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## Analysis of the fragility of the $\text{Zr}_{77}\text{Ni}_{23}$ metallic glass based on low-temperature heat capacity measurements

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We present an experimental investigation of the fragility and heat capacity of metallic glass  $\text{Zr}_{77}\text{Ni}_{23}$ . The ribbon sample was produced by melt-spinning technique. Glass transition temperature  $T_g$  obtained by differential scanning calorimetry with various heating rates was used to estimate fragility parameter  $m$ . Heat capacity measurements were performed in a wide temperature interval, ranging from 1.8 K up to room temperature, for as-cast and relaxed samples in different magnetic field strengths. Our results do not show any excess of vibrational density of states over the Debye contribution corresponding to the boson peak. Relaxation of the sample causes a slight decrease of Debye contribution consistent with the measured increase of Young modulus. The fact that no boson peak is observed in heat capacity, together with the obtained intermediate fragility of  $m = 53$ , positions  $\text{Zr}_{77}\text{Ni}_{23}$  well outside established correlations between fragility, boson peak strength, and glass forming ability.

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### I. INTRODUCTION

Glasses can be formed from a wide variety of covalent, metallic, ionic, and molecular liquids (or melts) [1,2] when cooled at sufficiently high rates to avoid crystallization [3]. The glass forming ability (GFA) can be quantified as the minimum cooling rate required for glass formation  $h_{\min}$  [3,4], or by the maximum diameter for glass formation  $d_{\max}$  [5].

In addition to the inherent amorphous structure, all glasses exhibit a number of characteristic features which can be classified within the spectrum from strong to fragile according to the concept of fragility [6–8]. The kinetic fragility index  $m$ , which describes how fast viscosity or relaxation time increases near the glass transition temperature  $T_g$  [9], is strongly correlated with different dynamical [10], thermodynamic [11], or structural [12,13] parameters, which can be considered as alternative fragility measures, although such a unified picture has been contested [14,15].

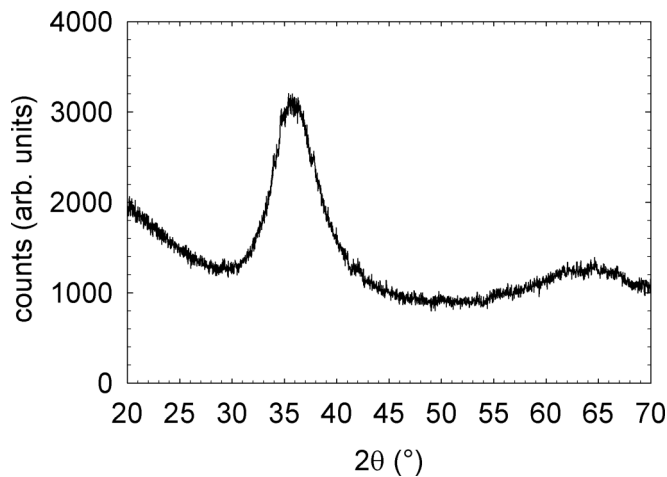
Strong glass formers with low  $m$  values typically have high GFA, while fragile ones with high  $m$  have low GFA. This relation has been studied particularly in metallic glasses (MGs) [16–19] where GFA can vary strongly with small compositional changes. An exact correlation [18,19] required another free parameter, reduced glass transition temperature  $T_{rg}$  [20], one of several similar empirical criteria used to predict GFA in MG [5]. Therefore it seems that thermodynamic and kinetic parameters governing the glass formation are not entirely interdependent. The fragility is also correlated with the boson peak (BP), representing the low energy vibrational density of states (VDOS) in excess to the acoustic (Debye) contribution, which is consistently observed in low temperature heat capacity [21], Raman [22], and inelastic neutron scattering

[23] of glasses. The strength of the BP, i.e., the maximum deviation from the Debye contribution, is shown to increase with the decrease of  $m$  [24–27]. Although the description of all the glass properties, based on the single parameter of fragility, is probably oversimplified [14,15,28,29], it is possible to establish a simple rule of thumb that good glass formers with high GFA have low fragility and prominent BP.

Early transition metal-late transition metal (TE-TL) MGs were among the first metal-only MGs obtained [30], but they are typically poor glass formers [31,32]. MG based on ZrNi alloys, despite their compositionally wide glass forming range (GFR) [33,34], have not yet been produced in bulk metallic glass (BMG) form [35], i.e., with thickness exceeding 1 mm. This is in accordance with their low values of  $T_{rg}$  [34]. However, except in one case [36], various approaches [35,37–40] suggest that GFA of ZrNi should be comparable to GFA of ZrCu alloys which represent a rare example of binary BMG [41]. In particular, it is suggested that GFA of ZrNi alloys should be highest close to the composition of deepest eutectic [39].

With respect to their low GFA, ZrNi MG is expected to show typical characteristics of fragile glasses and the fragility assessments in several ZrNi alloys based on viscosity [42], differential scanning calorimetry (DSC) [43] and structural [13] measurements tend to confirm it. Low temperature heat capacity ( $C_p$ ) measurements [44–47] for various compositions have not been performed in a sufficiently wide temperature range to determine BP, but they indicate it should be small [48]. On the other hand,  $\text{Zr}_{67}\text{Ni}_{33}$  has been described as a strong glass former [49], based on high BP in VDOS calculated from inelastic neutron scattering data [50] and the low fragility obtained from molecular dynamics (MD) simulations [51]. Such a conclusion has been disputed [48], however it leaves open the question of the relation between the fragility, GFA, and BP in metallic glasses.

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FIG. 1. XRD pattern of  $Zr_{77}Ni_{23}$  MG.

In this work we present the measurements of DSC and  $C_p$  on  $Zr_{77}Ni_{23}$  MG sample. This composition is close to the deepest eutectic  $Zr_{75.9}Ni_{24.1}$ . However, it is situated at the edge of experimentally determined GFR [33,34] and the GFA estimate based on the reduced glass transition temperature  $T_{rg}$  [20] is low [33,34]. DSC measurements of the heating rate dependence of  $T_g$  confirm low  $T_{rg}$  value, but give an intermediate value of  $m$ . On the other hand,  $C_p$  measurements on as-cast and relaxed samples show no indication of BP in this system, which is unusual even for very fragile glasses [24].

In order to give full information of our system in comparison to previously published results, our results under different magnetic field strengths, as well as characterisation of the SC transition, are discussed separately in the frame of similar investigations performed earlier by other groups [44–47].

## II. EXPERIMENT

The master alloy  $Zr_{77}Ni_{23}$  was prepared by arc melting under an argon atmosphere using high purity elements: Zr (99.85 %) and Ni (99.995 %). MG sample in the form of ribbon approximately 1.5 m long, 0.85 mm wide, and 30  $\mu$ m thick was prepared by the single roller chill block melt-spinning technique in an argon atmosphere using a home-made device [52]. The linear surface velocity of the rotating copper wheel was 30 m/s. The results of x-ray diffraction (XRD) analysis, shown in Fig. 1, confirms amorphous structure of the ribbon. The energy dispersive x-ray spectroscopy (EDS) results show a very homogenous distribution of nickel and zirconium in the ribbon. The agreement of nominal and EDS composition was within 1%.

In order to determine the dependence of  $T_g$  on the heating rate ( $h$ ) for the fragility determination, we chose from the same ribbon several samples approximately 1 cm long and heated them using DSC at  $h = 1, 3, 10,$  and 30 K/min. All thermal measurements were performed using the calorimeter NETZCH DTA 404 S/3/F in argon flow of 150 ml/min.

$C_p$  measurements were performed in the  $T$  range from 1.8 to 300 K with PPMS (Physical Properties Measurement System)-Model 6000, Quantum Design Inc. using a thermal relaxation technique. The sample was in the form of a disk

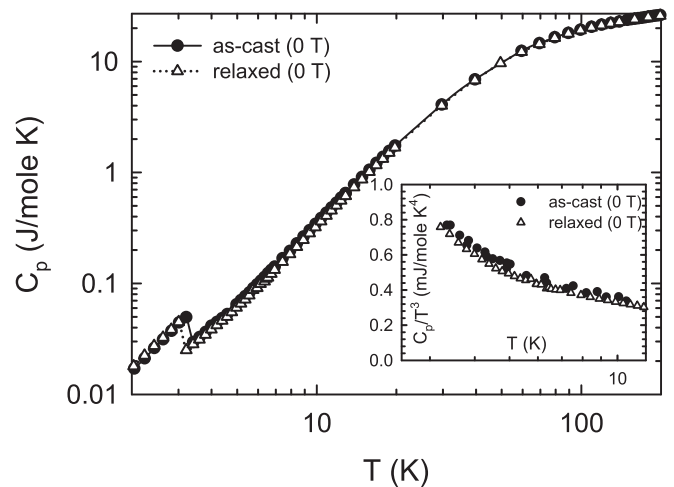


FIG. 2.  $C_p$  of  $Zr_{77}Ni_{23}$  as-cast and relaxed samples in zero magnetic field. The inset shows a  $C_p/T^3$  vs  $T$  plot for as-cast and relaxed samples.

made by compressing the ribbon using a 2 mm wide mold press. The mass of the sample was 15.7 mg. It was attached to the holder using Apiezon grease. The addenda contribution in total measured  $C_p$  was about 3% at 3 K and 50% at 300 K.

The annealing of the sample, which was used for the first  $C_p$  measurements, was performed by means of DSC. The sample was heated at a heating rate of 20 K/min from room temperature (RT) to  $T_a = 305^\circ\text{C}$ , 10 K below the  $T_g$ . At the maximum temperature  $T_a$ , the sample was isothermally relaxed for 10 min and then cooled to RT at the same rate.

Generally,  $C_p$  measurements are very sensitive to different factors. In order to check reproducibility, avoid errors, obtain wider  $T$  range for determination of  $C_p$  parameters, and characterize the SC transition, we made measurements under different magnetic fields:  $H = 0, 1, 2, 3, 4$  T for as-cast and relaxed samples. Finally, we also measured the velocity  $v_s$  of a 150 kHz ultrasound wave along the 100 mm long ribbon using pulse-echo technique at RT for the as-cast and relaxed samples [53]. In the long rod geometry the sound velocity is related to the Young modulus  $E$  as  $E = v_s^2 \rho$ .

## III. RESULTS AND DISCUSSION

$C_p$  of as-cast and relaxed samples of  $Zr_{77}Ni_{23}$  without magnetic field is presented in Fig. 2. At RT,  $C_p$  in both measurements reaches the Dulong-Petit value. As expected [44–47], at low temperatures the SC transition was detected. The inset of Fig. 2 shows  $C_p$  vs  $T^3$  dependence for as-cast and relaxed samples in zero magnetic field above the SC transition temperature  $T_c$ , indicating considerable linear term in  $C_p$  below 4 K. For better determination of  $C_p$  in metallic state, we have applied a magnetic field to suppress SC transition to lower  $T$ , as shown in Fig. 3.

$C_p$  of nonmagnetic metallic alloys is determined by electronic and phonon contributions [54] which, at sufficiently low temperature, can be written as  $C_p = \gamma T + \beta T^3$ . The parameter  $\gamma$  is related to the electron density of states  $n_F$  at Fermi level  $\gamma = \frac{\pi^3}{3} k_B^2 n_F$  and  $\beta$  to the Debye temperature  $\theta_D$ ,

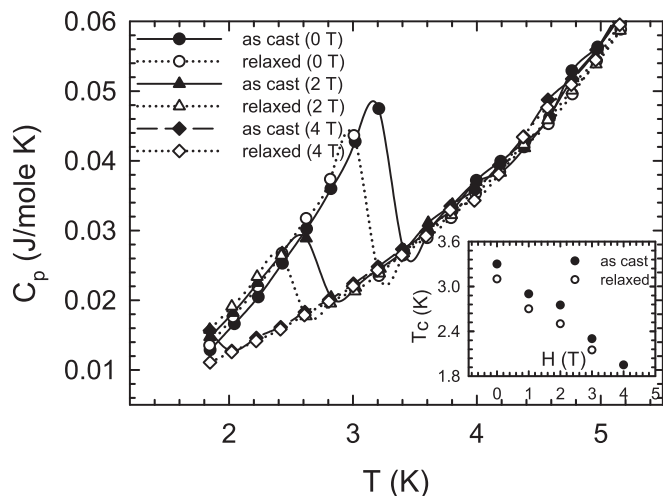


FIG. 3. Heat capacity in the range of SC transition for various magnetic fields. The inset shows the dependence of  $T_c$  on the magnetic field.

$\beta = \frac{12\pi^4 k_B}{5 \theta_D^3}$ , with  $k_B$  being Boltzmann constant. The usual way to obtain parameters  $\beta$  and  $\gamma$  is using  $\frac{C_p}{T}$  vs  $T^2$  plot where  $\beta$  is determined from the slope and  $\gamma$  from the intersection of linear function with ordinate, as shown in Fig. 4. Applying magnetic field pushes SC transition to lower  $T$ , giving us wider  $T$  range for an estimation of both contributions. On the other hand, the sample relaxation decreases  $C_p$ , but also lowers  $T_c$ , so in the following we analyze both influences, of annealing and of magnetic field.

#### A. Influence of annealing and magnetic field above SC transition

In Fig. 4 we show  $\frac{C_p}{T}$  dependence on  $T^2$  for as-cast and relaxed samples with magnetic fields set for clarity only to  $H = 0$  T and  $H = 4$  T. Our previous measurements on CuHfTi BMG [55] have highlighted the importance of careful measurements and proper analysis of  $C_p$  data, particularly with respect to the possible BP contribution. However, in  $Zr_{77}Ni_{23}$  there is no deviation from the linear dependence above  $T_c$ . The parameters  $\beta$  and  $\gamma$  obtained by fitting in the  $T$  range from  $T_c$  to 7 K, are given in Fig. 5. They are in a good agreement with previously published results [56] for our composition, with corresponding values  $n_F = 2.13$  1/at eV and  $\theta_D = 181$  K, or 186 K for the relaxed sample. It is clear that the magnetic field does not affect the values of  $\beta$  and  $\gamma$ . On the other hand, the slope, i.e.,  $\beta$  value, is reduced with relaxation, while  $\gamma$  (intersection) remains approximately the same.

Measured sound speed ( $v$ ) in as-cast and relaxed samples are 3049 and 3120 m/s, respectively, which is in very good agreement with previous results on  $Zr_{78}Ni_{22}$  [57]. Using the data for  $\rho$  [58], the  $E$  for as-cast and relaxed samples are 64 and 67 GPa, respectively. The increase of  $\theta_D$  and  $E$  after relaxation is proportional, as would be expected for an isotropic elastic solid [59]. However, direct comparison of two parameters in terms of Poisson's ratio would be too tenuous considering different temperature ranges of corresponding measurements.

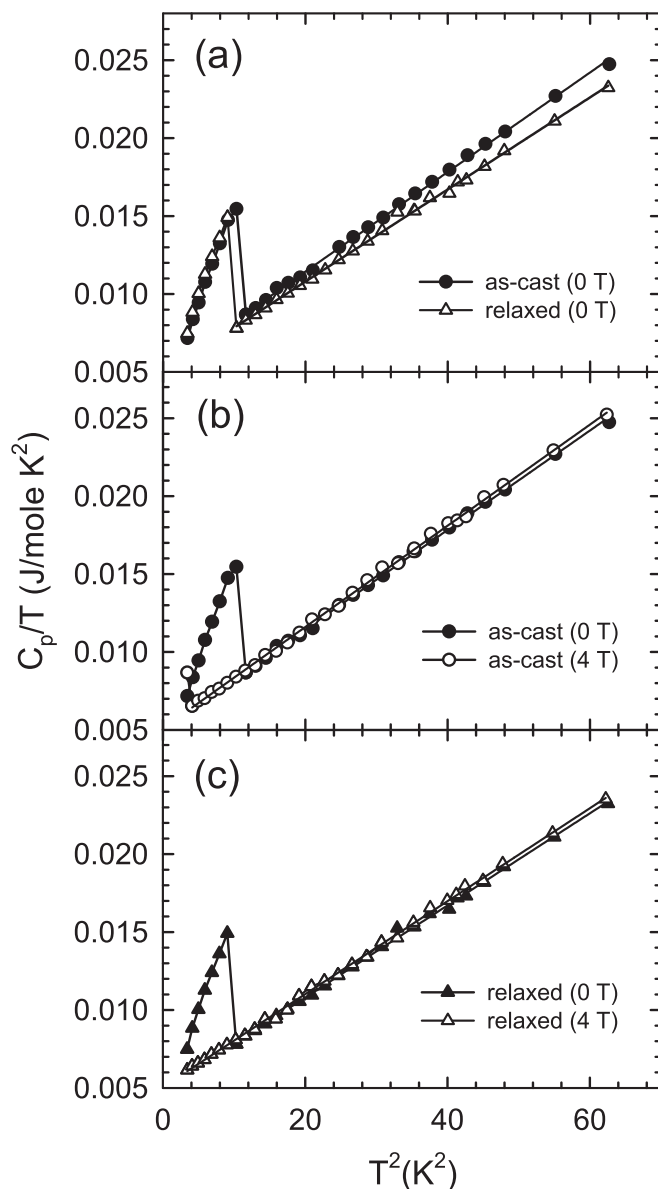


FIG. 4. The  $C_p/T$  vs  $T^2$  plots for (a) as-cast and relaxed samples without magnetic field, (b) as-cast sample with field  $H = 0$  T and  $H = 4$  T, and (c) relaxed sample with  $H = 0$  T and  $H = 4$  T.

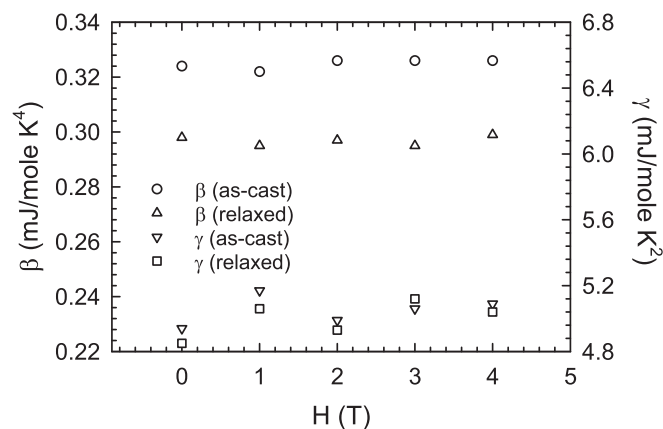


FIG. 5. Heat capacity parameters  $\beta$  and  $\gamma$  for as-cast and relaxed  $Zr_{77}Ni_{23}$  samples for different magnetic fields.



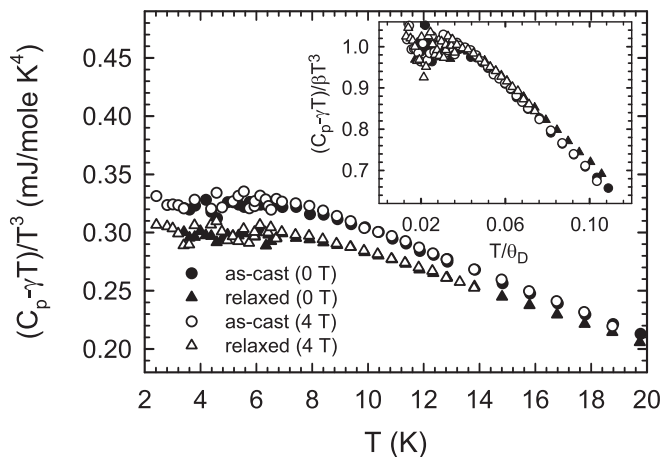


FIG. 6.  $\Delta C_p$  after subtracting the electronic contribution shows pure  $T^3$  behavior, but it demonstrates also the effect of relaxing. The inset shows a  $(C_p - \gamma T)/\beta T^3$  vs  $T/\theta_D$  plot.

### B. Is there a BP in $C_p$ ?

The vibrational  $C_p$ , obtained by subtracting the estimated electronic contribution  $\gamma T$  from the total  $C_p$ , is presented in Fig. 6 in the form  $(C_p - \gamma T)/T^3$  vs  $T$ . The data follow the  $T^3$  law until about  $\sim \theta_D/20$  where the downward deviation is observed. The BP in glasses manifests in  $C_p$  as the broad maximum in  $C_p/T^3$  in excess to constant  $\beta$  (Debye) background, usually situated in the temperature range near 10 K [21,24–27]. There is no indication of such a maximum in either as-cast or relaxed sample data, up to the data scattering of about 1%–2%.

It has been shown that the BP strength does not scale with the Debye parameters such as  $\beta$  or  $\theta_D$  [25,60]. Also, in MG the relaxation reduces both the BP strength and  $\beta$ , but not to the same extent, so BP becomes more pronounced [27,61–63] with respect to the Debye background. In the inset of Fig. 6 we present the data from the main panel, rescaled by Debye parameters, as  $(C_p - \gamma T)/\beta T^3$  vs  $T/\theta_D$ . The overlap of data indicates that the effect of relaxation is entirely due to the increase of stiffness, which has already been indicated by the proportionality of  $\theta_D$  and  $E$ . There is only a small deviation above about  $0.08 \theta_D \sim 15$  K, however even this does not amount to more than a few percent. The overall conclusion is that the BP peak is not present in  $Zr_{77}Ni_{23}$  MG, unless its strength is less than 1% of the Debye contribution. It is quite surprising, as even in canonical fragile glasses [64,65] BP have been observed in the low temperature  $C_p$ , its strength exceeding at least 10% of  $\beta$  value [25,27].

### C. Direct measurement of fragility

The lack of BP in  $Zr_{77}Ni_{23}$  would imply that this system should be highly fragile with extremely low GFA if it conforms to the scheme described in the Introduction. However, the melt-spinning technique, by which  $Zr_{77}Ni_{23}$  is formed, does not produce particularly high cooling rates, at least compared to the requirements for monoatomic MG formation [66]. Thus, although exact minimum cooling rate is not known, GFA of  $Zr_{77}Ni_{23}$  cannot be extremely low.

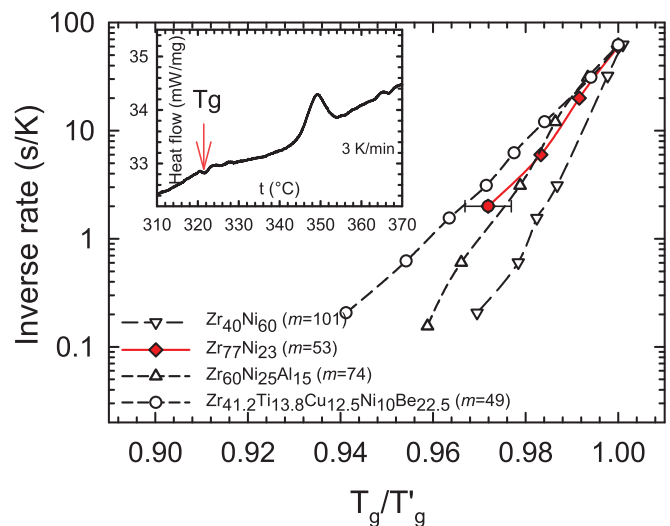


FIG. 7. Inverse heating rate against  $1/T$  normalized to  $T'_g$  at heating rate 1 K/min. All results except for  $Zr_{77}Ni_{23}$  are taken from [43]. Error bar is indicated for measurement at heating rate of 30 K/min. Inset figure shows DSC measurement for heating rate 3 K/min.

The viscosity of ZrNi melts have not been measured sufficiently close to  $T_g$  [42] for reliable direct evaluation of  $m$ , apart from unverified claims [51]. However, it is possible to estimate  $m$  from high temperature activated dependence of viscosity and the value of  $T_g$  [67] which gives  $m = 59$  for  $Zr_{76}Ni_{24}$  and 64 and 75 for  $Zr_{36}Ni_{64}$  and  $Zr_{57}Ni_{43}$ , respectively [42].

Another estimate of fragility can be obtained from the heating rate dependence of  $T_g$  in DSC measurements [43]. This method gives  $m = 90$  [48] for  $Zr_{60}Ni_{40}$ , reasonably close to the values estimated from viscosity measurements, so we have applied it to  $Zr_{77}Ni_{23}$  as well. Results obtained with heating rates of 1, 3, 10, and 30 K/min are presented in Fig. 7 together with data for several other systems [43]. The main panel of Fig. 7 shows  $T_g$  normalized to  $T'_g$  at lowest heating rate, plotted against the inverse heating rate. The onset of the glass transition has been identified as the downward break of the slope in the exotherm, found slightly below the crystallization peak  $T_x$  [68], shown in the inset of Fig. 7. Both  $T_x$  and  $T_g$  are in good agreement with previous measurements [33].

By definition, sufficiently close to  $T_g$   $m$  can be directly obtained as the slope of  $\log h$  vs  $T'_g/T_g$  dependence [9]. Our data give  $m = 53$ , in very good agreement with the value estimated from high temperature viscosity data. Other systems with similar, intermediate values of  $m$  [17–19] have sufficiently high GFA to be produced in bulk form, particularly those shown in Fig. 7 [68,69]. However, according to the empirical relation [19], the low value of  $T_{rg} = 0.482$  would offset the GFA in  $Zr_{77}Ni_{23}$  to lower values. Using a suggested formula [19], we have calculated  $d_{max} = 0.5$  mm, just below the limit of bulk glass formation. From  $m$  and  $T_{rg}$  it is also possible to estimate  $h_{min}$  [18] to be of the order of  $10^4$  K/s. This estimate is in accordance with experimentally determined  $h_{min}$  for several ZrNi alloys [35,70,71].

#### IV. DISCUSSION

Intermediate fragility, low GFA, and the absence of BP position Zr<sub>77</sub>Ni<sub>23</sub> MG are outside established correlations between glass forming ability, fragility, and boson peak strength. In the following we will consider the microscopic description of these properties and try to relate it to the peculiarities of our results.

Locally preferred atomic arrangement incompatible with long range crystalline order, typically with fivefold symmetry, is considered to have an important role in the suppression of crystallization [29,72–74]. In MG this short range order is predominantly represented by icosahedronlike clusters [75] and it has been directly associated with high GFA [76] of ZrCu MG. Structural investigations [77–79] show that ZrNi MG have a relatively smaller fraction of such clusters, which is attributed to stronger Zr-Ni bonding and corresponding chemical short range order [77,78,80]. Thus, while stronger bonding increases viscosity, particularly near eutectic composition, which would lead to smaller  $m$ , at the same time it promotes the crystal nucleation, resulting in a reduced  $T_{rg}$  value. The interplay of these two effects can lead to the reduced GFA despite intermediate  $m$  values. With respect to the suggested correlation between GFA,  $m$ , and  $T_{rg}$  [19] it would be interesting to see if relatively high calculated  $d_{max}$  can be achieved, despite a very low value of  $T_{rg}$ .

While the values of GFA and  $m$  in Zr<sub>77</sub>Ni<sub>23</sub> MG can be reconciled within the extended approach that considers independently thermodynamic and kinetic contributions to GFA [19], neither of them is sufficiently low to explain the lack of BP. It is widely accepted that the structural disorder is at the origin of BP in MG [81], although recent experimental results seem to contest this [82] in the case of oxide glasses. Thus it is not surprising that MD simulations of ZrNi MG indicate corresponding excess of VDOS [83,84]. More detailed analyses suggest that the vibrations contributing to BP in MG are quasilocalized in the regions of reduced density [85–87] characterized by strongly distorted clusters with substantial “free volume” of subatomic voids. The local atomic potential near the voids [86] is essentially the same as in the phenomenological soft-potential [88] or interstitialcy [89] models of BP.

The existence of free volume in MG has been confirmed by positron annihilation experiments [90]. However, free volume depends on sample history and decreases with annealing [91] or lower  $h$  [92]. This is consistent with the observed increase of density on annealing [93] and slow cooling [94]. At the same time, lower  $h$  [27,62] and particularly annealing [27,61–63] reduce the BP strength in  $C_p$ . This correlation gives an indirect, but compelling link between the free volume and BP strength. The annealing can actually completely remove BP [61], which has been correlated to the estimated density of interstitiality defects. In relation, complete reduction of free volume has been inferred from the saturation of relaxation time

in sequential annealing [93], after which the density remains constant.

The bottom line is that, given sufficient time, the free volume can be reduced and therefore eliminate BP. Whether it can be achieved by slow cooling remains to be confirmed in experiments. However, in Zr<sub>77</sub>Ni<sub>23</sub> the estimated  $h_{min}$  is quite high, barely lower than typical  $h$  for melt spinning [95]. We can tentatively suggest that the cooling rate close to  $h_{min} \sim 10^4$  K/s is responsible for lack of BP. This is not at odds with the results of MD simulations [83,84] as the effective  $h$  there is of the order of  $10^{12}$  K/s, i.e., 8 orders of magnitude higher. The stiffening observed both in the value of  $\beta$  in  $C_p$  and in  $E$  after relaxation can be related to the volume preserving reordering observed in structural dynamics [93]. A corollary to the discussion of BP is that the BP strength might not represent an intrinsic parameter of a particular glass former. However, it could be a good measure of relative GFA for glasses obtained under the same conditions, as it will be lower for glasses with  $h_{min}$  closer to actual  $h$ .

#### V. CONCLUSION

The relation between the fragility, GFA, and BP has been investigated in archetypal Zr<sub>77</sub>Ni<sub>23</sub> metallic glass in order to elucidate some open questions for this particular system with respect to widely established correlations in the field of glasses. The intermediate value of fragility parameter  $m$  deduced from the DSC analysis is clearly inconsistent with the marginal GFA of this alloy. Moreover, the absence of BP in the low temperature  $C_p$ , although in a broad accord with its poor GFA, also shows that BP is not a universal feature of amorphous solids. As intermediate fragility, low GFA and the absence of BP are at odds with the affirmed correlations between GFA, fragility, and BP strength, we propose the microscopic origin of this peculiarity. The absence of BP could be due to the strong reduction of free volume when the cooling rate used in sample production is close to the minimum cooling rate for glass formation. Therefore, only for metallic glasses obtained under the same conditions (same cooling rate), the strength of BP could be a good measure of relative GFA. Our results combined with literature results provide a basis for a deeper understanding of the relationships between GFA and parameters used for estimation of GFA in metallic glasses composed from early and late transition metals (or noble metals).

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