Elastic constants of $Pd_{39}Ni_{10}Cu_{30}P_{21}$ bulk metallic glass under high pressure

Li Min Wang,[a] L. L. Sun, W. H. Wang, R. J. Wang, Z. J. Zhan, D. Y. Dai, and W. K. Wang[b]
Center for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing, 100080, People's Republic of China

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The pressure-dependent acoustic velocities of a $Pd_{39}Ni_{10}Cu_{30}P_{21}$ bulk metallic glass (BMG) have been measured up to 0.5 GPa by using an ultrasonic technique with the pulse echo overlap method. The elastic constants, the Debye temperature, and their pressure dependence are obtained. The isothermal equation of state (EOS) of the BMG is established in terms of the Murnaghan form. The atomic configurations of the BMG are discussed by comparing the elastic constants and the EOS with those of its metallic component and of other amorphous materials. © *2000 American Institute of Physics.* [S0003-6951(00)04349-7]

Studies on elastic properties and Debye temperature can provide important information about structural and vibrational characteristics for a condensed matter.[1,2] However, in comparison with the crystalline state, the understanding on glassy metallic state has been impeded by the inability in preparing bulk metallic glasses (BMGs). Recently, multicomponent Pd- and Zr-based glass forming systems with a larger geometry have been developed by a conventional casting process at a low cooling rate.[3–7] Among the BMGs, PdNiCuP systems are of the highest reduced glass transition temperature of 0.72 known so far, and can be prepared into a glass with a maximum thickness of over 70 mm at a cooling rate less than 1 K/s.[3–5] It is believed that the BMGs have a considerable potential for both theoretical investigations and practical applications. Ultrasonic measurement provides a powerful tool for obtaining the elastic constants and Debye temperature of a solid matter, and the larger geometry of the BMGs is more suitable for the measurement of elastic wave propagation compared to conventional metallic glasses.[8] However, not much work has been done on this aspect, in particular, on the understanding of microstructural configuration under pressure. In this work, we investigate the pressure dependence of the acoustic velocities, the elastic constants, and the Debye temperature of a $Pd_{39}Ni_{10}Cu_{30}P_{21}$ BMG. With these results, we attempt to reveal the characteristics of the elastic behavior of the BMG and, further, to obtain structural information.

A 6-mm-diam rod of the PdNiCuP BMG was prepared by a water quenching method.[9] The composition was quantified to be $Pd_{39}Ni_{10}Cu_{30}P_{21}$ by chemical analyses. The amorphous nature as well as the homogeneity of the BMG was ascertained by x-ray diffraction and transmission electron microscopy. The BMG rod was cut into a length of about 10 mm and its ends were polished flat and parallel. The acoustic velocities and their pressure dependence of the BMG were measured at room temperature by using the pulse echo overlap method.[10] The travel time of ultrasonic waves propagating through the rod with a 10 MHz carry frequency was measured by using the MATEC 6600 ultrasonic system with x- and y-cut quartz transducers. The measuring sensitivity was of the order of 0.5 ns. The high pressure experiments were performed on a piston-cylinder high-pressure apparatus, and electric insulation oil was used for the pressure transmitting media, for which hydrostaticity has already been determined at room temperature.[8] The measurements were performed for several pressure load–unload cycle times to examine its reproducibility. The loading and unloading rate was 0.04 kbar/min. The density was measured by the Archimedean technique and the accuracy lies within 0.1%. Upon pressure loading, the density and the length of the rod were modified with the Richard Cook method.[11] Elastic constants (e. g., Young's modulus E, shear modulus G, bulk modulus K, and Poisson's ratio σ) and Debye temperatures Θ_D were derived from the acoustic velocities and the densities.[10]

The longitudinal, transverse velocities v_l, v_t, and the density ρ of the BMG at ambient condition are 4.744 km/s, 1.959 km/s, and 9.152 g/cm^3, respectively. E, G, K, σ, and Θ_D are calculated to be 98.2, 35.1, 159.2 GPa, 0.397, and 279 K. These values are rather close to those of crystalline Pd,[12] which means that the metallic bond is retained even if the BMG lacks long-range order. For a solid material, Poisson's ratio $\sigma=(v_l^2-2v_t^2)/2(v_l^2-v_t^2)$ and the expression of $K/G=(v_l/v_t)^2$-4/3 are often used to evaluate its microstructural characteristics, and $\sigma=0.25\,(K/G\sim1.7)$ is referred to as the typical value for isotropic materials with central interacting forces such as silicate glass.[10,13,14] Some σ and K/G values of the BMG and of other Pd-containing metallic glasses from Ref. 15 are listed in Table I. Compared to these conventional metallic glasses, which have lower GFA and require a higher cooling rate for glass formation, the $Pd_{39}Ni_{10}Cu_{30}P_{21}$ BMG shows smaller values of σ and *K/G*. A previous study confirms that the decrease of σ brings about more difficulties in atomic rearrangements, which results in higher GFA.[8] The present results are in agreement

[a] Author to whom all correspondence should be addressed; electronic mail: wanglm@aphy.iphy.ac.cn
[b] Also at: College of Material Sciences and Chemical Engineering, Yanshan University, Qinhuangdao, 066004, People's Republic of China.

TABLE I. Comparison of longitudinal and transverse acoustic velocities v_l, v_t, Poisson ratio σ, and the ratio of bulk modulus K to shear modulus G of various Pd-containing metallic glasses.

Sample	v_l (km/s)	v_t (km/s)	v_l/v_t	σ	K/G
$Pd_{39}Ni_{10}Cu_{30}P_{21}$	4.750	1.963	2.42	0.397	4.52
$Pd_{32}Ni_{48}P_{20}$ [a]	4.930	2.020	2.44	0.399	4.62
$Pd_{48}Ni_{32}P_{20}$ [a]	4.786	1.918	2.49	0.404	4.89
$Pd_{79.5}Cu_6Si_{16.5}$ [a]	4.6	1.797	2.56	0.411	5.22

[a]Data from Ref. 15

with the argument and the decrease in σ and *K/G* improves the GFA of the Pd-containing alloys.

Figure 1 shows the pressure dependence of the reduced longitudinal and transverse velocities, $\delta v(P)/v(P_0) = (v(P)\text{-}v(P_0)/v(P_0)$, for the $Pd_{39}Ni_{10}Cu_{30}P_{21}$ BMG at room temperature, where P_0 is the ambient pressure. Reversible behaviors in the acoustic velocities under P cycling are shown in Fig. 1 with slight hysteresis effects. And thus, the measurements are within the elastic region of the BMG, and no pressure-induced structural relaxation is visible. Upon pressure loading, v_l and v_t roughly linearly increase, and the pressure coefficients $(dv/dP)/v_0$ for v_l and v_t are yielded to be ~ 0.015 and $\sim 0.010\,\mathrm{GPa}^{-1}$, respectively. The longitudinal velocity is slightly more sensitive to the pressure variation than the transverse one.

The variations $\delta Y(P)/Y(P_0) = [Y(P)\text{-}Y(P_0)]/Y(P_0)$ of the calculated elastic constants E, G, K, and σ are shown in Fig. 2 as a function of pressure. The elastic constants monotonously increase with pressure, indicating the continuous stiffness of the elastic constants under the hydrostatic pressure. Bulk modulus K exhibits the biggest increase by $\sim 1.7\%$ up to 0.5 GPa, while E and G have relatively smaller changes. σ almost keeps constant within the experimental range, indicating little structural changes. When the BMG is treated as a monatomic lattice with an average cellular volume, the Debye temperature Θ_D is calculated using the formula

$$\Theta_D = \frac{h}{k_B}\left(\frac{9}{4\pi\Omega_0}\right)^{1/3}\left(\frac{1}{v_l^3}+\frac{2}{v_t^3}\right)^{-1/3}, \tag{1}$$

where h and k_B are the Planck constant and the Boltzman constant, respectively; Ω_0 is the atomic volume. As shown in Fig. 3, Θ_D increases by $\sim 0.62\%$ up to 0.5 GPa. Θ_D represents the temperature at which nearly all modes of vibration in a solid are excited, and its increase indicates a strengthening in the rigidity of the BMG with increasing pressure.

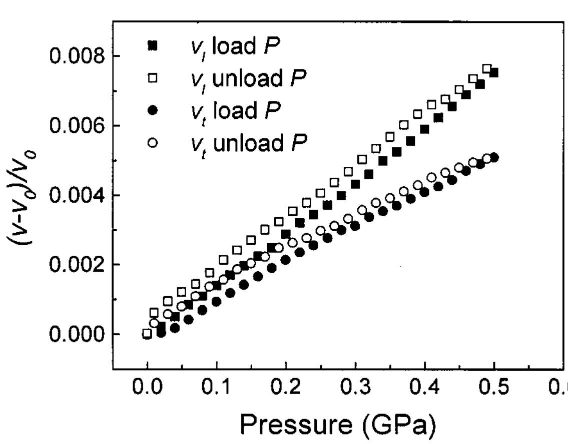

FIG. 1. Pressure dependence of the longitudinal and transverse acoustic velocities, v_l and v_t, of the $Pd_{39}Ni_{10}Cu_{30}P_{21}$ BMG. v_0 is the velocity at ambient pressure P_0.

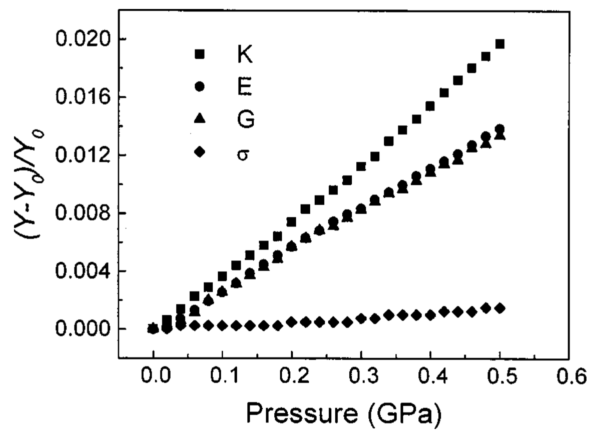

FIG. 2. Variation of the elastic constants of the $Pd_{39}Ni_{10}Cu_{30}P_{21}$ BMG with pressure ($Y = K,E,G,\sigma$). K, E, G, and σ stand for bulk modulus, Young's modulus, shear modulus, and Poisson's ratio. Y_0 is the modulus at ambient pressure.

On the basis of bulk modulus and its pressure dependence, an isothermal equation of state (EOS) is established in terms of the Murnaghan form,[16,17]

$$P = \frac{K_0}{K_0'}\left[\left(\frac{V_0}{V(P)}\right)^{K_0'} - 1\right], \tag{2}$$

where K_0 and K_0' are the bulk modulus and its pressure derivative at zero P, respectively, and V_0 is the volume at zero pressure. K_0' of the $Pd_{39}Ni_{10}Cu_{30}P_{21}$ BMG is derived to be 6.28 ± 0.01 from Fig. 2 and, accordingly, the isothermal EOS of the BMG in the elastic region is described as

$$P = 25.4\left[\left(\frac{V_0}{V(P)}\right)^{6.28} - 1\right]. \tag{3}$$

Figure 4 shows the volume compression curves $V_0/V(P)$ of various materials up to 0.5 GPa. Unlike other amorphous materials such as oxide glasses and amorphous carbon,[18] the Pd- and Zr-based BMGs exhibit small volume changes with pressure, as do their metallic components.[19] It

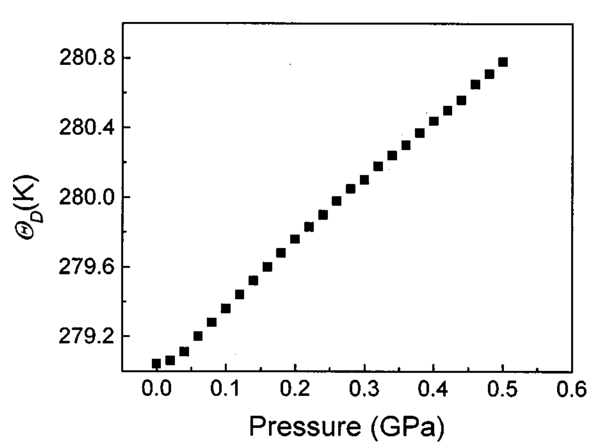

FIG. 3. Debye temperature of the $Pd_{39}Ni_{10}Cu_{30}P_{21}$ BMG as a function of pressure.

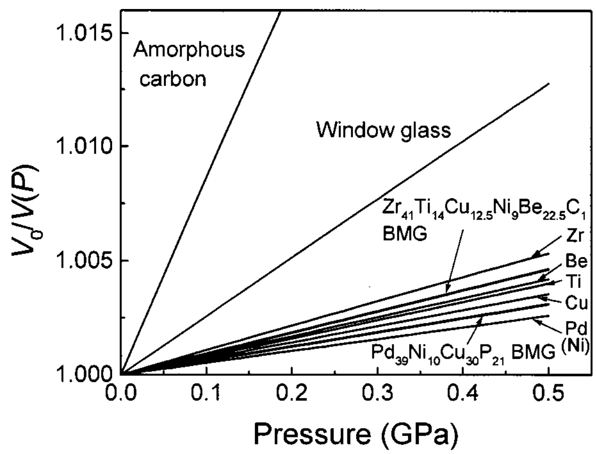

FIG. 4. Comparison of volume compression curves of various materials. V_0 is the volume under ambient pressure.

is seen that the compression curve of the $Pd_{39}Ni_{10}Cu_{30}P_{21}$ BMG is interposed among those of its metallic components Pd, Ni, and Cu. For comparison, the compression curves of the elements Zr, Ti, Be are plotted in Fig. 4 for the $Zr_{41}Ti_{14}Cu_{12.5}Ni_9Be_{22.5}C_1$ BMG. It is indicated that the compression curves of the two BMGs depend on their metallic components and exhibit an average result of these elements. The compressibility of a solid is determined by the nature of the interatomic potential and the atomic configurations,[19] and thus Fig. 4 implies that the short-range order structure of the $Pd_{39}Ni_{10}Cu_{30}P_{21}$ BMG has close correlation with the atomic configurations in its three metallic components. The existence of metalloid P in the BMG does not change the nature of the metallic bond. Since Pd, Ni, and Cu are of cubic close-packed structures, it is very likely that the same atomic close-packed configurations dominate the short-range structure of the $Pd_{39}Ni_{10}Cu_{30}P_{21}$ BMG.

In conclusion, the elastic constants, the Debye temperature, and their pressure dependence of the $Pd_{39}Ni_{10}Cu_{30}P_{21}$ BMG are obtained. It is found that for Pd-containing metallic glasses, the decrease of σ or K/G favors the improvement of the GFA. The isothermal equation of state of the BMG is established in terms of the Murnaghan form up to 0.5 GPa.

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[1] J. Xu and M. H. Manghnani, Phys. Rev. B **45**, 640 (1992).
[2] B. Golding, B. G. Bagley, and F. S. L. Hsu, Phys. Rev. Lett. **29**, 68 (1972).
[3] N. Nishiyama and A. Inoue, Mater. Trans., JIM **37**, 1531 (1996).
[4] A. Meyer, R. Busch, and H. Schober, Phys. Rev. Lett. **83**, 5027 (1999).
[5] A. Inoue, Mater. Sci. Eng., A **267**, 171 (1999).
[6] A. Peker and W. L. Johnson, Appl. Phys. Lett. **63**, 2342 (1993).
[7] X. P. Tang, U. Geyer, R. Busch, W. L. Johnson, and Y. Wu, Nature (London) **402**, 160 (1999).
[8] W. H. Wang, R. J. Wang, F. Y. Li, D. Q. Zhao, and M. X. Pan, Appl. Phys. Lett. **74**, 1803 (1999).
[9] L. M. Wang, W. H. Wang, L. L. Sun, J. H. Zhao, D. Y. Dai, and W. K. Wang, Sci. China, Ser. A: Math., Phys., Astron. **43**, 407 (2000).
[10] E. Schreiber, *Elastic Constants and Their Measurement* (McGraw–Hill, New York, 1973).
[11] Richard Cook, J. Acoust. Soc. Am. **29**, 445 (1957).
[12] D. E. Gray, *American Institute of Physics Handbook*, 3rd ed. (McGraw–Hill, New York, 1973).
[13] R. J. Wang, F. Y. Li, J. Xu, and H. S. Xie, J. High Press. Phys. **8**, 177 (1994). (in Chinese).
[14] H. S. Chen, J. Appl. Phys. **49**, 462 (1978).
[15] H. S. Chen, J. Non-Cryst. Solids **27**, 257 (1978).
[16] F. D. Murnaghan, *Finite Deformation of an Elastic Solid* (Wiley, New York, 1951).
[17] M. H. Manghnani, and S. Akimoto, *High-Pressure Research* (Academic, New York, 1977).
[18] J. F. Wang, R. J. Wang, and S. A. He, J. High Press. Phys. **2**, 34 (1988). (in Chinese).
[19] P. W. Bridgman, *The Physic of High Pressure* (Bell, London, 1931).