Effects of Network Topology on Low-Temperature Relaxation in Ge-As-Se Glasses, as Probed by Persistent Infrared Spectral Hole Burning

S. P. Love and A. J. Sievers
Laboratory of Atomic and Solid State Physics and Materials Science Center, Cornell University, Ithaca, New York 14853-2501

B. L. Halfpap and S. M. Lindsay
Department of Physics, Arizona State University, Tempe, Arizona 85287-1604

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The relaxation of persistent infrared spectral holes burned in the SeH vibrational absorption band at 1.5 K is studied for ten glass compositions in the Ge-As-Se system. It is found that the dominant spectral-hole relaxation rate increases by over 3 orders of magnitude as the average atomic coordination number varies from 2.0 to 2.8. Over the composition range studied, the quantitative form of the nonexponential hole relaxation depends solely on the average coordination number, independent of chemical composition.

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The role of microscopic topology in determining the properties of glass-forming compounds has been explored theoretically for several years. The concept of an average atomic coordination number was used by Phillips[1] in constraint-counting arguments explaining the strong glass-forming tendency of certain alloy compositions. These ideas were later refined by Thorpe and coworkers,[2-4] who, by evaluating the number of zero-frequency "floppy" modes as a function of the coordination number, predicted a rigidity percolation transition from a soft to a rigid structure should occur at a coordination number of 2.4.

The ternary Ge-As-Se system is particularly well suited to testing the validity of these topological concepts because its large glass-forming region makes it possible for a given value of the average coordination number $\langle r \rangle$ (given in this case by $\langle r \rangle = 4X_{\mathrm{Ge}} + 3X_{\mathrm{As}} + 2X_{\mathrm{Se}}$, where X is the mole fraction) to be realized with a continuous range of chemical compositions, allowing purely topological effects to be distinguished from chemical effects. Recent high-temperature experiments[5] on this system have shown the relevance of the average coordination number in determining the behavior of glass-forming liquids, and demonstrated that topological considerations play the dominant role in several key relaxational and thermodynamic properties of glass-forming liquids, including the "fragility" of the liquid and the glass transition temperature.

To explore the role of topology in the low-temperature regime, we have performed persistent-spectral-hole relaxation experiments on the SeH vibrational mode for ten compositions in the Ge-As-Se system, with the remarkable result that the hole relaxation behavior in these glasses appears to be determined solely by topological considerations, independent of chemical composition. The dominant relaxation rate characterizing the nonexponential hole relaxation is found to increase monotonically with $\langle r \rangle$ varying by over 3 orders of magnitude as $\langle r \rangle$ varies from 2.0 to 2.8.

The use of persistent-spectral-hole burning as a probe of the microscopic dynamics of amorphous systems at low temperatures has become well established in recent years.[6-10] Monitoring the size of a spectral hole as it refills in the dark, revealing relaxation processes on time scales of seconds to hours, is a new type of experiment possible in systems displaying nonphotochemical hole burning. Recall that in the standard model for nonphotochemical hole burning in glasses,[11] optical excitation of an impurity center with a narrow-band laser leads to a transition from one to another of the multiple quasi-ground-state configurations of the glassy host surrounding the impurity. This configuration change in turn shifts the transition frequencies of the affected impurities away from the laser frequency, resulting in a decrease in absorption strength, i.e., a spectral hole, in a region of the inhomogeneously broadened impurity absorption band centered at the laser frequency. Thus for systems of this type, in monitoring the time evolution of the spectral hole after burning ceases, one is in effect monitoring the relaxation among the glassy configurations involved in the hole burning.

Experiments of this type have been performed on a variety of amorphous systems, both organic and inorganic.[12-15] The one qualitative feature universal to all these systems is the highly nonexponential nature of the hole relaxation, indicating the existence of a broad distribution of relaxation rates for each system. Quantitatively, however, these distributions of relaxation rates vary widely from system to system, with the most probable relaxation rate varying by several orders of magnitude. So far, the diverse nature of the systems studied has made meaningful correlations between glass structure and hole relaxation behavior impossible.

Recently, however, it was discovered[9,10] that persistent infrared spectral holes burned in the SeH vibrational absorption band display radically different relaxation behavior in glassy Se and As_2Se_3, two glasses which appear superficially to be quite similar. The obvious difference between these two glasses is that Se glass consists of weakly interacting chains of twofold-coordinated Se atoms, while in As_2Se_3 these chains are cross-linked by threefold-coordinated As atoms. This result suggested a relation between the microscopic topology of the glass network and hole relaxation behavior, but chemical effects due to the presence or absence of As could not be ruled out. The importance of this result, however, is that both glasses are members of a large class of glass-forming alloys which allow continuous variation of structure by varying alloy composition, opening the way for a systematic study of the effects of network topology on spectral-hole behavior.

The samples used in this study are bulk melt-quenched glass ingots prepared by first synthesizing the binary and ternary alloy glasses from their elemental constituents, as described in Ref. 5. SeH centers are then introduced by heating each glass well above its glass transition in a sealed quartz tube containing hydrogen gas, as has previously been described in Refs. 9, 10, and 12. Samples are quenched either in air or in liquid nitrogen, depending upon the alloy composition.

Infrared absorption spectra showing the SeH stretch absorption bands produced in the various host glasses by this procedure are displayed in Fig. 1. Note that the SeH bands, all having maxima at roughly 2200 cm^{-1} and widths on the order of 50–100 cm^{-1}, have considerable frequency overlap among the various hosts, allowing hole burning experiments to be carried out at a single frequency in all samples. The ability to do so is very important for practical reasons, as explained below. In addition to the SeH stretch mode, samples with high germanium content also display a GeH stretch absorption at roughly 2020 cm^{-1}. At high Ge concentrations, the hydrogenation procedure favors the formation of GeH bonds over SeH, thereby limiting the range of $\langle r \rangle$ available for the SeH hole burning experiment. Finally note that, although there appears to be a general trend toward weaker SeH absorption features at higher values of $\langle r \rangle$, due to the variation in the peak absorption frequency the actual value of the absorption coefficient at the laser frequency is not correlated with $\langle r \rangle$. The laser frequency of 2227 cm^{-1} is chosen to fall near the absorption peak in the high-$\langle r \rangle$ samples.

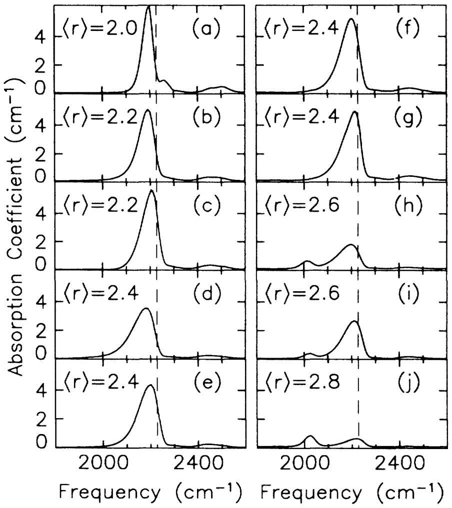

FIG. 1. Infrared absorption spectra at 1.5 K, showing the SeH stretch bands in ten glasses in the Ge-As-Se system: (a) glassy Se, (b) $As_{0.2}Se_{0.8}$, (c) $Ge_{0.089}As_{0.022}Se_{0.889}$, (d) As_2Se_3, (e) $Ge_{0.1}As_{0.2}Se_{0.7}$, (f) $Ge_{0.133}As_{0.133}Se_{0.733}$, (g) $Ge_{0.15}As_{0.10}Se_{0.75}$, (h) $Ge_{0.1}As_{0.4}Se_{0.5}$, (i) $Ge_{0.2}As_{0.2}Se_{0.6}$, and (j) $Ge_{0.3}As_{0.2}Se_{0.5}$. The value of the average coordination number $\langle r \rangle$ is noted for each spectrum. The vertical line indicates the laser frequency, 2227 cm^{-1}, used in the hole burning experiments.

Persistent-spectral-hole burning and relaxation experiments are carried out with the samples maintained at 1.5 K, immersed in superfluid helium inside an optical-access cryostat equipped with ZnSe inner and BaF_2 outer windows. Tunable radiation from a Pb-salt infrared diode laser operating near 2227 cm^{-1} is focused to an intensity of roughly 200 mW/cm^2 at the sample position. The transmitted radiation emerging from the sample is collected at an InSb detector operating at 77 K. For each sample, a hole is burned by holding the laser frequency constant at 2227 cm^{-1} for 2 min. The hole is then probed with the same laser by repeatedly sweeping its frequency through a 37-GHz wide region centered at the burn frequency.

Figure 2 shows the initial appearance and time evolu-

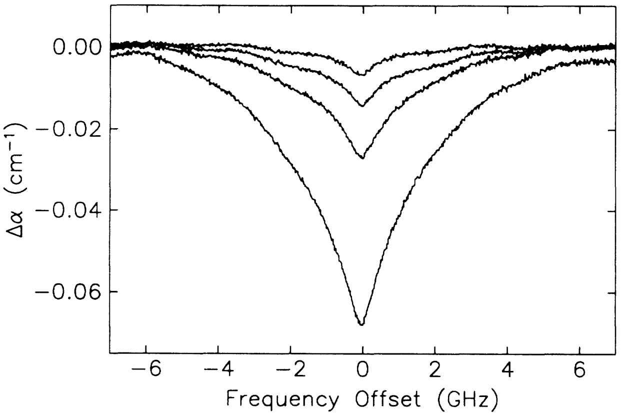

FIG. 2. Evolution of the spectral-hole line shape for SeH in $Ge_{0.1}As_{0.4}Se_{0.5}$ at 1.5 K. The four curves show the hole profile (laser-induced change in absorption coefficient vs the offset from the burn frequency) at 0.5 sec (deepest hole, corresponding to a 5.2% absorbance change at hole center), 10 sec (2.0% change), 30 sec (1.1% change), and 60 sec (0.5% change) after burning ceases. The hole, at 2227 cm^{-1}, was initially burned for 2 min at an intensity of roughly 200 mW/cm^2.

tion of a typical SeH vibrational hole burned and probed in this manner, in this case with $Ge_{0.1}As_{0.4}Se_{0.5}$ as the host glass. The non-Lorentzian spectral-hole line shape apparent throughout the relaxation in Fig. 2 is observed for all samples in this study and is typical of that produced in the deep-hole regime for glassy systems having a broad distribution of burning and relaxation rates.

A fundamental problem which arises in making comparisons of hole relaxation behavior in glassy systems having a broad distribution of barriers is that the distribution of hole relaxation rates selected in the hole burning process depends sensitively upon the intensity used to burn the hole.[12] Hence it is essential that hole burning be performed with identical intensities in all samples if meaningful comparisons are to be made. Because mid-infrared Pb-salt diode laser modes have spatial profiles which are notoriously non-Gaussian,[16] and which vary greatly according to the operating conditions, the only practical way of ensuring that identical intensities are used for all samples is to burn at the same frequency using the same laser mode throughout the experiment. The frequency overlap of the SeH modes in all the samples is therefore essential for this type of experiment.

In addition, it should be noted that the observed hole filling is a combination of spontaneous hole filling (i.e., direct relaxation among the quasi-ground-state configurations, requiring no photons) and laser-induced hole filling[6] (i.e., the inverse of the hole burning process, redistributing absorption frequencies from the antihole back to the hole) caused when the laser frequency is swept through the vicinity of the hole (and presumably through a portion of the antihole) during each measurement. This additional component of the hole relaxation again makes it essential that the experiment be performed in an identical manner for each alloy composition if meaningful comparisons are to be made. Thus, during probing, each sample must be exposed to the same laser intensity (in this case, the same as is used for burning), for the same duration, swept over the same frequency interval. (Sweeping over many homogeneous widths reduces the effective time-averaged intensity at a given center, in this case by roughly a factor of 100.)

Figure 3 displays the results of the 1.5-K hole relaxation experiment for ten compositions in the Ge-As-Se system, chosen so that there are two compositions having $\langle r \rangle = 2.2$, four having $\langle r \rangle = 2.4$, two having $\langle r \rangle = 2.6$, and one composition each for $\langle r \rangle = 2.0$ and $\langle r \rangle = 2.8$. The hole depth, plotted as a function of the time t after burning ceases, is normalized to unity at $t=0$ for each composition.

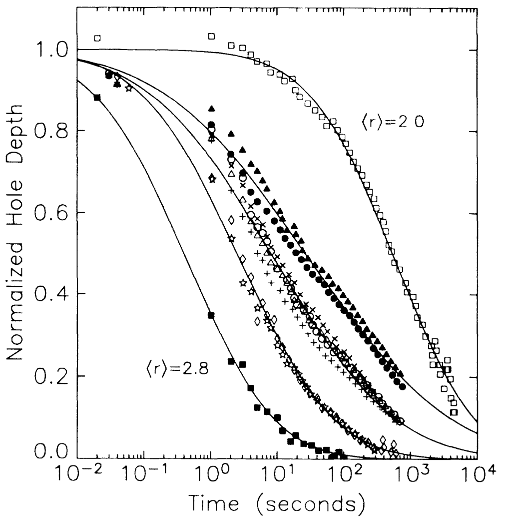

FIG. 3. Spectral-hole filling at 1.5 K for the SeH absorption in Ge-As-Se glasses. Data points show the hole depth, normalized to unity at $t=0$, as a function of time t after burning ceases for ten different compositions burned and probed under identical conditions. The average atomic correlation numbers $\langle r \rangle$ and compositions of the ten samples, listed in order of decreasing relaxation time, are as follows: $\langle r \rangle = 2.0$, glassy Se (open squares); $\langle r \rangle = 2.2$, $As_{0.2}Se_{0.8}$ (solid triangles), $Ge_{0.089}As_{0.022}Se_{0.889}$ (solid circles); $\langle r \rangle = 2.4$, $Ge_{0.15}As_{0.10}Se_{0.75}$ (crosses), As_2Se_3 (open circles), $Ge_{0.1}As_{0.2}Se_{0.7}$ (open triangles), $Ge_{0.133}As_{0.133}Se_{0.733}$ (plusses); $\langle r \rangle = 2.6$, $Ge_{0.1}As_{0.4}Se_{0.5}$ (open diamonds), $Ge_{0.2}As_{0.2}Se_{0.6}$ (open stars); $\langle r \rangle = 2.8$, $Ge_{0.3}As_{0.2}Se_{0.5}$ (solid squares). Solid lines are fits, for each set of compositions having a given value of $\langle r \rangle$, by a Gaussian distribution of tunneling parameters, described in the text.

The key result is that all compositions having a given value of $\langle r \rangle$ follow virtually identical hole relaxation curves. Throughout the composition range studied here, the overall hole relaxation rate increases monotonically with $\langle r \rangle$, with holes at $\langle r \rangle = 2.8$ decaying over 3 orders of magnitude faster than those at $\langle r \rangle = 2.0$. This monotonic variation with $\langle r \rangle$, however, shows no indication of a rigidity transition or any other unusual features at $\langle r \rangle = 2.4$. Both spontaneous and laser-induced hole filling contribute substantially to the relaxation under the experimentally convenient probing conditions used here. Preliminary investigations using different probe intensities and times between probings, thereby changing the relative contributions of the two filling mechanisms, indicate that the two mechanisms make roughly comparable contributions to Fig. 3. The general trends seen in Fig. 3, however, with faster filling at larger values of $\langle r \rangle$, continue to hold under all probing conditions, whether spontaneous or laser-induced processes dominate.

These nonexponential decay functions can be characterized more precisely by assuming relaxation occurs by tunneling from the hole-burned to the unburned configurations, so that the relaxation rate Γ for a single center is given by $\Gamma = \Gamma_0 e^{-\lambda}$, where λ is the tunneling parameter [of the general form $(2mV)^{1/2} d/\hbar$, where m is the mass of the tunneling entity, V the barrier height, and d the width of the barrier], and Γ_0 is an attempt frequency on the order of an optic-phonon frequency. Then, allowing λ to assume a Gaussian distribution of width σ centered at some value λ_0, the number of centers $N_B(t)$ remaining in the hole-burned configuration after time t is given by[9,10,12,17]

$$\frac{N_B(t)}{N_B(0)} = \frac{1}{\pi^{1/2}\sigma}\int_0^\infty \exp\left[-\frac{(\lambda-\lambda_0)^2}{\sigma^2}\right] \times \exp[-\Gamma_0 t e^{-\lambda}]d\lambda . \tag{1}$$

Fits by Eq. (1) for each value of the coordination number are shown by solid lines in Fig. 3. The fit parameters, width σ and dominant relaxation rate $\Gamma_0 e^{-\lambda_0}$, are listed for each value of $\langle r\rangle$ in Table I. Unlike $\Gamma_0 e^{-\lambda_0}$, σ does not vary monotonically with $\langle r\rangle$, but peaks at intermediate values of $\langle r\rangle$.

TABLE I. Values of fit parameters for fits of 1.5-K hole relaxation behavior (Fig. 3) by Gaussian distributions of tunneling parameters [Eq. (1)].

$\langle r\rangle$	σ	$\Gamma_0 e^{-\lambda_0}$ (sec^{-1})
2.0	2.70	1.1×10^{-3}
2.2	5.28	2.1×10^{-2}
2.4	4.44	7.1×10^{-2}
2.6	3.31	2.3×10^{-1}
2.8	3.04	1.5

The direction of the trend exhibited in the present results, slow relaxation at small $\langle r\rangle$ and rapid relaxation at large $\langle r\rangle$, is quite surprising if one takes the simplistic view that refilling rates are determined primarily by the height of the barriers between configurations, and that large barriers correspond to a more rigid structure. Such a view would predict that since systems with small values of $\langle r\rangle$ have the least rigid structures, relaxation would be most rapid in these systems, the opposite of the observed trend. Clearly, a more sophisticated approach of enumerating as a function of $\langle r\rangle$ the configurations available to hole burning and the barriers between them is required to explain these results.

Given the complexity of glassy systems, however, the existence of a single simple parameter, $\langle r\rangle$, which can predict spectral-hole relaxation behavior is remarkable indeed. The implication that simple geometrical considerations play the predominant role in determining spectral-hole burning behavior should prove an invaluable clue in the quest for a microscopic theoretical understanding of low-temperature relaxation phenomena in glasses.

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