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Pressure dependence of the elastic constants and vibrational anharmonicity of $Pd_{39}Ni_{10}Cu_{30}P_{21}$ bulk metallic glass

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Abstract

The pressure dependence of the acoustic velocities of a $Pd_{39}Ni_{10}Cu_{30}P_{21}$ bulk metallic glass have been investigated up to 0.5 GPa at room temperature with the pulse echo overlap method. Two independent second-order elastic coefficients C_{11} and C_{44} and their pressure derivatives are yielded. The vibrational anharmonicity is shown by calculating both the acoustic mode Grüneisen parameters in the long-wavelength limit and the thermal Grüneisen parameter, and this result is compared with that for the $Pd_{40}Ni_{40}P_{20}$ bulk glass.

1. Introduction

Acoustic and elastic studies have shown that the glassy materials possess some unique features different from those of the crystallized counterparts; considerable interest in the origin of the uniqueness has been aroused [1–4]. Inorganic glasses such as oxide-based glasses, BeF_2 and As-containing glasses have been widely investigated, and some theories have been established to explain the anomalous acoustic behaviours, such as the tunnelling model for the low-temperature anomalies in insulating glasses [3, 5]. However, so far, many phenomena remain poorly understood. Usually, ultrasonic measurements are used to give important information on the structural and vibrational features of condensed matter; in particular, the combination of ultrasonic measurements and the high-pressure technique can improve our understanding of the elastic and vibrational behaviours of glassy materials [6–8].

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In the glassy material family with various binding natures, metallic glasses have the simplest atomic configuration form, which is generally referred to as the randomly close-packed structure [9]. Studies on the metallic glasses clearly contribute to the new knowledge of the basic acoustic characteristics of glassy states, which will be helpful in exploring the physical origin of the anomalous behaviours in glassy states. However, to date, not many ultrasonic studies have been carried out on metallic glasses due to the difficulty in preparing bulk metallic glassy materials [10, 11]. The recent development of Zr- and Pd-based bulk metallic glasses (BMGs) with larger sizes (over a centimetre) has caused an upsurge in both fundamental and applications investigation [12–16]. As regards the acoustic study, BMGs allow more accurate measurements of ultrasonic wave propagation in comparison with those performed on the conventional amorphous alloy ribbons [17, 18]. It is believed that the investigation of these novel materials will open new windows helping to reveal the elastic and vibrational characteristics of the metallic glasses.

Our recent studies of BMGs based on ultrasonic measurements have shown lots of structural and phase transition characteristics of various BMGs [17–19]. In this work, we use this technique to study the elastic behaviours of a $Pd_{39}Ni_{10}Cu_{30}P_{21}$ BMG under high pressure at room temperature. The pressure dependence of the elastic constants is obtained and, further, the Grüneisen parameter is calculated, which is used to evaluate the vibrational anharmonicity. With these results, we attempt to get some further information on the structural and elastic characteristics of this excellent glass-former.

2. Experimental details

A 6 mm diameter rod of a PdNiCuP BMG was prepared by a water quenching method [18]. The composition was determined as $Pd_{39}Ni_{10}Cu_{30}P_{21}$ by chemical analyses. The amorphous nature as well as the homogeneity of the BMG were ascertained by means of x-ray diffraction and transmission electron microscopy. The BMG rod was cut to a length of about 10 mm and its ends were polished flat and parallel. The acoustic velocities and their pressure dependence were measured at room temperature by using the pulse echo overlap (PEO) method [20]. The travel time for ultrasonic waves propagating through the rod with a 10 MHz carrier frequency was measured by using a MATEC 6600 ultrasonic system with x- and y-cut quartz transducers. The travel time measurement error was of order 0.5 ns.

High-pressure experiments were performed on a piston–cylinder apparatus, and electric insulation oil was used as the pressure-transmitting medium. The measurements were performed for several pressure load–unload cycle times to guarantee reproducibility. The pressure loading and unloading rate was 0.04 kbar min^{-1}. The density of the BMG was measured at ambient pressure by the Archimedean method with an accuracy better than 0.1%. Upon pressure loading, the changes in the density and the length of the rod were modified using the Richard Cook method [21]. Elastic constants were derived from the acoustic velocities and the densities [20].

3. Results and discussion

Figure 1 gives the pressure dependence of the longitudinal and transverse velocities v_l, v_t of the as-quenched $Pd_{39}Ni_{10}Cu_{30}P_{21}$ BMG upon loading and unloading. One can see that, up to 0.5 GPa, the two acoustic velocities increase with a roughly linear trend. The pressure dependence of the acoustic velocities obtained during the loading can be roughly reproduced during the unloading processes, although there is a slight hysteresis during unloading.

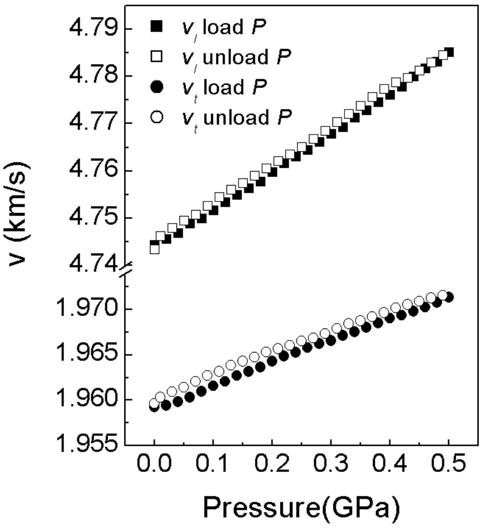

Figure 1. Pressure dependences of the longitudinal and transverse acoustic velocities of the $Pd_{39}Ni_{10}Cu_{30}P_{21}$ BMG at room temperature.

The results show that, within the experimental pressure range, the changes of the acoustic properties of the as-quenched BMG with pressure are reversible, and the measurements lie in the sample's elastic behaviour region.

Two independent second-order elastic coefficients $C_{11} = \rho v_l^2$ and $C_{44} = \rho v_t^2$ are obtained from the two acoustic velocities and the measured initial density of 9.15 g cm^{-3}. Also, the two elastic constants, $C_{12} = C_{11} - 2C_{44}$ and the bulk modulus K, often used in studying the elastic and vibrational properties of amorphous materials, are calculated, although they are not independent parameters. The pressure dependences of these moduli are shown in figure 2. It can also be seen that the elastic moduli increase linearly with pressure. Table 1 summarizes the moduli and their first-order pressure derivatives at ambient pressure from the present work and [11, 22–25]. It has been pointed out [8] that, under high pressure, the higher-order elastic stiffness is dominated by interatomic nearest-neighbour repulsive forces; most alloys of cubic crystals follow the common trend: $(\mathrm{d}C_{11}/\mathrm{d}P)_{P=0} > (\mathrm{d}C_{44}/\mathrm{d}P)_{P=0}$, the value of $(\mathrm{d}C_{11}/\mathrm{d}P)_{P=0}$ being the largest for most face-centred cubic (fcc) materials. It is also remarked that metals with close-packed structure have $\mathrm{d}K/\mathrm{d}P$ values higher than those of body-centred cubic (bcc) transition metals having comparable atomic volume [25]. From table 1 one can see that the Pd-based metallic glasses have $\mathrm{d}C_{11}/\mathrm{d}P$ and $\mathrm{d}K/\mathrm{d}P$ larger than those of the fcc and bcc crystalline metals. Our previous study confirms that the nature of metallic bond is retained in the BMG, although atomic long-range order is lacking [18]. In this context, the comparison in table 1 implies that the atomic configurations in the Pd-based metallic glasses are probably closely packed. The existence of this kind of atomic configuration in the BMG is possible, since the metallic components Pd, Ni, Cu have fcc atomic arrangement in the crystalline state. On the other hand, the larger $\mathrm{d}C_{11}/\mathrm{d}P$ and $\mathrm{d}K/\mathrm{d}P$ may be ascribed to the presence of the metalloid element P. It is also seen in table 1 that the shear moduli and their pressure derivatives of the Pd-based metallic glasses are relatively small. This is a common and pronounced feature of the elastic properties of amorphous materials. According to the conventional model, these low values arise from the relatively weak long-range Coulomb energy and its pressure dependence due to the lack of structurally atomic long-range ordering [26, 27].

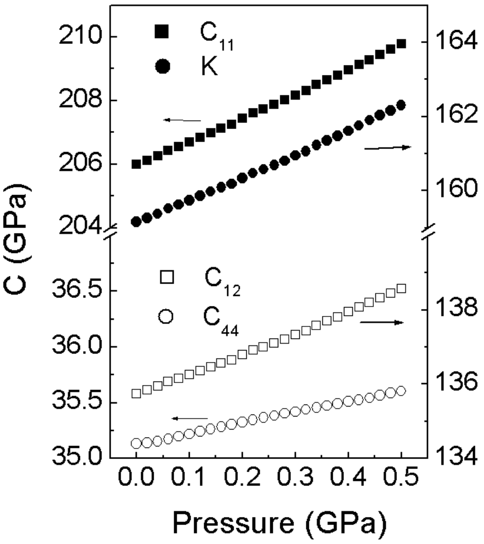

Figure 2. Elastic constants of the $Pd_{39}Ni_{10}Cu_{30}P_{21}$ BMG as functions of pressure at room temperature.

Table 1. Elastic constants of and their pressure derivatives at atmospheric pressure of the as-quenched $Pd_{39}Ni_{10}Cu_{30}P_{21}$ and $Pd_{40}Ni_{40}P_{20}$ BMGs, together with results for other metals at room temperature.

Sample	C_{11} (GPa)	C_{44} (GPa)	C_{12} (GPa)	K (GPa)	$\mathrm{d}C_{11}/\mathrm{d}P$	$\mathrm{d}C_{44}/\mathrm{d}P$	$\mathrm{d}C_{12}/\mathrm{d}P$	$\mathrm{d}K/\mathrm{d}P$	Reference
$Pd_{39}Ni_{10}Cu_{30}P_{21}$	206	35.1	135.8	159.2	7.56	0.96	5.64	6.28	Present
$Pd_{40}Ni_{40}P_{20}$	236	38.6	158.8	185	8.9	1.0	6.9	7.56	[11, 16]
Pd	224	71.6	173	189	6.1	2.4	5.2	5.42	[11, 17]
Ni	247	122	153	183	6.0	2.4	4.7	5.26	[11, 17]
Cu	168	75.1	121	137	6.25	2.35	5.1	5.48	[17, 18]
Nb	246.2	28.7	133	170	5.26	0.268	3.45	4.06	[19]
Ta	266	82.5	161	204	5.1	0.995	3.14	3.79	[19]

From the hydrostatic pressure derivatives of the elastic moduli listed in table 1, the acoustic mode Grüneisen parameters of the longitudinal and transverse waves in the long-wavelength limit γ_l, γ_t can be calculated as follows [28]:

$$\gamma_l = -\frac{K}{6C_{11}}\left(3 - \frac{2C_{12}}{K} - \frac{3\,\mathrm{d}K}{\mathrm{d}P} - \frac{4\,\mathrm{d}C_{44}}{\mathrm{d}P}\right) \tag{1}$$

$$\gamma_t = -\frac{1}{6C_{44}}\left(2C_{44} - 3K\frac{\mathrm{d}C_{44}}{\mathrm{d}P} - \frac{3}{2}K + \frac{3}{2}C_{12}\right). \tag{2}$$

Grüneisen parameters are associated with the vibrational anharmonicity of condensed matter, i.e. the nonlinearity of the interaction of atoms with respect to atomic displacements. An acoustic mode Grüneisen parameter reflects the volume or strain dependence of the vibrational frequency. According to equations (1) and (2), we obtain the two acoustic Grüneisen parameters $\gamma_l = 2.75$, $\gamma_t = 2.01$ for the as-quenched $Pd_{39}Ni_{10}Cu_{30}P_{21}$ BMG. The two values are both positive, indicating that the mode frequencies of the longitudinal and transverse acoustic branches in the long-wavelength limit increase with pressure. It has been shown that in the high-temperature region ($T > \Theta_D$; Θ_D is the Debye temperature), all vibrational modes are excited, and the mean acoustic Grüneisen parameter $\overline{\gamma}$ can be estimated using the following relation [11]:

$$\overline{\gamma} = \tfrac{1}{3}(\gamma_l + 2\gamma_t). \tag{3}$$

The Debye temperature of the as-quenched $Pd_{39}Ni_{10}Cu_{30}P_{21}$ BMG has been calculated [18] to be 279 K and, thus, equation (3) can be satisfied in this experiment at room temperature. Accordingly, the mean Grüneisen parameter $\overline{\gamma}$ in the long-wavelength limit for the $Pd_{39}Ni_{10}Cu_{30}P_{21}$ BMG is calculated to be 2.26. The value is higher than those of the crystalline metals Pd and Ni, which are 2.13 and 1.35, respectively [11]. Based on the values in table 1, the mean Grüneisen parameter $\overline{\gamma}$ of the $Pd_{40}Ni_{40}P_{20}$ metallic glass in the long-wavelength limit is calculated to be 2.59. Therefore, it is clear that the vibrational anharmonicity of the $Pd_{39}Ni_{10}Cu_{30}P_{21}$ BMG in the long-wavelength limit is slightly smaller than that for the conventional Pd-based metallic glasses.

After the long-wavelength Grüneisen parameter of the $Pd_{39}Ni_{10}Cu_{30}P_{21}$ BMG is obtained, it is necessary and useful to know the long-wavelength phonon contribution to the total Grüneisen parameter, i.e., the thermal Grüneisen parameter. In the quasiharmonic approximation, the thermal Grüneisen parameter γ_{th}, which is an average of the contributions of all of the phonons through the Brillouin zone to the total vibrational anharmonicity, can be yielded from the relation [11, 29]

$$\gamma_{th} = \frac{3\alpha^l K^S V}{C_P} \tag{4}$$

where α^l, K^S, V and C_P denote the linear thermal expansion coefficient, adiabatic bulk modulus, mole volume and specific heat, respectively. We have obtained the room temperature specific heat of the $Pd_{39}Ni_{10}Cu_{30}P_{21}$ BMG as 23.8 J mol^{-1} K^{-1} [18]. But, for the linear thermal expansion coefficient, so far, no room temperature data are available and, here, we use the value of a $Pd_{43}Ni_{10}Cu_{30}P_{27}$ BMG, 17×10^{-6} K^{-1} [30]. Then, the thermal Grüneisen parameter γ_{th} is calculated to be 2.72.

In table 2, we give a summary of the Grüneisen parameters of the $Pd_{39}Ni_{10}Cu_{30}P_{21}$ and the $Pd_{40}Ni_{40}P_{20}$ BMGs as well as corresponding physical properties involved in equation (4), which are from [11, 30–33]. One can see that, like those of the $Pd_{40}Ni_{40}P_{20}$ BMG, the thermal Grüneisen parameters of the $Pd_{39}Ni_{10}Cu_{30}P_{21}$ BMG are close to that of the long-wavelength acoustic mode. According to Saunders' studies [11], this similarity implies that the long-wavelength acoustic branches play an important role in governing the thermal properties of the metallic glass. Together with the positive pressure derivatives of elastic constants, the similarity of the thermal Grüneisen parameter to the mean acoustic Grüneisen parameter in the long-wavelength limit reflects a high atomic coordination number [29]. This is in agreement with the $Pd_{39}Ni_{10}Cu_{30}P_{21}$ BMG having a close-packed atomic configuration.

4. Conclusions

The pressure dependence of the acoustic velocities of the $Pd_{39}Ni_{10}Cu_{30}P_{21}$ BMG has been measured up to 0.5 GPa. The positive pressure derivatives of the two independent second-order elastic coefficients C_{11} and C_{44} have been obtained. These results reflect the structural stiffness of the metallic glass under pressure. The vibrational anharmonicity is shown by calculating both the acoustic mode Grüneisen parameters in the long-wavelength limit and the thermal Grüneisen parameter. It is found that the $Pd_{39}Ni_{10}Cu_{30}P_{21}$ BMG shows slightly smaller vibrational anharmonicity in the long-wavelength acoustic mode than the conventional Pd-based metallic glasses which require a higher critical cooling rate for glass forming; however, the value is still larger than for their crystalline metal components.

Table 2. Acoustic and thermal Grüneisen parameters γ (their definitions appear in the text) and corresponding thermodynamic parameters of the $Pd_{39}Ni_{10}Cu_{30}P_{21}$ and the $Pd_{40}Ni_{40}P_{20}$ BMGs at room temperature. ρ is the density, α the linear thermal expansion coefficient and C_P the specific heat. Note that the parameters of the two materials are for their as-quenched states.

	$Pd_{39}Ni_{10}Cu_{30}P_{21}$	$Pd_{40}Ni_{40}P_{20}$
γ_l	2.75	3.32[a]
γ_t	2.01	2.23[a]
$\overline{\gamma}$	2.26	2.59[a]
ρ (g cm^{-3})	9.152	9.4[a]
α (10^{-6} K^{-1})	17[b]	14[c]
C_P (J mol^{-1} K^{-1})	23.8	21.9[d]
γ_{th}	2.72	2.73[e]

[a] Reference [11].

[b] Reference [30]. This value is the room temperature linear thermal expansion coefficient value for the as-quenched $Pd_{43}Ni_{10}Cu_{30}P_{27}$ BMG.

[c] Reference [31].

[d] Reference [32]. This room temperature specific heat value is very close to ~21.3 J mol^{-1} K^{-1}, which is from [33].

[e] This is a new value calculated according to equation (4) using the values of the linear expansion coefficient and the specific heat of the $Pd_{40}Ni_{40}P_{40}$ BMG, and it is a little bigger than 2.24, which comes up in [11], where they use the values of the linear expansion coefficient and the specific heat for either a fully relaxed $Pd_{40}Ni_{40}P_{40}$ glassy sample or another $Pd_{48}Ni_{32}P_{20}$ glass.

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