PHYSICAL REVIEW B VOLUME 54, NUMBER 10 1 SEPTEMBER 1996-II

Microscope models of guest molecular vibrations in crystalline and glass hosts

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(Received 15 March 1996; revised manuscript received 27 June 1996)

Uebbing and Sievers [Phys. Rev. Lett. **76**, 932 (1996)] have shown with time-resolved saturation spectroscopy that the nonradiative decay rate γ of internal guest high-frequency H_2O symmetrical stretching vibrations in soft ternary Ge-As-Se host glasses is a function only of $\langle r\rangle$, the average host coordination number. A theoretical model based on the constraint theory of the structure of these network glasses explains the observed functional dependence, which is broadly linear with a break in slope at $\langle r\rangle=2.4$. The theoretical model also explains the width and asymmetry of the remarkable cusp which occurs in $\gamma(\langle r\rangle)$ at $\langle r\rangle=2.4$. [S0163-1829(96)50934-3]

I. INTRODUCTION

When a guest molecule (such as H_2O) is placed in a molecular crystal (such as a solid rare gas), there is a large difference between the internal molecular vibrational frequencies ω (of order 3000 cm^{-1}) of the guest molecule and the Debye frequency ω_A of the host crystal (of order 100 cm^{-1}). If one of the former high-frequency vibrational modes is excited, it might decay through multiphonon excitation of the soft host crystal. This problem was discussed long ago[2] and it was estimated that the number N_p of bulk host phonons would be of order $\omega/\omega_A \sim 30$. Subsequently many authors pointed out that local host vibrational and rotational modes would interact strongly with similar modes of the guest molecule.[3] These local modes will include both guest and host vibrations. Thus one might suppose that the localized vibrational frequencies ω_L would be given approximately by the harmonic average of the guest and host frequencies, $\omega_L^2 \sim \omega\omega_A$, so that the number of phonons $N_p \sim N_L \sim (\omega/\omega_A)^{1/2} \sim 5$–6. This supposition is in good agreement with the relatively weak experimental temperature dependence $\gamma(T) \sim T_L^N$ at low T.[4] In very soft host crystals (such as solid rare gases) one should recognize that substantial H bonding can occur.[5] In this case N_L can be reduced further to be ~ 1 or 2.

Most experimental studies of embedded vibrational relaxation have been carried out either with host crystals or liquids.[5] Host glasses are not easily studied because of the tendency of the guest molecules to precipitate in porous regions during quenching. Uebbing and Sievers, however, have found[1] that glasses formed from Ge-As-Se alloys with average coordination number $\langle r\rangle$ between 2.0 and 2.8 dissolve *isolated* H_2O molecules. These ternary glasses are of great interest, for studies of their intrinsic mechanical relaxation[6,7] have shown that they are close to being ideal network glasses, that is, continuous random networks, free of molecular clusters, of the kind originally envisioned by Zachariasen,[8] but which are seldom realized in practice.[9]

Before we turn to the analysis (Sec. IV) of $\gamma(\langle r\rangle)$ at $T=10$ K, we first review (Sec. II) microscopic valence force field constraint theory briefly in order to develop (Sec. III) a model of the localized cavity of such interfacial modes. When the numbers N_L and frequencies ω_L of these modes are known it is easy to understand the observed chemical trends.

II. CONSTRAINT THEORY OF NETWORK GLASSES

The formation of covalent networks does not, by itself, assure glass formation: Si and Ge form covalent networks, but when they are quenched from the melt they are always at least microcrystalline. However, it is true that covalent interatomic forces may (but do not always) form well-defined hierarchies, with bond energies and force strength decreasing from bond stretching (α, nearest neighbor) forces, to bond bending (β, second-nearest neighbor) to third neighbor ($\delta, \ldots$) and more remote forces. The strength of these forces decreases with distance, and qualitatively $\alpha \sim 3\beta \sim 9\delta$, and so on.[10] The corresponding phonon energies are of order 600 cm^{-1} (α forces), 200 cm^{-1} (β forces), and 70 cm^{-1} (δ forces). The average energies E_n of the nth neighbor forces may then satisfy the condition

$$E_1 > E_2 > bkT_g > E_3 \cdots, \tag{1}$$

where T_g is the glass transition temperature and $b \sim 1$. The meaning of this hierarchy is that when glass formation occurs at $T=T_g$, the α and β forces act as microscopic Lagrangian mechanical constraints,[7] while the δ forces do not. In the heavier solid rare gas crystals[5] the Debye energy is also of order $E_3 \sim 70$ cm^{-1}. These are the materials where guest hydrides exhibit strong hydrogen-bonding effects,[5] presumably because some of the hydrogen-bonded vibrational energies are also of order 70 cm^{-1}. It follows that if the α and β constraints do not exhaust the $d=3$ degrees of freedom per atom, there could be soft or ''floppy'' vibrational modes, with energies of order $E_3 \sim 70$ cm^{-1}, in the Ge-As-Se glass which resonantly form hydrogen bonds with hydrides such as H_2O similar to those found in solid rare gas hosts. However, to contribute to guest relaxation these soft modes must be localized near the guest hydride. The relaxation rate γ of the high-frequency guest vibrations in this model depends mainly on the concentration of high frequency host modes localized on the cavity surface. We now develop a microscopic model for the composition ($\langle r\rangle$) dependence of this concentration.

III. MODEL OF GUEST CAVITIES IN COVALENT NETWORK GLASS

The characteristic feature of melt-quenched covalent network glasses, such as SiO_2 and (Ge,As,Se) alloys with $\langle r\rangle$ near 2.40, is that the density of a glass closely approximates that of a (possibly metastable) crystalline phase. This behavior is not found in evaporated amorphous films of covalent non-glass-forming materials, which are generally porous. In host crystals the density of vacancies is so small that ordinarily one cannot dissolve large concentrations of guest molecules without exceeding the solid solubility limit of the guest species, which leads to precipitation of the latter. Phase separation and precipitation is generally an even greater problem in denser supercooled liquids, where solid solubility limits are greatly reduced compared to less dense normal liquids. While it is possible, at least in principle (although this is seldom done in practice for network materials) to estimate crystalline solid solubility limits theoretically, for glassy materials the solubility limits are actually determined by the limitations of guest diffusion kinetics, either during or after host glass formation. Here the data[1] clearly indicate that in the studied glass alloys individual water molecules have dissolved in the host network which has relaxed to form a cavity around the guest molecule. To determine the local structure of the guest and host would require a full molecular dynamics simulation, which lies outside the scope of the present short paper. However, the hierarchical nature of the host valence force fields, which is the necessary condition for the widespread success of this theory,[7] enables us to draw a surprisingly large number of quantitative conclusions regarding the microscopic content of these data.

In the absence of guest-host directional interactions it might seem that the natural shape for a guest cavity would be quasispherical. However, the crystalline forms of Ge-Se and As-Se compounds with $\langle r\rangle$ near 2.4, namely $GeSe_2$ and As_2Se_3, are both layered, with the outer atomic layers consisting of Se. From one sandwich to the next the Se outer layers are Van der Waals bonded. Then the spheroidal cavities should have boundary layers of Se atoms backbonded to As or Ge atoms. The first question is whether such cavities would retain their spheroidal symmetry in the presence of α and β stretching and bending constraints, respectively. The second question is the possible effects of hydrogen bonding between H_2O and the cavity surface Se atoms.

When the cavity structural problem is posed this way, its solution would seem to require a full-scale molecular dynamics simulation with very accurate interatomic force fields. The latter are known for simple covalent forces, notably Si,[10] but they are not yet known for hydrogen bonds. (As an aside, the hydride-rare gas matrix data[5] would seem to provide an ideal departure point for developing hydrogen bonding force fields.) Here we adopt a different approach, more in keeping with the topological hierarchical methods of constraint theory discussed above. We concede that this approach is heuristic and has been guided in part by knowledge of the experimental data which are discussed in the next section.

To begin let us imagine how the topology of the glassy alloy network changes with $\langle r\rangle$. At $\langle r\rangle = 2$ the network consists of Se_n chain fragments, where $n \sim 300$.[11] As $\langle r\rangle$ increases the chains become crosslinked, and near $\langle r\rangle = 2.4$ the structures are predominantly layered. Finally near $\langle r\rangle = 2.67$ a further morphological change to a three-dimensional structure occurs.[12,13] These topological changes seem complicated, but extensive numerical simulations by Thorpe and co-workers have shown[7] that all of the dynamical effects of varying $\langle r\rangle$ are described remarkably well by mean field theory, as follows.

First we recall that for fully intact α and β force fields the ideal glass-forming condition,

$$N_c = N_d, \tag{2}$$

where N_c is the number of constraints per atom and $N_d = d$ is the number of degrees of freedom, reduces to $\langle r\rangle = 2.4$. At this value of $\langle r\rangle$ the cavity is spheroidal. However, when $\langle r\rangle$ is below 2.4, some of the bulk modes are soft, and if there are enough of them, some can be localized on the cavity surface which can form H bonds with the guest H_2O. The fraction of host bonds which is soft is given by[9]

$$N_s = 5(\langle r\rangle_0 - \langle r\rangle)/2, \tag{3}$$

where $\langle r\rangle_0 = 2.4$.

Next we ask what is the radius of the spheroidal H_2O cavity at $\langle r\rangle = 2.4$. The Van der Waals radius of Se is[14] about 1.90 A. It has been suggested[15] that a good choice for the nonbonded radius of H_2O is half the distance of closest approach of nonbonded molecules in a high-pressure form of ice, which is about 1.6 A. With this radius there will be about ten Se atoms on the cavity surface, assuming that the Se-Se spacing (mediated by backbonded As or Ge) is similar to that in crystalline As_2Se_3 or $GeSe_2$.

When $\langle r\rangle$ is below 2.4, Eq. (3) tells us that with the soft modes concentrated on the twofold coordinated cavity surface Se atoms we can have one localized soft mode when $\langle r\rangle = 2.36$. This value is in good agreement with experiment and it is insensitive to the sphericity of the guest cavity. This localized mode can then H bond to guest hydrides much as soft rare gas modes do.[5] This dynamical mean-field calculation is less detailed but it is also much simpler than the hypothetical full-scale molecular dynamics simulation discussed above, and it explains one of the key features of the data, which is the cusp width. A similar estimate for the $\langle r\rangle$ width of a Te-centered cluster in glassy $Ge_x(Se_{0.99}Te_{0.01})_{1-x}$ alloys can be obtained from Mössbauer data.[16]

When $\langle r\rangle$ is larger than 2.4 there are more constraints than degrees of freedom. This will produce localized modes in which β bending constraints are replaced by α stretching constraints and so should have the effect of distorting the cavity so that it is no longer spheroidal. Indeed with increasing $\langle r\rangle$ the Tanaka medium-range order transition from isotropic to layered micromorphology at $\langle r\rangle = 2.67$ has been observed in several properties.[12,13] To first order in $\langle r\rangle - \langle r\rangle_0$ the cavity volume does not change but the degeneracy of the spheroidal major axes is lifted and the cavity becomes ellipsoidal. The guest molecule collides more often than before with the cavity walls and together with the average mechanical stiffening which occurs anyway as $\langle r\rangle$ in-

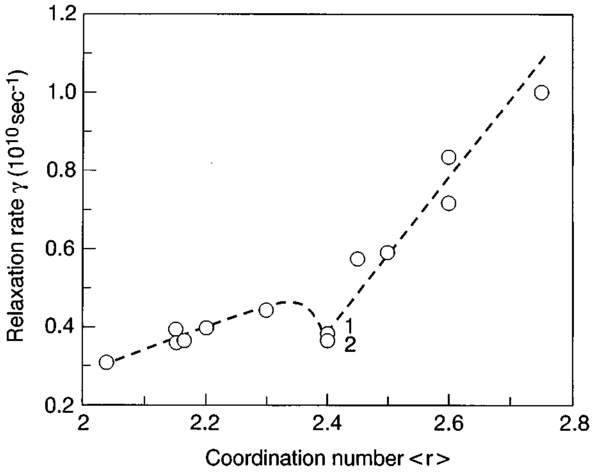

FIG. 1. The data of Ref. 1 have been replotted, together with a dashed line which represents the effects discussed in the present model. The points labeled 1 and 2 correspond to As_2Se_3 and $GeSe_4$. The relaxation rate measured is that of the H_2O symmetrical stretching mode at 3515 cm^{-1}.

creases this effect will increase $\gamma(\langle r\rangle)$ more rapidly for $\langle r\rangle$ above 2.4 than for $\langle r\rangle$ below 2.4. In fact the two slopes should roughly be in the ratio $\alpha/\beta\sim3$, as below 2.4, the number of β constraints and β localized modes is increasing as $\langle\beta\rangle$ stiffens, while above 2.4, the fraction of intact β constraints is decreasing as these are replaced by α constraints, leading to an increase in the concentration of α localized modes. The stiffening of the averaging force constants $\langle\alpha\rangle$ or $\langle\beta\rangle$ occurs, of course, because the number of β interactions increases linearly with increasing $\langle r\rangle$ for $\langle r\rangle$ below 2.4, while for r between 2.4 and $\langle r\rangle/2$, the numbers of both α and β interactions increase linearly, but only d/atom of these can be intact. This is one of the fundamental conclusions of constraint theory which is directly reflected in the experimental data.

IV. DISCUSSION OF EXPERIMENTAL DATA

We now turn to the experimental data for the relaxation rate γ of the H_2O symmetrical stretching mode, which are shown for the reader's convenience in Fig. 1. First we note the two broadly linear trends for $\langle r\rangle$ below and above 2.4. The break in slope is $\sim$ a factor of 3–4, which agrees well with the α/β ratio discussed above. One should also note here that it is nontrivial that this break in linearity occurs just at $\langle r\rangle=2.4$. In multiphonon rare earth relaxation of f electron crystal-field states it has been shown that the relaxation is not the result of a bilinear interaction carried to high order but that the process is better described as a strongly nonlinear interaction treated to first order.[17] It is far from obvious that $\langle r\rangle_0$ would have special significance in that case. It does here because anharmonic phonon-phonon interactions are weak and their effects can be linearized in crystals and glasses. A rigorous derivation of the two linearities of $\gamma(\langle r\rangle)$, for $\langle r\rangle$ below (<2.35) and above (>2.40), does not appear to be possible. This linearity is, however, what would be expected on general grounds. Coupling to local vibrational modes determines $\gamma(\langle r\rangle)$, and small variations in not only the stiffness but also the overall coupling strength will depend on the average strength of the weakest intact coupling. This is because the coupling is hierarchical and small variations make large changes only in the weakest coupling. This reflects the fact that in a democratic disordered structure the stronger couplings are always relaxed and fully intact.

Second we note that a similar break in slope of $\langle\omega^{-1}\rangle$ as a function of $\langle r\rangle$ has been observed by Mössbauer scattering with a Sn probe,[18] but not by neutron scattering. This has been attributed to local softening near the Sn.[19] The formation of the guest cavity can be regarded as a similar softening effect. The linearity in $\langle r\rangle$ is expected for $\langle r\rangle$ above 2.4 because ω is small compared to ω_A. However, it might seem that for $\langle r\rangle$ below 2.4 in addition to the softening linear in $\langle r\rangle$ one should also consider the possibility of H_2O forming two hydrogen bonds, for instance for $\langle r\rangle$ below 2.32. This possibility seems unlikely because the guest bond-bending vibrational energy is again much larger than the floppy mode and H bonding energies.

The new feature of the data which has not been observed before is the cusp at $\langle r\rangle=2.4$. It is clear that this is not the result of experimental scatter for two reasons. First the two independent data points corresponding to $GeSe_4$ and As_2Se_3 both indicate a cusp. Second the $\langle r\rangle=2.4$ points are part of the straight line extrapolated from $\langle r\rangle$ above 2.4 and represent the beginning of intrinsic stiffening due to replacement of β by α constraints. The present model predicts the existence, the location, the width and the asymmetry of the cusp, but not its magnitude. The latter can apparently be obtained theoretically only from a very accurate molecular dynamics simulation.

In addition to the relaxation data on H_2O there are also some results for the OH stretch relaxation at 3460 cm^{-1}.[1] At this frequency there is relatively more absorption in an $\langle r\rangle=2.5$ sample than in an $\langle r\rangle=2.3$ sample, as shown in Fig. 2 of Ref. 1. This indicates a larger $[OH]/[H_2O]$ ratio in the $\langle r\rangle=2.5$ sample. In spite of this, $\gamma(3460\ cm^{-1})$ is almost twice as large in the $\langle r\rangle=2.3$ sample. This suggests that OH is coupling strongly to a local cavity vibrational mode for $\langle r\rangle=2.3$ and that this coupling is largely absent for $\langle r\rangle=2.5$. The easiest way to explain this absence is to assume that the localized mode involves H bonding, and that the latter itself has disappeared for $\langle r\rangle=2.5$, in excellent accord with the predictions of the present model.

V. CONCLUSIONS

We have seen that the principal features of the recent elegant data[1] on vibrational relaxation of H_2O guest molecules in Ge-As-Se network glasses can be understood by microscopic valence force field constraint theory.[6,7] At first it might seem that such network glasses are much more complicated hosts than solid rare gases, which have been the most frequently studied host materials previously. It is true that considerable care was necessary in the preparation of the chalcogenide alloy glass samples,[19,1] whose chemistry and quenching kinetics are delicate. On the theoretical side, however, matters are, surprisingly, in some ways as simple for these network glass alloys as for the solid rare gases. This is because the covalent radii of Ge, As, and Se are the same.[20] This leaves $\langle r \rangle$ as the only relevant variable, which in turn produces broadly linear chemical trends because the number of constraints is linear in $\langle r \rangle$. It is especially satisfying that these include H bonding in much the same way as in the heavier rare gases, as this provides bonding evidence for the role of floppy modes which nicely compliments the direct evidence obtained in previous experimental and theoretical work.[7,19] Note that in the limit $\delta \rightarrow 0$ these floppy modes become true cyclical modes (called Goldstone modes by field theorists), so that the present analysis connects such modes to H bonds in two quite different host materials with essentially the same hydrogen bonding vibrational energies $\sim 70\ \mathrm{cm}^{-1}$.

I am grateful to M. Marcus for drawing my attention to Ref. 13.

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