



**Looking for footprint of bulk metallic glass in electronic and phonon heat capacities of Cu<sub>55</sub>Hf<sub>45</sub> x Ti x alloys**

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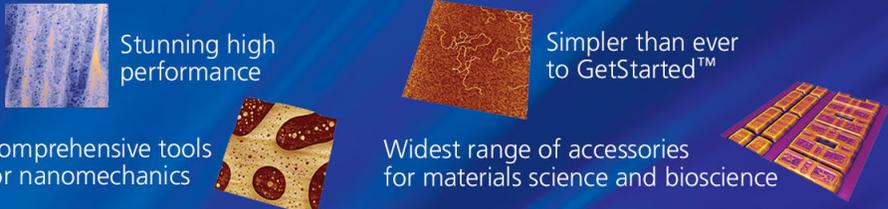
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# Looking for footprint of bulk metallic glass in electronic and phonon heat capacities of $\text{Cu}_{55}\text{Hf}_{45-x}\text{Ti}_x$ alloys

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We report on the heat capacity investigation of  $\text{Cu}_{55}\text{Hf}_{45-x}\text{Ti}_x$  metallic glasses. The most appropriate procedure to estimate low temperature electronic and phonon contributions has been determined. Both contributions exhibit monotonous Ti concentration dependence, demonstrating that there is no relation of either the electron density of states at the Fermi level or the Debye temperature to the increased glass forming ability in the Ti concentration range  $x = 15\text{--}30$ . The thermodynamic parameters (e.g., reduced glass temperature) remain better indicators in assessing the best composition for bulk metallic glass formation. © 2014 AIP Publishing LLC.

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Due to their exceptional mechanical and chemical properties, metallic glasses (MG) are very attractive for a wide range of applications.<sup>1–4</sup> The glass forming ability (GFA) determines the availability of MG in the bulk form required for large-scale applications. The *Liu's parameter*,<sup>5</sup>  $\Gamma = T_x/(T_L + T_G)$ , and the reduced glass temperature,<sup>6</sup>  $T_{RG} = T_G/T_L$ , are (among others) good measures of GFA,<sup>7</sup> based on thermodynamic and kinetic considerations.  $T_G$ ,  $T_L$ , and  $T_x$  are glass transition temperature, liquidus, and the onset crystallization temperature, respectively. However, in order to predict GFA, more fundamental MG models related to their specific atomic<sup>8–10</sup> and electronic<sup>11,12</sup> structure have been proposed. Semi-empirical models<sup>8,13</sup> enabled the development of numerous alloy compositions suitable for the synthesis of bulk MG (BMG).

Heat capacity ( $C_p$ ) measurements of typical ternary ( $\text{Cu}_{50}\text{Zr}_{50}$ )<sub>100-x</sub>Al<sub>x</sub> MG system<sup>14</sup> suggested yet another way to estimate GFA, since the electronic contribution to  $C_p$  showed a minimum for  $x$  exhibiting the highest GFA. This correlation seems to support the significance of electronic structure on the MG formation.<sup>11,12</sup> On the other hand, the variation of the phonon contribution to  $C_p$  did not show any systematic  $x$  dependence,<sup>14</sup> in contrast to the monotonous increase of elastic moduli and hardness.<sup>15</sup> However, a similar study of  $\text{Ca}_{75-x}\text{Mg}_{25}\text{Cu}_x$  system<sup>16</sup> has shown only a monotonous variation of electronic contribution in the  $x$ -range of the highest GFA.

We believe that a method determining GFA from the low temperature bulk properties, such as heat capacity, would be very valuable for BMG development. Therefore, we have performed a similar investigation of the  $\text{Cu}_{55}\text{Hf}_{45-x}\text{Ti}_x$  MG system, taking particular care of fitting procedure to test if electronic and phonon contributions reflect any specific features related to GFA.

Cu-based ternary BMGs with high Cu content have high GFA and strength.<sup>17,18</sup> In particular, the  $\text{Cu}_{55}\text{Hf}_{45-x}\text{Ti}_x$  alloy series has a pronounced maximum of the critical BMG formation diameter for  $x = 20\text{--}25$ , coinciding with the minimum in  $T_L$ <sup>19,20</sup> (i.e., maximum in  $T_{RG}$  and  $\Gamma$ —calculated by us), Fig. 1. On the other hand, mechanical properties (Young's modulus and microhardness), as well as magnetic susceptibility ( $\chi$ )<sup>21</sup> do not exhibit particular features in this composition range, hence do not indicate BMG favoring compositions.

We have investigated  $C_p$  of  $\text{Cu}_{55}\text{Hf}_{45-x}\text{Ti}_x$  ( $x = 0, 5, 10, 15, 20, 25, 35, 40, 45$ ) melt spun ribbon samples of average thickness  $\sim 25 \mu\text{m}$  and  $\sim 2 \text{mm}$  in width, previously thermally characterized.<sup>19,20</sup> The samples were piston pressed in the form of small disks, 2 mm in diameter and weighing up to 60 mg. To achieve the good thermal contact, samples were attached to the holder by a small amount of Apiezon N grease ( $< 0.1 \text{mg}$ ). Measurements on several samples have

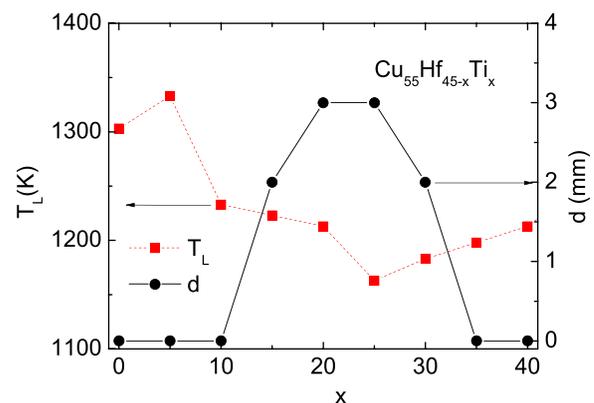


FIG. 1. The minimum in liquidus temperature  $T_L$  and the maximum of the critical glassy diameters of  $\text{Cu}_{55}\text{Hf}_{45-x}\text{Ti}_x$  alloys demonstrate the composition with the best GFA.

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been performed with the home made transient heat pulse technique in Zagreb, while the entire series has been measured in Grenoble, within the same T-range (1.9–320 K), with the Physical Property Measurement System (PPMS)-model 6000 from Quantum Design Inc. Sample to addenda  $C_p$  ratio was in general one order of magnitude below 50 K. Here, we present only the PPMS data, as the difference between two data sets is within the PPMS reproducibility (2%).

$C_p$  of  $\text{Cu}_{55}\text{Hf}_{45-x}\text{Ti}_x$  series is shown in Fig. 2. The inset plots  $C_p$  in the whole T-range from 1.9 K to the room temperature for the limiting Ti concentrations  $x=0$  and 45. In nonmagnetic metals,  $C_p$  is primarily determined by electronic and phonon contributions<sup>22</sup> ( $\sim T$  and  $\sim T^3$ , respectively), schematically indicated in Fig. 2

$$C_p = \gamma T + \beta T^3 \quad \gamma = \frac{\pi^2}{3} k_B^2 n_F \quad \beta = \frac{12\pi^4}{5} \frac{k_B}{\theta_D^3}, \quad (1)$$

$k_B$  being Boltzmann constant,  $n_F$  being electron density of states at the Fermi level, and  $\theta_D$  being the Debye temperature.

In *insulating glasses* a quasi linear contribution  $\sim T^\nu$  ( $\nu \sim 1$ ) is present below 1 K as well.<sup>23</sup> It is assigned to the localized two level systems (TLS) originating from small atomic clusters which change configuration and tunnel between two energetically close states.<sup>24</sup> In Cu-based superconducting MG,<sup>25,26</sup> such quasi linear contribution has been observed well below the superconducting transition ( $\sim 1$  K), with amplitude comparable to the one found in insulating glasses, almost 2 orders smaller than the regular electronic contribution. Therefore, we believe that this term can be neglected in our analysis.

We use the standard way to estimate parameters  $\gamma$  and  $\beta$  from the  $C_p/T$  vs.  $T^2$  presentation shown in Fig. 3;  $\beta$  from the slope and the  $\gamma$  from the ordinate intercept of the linear fit. Our fit in the 3–10 K range, typical for the evaluation of  $\gamma$  and  $\beta$ , resembles that one presented in Fig. 1 in Ref. 14.

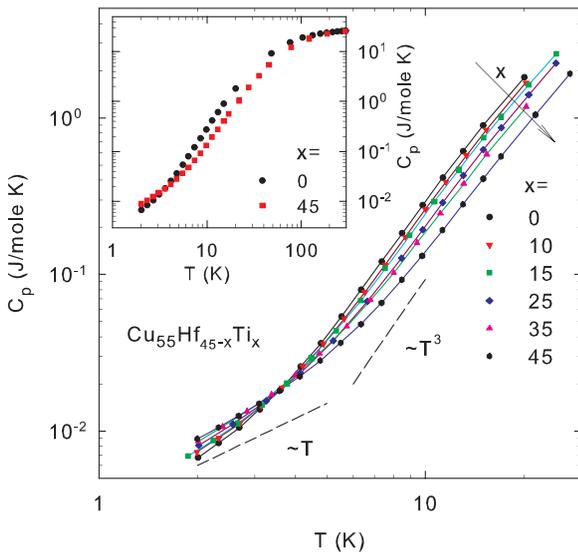


FIG. 2. Specific heat  $C_p$  of  $\text{Cu}_{55}\text{Hf}_{45-x}\text{Ti}_x$  MG series. Dashed lines indicate the electronic and the phonon contributions. The deviation from  $T^3$  dependence occurs at  $\sim \theta_D/10$ , well above 10 K. The inset shows  $C_p(T)$  approaching the Dulong-Petit value at ambient temperature.

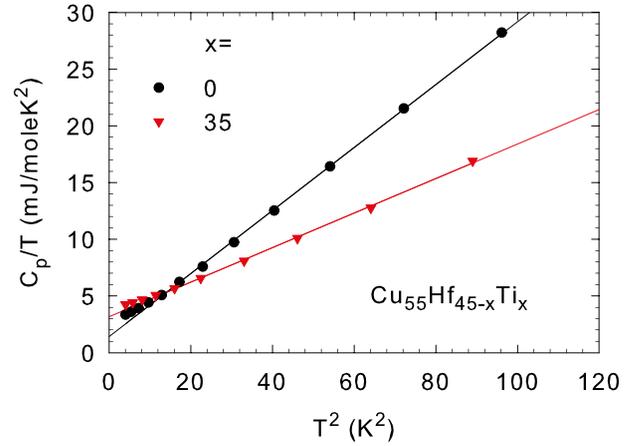


FIG. 3. Specific heat  $C_p$  of  $\text{Cu}_{55}\text{Hf}_{45-x}\text{Ti}_x$  in  $C_p/T$  vs.  $T^2$  presentation. Lines represent fits to Eq. (1) in 3–10 K range. Electronic contribution ( $\gamma$ ) and the phonon contribution ( $\beta$ ) are revealed from the ordinate intercept and the slope, respectively.

However, the experimental data show evident upturn below 4 K. It indicates that the quality of the fit and particularly the intercept might depend on the temperature interval of fits. Avoiding such artificial effects could be crucial in determination of correct  $\gamma(x)$ .

In order to demonstrate the influence of the temperature range used for fit, in Fig. 4 we show fit in the reduced range 1.9–5 K (full lines), which is more convincing at the lowest temperatures. Consequently, there is more pronounced deviation from the fitting line above 5 K. Therefore, one should fit with Eq. (1) only up to 5 K.

Deviations emerging at higher  $T$ , if fitting by Eq. (1), were well recognized already in the early works.<sup>27</sup> In the comprehensive low-T  $C_p$  investigation of Cu-Ti MG,<sup>28</sup> the correction to the phonon part has been taken into account as an additional quintic term<sup>27,28</sup>

$$C_p = \gamma T + \beta T^3 + \delta T^5. \quad (2)$$

The complete data in the range of 1.9–7 K are now well described by Eq. (2) (dashed lines in Fig. 4).

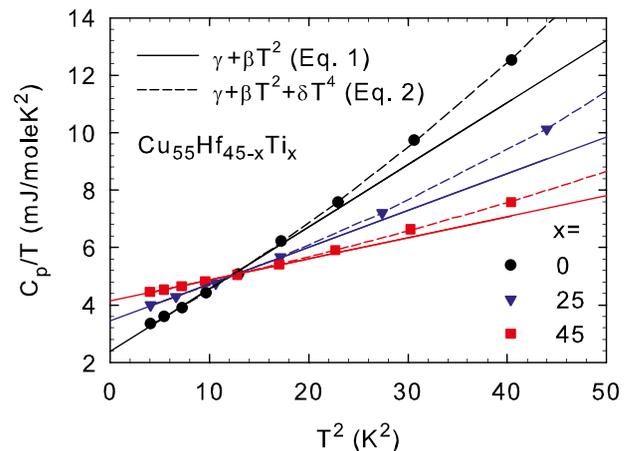


FIG. 4. Comparison between fits to different equations (indicated in the figure) in different T-ranges (1.9–5 K and 1.9–7 K for full and dashed lines, respectively) show good agreement below 4 K.

In the previous work, the physical significance of this additional phonon term was not discussed. Such upturn can occur in crystals due to the saturation in dispersion of acoustic phonons (van Hove singularities) and/or the excitation of optical phonons, as for instance in copper.<sup>29</sup> However, in glasses, this is the onset of a broad feature at  $\sim 10$  K, named Boson peak (BP).<sup>23</sup> BP is more appropriate for description of MG systems (for opposite view see discussion in Ref. 29).

We present the fit parameters obtained from both equations in different temperature ranges in Fig. 5 and the corresponding  $n_F$  and  $\theta_D$  in Fig. 6, together with values from previous studies of binary MG systems<sup>28,30,31</sup> (open symbols). Both  $\gamma$  and  $\beta$  depend monotonically on  $x$ . However, their absolute values depend on the temperature range in which they are determined. There is a good agreement between parameters obtained from the fits using Eqs. (1) and (2) below 5 and 7 K, respectively (Fig. 4). On the other hand, the fits in the broader temperature range (3–10 K), produced substantially different results. As the correction parameter  $\delta$  decreases with increasing Ti concentration, the difference between parameter values, obtained on broader and narrower ranges, becomes smaller. Reproducibility of parameters obtained on  $x=40$  and 45 samples is within deviation obtained using different fitting ranges, Fig. 5.

Mizutani and coworkers<sup>30</sup> measured  $C_p$  of  $\text{Cu}_{50}\text{Ti}_{50}$  and  $\text{Cu}_{60}\text{Ti}_{40}$  between 1.5 and 5 K, while Cooper<sup>31</sup> measured 4 alloys of  $\text{Cu}_{100-y}\text{Hf}_y$ ,  $y = 30, 40, 50, 65$  between 0.3 and 6 K.

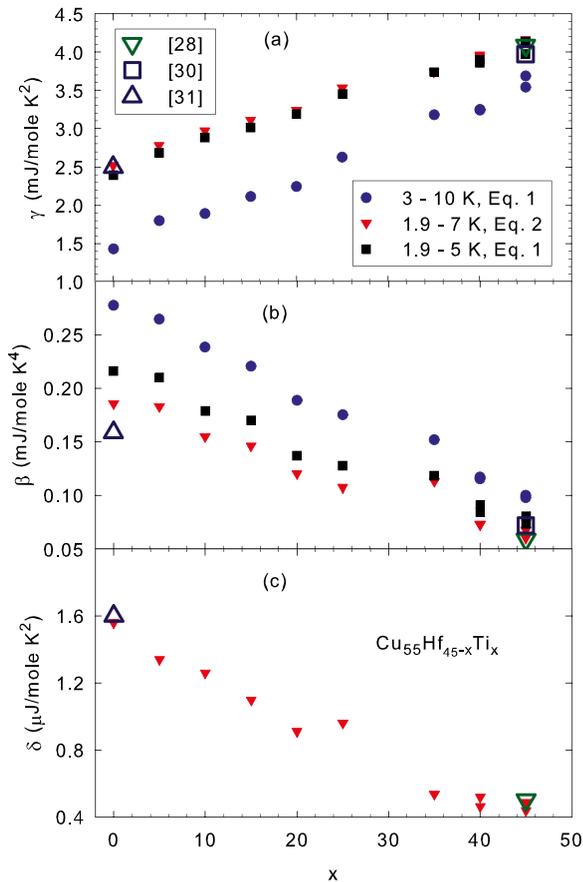


FIG. 5. Coefficients of electronic  $\gamma$  (a), phonon  $\beta$  (b), and  $\sim T^5$  correction  $\delta$  (c) contributions to  $C_p$  in different T-ranges (indicated in the figure) using both fit equations (closed symbols). Published data are indicated by the open symbols.

We have interpolated parameters from both experiments for  $\text{Cu}_{55}\text{Ti}_{45}$  and  $\text{Cu}_{55}\text{Hf}_{45}$  alloys. Moody and Ng<sup>28</sup> measured 10 alloys of  $\text{Cu}_{100-y}\text{Ti}_y$  between 1.1 and 4.2 K, including  $\text{Cu}_{55}\text{Ti}_{45}$ . Parameters, presented with empty symbols in Figs. 5 and 6, show very good agreement with the parameters obtained from our measurements in low-T range, including the values of the correction parameter  $\delta$ . Evidently, the  $C_p(T)$  dependence should be carefully studied to obtain reliable parameters of electronic and phonon contributions. The fit in high-T range overestimates the phonon contribution, due to the additional BP-like term, while reducing electronic contribution. This shows how carefully one has to make conclusions considering only one fitting parameter, as was done in Ref. 14. In following discussion, we therefore consider  $\gamma$  and  $\beta$  obtained from the fits in the low-T region.

The monotonous  $\gamma(x)$  and  $\beta(x)$  dependence is not particularly surprising. It has been shown that all properties of the amorphous alloys of early transition metals (TE = Ti, Zr, Hf) with copper exhibit simple solid solution dependence on composition.<sup>32</sup> Particularly, the properties which are directly related to  $n_F$ , such as  $\chi$ <sup>32</sup> and  $\gamma$ ,<sup>33</sup> reflect the predominantly TE d-like nature of the conduction band.<sup>34</sup> As the 3d orbitals in Ti are more tightly bound than the 5d orbitals in Hf,<sup>35</sup> the substitution of Hf by isoelectronic Ti narrows the conduction band, increasing  $n_F$  and consequently  $\chi$ <sup>32</sup> and  $\gamma$ . The relative increase of  $n_F$  by  $\sim 60\%$  from  $\text{Cu}_{55}\text{Hf}_{45}$  to  $\text{Cu}_{55}\text{Ti}_{45}$  is only slightly higher than expected from the electronic structure of pure Ti and Hf,<sup>35</sup> while the absolute values are substantially renormalized due to the reduced overlap and electron-phonon interaction.<sup>33</sup> We can therefore exclude the proposed relation between  $n_F$  and GFA<sup>11,12</sup> in the case of  $\text{Cu}_{55}\text{Hf}_{45-x}\text{Ti}_x$  alloys, which confirms that the nearly free-electron model might not be appropriate,<sup>27</sup> in agreement to the early findings.

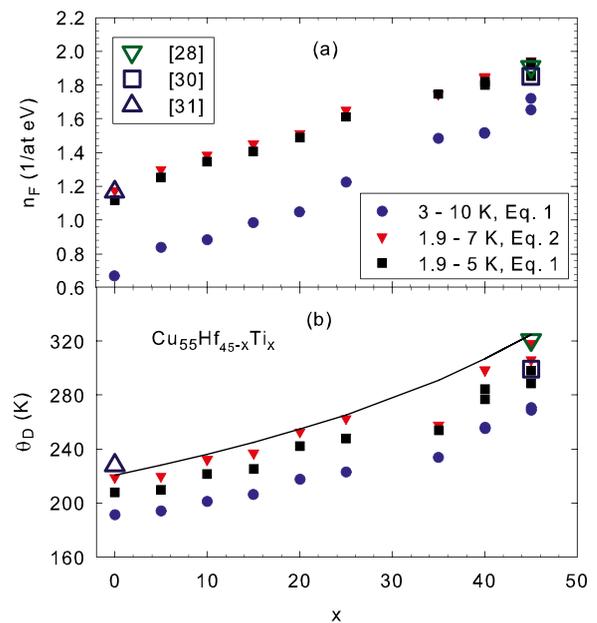


FIG. 6. Fermi density of states  $n_F$  (a) and Debye temperature  $\theta_D$  (b) calculated from fitting parameters using Eq. (1). Closed symbols—our work; open symbols—previously published data; full line—an estimate of  $\theta_D$  from the Young modulus,<sup>21</sup> Poisson ratio,<sup>18</sup> and mass density.

According to the theory of the isotropic elastic continuum (appropriate for homogeneous MG),<sup>36</sup>  $\theta_D$  can be estimated from the Young modulus,<sup>21</sup> Poisson ratio,<sup>18</sup> and mass density, which determine acoustic velocities, and atomic volume. As the density of Cu<sub>55</sub>Hf<sub>45-x</sub>Ti<sub>x</sub> BMGs has not been measured, we have used the experimental estimates of specific atomic volumes in TE-Cu amorphous alloys<sup>37</sup> to calculate average atomic volume and corresponding density using the average molar mass. The increase of  $\theta_D$ , presented by the solid line in Fig. 6(b), comes predominantly from the decrease of the molar mass, as Hf is more than 3× heavier than Ti.

Our investigation of Cu<sub>55</sub>Hf<sub>45-x</sub>Ti<sub>x</sub> MG sheds more light on some important issues on determination of the relevant relation between GFA and thermodynamic parameters, obtained from low-T  $C_p$ . We have clearly shown the justifiable criteria to fit the experimental data to obtain correct electronic and phonon contributions to  $C_p$ . Together with previously measured magnetic, mechanical, and thermal properties ( $T_L$ ,  $T_x$  and  $T_G$ ),<sup>19-21</sup> they exhibit a simple solid solution behavior—all parameters vary linearly with Ti composition.

Finally, we can conclude that, as we did not find in these simple model alloys any relation between the glass formation mechanism and the  $n_F$  or  $\theta_D$ , the thermal parameters,  $T_L$  and derived  $\Gamma$  and  $T_{RG}$ , remain the most assertive GFA indicators.<sup>21</sup> The glass formation mechanism should be searched in more subtle interrelations of the electronic and atomic subsystems.

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