Phase Separation in Frozen Microscale Eutectic Indium-Gallium and its Explosion upon Remelting

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Owing to its low vapor pressure, low toxicity, high thermal and electrical conductivities, eutectic Ga-In (EGaIn) has shown a great potential for smart material applications in flexible devices, cooling in micro-devices, self-healing reconfigurable materials, and actuators. For such applications, EGaIn is maintained above its melting point, below which it undergoes solidification and complex phase separation. A scientific understanding of the structural and compositional evolution during thermal cycling could help further assess the application range of Ga and other low-melting-point fusible alloys. Here, we use an integrated suite of cryogenically-enabled advanced microscopy & microanalysis to better understand phase separation and (re)mixing processes in EGaIn. We reveal an overlooked thermal-stimulus-response behavior for frozen mesoscale EGaIn at cryogenic temperatures, with a sudden volume expansion observed during in-situ heat-cycling, associated with the immiscibility between Ga and In during cooling and the formation of metastable Ga phases. These results emphasize the importance of the kinetics of rejuvenation, and open new paths for EGaIn in sensor applications.

The melting point of EGaIn is as low as 288 K, proving advantageous for applications that rely on its flexibility, deformability and ability to rejuvenate both its eutectic phase and oxide layer. The remelting process is intuitively perceived as an uneventful transition from a solid, eutectic microstructure to a liquid. Here, morphological observations using cryogenically-enabled scanning electron microscopy (SEM) combined with Xe-plasma focused ion beam (pFIB), and atom probe tomography (APT), reveal the intricate details in that remixing (remelting) reaction of Ga and In. Microdroplets of EGaIn (~50 µm in width), deposited on a flat Cu plate, were dropped in liquid-nitrogen to elicit solidification at a fast rate, leading to very fast and interrupted phase separation of the liquid EGaIn into Ga- and In-rich phases (see Fig. S1). This fast-cooled sample is referred to as f-EGaIn. On the other hand, slowly-cooled droplets, referred to as s-EGaIn, are cooled on the stage of the SEM, reaching 123 K in 100
Figure 1: In-situ SEM imaging of frozen f-EGaIn droplet on a temperature-controlled stage whilst remelting due to gradual increase in temperature (scale bars a: 50 µm, b: 40 µm, c: 50 µm, d: 50 µm).

Microdroplets were examined using cross-sectional scanning secondary electron (SE) imaging to identify the different phases in f-EGaIn at cryogenic temperatures and how they change upon reheating (Fig. 1). The phases with brighter contrast are attributed to the In-rich phase as confirmed by BSE imaging (Fig. S2a). Heavier elements lead to a locally brighter contrast: in all f-EGaIn droplets, we image a dendritic structure of an In-rich phase formed in a dark Ga-rich matrix phase. As the temperature gradually increases, from Fig. 1a to 1d, we observe in-situ a complex morphological evolution of f-EGaIn during the anticipated remixing and melting. While the In-rich phase maintains its shape, the Ga-rich phase seems to melt at sub-zero temperatures (263 K), causing a volumetric expansion by a factor of approx. 2 (Fig. 1b). At higher temperatures, from 271 K, remixing occurs with the remaining In-rich phase, that
progressively disappears and is fully integrated in the liquid metal at 294 K (Fig. 1c). This behavior contrasts with the heating process from a s-EGaIn droplet (Fig. S3), which shows an instantaneous remelting process happening at the eutectic temperature.

To elucidate the mechanism behind this volumetric explosion, we take a closer look at the atomic-scale chemistry in the frozen droplets. Fig. 2a shows a cross-sectional scanning electron micrograph of the f-EGaIn micro-structure following slicing with the pFIB. As evidenced from the close up in Fig. 2b, the width of the In precipitate is $2.6 \pm 1.7 \, \mu m$ with an area fraction of 6.2 % for the In-rich phase. We prepared specimens for APT analysis of each of the phases, at cryogenic temperature (123 K), following the approach used previously by El-Zoka et al., and guided by the BSE contrast. The successive steps leading to a suitable needle-shaped specimen for APT are depicted in Fig. 2c-f. Fig. 2g and 2h are the corresponding 3D atom maps of the In-rich and Ga-rich phases, respectively. Due to the rapid quenching, each phase is a mixture: the Ga-rich phase contains $1.17 \pm 0.02$ at. % of In that are homogeneously distributed (Fig. S4); the In-rich phase contains $2.74 \pm 0.01$ at. % of Ga, which show a slight tendency for agglomeration (Fig. S4). According to the binary equilibrium phase diagram, slow cooling bulk EGaIn to temperatures below the freezing point of EGaIn, i.e. 288 K, causes formation of two completely separated phases, namely orthorhombic $\alpha$-Ga and fcc-In, and each of these phases do not mix with one another. A one-dimensional composition profile across the interphase interface (along the arrow) shows a rough and diffuse interface over less than 10 nm (Fig. S5). Within its spatial resolution limits, APT indicates In kinetically entrapped within Ga, and vice versa, which can be ascribed to the fast cooling of the f-EGaIn sample that ‘freezes’ diffusing atoms in a metastable state.
Figure 2: (a,b) Cross-sectional FIB-SEM images of f-EGaIn sample (scale bar a: 10 µm, b: 5 µm). In b, the triangles are representative positions of where APT specimens were prepared. (c-e) Cryo-specimen preparation for the liquid metal (scale bar c: 500 µm, d: 200 µm, e: 20 µm). (f) Final atom probe specimen (scale bar f: 500 nm). 3D atom maps of (g) In- and (h) Ga-rich region from f-EGaIn (scale bar, g: 20 nm, h: 10 nm).

A similar set of analyses were performed on s-EGaIn droplets. The cross-sectional imaging in Fig. S6a and b reveal much larger In-rich regions, 9.6 ±0.7 µm in width, almost four times
larger than in f-EGaIn, with an area fraction of In-rich phase of 11.4%. APT analysis shows that only <0.0003 at.% In is detected within the Ga-rich region (see Fig. S6c), agreeing with the extremely low solubility of In in Ga-rich phase\textsuperscript{18}. On the other hand, the In-rich phase contains 0.73 ±0.01 at.% Ga, as expected from the higher solubility of Ga in fcc-In\textsuperscript{17}. Contrasting with f-EGaIn, the separate Ga and In phases in s-EGaIn are purer when sufficient time is given for diffusion to enable the demixing, and the compositions, reported in Table S1, confirm the low miscibility of these two metals below the eutectic point.

As the solubility of In in the Ga-rich phase is lower than that of Ga in the In-rich phase, In is expected to be an important limiting factor in the remixing or phase growth that happens. Therefore, we performed a series of in-situ heat-treatments at room temperature, inside the atom probe ultra-high vacuum (UHV) chamber, and measured the changes in In content within the Ga-rich phase in a f-EGaIn droplet, to explore intraphase interactions during heating. The concentration of In increases from 1.17 to 1.74 at. %, maintaining random distribution, after 1800 seconds of treatment as shown in Fig. S7. Similar in-situ heat treatments at room temperature on a heat-sensitive Al-based alloy showed no microstructural evolution\textsuperscript{19}, which was attributed to the annihilation of non-equilibrium vacancies at the free surface of the needle-shaped specimen. However, beyond non-equilibrium vacancies from the rapid quenching of f-EGaIn, heating at or near the melting point can introduce new vacancies, thereby facilitating the diffusion of In back into the Ga-rich phase within the specimen. These measurements confirm that, at cryogenic temperatures, mixing of In into Ga takes place before the fusion of the Ga-rich phase.

Let us now focus on the explosive volume change during remelting, to try and understand its origins and, potentially, how to control it. We performed temperature cycling on an initially fast quenched EGaIn droplet, as shown in Fig. 3: the same f-EGaIn droplet demonstrated
explosive behavior as expected during the first heating cycle. It was then cooled down again slowly and then re-heated for two more cycles. When the cooled droplet had a lower surface area of contact between the In rich phase and the Ga rich phase in the second and third cycles, the sudden expansion of the droplet was delayed to a higher temperature (268 K), and it did not last as long due to remixing soon after. Furthermore, we looked at remelting of EGaIn droplets that are not cross-sectioned to eliminate any possible contribution from the Xe-plasma ion milling. A fully intact oxide layer does not inhibit the observed morphological changes, as shown in supplementary video A. These explosions were not repeatable neither in small droplets, with a width below 30 μm, nor in larger ones with a width above approx. 100 μm.

Figure 3: in-situ SEM imaging of the f-EGaIn droplet (droplet width is ~ 60 μm and field of view is ~ 90 μm x 60 μm) during several cycles melting and stage cooling. (please see supplementary videos B-D)

The peculiar remelting behavior of frozen EGaIn is expected to result from the formation of metastable \( \gamma \)-Ga phase during the quenching at higher cooling rates resulting in higher undercooling of the liquid\(^{20} \). Ultimately, the dendritic In-rich phase in f-EGaIn in Fig. 1 proves
further that the cooling rate was too fast for a eutectic solidification that would lead to a lamellar or rod-like microstructures\textsuperscript{21}. The smaller difference between densities of $\gamma$-Ga and liquid Ga as compared to that of $\alpha$-Ga, leads theoretically to a lower nucleation barrier. Interestingly, a calculation of surface tensions between alpha and $\gamma$-Ga phases and In (Fig. S8) shows that $\gamma$-Ga is more likely to dominate at temperatures lower than 240K. The metastable $\gamma$-Ga shifts the entire system from eutectic to hypereutectic, as explained by the phase diagram in Fig. S9. Upon reheating, $\gamma$-Ga melts at a temperature lower than expected for $\alpha$-Ga, in agreement with previous measurements\textsuperscript{22,23} showing a size-effect in the melting points due to the formation of different metastable phases associated to the confinement within small Ga droplets. Tang et al. also observed by in-situ TEM study that during reheating that $\gamma$-Ga melted before In in phase-separated nanoparticles\textsuperscript{8}, and this is underpinned by a size dependence on the melting point depression in Ga-In nanoparticles\textsuperscript{24}.

The formation of one or more metastable Ga phases also explains the expansion behavior we are observing. Metastable Ga phases have higher densities, i.e. smaller molar volumes, than $\alpha$-Ga – i.e. the molar volume of $\gamma$-Ga is half of the equilibrium $\alpha$-Ga\textsuperscript{17}, which has a higher molar volume than liquid Ga\textsuperscript{25,26}. So, this expansion of frozen Ga upon heating could only happen from a metastable $\gamma$-Ga (or less likely $\beta$-Ga) phase rather than with $\alpha$-Ga. This leads to the formation of a “mushy” state containing liquid Ga and solid In phases, which transforms into liquid with the remnant proeutectic-In phases at higher temperatures, dissolving gradually as heating increases until the eventual full remixing. Future work shall address experimental ways of confirming the crystalline structures of supercooled EGaIn droplets. The small size of the droplets renders conventional techniques such as XRD (X-ray Diffraction) and DSC (Differential Scanning Calorimetry) not applicable in this case. The use of cryo-FIB along with APT and cryo-TEM (Transmission Electron Microscopy) techniques could address the
difficulties involved.

Figure 4: schematic showing a) the expansion upon remelting phenomenon observed in EGaIn and b) the proposed future use of the observations in this study.

To summarize, atomic-scale compositional analyses have shown that the two phases in EGaIn are practically immiscible, even at temperatures near the eutectic point, albeit there is some slow mixing seen using in-situ APT measurements, making the remixing process controllable. For now, we resort the origin of this behavior during rejuvenation of frozen EGaIn microdroplets to expansions of Ga metastable phases during melting in combination with their interaction with the In phase. Previous investigations have shown the surface tensions of Ga and In to rise with decreasing temperatures\textsuperscript{27,28}. Theoretical calculation correlates the interfacial energy in eutectic solids to the feature sizes of different phases, and thus the surface area of contact\textsuperscript{21}. We expect that future cryo-FIB tomography experiments could help clarify further the relationship between the surface area of In, undercooling, and size of droplet. The full extent of In’s contribution to the explosion of droplets is not completely clear, however we do observe expansion in the In-rich phase and increasing temperature is expected to cause a
volume expansion of pure In\textsuperscript{29} at cryogenic temperatures. Also, we can confirm from our experiments that the higher the surface area of the In phase, as defined by the extent of undercooling, the more probable is that the melting of Ga to result in these explosions.

To conclude, the results reported here highlight overlooked properties of EGaIn that could certainly help expand the usability of this alloy, and other low melting point alloys in general. The notion of repeatable volumetric expansion, summarized in Fig. 4a, in microscale EGaIn offer multiple opportunities for smart and flexible materials, where EGaIn droplets could be used for sensing different cooling rates and temperatures in cryogenic systems that rely on thermal cycling for functioning, as suggested in Fig. 4b. Exploiting the explosive expansion requires controlling both the size of the droplets and how finely and distributed is the In-rich phase throughout the EGaIn droplet which in turn depends on the cooling rate of these droplets. The size of the droplets reported here were expressed in terms of the shortest length, as each droplet has a non-uniform shape and thickness. Full realization of droplet volumes will also be done in the future using cryo-FIB tomography and better control of size and shapes could be reached by using e.g. microfluidics\textsuperscript{30}. Future work should delve into the possibilities lying behind this phenomenon and ways of controlling it.

**Methods**

*SEM Analysis*

Fastly-cooled droplets with dimensions of \(~1\text{ mm}\) were frozen by plunging in liquid nitrogen, followed by transferring via a cryo-enabled ultra-high-vacuum suitcase from a glovebox into the pFIB\textsuperscript{31}. Slowly-cooled droplets, were simply cooled on the stage of the cryo-pFIB (the cooling rate of 0.02 K sec\textsuperscript{-1}).
**APT on EGaIn**

We prepared atom probe specimens, following the approach outlined in Ref.\(^31\), from a liquid droplet of EGaIn attached to a commercial atom probe Cu clip (see Fig. S10) subsequently either fast or slow cooled. To avoid Ga ion beam damage, a Xe-plasma FIB (pFIB) equipped with a cryo-stage described in Ref.\(^{13,32}\) was used to perform cross-section SEM imaging. Two samples were quenched via different freezing processes. For slow-cooled EGaIn, referred to thereafter as s-EGaIn, a EGaIn droplet was transferred onto the stage of the pFIB. EGaIn has extremely low vapor pressure\(^33,34\) and, therefore, no deformation or phase transformation is likely occurred to the loaded EGaIn liquid droplet. Then, the pFIB stage was cooled by pouring liquid nitrogen (77 K) into the attached dewar until the stage temperature reached approx. 123 K. The temperature profiles for heating and cooling stage are shown in Fig. S11. This process took approx. 2h. For the fast quenched EGaIn sample (i.e. f-EGaIn), the EGaIn droplet was plunged into liquid nitrogen for 5 mins inside a glovebox. The sample was then loaded in a cryogenic ultra-high vacuum (cryo-UHV) suitcase and transferred to the pFIB for APT specimen fabrication. After fabrication, APT specimens were transferred via this cryo-UHV suitcase into a Cameca LEAP 5000 XS for atom probe analysis (see Fig. S12).

**In-situ APT analysis on f-EGaIn**

To investigate effects of temperature increase on the In content in Ga phase, f-EGaIn specimen was taken out of the analysis stage (30 K at 10 \(^{-11}\) torr) and was placed on a room-temperature buffer carousel (291 K at 10 \(^{-9}\) torr) for a certain times (0 to 1800 sec) for low-temperature heat treatment. Then the specimen was quickly loaded to the analysis stage again for APT measurement. This process was repeated for every 1.5 million ions collected to study heat-treated compositions.

We do not have a direct measurement of the temperature of the sample during each aging step, however, using a calculation outlined in the Supplementary Information, we could estimate the
temperature of the Cu puck after 1800 sec to be 284.4 K that is lower than the melting point. We are sure however that the specimen remained in the solid state due to the simple fact that the APT tip remained in shape.

Parameter Optimizations for APT on EGaIn
When operated in voltage-pulsing mode, APT analysis shows peaks pertaining to the two natural isotopes of Ga (69 and 71 Da). However, in laser-pulsing mode, despite sweeping through many experimental parameters, no peaks were detected (see Fig. S13a). This may be related to either a lack of laser light absorption or simply to the induced heating that generates a liquid layer that continuously field evaporated from the apex at the DC field35. This is rather likely since both Ga (15 V nm⁻¹) and In (12 V nm⁻¹) have amongst the lowest evaporation fields – i.e. the critical field necessary to provoke field evaporation36. To find optimal conditions for liquid metal APT measurement, voltage-mode field evaporations were performed at different pulse frequencies (Fig. S13b) and by sweeping the stage temperature from 30, 60, to 100 K (Fig. S14). Mass resolution, noise level, and detector histogram maps improve as the stage temperature decreases, which indicates that the liquid metal is more sensitive to the stage temperature than typical metal samples (e.g. steel37). The noise level at 30 K is three orders of magnitude lower than at 100 K and we were able to identify partial structural information from within the data38. Details on mass spectrum analysis are discussed in the Supplementary Information.
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**Author contributions**

All authors designed the experiments, discussed and interpreted the results. S.-H.K., A.A.E.-Z., and L.T.S. performed the experiment. A.A.E-Z. performed in-situ remelting pFIB experiments. L.T.S. and B.G. designed, managed and organized the cryo-UHV imaging, analysis and transfer system. S.-H.K. and A.A.E.-Z. prepared the samples, performed electron analyzed the atom probe datasets with B.G. A.KdS. performed the thermodynamic calculations. All author drafted the manuscript. All authors contributed and have given approval to the final version of the manuscript.
Supporting Information

Phase Separation in Frozen Microscale Eutectic Indium-Gallium and its Explosion upon Remelting

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**Fig S1.** A schematic illustration of solidification of a liquid EGaIn micro-droplet at different cooling rates.

**Fig S2.** BSE Images of (a) f-EGaIn and (b) s-EGaIn droplets before remelting for allocating of In (purple dot) and Ga (light-blue dot) Phases. Bright contrast indicates a heavier element region (In) (scale bars a: 30 μm, b: 40 μm).
**Fig S3.** In-situ SEM imaging of the s-EGaIn droplet on a temperature-controlled stage whilst remelting due to gradual increase in temperature (scale bars a: 40 µm, b: 50 µm, c: 50 µm).

**Fig. S4.** Experimental In-In (purple line) and Ga-Ga (yellow line) first nearest-neighbor distance along with simulated Gaussian curves (grey lines) from (a) In-rich and (b) Ga-rich regions in f-EGaIn.
Fig. S5. 1D atomic compositional profile along cylindrical region of interest across the interphase interface (ϕ10 x 30 nm³) in Fig. 2g. Inset tomogram shows an example of locally enriched Ga atoms within the reconstructed In-rich phase in the f-EGaIn sample (scale bar 5 nm).
Fig. S6. (a,b) Cross-sectional FIB-SEM images of s-EGaIn sample (scale bar a: 20 µm, b: 10 µm). 3D atom maps of (c) Ga region and (d) In region (scale bar c: 20 nm, d: 10 nm). The crystallography of Ga and segregation behavior of Ga in In rich phase are discussed in Fig. S15.

Table S1. Atomic compositions of each phase for f- and s-EGaIn samples obtained from APT analysis.

|                | Ga at.%   | In at.%   |
|----------------|-----------|-----------|
| f-EGaIn (plunge freezing in N\textsubscript{20}) |           |           |
| Ga-rich region | 98.83     | 1.17      |
| ±0.02          | ±0.02     | ±0.02     |
| In-rich region | 2.74      | 97.26     |
| ±0.01          | ±0.01     | ±0.01     |
| s-EGaIn (cooled on cryo-stage) |           |           |
| Ga-rich region | 99.99     | <0.0003   |
| In-rich region | 0.73      | 99.27     |
| ±0.01          | ±0.01     | ±0.01     |
Fig. S7. (a) In-situ heat treatment at room temperature of Ga-rich APT specimen from an f-EGaIn sample for 0, 2, 10, 20, 30, 40, 80, 120, 180, 300, 600 and 1800 sec. (b) The atomic compositions of solute In atoms in each aging time. Inset shows the Pearson coefficient variation for In (μIn) in Ga-rich phase along with each aging time. In-In nearest-neighbor analysis indicates no segregation at all. The Pearson coefficient associated to a χ² statistical test of the frequency distribution of In in the Ga-rich phase is measured to between 0.05 and 0.12 for all times (0 indicates complete randomness and 1 means a completely separated mixture) thereby confirming a tendency for randomness of In in Ga-rich phase.
Fig S8. Coherent interfacial energy between the possible Ga-rich phases (α-Ga and γ-Ga) and (a) the liquid phase and (b) BCT-A6 In-rich phase. The values were calculated using the Becker’s bond energy approach as implemented in the Thermo-Calc software in conjunction with the G35 Binary semiconductors thermodynamic database. Values should be use with care, since interfacial energy is dependent on many factors that are ignored in the coherent estimation (e.g., incoherency, orientation, and curvature).[1]
Fig S9. Explanation of the “mushy state” leading to explosion of microdroplets (scale bars: 20 µm).
Fig. S10. Liquid metal preparation for APT specimen fabrication. First, an EGaIn droplet was placed on a clean glassware. Then, a flat Cu clip was pressed down on the droplet. Ga-oxide layer has a high adhesive strength and therefore parts of a liquid EGaIn stuck with a commercial Cu clip and it could easily be placed on the clip.

Fig. S11. Temperature profiles when the cryo-FIB stage is (a) cooled down to -150 °C (with liquid nitrogen) and (b) heated up to 20 °C (with a 40 °C heating system).
**Fig. S12.** (a) Top view of the final APT specimen from s-EGaIn. Note that there are grain boundaries of EGaIn (scale bar: 300 µm). (b) An example of an APT specimen (scale bar: 500 nm). (c) Optical image of APT specimen and local electrode inside the 5000 XS analysis chamber.

**Fig. S13.** (a) Collected time-of-flight signals from pulsed-laser and pulsed-voltage mode. (b) Pulse frequency versus background level in voltage mode. For preliminary studies, we measured the liquid EGaIn metal using both laser and voltage mode in 5000 XS system. Using the voltage mode, we collected clear signals with distinct time-of-flights, however, using laser mode we were not able to collect any noticeable signals. Therefore, we measured all liquid metal sample using voltage mode.
The mass spectrum of the corresponding 3D atom map in Fig. S6c shows that major peaks detected are $^{69}\text{Ga}^+$ and $^{71}\text{Ga}^+$. Some Ga complex peaks are detected, as Ga evidently tends to evaporate in clusters. D.L. Barr investigated Ga ion emission from liquid Ga sources using a time-of-flight spectrometer and also found Ga$_n^+$ molecular ions with $n$ ranging up to 30 [2].
Fig. S15. (a) Normalized spatial distribution map of Ga atoms in Fig. S6c. (b) Ga-Ga nearest neighbor distance in Fig. S6d. We performed Ga-Ga nearest neighbor analysis from an In phase dataset. Ga phase in s-EGaIn sample was not investigated since the composition of solute In is too low to be analyzed (<10 ppm). The collected Ga-Ga distance distribution was compared with a randomized Ga distribution, in which the atomic position is unchanged but the mass-to-charge ratio are randomly swapped.

The analysis of the Ga-rich phase shows a crystallographic pole and the associated set of atomic planes in Fig S6c. The element-specific spatial distribution map (SDM) calculated along the pole orientation within the reconstructed dataset aids in determining the interplanar distance and could be used to optimize the reconstruction [3]. Here, due to the complexity of the α,γ-Ga structures, the orientation could not yet be identified. Nevertheless, we detected a periodicity of Ga atoms (see Fig. S15a) and with aids of cryo-electron diffraction in future work, the orientation can be identified. Fig. S15b shows the experimental Ga-Ga distribution, which deviates from the randomized Ga distribution, evidencing a tendency for Ga atoms to phase separate from the In-rich phase in the s-EGaIn sample.
Calculating the Cu puck temperature.

To estimate the temperature profile of EGaIn APT sample during the in-situ heat-treatment experiments, a semi-infinite solid, unsteady-state solution is used. The heat convection to the EGaIn specimen is negligible as the buffer pressure, where the sample is placed, is as low as 10⁻⁹ torr. When the Cu puck (with EGaIn specimen) is taken out from the analysis chamber to the buffer chamber, the puck is contacted with a room-temperature buffer carousel. Since the heat reservoir of a buffer carousel is much larger than that of the Cu holder, the following equation is used for the temperature estimation:

\[
\frac{T(x, t) - T_s}{T_i - T_s} = \text{erf} \left( \frac{x}{2\sqrt{\alpha t}} \right)
\]

, where \( T_s \) is the reservoir’s surface temperature (i.e. buffer carousel temperature), \( T_i \) is the initial temperature of Cu puck, \( x \) is distance from the contacted surface to EGaIn sample (0.02m), \( t \) is contacted time in sec, and \( \alpha \) is the thermal diffusivity of Cu (0.000111 m² sec⁻¹).

![Temperature-time profile for the surface of the Cu clip at different time contacted with a buffer carousel.](image)

**Fig. S16.** Temperature-time profile for the surface of the Cu clip at different time contacted with a buffer carousel.

The calculated temperature profile of the Cu clip is shown in Fig. S16. Although the EGaIn sample was taken out for 1800 sec on a buffer chamber, it did not undergo a phase transformation to a liquid phase and the APT was performed without any noticeable micro-fractures. The estimated temperature of a Cu holder is calculated to be 11.4 °C which is still below the melting temperature of EGaIn. Moreover, considering the additional heat transfer to a cooled bulk EGaIn droplet (Fig. 2c) from a heated Cu clip, a lower temperature is likely expected at the maximum time of 1800 sec. While we saw phase changes and explosion in micro droplets at temperatures close to 0 °C. These in situ APT experiments could only be done on much bigger droplets where no explosion was observed. Thus, the rise in temperature of the droplet above 0 °C did not change the shape of the tip.
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