copper concentrations x: circles, $x = 0.00$; squares, $x = 0.02$; triangles, $x = 0.04$; and diamonds, $x = 0.06$. All data were obtained at 73 MHz.

VIII. DISCUSSION

The relaxation-time measurements provide valuable microscopic information concerning the various transport and optical properties of amorphous semiconductors. In the metal-chalcogenide glasses these measurements can provide specific information about the inhomogeneities, low-frequency disorder modes and local atomic diffusion. The spin-lattice relaxation measurements of Cu NMR for Cu-As-Se and Cu-As-S glassy systems suggest that the spin-lattice relaxation rate T_1^{-1} is probably dominated by the two relaxation mechanisms discussed in Sec. I depending on the temperature. For $T < 300$ K, T_1^{-1} of ^{63}Cu NMR and ^{75}As NQR exhibits a weak temperature dependence which has been frequently observed for As in the chalcogenide and for other nuclei in the oxide glasses.[4,8,23] These results have been explained in terms of Raman-like processes which involve the excitation and de-excitation of two disorder modes or of one phonon and one disorder mode.[3,5]

Rubinstein *et al.*[3] showed that a power-law temperature dependence of the form $T_1 = T^{-\alpha}$ ($1 \leq \alpha \leq 2$) is expected in this case. The dependence of the parameter α on glass structure is related to the distribution of energy barriers between the two metastable equilibrium states of the disorder modes (density of states). This density of states is thought to be essentially independent of energy. Previous models[3,5] predict that a constant density of states of the disorder modes would yield $\alpha = 2$ and that departures from this value are probably indications of an energy-dependent density of states. A density of disorder modes that decreases with increasing energy yields $\alpha < 2$, and vice versa. The temperature dependence of T_1 for the ^{63}Cu NMR shows a similar power-law dependence with $\alpha = 2 \pm 0.2$. This value, which does not appear to be strongly affected by the copper concentration in the Cu-As-Se glassy systems, falls within the range of results observed previously.[8,23–25] This result suggests that the density of states of the disorder modes remains relatively unchanged as copper is added to the glass. One expects such insensitive behavior since the low-temperature specific heats, which probe these disorder modes more directly, are remarkably insensitive to glass composition and structure.[4,6] Preliminary measurements for the Cu-As-S glassy system indicate that the temperature dependence is probably similar.

Similar weak temperature dependences are also observed for T_1^{-1} using ^{75}As NQR in the Cu-As-S and Cu-As-Se glassy systems. For ^{75}As NQR, however, the parameter α in the $T_1^{-1} = T^{\alpha}$ power law seems to decrease appreciably as x increases in the $Cu_x(As_{0.4}Se_{0.6})_{1-x}$ glassy system. This decrease in α is probably due to a decrease in the density of states of the disorder modes with energy as discussed above. The smaller value of α for ^{75}As NQR when $x = 0.15$ (Fig. 12) may be consistent with the fact that the glass structure becomes "harder" (more highly coordinated) as Cu is added.[27]

At higher temperatures ($T > 300$ K) the situation is different. For ^{63}Cu NMR, the signals are generally strong and the measurements can be obtained at considerably higher temperatures. T_1^{-1} is found to increase rapidly with increasing temperature for $T > 300$ K. We take this deviation from the weak temperature dependence at lower temperatures to suggest that a more efficient mechanism dominates the relaxation processes for $T > 300$ K. Previous NMR measurements[18,28] have exhibited similar behaviors for Ag and Li in the $(AgI)_x(Ag_2SGeS_2)_{1-x}$ and the LiI_3 superionic compounds, respectively. Ionic conductivity measurements[18,28] obtained in these compounds, suggest that the increase of T_1^{-1} is related to the thermally activated motion of the metal ions. These results have been interpreted by a modified version of the classic Bloembergen, Purcell, and Pound (BPP) model.[16,17] This model, which was originally proposed to explain nuclear relaxation due to atomic motion in liquids, was modified to explain the relaxation results due to atomic motion in the superionic compounds. These modifications, which assume a distribution of correlation times to describe atomic motion, are consistent with the asymmetric broadening of the BPP peak observed in these compounds (Sec. III).

The increase of the ionic conductivity for $T > 300$ K, observed previously[9] in glassy Ag-As-S is probably due to the atomic diffusion of Ag. This result, combined with the results obtained for the superionic compounds, has led us to suggest that the sharp increase of T_1^{-1} for ^{63}Cu NMR in glassy Cu-As-Se for $T > 300$ K is probably induced by local diffusion of Cu atoms. If atomic motion does indeed occur in this glassy system, then the sharp increase of T_1^{-1} of ^{63}Cu NMR can be interpreted by the BPP model (Sec. III) with two additional complications.

First, atomic motion in glasses is much more complex than that in liquids and most crystals. In contrast to atomic motion in liquids, this motion is inhomogeneous and cannot be described by a single correlation time. Instead, it may be described by a distribution of correlation times. Since T_1^{-1} depends on these correlation rates, there may result a distribution of relaxation rates. The inhomogeneities of the spin environment are manifested in the nonexponential behavior of the magnetization recovery curves. The measured spin-lattice relaxation rate T_1^{-1} of the sample may then be taken as an inhomogeneous average of this distribution as described in Sec. IV.

It is surprising that a system (^{63}Cu NMR) that appears to have a well-defined value of T_2 will nonetheless exhibit an inhomogeneous distribution of T_1 values. It is perhaps even more surprising that this inhomogeneous distribution continues as the Cu atoms begin to diffuse locally. Although it is by no means certain, we believe that this behavior results from clustering of the Cu atoms in these glasses. Clustering is suggested from the calculations for T_2 as shown in Fig. 4. If the clusters of copper atoms are sufficiently separated, they may relax at different rates even though the copper may be moving locally within a cluster. The lack of any ionic contribution to the electrical conductivity in these glasses[29] is consistent with this picture.

One can explain the inhomogeneous behavior of T_1 in the ^{75}As NQR experiments more easily, because in this case the linewidths are so broad that only a small number of the total As sites is excited (those that have NQR frequencies within $\Delta\nu$ of the exciting frequency). In this case one might expect the spin diffusion between mutually resonant nuclei to be slow.

One effect of a distribution in spin-lattice relaxation rates on the BPP model is that the BPP maxima in the spin-lattice relaxation rates of the individual spins may occur over a range of temperatures (or correlation times). The distribution of the correlation times is limited, however, to the low-temperature side of the peak because on the high temperature side (extreme narrowing condition), the correlation time is unique. Only the low-temperature side of the peak has been observed in this study. Because of this fact, measurements of the spin-lattice relaxation time in the rotating frame $T_{1\rho}$ may be useful to probe the atomic motion more accurately.[30]

The second, and perhaps more serious, departure from the modified BPP model in these glasses arises when the magnitudes of T_1^{-1} and T_2^{-1} become comparable. When the interactions between the individual spins and the lattice are rapid enough so that some components of the inhomogeneous distribution of T_1^{-1} overlap with T_2^{-1}, then there must be interactions between some of the clusters. If this does indeed occur, then the spin diffusion rates will increase and, of course, the dispersion in T_1^{-1} must decrease. The high temperature data for T_1 in Fig. 7 ($T > 300$ K) can be fit by a single exponential as well as by an exponential in $t^{1/2}$. This fact may indicate that the sample is becoming more homogeneous as far as the ^{63}Cu NMR is concerned.

According to the above discussion, the rapidly increasing spin-lattice relaxation rates in glassy

$Cu_x(As_{0.4}Se_{0.6})_{1-x}$ for $T > 300$ K, are suggestive of a diffusive motion of the copper atoms, although the behavior is more complicated than the classic BPP model. The nonexponential nature of the relaxation rates in this temperature range indicates that there remain inhomogeneities in the environments of the copper spins. These inhomogeneities cause the individual spins to interact differently with the lattice producing a distribution of T_1^{-1}. One would expect the copper diffusion to be thermally activated and the relaxation rates to reach the modified BPP peak as the correlation frequency approaches the Larmor frequency. Clearly, this peak has not been reached in the temperature range available in this study. This temperature range, however, may be the only range available for measurements on these systems because increasing the temperature beyond 480 K, introduces partial crystallization of the samples. Even at about 500 K we observe no decrease of T_1^{-1} suggesting that a considerably higher temperature is needed to access the BPP peak.

The T_2 transients of ^{75}As NQR in the Cu-As-S and Cu-As-Se glassy systems are also not well understood. These transients start with a Gaussian decay followed by a slight increase and then decay exponentially thereafter. The nonmonotonic behavior in the T_2 transients has been observed previously[7] for ^{75}As NQR in the binary As_2S_3 and As_2Se_3 systems. The origin of this behavior is not known.

Since the temperature range available for this study is not high enough to obtain the BPP peak in T_1^{-1}, we can only speculate that the anomalous increase in T_2^{-1} above 300 K (Fig. 9) is probably driven by increasing interactions between clusters. Any further conclusion requires the determination of the width parameter of the distribution of correlation times and consequently of the relaxation times. The importance of this parameter lies in the fact that it can determine the components of T_1^{-1}. This parameter may be determined by the Cole-Davidson distribution function which has been used successfully to fit the temperature dependences of the relaxation rates in many inhomogeneous systems.[17,31] This distribution can only be determined, however, when the BPP peak is well defined.

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