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Specific volume study of a bulk metallic glass far below its calorimetrically determined glass transition temperature

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High-precision LASER dilatometry with a unique measurement setup was applied to the bulk metallic glass alloy $Zr_{52.5}Ti_5Cu_{17.9}Ni_{14.6}Al_{10}$ (Vit105) for specific volume studies. Employing small temperature steps of $\Delta T =$ 5 and 10 K and long measurement times effective heating rates of the order of 10^{-2} K/min were realized and changes of the specific volume were measured with a resolution of $\Delta V/V = 10^{-6}$ down to 573 K. The temperature regime of these experiments is far below a calorimetrically determined glass transition of $T_g^{\mathrm{calor}} =$ 659 K (5 K/min). The experimental results strongly support theoretical predictions for the existence of an ideal glass transition that was observed in this study at $T_g = 628$ K for this bulk metallic glass model alloy.

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I. INTRODUCTION

When a glass forming liquid approaches its glass transition certain physical properties can change by orders of magnitude. Whilst experimentally characterized by a variety of measurement techniques the question whether there is a real phase transition at a glass transition temperature T_g is still unanswered [1,2]. The slowing down of molecular or atomic motion makes it difficult to assess the behavior at temperatures well below an apparent glass transition, e.g., experimentally determined from calorimetry at T_g' (see Fig. 1). The structural relaxation time, usually termed τ_α, which is the decay time of correlated motion after a perturbation of the system is readily accessible only at temperatures above T_g because this quantity becomes strongly time dependent when the system falls out of equilibrium [3]. It is one of the most challenging questions regarding the glass transition [3–5] whether τ_α distinctly diverges at a finite, ideal temperature T_g, or whether τ_α just continuously increases with decreasing temperature; see Fig. 1 curve (1) and curve (2), respectively.

In contrast to the relaxation time τ_α other physical quantities that are linked to structural equilibration, e.g., changes in the specific volume, $\Delta V/V$, or changes in the specific heat, $\Delta Q/Q$, of the system are more conveniently accessible in the glassy state [6]. Such measurements can, in principle, answer the crucial question whether the glass equilibrates to the supercooled liquid even at temperatures far below T_g'. However, highly stable measurement conditions are necessary to examine the equilibration processes in the glassy state due to the usually very small signal per unit-time ratio. A divergence of the structural relaxation time τ_α at a finite temperature would also cause a significant change in the equilibration behavior of the specific volume because only secondary volume affecting processes like, e.g., defect diffusion mechanisms would remain at lower temperatures.

A direct access to the equilibration behavior of metallic glasses is provided by dilatometric measurements, i.e., the measurement of changes in the specific volume. However, most conventional dilatometric measurements are performed with continuous heating rates in the several K/min range (see, e.g., Ref [7]). At these rates volume changes below the apparent glass transition T_g' are caused by the instantaneous thermal expansion. For assessing the equilibration of the specific volume, i.e., the real glass transition temperature T_g, much lower heating rates are required.

Furthermore, depending on the type of glass the viscosity will show a more or less strong decrease upon reaching T_g. With a mechanical push-rod dilatometer a deformation of the sample is unavoidable at temperatures close to T_g [8]. Also, in isothermal measurements creeplike phenomena will start to play an increasingly important role when temperature or measurement time is increased near the glass transition where the kinetics becomes faster [9,10].

Because of these difficulties only a few dilatometric measurements on bulk metallic glasses below the glass transition are available in the literature [7,8,11]. An example for isothermal long-time measurements is given in Ref. [12] but no information about the specific volume evolution is given there.

In this paper we report dilatometric results from the equilibration behavior of the specific volume of a bulk metallic glass far below its calorimetrically determined glass transition temperature, T_g^{calor} ($=T_g'$). In the experiments an effective heating rate of the order of 10^{-2}K/min was realized. To achieve the necessary length resolution and measurement stability a high-resolution dilatometer based on two-beam LASER interferometry was developed and applied.

II. EXPERIMENTAL PROCEDURE

A. Sample preparation

For the presented measurements the Zr-based glass-forming alloy $Zr_{52.5}Ti_5Cu_{17.9}Ni_{14.6}Al_{10}$ (Vit105) was used as a model alloy because it exhibits an outstanding glass forming ability and good resistance to crystallization. The samples were produced by copper-mold suction casting into a form of a

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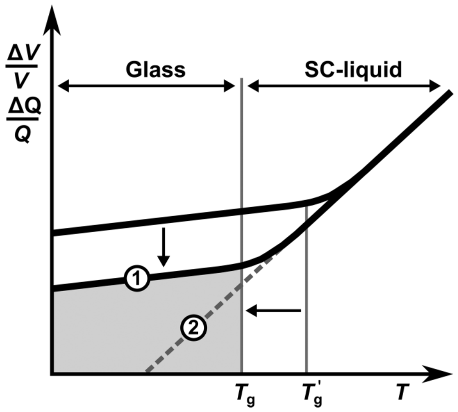

FIG. 1. Schematic representation of how the specific volume $\Delta V/V$ or the specific heat $\Delta Q/Q$ of a supercooled liquid could change upon cooling: (1) at the ideal glass transition T_g there is a distinct transition from a supercooled liquid state into the glassy state; (2) the glassy state is a frozen-in supercooled liquid state. An apparent glass transition T_g' is also indicated which is often measured if the supercooled liquid is not in its metastable equilibrated state or if cooling occurs too fast. In the case of behavior (1) states inside the gray area are fundamentally inaccessible.

rectangular prism with dimensions of $6 \times 3 \times 40$ mm^3. From this prism, a final L-shaped sample was cut with a diamond saw giving two parallel front faces a distance of 20 mm apart (see Fig. 2). These two faces were specially polished to achieve minimum deviation from parallelism and maximum optical reflectivity as they serve as the reflecting planes for the LASER interferometer.

B. Measurement setup

All measurements were performed using a unique, self-developed, high-resolution LASER dilatometer. The basic idea underlying the development of this device was the construction of a dilatometer for long-time, isothermal measurements after fast temperature changes. This type of measurement is necessary for direct studies of slow volume equilibration processes found in a variety of materials, e.g., in some intermetallic compounds [13,14] or especially in bulk metallic glasses below T_g' [15].

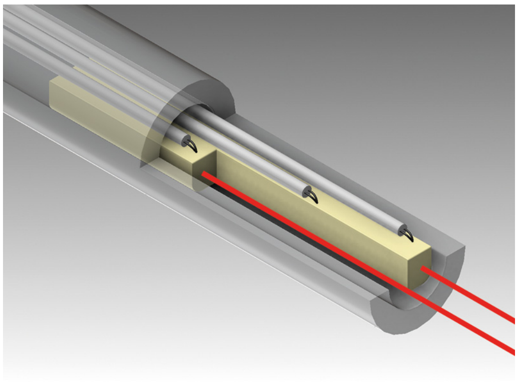

FIG. 2. (Color online) Sample (yellow) with its specific L-shape (for preparation details see text) placed in a holder (gray) cut from an alumina tube. The two LASER beams indicated by red lines are reflected by two parallel, mirror polished surfaces of the sample. The resulting resolution for the net length change is 10 nm. Temperature monitoring and control is achieved by three thermocouples spot-welded to the sample. This setting also allows the control of the temperature gradient along the sample length (not shown).

The measurement principle is based on a two-beam Michelson LASER interferometer (SIOS Messtechnik GmbH, Ilmenau Germany). The interferometer uses a 632.8 nm He-Ne LASER as light source. The minimum resolvable length change is limited by the detector unit and is given by $\lambda/512 \approx 1.2$ nm. Identical optical components are used for the two LASER beams to best cancel out systematic errors (difference method). The sample is placed in a vacuum chamber with a transparent glass window as entrance for the LASER beams. All measurements were performed in a vacuum at a pressure lower than $p < 10^{-6}$ mbar.

Based on the measurement setup reported earlier by Ye *et al.* [15] a new, significantly improved sample holder was designed (see Fig. 2) and a refined temperature control with an additional temperature-gradient control unit was developed. The sample holder now satisfies two crucial requirements for long-time measurements as follows. (i) The sample is placed horizontally inside the holder with no force acting upon it except its own weight (zero-force principle). (ii) The contact area between the sample and the holder is reduced to a minimum (zero-friction principle). Both aspects are vital for long-time isothermal measurements in glassy systems especially near the glass transition temperature because of the ability of the material to flow, at least on very long time scales. Figure 2 shows a schematic drawing of the sample holder. Due to the relatively high net length of the sample of 20 mm three thermocouples that are spot-welded to the sample are used to monitor and control both the temperature and the temperature gradient of the sample.

For sample heating, a conventional radiation furnace around the sample holder using electrical resistance heating is used. It consists of an alumina tube with 28 axial holes through which a $\varnothing = 0.25$ mm tantalum wire is threaded. A secondary furnace is used that only heats the alumina tube of the sample holder close to the rear reflective sample plane to minimize the temperature gradient along the sample length. The control of this temperature gradient compensation is coupled to the sample temperature control unit and adjusted accordingly whenever the sample is subjected to a temperature change. For all measurements, the temperature gradient along the 20 mm sample length was kept within ± 1.5 K, which is in the accuracy limits of the spot-welded thermocouples. With this kind of experimental setup it is possible to get a final resolution for the length change of ΔL down to 10 nm (see Fig. 4).

To achieve thermal long-term stability for the equilibration measurements it is further crucial that any thermal drift of the environment temperature of the experiment has to be minimized. Therefore, the complete experimental setup is located in an air-conditioned laboratory. Furthermore, the temperature of the vacuum chamber walls and the interferometer is kept at constant temperature ($T \pm 0.02$ K) using a thermostat (HAAKE K15-DC10). It allows for stable measurement conditions in the time range from 10^2 to 10^6 s.

C. Measurement procedure

For reproducible studies in the glassy state, i.e., at temperatures below the glass transition temperature T_g', it is necessary to first equilibrate the sample to obtain a distinct, well defined condition of thermodynamic, quasi- or near-equilibrium. For a bulk metallic glass such as Vit105 the corresponding temperature and time ranges can be obtained from the structural relaxation time scale of the system [16]. As the relaxation time scale increases strongly with decreasing temperature and finally should diverge at an ideal T_g [3] it is necessary to find an equilibration temperature with a structural relaxation time still accessible on laboratory time scales. According to these assumptions, the Vit105 sample was long-term annealed for 27 days with a final temperature of 573 K, i.e., 86 K below the onset temperature of the calorimetrically determined glass transition temperature $T_g^{\mathrm{calor}} = 659$ K. The annealing of the sample was performed in evacuated and sealed glass ampules in a standard laboratory furnace. The value of T_g^{calor} had been determined beforehand experimentally from the same sample material using differential scanning calorimetry (DSC) with a linear heating rate of 5 K/min. The final temperature of 573 K of the long-term annealing gave also the low temperature limit for the succeeding dilatometric measurements. The amorphous structure after the long-term annealing and prior to dilatometry was confirmed by x-ray diffraction (XRD).

The dilatometric measurement procedure is schematically shown in Fig. 3. The basic idea is to approximate an infinitesimal low heating rate, $\Delta T/\Delta t \rightarrow 0$, necessary to satisfy the equilibrium condition by isothermal measurements after finite, but small temperature changes in steps of ΔT. After each temperature step the isothermal volume equilibration is monitored until no further change in length is measurable with respect to the resolution of the dilatometer. The total length change ΔL

$$\Delta L = \Delta L_{\mathrm{inst}} + \Delta L(t) \qquad (1)$$

comprises the immediate, instantaneous length change ΔL_{inst} and the time-dependent length change $\Delta L(t)$. From ΔL_{inst} it is possible to obtain the temperature evolution of the thermal expansion coefficient α of the equilibrium state of the material. From $\Delta L(t)$ the total amount of the specific volume changes can be deduced by the simple approximation $\Delta V/V = 3(\Delta L/L)$ if an isotropic length change is assumed. Finally, values of the time dependent length changes are normalized to the total sample length $L(T)$. The initial sample length L_0 was of the order of 20 mm.

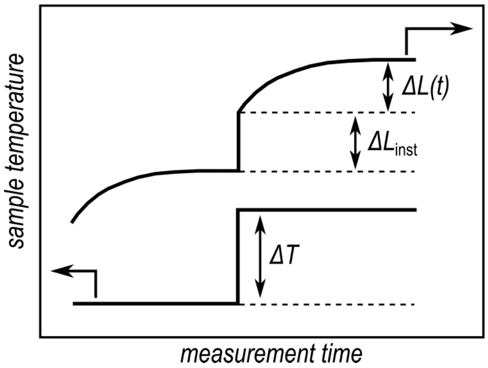

FIG. 3. Dilatometric experimental procedure is a sequence of measurement units where each unit consists of a fast temperature change ΔT with thermal stability of the system ideally within less than 100 s, followed by a long-time measurement period (up to $t = 10^5$ s) at a constant temperature to assess the equilibration process by measuring the time-dependent length change $\Delta L(t)$; ΔL_{inst} denotes the immediate, instantaneous length change.

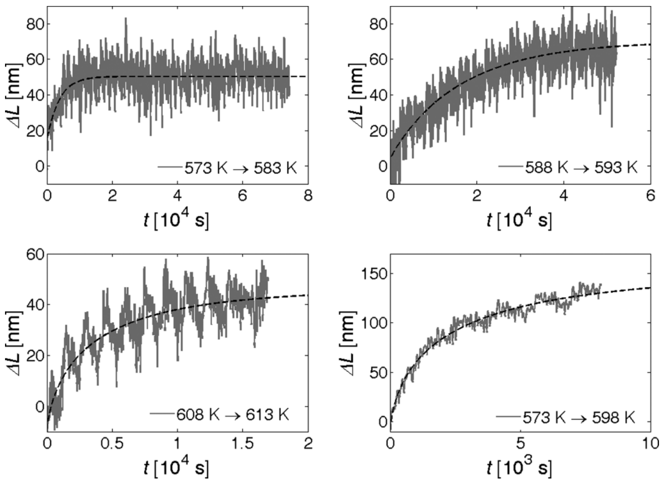

FIG. 4. Examples of absolute length changes (expansion) as function of time, $\Delta L(t)$, upon stepwise heating, ΔT, as indicated in the graph. Only the time-dependent part is shown (length scale in the 100 nm range). The contribution of the initial, instantaneous length change, ΔL_{inst}, of the order of 1000 to 2000 nm is omitted. The dashed lines are drawn for guiding the eye.

From previous metallic-glass measurements, the length change of the sample associated to isothermal volume equilibration after small temperature steps was expected to be at the resolution limit of the dilatometer for long-time measurements. According to preceding test measurements on the same sample material a minimum necessary temperature step $\Delta T = 5$ K was determined to get measurable length changes in the equilibrium state just slightly above the resolution limit of the dilatometer of $\Delta L = 10$ nm, i.e., $\Delta L/L_0 = 10^{-6}$ for $L_0 = 20$ mm (see Fig. 4). Each measurement was started after the sample temperature was stable. Times of about 400 s to 600 s were necessary to attain temperature stability of the measurement setup for temperature steps of $\Delta T = 5$ K or $\Delta T = 10$ K, respectively. These times are short and negligible compared to any of the following volume equilibration times in the investigated sub T_g' temperature range.

III. RESULTS

At first the stability of the sample length was monitored at 573 K to verify that the glass was in equilibrium with respect to the length change resolution of 10 nm of the dilatometer. As a result it was found that the sample length was constant within ±20 nm during an investigated time period of 10^5 s. Examples of the then following isothermal length change data for different temperature steps are shown in Fig. 4. The noise in

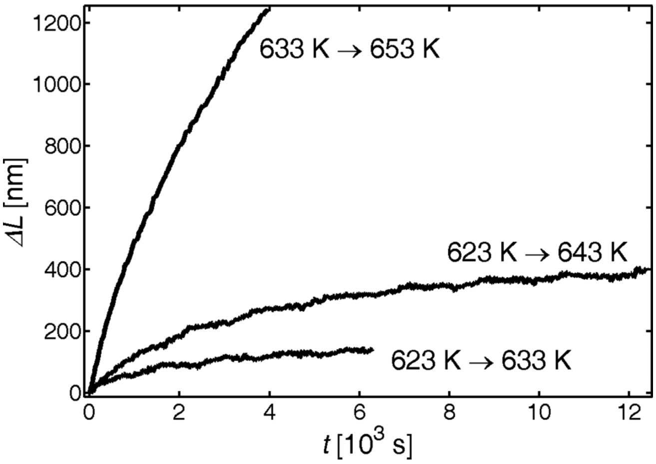

FIG. 5. Three examples of absolute length changes (expansion) as function of time: $\Delta L(t)$. The length scale is of the order of several 100 nm to 1200 nm after a temperature change by up-quenching to 633, 643, and 653 K. Only the time-dependent part is shown; the contribution of the instantaneous length change, i.e., ΔL_{inst} is omitted. The curve for temperature step, 633 K to 653 K, was the last dilatometric measurement and was interrupted due to the huge amount of volume formation.

the data mainly originate from small temperature instabilities in the experimental environment during the long measurement times. For the measurement at 583 K with the smallest length change amplitude the time was deliberately chosen longer to definitely detect the equilibrium state. This measurement also demonstrates the long-term stability of the experimental setup.

Figure 5 shows the equilibration curves for three temperature steps upon heating in the higher temperature regime. It is obvious that a significant change in the volume formation has occurred if compared to the lower temperature measurements (Fig. 4). Especially, the curve for 653 K shows a steep increase in length. It should again be noted that also these measurements are still well below the calorimetrically determined onset temperature of the glass transition which was found to be $T_g^{\text{calor}} = 659$ K for a heating rate of 5 K/min.

The cumulated isothermal volume formation amplitudes are plotted in Fig. 6. The starting volume at 573 K was used as a reference point and set to a value of zero. In Fig. 6 the reversibility of the first four temperature steps up to 598 K is demonstrated by the following procedure: after the sample was equilibrated at 598 K it was cooled to remove the formed volume and again kept at 573 K until no more decrease in length was measurable. Subsequently, the temperature was changed in one step to 598 K again and the volume equilibration was measured (see graph in the lower right of Fig. 4). The amount of isothermal volume gain is represented in Fig. 6 by the symbol triangle up. The volume change caused by the single, larger temperature step is completely equivalent to the cumulated smaller temperature steps with the same final temperature.

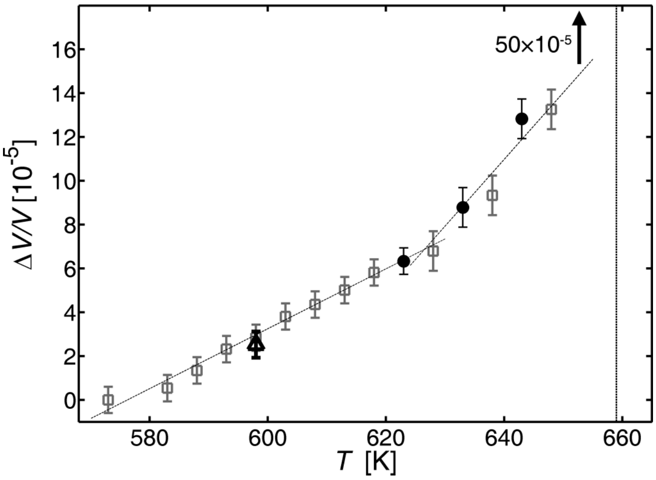

FIG. 6. Change of the specific volume $\Delta V/V$ as function of temperature T obtained from the time-dependent contribution $\Delta L(t)$ of dilatometry upon stepwise heating (open squares); the data indicated by the open triangle was obtained after again equilibrating at 573 K after the first four steps and then heating in one step to 598 K (see text). The data points represented by the filled circles and one indicated only by the arrow for the final heating up to 653 K were obtained in a second run after reequilibration at 623 K. The value of the last data point of 50×10^{-5} is significantly higher than the previous ones as indicated by the arrow. The vertical dashed line indicates the position of the temperature of $T_g^{\text{calor}} = 659$ K.

At approximately 630 K the equilibrium volume shows a distinct deviation from a nearly linear behavior for $573 \text{ K} < T < 630$ K (Fig. 6). To prove the reversibility of this deviation/kink in the equilibrium volume the sample was cooled and again annealed at 623 K. Then a second heating sequence with slightly different target temperatures confirmed the length change results and the deviation from the preceding sequence within the measurement uncertainties. Whilst at the lower temperatures below the kink a rather modest change in volume with equilibration temperature could be expected, this should not be the case at higher temperatures. In standard dilatometric experiments it was found that the expansion of the sample material increases rapidly upon reaching the calorimetric glass transition [7]. Actually, this behavior is confirmed by the data for heating to $T = 653$ K with $\Delta V/V = 50 \times 10^{-5}$ for the last measurement indicated only by an arrow in Fig. 6 due to its high value. Thus the volume increase per temperature step changes from an apparently linear behavior below 630 K to an exponential or even stronger dependence above 630 K. It should be noted here that this temperature, i.e., the temperature of the observed deviation from linearity, is nearly 30 K below the calorimetrically determined glass transition temperature T_g^{calor} of 659 K.

The temperature dependence of the thermal expansion coefficient α can also be derived from the experiments according to

$$\alpha(T) = \frac{1}{L(T)} \frac{\Delta L_{\text{ins}}(T)}{\Delta T}, \tag{2}$$

with $L(T)$ as the total sample length $(L_0 + \Delta L)$ taken at the end of each equilibration step at temperature T. In Fig. 7 the obtained values for α are plotted as function of temperature (open squares). For comparison also low temperature values obtained by cooling down the sample from 583 K are shown (filled circles). The equilibrium value for α changes from

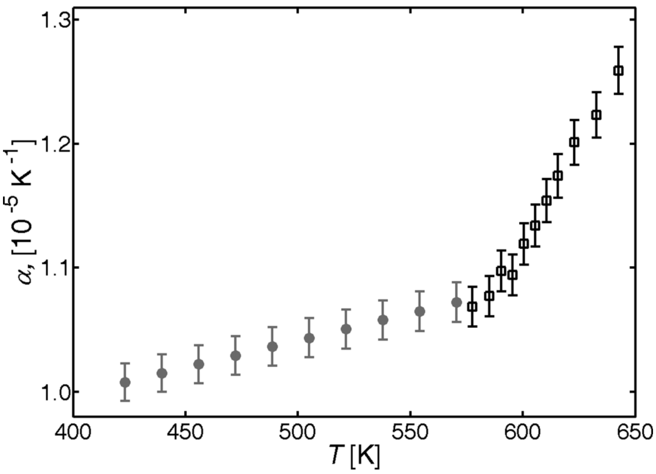

FIG. 7. Temperature dependence of the thermal expansion coefficient α. Data obtained from stepwise heating (see text) are shown as open squares; data obtained from cooling down in steps $\Delta T = 16$ K from 583 K of the long-time annealed sample are shown for comparison as filled circles.

1.01×10^{-5} K^{-1} at 423 K to 1.26×10^{-5} K^{-1} for 643 K by about 25%. The shape of $\alpha(T)$ curve shows a distinct deviation from linearity (kink) at about 590 K separating two regions with more or less linear $d\alpha/dT = 4.8 \times 10^{-9}$ K^{-2} for $T <$ 590 K and $d\alpha/dT = 32 \times 10^{-9}$ K^{-2} for $T >$ 590 K behavior.

IV. DISCUSSION

In the present experimental study reversible formation of specific volume was observed from time-dependent length change measurements. From the instantaneous volume changes the temperature dependence of the thermal expansion coefficient was also observed. Both quantities were measured far below the glass transition temperature T_g^{calor} as determined by calorimetry. At well-defined temperatures both quantities show a distinct kink/change in the temperature dependence that can be attributed to a glass transition in the equilibrium state.

For the lowest temperature the specific volume increases upon heating with ΔT temperature steps of 5 K. During these experiments definitely no decrease in the specific volume was observed even after times of the order of 10^6 s and a measurement sensitivity of $\Delta V/V = 1.5 \times 10^{-6}$. This behavior is completely reversible and the data are raw data obtained directly from the volume specific dilatometric method. Thus the results suggest that with these experiments the lowest thermodynamic stable state of the supercooled liquid has been reached. They further indicate that most probably the ideal glass transition has been observed in this bulk metallic glass as described by curve (1) in Fig. 1. The present results do not support approaches or theories that would describe the glassy state only as a frozen-in supercooled liquid state.

A manifestation of the grade of equilibration of a glass is the so-called enthalpy overshoot which is accessible in DSC experiments [6,12,17]. Depending on the time and temperature of structural equilibration in the glassy state additional energy is needed to heat the glass to the supercooled liquid state. This amount of energy is compared to the energy needed to heat a quenched sample (which usually represents a structural configuration at or even above T_g'). Although, in principle, it is possible we are unaware of any systematic study revealing the equilibrium specific volume or heat evolution below T_g' with this technique.

One very promising method to determine equilibrium properties below the glass transition temperature is isothermal dynamical mechanical analysis (DMA). Usually in DMA experiments the frequency or temperature dependent elastic moduli are studied and the structural relaxation time is determined. However, this is only possible if the structure of the glass is in equilibrium at any time of the experiment, i.e., the material must exhibit a liquidlike behavior and therefore these measurements are limited to higher temperatures, usually above T_g [18–21].

In contrast, in isothermal DMA measurements below the glass transition the evolution of the elastic moduli towards equilibrium is studied at a fixed frequency. In such measurements a similar behavior as in the dilatometric measurements presented in this paper could be observed: during the experiment, e.g., the shear modulus changes to its equilibrium value after the sample is heated or cooled faster than its structural relaxation time [18,22,23]. It is found that the shear modulus equilibrates on time scales equivalent to the time scales of specific volume equilibration and reaches its highest value at the lowest specific volume state [22].

In high-frequency shear modulus measurements Mitrofanov *et al.* showed that the equilibrium value of the shear modulus for a Pd-based bulk metallic glass shows the same behavior as the specific volume reported herein [23]. At a temperature approximately 40 K below T_g^{calor} a significant change in slope in the shear modulus evolution with temperature is observed. This is in very good agreement with the temperature range where the kink of the specific volume evolution is found in the present study.

In Ref. [24] it is argued that the kink temperature corresponds to the pseudocritical temperature first introduced by Kauzmann to find a solution to the paradoxon which was later named after him [25]. The idea is that below a certain temperature T_{pc} which is higher than the Kauzmann temperature T_K the supercooled liquid cannot exist and therefore the extrapolation of the supercooled liquid entropy to lower temperatures is not permissible. Although the experimental results presented in this paper are in excellent agreement with Kauzmann's idea a precise theoretical explanation of the observed behavior is still missing [25]. In fact, there is no fundamental restriction for the entropy of a liquid to become smaller than the entropy of its corresponding crystal. Because of such insights the question if the Kauzmann paradox is still important today is highly debated [2].

Far more important in the authors' opinion is the question whether the kink temperature corresponds to T_0, the temperature at which the primary relaxation time τ_α diverges. If this is the case, then the number of accessible glassy states below the observed T_g of the present study would become subexponential and the system would form an ideal glass [26]. To answer this question in detail further measurements in combination with other techniques are necessary primarily to detect and or distinguish possible different volume affecting processes in the glassy state.

V. SUMMARY

With a unique experimental setup, high-precision dilatometry was applied to the bulk metallic glass alloy $Zr_{52.5}Ti_5Cu_{17.9}Ni_{14.6}Al_{10}$ (Vit105) under equilibrium condition of nearly 90 K below the onset of the calorimetrically determined glass transition T_g^{calor}. This was achieved by realizing effective heating rates of the order of 10^{-2} K/min. Reversible volume changes and linear thermal expansion coefficients were accessible. The results suggest that with these experiments the lowest thermodynamic stable state of the supercooled liquid has been reached. Furthermore, the observed temperature dependence of the specific volume with a distinct kink at $T = 628$ K is completely reversible. The results indicate that most probably the ideal, glass transition T_g of this bulk metallic glass alloy has been observed at $T = 628$ K.

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