



HAL
open science

Hierarchical aging pathways and reversible fragile-to-strong transition upon annealing of a metallic glass former

Isabella Gallino, Daniele Cangialosi, Zach Evenson, Lisa Schmitt, Simon Hechler, Moritz Stolpe, Beatrice Ruta

► **To cite this version:**

Isabella Gallino, Daniele Cangialosi, Zach Evenson, Lisa Schmitt, Simon Hechler, et al.. Hierarchical aging pathways and reversible fragile-to-strong transition upon annealing of a metallic glass former. *Acta Materialia*, 2018, 144, pp.400-410. 10.1016/j.actamat.2017.10.060 . hal-02285759

HAL Id: hal-02285759

<https://hal.science/hal-02285759>

Submitted on 26 Apr 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Hierarchical aging pathways and reversible fragile-to-strong transition upon annealing of a metallic glass former

Isabella Gallino^{1,*}, Daniele Cangialosi², Zach Evenson³, Lisa Schmitt^{1,4}, Simon Hechler^{1,5}, Moritz Stolpe^{1,6}, and Beatrice Ruta^{5,7}

¹ Chair of Metallic Materials, Saarland University, Campus C6.3, 66123 Saarbrücken, Germany

² Materials Physics Center (CFM/MPC), Paseo Lardizabal 5, 20018 San Sebastian, Spain

³ Heinz Maier-Leibnitz Zentrum (MLZ) and Physik Department, Technische Universität München, Lichtenbergstrasse 1, 85748 Garching, Germany

⁴ fem Research Institute for Precious Metals & Metals Chemistry, Katharinenstrasse 17, 73525 Schwäbisch Gmünd, Germany

⁵ ESRF—The European Synchrotron, CS40220, 38043 Grenoble, France

⁶ Heraeus Additive Manufacturing GmbH, Heraeusstrasse 12-14, 63450 Hanau, Germany

⁷ Institute of Light and Matter, UMR5306 Université Lyon 1-CNRS, Université de Lyon, 69622 Villeurbanne Cedex, France.

*corresponding author: Isabella Gallino. E-mail address: i.gallino@mx.uni-saarland.de. Tel: +49 (0)681 302 2052

Abstract: The change of physical properties during aging and the associated microscopic dynamics of the $\text{Au}_{49}\text{Cu}_{26.9}\text{Si}_{16.3}\text{Ag}_{5.5}\text{Pd}_{2.3}$ bulk metallic glass are investigated using a broad collection of laboratory and synchrotron-based techniques, such as differential- and fast-scanning calorimetry, thermal-mechanical testing, and x-ray photon correlation spectroscopy. At low annealing temperatures, we observe multiple decays in the enthalpy change, which is reflected by a microscopic ordering pathway consisting of distinct stationary dynamical regimes interconnected by abrupt aging regimes, representative of states of local and transient equilibrium with increasingly higher activation energies. Furthermore, the aging study is conducted with the kinetically *fragile* frozen-in structure and the underlying fragile-to-strong transition is accessed by the ultra-viscous liquid state during annealing on a long-time scale and corresponds to the last observed enthalpy equilibration decay. The experimental work verifies, for the first time, that in a metallic glass forming system, the fragile-to-strong transition can also occur below the conventional glass transition temperature. Upon reheating, the reverse transformation, i.e. the strong-to-fragile transition, is observed with an entropy change of 0.19 J/(g-atom K), which is 2.4% of the entropy of fusion.

Keywords: bulk metallic glass, aging, differential scanning calorimetry, x-ray photon correlation spectroscopy, liquid-liquid transition

1. Introduction

At temperatures below the glass transition temperature, T_g , the extensive and macroscopic physical properties of glasses, such as density or enthalpy, as well as viscosity or electrical resistivity, slowly evolve in time [1]. This physical aging process occurs in all classes of glasses and leads to significant structural changes at the microscopic level. Even though the aging pathways are ruled by the thermodynamics as the unstable state attempts to re-attain thermodynamic equilibrium, they are steered by sluggish atomic dynamics [1]. In the case of bulk metallic glasses (BMG), sluggish liquid kinetics that impedes the nucleation and growth of crystals during solidification [2] reflects sluggish atomic mobility during the annealing of the glass. In contrast to conventional crystalline metals and alloys, BMG-forming liquids are multi-component liquids with highly dense random-packed structures that involve a large size distribution of different atomic species and a negative heat of mixing between most of the species [3]. These factors contribute to considerable local microscopic order and to a hierarchy of relaxation processes with distinct timescales and activation energies [4–10], representative of a complex system of energy wells involving the activated motion of atoms or group of atoms. Especially at low temperatures where it is expected to encounter weakly coupled frozen-in relaxation processes, the concept of a local equilibrium within a restricted energy range can be used [7]. In addition, for systems that were slowly frozen, the distributions of the structural relaxation processes are expected to be sparse and yield higher activation barriers [11].

In this work, we have studied the activation energy spectrum for enthalpy relaxation of a slowly frozen $\text{Au}_{49}\text{Ag}_{5.5}\text{Pd}_{2.3}\text{Cu}_{26.9}\text{Si}_{16.3}$ BMG. The initial state was obtained by a standard treatment, prior to annealing, that cooled the supercooled liquid state with a constant slow cooling rate. The

annealing treatments were selected for times from less than one second up to several days at temperatures 50 to 20 degrees below T_g . This composition is robust against crystallization [12] and the melting point is low enough that the glass can be obtained from the stable melt upon solidification using fast scanning calorimetry (FSC) [13]. Thermodynamic and kinetic analyses are performed using FSC, conventional power-compensated differential scanning calorimetry (DSC), and thermal mechanical analyses (TMA). The results from these laboratory experiments are compared with detailed microscopic information on the collective atomic motion obtained using the novel X-ray Photon Correlation Spectroscopy (XPCS) synchrotron technique [14].

Our results reveal distinct multiple decays in the enthalpy recovery behavior, representative of states of local and transient equilibrium with increasingly higher activation energies. This hierarchical relaxation behavior is confirmed at the atomic level, where we observe different regimes of stationary dynamics separated by intermittent temporary aging regimes. In the framework of the potential energy landscape approach [15], we ascribe the observed relaxation process to transitions from a high-energy local minimum to energetically lower, more deeply relaxed states [8,9,16–18].

In this work, we find also the direct thermodynamic and kinetic evidence of a fragile-to-strong fragility crossover connected to a polyamorphic liquid-liquid transition (LLT) in the ultra-viscous liquid state where the viscosity is greater than 10^{12} Pa s and relaxation times greater than 100 s, as a consequence of the physical aging process of a frozen-in fragile structure. The observation of a LLT during annealing is, to our knowledge, the first of this type for BMGs and it is in agreement with some anomalous behaviors in sub- T_g enthalpy relaxation studies of BMGs [19–23]. In Ref. [24] we have observed with the microscopic signature of the LLT of this glass former upon cooling. The transition was observed at a temperature slightly below the conventional T_g and it

was revealed by applying a quasi-static cooling protocol that shifted the T_g to lower values [24]. The transition resulted in a dramatic change of the kinetic fragility of the glass-forming liquid, which we define in the following. The kinetic fragility is described with the empirical Vogel-Fulcher-Tammann (VFT) equation,

$$f(T) = f_0 \exp\left(\frac{T_0 D^*}{T - T_0}\right) \quad [\text{Eq. 1}],$$

where f is either viscosity η or relaxation time τ . T_0 is the putative temperature, at which the barrier to viscous flow would become infinite. The combined parameters T_0 and D^* model the temperature dependence of the liquid relaxation kinetics. The larger the D^* , the ‘stronger’ the liquid, which more closely obeys the Arrhenius law. At high temperatures most BMG-forming liquids display fragile liquid behavior ($D^* < 12$) above T_m and stronger liquid behavior ($D^* > 20$) when equilibrated below T_g [25–27]. Upon cooling the studied BMG forming liquid was seen to transform spontaneously into more ordered, kinetically stronger structure without changing chemical composition and density [24], thereby leading to a fragile-to-strong LLT, similar to the LLT observed in other glass-forming systems [2,26–35].

In this work, we observe not only the occurrence of a fragile-to-strong LLT upon long time annealing below the conventional glass transition, but we observe also the reverse transition (strong-to-fragile) upon re-heating. Such reversibility was recently observed for the first time for a molecular liquid [35], but never before in a metallic glass-former.

2. Materials and methods

2.1 Materials preparation. To prepare $\text{Au}_{49}\text{Ag}_{5.5}\text{Pd}_{2.3}\text{Cu}_{26.9}\text{Si}_{16.3}$ glassy specimens, the mixture of elements (purity 99.995%) were melted and homogenized at a temperature of ~ 1100 K in an alumina crucible in an Indutherm MC15 casting apparatus and tilt-cast into their glassy state in a

water-cooled Cu-mold. A few rods of 5 mm diameter and length of 34 mm and plates of 3x13x34 mm dimension were produced by applying identical tilt-casting procedures. Some of the rods were re-melted in a quartz tube and injected onto a rotating copper well under argon atmosphere conditions to obtain glassy ribbons of approximately 5 to 10 μm of thickness. Prior to all experiments, the specimens were shown to be x-ray amorphous by X-ray diffraction. To prevent room temperature aging, the material was stored in a freezer at roughly $\sim 290\text{ K}$.

2.2 Calorimetry. Conventional differential scanning calorimetry (DSC) was carried out under a constant argon flow in a power-compensated Perkin Elmer Hyper DSC 8500, equipped with an intracooler and calibrated according to the melting transitions of n-decane ($\text{C}_{10}\text{H}_{22}$), indium and tin. Approximately 200 mg of material was used for each DSC experiment. Fast scanning calorimetry (FSC) measurements were carried out in a Mettler Toledo Flash DSC 1. This was coupled with a temperature controller based on a two-stage intracooler. Calibration of the FSC was carried out according to the melting of indium at different rates. The conventional glass transition temperature is defined as the onset value of the DSC glass transition signal during a scan with a heating rate of $q_h = 0.333\text{ K s}^{-1}$. For both the bulk specimens (rods and plates as described above) and the melt spun ribbons the conventional T_g is observed at 396 K.

2.3 Standard treatment and annealing protocol. Prior to the enthalpy relaxation experiments, a standard treatment was applied to sample by heating in with a rate of $q_h = 0.333\text{ K s}^{-1}$ to a temperature of 418 K, which is above the end of the calorimetric glass transition and then cooled to 273 K with a rate of $q_c = 0.333\text{ K s}^{-1}$. This assured the same enthalpic state for each specimen. After completion of annealing, the sample was first cooled to 273 K and then re-heated with $q_h = 0.333\text{ K s}^{-1}$ to the end of the crystallization process for the detection of the enthalpy recovery. Matching cooling and heating rates were applied in order to produce a realistic measurement of

fragility and, therefore, of activation energy as discussed elsewhere [36]. The crystalline baselines were produced by repeating the measurement in a second up-scan of the reacted material under identical conditions without removing the sample.

The enthalpy recovery data at 378 K and all those corresponding to $t_a \leq 100$ s for the other temperatures indicated in Fig. 1 are measured with the FSC using one sample for each annealing set. Each FSC specimen was directly placed onto the chip and the mass was estimated by comparing the heat of fusion obtained with this technique to that obtained with the conventional DSC with a known mass. A typical mass was in the range of 0.001 to 0.005 mg. Conventional DSC was used to acquire the enthalpy recovery data at longer t_a and for the detection of the enthalpy released. In this latter case one sample was used for each experiment.

2.4 Thermal step- protocol. For this treatment the as-spun material was heated from RT by performing 3 h isothermal steps of 5 K up to 363 K and of 2 K up to 397 K, with a heating rate of 3 K/min. At the highest temperatures (between 383 and 397 K) the isotherms last ≈ 30 -60 minutes. The specimen was subsequently cooled by performing isothermal steps of 0.5 K, with a cooling rate of 0.1 K/min and an annealing time of 1 to 4 h depending on the dynamics. This step- protocol was used to collect the XPCS data of Fig. 6 and as pre-treatment for the DSC dashed-dotted up-scan curve of Fig. 1. In all cases the isotherms last a factor 5 to 40 longer than the corresponding relaxation time, thus assuring the correct evaluation of a stationary dynamics. For instance, for a $\tau(\text{XPCS}) \sim 200$ s at 383 K, the isotherm lasts ≈ 4000 s, thus a factor 20 longer.

2.5 Specific heat capacity measurement. The $C_p(T)$ data of Fig. 4 were determined in DSC using a discontinuous step-method with $q_h = 0.333$ K s⁻¹ and isothermal holding time of 120 s. The specimen was cut from an amorphous rod of 3 mm in diameter and had a mass of approximately 200 mg. The resulting step in the DSC heat flow of the sample was compared with

that of a sapphire reference and empty measurement pan. The equations used to calculate the C_p values from the heat flow signals are described elsewhere [37]. The specific heat capacities of the glassy and crystalline states were determined using aluminum pans in 10 K temperature intervals beginning from 193 K. The specific heat capacity of the equilibrium liquid above the melting point was determined using Al_2O_3 pans in 20 K intervals from 656 K up to 756 K. In a separate set of experiments, individual samples were heated in Al_2O_3 pans to a temperature of 723 K and undercooled in temperature intervals ranging from 20 K to 5 K. The sample was held at this temperature isothermally for 120 s and, in the case that the sample had not crystallized, the specific heat capacity of the supercooled liquid was determined using the method described in Ref. [38]. Additionally, the C_p on a long timescale was estimated by determining the difference in specific heat capacities of the glassy state, $C_p(\text{glass}, T_i)$, and the equilibrium liquid, $C_p(\text{liquid}, T_i)$, at a temperature $T_i = T_1 + (T_2 - T_1)/2$, and approximating as $\Delta C_p(\text{liquid-glass}, T_i) \approx [\Delta H(\text{tot}, T_1) - \Delta H(\text{tot}, T_2)] / (T_2 - T_1)$, where $\Delta H(\text{tot}, T_1)$ and $\Delta H(\text{tot}, T_2)$ are the total endothermic enthalpy recovery, which was measured after equilibration at the specified temperature T_1 and T_2 , respectively. This methodology was previously successfully applied [37,39]. For each temperature one bulk specimen of approximately 200 mg was used. The C_p values at long timescale are shown in Fig. 2 together with the corresponding error bars.

2.6 Viscosity relaxation measurement. Isothermal three-point beam-bending experiments were performed to measure viscosity. Two sets of experiments were performed are reported in Refs. [32,40]. Each employed a different thermomechanical analyzer, i.e., a Netzsch TMA 402 and a NETZSCH TMA 402 F3 Hyperion. For each set of experiment, amorphous beams with rectangular cross-sectional areas of 0.3 to 1.1 mm^2 and a length of 13 mm were cut from a single as-cast plate with 3x13x34 mm dimensions. Each beam was positioned on two sharp supporting edges with span of 1.196×10^{-2} m. A load of 10 g was centrally applied by a silica probe with a

wedge-shaped head. The samples were heated to the desired temperature with a constant rate of 0.333 K/s. There they were held isothermally at least until the end of the relaxation process while the beam deflection during relaxation was measured. The viscosity was calculated from the midpoint deflection rate according to the methodology described elsewhere [26,41].

2.7 X-ray photon correlation spectroscopy. The ribbon used for the XPCS was approximately $8 \pm 1 \mu\text{m}$ thick and was mounted in a resistively-heated Ni furnace with temperature stability better than 0.05 K. The experiment was carried out for a fixed incoming energy of 8.1 keV ($\lambda = 1.53 \text{ \AA}$), by using a partial coherent beam of $10 \times 7 \mu\text{m}$ (HxV) with $\approx 10^{11}$ ph/s/200 mA. Speckles patterns were collected by a CCD detector (Andor Ikon-M, $13 \mu\text{m}$ pixel size) placed at ≈ 70 cm downstream of the sample, mounted horizontally in the scattering plane for an angle $2\theta \sim 39.6$ degrees, thus measuring the dynamics in correspondence of the maximum of the structure factor $q_p = 2.78 \text{ \AA}^{-1}$, which corresponds to an average interatomic distance [14]. The observed decorrelations are characteristic of atomic motions that interest, all at once, a large volume of material of approximately $560 \pm 70 \mu\text{m}^3$ (beam size x specimen thickness).

The thermal step-protocol described above was applied to the sample while the time evolution of the microscopic dynamics is directly captured in XPCS by the intensity two-time correlation function $G(q, t_1, t_2)$ (TTCF). This quantity reflects the statistical similarity between speckles patterns measured at times t_1 and t_2 and is defined as

$$G(q, t_1, t_2) = (\langle I(q, t_1) \rangle_p \langle I(q, t_2) \rangle_p) / (\langle I(q, t_1) \rangle_p \langle I(q, t_2) \rangle_p) \quad [\text{Eq. 2}],$$

where $\langle \dots \rangle_p$ denotes an ensemble averaging performed on all pixels of the detector which in our case correspond to q_p . The time-averaged dynamics can be extracted from the TTCF over different time interval in order to get the standard intensity-intensity correlation function, $g_2(q, t) = \langle G(q, t_i, \Delta t) \rangle$. This quantity can be directly related to the decay of density fluctuations in the

glass, through the Siegert relation, $g_2(q, t) = 1 + \gamma |\Phi(q, t)|^2$, providing thus direct information on the dynamics. Here, γ is the experimental speckle contrast and $\Phi(q, t) = S(q, t)/S(q, 0)$ is the normalized density-density correlation function. During the whole experiment, the experimental contrast was found $\approx 3\%$ independently on the annealing time and temperature. Before and after each measurement at each temperature, we measured also the intensity profile in the [1.77-3.15] \AA^{-1} q-range in order to control possible structural evolution in the probed scale.

3. Results

3.1 Macroscopic aging pathways

During annealing, the glass drifts towards a state of lower free energy and the system releases enthalpy. The released enthalpy is recovered back into the system when the relaxed glass is heated up through the glass transition, manifesting itself as an endothermic overshooting of the heat flow signal. Figure 1 shows the time evolution of the enthalpy recovery of the studied glass after annealing below T_g . The $\Delta H(\text{rec}, t)$ and the $\Delta H(\text{tot})$ values are obtained from the integration of the endothermic overshooting signal with respect to the heat flow signal of a reference, i.e. the standard treated material. Examples of up-scans of standard treated glasses relaxed for different annealing times t_a at 373 K are shown in Fig. 1a. The other up-scans performed in this work are reported in Ref. [32,40]. The temperature of 373 K is 23 degrees below the conventional T_g , and Fig. 1a shows that during the re-heating after annealing at this temperature, for values of t_a up to 10,000 s, the onset of the endothermic overshoot is the same as the T_g of the reference state, which is the standard treated glass. After 10,000 s, the onset shifts to higher temperatures, reflecting the transition toward a state with higher kinetic stability of the relaxed glass on a long timescale.

The equilibrium recovery behavior can be described by stretched exponential Kohlrausch-Williams-Watts (KWW) functions. This approach neglects non-linearity effects, that is, the structure dependence of the relaxation time [42–46]. However, the treatment based on a single KWW function is not sufficiently adequate for the treatment of the data of Fig. 1b, in agreement with Ref. [10]. In fact, we do observe a separation of enthalpy recovery processes as the annealing temperature decreases. Only the high temperature data at 378 K can be adequately reproduced with a single stretched-exponential decay, with an exponent $\beta < 1$, i.e.

$$f(t) = \exp(-(t/\tau)^\beta) \quad [\text{Eq. 3}].$$

At lower temperatures, the decay clearly splits into different steps, which we model as a sum of simple exponential decays:

$$f(t) = A + \sum_{i=1}^N h_i \exp(-t/\tau_i) \quad [\text{Eq. 4}].$$

Here, A is the baseline. The values of h_i and τ_i correspond to the relaxation amplitude and to the characteristic relaxation time of the observed enthalpy decay, respectively. We wish to note here that each DSC data point shown in Fig. 1b corresponds to the measurement of a single sample. DSC and FSC reproducibility tests have shown that the error bar for each $\Delta H(\text{rec}, t)$ data point is in the order or smaller of the symbol size [40]. The fitting procedure assured that always the same identical relaxation decays were identified independently of the number of the exponential terms assumed. Figure 1b shows the best fits as continuous lines obtained with equation 4, while the corresponding parameters are reported in the SI, together with the value for the activation energy Q_i of each decay. The latter are obtained by fitting the temperature dependence of the resulting τ_i to the Arrhenius equation. The values of τ_i , named hereafter as $\tau_i(\Delta H_{\text{rec}})$ and Q_i are given in the inset of Fig. 1b.

The time-dependence of the enthalpy released during relaxation of the standard treated glass was directly studied by analyzing the calorimetric signal recorded during isothermal DSC measurements between 368 and 390 K. The isothermal heat flow signals are integrated as a function of time to obtain the $\Delta H(\text{released}, t)$ functions as in Ref. [37]. An example of heat flow for the annealing at 373 K is shown in the inset of Fig. 2. Here, the relaxation process proceeds via a gradual exothermic heat release. The amount of enthalpy that is released from the system decreases with time during the relaxation until the thermodynamic metastable equilibrium liquid state is reached. The isothermal heat flow signal at 373 K show abnormal step-behavior after a annealing time of 1×10^4 s, which is the onset time of the final enthalpy recovery decay seen in Fig. 1. The overall signal was integrated as a function of time to obtain the $\Delta H(\text{released}, t)$ function, which is modeled with the single KWW equation as in Ref. [34]. The procedure was applied to various DSC isothermal signals performed between 368 and 390 K, and the resulting characteristic relaxation time values $\tau(\Delta H_{\text{released}})$ are plotted in Fig. 7 as open red squares on the left y-axis as a function of annealing temperature.

In Fig. 3 the time-evolution of the viscosity of the studied alloy is plotted as measured by isothermal three-point beam-bending (ITPBB). The data are fitted to the KWW equation using the same procedure that is described in Ref. [26,41,47]. It can be observed that, during the structural relaxation, the measured apparent viscosity rapidly rises and eventually starts to saturate towards an equilibrium value η_{eq} at longer annealing times. The resulting equilibrium values are plotted on the right y-axis of Fig. 7 as filled blue circles as a function of annealing temperature.

Figure 4 shows for the studied alloy composition the isothermal specific heat capacity, $C_p(T)$, of the glassy (open squares), crystalline (open triangles) and equilibrium supercooled liquid (SCL)

(open circles) states. The data for the liquid below the liquidus temperatures (between 565 and 630 K) are measured by means of isothermal undercooling experiments of the stable melt. The continuous curves correspond to the temperature dependence of C_p for the equilibrium liquid, the crystalline state and the glassy state as determined through fitting of the experimental data to the empirical equations [48,49]:

$$C_p(\text{liquid}, T) = 3R + aT + bT^{-2} \quad [\text{Eq. 5}]$$

$$C_p(\text{crystal}, T) = 3R + cT + dT^2 \quad [\text{Eq. 6}]$$

$$C_p(\text{glass}, T) = \frac{3R}{M} (1 - \exp(1.5 (T/T_D))) \quad [\text{Eq. 7}]$$

where R is the ideal gas constant and a - d are fitting constants, T_D is the Debye temperature and M a scaling factor close to unity [49]. The fitting parameters are listed in the SI.

Figure 4 also shows the values of $C_p(T)$ of the deeply undercooled liquid in its ultra-viscous state, as obtained from the enthalpy recovery values measured after long-time annealing below T_g (shaded circles). The determination of these values is described in the methods, and follows a methodology developed previously [37,39]. These values for the equilibrated SCL on a long timescale represent two distinct, albeit metastable, thermodynamic equilibrium states. The $\Delta C_p(\text{SCL-crystal}, T_g)$ values for these two equilibrium states are $14.6 \pm 2.0 \text{ J g-atom}^{-1} \text{ K}^{-1}$ and $20.3 \pm 2.0 \text{ J g-atom}^{-1} \text{ K}^{-1}$ for the blue and the grey symbols, respectively.

3.2 Atomic dynamics during physical aging

The occurrence of intermittent aging regimes is revealed by microscopic studies of the atomic dynamics in the glassy state using XPCS during long-time isothermal anneals below T_g . We observe this to go hand-in-hand with the existence of different decays in the time evolution of the enthalpy recovery. The XPCS technique provides information on the microscopic time necessary

for structural rearrangements at the atomic level [14,18]. Data taken with an $\text{Au}_{49}\text{Cu}_{26.9}\text{Si}_{16.3}\text{Ag}_{5.5}\text{Pd}_{2.3}$ as-spun ribbon during isothermal annealing at different temperatures from room temperature up to T_g reveal that the collective atomic motion is persistent and stationary, with no immediate signs of physical aging. However, after long-time regimes of approximately 10^3 to 10^4 s of stationary dynamics, sudden physical aging events are observed to occur, reflected in an abrupt slowdown of the atomic dynamics.

Figure 5a shows an example of this behavior for the annealing step at 377 K by reporting the direct correlation between a given atomic configuration and its spontaneous temporal evolution, the so called two-times correlation function TTCF [50]. The center diagonal from the bottom left corner to the upper right corner corresponds to the elapsed time of the measurement. The width of the yellowish diagonal contour is proportional to the characteristic timescale on which any given atomic configuration no longer correlates to that measured at a later time and it thus directly relates to the structural relaxation time τ . If the width becomes larger with time, the corresponding atomic dynamics decelerates, which is a characteristic feature of physical aging. In Fig. 5a, the width of the diagonal contour is constant for about 5,500 s until a transitory aging regime occurs, as marked by the sudden broadening of the intensity profile of the TTCF at about $t_a = 6,040$ s. The TTCF in Fig. 3b corresponds to the continuation of the measurement at $T = 377$ K shown in Fig. 5a.

Quantitative information on the microscopic dynamics can be obtained by extracting from the TTCF the standard intensity-intensity correlation functions [51], $g_2(q_0, t)$, for the two stationary regimes prior to and after the aging regime. These are shown in Fig. 3c together with the fit using a KWW expression of the form [18]

$$g_2(q_0, t) = 1 + c \exp[2(t/\tau)^\beta] \quad [\text{Eq. 8}].$$

Here, $\tau = \tau(\text{XPCS})$ is the relaxation time measured in XPCS, β is the shape parameter and the pre-factor $c = \gamma f_q^2$ is the product between the experimental contrast γ and the square of the Debye-Waller factor f_q . The elapsed time of the aging regime is ~ 500 s, during which a steady slowdown of the atomic dynamics is observed, in agreement with other XPCS investigations [18,50,52]. In this case, thus, the continuous microscopic aging occurs through transitions between distinct stationary regimes. In fact, after the observed regime of physical aging, the atomic dynamics becomes overall slower – marked by an increase in τ from 570 ± 26 to 1650 ± 7 s – but remains persistently constant afterwards within the experimental timescale. The stationary regime labeled with b was observed to persist for at least 7,050 s.

Long-time stationary dynamics is observed at all other annealing temperatures of the XPCS experiment. Aging events, similar to that reported in Fig. 5, are observed only at temperatures below 377 K. Above this temperature, the atomic dynamics are stationary and persistent for annealing times many orders of magnitude greater than the corresponding XPCS relaxation times. For this high-temperature regime, the corresponding normalized $g_2(q_0, t)$ functions are shown in the plot of Fig. 6, while the resulting $\tau(\text{XPCS}, T)$ data are shown in the inset. The $\tau(\text{XPCS}, T)$ data for the low-temperature regime are reported in the SI. The $\tau(\text{XPCS}, T)$ values of the high-T regime are best fitted to an Arrhenius equation with an activation energy of 4.03 eV, thus comparable to that reported in Fig. 1b for the second-to-last step in enthalpy relaxation.

The transition from the glass to the supercooled liquid (SCL) is finally observed during continuous heating from 393 to 395 K, and it corresponds to a sudden increase of τ and to an abrupt change of the shape parameter of the $g_2(q, t)$ from $\beta \approx 1.8$ towards values close to unity. This dynamical crossover has been also reported in other metallic glasses [18] and is further discussed elsewhere [24] together with the corresponding dynamics in the ultra-viscous SCL. The

fact that the SCL is finally reached at this temperature is not a surprise considering that 396 K corresponds to the calorimetric T_g in heating [53,54].

4. Discussion

4.1 Hierarchical aging pathways

The atomic dynamics in the glassy state of $\text{Au}_{49}\text{Cu}_{26.9}\text{Si}_{16.3}\text{Ag}_{5.5}\text{Pd}_{2.3}$ displays temporally intermittent aging behavior similar to that observed recently by XPCS in other fragile BMG systems based on Pd where the aging mechanism studied by applying a similar slow heating protocol involves avalanche-like relaxations from a high energy local minimum to a deeper relaxed state [11,17,52]. Differently from those cases, however, aging here only occurs on relatively short timescales and is accompanied by long stationary regimes (see Fig. 5). We interpret this behavior as the ability of the system to visit several local and distinct metastable states of high stability during aging, reflecting a hierarchical structural relaxation process that does not involve appreciable rearrangement of an atomic backbone structure connected to the α -relaxation. The observed persistent stationary atomic dynamics is indicative of a higher resistance to diffusive processes, and could be related to microscopic ordering processes not involving density changes [52].

The high-temperature glass configuration that is observed during aging at temperatures between 377 and 391 K (see Fig. 6), can be interpreted as a state trapped in a deep local energy minimum. Here, even though the atomic dynamics becomes increasingly faster as the temperature increases [$\tau(\text{XPCS}) \sim 10$ s], we do not observe any sign of physical aging. The corresponding TTCFs show constant center diagonal contours that persist over the entire length of the measurement, similar the TTCF shown in Fig. 5b. The thermal energy is apparently not enough to immediately overcome the high local activation energy barriers during a single isothermal treatment. Only

upon approaching the calorimetric T_g the entire backbone structure starts to flow, facilitating the transition back into the ultra-viscous SCL. This surprising behavior strongly contradicts macroscopic measurements where aging close to T_g occurs on timescales similar to the intrinsic relaxation time, and strengthens the idea of a strong length scale dependence of the dynamics in the glassy state.

The hierarchy of relaxation modes reported here for $\text{Au}_{49}\text{Cu}_{26.9}\text{Si}_{16.3}\text{Ag}_{5.5}\text{Pd}_{2.3}$ seems to be an universal feature of glass-forming systems, independent of the nature of the relaxation processes. In fact, multiple relaxation behaviors were observed not only in metallic glass-forming systems [17,20,23,55], but also in numerous studies on non-metallic glass formers [56–61]. This distribution differs from the mostly single peaked distributions found in equilibrium metallic supercooled liquids [62–64].

The atomic mobility in BMGs can be directly probed, for example, in radiotracer experiments. A diffusion process in metallic glasses on the order of one atomic displacement can involve thermally activated, highly cooperative atomic motions of 10 to 20 atoms in a chainlike manner [65]. In addition, BMG-formers are typically multi-component systems characterized by large atomic mismatch among the atomic species. Thus, it is expected that, at low temperature where there are fewer active degrees of freedom, some of the more sluggish processes, controlled by the slower diffusive species, remain frozen, leading to a more visible separation of the relaxation modes. The presence of multiple decays in the enthalpy change during aging could be justified, therefore, by relaxation processes involving cooperative structural rearrangements led by atoms of predominately small and intermediate sizes. These processes do not necessarily involve the motion of the entire glassy matrix, the cause for macroscopic plastic flow. On the other hand, these intermediate timescale relaxation processes appear to be much slower than the faster

motions usually associated with the β -relaxation process, which has been attributed to fast, string-like motions of atoms [62–64].

The observed hierarchy of relaxation modes can be, however, explained in terms of ‘slower’ β -relaxation-type of atomic rearrangements in the glassy state. It is known that β -relaxation events are confined in rapidly quenched metallic glasses mainly to short time scales and short-range order length scales (less than ~ 5 Å) [53,65–67]. This appears to be in line with the isochronal synchrotron X-ray diffraction experiments of Ref. [53] performed with the $\text{Au}_{49}\text{Cu}_{26.9}\text{Si}_{16.3}\text{Ag}_{5.5}\text{Pd}_{2.3}$ composition, which did not show any significant atomic rearrangements occurring on length scales larger than ~ 5 Å. In the current study, the slow thermal history applied to the sample prior annealing, e.g., the slow cooling rate of the standard treatment or the quasi-static step-heating protocol of the XPCS experiments might have indeed increased the size of the structural units responsible for such relaxation events, thereby necessitating atomic rearrangements over much larger length scales. If we relate our experimental observations to the potential energy landscape approach, e.g. to the relaxation events observed by atomistic simulations on slowly cooled systems [67], we can well relate the observed hierarchy of relaxation modes to sparse distributions of sub-basins with large average separations, which makes the β activation energy barriers higher with respect to a rapidly quenched system (see [67]).

Our finding of hierarchical relaxation processes is also in agreement with a few radiotracer or nuclear magnetic resonance (NMR) experiments performed with Pd-based and Zr-based multicomponent glass forming alloys [4,64,68,69]. The diffusivity of the large atoms like Pd, Au and Zr, seems to decouple from the diffusivity of the smaller components. Only for the large atomic species does the relation between the equilibrium viscosity and diffusion coefficient D , (D

$\propto T/\eta$), hold over a change in diffusivity of several orders of magnitude [4,64]. The smaller components are seen to strongly deviate from the $D \propto T/\eta$ relation below a certain temperature. This is the case for P, Si, and highly polarizable atoms like Cu, Co, and Cr. Thus, the apparent viscosity values extracted from the self-diffusion coefficients of these very mobile atoms would fall below the macroscopic equilibrium viscosity data, which is well represented by the diffusion of large-size components. The difference increases monotonically with decreasing temperature, and at T_g the difference is some 4 orders of magnitude [4,64]. Although radiotracer experiments or NMR experiments have not yet available for the studied Au-Cu-Si-Ag-Pd system, it is likely that similar tremendous asymmetries in the mobility of the different species during aging must be present in this particular system. We argue that the observed intermediate timescale relaxation processes are induced by cooperative rearrangements involving the asymmetric diffusion of Cu considerably enhanced by the presence of Si as discussed elsewhere [53,70].

4.2 The fragile-to-strong transition in the ultra-viscous state

Apart from the robust evidence of the presence of multiple mechanisms in the enthalpy relaxation process, the main novelty of this work lies in the detection of the thermodynamic signature of a fragile-to-strong transition in a metallic glass system as a consequence of physical aging below T_g . We have recently observed structural anomalies in this same alloy composition upon quasi-static cooling that correspond to the structural signature of a liquid-liquid polyamorphic transformation [24]. Here, a dynamic and thermodynamic fragility crossover is observed in the ultra-viscous liquid state upon aging from the glass. As a result, the supercooled liquid state obtained on a long timescale below a certain temperature is thermodynamically more stable than the state obtained above. Through annealing, we are able to experimentally access this state, which is evidenced in Fig. 4 by the different values of C_p for the SCL on a long timescale (blue

vs. grey shaded circles). A certain amount of undercooling with respect to the critical temperature, i.e. T_{LLT} , is necessary for the transition, indicating the first order nature of the transition. In terms of the jump of C_p at T_g , the low-temperature equilibrated state (blue shaded circles) reflects a stronger thermodynamic fragility behavior than the high-temperature equilibrated state (grey shaded circles), in agreement with the thermodynamic fragility concept of Angell [71]. This difference in C_p is expected to reflect distinct underlying kinetic fragility values for each state [38,72], which we quantify in the following.

We quantify in Fig. 7 the kinetic fragility of the two distinct liquids discussed above using an Angell-type, or fragility, plot that represents the temperature dependence of the measured relaxation time. The data are rescaled as a function of $(389 \text{ K})/T$, where 389 K is the critical temperature associated with the liquid-liquid transition as detected at the atomic level in Ref. [24]. In Fig. 7 the scaling relation between equilibrium viscosity and relaxation time is the Maxwell relation: $\eta = G^\infty \tau$, with a G^∞ value of $4.5 \times 10^8 \text{ Pa}$. Here, the isothermal equilibrium viscosities (filled blue circles), the relaxation times obtained for the decays of the isothermal enthalpy release, $\tau(\Delta H_{\text{released}})$ (open red squares), and the final enthalpy recovery relaxation time all show a similar VFT temperature dependence. The VFT fit shown in Fig. 7 with $D^* = 21.5 \pm 0.7$ and $T_0 = 244.6 \pm 2.8$ and $\eta_0 = 4 \times 10^5 \text{ Pa s}$ (blue dashed line) was obtained considering only the η_{eq} isothermal data (blue filled circles). This corresponds to a fragility steepness index [71] m of 45.2 and it is characteristic of a relatively strong BMG-forming liquid [38,73]. The two $\tau(\Delta H_{\text{released}})$ data points (red open square) measured at 388 and 390 K follow a steeper trend, which is in agreement with the more fragile behavior of the DMA alpha relaxation time, τ_α [24,53] (open triangles), and the $\tau(\text{XPCS})$ data in the SCL (open red circle symbols at 395 and 396 K). These three sets of data are fit together to the VFT equation, with $D^* = 9.78 \pm 0.4$ ($m =$

79.7) and $T_0 = 311.0 \pm 3.5$ K. These value of kinetic fragility corresponds to one of the most fragile liquids behavior observed in BMGs [38,73]. The open crossed circles in Fig. 7 are calorimetric data taken from Ref. [22] and actually appear to be characteristic of two distinct systems, in agreement with the extrapolations of our VFT fits.

In Fig. 7, the Arrhenius fit obtained from the $\tau(\text{XPCS})$ in the glassy state agrees well with the activation energy of the second-to-last enthalpy recovery decay (see top dashed-dot line). The VFT and the Arrhenius curves shown in Fig. 7 are also reproduced in Fig. 8, which corresponds to a temperature-time-transformation (TTT) diagram for $\text{Au}_{49}\text{Ag}_{5.5}\text{Pd}_{2.3}\text{Cu}_{26.9}\text{Si}_{16.3}$. The temperature dependence of the two data points corresponding to τ_5 , obtained from the last enthalpy recovery decay (open diamonds symbols), appears in Fig. 7 to be comparable to the temperature dependence of the equilibrium viscosity data (filled blue circles). Even from a cursory inspection, it is clear that these two points would have higher activation energy than all other diamond symbols, and that viscous flow might well be connected to those structural rearrangements responsible for the slowest relaxation mode detectable in our enthalpy recovery decay analysis.

The microscopic signature of the polyamorphic LLT upon cooling has been recently reported elsewhere [24] by combining advanced structural and dynamical synchrotron measurements using the same identical step protocol applied to the aforementioned DSC experiment. The resulting relaxation times measured during cooling from the fragile liquid are shown in Fig. 8 as blue open circles. They show a distinct change in the VFT temperature-dependence at 389 K from a D^* value of 8.9 to 23.7, which marks the transition from a kinetically highly fragile to a stronger liquid [24].

The critical transition temperature is at 389 K, slightly below the conventional T_g of 396 K. This transition should not be confused with the ideal glass transition that occurs at a much lower temperature just before the Kauzmann temperature that for this system is at 318K (see Table in the SI). The ideal glass transition is understood as a second order thermodynamic transition [74,75], which is in contrast to our observation of the first-order nature of the LLT. Moreover at the ideal glass transition the entropy of the glass is equal to the entropy of the crystal. In the case studied here, at the temperatures where we observe the fragility crossover the entropy of the crystalline mixture is still well below the entropy of the undercooled system.

4.3 Reversibility of the fragile-to-strong transition

The endothermic overshoot signal after final equilibration has two contributions. The first is due to the enthalpy recovery event of a highly relaxed structure; the second is the endothermic signature of the polyamorphic strong-to-fragile transition, i.e. the reverse transition [29,35,76] of what we have observed during the last physical aging decay. If we consider the annealing at 373 K, i.e. in Fig. 1a, the maximum amount of enthalpy recovered solely due to the relaxation of the fragile glass is $200 \pm 25 \text{ J g-atom}^{-1}$, which is the value obtained after annealing for $t_a = 10,000 \text{ s}$. If we subtract this value from the total area of the endothermic overshoot after equilibration ($270 \pm 10 \text{ J g-atom}^{-1}$), the difference is the enthalpy contribution of the reverse transition to the endothermic overshoot, $\Delta H(\text{LLT}) = 70 \pm 25 \text{ J g-atom}^{-1}$. In terms of restored disorder, it corresponds to an entropy change $\Delta S(\text{ordering}) = 0.187 \pm 0.06 \text{ J g-atom}^{-1} \text{ K}^{-1}$, if we take 373 K as a reference. This corresponds to 2.4 % of the entropy of fusion. In the inset of Fig. 4 we compare this value to the entropy change associated to the liquid-liquid transition of the Vit106a and the Vit1 BMG systems [28,29]. The $\Delta S(\text{ordering})$ is linearly proportional to the temperature of the crossover between the two liquid states, indicating that the higher the ordering energy, the higher

the entropy change that accompanies an order-disorder transition, and the higher the transition temperature [77,78].

The endothermic overshoot of the enthalpy recovery starts to shift to higher temperatures only as soon as the last equilibration enthalpy decay begins to occur. The maximum temperature shift is obtained when the entire volume of the specimen has transformed, which in this study is determined as 10 K. In Ref. [22], a shift of the endothermic overshoot to higher temperatures is also observable and even more pronounced than in our case (~28 K) due to the applied heating rate of the up-scan of 1000 K s^{-1} – some four orders of magnitude higher than our DSC experiments. In fact, according to the extrapolation of the VFT-fits in the TTT diagram of Fig. 8, upon reheating, the onset of the glass transition of the strong system occurs at a higher temperature than that of the fragile system, and the onset temperature difference increases as relaxation time decreases. For this reason, the maximum shift of the onset of the endothermic overshoot is greater when a faster scanning rate is applied.

During the relaxation experiments carried out in this work, the long-time annealing seems to result in an equilibrium state that has the same thermodynamic stability as a liquid cooled slowly enough to maintain an internal equilibrium, in agreement with the literature [79]. The fact that the two liquid states have reached the same level of thermodynamic stability is supported by calorimetry, as the area under the endothermic signals detected from both the specimen after the step thermal protocol (dashed curve in Fig. 1a), and from the fully equilibrated glass at 373 K corresponds to an equal value of enthalpy recovery change of $270 \pm 10 \text{ J g-atom}^{-1}$.

5. Conclusions

The peculiarity of the $\text{Au}_{49}\text{Cu}_{26.9}\text{Si}_{16.3}\text{Ag}_{5.5}\text{Pd}_{2.3}$ glass-forming system is that, during annealing below T_g , it exhibits at the microscopic scale a persistent and stationary regime of atomic

dynamics, and at the macroscopic scale a hierarchical activation energy spectrum of enthalpy relaxation modes. Like many BMGs, $\text{Au}_{49}\text{Cu}_{26.9}\text{Si}_{16.3}\text{Ag}_{5.5}\text{Pd}_{2.3}$ is a multi-component system with large atomic size mismatches that result a dense atomic packing. However, in this system, the presence of a large amount of mobile atoms like Cu and Si contributes to the acceleration of secondary collective diffusion processes to the point that intermediate relaxation processes branch off from the slow motion of the backbone structure represented by the sluggish diffusion of the large size atoms. This seems to be enhanced by the thermal history of the material and it is in agreement with the potential energy landscape approach of relaxation events in slowly cooled glasses [67].

Our finding of a thermodynamic signature of a fragile-to-strong transition below conventional T_g implies that the frozen-in state during processing has retained the structure of the high-temperature fragile liquid, and that during annealing the system is driven to equilibrate into a more ordered, stronger liquid. This transition exhibits a behavior similar to that recently observed for the first time in an organic glass-former [35], but never before in a metallic glass-former. The process involves ordering kinetics with relaxation times of the order of thousands of seconds and is found to be reversible. Our results are in agreement with the observed structural evidence of a polyamorphic liquid-liquid transition that takes place upon cooling when the T_g of the solidifying system is shifted to a lower temperature by applying a quasi-static cooling rate [24]. The transition is reversible (strong-to-fragile) upon reheating in DSC in the glass transition range, marked by a small value of the entropy change of $\sim 0.19 \text{ J g-atom}^{-1} \text{ K}^{-1}$. This value is as low as 2.4 % of the entropy of fusion of this system and it is the reason why the associated transition temperature is found for $\text{Au}_{49}\text{Cu}_{26.9}\text{Si}_{16.3}\text{Ag}_{5.5}\text{Pd}_{2.3}$ at a very low temperature, which is slightly below the T_g observed on the typical laboratory timescale.

Acknowledgements: This work was supported by the German Research Foundation (DFG) through [Grant No. GA 1721/2-2]. D. Cangialosi acknowledges the University of the Basque Country and Basque Country Government (Ref. No. IT-654-13 (GV)), Depto. Educación, Universidades e investigación; and Spanish Government (Grant No. MAT2015-63704-P, (MINECO/FEDER, UE)) for their financial support. We express our gratitude to C. Hafner Edemetall Technologie for the noble metals supply. We acknowledge and thank H. Vitoux and K.L. L’Hoste from the ESRF and W. Hembree for the support with the XPCS experiment, the CFM/MPC institute for the support with the flash calorimetry experiments, and G. Fiore for the experimental support with the melt spinning. We would like to thank O. Gross, S. Wei, M.H. Müser, S.V. Sukhomlinov, W. Possart, and especially R. Busch for discussions throughout the interpretation process.

References

- [1] I. Gallino, R. Busch, Relaxation Pathways in Metallic Glasses, JOM. (2017). doi:10.1007/s11837-017-2573-6.
- [2] R. Busch, I. Gallino, Kinetics, Thermodynamics, and Structure of Bulk Metallic Glass Forming Liquids, JOM. (2017). doi:10.1007/s11837-017-2574-5.
- [3] R. Busch, The thermophysical properties of bulk metallic glass-forming liquids, JOM. 52 (2000) 39–42. doi:10.1007/s11837-000-0160-7.
- [4] A. Masuhr, T. Waniuk, R. Busch, W. Johnson, Time scales for viscous flow, atomic transport, and crystallization in the liquid and supercooled liquid states of $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$, Phys. Rev. Lett. 82 (1999) 2290–2293.
- [5] A. Bartsch, K. Rätzke, A. Meyer, F. Faupel, Dynamic Arrest in Multicomponent Glass-Forming Alloys, Phys. Rev. Lett. 104 (2010) 195901. doi:10.1103/PhysRevLett.104.195901.
- [6] X. Tang, U. Geyer, R. Busch, W.L. Johnson, Y. Wu, Diffusion mechanisms in metallic supercooled liquids and glasses, Nature. 402 (1999) 160–162. doi:10.1038/45996.
- [7] M.R.J. Gibbs, J.E. Evetts, J.A. Leake, Activation energy spectra and relaxation in amorphous materials, J. Mater. Sci. 18 (1983) 278–288. doi:10.1007/BF00543836.
- [8] A.S. Keys, L.O. Hedges, J.P. Garrahan, S.C. Glotzer, D. Chandler, Excitations Are Localized and Relaxation Is Hierarchical in Glass-Forming Liquids, Phys. Rev. X. 1 (2011) 1–15. doi:10.1103/PhysRevX.1.021013.
- [9] P. Luo, P. Wen, H.Y. Bai, B. Ruta, W.H. Wang, Relaxation Decoupling in Metallic Glasses at Low Temperatures, Phys. Rev. Lett. 118 (2017) 1–6. doi:10.1103/PhysRevLett.118.225901.
- [10] J.D. Ju, D. Jang, A. Nwankpa, M. Atzmon, An atomically quantized hierarchy of shear

- transformation zones in a metallic glass, *J. Appl. Phys.* 109 (2011) 0–8.
doi:10.1063/1.3552300.
- [11] Y. Fan, T. Iwashita, T. Egami, Crossover from Localized to Cascade Relaxations in Metallic Glasses, *Phys. Rev. Lett.* 115 (2015) 1–5. doi:10.1103/PhysRevLett.115.045501.
- [12] G. Fiore, I. Ichim, L. Battezzati, Thermal analysis, fragility and viscosity of Au-based metallic glasses, *J. Non. Cryst. Solids.* 356 (2010) 2218–2222.
doi:10.1016/j.jnoncrysol.2010.08.032.
- [13] C. Schick, V. Mathot, *Fast Scanning Calorimetry*, Springer International Publishing, 2016.
- [14] A. Madsen, A. Fluerasu, B. Ruta, Structural Dynamics of Materials Probed by X-Ray Photon Correlation Spectroscopy, in: *Synchrotron Light Sources Free. Lasers*, Springer International Publishing, Cham, 2015: pp. 1–21. doi:10.1007/978-3-319-04507-8_29-1.
- [15] A. Heuer, Exploring the potential energy landscape of glass-forming systems: from inherent structures via metabasins to macroscopic transport, *J. Phys. Condens. Matter.* 20 (2008) 373101.
- [16] T. Yanagishima, J. Russo, H. Tanaka, and Mechanical Origin for Ageing and Crystallization of Glasses, *Nat. Commun.* 8 (2017) 1–10. doi:10.1038/ncomms15954.
- [17] Z. Evenson, B. Ruta, S. Hechler, M. Stolpe, E. Pineda, I. Gallino, R. Busch, X-ray photon correlation spectroscopy reveals intermittent aging dynamics in a metallic glass, *Phys. Rev. Lett.* 115 (2015) 1–5. doi:10.1103/PhysRevLett.115.175701.
- [18] B. Ruta, Y. Chushkin, G. Monaco, L. Cipelletti, E. Pineda, P. Bruna, V.M. Giordano, M. Gonzalez-Silveira, Atomic-scale relaxation dynamics and aging in a metallic glass probed by X-ray photon correlation spectroscopy, *Phys. Rev. Lett.* 109 (2012) 1–5.
doi:10.1103/PhysRevLett.109.165701.
- [19] Q.S. Zeng, Y.C. Li, C.M. Feng, P. Liermann, M. Somayazulu, G.Y. Shen, H. -k. Mao, R. Yang, J. Liu, T.D. Hu, J.Z. Jiang, Anomalous compression behavior in lanthanum/ceium-based metallic glass under high pressure, *Proc. Natl. Acad. Sci.* 104 (2007) 13565–13568.
doi:10.1073/pnas.0705999104.
- [20] L. Hu, Y. Yue, C. Zhang, Abnormal sub- T_g enthalpy relaxation in the CuZrAl metallic glasses far from equilibrium, *Appl. Phys.Lett.* 98 (2011) 81904.
- [21] Z.F. Zhao, P. Wen, C.H. Shek, W.H. Wang, Measurements of slow β -relaxations in metallic glasses and supercooled liquids, *Phys. Rev. B - Condens. Matter Mater. Phys.* 75 (2007) 1–5. doi:10.1103/PhysRevB.75.174201.
- [22] J.Q. Wang, Y. Shen, J.H. Perepezko, M.D. Ediger, Increasing the kinetic stability of bulk metallic glasses, *Acta Mater.* 104 (2016) 25–32. doi:10.1016/j.actamat.2015.11.048.
- [23] D. V. Louzguine-Luzgin, I. Seki, S. V. Ketov, L. V. Louzguina-Luzgina, V.I. Polkin, N. Chen, H. Fecht, A.N. Vasiliev, H. Kawaji, Glass-transition process in an Au-based metallic glass, *J. Non. Cryst. Solids.* 419 (2015) 12–15.
doi:10.1016/j.jnoncrysol.2015.03.018.
- [24] S. Hechler, B. Ruta, M. Stolpe, E. Pineda, Z. Evenson, O. Gross, W. Hembree, A. Bernasconi, R. Busch, I. Gallino, Liquid-liquid transition revealed by quasi-static cooling of an ultra-viscous metallic liquid, *ArXiv.* (2017) 1704.06703.

- [25] Z. Evenson, T. Schmitt, M. Nicola, I. Gallino, R. Busch, High temperature melt viscosity and fragile to strong transition in Zr-Cu-Ni-Al-Nb(Ti) and Cu₄₇Ti₃₄Zr₁₁Ni₈ bulk metallic glasses, *Acta Mater.* 60 (2012) 4712–4719. doi:10.1016/j.actamat.2012.05.019.
- [26] B. Bochtler, O. Gross, I. Gallino, R. Busch, Thermo-physical characterization of the Fe₆₇Mo₆Ni_{3.5}Cr_{3.5}P₁₂C_{5.5}B_{2.5} bulk metallic glass forming alloy, *Acta Mater.* 118 (2016) 129–139. doi:10.1016/j.actamat.2016.07.031.
- [27] W. Xu, M.T. Sandor, Y. Yu, H.-B. Ke, H.-P. Zhang, M.-Z. Li, W.-H. Wang, L. Liu, Y. Wu, Evidence of liquid–liquid transition in glass-forming La₅₀Al₃₅Ni₁₅ melt above liquidus temperature, *Nat. Commun.* 6 (2015) 7696. doi:10.1038/ncomms8696.
- [28] M. Stolpe, I. Jonas, S. Wei, Z. Evenson, W. Hembree, F. Yang, A. Meyer, R. Busch, Structural changes during a liquid-liquid transition in the deeply undercooled Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8} bulk metallic glass forming melt, *Phys. Rev. B - Condens. Matter Mater. Phys.* 93 (2016) 1–7. doi:10.1103/PhysRevB.93.014201.
- [29] S. Wei, F. Yang, J. Bednarcik, I. Kaban, O. Shuleshova, A. Meyer, R. Busch, Liquid–liquid transition in a strong bulk metallic glass-forming liquid, *Nat. Commun.* 4 (2013) 1–9. doi:10.1038/ncomms3083.
- [30] H.W. Sheng, H.Z. Liu, Y.Q. Cheng, J. Wen, P.L. Lee, W.K. Luo, S.D. Shastri, E. Ma, Polyamorphism in a metallic glass., *Nat. Mater.* 6 (2007) 192–197. doi:10.1038/nmat1839.
- [31] C. Way, P. Wadhwa, R. Busch, The influence of shear rate and temperature on the viscosity and fragility of the Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5} metallic-glass-forming liquid, *Acta Mater.* 55 (2007) 2977–2983. doi:10.1016/j.actamat.2006.12.032.
- [32] Z. Evenson, On the thermodynamic and kinetic properties of bulk glass forming metallic systems, Dissertation, Saarland University, 2012.
- [33] I. Saika-Voivod, P.H. Poole, F. Sciortino, Fragile-to-strong transition and polyamorphism in the energy landscape of liquid silica., *Nature.* 412 (2001) 514–517. doi:10.1038/35087524.
- [34] P. Gallo, K. Amann-Winkel, C.A. Angell, M.A. Anisimov, F. Caupin, C. Chakravarty, E. Lascaris, T. Loerting, A.Z. Panagiotopoulos, J. Russo, J.A. Sellberg, H.E. Stanley, H. Tanaka, C. Vega, L. Xu, L.G.M. Pettersson, Water: A Tale of Two Liquids, *Chem. Rev.* 116 (2016) 7463–7500. doi:10.1021/acs.chemrev.5b00750.
- [35] M. Kobayashi, H. Tanaka, The reversibility and first-order nature of liquid–liquid transition in a molecular liquid, *Nat. Commun.* 7 (2016) 13438. doi:10.1038/ncomms13438.
- [36] Z. Evenson, I. Gallino, R. Busch, The effect of cooling rates on the apparent fragility of Zr-based bulk metallic glasses, *J. Appl. Phys.* 107 (2010) 1–7. doi:10.1063/1.3452381.
- [37] I. Gallino, M.B. Shah, R. Busch, Enthalpy relaxation and its relation to the thermodynamics and crystallization of the Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8} bulk metallic glass-forming alloy, *Acta Mater.* 55 (2007) 1367–1376. doi:10.1016/j.actamat.2006.09.040.
- [38] I. Gallino, J. Schroers, R. Busch, Kinetic and thermodynamic studies of the fragility of bulk metallic glass forming liquids, *J. Appl. Phys.* 108 (2010) 63501. doi:10.1063/1.3480805.

- [39] R. Busch, W.L. Johnson, The kinetic glass transition of the $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ bulk metallic glass former-supercooled liquids on a long time scale, *Appl. Phys. Lett.* 72 (1998) 2695–2697. doi:10.1063/1.121102.
- [40] L.-Y. Schmitt, Relaxation studies with a 18 carat Au-based glass-forming alloy, Master Thesis, Saarland University, 2017.
- [41] O. Gross, B. Bochtler, M. Stolpe, S. Hechler, W. Hembree, R. Busch, I. Gallino, The kinetic fragility of Pt-P- and Ni-P-based bulk glass-forming liquids and its thermodynamic and structural signature, *Acta Mater.* 132 (2017) 118–127. doi:10.1016/j.actamat.2017.04.030.
- [42] A. Kovacs, Glass transition in amorphous polymers: a phenomenological study, *Fortsch. Hochpolym. Fo.* 3 (1963) 394–508.
- [43] A.Q. Tool, Relation between inelastic deformability and thermal expansion of glass in its annealing range, *J. Am. Chem. Soc.* 29 (1946) 240–253.
- [44] O. Narayanaswamy, A model of structural relaxation in glass, *J. Am. Ceram. Soc.* 54 (1971) 491–498.
- [45] I.M. Hodge, Enthalpy relaxation and recovery in amorphous materials, *J. Non-Cryst. Sol.* (1994) 211–266.
- [46] D. Cangialosi, V.M. Boucher, A. Alegria, J. Colmenero, Physical aging in polymers and polymer nanocomposites: recent results and open questions, *Soft Matter.* 9 (2013) 8619–8630.
- [47] R. Busch, W. Liu, W.L. Johnson, Thermodynamics and kinetics of the $Mg_{65}Cu_{25}Y_{10}$ bulk metallic glass forming liquid, *J. Appl. Phys.* 83 (1998) 4134–4141.
- [48] O. Kubaschewski, C. Alcock, P. Spencer, *Materials Thermochemistry*, 6th ed., Pergamon Press, New York, 1993.
- [49] S. Inaba, S. Oda, K. Morinaga, Heat capacity of oxide glasses at high temperature region, *J. Non. Cryst. Solids.* 325 (2003) 258–266. doi:10.1016/S0022-3093(03)00315-6.
- [50] B. Ruta, G. Baldi, G. Monaco, Y. Chushkin, Compressed correlation functions and fast aging dynamics in metallic glasses, *J. Chem. Phys.* 138 (2013) 54508. doi:10.1063/1.4790131.
- [51] Y. Chushkin, C. Caronna, A. Madsen, A novel event correlation scheme for X-ray photon correlation spectroscopy, *J. Appl. Crystallogr.* 45 (2012) 807–813. doi:10.1107/S0021889812023321.
- [52] V.M. Giordano, B. Ruta, Unveiling the structural arrangements responsible for the atomic dynamics in metallic glasses during physical aging, *Nat. Commun.* 7 (2016) 1–8. doi:10.1038/ncomms10344.
- [53] Z. Evenson, S.E. Naleway, S. Wei, O. Gross, J.J. Kruzic, I. Gallino, W. Possart, M. Stommel, R. Busch, β -relaxation and low-temperature aging in a Au-based bulk metallic glass: From elastic properties to atomic-scale structure, *Phys. Rev. B - Condens. Matter Mater. Phys.* 89 (2014) 1–14. doi:10.1103/PhysRevB.89.174204.
- [54] J. Schroers, B. Lohwongwatana, W.L. Johnson, A. Peker, Gold based bulk metallic glass, *Appl. Phys. Lett.* 87 (2005) 2005–2007. doi:10.1063/1.2008374.

- [55] H.S. Chen, A. Inoue, T. Masumoto, Two-stage enthalpy relaxation behaviour of (Fe_{0.5}Ni_{0.5})₈₃P₁₇ and (Fe_{0.5}Ni_{0.5})₈₃B₁₇ amorphous alloys upon annealing, *J. Mater. Sci.* 20 (1985) 2417–2438. doi:10.1007/BF00556071.
- [56] J.M.M. Duenas, A.V. Garayo, F.R. Colomer, J.M. Estelles, J.L.G. Ribelles, M.M. Pradas, Structural relaxation of glass-forming polymers based on an equation for configurational entropy, 4. Structural relaxation in styrene-acrylonitrile copolymer, *J. Polym. Sci. Part B Polym. Phys.* 35 (1997) 2201–2217. doi:10.1002/(SICI)1099-0488(199710)35:14<2201::AID-POLB2>3.0.CO;2-Z.
- [57] A. Brunacci, J.M.G. Cowie, R. Ferguson, I.J. McEwen, Enthalpy relaxation in glassy polystyrenes: 1, *Polymer (Guildf)*. 38 (1997) 865–870. doi:10.1016/S0032-3861(96)00575-7.
- [58] L. Andreozzi, M. Faetti, M. Giordano, F. Zulli, Molecular-Weight Dependence of Enthalpy Relaxation of PMMA, *Macromolecules*. 38 (2005) 6056–6067. doi:10.1021/ma0507037.
- [59] D. Cangialosi, V.M. Boucher, A. Alegría, J. Colmenero, Direct Evidence of Two Equilibration Mechanisms in Glassy Polymers, *Phys. Rev. Lett.* 111 (2013) 95701. doi:10.1103/PhysRevLett.111.095701.
- [60] R.C. Welch, J.R. Smith, M. Potuzak, X. Guo, B.F. Bowden, T.J. Kiczanski, D.C. Allan, E.A. King, A.J. Ellison, J.C. Mauro, Dynamics of Glass Relaxation at Room Temperature, *Phys. Rev. Lett.* 110 (2013) 265901. doi:10.1103/PhysRevLett.110.265901.
- [61] R. Golovchak, A. Kozdras, O. Shpotyuk, V. Balitska, Crossover between cooperative and fractal relaxation in complex glass-formers, *J. Phys. Condens. Matter*. 28 (2016) 355101. doi:10.1088/0953-8984/28/35/355101.
- [62] H.B. Yu, K. Samwer, W.H. Wang, H.Y. Bai, Chemical influence on β -relaxations and the formation of molecule-like metallic glasses., *Nat. Commun.* 4 (2013) 2204. doi:10.1038/ncomms3204.
- [63] H.B. Yu, K. Samwer, Y. Wu, W.H. Wang, Correlation between β Relaxation and Self-Diffusion of the Smallest Constituting Atoms in Metallic Glasses, *Phys. Rev. Lett.* 109 (2012) 95508. doi:10.1103/PhysRevLett.109.095508.
- [64] K.L. Ngai, S. Capaccioli, An explanation of the differences in diffusivity of the components of the metallic glass Pd₄₃Cu₂₇Ni₁₀P₂₀, *J. Chem. Phys.* 138 (2013) 94504. doi:10.1063/1.4793597.
- [65] F. Faupel, W. Frank, M.-P. Macht, H. Mehrer, V. Naundorf, K. Rätzke, H.R. Schober, S.K. Sharma, H. Teichler, Diffusion in metallic glasses and supercooled melts, *Rev. Mod. Phys.* 75 (2003) 237–280. doi:10.1103/RevModPhys.75.237.
- [66] Z. Evenson, T. Koschine, S. Wei, O. Gross, J. Bednarcik, I. Gallino, J.J. Kruzic, K. Rätzke, F. Faupel, R. Busch, The effect of low-temperature structural relaxation on free volume and chemical short-range ordering in a Au₄₉Cu_{26.9}Si_{16.3}Ag_{5.5}Pd_{2.3} bulk metallic glass, *Scr. Mater.* 103 (2015) 14–17. doi:10.1016/j.scriptamat.2015.02.026.
- [67] Y. Fan, T. Iwashita, T. Egami, How thermally activated deformation starts in metallic glass., *Nat. Commun.* 5 (2014) 5083. doi:10.1038/ncomms6083.
- [68] U. Geyer, S. Schneider, W.L. Johnson, Y. Qiu, T.A. Tombrello, M.P. Macht, Atomic

- diffusion in the supercooled liquid and glassy states of the Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni₁₀Be_{22.5} alloy, *Phys. Rev. Lett.* 75 (1995) 2364–2367.
- [69] A. Meyer, J. Wuttke, W. Petry, O. Randl, H. Schober, Slow motion in a metallic liquid, *Phys. Rev. Lett.* 80 (1998) 4454–4457.
- [70] M. Eisenbart, U.E. Klotz, R. Busch, I. Gallino, A colourimetric and microstructural study of the tarnishing of gold-based bulk metallic glasses, *Corros. Sci.* 85 (2014) 258–269. doi:10.1016/j.corsci.2014.04.024.
- [71] C.A. Angell, Formation of glasses from liquids and biopolymers., *Science.* 267 (1995) 1924–1935. doi:10.1126/science.267.5206.1924.
- [72] G.D. Fontana, L. Battezzati, Thermodynamic and dynamic fragility in metallic glass-formers, *Acta Mater.* 61 (2013) 2260–2267. doi:10.1016/j.actamat.2012.12.045.
- [73] I. Gallino, On the Fragility of Bulk Metallic Glass Forming Liquids, *Entropy.* 19 (2017) 483. doi:10.3390/e19090483.
- [74] V.M. Boucher, D. Cangialosi, A. Alegría, J. Colmenero, J. Rodriguez-Viejo, T. Scopigno, B.E. Dom, P.W. Drake, A.J. Eastel, P.B. Elterman, R.P. Moeller, H. Sasabe, J.A. Wilder, Reaching the ideal glass transition by aging polymer films, *Phys. Chem. Chem. Phys.* 19 (2017) 961–965. doi:10.1039/C6CP07139B.
- [75] M. Ozawa, W. Kob, A. Ikeda, K. Miyazaki, Equilibrium phase diagram of a randomly pinned glass-former, *Proc. Natl. Acad. Sci.* 112 (2015) 6914–6919. doi:10.1073/pnas.1500730112.
- [76] M. Zhu, J.Q. Wang, J.H. Perepezko, L. Yu, Possible existence of two amorphous phases of d-mannitol related by a first-order transition, *J. Chem. Phys.* 142 (2015). doi:10.1063/1.4922543.
- [77] P. Haasen, *Physical Metallurgy*, 3rd ed., Cambridge Press, 1996.
- [78] F. Nix, W. Shockley, Order-disorder transformations in alloys, *Rev. Mod. Phys.* 10 (1938) 1–71.
- [79] E. Tombari, G.P. Johari, Change in entropy in thermal hysteresis of liquid-glass-liquid transition and consequences of violating the Clausius theorem, *J. Chem. Phys.* 141 (2014) 74502. doi:10.1063/1.4892588.

Figure labels:

Fig. 1 Time evolution of the enthalpy recovery change for the relaxed Au₄₉Ag_{5.5}Pd_{2.3}Cu_{26.9}Si_{16.3} BMG. a) Heat flow signals in the glass transition region of relaxed glasses after annealing at 373 K for the indicated annealing time t_a (continuous curves) and of an as-spun specimen after a step protocol (dashed-dot curve). The enthalpy change $\Delta H(\text{rec}, t)$ associated with the endothermic overshoot is obtained by integrating the area under signal with respect to the up-scan of a standard treated specimen. A thermodynamic crossover is identifiable after $t_a = 10,000$ s as the onset of the endothermic overshoot signal shifts suddenly up to a maximum of 10 K, while the endothermic peak height accelerates in growth, with an increase of 70 J/g-atom. b) Plot of the

normalized enthalpy recovery after annealing for the indicated temperatures as a function of t_a . $\Delta H(\text{tot})$ is the maximum enthalpy change to reach equilibrium. Each data point corresponds to a single measurement sample. The continuous lines are the fits to Eq. 4. Inset) The $\tau_i(\Delta H_{\text{rec}})$ values of Eq. 4 are plotted versus $T_g (=396 \text{ K})$ scaled inverse temperature. The Q_i are the assigned values of activation energy for the enthalpy recovery decays based on the Arrhenius equation and compared to that for the β -relaxation (dashed curve) of as-quenched ribbons based on DMA (triangle) and DSC experiments [53].

Fig. 2 Selected normalized enthalpy released curves $\Delta H(t)/\Delta H_{\text{total}}$ for the $\text{Au}_{49}\text{Ag}_{5.5}\text{Pd}_{2.3}\text{Cu}_{26.9}\text{Si}_{16.3}$ BMG in the standard treated condition for the indicated isothermal annealing. Inset) Heat flow change during the annealing at 373 K subtracted by the heat flow change of a fully crystallized sample. The shaded area represents the total enthalpy that was released during aging.

Fig. 3 Viscosity change measured using isothermal three points beam bending at the indicated annealing temperatures for the $\text{Au}_{49}\text{Ag}_{5.5}\text{Pd}_{2.3}\text{Cu}_{26.9}\text{Si}_{16.3}$ BMG in as-cast condition. The dashed lines are the KWW-fits from which the equilibrium viscosity values are obtained. The curves at other temperatures are reported elsewhere [32,40].

Fig. 4 Specific heat capacity $C_p(T)$ of $\text{Au}_{49}\text{Ag}_{5.5}\text{Pd}_{2.3}\text{Cu}_{26.9}\text{Si}_{16.3}$ determined in DSC using a step-method for the glass (squares), crystalline (triangles) and liquid (circles) states [32]. The curves are the fits with Eqs. 5-7. The shaded circles with the error bars represent the values of C_p for the supercooled liquid estimated from calorimetric experiments on a long timescale. For the other data, the error bars are smaller than the size of the symbols. Inset) Entropy change for the thermodynamic crossover as a function of the liquid-liquid transition temperature T_{LLT} for the studied alloy in comparison with the literature values for other BMGs [28,29]. The red line is a linear fit through the data.

Fig. 5 Two-time XPCS correlation function (TTCF) for $\text{Au}_{49}\text{Ag}_{5.5}\text{Pd}_{2.3}\text{Cu}_{26.9}\text{Si}_{16.3}$ measured during isothermal annealing at 377 K for 5 h. a) TTCF during the first 9,400 s of annealing. b) TTCF for the last 7,000 s of annealing. The annealing followed a step-wise heating protocol from ambient temperature to 377 K, described in the methods. The axes correspond to the annealing time elapsed from the beginning of the data acquisition, while the width of the diagonal intensity profile is proportional to the microscopic structural relaxation time. c) Normalized one-time correlation functions extracted from the TTCF in the two stationary regimes labeled 'a' (from 0 to 6,000 s in Fig. 5a), and 'b' (over the entire length of the measurement of Fig. 5b). The solid lines through the data are fits to the Eq. 8, yielding $\tau_a = 570 \pm 26 \text{ s}$ and $\beta_a = 1.62 \pm 0.03$, and $\tau_b = 1650 \pm 7 \text{ s}$ and $\beta_b = 1.39 \pm 0.03$.

Fig. 6 Normalized intensity-intensity correlation functions for $\text{Au}_{49}\text{Ag}_{5.5}\text{Pd}_{2.3}\text{Cu}_{26.9}\text{Si}_{16.3}$ measured with XPCS at the indicated temperatures. a) The solid lines through the data are fits to the Eq. 8. The data at 377 K are for the stationary dynamics labeled ‘b’ of Fig. 5c. Inset) temperature evolution of the corresponding relaxation times. The continuous line is the Arrhenius-fit corresponding to an activation energy of $Q = 4.03 \pm 0.01$ eV. The additional annealing at 395 and 396 K shows that the transition to the liquid state occurred during the heating step from 393 to 395 K.

Fig. 7 Kinetic fragility diagram for $\text{Au}_{49}\text{Ag}_{5.5}\text{Pd}_{2.3}\text{Cu}_{26.9}\text{Si}_{16.3}$ of the relaxation times and equilibrium viscosities as a function of $T_{\text{LLT}} (= 389 \text{ K})$ -scaled inverse temperature. On the left y-axis is plotted the relaxation time using black diamonds for the enthalpy recovery values $\tau_i(\Delta H_{\text{rec}})$; open red circles for the for the XPCS data; red open squares for the equilibrium characteristic relaxation times $\tau(\Delta H_{\text{released}})$; the open triangles for the frequency dependence of the DMA loss modulus taken from [24,53]; the crossed circles for the literature calorimetric data of Ref. [22]. The dotted line represents the onset time of isothermal crystallization [12]. On the right y-axis is plotted the viscosity using filled blue circles for isothermal equilibrium viscosities η_{eq} . The dashed line and the solid lines are the fits to the VFT-equation (see text). The dash-dotted lines are Arrhenius-fits with activation energy Q_i from the enthalpy recovery spectrum analysis of Fig. 1.

Fig. 8 Temperature-time-transformation (TTT) diagram for $\text{Au}_{49}\text{Ag}_{5.5}\text{Pd}_{2.3}\text{Cu}_{26.9}\text{Si}_{16.3}$, based on the observed relaxation processes. The diamonds with the Arrhenius fits (dash-dotted lines) represent the relaxation times for the enthalpy recovery multi-stage process. The open circles are the XPCS τ data obtained upon quasi-static heating (red circles) and quasi-static cooling (blue circles [24]), respectively. See legend of Fig. 7 for more information.

















