Low-temperature elastic moduli of a Pd-based metallic glass showing positive phonon dispersion

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We have recently shown that the sound velocity obtained from the inelastic x-ray scattering (IXS) measurement exceeds the ultrasonic wave velocity of a Pd-based metallic glass in a rigid glass state far below its glass transition temperature. Here we report that no obvious evidence of faster processes, which are supposed to be an origin of the phenomenon, was detected in the low-temperature dependence of the elastic moduli and internal friction of the Pd-based metallic glass showing such a positive dispersion. The longitudinal elastic modulus at low temperatures, where any processes are considered frozen out, is less than the elastic modulus deduced from the IXS measurement at room temperature. These suggest that the positive dispersion observed in this metallic glass is not a time-dependent phenomenon.

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Disordered materials, such as liquids and glasses, show many intriguing physical properties. Positive phonon dispersion phenomena, so-called "fast sound," are frequently observed in many disordered systems.[1,2] Especially for liquids, the positive dispersion is successfully explained within the framework of the mode coupling theory (MCT), in which a certain faster process, which is rattling movement (see for details Ref. 3) and different from α or (Johari-Goldstein) β relaxation processes, is supposed to be present.[1,2] Recently, we have experimentally measured the longitudinal sound velocity, V_L, by the inelastic x-ray scattering (IXS) measurement (see Fig. 1); it was found that the IXS sound velocity evidently exceeds the ultrasonic wave velocity of $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ in a rigid glass state far below its glass transition temperature (at about $0.38T_m$ or $0.52T_g$ with T_m as the melting temperature and T_g as the glass transition temperature).[4] A similar phenomenon on rigid glasses was observed earlier on a simple-glass selenium[5] and a silica glass,[6] and the phenomenon has been attributed to the residual fast process in the glass.[1,2,6] As was shown by Buchenau and Wischnewski,[7] elastic moduli of glasses are frequency dependent at sufficiently high temperatures where α or β relaxations can take place. Hence, the fast process is surely one of the candidates of the positive dispersion mechanism for relatively low-density glassy materials, but the existence of such a faster process may be uncertain, especially, for frozen-out rigid metallic glasses consisting of closely packed atoms. In our opinion, such a positive dispersion can be caused by two kinds of possible origins: one is frequency dependent due to such a fast process and the other is wavelength dependent associated with an intrinsic spatial inhomogeneity.

Based on the energy landscape concept,[8–10] since the dynamics far below T_g is dominated by the potential barriers in a glassy solid state (i.e., in the "landscape-dominated" regime), we need to confirm that the fast process of the order of megahertz-terahertz is indeed alive in such a sufficiently frozen glassy solid. In addition to the fast process, the double-well potential (DWP) or two-level system (TLS) (Refs. 11 and 12) may affect ultrasonic attenuation or sound velocity. As was demonstrated by Keppens *et al.*,[13] measuring of the temperature dependence of the elastic moduli may be a straightforward way for detecting such a localized vibration modes due to TLS. Thus, to obtain an evidence whether the faster process indeed remains in the Pd-based metallic glasses or not, we have measured the resonant frequencies, corresponding internal frictions and elastic moduli of the Pd-based metallic glass showing the positive dispersion at low temperatures down to 10 K, where most of dynamic processes (e.g., α and β relaxations, etc.) are considered to be frozen. In this Brief Report, we show that obvious anomaly in the low-temperature dependence of the elastic moduli can hardly be detected in the Pd-based metallic glass. Furthermore, the longitudinal elastic modulus at very low temperatures measured by ultrasound is less than that deduced from the sound velocity by IXS at room temperature. These results strongly indicate that the positive dispersion phenomenon observed in the Pd-based rigid metallic glass is not a time-dependent one.

We have employed the resonant ultrasound spectroscopy

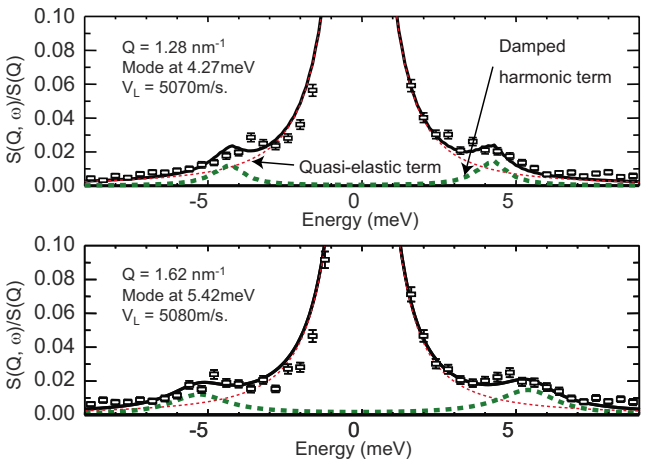

FIG. 1. (Color online) Normalized dynamic structure factor $S(Q,\omega)/S(Q)$ measured by IXS for $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ (PNCP) metallic glass at $Q=1.28$ and 1.62 nm^{-1}. The mode energy Ω_Q at each Q value was determined with the damped harmonic-oscillator model. The sound velocities at respective Q values are $V_L=5070$ and 5080 m/s, which exceed the ultrasonic sound velocity of 4760 m/s (see, for details, Ref. 4).

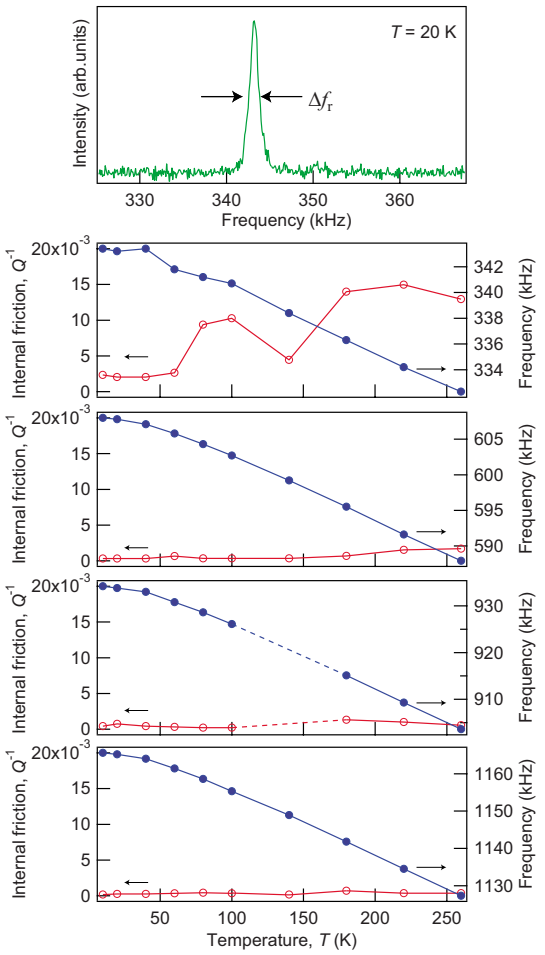

FIG. 2. (Color online) The resonance peak around 300 kHz at 20 K (top), the low-temperature dependence of several resonance frequencies (right axis), and their corresponding internal frictions (left axis) of $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$. Half width of the peak gives the internal friction corresponding to the resonance peak.

(RUS) technique[14–17] to measure the elastic moduli at low temperatures. By using the same sample (rectangular parallelepiped of $1.602\times1.632\times2.680$ mm^3 in dimensions and mass density of 9237 kg/m^3) used for the RUS and IXS measurements in the previous work,[4] the resonance frequencies were measured in the temperature range between 10 and 260 K in a helium-gas atmosphere. The resonance spectrum consisting of about 30–40 resonant peaks was obtained at each temperature in the frequency range of 200–1500 kHz at a step of 0.1 kHz, through the results of which the inverse iterative calculations were carried out to determine the longitudinal elastic modulus, c_L, and the transverse (shear) modulus, c_T, from the measured resonance spectrum.

Figure 2 shows the temperature dependence of the resonance frequency f_r and corresponding internal friction Q^{-1}, defined as

$$Q^{-1}(T) = \Delta f_r/f_r(T), \tag{1}$$

where Δf_r is the half width of the resonance frequency $f_r(T)$ at a temperature T (see the top figure in Fig. 2). Although it may be noticeable that a peak in Q^{-1} for $f_r\sim340$ kHz is seemingly seen around 100 K, no anomaly is substantially detected in $Q^{-1}(T)$ curves of the other vibration modes. If the apparent peak is due to the thermal activation process, similar peak should be observed at a higher temperature for a higher resonance frequency, but this is not the case. Namely, when we suppose that it is a real (not artifact) peak, the process is not a thermal activation process.

Figure 3 shows the low-temperature dependence of the elastic moduli (c_L, c_T, Young's modulus E, bulk modulus B, Poisson's ratio, and c_T/B). The temperature dependence is known to be well expressed with the Varshni equation,[18]

$$c(T) = c(0) - \frac{s}{\exp(\theta/T) - 1}, \tag{2}$$

where T is the temperature, $c(0)$ is the elastic modulus at 0 K, and s and θ are fitting parameters. All the elastic moduli can be well fitted by the Varshni[18] equation; the fitted curves are also shown by solid lines in the figure. Table I summarizes the fitting parameters for various metallic glasses[19,20] including the present $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ metallic glass. Interestingly, the elastic moduli c_L and B of $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ exhibit a strong temperature dependence; this corresponds to the lowering of θ for c_L and B. According to Keppens *et al.*,[13] this is suggestive of unusual low-energy vibrational modes in addition to the normal acoustic phonons. As seen in Table I, in common metallic glasses, θ for c_L is higher than that for c_T, but this relation is reversed for $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$, and it is surely anomalous behavior, which might be attributed to a certain faster process residual in the glass. However, as seen in the curves of the normalized moduli versus normalized temperature (T/T_l: T_l is the melting temperature) in Fig. 3, the overall temperature dependence of $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ is quite normal compared to that of $Zr_{50}Cu_{40}Al_{10}$ metallic glass. As shown in the recent work by Tarumi *et al.*,[20] the transverse elastic modulus c_T decreases with increase in temperature more steeply than the longitudinal modulus c_L, and this trend is also the case for $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$, and accompanied by this, Poisson's ratio increases and c_T/B decreases with increase in temperature. What is the most important here is that $c_L^{\mathrm{US}}(0)=221$ GPa at 0 K is still less than the value, $c_L^{\mathrm{IXS}}=237(8)$ GPa, evaluated from the IXS sound velocity at room temperature. Thus, considering some anomalous behaviors in the temperature dependence of elastic moduli of $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$, although it may be premature to affirm that any faster process does not remain in the Pd-based metallic glass, at least, we can conclude that it is not the main cause of the positive dispersion shown in Fig. 1.

An alternative candidate for the possible origin is the spatial elastic inhomogeneity that exists intrinsically in the glass.[21,22] In fact, there are several structural models of glasses that explicitly take into account of the intrinsic structural fluctuation in a glass substance in terms of thermodynamics, rheology, fragility, mechanical response, etc.[23–29] In order to reveal the nanoscale inhomogeneity, we have previously used ultrasound-induced instability phenomena in metallic glasses;[22,30,31] in that work glasses are crystallized by atomic jumps during the [Johari-Goldstein (Ref. 25)] β re-

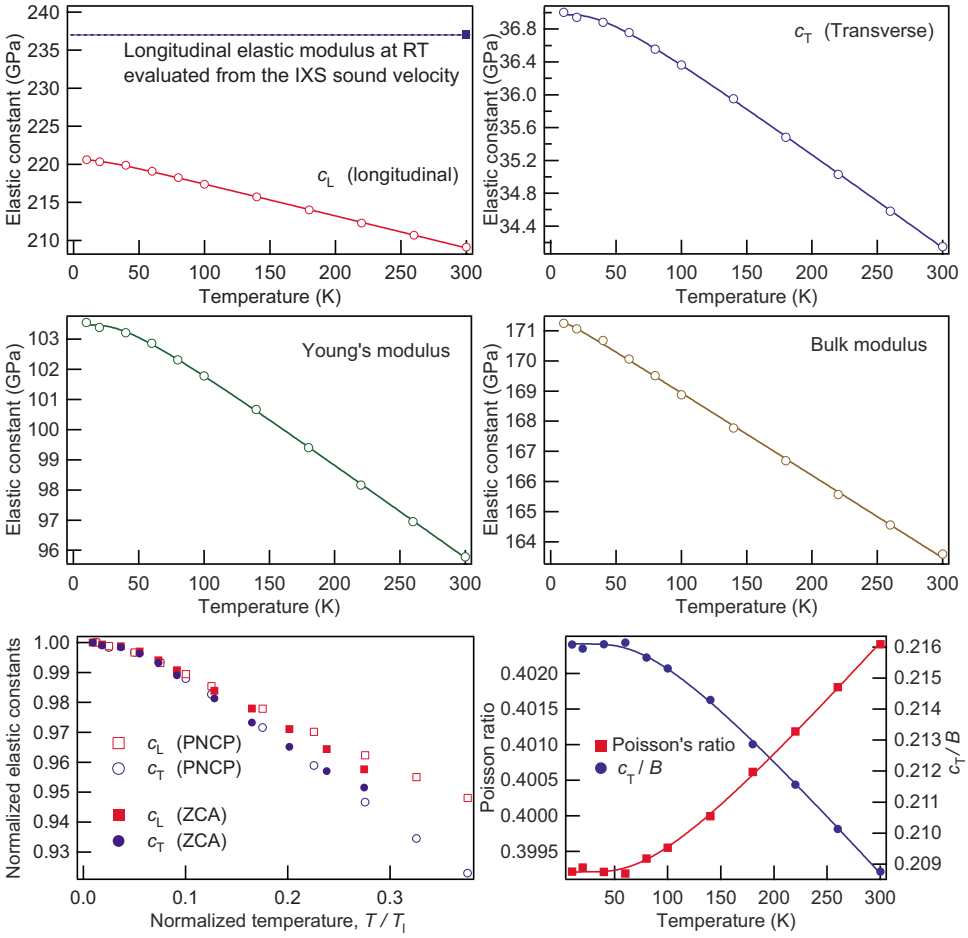

FIG. 3. (Color online) Low-temperature dependence of the elastic moduli of $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ showing positive dispersion. For comparison, those of $Zr_{50}Cu_{40}Al_{10}$ (ZCA) metallic glass (Ref. 19) are also shown. The solid lines are obtained by fitting the Varshni (Ref. 18) equation to the experimental data.

laxation resonant with a periodic strain field, and the partially crystallized microstructure of the glass is observed using high-resolution transmission electron microscopy from the results of which the structure of fragile metallic glasses is expected to consist of strongly bonded regions surrounded by weakly bonded regions. Such an structural inhomogeneity

TABLE I. Elastic modulus c_L (in units of GPa) measured by RUS and IXS at room temperature and fitting parameters of the Varshni (Ref. 18) equation for elastic moduli of various metallic glasses. The longitudinal modulus c_L of IXS is evaluated with $c_L=\rho V_L^2$ ($\rho=9237$ kg/m^3 for $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$) from the phonon excitation energy measured at $Q=1.28$ and 1.62 nm^{-14}. The value of $c(0)$ means the low-temperature elastic modulus at 0 K.

Measurement		U.S.	IXS		Refs.
	Q	~0	1.28	1.62	
$Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$	c_L(RT)	209	237	238	4
Parameters in Eq. (2)		$c(0)$	s	θ	
$Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$	c_L	221	2.30	54.4	Present
	c_T	37.0	1.33	115	Present
	E	103	3.47	111	Present
	B	171	0.73	26.7	Present
$Zr_{50}Cu_{40}Al_{10}$	c_L	165	3.41	119	19
	c_T	35.3	0.80	113	19
$Cu_{60}Zr_{30}Ti_{10}$	c_L	179	4.7	183	20
	c_T	37.8	1.15	123	20
$Cu_{60}Hf_{25}Ti_{15}$	c_L	181	3.72	147	20
	c_T	39.6	1.18	123	20

strongly supports the idea of Ngai[32] or Johari[33] that not all molecules or atoms may contribute to the Johari-Goldstein[25] β relaxation process, which is recently investigated deeply by Lunkenheimer *et al.*,[3] Buchenau,[34] and Zhao *et al.*[35] Thus, the present result that the sound velocities of nanoscale wavelengths (corresponding to the local elastic modulus) exceed the ultrasound velocity at zero temperature, corresponding to $c_{ij}(0)$, strongly indicates that this phenomenon is not time dependent but spatial dependent, and elastically harder regions should be present in the glassy matrix (hence, the existence of elastically softer regions is also needed so as to realize the relatively low elasticity of the whole glass substance). It should be noted that works being focused on the elastic inhomogeneity of glasses have been frequently reported in various viewpoints.[36–41] Among them, our concept may be similar to the recently proposed Buchenau-Schober model[42] to account for the boson peak in metallic glasses and may link to the cooperative shear model proposed by Johnson and Samwer.[43]

In summary, we have measured the low-temperature elastic moduli and internal frictions of $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ that exhibits the positive phonon dispersion in inelastic x-ray scattering, compared to other metallic glasses. We have observed no anomaly of temperature dependencies of elastic moduli and internal frictions. It is emphasized here that the zero-temperature elastic modulus $c_L^{\mathrm{US}}(0)$, which is not affected by any relaxation process, is lower than c_L^{IXS} evaluated by the IXS measurement at room temperature. Thus, it is suggested that spatial elastic inhomogeneity causes positive dispersion and causes IXS velocity to exceed ultrasound velocity.

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