

Liquid-Liquid Transitions due to Melting Temperatures of Residual Glassy Phases Expected in $Pt_{57}Cu_{23}P_{20}$

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Abstract

Bulk glasses are obtained by quenching melts of various compositions. The initial temperature is chosen above the liquidus temperature (T_l) of materials assuming that the melt is homogenous. Glassy items are formatted above the glass transition temperature T_g below a crystallization temperature called T_x . First-order transitions at T_x transform melts into composites containing crystals and new glassy phases, melting at temperatures (T_{n+}) much higher than (T_l). These first-order transitions were studied at Caltech Pasadena by cooling and heating a melt of $Pt_{57}Cu_{23}P_{20}$. A recent model predicting the formation enthalpies of these new composites at T_x and the melting temperatures (T_{n+}) of glassy fractions is applied to this alloy.

Keywords: Crystallization; Liquid; Temperature; Transitions

Introduction

A detailed study of first-order transitions, occurring in the melt $Pt_{57}Cu_{23}P_{20}$ during cooling and heating below its liquidus temperature, was recently published by J H Na et al. [1]. A theoretical description was proposed, considering that all these transitions lead to a full crystallization even far below the melting temperature. Another interpretation of these results is proposed in this paper in the light of a recent discovery of complementary melting temperatures of multiple glass phases surviving in glass-forming melts above the melting temperature [2,3].

The glass transition in $Pt_{57}Cu_{23}P_{20}$ melt occurred at $T_g=505K$, the solidus melting temperature at $T_s=T_m=823.8K$ and the liquidus temperature at $T_l=827.9K$. In spite of an overheating temperature higher than 1173K, Fifteen thermal cycles were necessary to attain the highest undercooling rate ($\Delta T@286K$). First-order transitions were observed near T_g' after annealing the glass during 15 hours at 503K. The melting heat was 68.5J/g [1].

The first objective, in this paper, is to attribute the first-order transitions near T_g to the formation of glacial phases as already observed in triphenyl phosphite, d-mannitol, n-butanol and water [4-11]. A non-classical model of homogeneous nucleation, built from the knowledge of T_g and T_m' , had explained the glacial phase formation by considering that the first-order transition was driven by the entropy of a new phase called Phase 3 [12,13]. The existence of entropically-driven transitions in $Al_2O_3-Y_2O_3$ system was recognized, for the first time, by Assland & McMillan [14] while the formation of Phase 3 was proposed by heating supercooled water [15,16].

Phase 3 obtained by heating the melt from the glassy state, has been attributed to the presence, above T_g' , of residual bonds in all glasses, melted at temperatures T_{n+} higher than T_m [17]. The non-classical model of homogeneous nucleation was recently completed, leading to the prediction of Phase 3 transformations in glassy phases at new temperatures T_x which are driven by enthalpy [3]. The melt above T_g is viewed as containing residual bonds (after configurons formation [18-21]) at a critical threshold up to a first-order transition at $T=T_x$ [17]. Above T_x , new glassy Phases 3 of lower enthalpy, could be formed with a glass transition temperature T_g' equal to $(2T_m-T_g) = 1142.6K$ which remains virtual because (T_g') is higher than their melting temperatures (T_{n+}) [3].

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First-order transitions occurring near $T_g=505K$ in $Pt_{57}Cu_{23}P_{20}$ were varying between $T_x=535.6K$ and $548.8K$ during heating. These transition temperatures slightly increased because the liquid enthalpy, relaxed at low heating rates, induced entropy and enthalpy variations due to the long annealing (15 hours) initially applied at T_g and to very low heating rates (0.2-10K/mn) up to T_m [1] Figure

1. All latent heats of transitions at T_x , including those observed by under cooling, were attributed to the melt crystallization which increased from 20J/g near T_g to 68.5J/g at T_m [1] in contradiction with our description of a new phase formation which is entropically driven.

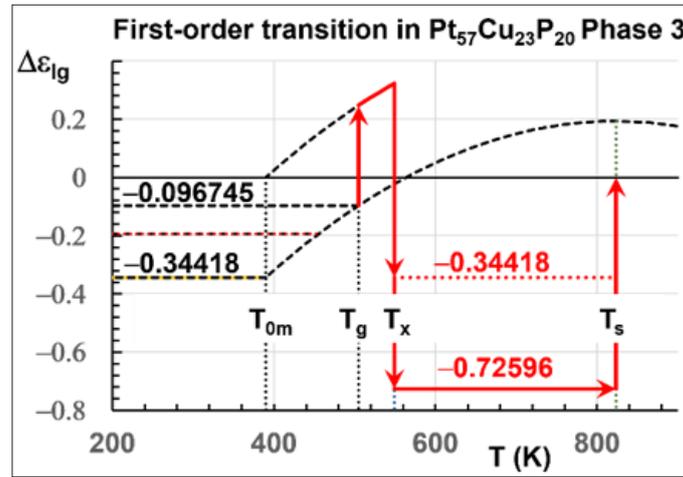


Figure 1: First-order transition at $T_x=548.8K$ during heating. Observed in [1] Figure 1E. $T_{0m}=389.9K$. Increase of the enthalpy after 15 hours of annealing at $T_g=505K$. Melting temperature $T_s=T_m=823.8K$. Enthalpy coefficient (-0.34418) resulting from the transition driven by the entropy at T_x . Transformation of Phase 3 in a new glass at $T_x=548.8K$ with an enthalpy coefficient during the first heating and melting at $T_m=823.8K$.

The second objective is to determine when these findings are compatible with a glass formation, following an increase of residual bond fraction at the transition at T_x , driven by the configuron entropy toward a new Phase 3 of lower enthalpy. These bonds may disappear at temperatures T_{n+} higher than T_m as already observed in many glasses and predicted by non-classical nucleation equation [17,22,23]. They give rise to a glass phase fraction in the melt above T_x . The maximum fraction of atoms involved into the glass phase is defined by the latent heat inducing transition at T_x .

The third objective is to predict the multiple melting temperatures (T_{n+}), higher than T_m , of these new glassy fractions and the total melting heat of $Pt_{57}Cu_{23}P_{20}$, including the additional latent heat recovered at T_{n+} .

2-Practical Equations Applied to Liquid Pt57Cu23P20 Enthalpies

There are 3 fragile liquid states having enthalpies equal to ϵ_{ls}, H_m , ϵ_{gs}, H_m and $\Delta\epsilon_{lg}, H_m$ where H_m is the melting enthalpy [24]:

$$\epsilon_{ls}(\theta=0) = \epsilon_{ls0} = \theta_g + 2$$

$$\epsilon_{gs}(\theta=0) = \epsilon_{gs0} = 1.5\theta_g + 2$$

$$\theta_{0m}^2 = \frac{8}{9}\epsilon_{ls0} - \frac{4}{9}\epsilon_{ls0}^2$$

$$\theta_{0g}^2 = \frac{8}{9}\epsilon_{gs0} - \frac{4}{9}\epsilon_{gs0}^2$$

$$\Delta\epsilon_{lg}(\theta) = [\epsilon_{ls} - \epsilon_{gs}] = \left[\epsilon_{ls0} - \epsilon_{gs0} - \theta^2 \left(\frac{\epsilon_{ls0}}{\theta_{0m}^2} - \frac{\epsilon_{gs0}}{\theta_{0g}^2} \right) \right]$$

where (θ_m) and (θ_g) are the reduced and calculated Vogel-Fulcher-Tammann (VFT) temperatures higher than $(-2/3)$ for fragile liquids. The enthalpy coefficients devoted to $Pt_{57}Cu_{23}P_{20}$ are:

Liquid 1

$$\epsilon_{ls} = 1.61301 \left(1 - \frac{\theta^2}{0.27743} \right) \quad (1)$$

Liquid 2

$$\epsilon_{gs} = 1.41952 \left(1 - \frac{\theta^2}{0.36622} \right) \quad (2)$$

Phase 3

$$\Delta\epsilon_{lg}(\theta) = [\epsilon_{ls} - \epsilon_{gs}] = [0.19349 - 1.93805 \times \theta^2] \quad (3)$$

3-First-Order Transitions Driven by the Entropy of Phase 3 during the First Heating

The singular enthalpy coefficients $\Delta\epsilon_{lg}$ of Phase 3 are: 0, $\Delta\epsilon_{lg0}/2 = -0.096745$, $\pm 0.14993^*$, $\Delta\epsilon_{lg0} = \pm 0.19349$, $\Delta\epsilon_{lg}(\theta_m) = -0.34418$, and $(-0.33342 = -0.14933 - 0.19349)$ and expected to correspond to various percolation thresholds [3,17,25]. The entropy variation of Phase 3 from the solidus melting temperature ($T_s=T_m=823.8K$) down to the Kauzmann temperature $T_K=364.43K$ is equal to $(-1/T_m)$ assuming that $H_m=1J/g$. The entropy variation of Phase 3 in Eq. (4), up to a temperature T , starts from the temperature T_K :

$$\Delta S(T) = 2(1.93805) \Delta S_m \left(\frac{T - T_x}{T_m} \right) - 2 \Delta S_m L_m \left(\frac{T}{T_x} \right) (1.93905) \quad (4)$$

For $T = T_x$, $\Delta S(T_x)$ is equal to the entropy change produced by the first-order transition which is equal to $[\Delta \epsilon_{lg}(T_x) + 0.34418] / T_x = 0.47928 / T_x = 0.0008719 \text{ J/K/g}$ at $T_x = 548.8 \text{ K}$ with $H_m = 1 \text{ J/g}$, $\Delta \epsilon_{lg}(T_x) = 0.13342$ and $T_K = 364.63 \text{ K}$. The enthalpy coefficient inducing the first-order transition is equal to (-0.34418) deduced from $\theta^2 = \theta_m^2$ in Eq. (1) and $\Delta \epsilon_{lg}(\theta_m^2) = -0.34418$ in Eq. (3). The measured latent heat at T_x is $(49 \text{ J/g}) = 0.71533 \times H_m = 0.71533 \times 68.5 \text{ J/g}$ [1] and the latent heat coefficient, being higher than (0.47928) , is enhanced by adding the singular enthalpy coefficients $(0.096745 + 0.14993)$, leading to the theoretical value $(0.72596 \times 68.5 = 49.7 \text{ J/g})$. This glassy phase, having a very low enthalpy, cannot exist above T_m with a melting temperature $T_{n+} = 1.72596 T_m$, which would be higher than $T'_g = 1.38699 T_m = 1142.3 \text{ K}$. This glassy phase is melted at $T_m = 823.8 \text{ K}$.

First-order transitions temperatures lower than $T_x = 548.8 \text{ K}$ are calculated with Eq. (4) and temperature (T_K) equal to 364.4 K in agreement with experimental latent heats. For $T_x = 535.6 \text{ K}$, the measured latent heat (38.7 J/g) corresponds to a fraction $(38.7/68.5 = 0.56496)$ of H_m and to an entropy of transition $(0.0008327 \text{ J/K/g} = (0.34418 + \Delta \epsilon_{lg}) / T_x = 0.44598 / 535.6)$ with $T_K = 364.63 \text{ K}$ and $\Delta \epsilon_{lg} = 0.1018$. The singular latent heat coefficient (0.096745) is added to (0.44598) to attain the theoretical value (0.54273) during the transition and a latent heat of 37.2 J/g . For $T_x = T_g = 505 \text{ K}$, the highest relaxed entropy after isothermal annealing could be $(0.0007306 = (0.34418 + \Delta \epsilon_{lg}) / T_x)$ for $\Delta \epsilon_{lg} = 0.02482$ and $T_K = 364.63 \text{ K}$ and the relaxed enthalpy $(0.369 \times 68.5 = 25.3 \text{ J/g})$ [1]. The various values of $\Delta \epsilon_{lg}$ depend on the enthalpy which is relaxed during annealing at T_g and slow heating

up to T_x . All these enthalpy changes are driven by the entropy of Phase 3 without any crystallization.

4-First-Order Transitions Driven by the Enthalpy of Phase 3 during Supercooling

Temperatures of undercooling are predicted using the non-classical nucleation model leading to nucleation temperatures (θ_{n-}) in Liquid 2 defined in Eq. (5) [26]:

$$\epsilon_{g0} \frac{\theta_{n-}^2}{\theta_{0g}^2} + 3\theta_{n-} + 2 - \epsilon_{g0} - \Delta \epsilon = 0 \quad \text{or}$$

$$\epsilon_{g0} (\theta = 0) = (3\theta_{n-} + 2 - \Delta \epsilon) / \left(1 - \frac{\theta_{n-}^2}{\theta_{0g}^2} \right) \quad (5)$$

where $\Delta \epsilon$ is equal to singular values of the enthalpy coefficient of Phase 3. The initial enthalpy coefficient $\Delta \epsilon_{lg}$ at the supercooling temperature would be much higher than (-0.34418) after 15 Differential Scanning Calorimetry (DSC) cycles at 0.17 K/s from 1173 K to 373 K [1] and equal to the enthalpy coefficient $(\Delta \epsilon_{lg} = 0)$ of homogeneous liquid. The transitions during undercooling occur between 635 K and 689 K starting from the cooling enthalpy $(\Delta \epsilon_{lg} = 0)$ as shown in Figure 2, using Eq. (5), $\Delta \epsilon = 0.096745, 0.19349, 0.246675$, and 0.34418 respectively and ϵ_{g0} and θ_{0g}^2 given by Eq. (2). These new transitions lead to new glassy Phases 3 which are accompanied by crystallization of the other liquid fraction.

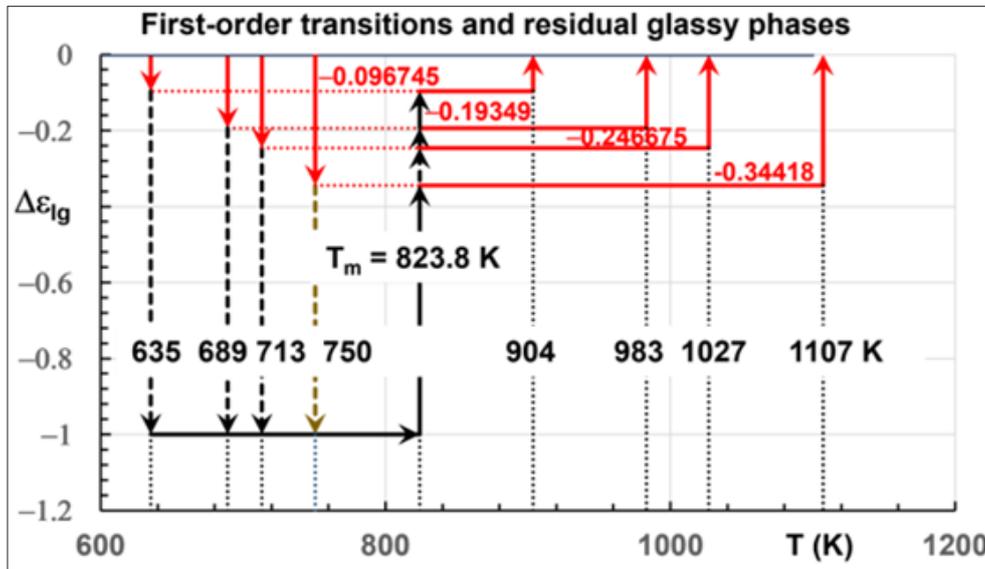


Figure 2: First-order transitions starting from the homogeneous liquid state ($\Delta \epsilon_{lg} = 0$). Nucleation of Phase 3 leading to crystallization for various undercooling rates (from 74 to 189K). The enthalpy change starts from 0 toward four singular values of $\Delta \epsilon_{lg}$ in Eq. (5) equal to $-0.096745, -0.19349, -0.246675$ at $635, 689 \text{ K}, 713 \text{ K}$ and 750 K leading to the formation of glassy phases 3 and to spontaneous crystallization. Melting temperatures $T_{n+} = 903.5 \text{ K}, 983.2 \text{ K}, 1027 \text{ K}$ and 1107.3 K . Transitions at T_x described in [1] Figure S4c. The crystallization heat is equal to h_{cr} for .

There is an experimental jump of undercooling rate between 689K and 713K corresponding to that of singular values from (-0.19349) to (-0.246675) in rough agreement with a group of 25 undercooling rates between 140 and 189K following 15 previous thermal cycles [1] Figure S4c. The residual glassy phases, in these conditions, are formed at temperatures $T_x=635, 689, 713K$ and 750K through first-order transitions inducing crystallization and melted after reheating at $T_{n+}=903.5K, 983.2K, 1027K$ and 1107K respectively. The lowest enthalpy of Phase 3 is found again for $\Delta\varepsilon = 0.34418$ without being accompanied by supplementary enthalpy coefficients at $T_x=750K$ leading to $T_{n+}=1107K$.

The nucleation of crystallization, at weak undercooling rate, starts in Figure 3 from $\Delta\varepsilon_g = -0.34418$ instead of zero in Figure 2. A first-order transition is expected at $T_{n+}=1107K$ in spite of an overheating at 1173K. Eq. (5) is applied for ($\varepsilon_{g0} = 1.41952 - 0.34418 = 1.07534$), ($\theta_{g0}^2 = 0.36622$) as in Eq. (2), ($\Delta\varepsilon = 1 - 0.34418 = 0.65582$) and leads to a nucleation temperature (742.1K) near the experimental value (737.4K). All measured latent heats [1] were viewed as “crystallization” enthalpies including those of glassy fractions from T_g to T_m and were represented by Eq. (6) including the latent heats of Phases 3 at $T_x < 548.8K$:

$$h_{cr}(T) = 70.2 \left[1 - \frac{484}{T} \right]^{8.04} \quad (6)$$

The “crystallization” heat h_{cr} at $T_m=823.8K$ was 69.2J/g, applying Eq. (6). The highest crystallization temperature occurred at 737.4K instead of 742.1K with a “crystallization” heat ($h_{cr}=67.82J/g$). This homogeneous nucleation temperature is obtained with Eq. (5) for $\varepsilon_{g0} = 1.06795$ instead of 1.07534, and $\Delta\varepsilon = 0.64883$. The initial enthalpy ($\Delta\varepsilon_g$) before supercooling is (1.06795-1.41952=-0.35157) instead of (-0.34418) corresponding to a “crystallization” heat (67.82J/g) deduced from Eq. (6). The crystallization at 737.4K starts from an undercooling rate (86K) during the first thermal cycle and at 720.9K with an undercooling rate (103K) for the 15th thermal cycle and a “crystallization” heat (67.35J/g), weakly reduced (67.82-67.35=0.47J/g) and associated with a weak increase of $\Delta\varepsilon$ up to 0.3585. This result confirms the existence of a second group of undercooling rates between 86 and 103K inducing crystallization during the first DSC cycles [1]. The glassy Phase 3 would be formed and melted through a first-order transition at 1107.3K during the first thermal cycles as shown in Figure 3 and as already observed in $Cu_{46}Zr_{46}Al_8$ [3,27].

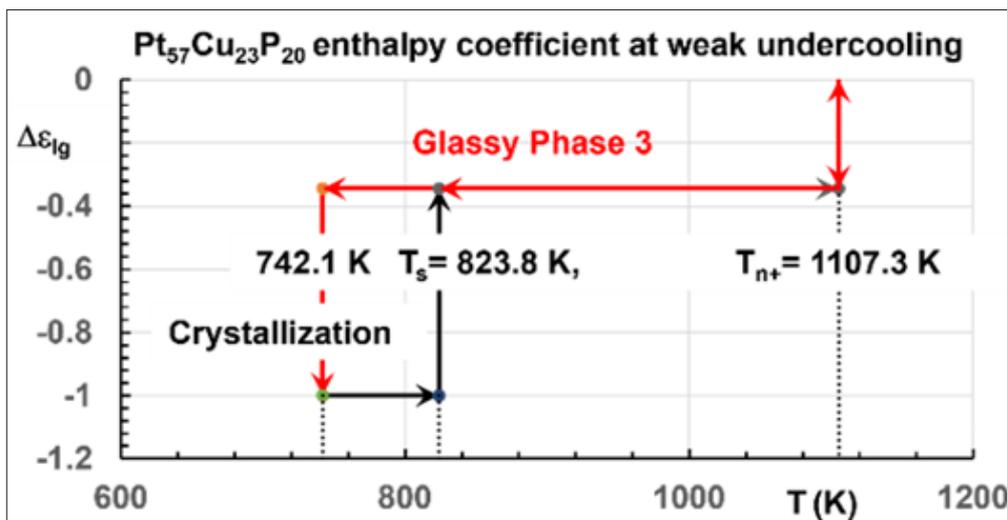


Figure 3: Nucleation of crystallization at weak undercooling rate (82K) from $\Delta\varepsilon_g = -0.34418$. The enthalpy coefficient change starting from -0.34418 toward -1, the crystal enthalpy coefficient with in Eq. (5). Transitions at T_x described in [1] Figure S4c. The crystallization heat is equal to h_{cr} for $\Delta\varepsilon_g = -1$.

The “crystallization” heat h_{cr} during supercooling, including the latent heat of glassy Phase 3, depends on singular value ($\Delta\varepsilon$). For $\Delta\varepsilon = 0.096745$ and $T_x=635K$, the latent heat h_{cr} is equal to -62.9J/mole in Eq. (6). For $\Delta\varepsilon = 0.19349$, $T_x=689K$, $h_{cr}=-66.1J/mole$ in Eq. (6). For $\Delta\varepsilon = 0.246675$, $T_x=713K$, $h_{cr}=-67.1J/mole$ as shown in Figure 2. The missing melting heats ($0.096745H_m$), ($0.19349H_m$), ($0.246675H_m$) and ($0.34418H_m$) of Phases 3 are recovered at $T_{n+}=1.096745T_m$, $1.19349T_m$, $1.246675T_m$ and $1.34418T_m$ respectively. The enthalpy of the crystallized fraction included in the crystallization heat h_{cr} is weakly reduced from $H_m=68.5$ to 62.9J/g when the elapsed

time in the undercooling rate ΔT increases. This phenomenon was observed after annealing a glass-forming melt at temperatures lower than T_x [3,28].

A measurement of melting heat H_m must eliminate the glassy fraction of configurons. The melt must be overheated above T_g' if possible, annealed above T_m to induce new growth nuclei able to crystallize the melt at T_m without undercooling. Eq. (5) predicts here a nucleation temperature of complete crystallization at 844K with $\Delta\varepsilon = 1$. The glassy fractions have been melted in $Pt_{57}Cu_{23}P_{20}$ leading to $H_m = 68.5J/g$ [1].

Conclusion

First-order transitions observed near $T_g=505\text{K}$ in $\text{Pt}_{57}\text{Cu}_{23}\text{P}_{20}$ at various temperatures (T_x), varying from 535.6 to 548.8K, are entropically driven during heating and lead to the formation of glassy Phases 3 with a lower enthalpy at T_x without crystallization at these temperatures. Those observed by supercooling at homogeneous nucleation temperatures $T_n=T_x$ between 635 and 750K are driven by an increase of singular values of configuron enthalpies and lead to the formation of various Phases 3, being glassy from T_x to their melting temperature (T_m). All these first-order transitions are accompanied by crystallization.

The measured crystallization enthalpy h_{cr} , equal to 68.5J/g, observed at the solidus temperature T_s , is complete. The total melting heat, including the latent heat expected at T_m above T_m , resulting from the melting of glassy Phase 3, which are formed at T_x by undercooling, is equal to $h_{cr}\leq 68.5\text{J/g}$. The crystallization heat slightly decreases with the elapsed time in the undercooled state and the annealing time between T_g and T_x .

This work shows that glass-forming melts are composed of crystallized fractions or liquid fractions and glassy fractions, melting at temperatures T_m much higher than the crystal melting temperature.

The presence of glassy phases above the crystal melting temperature, after a first-order transition at T_x , obtained by undercooling below T_g and reheating, has for consequence that the crystallization heat must be measured by cooling the melt, if possible, from the second glass transition temperature (T_g), and in all cases, by annealing it above T_m to grow new nuclei and crystallizing it without undercooling.

*A latent heat is expected at $T_m=1.14766\times T_m$ in the absence of long annealing at T_g [17,23].

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