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13. ABSTRACT (Maximum 200 words)

The mechanisms of atomic transport in the supercooled liquid state (SLS) and the nature of glass transition have been challenging problems for decades. It is believed that collective atomic motion plays a key role in the dramatic slow-down of kinetics near the glass transition temperature Tg. Thus, understanding the mechanisms of atomic transport is directly linked to the understanding of the glass forming ability of metallic alloys. Measurements on both macroscopic and microscopic scales are required for the understanding of atomic motions in SLS and glasses. We have developed a nuclear magnetic resonance technique, the Be-9 spin alignment echo technique (SAE), to probe slow atomic motions on microscopic scales. Systems of focus are Vitreloy1 and Vitreloy4, two of the Zr-Ti-Ni-Cu-Be bulk metallic glasses with extraordinary glass forming ability. By combining SAE and diffusion measurements it was revealed that long-range transport of Be atoms in the SLS is due to two diffusion processes, one of these is single-atom hopping assisted by thermal fluctuation of spread-out free volume. However, collective motion of atomic clusters dominates in the SLS. Further understanding of the influence of composition and processing on such atomic motions could lead to the improvement of glass forming ability.

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Statement of the problem studied

It was shown that some Zr-based alloys are very good glass formers forming bulk metallic glasses (BMG). In particular, the addition of Be in the Vitreloy systems, $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ (Vit1) and $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10.0}Be_{27.5}$ (Vit4) improves the glass forming ability (GFA) dramatically (1). The understanding of atomic motion and diffusion mechanisms are crucial for the understanding of the GFA, the nature of glass transition, and the crystallization and growth processes in these systems of BMG. Unlike in crystalline systems, the link between macroscopic and microscopic worlds is quite complicated in supercooled liquids and glasses. Measurements on both macroscopic and microscopic scales are required for the understanding of atomic motions in systems such as Vit1 and Vit4. We have developed a method using nuclear magnetic resonance (NMR) to probe atomic motions on microscopic scales. Combining with diffusion measurements, important understanding of the mechanisms of atomic motions in Vitreloy systems have been obtained.

Summary of the most important results

Our research can be divided into three stages, the development of the alignment echo technique for ^{9}Be, the understanding of the diffusion mechanism in the glassy state, and the understanding of diffusion mechanisms in the supercooled liquid state (SLS).

Alignment Echo Technique

One of the common approaches in the study of motion is the measurement of the relaxation response function of some quantity in time domain, $g_\nu(t)$, to a weak external perturbations ν which can be mechanical, electrical, thermal, optical, and so forth. For instance, $g_\nu(t)$ can be the electric polarization which relaxes when the electric field is turned off as illustrated below. The rate of relaxation depends on ease of atomic motions in the system; thus, the relaxation rates depend on the temperature. It is found that the

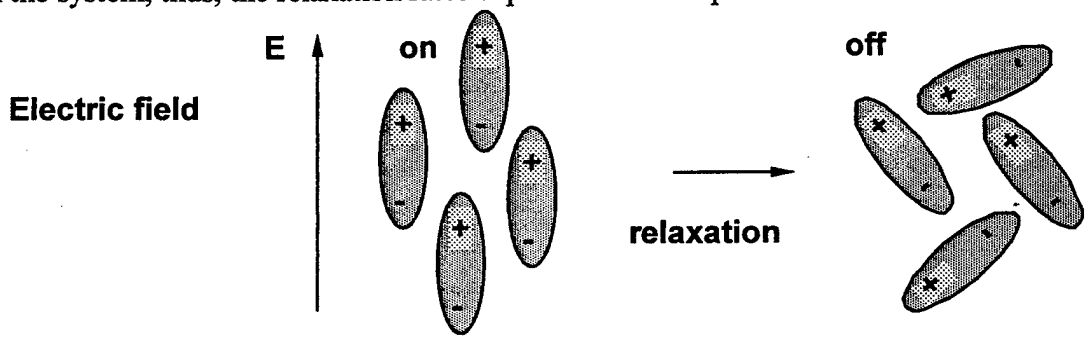

Figure 1

relaxation function $g_\nu(t)$ in glasses follows the Kohlrausch-Williams-Watts (KWW) stretched exponential decay (2)

$$g_\nu(t) = g_0 \exp[-(t/\tau_\nu)^\beta]$$

and the temperature dependence of the relaxation time τ_ν follows the well known Vogel-Tammann-Fulcher (VTF) relation (2)

$$\tau_\nu(T) = \tau_0 \exp[A/(T - T_0)].$$

For the understanding of the nature of glass transition and the resistance of metallic glasses again crystallization, it is important to measure the relaxation time τ_ν associated

with microscopic motions. Measurements of viscosity and diffusion, for instance, probe the cumulative effects of atomic motion (a huge number of steps) on a macroscopic scale. Dielectric measurements are used to probe atomic motion in glasses on a microscopic scale. However, because of the presence of conduction electrons and the lack of well-defined dipole-carrying molecules, this technique cannot be used for the study of metallic glasses. To our knowledge, measurements of atomic motion on a microscopic scale have not been conducted in metallic glasses prior to our study.

A quadrupolar nuclear spin such as ^{9}B is strongly coupled with the local electric field gradient (EFG). Using the quadrupole alignment echo technique, a ^{9}Be nuclear spin is labelled by its local EFG at the nucleus through the first two radio frequency (rf) pulses, as shown in Fig. 2, and the information is stored in the form of the so-called quadrupolar order (or spin alignment) (3). There is no evolution of the spin system after the second rf pulse during the period t in the absence of motion. The ^{9}Be spin will remember its local EFG during the period t and such memory is evidenced by the formation of an echo created by the third rf pulse. However, if the spin has moved during the period t, the spin will lose its memory of its original local EFG and will not contribute to the echo. For instance, if the local EFG of half of the spins (e.g., Be atoms) have changed during the period t, the echo intensity will drop to half of its intensity at t =0. Clearly, meaning of the echo height versus t is exactly the same as the function $g_\nu(t)$ where t is the time between the second and the third rf pulses. Here ν is the response of the local EFG at the given spin (e.g.^{9}Be) to the change of the local environment (microscopic) caused by atomic motion. There is a limitation to this technique. Since a spin can also lose its memory of its local EFG resulting from the spin-lattice relaxation without atomic motion, atomic motion slower than the time scale of the spin-lattice relaxation time (T_1) cannot be detected. A key realization is that T_1 of ^{9}Be is quite long (on the order of a few seconds). Therefore, very slow atomic motion, which is most relevant to glass transition, can be probed by the alignment echo technique. This work is described in an article in *Journal of Magnetic Resonance* **133**, 155 (1998).

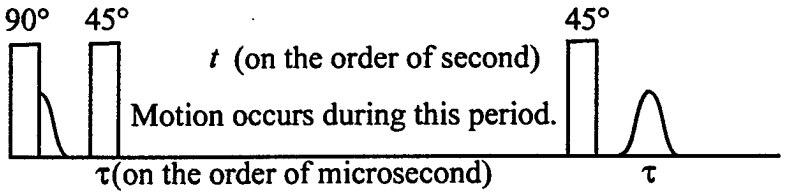

Figure 2

Diffusion Mechanism in the Glassy State

There is a long standing controversy about the mechanism of diffusion in metallic glasses (4). One opinion claims that vacancy mechanism is responsible for diffusion similar to that in crystalline solids. The other opinion favors collective motion mechanism. The controversy originates, partly, from the lack of information on microscopic scale.

Figure 3 shows the time dependence of the alignment echo height versus t. It follows a perfect exponential decay (over nearly three orders of magnitude) at all temperatures. The rate of atomic motion, determined from fitting of curves in Fig.3, is shown in Fig. 4 as a function of temperature. A key difference between vacancy model and models of collective motion is that the former is inhomogeneous on microscopic scales. The probability of atomic jump at a given time is different for an atom that is near a vacancy than that far from vacancies. As a result, the decay curve should be non-

exponential (a stretched exponential according to Monte-Carlo simulation) unlike those displayed in Fig.3. The probability of jumps averaged over many jumps should be homogeneous in both vacancy and collective motion models. Detailed analysis shows that

(1) Be motions are not consistent with vacancy-assisted diffusion and interstitial diffusion. The result is consistent with the thermal fluctuation of spread-out free volume involving many atoms (5,6).

(2) It is shown that the energy barrier for short-range Be motion is identical to that for long-range diffusion in Vit1 and Vit4. In an amorphous system, a large distribution of energy barrier is expected. For long-range diffusion high energy barriers provide the main hindrance to diffusion whereas for short-range displacement, atoms would most likely jump over the low energy barriers. The fact that the energy barriers are the same for short- and long-range Be motions indicate that collective motions are involved in the diffusion process which averages out the distribution of barrier height (5).

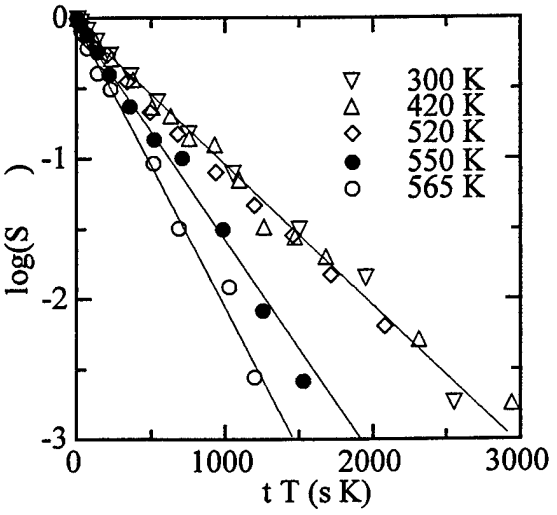

Fig. 3

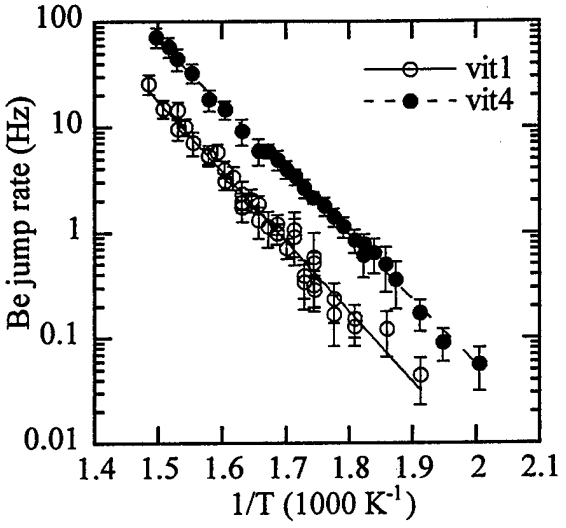

Fig. 4

Diffusion Mechanisms in the Supercooled Liquid State

Figure 5 shows the temperature dependence of the interdiffusion coefficients D of Be in Vit1 and Vit4. Below 620 K, which lies in the calorimetric glass transition regime, Be diffusion shows Arrhenius behavior with activation energies of about 1.1 eV in both alloys (7,8). At higher temperatures, the temperature dependence of Be diffusion increases significantly, resulting in kinks in the Arrhenius plot of D. Similarly, a kink was also observed in the $D(T)$ data for other elements including Ni (9), B, Fe (10), and Co (9,10) in Vit4. For comparison, the atomic jump rate Ω measured by NMR is shown in Fig. 5. Here, Ω follows the Arrhenius behavior in both Vit1 and Vit4. Fitting the measured Ω using $\Omega(T)=\Omega_0\exp(-E_a/k_BT)$ yields $E_a=(1.2\pm0.15)$ eV for both Vit1 and Vit4. Within the experimental uncertainty this E_a is identical to those obtained by diffusion measurements below the kink temperature. Also, Ω in Vit4 is larger than that in Vit1 similar to the trend of the diffusion constant below the kink temperature. Based on the equation $D=f\Omega\lambda^2/6$ where f is the correlation factor ($0<f\leq1$) and λ^2 is the mean square displacement per jump, $f\lambda^2$ values can be derived from data shown in Fig. 1. They are (4.5 Å)^2 and (2.8 Å)^2 for Vit1 and Vit4, respectively, and is consistent with the estimated hopping distance based on the structure.

The NMR measurement extends above the kink temperature. Surprisingly, no kink is observed in the Arrhenius plot of Ω. The measured Ω in the SLS obeys the same Arrhenius behavior as that below 620 K in both Vit1 and Vit4. This demonstrates that single-atom Be hopping is an intrinsic property of both the SLS and the relaxed glassy state. The combined SAE and diffusion studies indicate that the long-range transport of Be atoms in the SLS is due to two diffusion processes, one of these is single-atom hopping. The other process, which dominates in the SLS, does not change significantly the truncated quadrupole interactions at most Be sites over the average time interval between two hopping events. This suggests that this process is collective involving most of the nearest neighbors of Be atoms as suggested by some theories (11,12).

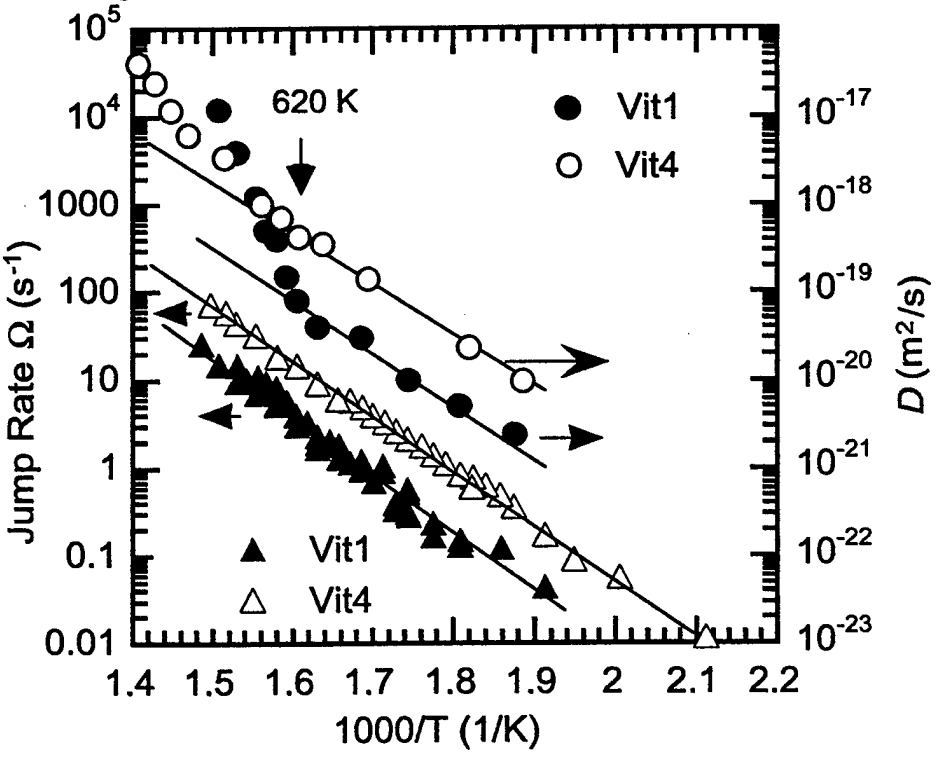

Figure 5

List of all publications and technical reports

Alignment Echo of Spin-3/2 9Be Nuclei: Detection of Ultraslow Motion
X.-P. Tang and Y. Wu
Journal of Magnetic Resonance **133**, 155-165 (1998).

Slow Atomic Motion in Zr-Ti-Cu-Ni-Be Metallic Glasses Studied by NMR
X.-P. Tang, R. Busch, W. L. Johnson, and Y. Wu
Physical Review Letters **81**, 5358-5361 (1998).

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X.-P. Tang, Ralf Busch, William L. Johnson, and Yue Wu
Materials Research Society Symposium Proceedings **554**, 87-92 (1999).

Diffusion mechanisms in metallic supercooled liquids and glasses
X.-P. Tang, Ulrich Geyer, Ralf Busch, William L. Johnson, and Yue Wu
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Solutions of Spin Lattice Relaxation for All Spin Orders of Quadrupolar Nuclei
Xiao-Ping Tang and Yue Wu, to be submitted.

Participating Scientific Personnel

Yue Wu: Associate Professor, Ph. D., summer salary.

Xiao-Ping Tang: Postdoctoral fellow, Ph.D., salary.

Chunlei Liu: Research Assistant, salary.

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