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Development of Gallium and Gallium-Based Small-Size Eutectic Melting Fixed Points for Calibration Procedures on Autonomous Platforms

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Abstract Melting/freezing temperature curves are studied for the single-component Ga and bimetallic eutectic alloys Ga–In, Ga–Sn, Ga–Zn, and Ga–Al in small-size cells. These phase-transition studies were conducted at VNIIOFI in order to design small-size fixed-point devices for metrological monitoring of temperature sensors on autonomous (e.g., space borne) platforms. The results show that Ga and some Ga-based eutectic alloys in small cells can be used as melting fixed points. The repeatability of melting temperatures of Ga, Ga–In, Ga–Sn, and Ga–Zn fixed points is studied. The effects of the concentration of the second element of Ga-based eutectic alloys and the thermal history on the melting plateau's shape and the melting temperature are studied.

Keywords Calibration · Gallium · Gallium-based eutectic · Small-size melting fixed point

1 Introduction

Along with ensuring that the practical temperature scale approaches the thermodynamic one with increasing accuracy, an important task is to add more (secondary) fixed points to the existing temperature scale. In this respect, the use of the isothermal eutectic phase transition looks especially promising as the list of eutectic alloys that can serve as fixed points greatly exceeds the list of pure metals.

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Along with possible improvements to the temperature scale, this approach may allow us to solve another important problem: to develop standard radiation sources based on phase transitions within the temperature range from 273 K to 310 K for the calibration of IR sensors installed on Earth observation space-borne platforms [1–3]. To properly monitor the stability of the instruments, onboard calibration devices having two or three fixed points within the afore-mentioned temperature range are needed. In addition to pure Ga, Ga-based bi- and tri-metallic eutectic alloys are possible candidates for this purpose.

The onboard (e.g., satellite borne) devices for fixed-point realization should be small, light, and consume a little power. Therefore, it is necessary to study the behavior of single- and multiple-component fixed points in cells that are much smaller than the standard cells used in precision thermometry. Hence, this work, mostly conducted at VNIIOFI, describe studies of small-size melting points on the basis of single-component Ga and the bi-metallic alloys Ga–In, Ga–Sn, Ga–Zn, and Ga–Al. The small cells, typically, contained (115–125) g of Ga or Ga-based alloys; note that the mass of substance in the standard metrological cell normally amounts to approximately 1 kg.

The melting/freezing eutectic transition is a much more complex phenomenon than the melting and freezing of a single-component metal, and we still do not have any eutectic fixed point of the same metrological quality as those of the fixed points based on pure metals. In order to execute the transfer from simple substances to eutectic alloys, one has to investigate the eutectic melting and freezing transitions that differ appreciably from the melting/freezing mechanisms for single-component metals. As the earliest studies of potential eutectic-based fixed points showed, unlike the case of single-component metals, the eutectic freezing temperatures have poor reproducibility. (This experimental fact highlights the significant differences between the melting/freezing-transition mechanisms in pure metals and eutectic alloys). Hence, the eutectic fixed points should be defined as melting points while all pure-metal fixed points of the ITS-90, with the exception of Ga, are defined as freezing temperatures.

2 Realization of Melting Fixed Points and Instrumentation

In our experiments with Ga and Ga-based eutectics, we used the dynamic method of melting as the fixed-point realization. A cell was placed into a liquid thermostat with a preset temperature offset above the melting temperature of the cell's substance. In this way, the melting process begins at the periphery of the cell; the offset value determines the melting rate of the substance. The experiments with prospective fixed points based on gallium and gallium eutectics were conducted under automatically repeated melt/freeze cycles, with 3–7 cycles per measurement series. The time and temperature parameters of these thermal cycles were selected on the basis of preliminary studies of the effects of melting rate and thermal history on the quality of the melting plateau. ("Thermal history" is the succession of preceding melt/freeze cycles).

Normally, a cell filled with one substance was changed to a cell filled with another substance after each series of measurements. Thus, the series of measurements with the same substance were separated by time intervals during which other substances were studied. It was believed that the results accumulated with such a protocol are

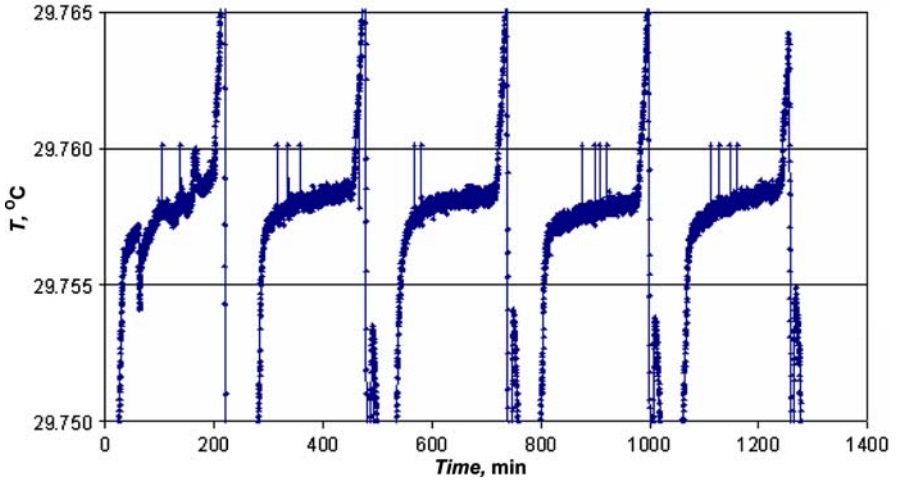

Fig. 1 Series of high-quality Ga melting plateaux

more reliable with respect to the overall repeatability of the fixed point under study. The thermal cycles were organized in such a way that, by the beginning of the current measuring melting stage, the substance within the cell would be to the maximum possible degree in the same state with respect to its thermal history.

The temperature within the cell's thermowell was measured with a miniature reference PRT (stability 2.5 mK per year at 0 °C) that was always placed at the bottom of the thermowell. To improve the thermal contact between the PRT and the cell, the cell's thermowell was filled with mineral oil. The entire measurement system was calibrated using a secondary temperature standard traceable to the Russian National Temperature Scale. The calibration was based on three points: the gallium melting point, 0 °C, and 20 °C, the latter two as realized in the temperature standard's thermostat within ±1 mK of the desired value. The intermediate point at 20 °C was selected because of its position in the middle of the interval between the lowest and highest melting temperatures of our eutectic alloys: ∼15.7 °C for Ga–In, ∼27 °C for Ga–Al; it is also close to the melting temperature of Ga–Sn (∼20.5 °C).

3 Determining the Melting Temperatures of Gallium and Gallium-Based Eutectic Fixed Points

Determining the gallium melting temperature in a small cell created no problems; as a rule, the Ga melting plateau stayed practically horizontal for about 2 h, and the Ga heating curve had a short relaxation time (Fig. 1). Fluctuations of temperature on the melting plateau did not exceed 1 mK so that the average temperature within the steady part of the plateau could be regarded as the Ga melting fixed point. In those cases when a slight drift was observed in the melting temperature (2–3 mK in 2–2.5 h), the Ga melting fixed point was taken to coincide with the "run-off point." The latter is defined as the end point of the linear portion of the melting curve [4].

For the eutectic alloys Ga–In, Ga–Sn, Ga–Zn, and Ga–Al whose melting plateaux were always tilted (the degree of tilt depended mostly upon the type of eutectic), the fixed point was always defined as the run-off point. In our mode of fixed-point realization, when the melting process is initiated only from the periphery of the cell, the melting front passes the vicinity of the thermowell at the later, final part of the plateau. Consequently, the thermometer's readings at the run-off point are close to the temperature at the boundary between the liquid and solid phases, that is, to the liquid–solid equilibrium temperature.

The experience acquired in the course of this study shows that the difference between the run-off point and the melt-off point (the temperature at which the eutectic part of the sample is fully melted) does not exceed (2–3) mK and is practically independent of the type of eutectic (with the exception of Ga–Al). However, estimates of the melt-off point (when the temperature of the sample starts to increase rapidly [4]) are more subjective than the determination of the run-off point that is both easier to see and to computerize. At the same time, it should be noted that estimates of any characteristic points on the melting curves contain a certain degree of subjectivity.

4 Results of Investigating the Gallium Melting Point in a Small Cell

First, the Ga melting point in a small cell containing 123 g of gallium was compared with its analog in a standard metrological cell. The temperature in the standard cell was measured using the secondary Ga melting fixed-point standard traceable to the Russian National Temperature Scale. All measurements were made with the same equipment, including the miniature thermometer. The Ga melting temperature measured in the small cell immediately after the measurements in the standard cell was 8 mK lower (Fig. 1). The high quality of the melting plateaux of Ga in the small cell proves that the difference cannot be ascribed to impurities in the Ga (one of the best series of the Ga melting plateau is shown in Fig. 1).

The temperature drift on the Ga melting plateau remains within (2–3) mK over (2–2.5) h even for relatively low-quality plateaux (see the first plateau in Fig. 1). The high quality of the Ga melting plateaux realized in a small cell containing only 123 g of substance looks especially significant if one takes into account that the melting rate of the substance was intentionally set much higher than in the standard case. (In our experiments, the temperature offset was about 1.24 °C, which is much higher than for the standard approach to realize the metrological Ga melting point when the plateau may last for dozens of hours). In addition to the higher melting rate, we never initiated an internal melting front around the thermowell—another intentional simplification of the standard procedure. This "coarsening" of the experiment was believed to be necessary to study automated calibration procedures on autonomous platforms using the simplest possible approach to the melting fixed-point realization.

After comparing the Ga melting temperature in standard and small cells, the repeatability of the small-size Ga melting point was thoroughly studied. For these experiments, the thermostat temperature was always set at 31 °C during the melting (measuring) stage. The repeatability of the small-size Ga melting point within each series of measurements turned out to be very high (0.5–1.5) mK. Commonly, the repeatability in

Table 1 Summary of measurements of the repeatability (1σ) of gallium melting fixed point in a small cell

Substance	Repeatability (1σ) in individual series (mK)	Overall repeatability ($1\sigma_{ov}$) (mK)
Ga	0.5–1.5	2.3

individual series of melt/freeze cycles is understood as the actual fixed-point repeatability observed under identical (to the maximum possible extent) experiment conditions. The repeatability of the entire dataset (the overall repeatability) defines the upper limit for the variability of measured melt transition temperatures (Table 1). The overall repeatability is lower than the repeatability in individual series, yet its value looks quite optimistic with regard to the development of the small-size Ga melting point.

It is often mentioned in the literature that Ga has a tendency for deep (sometimes even "gigantic": up to (50–70) °C) supercooling during the freezing stage. This property of high-purity Ga would be very inconvenient if a gallium-based fixed point is used to automatically calibrate sensors installed on autonomous platforms. However, in all our experiments with Ga in a small Teflon cell that included more than 50 melt/freeze cycles, the supercooling never exceeded ∼1 °C. An ∼5 °C supercooling was observed after intentional overheating of the melted Ga to (50–60) °C. This dependence of supercooling upon the degree of the previous overheating means that, in the vicinity of the phase-transition temperature, liquid Ga has a clustered structure. The clustering of liquid Ga under those conditions may be regarded as an alternative reason why Ga can only be used for a melting point. (In this respect, Ga seems to be closer to eutectic-based fixed points than to single-component metal-based fixed points).

The freezing of high-purity Ga occurring without deep supercooling was described as long ago as 1978 [5]. Similar to our study, those experiments were conducted with a small cell containing about 40 g of Ga; the cell materials were both Teflon and nylon. The authors of [5] assume cautiously that no deep-supercooling effect can be explained by the use of nylon for the thermowell since nylon, in contrast to Teflon, is well wetted with liquid Ga. Indeed, this effect is well known in the theory of crystallization: the freezing on the surface of the melt begins with no supercooling if the underlying material is well wetted with the melt. However, the moderate supercooling found in this study must have been caused by other physical factors because our cells were made entirely of Teflon. According to our conjecture, the size of the cell seems to be the most probable factor that might have caused this phenomenon.

Though we still do not fully understand why Ga behaves in such a way in small cells, this low-supercooling behavior makes it easier to apply the small-size Ga melting point to automatic calibrations of instruments on autonomous platforms. If one has a Ga melting point in a small cell with sufficiently good metrological characteristics, just 1 or 2 additional eutectic fixed points in a small cell would be enough for the purpose (1 or 2 eutectic fixed points that showed the best melting plateau shape and repeatability among all the studied gallium-based eutectics). This set of fixed points will be sufficient to develop a detailed calibration scale for sensors on autonomous platforms that would be based on a pure Ga fixed point along with eutectic fixed points within the temperature range from 10 °C to 30 °C. (Obviously, it is desirable that the interval between the selected fixed points would be as wide as possible).

Table 2 Composition of gallium-based eutectics

Gallium eutectic alloys	Sample marking	Alloy mass (g)	Composition (mass%)	Nominal eutectic composition[a] (mass%)
Ga–In	Ga–In-1	124.3	∼18% In	(18.8–22.9)% In
	Ga–In-2	130.2	24.4% In	
Ga–Sn	Ga–Sn-1	119.3	13.8% Sn	(12.8–13.8)% Sn
	Ga–Sn-2	120.0	20% Sn	
Ga–Zn	Ga–Zn-1	116.5	3.7 % Zn	(3.5–5.1)% Zn
Ga–Al	Ga–Al-1	125.9	1.68% Al	∼ 1.67% Al
	Ga–Al-2	120.5	2.65% Al	

[a] Eutectic composition is shown according to [6]

5 Composition of Gallium-Based Eutectic Alloys Selected for the Fixed Points

The parameters of the cells filled with Ga-based eutectic alloys and with pure gallium are given in Table 2 below (all cells were made of Teflon). The purity of metals used in our experiments was 6 N for Ga and In, 5 N for Zn, and 5–6 N for tin and aluminum.

We varied the concentration of the second component (Table 2) with respect to the nominal eutectic composition [6] in order to study the influence of the alloy's composition upon the eutectic melting temperature as measured in our experiments. ("Eutectic melting temperature" means the melting temperature of the eutectic part of the sample. It coincides with the liquidus point for the whole sample in the case when the latter has the unique/true eutectic composition). As seen from Table 2, finding the true eutectic composition remains an unresolved problem. At best, it is known to a 10th of a percent, but usually within only a few percent (see Table 2). However, many authors (e.g., [7,8]) believe that eutectic fixed points should be prepared in accordance with the best knowledge of the true eutectic composition; according to their experience, the alloy's composition influences the eutectic melting temperature determined experimentally as well as its repeatability. However, in a recent paper [4], it was shown that the eutectic melting temperature determined experimentally (repeatability of the order of 1 mK) for the Cu–Al eutectic alloy is independent of the mixing ratio of the components. In this work, we tried to shed some light on this problem as well.

6 Results of Investigating Gallium-Based Eutectic Melting Points in a Small Cell

This part of the study included the following stages:

- Studying the heating curves of Ga–In, Ga–Sn, Ga–Zn, and Ga–Al in small cells and determining the eutectic melting temperatures and their repeatability for prospective small-size Ga–In, Ga–Sn and Ga–Zn melting points.
- Studying the dependence of the measured eutectic melting temperature of alloys $Ga(1-x)In(x)$, $Ga(1-x)Sn(x)$, and $Ga(1-x)Al(x)$ on the concentration x of the second component. These experiments were conducted in three pairs of cells, two

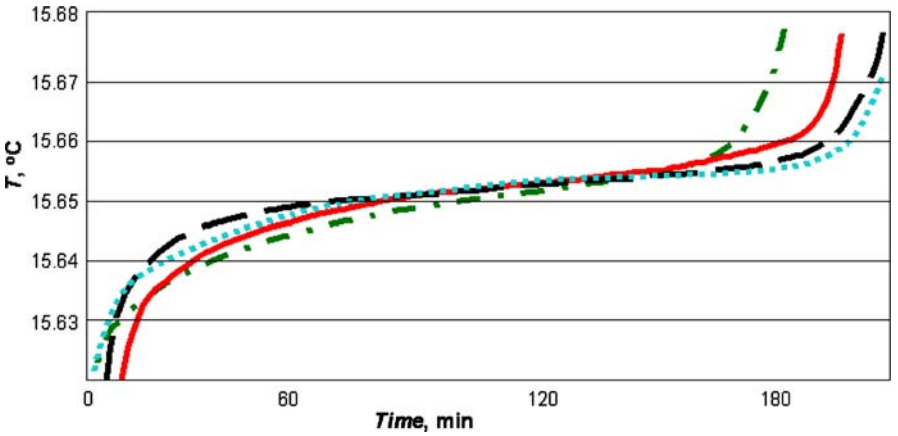

Fig. 2 Series of high-quality Ga–In-2 melting plateaux

for each eutectic alloy with different concentrations of the second component—In, Sn, and Al (Table 2).

- Studying the dependence of melting plateau quality on the thermal history of the eutectic alloy. In these experiments conducted for Ga–In, Ga–Sn, and Ga–Zn fixed points, the parameters of preceding melt/freeze cycles were varied.

Similar to the experiments with pure Ga, the experiments with Ga-based eutectics were executed as an automated series of melt/freeze cycles. The temperature within the thermostat during the cycles was higher than the eutectic melting temperatures by approximately 1.5 °C. The optimal value of this offset was selected mostly on the basis of the melting plateau's quality and the ability to accurately determine the run-off point on the curves. However, the desirable velocity (time) of melting fixed-point realization during automated calibration procedures on autonomous (e.g., space borne) platforms was also taken into account.

6.1 Melting Temperature and Repeatability of $Ga(1-x)In(x)$ Eutectic Melting Points in a Small Cell

The compositions of the alloys in cells Ga–In-1 and Ga–In-2 were selected in such a way that they would not differ much from the approximate eutectic composition [6]. With a large degree of certainty, the Ga–In-1 cell contained a slightly hypoeutectic alloy while the substance in the Ga–In-2 cell was slightly hypereutectic.

The thermostat temperature during the melting stage was set at 17 °C in all series of measurements during the experiments with the Ga–In eutectic fixed point (temperature offset ∼1.35 °C). High-quality melting plateaux of the Ga–In-2 eutectic fixed point are shown in Fig. 2. A steady part as observed on the best melting plateaux for pure Ga is never revealed clearly on the melting plateaux of Ga–In and other eutectic alloys. This difference, which has been observed in many experiments, can only be explained by the much more complicated mechanism of the eutectic phase transition.

Table 3 Summary of measurements of the average melting temperature and repeatability (1σ) of $Ga(1-x)In(x)$ eutectic melting fixed points in a small cell

Alloy	Average melting temperature (°C)	Repeatability (1σ) in individual series (mK)	Overall repeatability ($1\sigma_{ov}$) (mK)
Ga–In-1	15.655	1–1.5	2.2
Ga–In-2	15.655	1.5–2	3.0

Table 3 gives the average eutectic melting temperature and its repeatability (1σ) for the Ga–In-1 and Ga–In-2 eutectic alloys estimated on the basis of 17 and 24 melting plateaux, respectively. As seen from the table, the repeatability within individual series of experiments with the Ga–In fixed point is markedly higher than the overall repeatability, which is determined over the entire set of data. Similar to the single-component Ga, this is true for all other Ga-based eutectic alloys.

The exact agreement of the estimated average Ga–In-1 and Ga–In-2 fixed points (within 1 mK) must be fortuitous, but the high overall repeatability of the Ga–In-1 and Ga–In-2 melting temperatures allows us to arrive at the preliminary conclusion that the measured melting temperature of the eutectic alloy $Ga(1-x)In(x)$ does not depend on the concentration x of the second component.

6.2 Melting Temperature and Repeatability of $Ga(1-x)Sn(x)$ Eutectic Melting Points in a Small Cell

The compositions of the alloys Ga–Sn-1 and Ga–Sn-2 were selected in such a way that Ga–Sn-1 was approximately eutectic [6] while the cell with Ga–Sn-2 was definitely hypereutectic. The thermostat temperature during the melting stage was set at 22 °C for all the measurements with the Ga–Sn eutectic fixed point (temperature offset ∼1.5 °C). High-quality melting plateaux of the Ga–Sn-1 eutectic fixed point are shown in Fig. 3.

Table 4 gives the average eutectic melting temperature and its repeatability (1σ) for the Ga–Sn-1 and Ga–Sn-2 eutectic alloys estimated on the basis of 15 and 13 melting plateaux, respectively. Similar to the Ga–In case, it can be suggested that the high overall repeatability of the Ga–Sn-1 and Ga–Sn-2 melting fixed points allows us to arrive at a preliminary conclusion that the melting temperature of the eutectic alloy $Ga(1-x)Sn(x)$ is independent of the concentration x of the second component.

6.3 Melting Temperature and Repeatability of Ga–Zn Eutectic Melting Point in a Small Cell

Experiments with the Ga–Zn alloy were conducted in one cell only. The composition of the alloy seems close to the eutectic [6]. In contrast to the experiments with Ga–In and Ga–Sn, the measurements with the Ga–Zn-1 cell were made with different thermostat temperatures during the melting ((26.5, 27, and 27.5) °C). This was done in order to find the optimal thermal parameters for experiments with the Ga–Zn melting point. A typical series of Ga–Zn-1 melting plateaux is shown in Fig. 4 (thermostat temperature

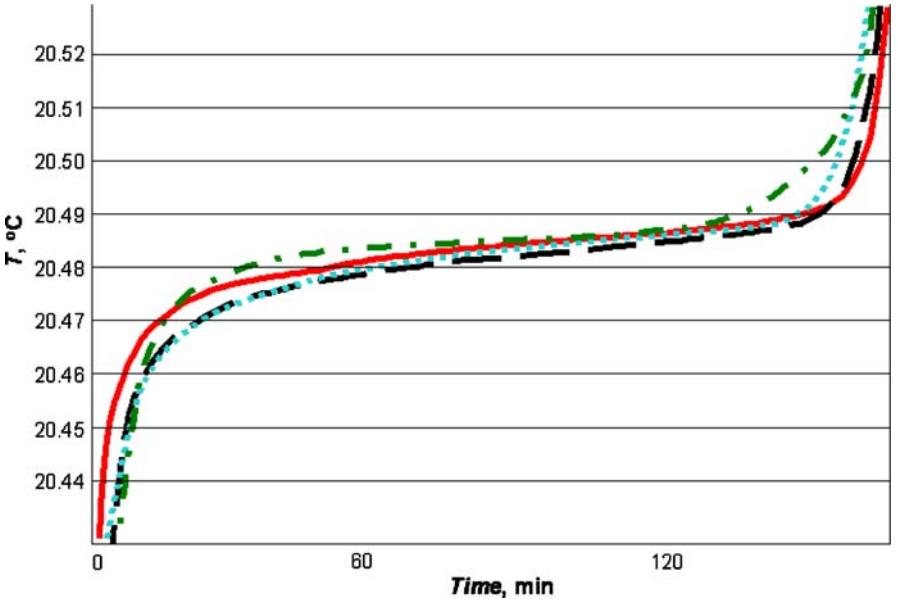

Fig. 3 Series of high-quality Ga–Sn-1 melting plateaux

Table 4 Summary of measurements of the average melting temperature and repeatability (1σ) of $Ga(1-x)Sn(x)$ eutectic melting fixed points in a small cell

Alloy	Average melting temperature (°C)	Repeatability (1σ) in individual series (mK)	Overall repeatability ($1\sigma_{ov}$) (mK)
Ga–Sn-1	20.482	0.8–1	2.7
Ga–Sn-2	20.483	1–1.5	2.4

27 °C, temperature offset ∼1.8 °C). This figure demonstrates why the search for an optimal thermal mode for the Ga–Zn melting fixed point took so much effort: the scatter of the Ga–Zn melting plateaux is much greater than in the cases of Ga–In and Ga–Sn. Changing the thermostat temperature (that is, changing the melting rate) did not result in a more stable melting plateau nor a smaller uncertainty of the melting temperature estimates. Therefore, we do not show the measurements with the Ga–Zn-1 cell obtained for other thermostat temperatures; in general, these results are sufficient only to estimate the average Ga–Zn eutectic melting temperature. Respective quantities obtained on the basis of 29 melting plateaux are given in Table 5. However, we believe that the Ga–Zn eutectic fixed point should be studied further because it has a well-shaped melting plateau with a well-defined run-off point (Fig. 4).

A feature of this alloy is the slow increase in its temperature beyond the end of the eutectic melting plateau as compared to Ga–In and Ga–Sn. The rate of growth may become so low (admittedly, depending on thermal history) that the Ga–Zn alloy's temperature does not reach the temperature of the thermostat (27 °C) even after 4 h.

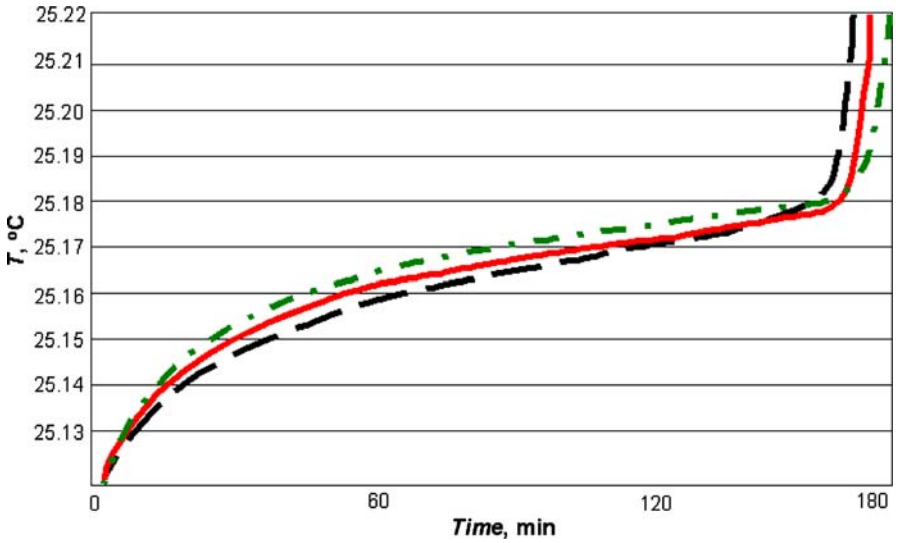

Fig. 4 Typical series of Ga–Zn-1 melting plateaux

Table 5 Summary of measurements of the average melting temperature and repeatability (1σ) of Ga–Zn eutectic melting fixed point in a small cell

Alloy	Average melting temperature (°C)	Repeatability (1σ) in individual series (mK)	Overall repeatability ($1\sigma_{ov}$)(mK)
Ga–Zn-1	~ 25.19	2–3.5	8

(Ga–In and Ga–Sn alloys come to thermal equilibrium with the thermostat in ~1.5 h after the eutectic part of the sample has melted).

6.4 Investigation of Ga–Al Melting Plateaus in a Small Cell

The compositions of the alloys Ga–Al-1 and Ga–Al-2 were selected in such a way that Ga–Al-1 was approximately eutectic [6] while the cell with Ga–Al-2 was definitely hypereutectic. The thermostat temperature was set at 28.5 °C during the melting stage for all measurements so that, similar to the Ga–In and Ga–Sn cases, the offset with respect to the eutectic melting temperature was close to 1.5 °C. However, in spite of the similarity in the thermal conditions, the Ga–Al melting plateaux differ markedly from the plateaux of Ga–In, Ga–Sn, and Ga–Zn: it is 10 times shorter and badly tilted (Fig. 5 shows the Ga–Al-1 plateaux).

Surprisingly, the rate of temperature growth in the Ga–Al cell after the eutectic melting plateau, on the contrary, becomes much slower than in the cells with Ga–In and Ga–Sn. (This is similar to the Ga–Zn alloy, although melting plateaux of Ga–Zn and Ga–Al per se drastically differ). A possible explanation is the gradual randomization of the clustered quasi-eutectic structure that exists in the liquid eutectic phase of the

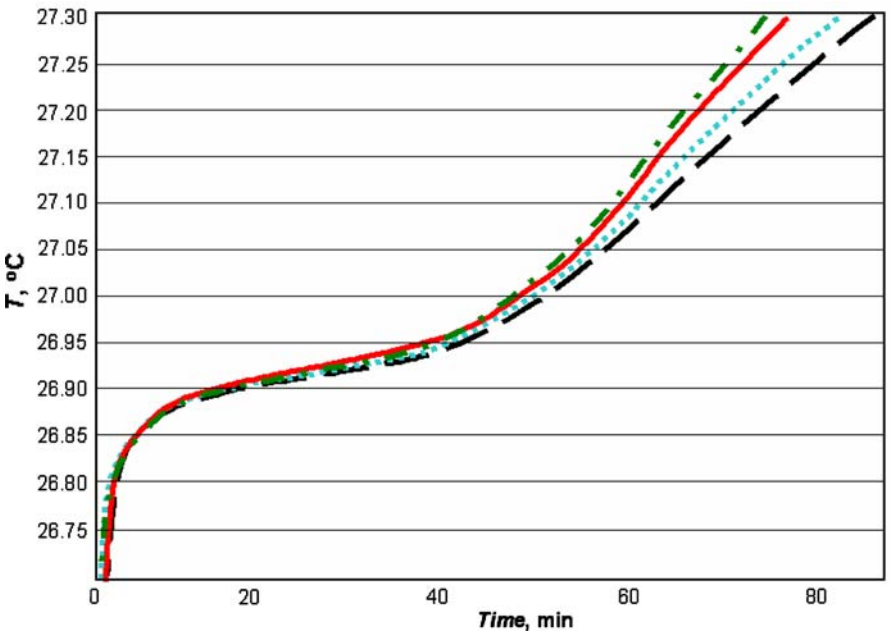

Fig. 5 Typical series of Ga–Al-1 melting plateaux

Ga–Al and Ga–Zn alloys near the transition point. This randomization occurs beyond the melting plateau with the alloy's temperature growth and presumably results in the change of the system's enthalpy. This may also be true for the Ga–In and Ga–Sn alloys, although the randomization processes above the eutectic transition temperature in these cases are probably faster and produce less thermal effects.

The Ga–Al-2 melting plateaux are identical, so we do not show them. Nevertheless, our approximate estimate of the average Ga–Al-1 and Ga–Al-2 melting temperatures (∼27 °C for both cells) do not contradict our preliminary conclusion that the eutectic melting temperature is independent of alloy concentration.

7 Effect of Thermal History on the Eutectic Melting Plateau

We began this study on the basis of the results obtained in [8] where recommendations for the thermal preparation of gallium-containing eutectic alloys for the purpose of obtaining a fixed point were proposed using a Ga–Sn alloy as an example. According to [8], the melting stage during which the fixed-point temperature is measured should follow crystallization of the sample from the state of partial melting (velocity of crystallization is not a key parameter). After that, the Ga–Sn melting plateau turned out to be flat, and the fixed-point temperature value, detected from the melting curve, proved to be highly reproducible.

Experiments with Ga–In, Ga–Sn, Ga–Zn, and Ga–Al alloys were conducted, inter alia, to check the proposed method and clarify the physical basis for the observed

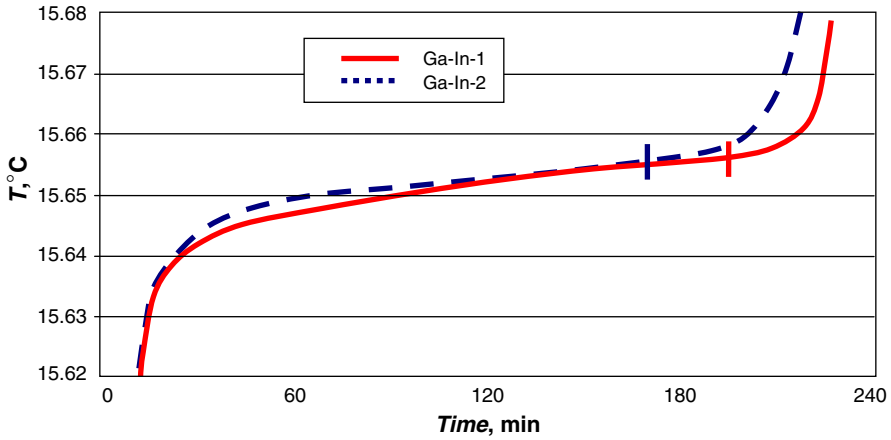

Fig. 6 High-quality Ga–In plateaux depending on thermal history

correlation between the parameters of the preliminary thermal cycle and the subsequent melting plateau's temperature characteristics. The study demonstrated that the method of 'partial melting' during the preliminary melt/freeze cycle improves the melting curve's shape. Recently, the same result was obtained for the Cu–Al eutectic [4], with a substantially higher melting temperature, proving the similarity of the eutectic melt/freeze transition mechanisms for eutectic alloys of different chemical elements. More detailed investigation showed that the proposed method is not a unique way to obtain eutectic melting plateaux of high quality. Actually, the eutectic part of the sample can be fully melted at the preliminary stage but, according to the available results, the key parameter affecting the quality of the next melting plateau is the degree of overheating above the eutectic melting temperature. ("Degree of overheating" implies the maximum temperature that the sample reaches after the eutectic part is fully melted, and before cooling is initiated). Low overheating in the preliminary melt/freeze cycle leads to solidification with negligible supercooling, apparently under quasi-equilibrium conditions. Seemingly, such a freezing mode favors a good shape of the next (measuring) melting plateau.

Some typical melting plateaux depending on the thermal history are shown in Figs. 6 and 7 for the Ga–In-1 and Ga–In-2 cells. High-quality plateaux (Fig. 6) were obtained after low-supercooling crystallization preceded by either partial melting or low overheating (∼(0.2–0.3) °C) after the end of the melting plateau. Relatively, poor quality plateaux (Fig. 7) were obtained after crystallization was preceded by greater overheating (∼1.5 °C or more) above the melting temperature. Then, crystallization occurred with noticeable supercooling; in the case of intentionally "superfluous" overheating (to 60 °C), the supercooling turned out to be unexpectedly large (up to (15–18) °C) for all the investigated eutectics (Ga–In, Ga–Sn, Ga–Zn, and Ga–Al).

"Poor quality" plateaux are shorter, in many cases they are badly shaped (see Ga–In-2 melting curve in Fig. 7), and usually have a larger melting range. (The same pattern was observed for Ga–Sn and Ga–Zn melting plateaux depending on their thermal history). Vertical bars in Figs. 6 and 7 indicate the discrepancy of the position of

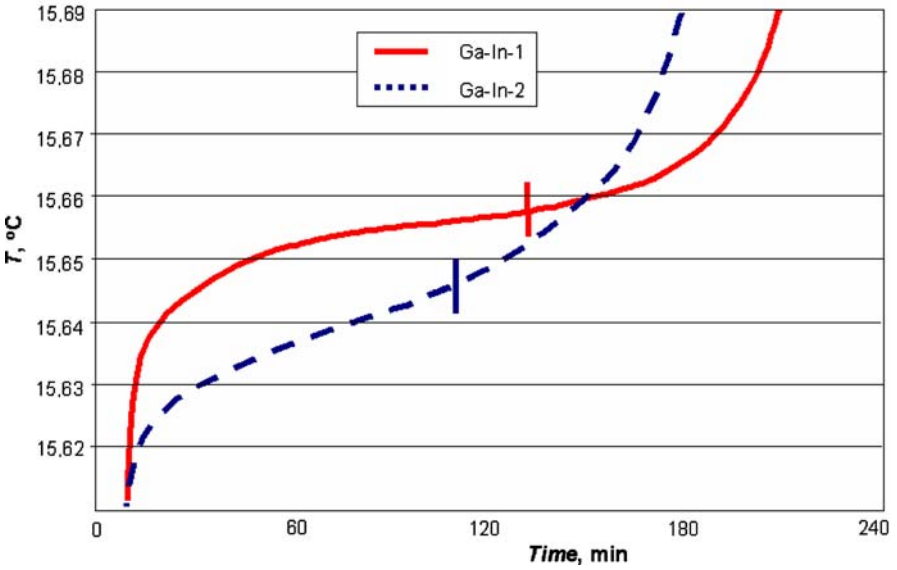

Fig. 7 "Poor-quality" Ga–In plateaux depending on thermal history

the plateaux (in other words, the discrepancy of the initial, unprocessed experimental data). The discrepancy of "poor quality" plateaux is greater than that of high-quality plateaux that look quite natural. (The bars in Figs. 6 and 7 are placed close to the run-off points just to indicate the positions of the latter).

In addition to showing the effect of thermal history on the melting plateau, Figs. 6 and 7 also illustrate the deduction made earlier in this article on the basis of investigating the $Ga(1-x)In(x)$ and $Ga(1-x)Sn(x)$ alloys: the eutectic melting temperature as measured by experiment is independent of concentration x of the second component (see Tables 3 and 4 and positions of vertical bars in Figs. 6 and 7). Of course, this property of near-eutectic alloys is much more evidently illustrated by the high-quality melting plateaux presented in Fig. 6.

The experience acquired in the course of this study shows (see, e.g., Figs. 6 and 7) that the thermal history of the eutectic fixed point affects the position of the run-off point to a lesser degree than the position of the initial and middle parts of the melting plateau. This invariability of the run-off point with respect to the preceding thermal processing explains the relatively high repeatability of our measurements for the Ga–In and Ga–Sn fixed points. This shows that the run-off point must be quite close to the true equilibrium temperature, and its selection as the estimate of the true eutectic melting point seems to be justified.

At the same time, this issue obviously requires further, more detailed studies; the effect of thermal history on the eutectic melting plateau's shape and repeatability was reported in a number of publications (e.g., [8–12]) whose authors suggested that investigations of this crucial problem should be continued by means of different methods and instruments. In [12], the heating curves of a Ga–Sn alloy with 12 mass% Sn were obtained (Fig. 8) by means of a differential scanning calorimeter (DSC). (The

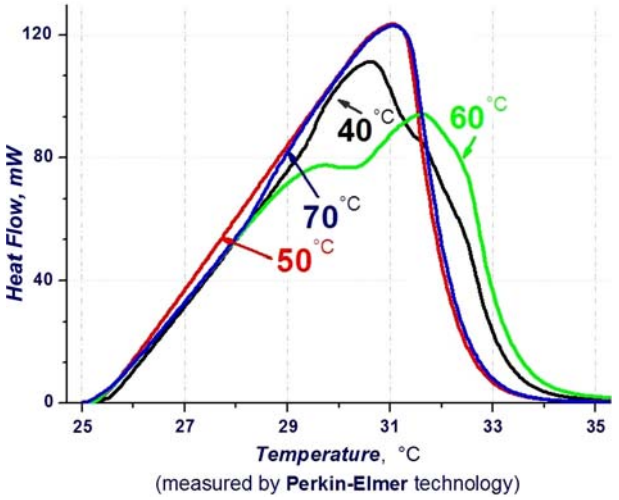

Fig. 8 Ga–Sn heating curves (measured with "Pyris-1 DSC" by Perkin–Elmer technology) [12]

calorimetry of melting appears on the vertical axis; the temperature of the sample is on the horizontal axis). Some essential features of the eutectic melting were discovered, such as the dependence on the overheating above the melting temperature in the preceding melt/freeze cycle for the Ga–Sn sample. The arrows in Fig. 8 point to the curves corresponding to different overheating values during the preceding melt (the succession of melt/freeze cycles begins with overheating of 40 °C, followed by (50, 60, and 70) °C overheating).

Referring to [12], overheating during the preceding cycle, in contrast to our experience, affects the position of the "stop-point" on the melting plateau rather than the temperature at which the melting process starts. (The "stop-point" is the author's expression; according to commonly accepted terminology, it is the break-off point or run-off point). However, we regard as most important the fact that the results obtained by another DSC procedure confirm the measurements conducted at VNIIOFI with respect to the dependence of the eutectic melting plateau quality upon thermal history. Hence, the heat-flow measurements showed that the duration of melting changes with the degree of the preceding overheating (Fig. 8). In turn, the shape of the heating curves in the vicinity of the heat-flow extremum (especially the extremum's left side, which corresponds to the main part of the melting plateau [12]) indicates the melting plateau's stability dependence on the overheating value. A special case is the curve obtained after the preceding overheating to 60 °C (Fig. 8). Two extremes on this curve (the first, barely visible, and the second, distinct extremum) allow one to cautiously assume that a sort of "two-stage phase transition" was observed in the Ga–Sn eutectic after the corresponding heat treatment.

Differential scanning calorimeter experiments [12] are in full agreement with experiments conducted at VNIIOFI with respect to the observation of substantial supercooling at the stage of eutectic alloy crystallization following substantial overheating above the melting temperature (Fig. 9). Maximal supercooling follows overheating to 60 °C

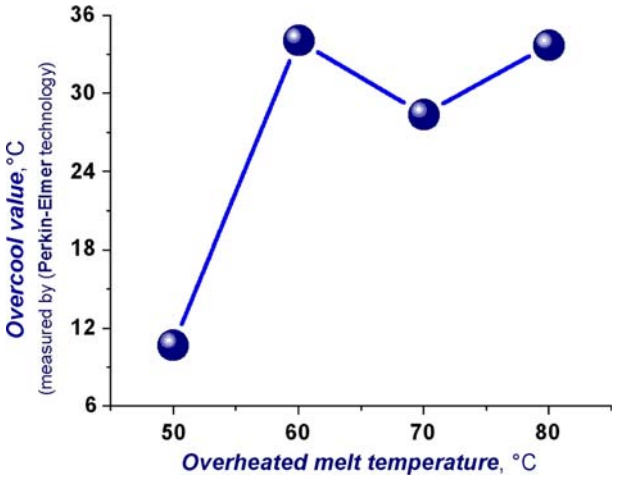

Fig. 9 Supercool value under Ga–Sn crystallization depending on overheated melt temperature [12]

and reaches as much as (35–36) °C (Fig. 9). The non-monotonic dependence of the supercooling depth on the overheating temperature (Fig. 9) has as yet no explanation. We can just note that both the deviation from monotonic increase of the supercooling with overheating and the aforementioned peculiarity of the Ga–Sn heating curve are observed for the same overheating temperature of 60 °C (compare Figs. 8 and 9).

On the whole, studies of properties of the melting plateau as a function of the thermal history of the eutectic alloy and the thermal mode of the melting fixed-point realization show the necessity of two equally important stages:

- starting from the proper initial state of the molten alloy, it is necessary to obtain a eutectic alloy whose structure would ensure the maximally isothermal character of the subsequent (measuring) melting process;
- conduct the melting stage under the thermal conditions (melting rate, constancy of the heat flow, etc.) optimal for obtaining a stable, isothermal plateau.

The structure of the liquid eutectic above, but close to, the phase-transition temperature is especially important to obtain the fine- and even-grained structure that ensures maximally isothermal melting of the eutectic alloy. It is the interaction among the nano-size clusters in the liquid phase that mostly determines the character of the starting structure of the eutectic fixed point obtained under freezing at the preliminary stage [11].

Having obtained the eutectic fixed point with optimal starting structure, then, at the measuring melting stage, it is important to take into account the actual mechanism and kinetics of the eutectic phase transition when choosing the parameters of the fixed-point realization. The fixed point should be realized during the melting stage by taking into account the thermal and technological factors that may affect the shape of the plateau and—even more important—the determination of the conventional fixed-point value within the phase-transition temperature range. We anticipate this will be the subject of a separate article.

8 Conclusion

- It has been shown that, in principle, fixed points based on the melting phase transition of Ga and Ga-based eutectic alloys can be realized in a small cell.
- The insignificant effect of supercooling in our experiments with the pure Ga melting fixed point in small cells allows one to hope that this fixed point can be used for automatic calibrations of spacecraft instruments operating within the temperature range from 273 K to 310 K.
- In addition to pure Ga, the alloys of Ga with In and Sn can also be used for the same purpose. The Ga–Zn alloy showed relatively poorer qualities but we believe that the Ga–Zn eutectic fixed point should be studied further because it usually has a well-shaped melting plateau with a clearly defined run-off point.
- Our results for the $Ga(1-x)In(x)$, $Ga(1-x)Sn(x)$ alloys are sufficient for a preliminary conclusion that the experimentally detected eutectic melting fixed point is independent of the concentration x of the second component. Nevertheless, this issue requires further study.
- Preceding melting/freeze cycles (i.e., thermal history) play an important role in obtaining the best shape of the subsequent melting plateau.
- The conclusions regarding the practicality of using Ga, Ga–In, and Ga–Sn (and possibly other Ga-based bi- and tri-metallic eutectic alloys) for the in-flight calibration of space-borne instruments are preliminary and require experiments with the phase-transition phenomenon under microgravity conditions.

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