Solid–solid phase transitions via melting in metals

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Observing solid–solid phase transitions in-situ with sufficient temporal and spatial resolution is a great challenge, and is often only possible via computer simulations or in model systems. Recently, a study of polymeric colloidal particles, where the particles mimic atoms, revealed an intermediate liquid state in the transition from one solid to another. While not yet observed there, this finding suggests that such phenomena may also occur in metals and alloys. Here we present experimental evidence for a solid–solid transition via the formation of a metastable liquid in a ‘real’ atomic system. We observe this transition in a bulk glass-forming metallic system in-situ using fast differential scanning calorimetry. We investigate the corresponding transformation kinetics and discuss the underlying thermodynamics. The mechanism is likely to be a feature of many metallic glasses and metals in general, and may provide further insight into phase transition theory.
Nearly all classes of materials show solid-state phase transitions. Understanding transformations from one crystal to another is a key topic in materials science because in many cases they determine material properties. The transition from graphite to diamond, the property design of steels or the formation of metastable phases to strengthen amorphous to crystalline or even vice versa have also been reported in metals, and they are also of great importance in other fields. For example, pharmaceutical substances can drastically alter their bioavailability in the human body via transitions from a metastable to a stable polymorphic modification. These mechanisms are complex and in most cases difficult to investigate via in-situ experiments. The atomistic mechanisms of solid–solid phase transitions are therefore still poorly understood.

In the past this limitation was circumvented by deploying colloidal model systems, where the motion of particles can be directly observed via video microscopy. Recently, one such study on micron-sized polymer particles discovered an intermediate liquid state in the transition from one solid to another. This suggests that such phenomena may also occur in 'real' atomic systems such as metals and alloys. However, because of the spatial localization and rapid kinetics of such transitions, this phenomenon has not yet been demonstrated in metallic systems.

Orava et al. illustrated the power of novel chip-based fast differential scanning calorimetry (FDSC) in studying the rapid crystallization of an amorphous Ge₃Sb₂Te₃ phase-change material. In their study, small-scale samples on a chip sensor with low thermal mass facilitated precise measurements of thermodynamic data at high speed. The slowest known transformation kinetics within metallic materials has been obtained for metallic glasses. The first metallic glass discovered was a Au–Si system. Since then Au-based bulk metallic glasses (BMGs) with very slow crystallization kinetics have been found and their suitability for FDSC investigations has recently been demonstrated. They are also of interest for future applications, for example, in small-scale devices for information technology and are known to form various metastable crystalline states.

By deploying a Au₇₀Cu₅.₅Ag₅.₅Si₁₇ BMG and FDSC we are in the unique situation of being able to measure a slowly transforming metallic system using a very fast detection technique. With this method we have been able to demonstrate unambiguously that a metallic system can transform from a metastable crystalline state into a more stable crystalline state via the formation of a metastable liquid at a temperature far below the deepest equilibrium eutectic temperature. This transformation differs from the usual crystallization pathway of metallic glasses, which often occurs via primary crystallization at low temperature and eutectic crystallization of the residual supercooled liquid (which now has a composition different from that of the original glass) at elevated temperature.

Results

Metastable melting upon rapid heating. Figure 1a illustrates FDSC heating curves of small-scale Au₇₀Cu₅.₅Ag₅.₅Si₁₇ specimens, which have been amorphized in-situ via rapid cooling from 748 K at a rate of 5,000 K s⁻¹. The FDSC curve at a heating rate of 300 K s⁻¹ shows a glass transition (Tg), two exothermic events (Te and Tm) and melting (Tm) towards an equilibrium liquid. This behaviour agrees well with results for Au₇₀Cu₅.₅Ag₅.₅Si₁₇ BMGs measured via conventional DSC, and the onset of melting corresponds to the deepest eutectic temperature reported for the Au–Si–Cu system. Increasing the heating rate to 350 K s⁻¹ shifts T1 and T2 to higher temperatures, which is commonly expected for the crystallization of supercooled liquids and most solid–solid transitions. A further increase in the heating rate to 1,000 K s⁻¹ clearly reveals the surprising occurrence of an endothermic effect at Tc (≈ 558 K) after the T1 peak and right before the T2 peak.

Figure 1b shows a close-up of the endothermic effect and the T2 peak at heating rates of 350–500 K s⁻¹. While the peak at T2 shifts to higher temperatures when the rate increases, the endothermic effect shows no rate dependence, which is a common sign of melting. Note that Tc is far below Te that is, the temperature Tc corresponds to that of a metastable liquid. This metastable liquid re-transforms very rapidly (within a few ms) towards a more stable crystalline state within the subsequent exothermic event at T2. For comparison, Fig. 1b also shows the T2 peak.
peak at a rate of 80 K s$^{-1}$, where it clearly occurs below $T_e$, (such that the metastable melting at $T_e$ does not occur). Comparing the rates at 80 K s$^{-1}$ and above 350 K s$^{-1}$, it is obvious that the $T_2$ peaks are remarkably different in shape and size.

If we examine the enthalpies of these transformations it becomes obvious that the crystallization enthalpy at $T_1$ only exhibits a low heating rate dependency, whereas the enthalpy of the $T_2$ peak is roughly 1/3 of the $T_1$ peak if $T_2 < T_e$ ($\approx 558$ K) but strongly increases to $\approx 3/2$ of the $T_1$ peak if $T_2 > T_e$.

(Figure 3b illustrates how the $T_2$ enthalpy peak is separated from the $T_1$ exothermic peak.) Because the enthalpy of melting at $T_m$ remains similar for all heating curves in Fig. 1, this simple energetic consideration indicates clearly that the Au-based BMG must transform through a metastable liquid upon heating, that is, glass $\rightarrow$ undercooled liquid $\rightarrow$ metastable crystalline state $\rightarrow$ metastable liquid $\rightarrow$ more stable crystalline state $\rightarrow$ equilibrium liquid. The metastable state appears to consist of one major metastable phase, which transforms via metastable melting (see also Supplementary Fig. 1) into stable primary crystals within an eutectic microstructure. The latter can be concluded from the melting event at $T_m$, which contains one sharp endothermic peak (corresponding to eutectic melting), followed by a broader endothermic event (see Fig. 1a).

**Freezing the non-equilibrium states.** In the following we present further evidence for the unusual solid–solid phase transition via melting. We first prepared glassy Au$_{70}$Cu$_{5,5}$Ag$_{2,5}$Si$_{17}$ in-situ in the FDSC via rapid cooling from 748 K at a rate of 5,000 K s$^{-1}$. We then processed the alloys according to the upper image in Fig. 2: after heating with $H_1 = 2,000$ K s$^{-1}$ to $T_{freeze(1,2)}$ the specimens were cooled at a freezing rate $F$ of 5,000 K s$^{-1}$ to room temperature and then re-heated at $H_2 = 2,000$ K s$^{-1}$ to 748 K. The lower images in Fig. 2 show the corresponding heat flow curves. The blue dash-dotted curve indicates heating with $H_1$ to $T_{freeze1}$, which is above $T_1$ but slightly below $T_e$. In this case a glass transition occurs, followed by the formation of a metastable crystalline state at $T_1$. Upon freezing with $F = 5,000$ K s$^{-1}$ (dotted blue curve) no further crystallization is observed and no glass transition detected. This implies that the supercooled liquid was mostly crystallized at $T_{freeze1}$. Only upon reheating with $H_2 = 2,000$ K s$^{-1}$ (solid blue curve) are additional peaks observed above $T_{freeze1}$ illustrating the melting of the metastable crystalline state at $T_1$ and its subsequent re-crystallization at $T_2$. If the material is frozen during the formation of the metastable liquid at $T_{freeze2}$ partial crystallization occurs upon freezing (dotted red curve) and a small glass transition and a small first crystallization event are observed upon reheating (solid red curve). This is further proof that metastable melting is indeed observed at $T_e$. However, the overlapping transition to a ‘stable’ crystalline state at $T_2$ prevents freezing to a fully amorphous state.

**Rate dependence of the phase transitions.** We now turn to the rate dependence of the formation of the solids. Figure 3a shows a Kissinger plot$^{24}$, from which the effective activation energies of the transitions can be deduced$^{17}$. Such activation energies are a common measure of phase transformation kinetics$^{25}$. As seen in Fig. 3a, the activation energy required to form the metastable crystalline state is lower by nearly a factor of two compared with that needed to form the ‘stable’ state, which is thus much more difficult to form kinetically. This also supports the idea that it is easier for the metastable crystalline state to transform into a metastable liquid than into a ‘stable’ crystalline state.

Figure 3b details the rate dependence of the transition enthalpy from the metastable to the ‘stable’ crystalline state. Figure 1 revealed a Gaussian shape of the corresponding transition peak ($T_2$) for temperatures $< T_e$ (heating rate $< 100$ K s$^{-1}$), but a strong influence of the overlapping melting of the metastable state for temperatures $> T_e$ (rate $> 100$ K s$^{-1}$), which also made the $T_2$ peak much sharper for $T > T_e$. To separate the melting peak from the $T_2$ crystallization peak, the transition from metastable to ‘stable’ was thus fitted with a Gaussian and, for melting of the metastable state, with a BiGaussian function. This is illustrated in the insert to Fig. 3b for a heating rate of 600 K s$^{-1}$. The transition enthalpy increases above a rate of 100 K s$^{-1}$, where the transition from metastable to ‘stable’ starts to overlap with the formation of the metastable liquid at $T_e$. This behaviour is so pronounced that it is still obvious if the transition peak resulting from the overlap of metastable melting and crystallization is integrated using a horizontal baseline. Note also that at high rates above 1,000 K s$^{-1}$ the formation of the ‘stable’ state cannot be completed kinetically before the temperature approaches $T_m$, which is why the enthalpy decreases again. At even higher rates the melting peak at $T_e$ no longer overlaps significantly with the $T_2$ crystallization peak, which is illustrated in the Supplementary Fig. 1a for a heating rate of 3,000 K s$^{-1}$. Here the melting of the metastable crystalline
state becomes very obvious and can be clearly distinguished from a \(c_p\) step, which would result from an additional glass transition.

**Discussion**

In the following, we discuss our FDSC data by evaluating the thermodynamics of the Au\(_{70}\)Cu\(_{5.5}\)Ag\(_{7.5}\)Si\(_{17}\) BMG. The thermodynamic data are obtained from the specific heat capacities (\(c_p\)) of the liquid and the metastable and ‘stable’ states, and their corresponding transition enthalpies and temperatures. Conventional DSC was deployed to determine the transition temperatures and specific enthalpies, because of the relatively high uncertainty of the sample mass determination in FDSC. Specific heat capacities were measured by temperature-modulated DSC (TM-DSC)\(^{26}\) and fitted by polynomials\(^{27,28}\) (provided in the Supplementary Discussion). The resulting DSC/TM-DSC heat flow curves are comparable with the curves measured by FDSC at 60 K s\(^{-1}\), presented in Fig. 1a. The relative specific enthalpies, as shown in Fig. 4a, were calculated according to \(\Delta h(T) = \int_T^{T_0} c_p\,dT\), where \(T_0\) is the melting temperature of the ‘stable’ state (more details are presented in the Supplementary Discussion). Figure 4a shows that at low heating rates only the small transition enthalpy from metastable to ‘stable’ (small arrows pointing downwards) is observed, while at fast heating rates the transition enthalpies following the path metastable crystalline → metastable liquid → ‘stable’ crystalline (dashed arrows) become visible. The values from Fig. 4a correspond well to the FDSC data in Fig. 3b, taking into account the uncertainty of the mass determination in FDSC (~10%).

In this context it should be mentioned that we work with a four-component BMG to ensure sluggish transformation kinetics. The metastable crystalline state may thus contain more than one phase, but the transformation enthalpies measured reveal clearly that the majority of the material follows the proposed transition path. In fact, the FDSC data of the Supplementary Fig. 1 and the melting events shown in Fig. 1a indicate that this major metastable phase transforms via metastable melting to stable primary crystals within an eutectic microstructure. Future transmission electron microscopy studies may further illustrate these microstructural features.

Figure 4b shows the relative Gibbs free energies (\(\Delta g\)) of the various states, which can be calculated from \(\Delta g = \Delta h - T\Delta s\), where \(\Delta s(T) = \Delta s^0 - \int_T^{T_0} \left(\frac{c_p}{T}\right)\,dT\) is the relative entropy and \(\Delta s^0\) is approximated by \(\Delta h^0/T_0\), with \(\Delta s^0\), \(\Delta h^0\) and \(T_0\) as the entropy, enthalpy and temperature of the solid-to-equilibrium liquid transition. All data for the ‘stable’ state and liquid are accessible via DSC and TM-DSC, while the temperature of metastable melting (\(T_m \approx 558\) K) is estimated from FDSC and the corresponding specific enthalpy (35.1 J g\(^{-1}\)) is read from Fig. 4a. For better visualization Fig. 4b plots the relative Gibbs free energy with reference to the ‘stable’ state. The mangenta dotted line schematically illustrates the kinetic transition path of the solid–solid transition via melting. Starting from the supercooled liquid, \(\Delta g\) is abruptly reduced at \(T_0\) by the formation of the metastable crystalline state. The kinetically difficult solid–solid transition to the ‘stable’ state (see also Fig. 3a) enables the lowering of \(\Delta g\) via the formation of a metastable liquid at \(T_m\). Figure 4b thus illustrates that there is a thermodynamic driving force\(^3\) for the formation of a metastable liquid, and from refs \(8,9\) it can be concluded that the liquid–solid interfacial free energy is likely to be lower than that between the solids. This triggers the transition to the ‘stable’ state at \(T_m\), where \(\Delta g\) is again abruptly lowered. Finally, the transition to the equilibrium liquid occurs at \(T_m\).

We have thus documented the discovery of a solid–solid transition via melting in a metallic system. The Au\(_{70}\)Cu\(_{5.5}\)Ag\(_{7.5}\)Si\(_{17}\) BMG exhibits the following unusual transition path upon heating: glass → undercooled liquid → metastable crystalline → metastable liquid → ‘stable’ crystalline → equilibrium liquid. With FDSC we are able to explore this new transition path in-situ and, using also conventional DSC, gain new insights into the underlying thermodynamics.
In conclusion, we suggest that the observed fundamental solid–solid transition via metastable melting is a feature of many metallic glasses and metals, where different formation sequences of solid phases with varying thermodynamic stability are frequently observed. The concept presented can be applied to any metastable to more stable transformation of crystals and does not require the glassy state. This is illustrated in Supplementary Fig. 1b, where a metastable crystalline state can transform into a ‘stable’ crystalline state even if no glass has formed beforehand upon slow cooling. The possibility of studying solid–solid transitions via melting in real atomic systems demonstrated here is thus expected to provide further insight into phase transition theory, and may also trigger the development of new materials. For example, FDSC may be deployed to gain a deeper understanding of the reversion of precipitates upon heating in conventional metallurgy. Finally, the concept presented may also be of great importance for the understanding of new processing techniques, involving metals and BMGs, where rapid cooling and heating are applied (for example, 3D printing of metals) and metastable phases form frequently.

Methods
Sample preparation. The elements Au (purity 99.99 wt%), Ag (99.99 wt%) and Cu (99.995 wt%) were weighed according to the atomic composition Au70Cu5.5Ag7.5Si17 and inserted into quartz glass tubes of 5 mm diameter. After repeated purging with Ar pressure and the element pieces were induction-melted to a pre-alloy. From this pre-alloy, thin (30 μm) and chemically homogeneous glassy ribbons were produced by melt spinning under a 500 mbar He atmosphere.

Fast differential scanning calorimetry. FDSC was performed in power compensation mode using a Mettler-Toledo Flash-DSC 1. The sample support temperature of the FDSC was set to 183 K using a Huber intracooler TC30. The FDSC samples were prepared by cutting the melt-spin ribbons into small pieces under a stereomicroscope and then transferred using an electrostatic manipulator onto a conditioned MultiSTAR UFS1 sensor. The sample masses were estimated to be 1.7 to 3 μg according to the procedure given in ref. 18. Reproducibility was checked by comparing the same thermal cycles at the start and end of each measurement series.

Conventional and temperature-modulated DSC. Conventional DSC was performed using a differential scanning calorimeter (Mettler-Toledo DSC1) to determine the temperatures and enthalpies of the transitions. The measurements were conducted at a heating rate of 0.16 K s⁻¹ using aluminium pans on the sample and reference platforms. Heat flow calibration was performed with indium and zinc.

Specific heat capacity measurements were performed using TMDSC in a Mettler-Toledo DSC1 equipped with TOPEM stochastic temperature modulation. Sapphire was used as reference substance for the specific heat capacity determination. The measurements were conducted at heating and cooling rates of 0.033 K s⁻¹ and a temperature modulation of 2 K, using aluminium pans on the sample and reference platforms. Data processing was performed with a calculation window width of 300 s and a corresponding shift of 10 s. For the specific heat capacity determination of the liquid phase, heating and cooling measurements were combined to increase the temperature range of the measured data.

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Author contributions
S.P. and J.F.L. conceived the study. S.P. and D.L. produced the alloys and performed the FDSC tests. J.E.K.S. conducted the TMDSC and DSC measurements. P.J.U. and J.F.L. supervised the work. All authors contributed extensively to the data analysis and discussion. S.P. and J.F.L. wrote the paper.

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