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Elastic behavior and vibrational anharmonicity of a bulk $Pd_{40}Ni_{40}P_{20}$ metallic glass

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The elastic behavior has been studied of a bulk metallic glass of composition $Pd_{40}Ni_{40}P_{20}$, prepared by the recently developed technique of slow cooling from a dehydrated flux of boric oxide in an ultraclean environment. A large ratio ($B^S/\mu = 4.56$) of the bulk to shear moduli and a large Poisson's ratio (0.40) at room temperature indicate intrinsic softening of transverse acoustic phonons. Pulse-echo-overlap measurements have been made of both ultrasonic modes between 4.2 and 293 K. Both C_{11} and C_{44} decrease with temperature and show enhanced stiffening at low temperatures which can be associated with two-level systems. To examine nonlinear acoustic properties of a metallic glass the hydrostatic pressure dependence of the ultrasonic wave velocities has been measured. Both dB^S/dP ($=7.52$) and dC_{44}/dP ($=1.0$) are positive, showing that the modes stiffen under hydrostatic pressure in the normal way. The results are used to examine quantitatively the vibrational anharmonicity of a metallic glass by recourse to the mode Grüneisen parameters ($\gamma_l = 3.20$, $\gamma_t = 2.23$). The mean long-wavelength acoustic mode Grüneisen parameter $\bar{\gamma}_H^{\text{el}}$ ($=2.59$) at room temperature is comparable with the thermal Grüneisen parameter γ_H^{th} ($=2.24$). In general, the temperature and pressure dependences of the elastic constants show that metallic glasses, unlike many SiO_2-based insulating glasses, have elastic and anharmonic properties similar in kind to the crystalline state (in this case to the component transition metals nickel and palladium). An equation of state for a metallic glass is presented for the first time: The compression is found to be small, being similar to that of nickel.

I. INTRODUCTION

The vibrational excitations in metallic glasses are not well understood. The considerable theoretical difficulties involved in their assessment are increased by lack of precise experimental information on the vibrational spectra and in particular on vibrational anharmonicity. A central reason for the paucity of data is the limitation imposed on specimen geometry by fast-quenching techniques: Specimens made this way are not well suited to pulse-echo ultrasonic investigations of elastic behavior. Recently, however, bulk samples of the alloy $Pd_{40}Ni_{40}P_{20}$ have been prepared by cooling its melt in molten B_2O_3 fluxes.[1] Measurements of the hydrostatic pressure and temperature dependences of ultrasonic wave velocities have now been made on this bulk metallic glass and the results provide quantitative details of its elastic behavior.

In the absence of the periodicity typical of a crystalline solid, the proper normal modes in an amorphous solid are not plane waves. Anharmonic effects couple the modes and this damping limits lifetimes, especially as the wavelength approaches the interatomic spacing. Hence as the wave vector is increased, the dispersion curve becomes progressively more smeared out and phonons in the usual sense do not exist. However, at low frequencies an amorphous material behaves as an elastic continuum with a well-defined dispersion relation so that ultrasonic waves can be propagated. Elastic constant measurements are of central importance in investigations of the vibrational properties of a metallic glass because they define the slope of the dispersion curves in the long-wavelength limit. The pressure dependences of the elastic constants provide information on the shift of the mode energies with compression and characterize the vibrational anharmonicity, that is, the nonlinearity of the atomic forces with respect to atomic displacement. Thus this study of the hydrostatic pressure derivatives of the elastic constants has the aim of providing details of the vibrational anharmonicity of a bulk metallic glass. To gain physical insight into the vibrational anharmonicity, the results are used to obtain the acoustic mode Grüneisen parameters, which quantify the volume dependence ($-\partial \ln \omega_i / \partial \ln V$) of the normal mode frequencies ω_i and are compared with an estimate of the thermal Grüneisen parameter.

II. EXPERIMENTAL TECHNIQUES

The term metallic glass is conventionally used to describe a metallic alloy which has been so rapidly cooled from the melt (cooling rates of $10^6\ \mathrm{K\,s^{-1}}$ are not atypical) that it is amorphous. The requirement of such rapid cooling leads to specimens in the form of thin anisotropic ribbons or wires, neither of which are ideal geometries for ultrasonic measurements. However, the material under investigation here has been produced by the recently developed technique[1] of slow undercooling of nominal composition $Pd_{40}Ni_{40}P_{20}$ in ultraclean conditions in a molten flux of dehydrated boric oxide. The absence of crystallinity in this sample has been confirmed by x-ray and electron diffraction. The ultrasonic specimen was prepared by polishing two faces flat and parallel to better than 10^{-4} rad, the faces being 5.5 mm apart and the other dimensions about the same. Confirmation that the specimen remained amorphous after handling during the experimental program was established by x-ray and electron diffraction from the polished surfaces: Diffuse halos only were observed. X-ray energy dispersive analysis of the surface prepared for the transducer gave the composition as $Pd_{45}Ni_{35.7}P_{19.3}$. Physical properties of metallic glasses depend in a complicated way on the thermomechanical history of the sample. A particular value of a physical property need not imply a unique atomic arrangement;[2] continuous transformations within the glassy phase are possible, with concomitant changes in properties. In the present context it may be noted that previously a complex dependence has been observed of the velocity of sound in $Fe_{40}Ni_{40}B_{20}$ on annealing treatment.[3] The present measurements can be taken to represent results on a material which has undergone considerable structural relaxation during the slow cooling at the production stage. Since the specimen has been kept at room temperature or cooled slowly below, no thermal treatments have been imposed on it that will have significantly added to this relaxation—the results can be regarded as coming from a fixed atomic configuration. It is often observed that melt-spun metallic glasses are structurally anisotropic,[4] which arises from the inherent directionality of the quenching process. The material studied here has not experienced any directional solidification and can be regarded as being structurally isotropic. The crystallization temperature of this alloy is 650 K when measured at a 10 K min^{-1} heating rate, the glass-transition temperature being 590 K at the same heating rate.[1]

Ultrasonic wave transit times were measured by the single-ended pulse-echo-overlap technique, capable of resolving changes to better than 1 part in 10^5. Hydrostatic pressures were applied in a piston and cylinder apparatus described elsewhere.[5]

III. ELASTIC CONSTANTS OF AMORPHOUS $Pd_{40}Ni_{40}P_{20}$

The two independent second-order elastic stiffness moduli have been obtained from the ultrasonic wave velocities (V_l and V_t) for longitudinal and shear modes (Table I). Previously the ultrasonic wave velocities had been measured at room temperature in a series of $(Pd_{1-x}Ni_x)_{80}P_{20}$ $(x=0.0,0.2,0.4,0.6,0.8,1.0)$ metallic glass.[6] Agreement between this data interpolated for $x=0.5$ and the present results at room temperature (293 K) is good (Table I). The thin cylindrical rod geometry ($\sim$1—2 mm diameter, 10 mm long) used in that work did not comply strictly with the requirements for pulse echo ultrasonics: At the driving frequency (20 MHz) used, diffraction and nonplane wavefront effects would have occurred but apparently did not significantly influence the results.

The most striking feature of the elastic behavior of these metallic glasses is that they are much stiffer than other amorphous materials; see Refs. 7—9. In fact the bulk modulus of this metallic glass is similar to those of the crystalline transition metals nickel and palladium (Table II), suggesting that the interatomic bonding is similar. For transition metals the valence *s* electrons provide the repulsive pressure to counter the strongly attractive *d*-electron contributions and hence play an important part in the bulk modulus (the *d* electrons largely determine the cohesive energy). For palladium the *s*-electron contribution to the bulk modulus has been estimated[10] on the basis of self-consistent local-density-function theory to be about $1\frac{1}{4}$ times that of the *d* electrons; *sd* hybridization is also involved significantly.

A second difference in kind rather than in degree between the elastic behavior of the metallic glass ($B^S/\mu=4.56$) and those of other amorphous materials [for silica-based glasses, $B^S/\mu\sim1.2$; for chalcogenide and related glasses, $B^S/\mu\sim1.9\pm0.2$ (Refs. 7 and 8); for amorphous TeO_2, $B^S/\mu=1.54$ (Ref. 9)] is that the metallic glass has a much larger bulk than shear modulus. For amorphous $Fe_{79}P_{21}$ and $Co_{77}P_{23}$ the B^S/μ ratios are 3.0 and 3.8, respectively.[11] A large B^S/μ ratio could be a characteristic of metallic glasses based on transition elements. Both crystalline nickel and palladium have quite large bulk moduli in comparison to shear moduli ($B^S/\mu\sim2.5$), this being a general feature of transition metals. Nevertheless, B^S/μ for the amorphous $Pd_{40}Ni_{40}P_{20}$ is exceptionally large and this may be due to an intrinsic softening of transverse phonons in the amorphous state.[12,13] Amorphous Ni-P alloys[14,15] and Pd-Si alloys[13,16—18] are appreciably more compliant, especially in

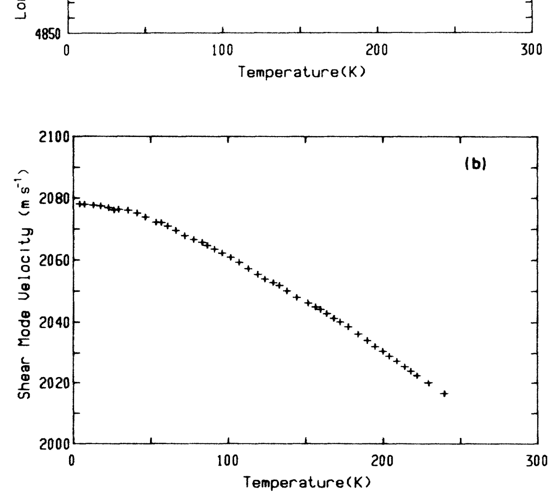

FIG. 1. Temperature dependence of (a) the longitudinal and (b) the shear ultrasonic modes propagated in $Pd_{40}Ni_{40}P_{20}$ bulk metallic glass.

response to a shear stress, than the crystalline phases; whereas the bulk modulus is only about 5% smaller in the amorphous state than in the polycrystalline forms, the shear and Young moduli are about 30% smaller. A reduced resistance to shear due to the possibility of nonuniform changes in the local atomic density in the somewhat looser glass structure was anticipated theoretically from model calculations for a single metallic species interacting with short-range repulsive forces.[12]

The $Pd_{40}Ni_{40}P_{20}$ metallic glass has a large Poisson's ratio σ (0.40) compared with that of other glasses (see Table 2 of Ref. 9). The fourfold-coordinated silica-based glasses tend to have a small σ (<0.2), those of chalcogenide glasses range between 0.25 and 0.3, and a fluorozirconate glass has a σ of 0.279. For an isotropic solid the Poisson's ratio can be written in terms of the elastic stiffnesses as

$$\sigma=(C_{11}-2C_{44})/2(C_{11}-C_{44}) \ . \tag{1}$$

Inspection of this equation shows that the large Poisson's ratio of the metallic glass can be viewed as a consequence of the much larger value of C_{11} than C_{44} and hence of the combination of transition-metal bonding [nickel and palladium have large Poisson's ratios (Table II)] and the intrinsic transverse phonon softening in the loose glass structure.

The temperature dependences of the longitudinal and shear wave velocities measured between 4.2 K and room temperature are shown in Fig. 1. Modulus values determined at 4.2 K are given in Table I and the temperature derivatives at room temperature in Table II. At low temperatures metallic glasses show a nearly linear temperature-dependent contribution to their specific heats[19] and other phenomena which are usually interpreted by describing amorphous solids as including a broad distribution of multilevel atomic tunneling systems (two level in its simplest formalism) due to their disorder. Acoustic measurements on rodlike metallic glass specimens are characterized by a linearly increasing acoustic wave velocity for longitudinal and shear modes with decreasing temperature in the range 2–20 K.[20–24] The wave velocity peaks at about 2 K, below which the velocity exhibits a logarithmic temperature dependence[20–22] and the attenuation is intensity dependent.[23] These effects, which are similar in kind to those observed in insulating glasses but an order of magnitude less in scale, have also been interpreted generally in terms of two-level systems.[24] The present results can be compared with those from rapidly quenched samples in the linear region between 4.2 and 30 K: Lower temperatures are currently unavailable at our laboratory. The relative changes in wave velocity in this temperature range $\delta=V^{-1}\Delta V/\Delta T$ for longitudinal and shear modes in amorphous $Pd_{40}Ni_{40}P_{20}$ are $\delta_l=-3.2\times10^{-5}\ K^{-1}$ and $\delta_t=-2.6\times10^{-5}\ K^{-1}$ as compared to $\delta_l=-2.8\times10^{-5}\ K^{-1}$ and $\delta_t=-8.2\times10^{-5}\ K^{-1}$ in amorphous $Ni_{81}P_{19}$,[21] and $\delta_l=-2.3\times10^{-5}\ K^{-1}$, $\delta_t=-9.2\times10^{-5}\ K^{-1}$ in amorphous $Co_{82}P_{18}$:[22] δ_l for the slowly cooled $Pd_{40}Ni_{40}P_{20}$ is similar to that of the two rapidly quenched samples $Ni_{81}P_{19}$ and $Co_{82}P_{18}$ whereas δ_t is much smaller in $Pd_{40}Ni_{40}P_{20}$ than in the other two materials. It should be noted that substantial changes in $\Delta V/V$ at low temperatures have been observed to result from heat treatment.[24]

IV. HYDROSTATIC PRESSURE DERIVATIVES OF THE ELASTIC CONSTANTS AND VIBRATIONAL ANHARMONICITY

For both longitudinal and shear modes the velocity of ultrasound increases linearly with hydrostatic pressure in the pressure range (up to 3×10^{8} Pa) studied. This is the usual behavior observed in materials which do not have soft long-wavelength acoustic modes. From the slopes of the pressure dependences of the natural velocity, the hydrostatic pressure derivatives of the elastic constants have

TABLE I. The bulk elastic properties of $Pd_{40}Ni_{40}P_{20}$ metallic glass. The data shown in the last column have been estimated graphically from measurements made at room temperature on a series of $(Pd_{1-x}Ni_x)_{0.8}P_{0.2}$ metallic glass rods (Ref. 6).

	4.2 K	293 K	293 K[a]
Density ρ_0 ($kg\,m^{-3}$)	9455	9405	9500
Longitudinal wave velocity V_l ($m\,s^{-1}$)	5115	5013	4900
Shear wave velocity V_t ($m\,s^{-1}$)	2105	2025	1960
Elastic stiffness (10^{10} $N\,m^{-2}$)			
C_{11}^S	24.6	23.6±0.2	22.8
C_{44}^S	4.17	3.86±0.05	3.65
C_{12}^S	16.2	15.9±0.3	15.5
Elastic compliance (10^{-11} m^2N^{-1})			
S_{11}	0.857	0.925	0.975
S_{12}	−0.338	−0.373	−0.395
S_{44}	2.40	2.59	2.74
Bulk modulus B^S (10^{10} $N\,m^{-2}$)	19.0	18.5	17.5
Volume compressibility κ_v (10^{-11} m^2N^{-1})	0.525	0.54	0.57
Linear compressibility κ_L (10^{-11} m^2N^{-1})	0.175	0.18	0.19
Young's modulus E^S (10^{10} $N\,m^{-2}$)	11.7	10.8	10.5
Poisson's ratio σ^S	0.40	0.40	0.4
Debye temperature Θ_D^{el} (K)	301		

[a] Data from Ref. 6.

TABLE II. Comparison of the room-temperature (293 K) elastic properties of amorphous $Pd_{40}Ni_{40}P_{20}$ with those of crystalline Ni and Pd.

	$Pd_{40}Ni_{40}P_{20}$	Ni	Pd
Elastic stiffness constants (10^{10} N m^{-2})			
C_{11}^S	23.6	24.7	22.4
C_{44}	3.86	12.2	7.16
C_{12}^S	15.9	15.3	17.3
$\frac{1}{2}(C_{11}^S - C_{12}^S)$	3.86	4.7	2.55
Elastic compliances (10^{-11} m^2 N^{-1})			
S_{11}	0.925	0.769	1.37
S_{44}	2.59	0.820	1.40
S_{12}	-0.373	-0.29	-0.60
Density (kg m^{-3})	9405	8900	12 000
Bulk modulus B_0^S (10^{10} N m^{-2})	18.5	18.4	19.0
Linear thermal expansion (10^{-6} K^{-1})	12	12.8	
dC_{11}^S/dP	8.9	6.0	6.1
dC_{44}/dP	1.0	2.4	2.4
dC_{12}^S/dP	6.9	4.7	5.2
dB_0^S/dP	7.52	5.3	5.5
dE^S/dP	2.86		
B_{11}	10.3		
B_{44}	2.07		
$(1/C_{11}^S)(dC_{11}^S/dP)$ (10^{-11} m^2 N^{-1})	3.8	2.4	2.7
$(1/C_{44})(dC_{44}/dP)$	2.6	2.0	3.4
$(1/C_{12}^S)(dC_{12}^S/dP)$	4.3	3.1	3.0
$(1/B^S)(dB^S/dP)$	4.1	2.9	2.9
$(1/C_{11}^S)(dC_{11}^S/dT)$ (10^{-4} K^{-1})	-1.6	-1.8	-1.7
$(1/C_{44})(dC_{44}/dT)$	-3.4	-2.6	$+0.8$
$(1/C_{12}^S)(dC_{12}^S/dT)$	-0.8	-0.3	-1.1
$(1/B^S)(dB^S/dT)$	-1.1	-1.0	-1.3
Mean Grüneisen parameter			
$\bar{\gamma}_H^{el}$	2.59	1.35	2.13
γ_l	3.30	2.28	2.82
γ_s	2.23	0.89	1.79
Poisson's ratio	0.403 (mean)		
stress strain			
[001] (001) plane		0.383	0.436
[111] (111) plane		0.228	0.333
[110] [001] direction		0.652	0.807
[110] $[1\bar{1}0]$ direction		-0.078	-0.051

been calculated at atmospheric pressure by using

$$\left[\frac{\partial C_{IJ}}{\partial P}\right]_{P=0} = 2\rho_0 W_0^2 \left[\frac{\partial}{\partial P}\left[\frac{\Delta W}{W_0}\right]\right]_{P=0} + \frac{1}{3}\left[\frac{C_{IJ}}{B^T}\right]_{P=0} . \tag{2}$$

The second term here is a correction which accounts for the reduction in dimensions of the sample under pressure. The pressure derivatives of the elastic constants of $Pd_{40}Ni_{40}P_{20}$, given in Table II, are similar to those of crystalline Ni and Pd except that $\partial C_{44}/\partial P$ is smaller in the glass. $(1/C_{44})(\partial C_{44}/\partial P)$ is 0.26 for the metallic glass, lying between that 0.20 for crystalline nickel and 0.34 for crystalline palladium. The similarity of elastic behavior to that of crystalline nickel and palladium reinforces the suggestions that the interatomic bonding in the amorphous metal resembles that of the transition metals. For the bulk metallic glass, the positive sign of $\partial C_{44}/\partial P$ shows that while C_{44} is soft compared with that in a corresponding crystalline solid, this intrinsic softness is not enhanced by application of pressure.

Glasses fall into two distinct categories so far as the temperature and pressure dependences of their elastic constants are concerned. The negative temperature dependences and positive pressure dependences of ultrasonic wave velocities establish that, as far as its elastic properties are concerned, the metallic glass is "well behaved" in the sense that when the material is compressed or cooled it becomes stiffer. This is in marked contrast to the anomalous elastic behaviors of fused SiO_2 and amorphous GeO_2 and BeF_2 which have positive temperature coefficients and negative pressure coefficients of shear and bulk moduli (see Table II of Ref. 9 which includes references to the original studies), associated with the low (fourfold) coordination which allows large bending vibrations in the form of motion of the bridging oxygen or fluorine ions.

It can be shown that the hydrostatic pressure derivative of Poisson's ratio σ for an isotropic material is

$$\left[\frac{\partial\sigma}{\partial P}\right]_{P=0,\,T}=(1-\sigma)(1-2\sigma)\left[\frac{1}{C_{11}}\frac{\partial C_{11}}{\partial P}-\frac{1}{C_{44}}\frac{\partial C_{44}}{\partial P}\right]$$

$$=+1.40\times10^{-12}\ (\mathrm{N\,m^{-2}})^{-1} \qquad (3)$$

for the metallic glass.

By recourse to an equation of state, the ultrasonic data for the bulk modulus and its hydrostatic pressure derivative can be used in an extrapolation procedure to estimate the compression of a material at very high pressures. This has been carried out for this metallic glass by using the Murnaghan[25] equation of state

$$\ln\left[\frac{V_0}{V(P)}\right]=\frac{1}{(B_0^T)'}\ln\left[(B_0^T)'\left[\frac{P}{B_0^T}\right]+1\right], \qquad (4)$$

which rests upon the assumption that the isothermal bulk modulus depends linearly upon pressure:

$$B^T(P)=-V\left[\frac{\partial P}{\partial V}\right]_T=B_0^T+P\left[\frac{\partial B^T}{\partial P}\right]_{P=0,\,T}. \qquad (5)$$

Ultrasonic pulse-echo experiments give adiabatic elastic constants. The isothermal bulk modulus has been obtained from the adiabatic quantity by using

$$B_0^T=B_0^S/(1+\gamma\alpha T)=18.3\times10^{10}\ \mathrm{N\,m^{-2}} \qquad (6)$$

The thermal expansion coefficient α of this particular metallic glass has not been measured, so the value found for a rapidly quenched and annealed metallic glass of the same nominal composition [$\alpha=1.45\times10^{-5}\ \mathrm{K}^{-1}$ (Ref. 26)] has been employed. Since the thermal expansion only occurs in small correction terms for the parameters used in the equation of state, taking this value of α should be adequate. The temperature dependence of the isothermal bulk modulus has been estimated from

$$\left[\frac{\partial B^T}{\partial T}\right]_P=\left[\frac{\partial B_0^S}{\partial T}\right]_P\Big/(1+T\alpha\gamma)$$

$$=-2.1\times10^{7}\ \mathrm{N\,m^{-2}\,K^{-1}} \qquad (7)$$

and hence to a first approximation the pressure derivative $(B_0^T)'$ $(=\partial B^T/\partial P)_{P=0}$ from[27,28]

$$(B_0^T)'=(B_0^S)'+T\alpha\gamma\left[\frac{B_0^T}{B_0^S}\right]\left[1-\frac{2}{\alpha B_0^T}\left[\frac{\partial B_0^T}{\partial T}\right]_P-2(B_0^S)'\right]$$

$$=7.57\,. \qquad (8)$$

The compression of this metallic glass calculated using the Murnaghan equation of state (4) is plotted in Fig. 2. There are no previous estimates of the equation of state (or of the hydrostatic pressure derivatives of the elastic constants) of a metallic glass with which to compare these results. However the compression is similar to those in crystalline nickel and palladium.

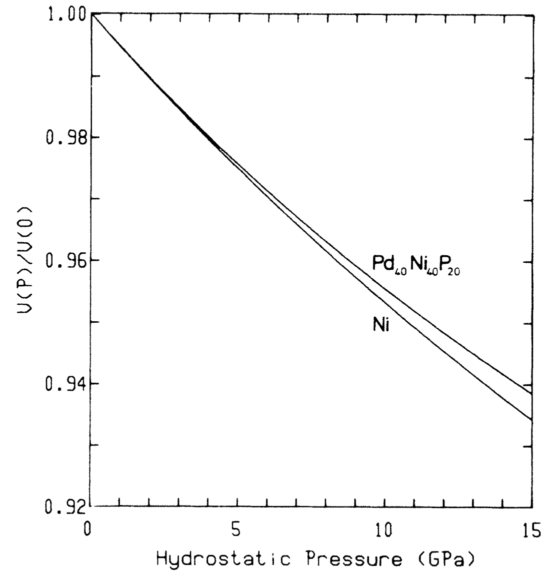

FIG. 2. Isothermal compression of the $Pd_{40}Ni_{40}P_{20}$ metallic glass calculated on the basis of the Murnaghan equation-of-state in comparison with that of crystalline nickel.

Vibrational anharmonicity is responsible for the nonlinear elastic behavior of a material under a finite strain and for physical properties, which are governed by thermal motion, such as thermal expansion. The first report of anharmonicity in a metallic glass appeared as the uniaxial stress (σ) dependence of the Young's modulus (E) in $Pd_{77.5}Si_{16.5}Cu_6$ ribbon.[18] Unusually large values of $dE/d\sigma$ of -12 and -16 were found at low stresses in amorphous and crystalline phases, respectively, suggesting pronounced vibrational anharmonicity. However, data on $\partial E/\partial\sigma$ alone are not sufficient to quantify vibrational anharmonicity. The hydrostatic and uniaxial pressure dependences of the second-order elastic constants provide a measure of the elastic anharmonicity of long-wavelength acoustic modes which can be expressed by acoustic mode Grüneisen parameters. These define the volume (or strain) dependence of the normal mode frequency ω_i,

$$\gamma_i=-d\ln\omega_i/d\ln V\,. \qquad (9)$$

For an isotropic solid there are only two components of long-wavelength acoustic mode Grüneisen parameter: γ_l^{el} and γ_t^{el} which refer to the longitudinal and shear elastic waves, respectively, and are given by[9]

$$\gamma_l^{\mathrm{el}}=-\frac{B}{C_{11}}\left[3-\frac{2C_{12}}{B}-\frac{3dB}{dP}-4\frac{d\mu}{dP}\right], \qquad (10)$$

$$\gamma_t^{\mathrm{el}}=-\frac{1}{6\mu}\left[2\mu-3B\frac{d\mu}{dP}-\frac{3}{2}B+\frac{3}{2}C_{12}\right], \qquad (11)$$

where the Lame constant μ is C_{44}. From the measurements of the elastic constants and their hydrostatic pressure derivatives, it has been found that γ_l^{el} is 3.30 and γ_t^{el} is 2.23. The mean acoustic Grüneisen parameter $\bar{\gamma}^{\mathrm{el}}$ can be obtained from γ_l^{el} and γ_t^{el} by means of weighting functions, but at a high enough temperature ($T>\Theta_D$) to ensure that all the vibrational modes are excited, i.e., in the high-temperature limit,

$$\bar{\gamma}_H^{\mathrm{el}} = (\gamma_l^{\mathrm{el}} + 2\gamma_t^{\mathrm{el}})/3 \qquad (12)$$

holds. For this metallic glass the elastic Debye temperature Θ_D^{el}, calculated from the low-temperature velocities, is 301 K—so that room temperature is reasonably close to the high-temperature limit and the $\bar{\gamma}_H^{\mathrm{el}}$ value of 2.59, obtained from γ_l^{el} and γ_t^{el} using Eq. (12), should be a good approximation to the mean acoustic mode Grüneisen parameter. In addition to determining the nonlinear acoustic behavior under finite strain, the vibrational anharmonicity is responsible for thermal expansion and contributes to the high-temperature specific heat. The pressure dependences of the elastic constants quantify cubic terms in the elastic strain free energy and thus the anharmonicity of the long-wavelength acoustic modes. Comparison between the thermal Grüneisen parameter

$$\gamma_H^{\mathrm{th}} = 3\alpha V/\kappa_v^S C_p = 3\alpha V/\kappa_v^T C_v \qquad (13)$$

and the $\bar{\gamma}_H^{\mathrm{el}}$ forges a link between the thermal properties and the pressure dependences of the elastic constants. Values of the thermal expansion coefficient α and the specific heat C_p are not available for our specimen. However α ($=14.5\times10^{-6}$ K^{-1}) has been measured for a fully relaxed rapidly quenched sample of the same composition;[26] this should be close to the value for the present type of metallic glass. The specific heat C_p (27.6 ± 0.9 J mol^{-1} K^{-1} at room temperature) has been measured[29] for a material of composition ($Pd_{48}Ni_{32}P_{20}$) close to that of the present work. These data lead to a value of 2.24 for γ^{th} at room temperature, which is quite close to that (2.59) found for γ_H^{el}: Either the long-wavelength acoustic modes play a central role in the thermal properties or those shorter wavelengths excitations which also contribute have similar mode Grüneisen parameters ($\sim$2) to those of the long-wavelength acoustic mode. It is likely that both these comments hold. The positive signs of γ_l^{el} and γ_t^{el} are due to the increase in the long-wavelength acoustic mode frequencies with applied pressure. Similar behavior is found in many other glasses: amorphous arsenic,[7] As_2S_3,[30] a fluorozirconate glass,[8] amorphous TeO_2.[9] In contrast for both Pyrex and fused silica both acoustic mode Grüneisen parameters are negative: The acoustic modes in these glasses soften under pressure.[7] The more normal—positive—acoustic mode Grüneisen parameters and negative temperature dependences of the ultrasonic wave velocities of the metallic glass can be ascribed to its high coordination number, which inhibits the transverse vibrations that are the source of the anomalous elastic properties of the tetrahedrally coordinated silica-based glasses BeF_2, SiO_2, and GeO_2. The mean Grüneisen parameter $\bar{\gamma}_H^{\mathrm{el}}$ of the acoustic modes at the long-wavelength limit of the metallic glass is substantially larger than the $\bar{\gamma}_H^{\mathrm{el}}$ of the crystalline elements nickel and palladium (Table II) and also of other "well-behaved" glasses. The mean value $\bar{\gamma}_H^{\mathrm{el}}$ of 2.59 found for the metallic glass shows that the vibrational anharmonicity of the acoustic modes in the long-wavelength limit is large but not excessively so.

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