

## Relationship between low-temperature boson heat capacity peak and high-temperature shear modulus relaxation in a metallic glass

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Low-temperature ( $2\text{ K} \leq T \leq 350\text{ K}$ ) heat capacity and room-temperature shear modulus measurements ( $\nu = 1.4\text{ MHz}$ ) have been performed on bulk  $\text{Pd}_{41.25}\text{Cu}_{41.25}\text{P}_{17.5}$  in the initial glassy, relaxed glassy, and crystallized states. It has been found that the height of the low-temperature Boson heat capacity peak strongly correlates with the changes in the shear modulus upon high-temperature annealing. It is this behavior that was earlier predicted by the interstitialcy theory, according to which dumbbell interstitialcy defects are responsible for a number of thermodynamic and kinetic properties of crystalline, (supercooled) liquid, and solid glassy states.

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We found that the Boson peak (BP) in the specific heat of a metallic glass tracks with the shear modulus change upon annealing within the glassy state as well as after partial or complete crystallization. This is just as predicted by the interstitialcy theory of condensed matter (ITCM) (Ref. 1); although by no other theory.

The BP is a peak in the specific heat divided by the cube of the temperature ( $C/T^3$ ) in the 5–15 K temperature region. It arises from excess vibrational states in the glass not found in crystalline materials. These states are detected by Raman and inelastic neutron scattering as well as by a plateau in the thermal conductivity over the same temperatures. They are also directly observed in phonon spectra in the  $10^{12}$  Hz range<sup>2</sup> and are thought to be characteristic fingerprints of the glassy state. There is an enormous literature of hundreds of articles on the subject. However, there has been much confusion, particularly for the specific heat, because it is difficult to separate the Boson peak from other simultaneous and overlapping effects at these low temperatures. In general, these include: (i) Schottky effects from magnetic ions dominant at the lowest temperatures, (ii) electronic and tunneling effects (important below 1 K), (iii) Debye continuum excitations, and (iv) lattice dispersions including van-Hove singularities (in the 15–25 K range), as schematized in Fig. 1. These effects can be in principle separated by their characteristic temperature dependencies and, as we find here, by annealing above the glass transition temperature  $T_g$ . To avoid magnetic effects, we used a nonmagnetic glass annealed above  $T_g$  to the crystalline state.

There have been many suggestions for the source of the BP not being part of a general theory of amorphous materials. They usually include fitting parameters not specified in advance. One can mention in this regard the models of soft anharmonic potentials,<sup>3–6</sup> loose structural units,<sup>7,8</sup> spatially fluctuating force constants,<sup>9</sup> and/or density.<sup>10</sup> A sample of some recent discussions emphasizing different viewpoints is given in Refs. 11–15. None of these is a part of a comprehensive theory.

Most measurements have been done on complex systems

but as the effect is universal, it is best studied in simple ones. Bulk metallic glasses have proven to be such systems, allowing for high sensitivity measurements of the shear modulus (four orders of magnitude more precise than specific-heat changes). We found that on annealing of glassy  $\text{Pd}_{41.25}\text{Cu}_{41.25}\text{P}_{17.5}$  above  $T_g$ , the Boson peak disappears with crystallization in the same temperature range as the shear modulus increases, just as predicted by the ITCM. According to the ITCM, a liquid contains a few percent of interstitialcies (which provide its fluidity) while a glass is a frozen liquid below  $T_g$ . Interstitialcies are interstitials in the dumbbell form with two atoms occupying a potential well normally occupied by one atom. As the interstitialcy configuration is spread out over several atoms, the interstitialcy definition applies as well in alloys.<sup>16</sup> The ITCM is developed with quantitative predictions that have been confirmed for different thermodynamic and kinetic properties, for a review see Refs. 17–19. The vibrational and quasistatic shear elastic response of crystals containing interstitialcies is unexpectedly large on a per defect basis but has been well established and understood in radiation damage studies about 50 years ago (see, for example, Ref. 20). The measurements given here explicitly relate low-temperature and high-temperature effects in the glassy state to the dynamic and quasistatic properties of the interstitialcy configuration, heretofore considered separately.

The ITCM (Ref. 1) considers the BP as originating from low-frequency resonance vibration modes of interstitialcies, resulting mainly from excitation to their first excited state. The height of the BP,  $H_B = (C_B/C_D)_{\max}$  (where  $C_B$  and  $C_D$  are the interstitialcy and Debye heat capacity contributions, respectively), is proportional to their concentration  $c_I$ , namely,<sup>21</sup>

$$H_B \approx 4.6 \frac{c_I}{0.035} f \left( \frac{\omega_D}{7\omega_R} \right)^3, \quad (1)$$

where  $f$  is the number of resonance modes per interstitialcy,  $\omega_D$  the Debye frequency, and  $\omega_R$  the interstitialcy resonant frequency. The BP temperature is given as<sup>21</sup>

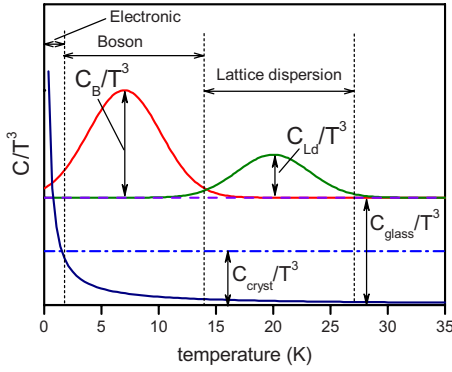


FIG. 1. (Color online) Schematic representation of electronic Boson, lattice dispersion, and Debye (for glassy and crystalline states) contributions to the low-temperature specific heat (in the units of  $C/T^3$ ) of a metallic glass. As the glass is annealed to the crystalline state, the Boson heat capacity  $C_B$  gradually approaches zero while  $C_{glass} \rightarrow C_{cryst}$ .

$$T_B \approx \frac{\Theta_g}{35} \left( \frac{7\omega_R}{\omega_D} \right), \quad (2)$$

where  $\Theta_g$  is the Debye temperature of the glass. With the theoretically expected  $7\omega_R/\omega_D \approx 1$ , Eq. (2) gives  $T_B = \Theta_g/35$ , in fair agreement with experimental data on different glasses.<sup>22</sup>

The key physical quantity of the ITCM is the unrelaxed (=high-frequency) shear modulus  $G$ . This is related to the interstitially defect concentration  $c_I$  as<sup>1</sup>

$$G = G_{cryst} \exp(-\beta c_I), \quad (3)$$

where  $G_{cryst}$  is the unrelaxed shear modulus of the reference crystal and  $\beta$  the dimensionless “shear susceptibility.” For the whole glass  $\rightarrow$  crystal transformation range, a sufficiently accurate approximation is

$$\Delta G/G = (G_{cryst} - G)/G \approx \beta c_I. \quad (4)$$

Structural relaxation and crystallization occurring upon annealing of glass, decrease the interstitially concentration and, therefore, increase the shear modulus according to Eq. (4). This effect can be measured accurately allowing calculation of the defect concentration available for further thermal activation. The latter is expected to define the Boson heat capacity peak height through Eq. (1). Therefore, one should expect (i) a decrease in the BP height during structural relaxation and crystallization according to Eq. (1) and (ii) this decrease should be governed by the relationship [Eq. (4)]. The purpose of the present Brief Report is to validate these predictions.

Bulk glassy  $\text{Pd}_{41.25}\text{Cu}_{41.25}\text{P}_{17.5}$  (at. %) was used for the investigation. This composition is close to  $\text{Pd}_2\text{Cu}_2\text{P}$ , which polymorphically crystallizes into the tetragonal phase of the same composition.<sup>23</sup> The initial master alloy was produced by direct remelting of the components (purity not worse than 99.95) by a two-temperature method upon controlled phosphorus pressure. The alloy was next melt jet quenched (quenching rate  $\approx 200$  K/s) into a copper mold with a  $2$

$\times 5 \times 65$  mm<sup>3</sup> cavity.  $T_g$  and the crystallization onset temperature  $T_c$  were found at  $dT/dt = 5$  K/min by differential thermal analysis (DTA PYRIS) to be 545 and 586 K, respectively. The casting was checked by x rays (Thermo Scientific ARL X’TRA diffractometer) to be fully amorphous and next cut into pieces for  $C$  and  $G$  measurements. The former were performed with a physical property measurement system (PPMS) from Quantum Design Inc. in the temperature range  $2 \text{ K} \leq T \leq 350 \text{ K}$ . Shear modulus measurements (sample’s size  $4 \times 5 \times 0.8$  mm<sup>3</sup>) in the initial state and after annealing of the same specimen were made by an electromagnetic acoustic transformation method at a transverse resonant frequency  $\nu \approx 1.4$  MHz measured with a relative precision of  $\approx 10^{-5}$  as described elsewhere.<sup>24,25</sup> The normalized shear modulus was calculated using  $\frac{G}{G_0} = \frac{\rho}{\rho_0} \left( \frac{\nu}{\nu_0} \right)^2$ , where the density  $\rho$  was determined by hydrostatic weighing (with a 0.3% error) and the subscript “0” refers to the initial state of the sample. Heat capacity and modulus measurements were carried out for the as-cast state and after heating up to temperatures  $T_a = 473, 573, 603, 633, 703, \text{ and } 773 \text{ K}$  in a vacuum at a rate of 5 K/min. Additional measurements were performed on a sample annealed at  $T_a = 773 \text{ K}$  for 12 h. X-ray measurements showed that heat treatment at 473 and 573 K does not lead to any traces of crystallization. Heating up to  $T_a = 633 \text{ K}$  results in partial crystallization while annealing at  $T_a = 733 \text{ K}$  produces Bragg reflections, which mostly belong to tetragonal  $\text{Pd}_2\text{Cu}_2\text{P}$ .

In the analysis given below, we omit the data above 15 K because it brings up more topics not directly involved in the comparison of the BP height and change in the shear modulus. These, with a comparison of low-temperature and high-temperature determinations of  $\beta$  and  $f$  and an Einstein term, will be discussed in a later fuller article also containing more data for the transition region.

Standard replotting of the data as  $C/T^3$  vs  $T$  reveals an excess peak of the vibrational density of states, as shown in Fig. 2(a). The height of this peak does not change due to structural relaxation at  $T_a = 473 \text{ K}$ . Further annealing in the supercooled liquid region (i.e., at  $T_g \leq T_a \leq T_c$ ) and at higher temperatures producing partial ( $T_a = 633 \text{ K}$ ) or complete ( $T_a = 773 \text{ K}$ ) crystallization leads to a decrease in this peak (see also Ref. 26). As discussed above, the Boson peak in glassy structure can be separated by subtracting the reference crystalline  $C/T^3$  peak. This is done in Fig. 2(b), where the crystalline state obtained by heating up to  $T_a = 773 \text{ K}$  is taken as a reference. It is seen that the BP temperature  $T_B = 8\text{--}9 \text{ K}$  with only about a 1 K increase on annealing into the crystalline state, in good accord with Eq. (2). For the  $5 \text{ K} \leq T \leq 15 \text{ K}$  range, the heat capacity of the glass can be accepted as a sum of the Boson contribution induced by interstitialcies,  $C_B = c_I f N k_B x^2 e^{-x}$  (where  $x = \hbar\omega_R/k_B T = \Theta_R/T$ , see Ref. 21), and standard Debye component  $C_g = 234 N k_B (T/\Theta_g)^3$ . Expanding into a Taylor series,  $\Theta_g(c_I) \approx \Theta_{cryst} \left( 1 + \frac{c_I}{\Theta_{cryst}} \frac{d\Theta_g}{dc_I} \right)$  one arrives at  $1/\Theta_g^3(c_I) = \left( 1 - \frac{3c_I}{\Theta_{cryst}} \frac{d\Theta_g}{dc_I} \right) / \Theta_{cryst}^3$ , where the subscripts “g” and “cryst” refer to the glassy and crystalline states, respectively. Taking into account that the Debye temperature is proportional to the square root of the shear modulus, using Eq. (3) and accepting that  $\frac{1}{\Theta_{cryst}} \frac{d\Theta_g}{dc_I} \approx \frac{1}{2G} \frac{dG}{dc_I}$ , one can derive a more useful

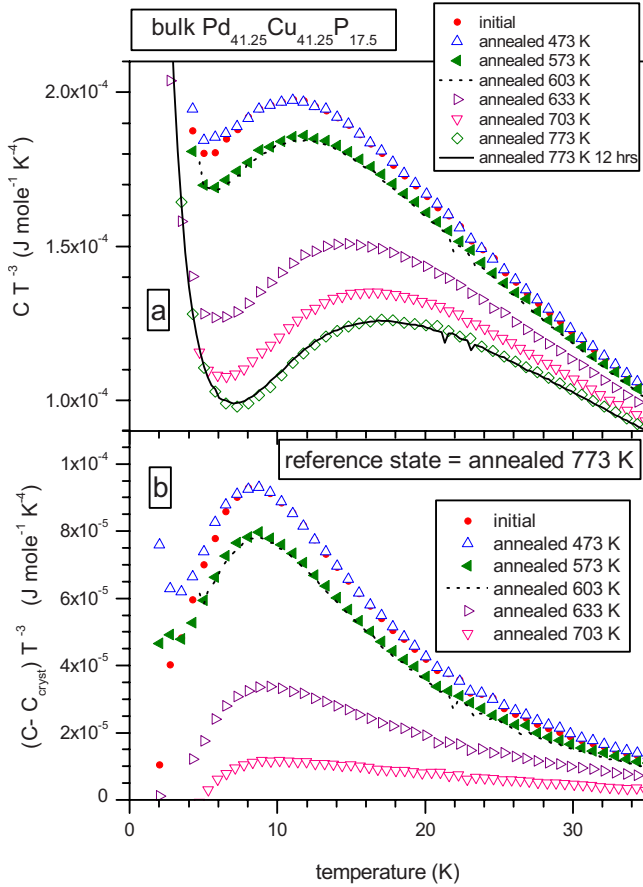


FIG. 2. (Color online) (a)—Experimental  $C_p/T^3$  data in the initial and annealed states. (b)—Bosc peak obtained by subtracting the reference crystalline state (obtained by annealing at  $773$  K for  $12$  h) from the heat capacity data given in the upper part of figure.

form for describing the BP changes with annealing to the crystalline state as

$$\frac{C - C_{\text{cryst}}}{T^3} = \frac{234Nk_B}{\Theta_{\text{cryst}}^3} \left[ f x^5 e^{-x} \frac{(\Theta_{\text{cryst}}/\Theta_g)^3}{234} + \frac{3}{2}\beta \right] c_I, \quad (5)$$

The maximum change in the BP is then given by

$$\left[ \frac{C - C_{\text{cryst}}}{T^3} \right]_{\text{max}} = \frac{234Nk_B}{\Theta_{\text{cryst}}^3} \left[ 30.7f + \frac{3}{2}\beta \right] c_I. \quad (6)$$

It is accepted in this equation that since  $\frac{d}{dx}(x^5 e^{-x})_{x=x_{\text{max}}} = 0$ , then  $x_{\text{max}} = 5$  and, therefore,  $x_{\text{max}}^5 e^{-x_{\text{max}}} = 21$ . Equation (6) also neglects a smaller decrease in  $(C/T^3)_{\text{cryst}}$  expected from the lattice dispersion near  $15$  K. Then, with the Debye temperatures of the glass and crystal,  $\Theta_g = 290$  K (that coincides with  $\Theta_g$  for a similar glass  $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ , see Ref. 28) and  $\Theta_{\text{cryst}} = 340$  K taken from the  $2$ – $4$  K range using the standard Debye expression given above,  $\beta c_I = 0.36$  determined from the high-temperature shear modulus [Eq. (4) and Fig. 3, see below],  $f = 5$  and  $c_I \approx 0.01$  calculated from Eq. (6) with the Bosc peak height equal to  $9.3 \times 10^{-5}$  J/mole  $\text{K}^4$  [Fig. 2(b)], one finds  $\beta \approx 30$ . This is fairly close to earlier expectations.<sup>1,19</sup> The rule  $T_B \approx \Theta_g/35 = 8.5$  K [see Eq. (2)] is also well followed. We expect the values  $c_I$  and  $\beta$  to be

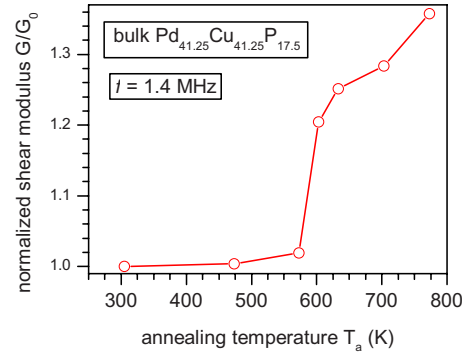


FIG. 3. (Color online) Room-temperature normalized shear modulus as a function of the annealing temperature  $T_a$ .

accurate to within about 30%. The calculated  $c_I$  could increase somewhat for an expected distribution of resonant modes while  $\beta$  would have a corresponding reduction.

It is to be emphasized that the procedure for subtracting the background  $C$  applied above differs from that reported by others (e.g., Ref. 11). In the present work, the maximum temperature of consideration (approximately  $15$  K) was limited to assure that the measured excess specific heat arose mainly from the contribution of the interstitialcy defect. In contrast, the previous investigators have analyzed their specific-heat data to much higher temperatures, thereby including contributions to  $C$  from lattice dispersions as well.

The dependence of the room-temperature normalized shear modulus  $G/G_0$  as a function of the annealing temperature  $T_a$  is given in Fig. 3. With  $\beta = 30$  one obtains a change in the defect concentration  $c_I$  with the annealing temperature  $T_a$  as given in Fig. 4. Equation (4) shows that the frozen-in concentration of interstitialcies in the as-cast glass is about 1%, in rough agreement with the value of  $c_I$  ( $\approx 2\%$ ) found for a Zr-based glass<sup>19</sup> but very close to  $c_I = 1.08\%$  derived for a similar Pd-based glass.<sup>29</sup> The frozen-in interstitialcy defects anneal out upon heat treatment so that  $c_I$  vanishes in the

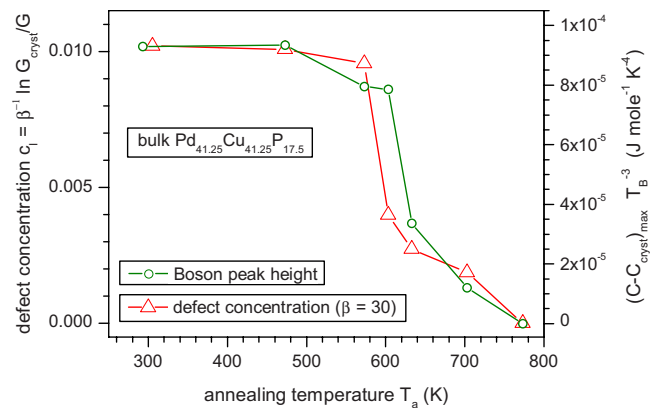


FIG. 4. (Color online) Defect concentration calculated using Eq. (4) from the shear modulus data shown in Fig. 3 together with the Bosc peak height taken from Fig. 2(b) as a function of the annealing temperature  $T_a$ . The curves are drawn as guides for the eye. It is seen that the dependencies of  $c_I$  and peak height on  $T_a$  can be superposed indicating direct proportionality between them, in line with Eqs. (1) and (6).

reference crystalline state. Figure 4 also gives the BP height  $(C - C_{cryst})/T^3$  as a function of  $T_a$ . It is seen that this dependence nearly coincides with the defect concentration  $c_I(T_a)$ . This means that the Boson peak height and interstitialcy defect concentration as determined from shear modulus changes using Eq. (4) are proportional to each other, just as predicted by Eqs. (1) and (6).

In summary, we performed heat capacity and shear modulus measurements on bulk  $\text{Pd}_{41.5}\text{Cu}_{41.5}\text{P}_{17.5}$  in the as-cast glassy, relaxed glassy, and crystallized states. Heat capacity measurements revealed an excess contribution in the vibrational density of states at temperatures  $5 \text{ K} \leq T \leq 25 \text{ K}$ , which is maximal in the as-cast state and decreases upon continued annealing. Crystallization, however, does not lead to its vanishing, as shown in Fig. 2(a). The Boson heat capacity peak obtained by subtracting the  $C/T^3$  contribution in the reference crystalline state was found at  $T_B = 8-9 \text{ K}$  with a small increase in temperature upon annealing. The characteristics of this peak are in agreement with the interstitialcy

theory,<sup>1,21</sup> which connects this peak with low-frequency resonant localized vibrations of interstitialcy defects frozen in upon glass production. The height of this peak is predicted to be proportional to the concentration of these defects. It is these defects that provide shear softening of the glass with respect to the reference crystal. Using high-frequency shear modulus measurements and basic Eq. (3) of the interstitialcy theory, we showed that the Boson heat capacity peak height is indeed directly proportional to the defect concentration derived from this equation. The performed investigation together with earlier findings provides further evidence that interstitialcies are the basic entities responsible for this and a number of other thermodynamic and kinetics properties of glassy, (supercooled) liquid, and crystalline states and the generic relationship between these.

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<sup>26</sup>In Ref. 27, the height of the excess heat capacity peak in the glassy state of a similar alloy  $\text{Pd}_{40}\text{Cu}_{40}\text{P}_{20}$  was found *smaller* than that in the crystalline state, contrary to the data shown in Fig. 3. The reason for this could be in the smaller height of the Boson peak as compared with the lattice dispersions excess  $C$  peak in this glass.  
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