

Nanoscale Elastic Inhomogeneity in a Pd-based Metallic Glass Observed by Inelastic X-ray Scattering and Ultrasonic Experiments

The structures of vitreous substances are one of the attractive subjects of ongoing research in glass science. In general, glasses roughly fall into two classes, “strong” and “fragile” glass-forming liquids, from the viewpoint of their deviation from the Arrhenius behavior in the temperature dependence of viscosity. It is known that strong glasses such as those formed from SiO_2 and GeO_2 consist of a network of covalently bonded clusters. In contrast, the structure of fragile glasses is still unclear, and they exhibit aspects in their physical properties that are not yet understood. In general, the microstructure frequently governs physical properties, but the microstructure of fragile glasses has not been established yet, despite the fact that several models have been proposed to date. In a series of recent experiments using inelastic X-ray scattering (IXS) and ultrasonic (US) techniques [1,2], we have shown that the sound velocity of nanometer-order wavelengths “exceeds” that of millimeter-order wavelengths. This fact indicates that elastically harder and softer regions coexist in the glass matrix, i.e., there is nanoscale elastic inhomogeneity in a metallic glass.

An intriguing behavior of metallic glasses that we have reported is that their structural stability is significantly deteriorated under radio-frequency ultrasonic perturbation at relatively low temperatures near or below the glass transition temperature T_g , even in thermally stable glasses such as Pd-Ni-Cu-P, Pd-Ni-P and Zr-Al-Ni-Cu bulk metallic glasses [3]. Similar instability phenomena have been observed in other metallic glasses (see the references in [3]), but the mechanism causing the instability was unclear. Our mechanical spectroscopy analysis indicates that the instability is caused by atomic motion resonant with the dynamic ultrasonic-strain field and such that

atomic jumps are associated with β relaxation, which is usually observed for low frequencies of the order 1 Hz at temperatures far below T_g . Figure 1(a) shows the microstructure observed by transmission electron microscopy for a Pd-Ni-Cu-P sample subjected to ultrasonic annealing near/below T_g , in which the crystallized region is colored yellow and the remaining amorphous region is colored blue. Such atomic motion at temperatures lower than the so-called “kinetic freezing temperature T_g ” is considered to originate from the relatively weakly bonded (and/or low-density) regions in the microstructure of glass with nanoscale inhomogeneities. On the basis of this result, we have proposed a plausible microstructural model of fragile glasses, shown in Fig. 1(b), which consists of strongly bonded regions (SBRs) surrounded by weakly bonded regions (WBRs).

If this structural model is correct, it is predicted that the sound velocity for the nanometer-order wavelength, which mainly represents the elasticity of SBRs, should be faster than that of millimeter-order wavelength, which reflects the macroscopic elastic stiffness of the overall substance including SBRs and WBRs, although the longer-wavelength wave in a homogeneous solid is usually faster. To obtain these sound velocities, two measurement techniques are available: the IXS method for the former sound velocity and the US measurement for the latter. Near the Q value corresponding to the typical domain size ξ , the phonon-dispersion relation is expected to branch positively and negatively from the US line due to the SBR and WBR elasticities, respectively, as shown in Fig. 2(a). To confirm the existence of a “static” structural inhomogeneity, however, we have to eliminate any effects of the hardening/softening due to the relaxation processes that frequently appear in glass substances. Then, in the present work, using one of the most stable bulk metallic glasses (Pd-Ni-Cu-P), we performed the IXS and US measurements far below the glass transition temperature (about $0.5 T_g$). As shown in Fig. 2(b), in this metallic-glass system, most of relaxation processes are expected to be excluded from the MHz-ultrasonic measurement and, of course, this is also the case for much higher frequencies such as those in the THz region. Namely, the two kinds of sound velocities (US: MHz, IXS: THz) measured at such a low temperature are both at the high-frequency limit, so that the velocity difference caused in this situation, if present, is limited only to what is caused by the difference between the wavelengths of the probes. We can, thereby, discuss

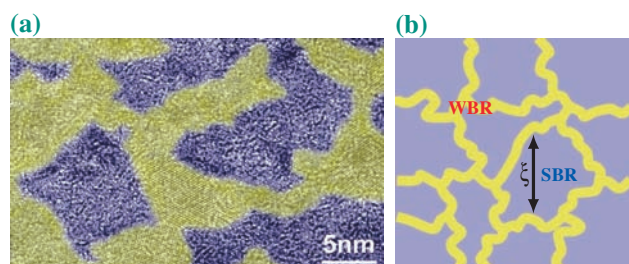


Fig. 1. (a) Partially crystallized microstructure of a Pd-based metallic glass obtained by annealing under ultrasonic vibrations slightly below the glass transition temperature. It was found that amorphous regions (blue) are surrounded by the crystallized wall (yellow). (b) On the basis of the inhomogeneous microstructure, a two-component microstructural model shown in the right figure is inferred; the blue parts denote strongly bonded regions and the yellow parts denote weakly bonded regions.

the “static structure” of the glass through the IXS and US “dynamic” measurements.

The IXS measurement was performed at the high-resolution IXS beamline **BL35XU**. Figure 3(a) shows the typical IXS spectra measured at very low Q values. To obtain the excitation energy, the present IXS spectra were fitted to the damped harmonic oscillator (DHO) function. Figure 3(b) shows the phonon-dispersion relation (lower panel) and compares the phase velocity of longitudinal sound obtained from the IXS data with the US velocities (upper panel). Usually, the US velocity ($\lambda \sim 1$ nm) in homogeneous solids is substantially equivalent to the fastest sound velocity at the long-wavelength limit. However, as shown in Fig. 3(b), the sound velocities in the low- Q region are found to be apparently higher than the US velocity in this case. The sound velocity at $Q \sim 4$ nm⁻¹ is virtually equal to the US velocity, indicating that the plots at $Q < 4$ nm⁻¹ deviate positively from the US linear function. For consistency, the sound-velocity plots in the low- Q region should be connected to the long-wavelength limit as shown by curve “A” in the figure. If we had

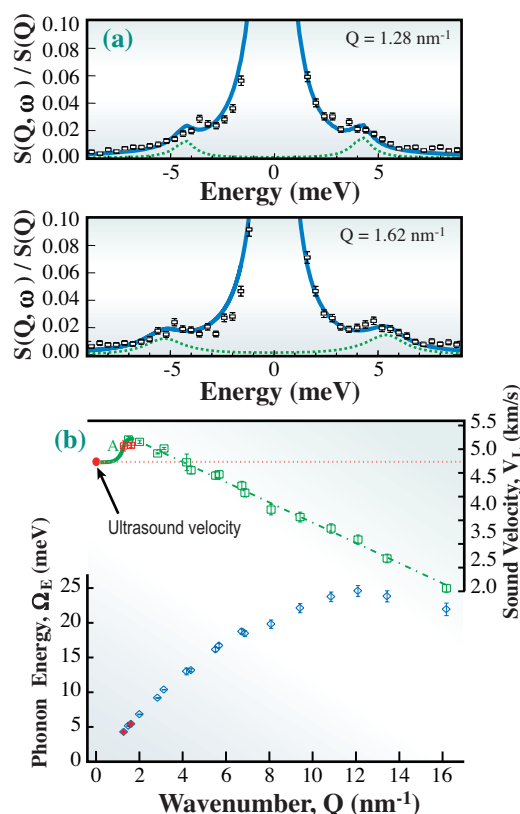


Fig. 3. (a) IXS spectra at very low Q values and (b) phonon-dispersion curve obtained from the IXS data for a Pd_{42.5}Ni_{7.5}Cu₃₀P₂₀ bulk metallic glass (lower), and comparison of the velocity of longitudinal sound obtained from the IXS data and the US velocities (upper).

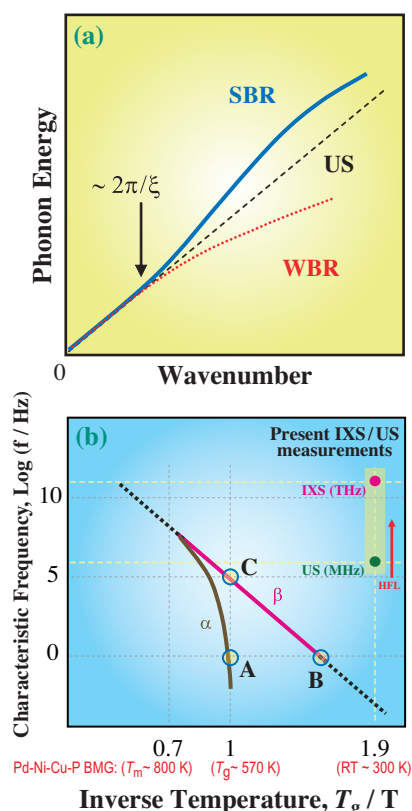


Fig. 2. Schematic illustrations showing (a) phonon-dispersion relation in a very small Q region predicted from the model, and (b) inverse-temperature dependence of the characteristic frequencies of α and β relaxations. The set of characteristic temperatures in (b) is an example for the case of Pd-Ni-Cu-P metallic glass; Point A denotes the glass transition, B and C are obtained from the experiments.

obtained a critical point that deviated from the US line by measuring the excitation energy at Q values less than 1.28 nm⁻¹, we would know the typical domain size ξ in Fig. 1(b). Finally, we remark that a higher-energy mode is present in this metallic glass and that it should be further investigated in detail.

Tetsu Ichitsubo^{a,*}, Eiichiro Matsubara^a, Shinya Hosokawa^b and Alfred Q.R. Baron^c

^a Department of Materials Science and Engineering, Kyoto University

^b Center for Materials Research using Third-Generation Synchrotron Radiation Facilities, Hiroshima Institute of Technology

^c SPring-8 / JASRI · RIKEN

*E-mail: tichi@mtl.kyoto-u.ac.jp

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