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Realization of the Indium Fixed Point by an Adiabatic Technique

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Abstract This work investigates the effect of heating techniques on the realization of the ITS-90 fixed points above room temperature. For that purpose, LNE has constructed a new apparatus to realize the indium fixed point under adiabatic conditions using the "calorimetric" method. The adiabatic condition, in general, is established by maintaining a temperature difference between the fixed-point cell and its surroundings that is as small as possible. In this work, the indium fixed-point cell is located within thermally controlled heat shields whose walls also contain indium. Thus, the shields themselves are also indium cells. The experiments realizing the melting and freezing temperatures of indium using the calorimetric method are described. The results revealed the existence of thermal effects in the realization of the indium fixed-point cell by the conventional "continuous heat flux" method. The advantages of the "cell-within-cell" technique are presented.

Keywords Adiabatic · Calorimetric · Indium · Heat pulse · Continuous heat flux

1 Introduction

Above room temperature, the defining fixed points of the international temperature scale of 1990 (ITS-90) [1] are generally realized using the conventional "continuous heat flux" method [2]. This method introduces time in the realization of thermodynamic phase transitions. During freezing or melting, the fixed-point substance is expected to provide a stable and uniform temperature. To approximate these conditions, the amount of metal must be relatively large. The freezing point has an advantage: the maximum value of the observed temperature is quite repeatable if specific procedures

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are followed [2]. However, the fixed-point cell is not in ideal thermal equilibrium. In particular, the observed temperature is quite different from that of the solid/liquid interface at the end of melting ("run-off" point) and during freezing when slowly recovering from the supercool. The first consequence is that solid/liquid fractions along the freezing curves cannot be determined accurately [3]. Secondly, the lack of thermal models to account for the real behavior of fixed points during the entire phase change results in difficulty in distinguishing thermal and impurity effects [4], especially following recalescence. Consequently, the reliability of the deduced impurity effect [5,6] and the value of the extrapolated liquidus point using the continuous heat-flux method are questionable. The results of CCT-K3 [7] revealed larger differences among the fixed points than expected based on the reported uncertainties. This could be due to the lack of an accurate definition of the ITS-90 fixed points and/or underestimation of the uncertainties due to thermal influences.

ITS-90 fixed points can also be realized under adiabatic conditions using the "calorimetric" method. The absence of heat flux results in an isothermal system. Compared to the situation described above, the thermometer should ideally indicate the temperature of the solid/liquid interface no matter what the direction of the phase transition, solid-to-liquid or liquid-to-solid. During the CCT workshop held in Cavtat in 2004 [8], Hill discussed selected investigations of metal fixed points realized both under heat flux and adiabatic conditions [3,4,9,10]. In particular, he concluded his talk with the following question "Do temperatures realized by adiabatic and continuous heat-flux techniques differ in principle?"

A new apparatus and associated procedures were developed at LNE within the framework of a Euromet project [11] to realize the indium fixed point by the calorimetric method; full details are provided in this paper. In the real world, adiabatic conditions can only be approximated. Therefore, 'adiabatic' in this paper means almost adiabatic conditions, except during heating periods. The effect of heat fluxes on measurements performed under adiabatic conditions is reported in the following. Results of experiments performed under adiabatic conditions are compared to those obtained using the continuous heat-flux method to investigate possible thermal influences when realizing ITS-90 metal fixed points.

2 Experimental Setup: Principle and Technical Features

In the cryogenic range, the calorimetric method is widely used because the thermal conductivity of substances is poor and their enthalpy is low. The adiabatic condition is more easily approached at low temperatures where radiative heat exchange is very small; this is no longer true above room temperature. Nevertheless, several experiments under adiabatic conditions have already been reported in the field of metal fixed points. These generally consisted of keeping the surroundings as isothermal as possible, with respect to the fixed-point cell, by means of heaters and shields [3,4,10,12,13].

In this work, exchange of heat between the fixed-point cell and its shields can be minimized by using a "cell-within-cell" design. Such a design was already used at LNE-INM to realize the Hg triple point [14]. The fixed-point cell is completely surrounded by two external cells, the guards (see Fig. 1), both of which are filled

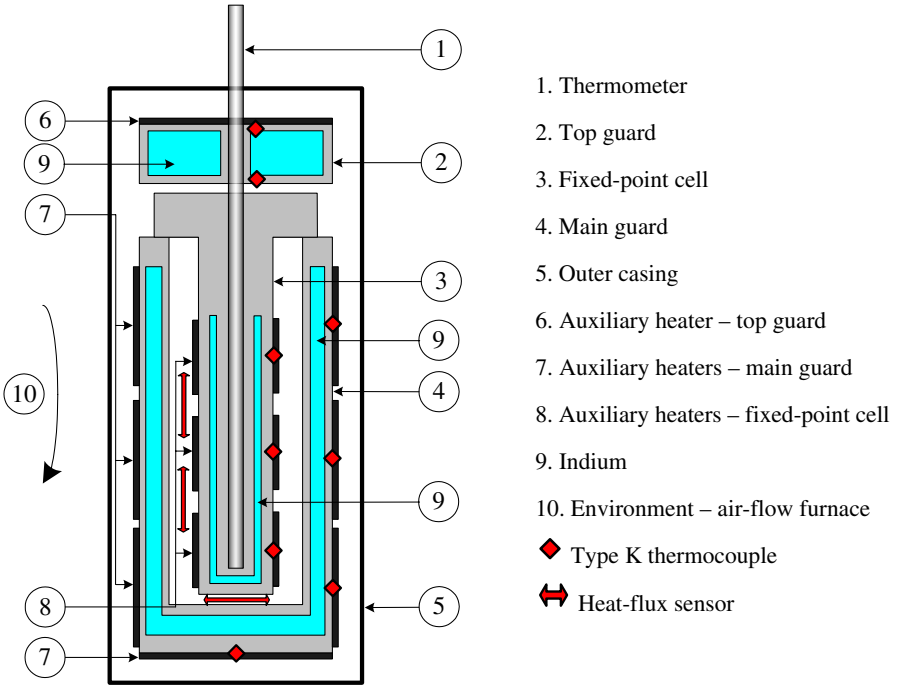

Fig. 1 Cell-within-cell apparatus

with indium. The system is located in a furnace, with the temperature kept below the phase-transition temperature of the metal. Several auxiliary heaters can heat both the fixed-point cell and the guards to the melting temperature. Adiabaticity is established as long as the fixed-point cell and the guards are simultaneously undergoing a phase transition. The guards serve as adiabatic walls, preventing any thermal exchange between the fixed-point cell and the furnace.

The conventional fixed-point cell design used in these experiments is shown in Fig. 2. It consists of a PTFE crucible (28 mm to 32 mm outer diameter, 24 mm inner diameter, and 207 mm outer length) containing an indium sample of 99.999 % nominal purity (metal basis). The mass of the indium sample is 0.316 kg. A 5.5 mm thick indium layer surrounds the PTFE thermometer well over 160 mm. A 5 mm thick tissue is placed at the bottom of the well. Three auxiliary heaters, individually shielded using aluminum foil, are installed along the crucible. During the experiments, this open fixed-point cell is maintained in pure argon (99.9999 % purity) a few hundred pascal above ambient pressure. The fixed-point cell is suspended within the "main guard" (66 mm diameter and 238 mm high) using its PTFE holder, as shown in Fig. 1. This assembly prevents any heat shunt between the two metal ingots. The "top guard" (70 mm diameter and 30 mm high) is located just above the indium fixed-point cell. Its central sleeve is fitted to the thermometer to stop heat from flowing through the stem as effectively as possible. The main and the top guards contain, respectively, (1.1 and 0.2) kg indium of 99.999 % purity. The main guard has four heaters while the top guard has only one. This enables careful monitoring of the position of the solid/liquid interface in the guards while the fixed-point cell is undergoing its phase transition.

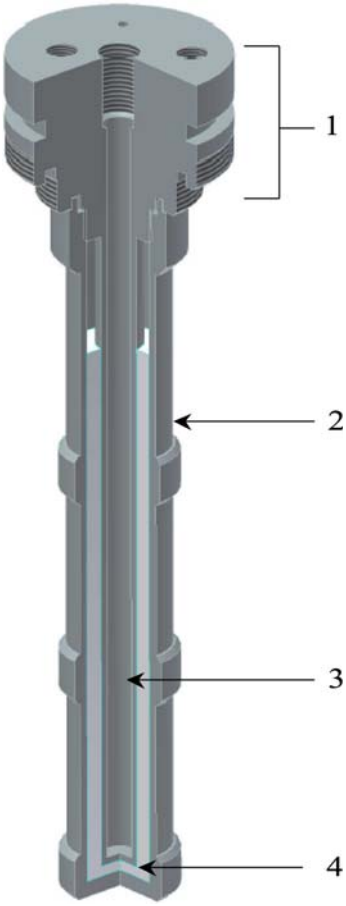

Fig. 2 Indium cell: (1) holder, (2) crucible, (3) thermometer well, (4) indium sample

The device is located in an air-flow furnace. The outer casing shown in Fig. 1 reduces the convective heat exchange between the guard heaters and the air-flow furnace. At the present time, the apparatus is designed to work at atmospheric pressure only.

Temperature measurements were performed using a Tinsley 5187SA platinum resistance thermometer connected to an ASL F900 bridge. The resistance of the thermometer was periodically measured at the gallium melting point. During the experiments, the temperature of each auxiliary heater was checked by means of Type K thermocouples. Three heat-flux sensors indicated the heat exchanged between the fixed-point cell and the guards.

3 Measurements

The phase transformation of indium was realized with the same layout using successively the "continuous heat-flux" and the "calorimetric" methods. The liquidus

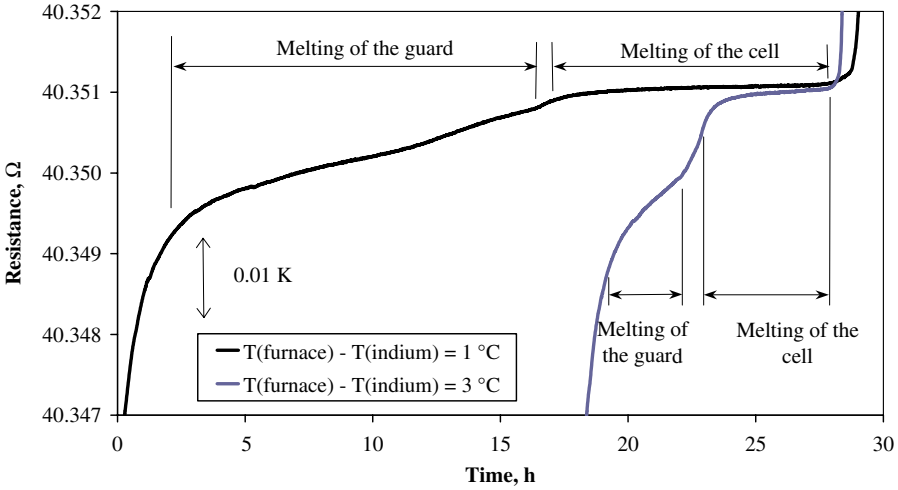

Fig. 3 Typical melting of the indium guard followed by melting of the indium cell using the continuous heat-flux method when the furnace temperature T(furnace) is set (1 and 3) °C above 156.5985 °C = T(indium)

point was determined from the solid-to-liquid phase transition (melting), and also from the liquid-to-solid phase change (freezing). The measurement procedures are presented below.

3.1 Preliminary Realization Using the "Continuous Heat-Flux" Method

Figure 3 shows typical results for fast melting and slow melting when the furnace temperature was set, respectively, (3 and 1) °C above the melting point of indium. Fast melting starts with the melting of indium in the main guard followed by the melting of indium in the fixed-point cell. Similar behavior was observed for slow melting. The effect of the top guard was also observed: half-way through the melting of the indium fixed-point cell (fast melting realization), the temperature of the top guard was increased by 3 °C without noticeable effects.

Slow melting of the fixed-point cell required about 10 h. The melting range was 0.5 mK to 1 mK (Fig. 4). Run-off was followed by melt-off [3], showing the difficulty in estimating the liquidus point and the melting time using the continuous heat-flux method.

3.2 Realization Using the "Calorimetric" Method

3.2.1 Solid-to-Liquid Transformation

The indium fixed-point cell and the associated guard system were maintained 0.5 °C below their phase-transition temperature in the air-flow furnace. Then, heat pulses were applied to the guards to initiate melting. The presence of the solid/liquid interface was

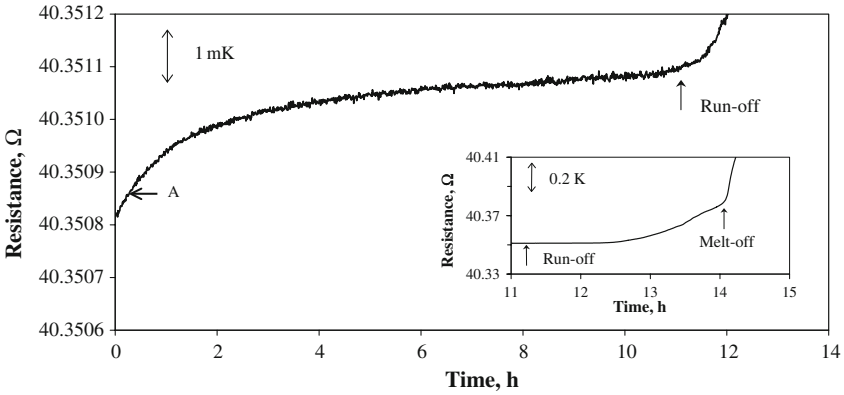

Fig. 4 Melting of the indium cell with the continuous heat flux method (furnace set 1 °C above melting). "Run-off" is observed ∼11 h after the beginning of melting. The metal is fully liquid ∼3 h after "run-off." Point "A" plotted on the curve is taken as $F = 0$ (information drawn from realizations under adiabatic conditions)

detected by thermocouples attached to the auxiliary heaters. Once the phase transition was detected, the heaters were turned off. However, heat pulses were applied from time to time to maintain the guards in their melting state. Finally, the first heat pulse was applied to the fixed-point cell to initiate melting. The total heat required to reach the beginning of the melting curve was less than 15 J. The presence of the solid/liquid interface was detected in the same way as for the guards. The total heat of fusion was about 9 kJ. The adiabaticity was monitored during melting using heat-flux sensors.

The result of a typical melting experiment is shown in Fig. 5. Temperatures were measured outside the heating periods with (1 and $\sqrt{2}$) mA measuring currents. The heat pulses applied to the fixed-point cell are shown below the melting curve. These were not observed in the thermometer well as long as it was entirely surrounded by a

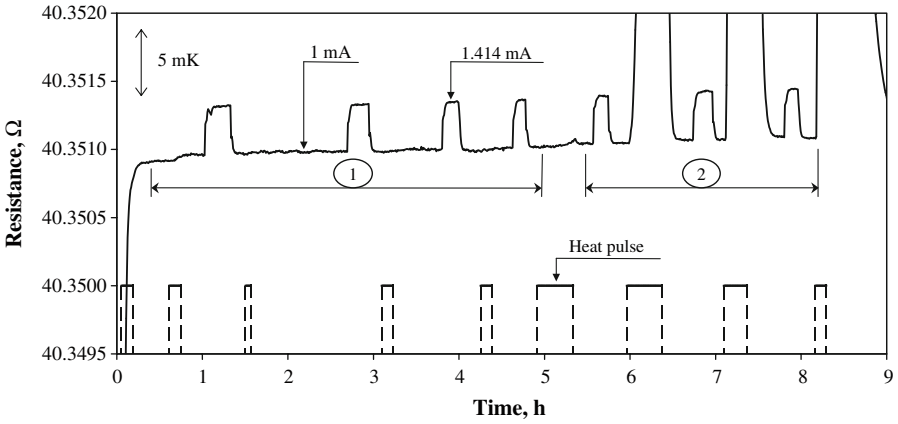

Fig. 5 Phase transition of the indium cell from solid-to-liquid with the calorimetric method. Temperatures are measured after stabilization for (1 and $\sqrt{2}$) mA measuring currents

solid indium shell, as shown in part '1' of the melting curve in Fig. 5. However, the well rapidly came into contact with liquid indium as shown by the peaks observed in part '2' of the curve.

3.2.2 Liquid-to-Solid Transformation

The air-flow furnace was maintained 0.5 °C below the melting temperature of both the fixed-point cell and the guards, just as for the solid-to-liquid transformation. A preliminary step consisted of melting completely the indium fixed-point cell using its auxiliary heaters. Then, the guards were partially melted using the procedure described above. Next, the thermometer was removed from the fixed-point cell and an alumina tube of 4 mm outer diameter was inserted into the well to a depth of 10 mm from the bottom. The fixed-point cell was cooled by blowing air through the tube at a rate of $10\,\mathrm{L}\cdot\mathrm{min}^{-1}$ for 20 s. Afterward, the tube was replaced by the thermometer and readings were taken once the thermometer had stabilized. This procedure was repeated until the indium fixed-point cell was completely frozen. Temperature measurements drawn from this experiment were exploited together with those obtained for the solid-to-liquid transformation, as further described.

3.2.3 The "Adiabatic" Condition: Effect of Heat Flux

In principle, the temperature difference between the metal of the fixed-point cell and the guards during phase transitions does not exceed a few mK for metal purities of at least 99.999 % [12]. The high thermal resistance between the fixed-point cell and the guards results in a limited effect on the temperature of the fixed-point cell. In fact, the presence of small sources of heat flux is inevitable. A numerical model, reported in a separate paper [15], evaluated the transient thermal behavior of the apparatus and highlighted the presence of heat flux even when the metals in both the fixed-point cell and guards were in a phase transition.

Measurements of the temperature distribution along the thermometer well of the indium fixed-point cell up to the top guard were performed using the platinum resistance thermometer described above. Figure 6 shows the temperature profile along the thermometer well at $1/F = 5$ and $1/F = 1.5$ (respectively, $F = 20\,\%$ and $F = 66\,\%$, F being the liquid fraction with solid and liquid in equilibrium). The immersion profile follows the theoretical line even near run-off at $1/F = 1.5$. The temperature dropped by about 20 mK near the crucible holder shown in Fig. 2, 80 mm above the surface of the indium sample.

The nearly adiabatic condition was monitored using heat-flux sensors located between the fixed-point cell and the main guard. The possible deviation of the main guard from a stable condition was quantified in terms of energy using the heat-flux sensors. The effect of these deviations on temperature was observed in the thermometer well. In a preliminary step, the heat-flux sensors were verified in situ. The offset of the heat-flux sensors was determined when the environment was in thermal equilibrium. Afterward, the indium fixed-point cell was realized by the continuous heat-flux method to compare heat-flux measurements, converted to energy, with the theoretical heat of fusion ($0.316\,\mathrm{kg}\times 28{,}500\,\mathrm{J}\cdot\mathrm{kg}^{-1} = 9{,}006\,\mathrm{J}$) of the indium sample. The difference in

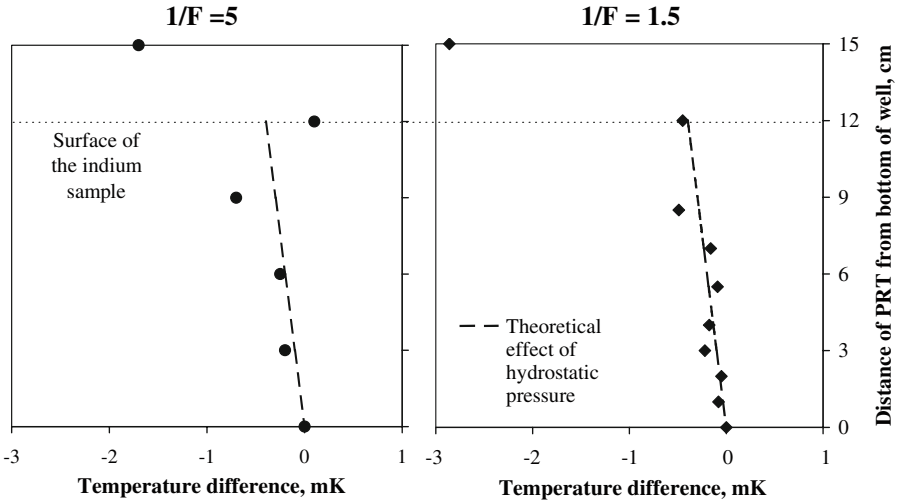

Fig. 6 Temperature profile in the thermometer well under adiabatic conditions at $1/F = 5$ and $1/F = 1.5$

the energies was less than 10 %. Finally, the indium sample was melted by means of electrical heaters inserted into the thermometer well while maintaining adiabatic conditions. The energy supplied, 9,191 J, was in good agreement with the theoretical value of 9,006 J. Following these results, a relative uncertainty of 10 % was associated with the heat flux measurements. Subsequently, the effect of heat flux was assessed while maintaining the fixed-point cell and guards in phase transition:

- Under adiabatic conditions, the heat-flux sensors were stable within the detection limit of approximately $\pm 0.1\,\mathrm{W \cdot m^{-2}}$, except at $F > 0.85$ during the solid-to-liquid transformation. This corresponds to a possible deviation of the main guard from stability of about 90 J for an 11 h transition.
- At $F > 0.85$, a gradual deviation of approximately $0.3\,\mathrm{W \cdot m^{-2}}$ produced a temperature increase of up to 0.4 mK in the thermometer well.
- The guards were heated until completely melted (13 h melting) while keeping the metal in the fixed-point cell at a fixed liquid fraction ($F < 0.85$). The temperature observed in the thermometer well was stable to within 0.2 mK. The heat-flux sensors remained stable in the meantime.

In the course of some experiments, the main guard re-solidified temporarily (< 30 min), leading to a local deviation of $0.3\,\mathrm{W \cdot m^{-2}}$. However, temperatures measured in the thermometer well were not taken into account if a significant heat flux was detected by the heat-flux sensors. Temperature measurements presented in the results below correspond to this "adiabatic condition."

4 Results and Discussion

Figure 7—series 2 to 5—shows the results of four experiments under adiabatic conditions carried out during a three-week period. The apparatus was cooled to room

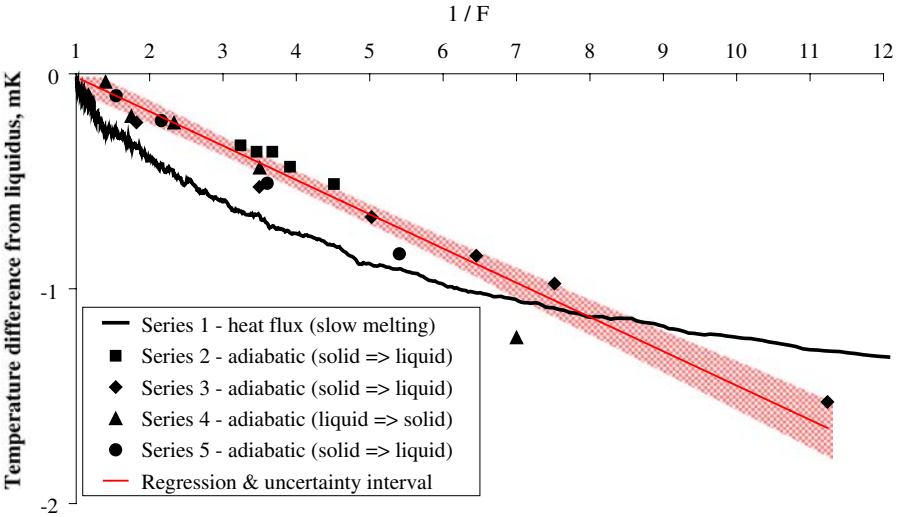

Fig. 7 Difference from the extrapolated liquidus point of each experimental series. Series 1 is a 10 h melting realized using the continuous heat-flux method. Series 2–5 were obtained under adiabatic conditions

temperature after the fourth series in order to repair one of the heaters. Fractions F of the melted sample were determined from the heat supplied by the auxiliary heaters installed along the fixed-point cell. Differences from the extrapolated liquidus points are plotted as a function of $1/F$. Results obtained for liquid-to-solid transformations are consistent with those for solid-to-liquid transformations. The first melting point (near the solidus) is 2.5 mK below the liquidus point. The indium sample is of 99.999 % nominal purity [16]. Nevertheless, the observed melting range was similar to the ones observed for 99.9999+ % purity samples under adiabatic conditions [12] and with continuous heat flux [17]. Therefore, further investigations will be carried out to determine the purity of the sample. A polynomial regression and associated uncertainty interval for series 2–5 is presented in Fig. 7. The optimal model is a polynomial of degree one; temperatures are a nearly linear function of $1/F$.

The values shown as series 1 in Fig. 7 were obtained using the continuous heat-flux method. Conventionally, it is only the linear part of the melting curve, the plateau, which is used to calculate the $1/F$ values. Nevertheless, with the aid of the adiabatic data, the first point was taken on the rounded part of the melting curve preceding the plateau (see Fig. 3, point "A" plotted on the curve). These $1/F$ values differ considerably from the adiabatic data. Temperatures are affected by thermal effects. Near the end of melting, the temperatures ran off the plateau well before melt-off; the liquidus point cannot be clearly identified (arbitrary in Fig. 7). It is not possible to distinguish the impurity effect from thermal influences.

When using the continuous heat-flux method, the highest accuracy measurements can be facilitated by establishing two solid/liquid interfaces within the fixed-point cell [2]. This technique overcomes the heat-flux effects described above. Although measurements are stable, the inner interface surrounding the thermometer well is essentially static. Using the cell-within-cell technique, both interfaces are physically

separated. The solid/liquid interface in the guards prevents thermal exchange between the fixed-point cell and the furnace, while the thermal resistance between the fixed-point cell and guards is kept high. The inner interface is not static and temperatures in the thermometer well can be observed for different fractions of melted sample while in thermal equilibrium.

Results obtained under adiabatic conditions emphasize the importance of keeping the heat flux as small as possible during experiments. Deviation from adiabaticity will of course result in a heat-flux condition. In this experimental arrangement, about half of the heat supplied to the fixed-point cell by the heaters (about 9 kJ) leaked toward the guards. This indicates the difficulty of keeping the main guard in phase transition to achieve the adiabaticity. Although the design is not optimal at this stage, the apparatus demonstrated the cell-within-cell technique. The temperature of the guards was kept constant and temperature measurements in the thermometer well were moderately affected by heat flux between the fixed-point cell and its surroundings, as described above. In order to improve this experimental arrangement, several modifications are being considered. The apparatus will be modified to use vacuum. The heat conductivity of the crucible will be improved. The mass of indium in the fixed-point cell will be decreased to reduce the power of the heat pulses.

5 Conclusion

The new apparatus presented in this paper achieves nearly adiabatic conditions. Results produced using the "calorimetric" method are distinctly different from the conventional, "continuous heat-flux" method as shown by $1/F$ curves. This establishes that there exist thermal influences with conventional fixed-point cells and procedures that bias temperature observations during the phase transition and make their interpretation difficult.

Experiments carried out with a continuous heat flux showed highly transient thermal conditions, particularly at the beginning and at the end of the phase transition. It is also likely that impurities were redistributed during the realization, consequently affecting the results. In such a furnace environment, this technique is not suitable for obtaining equilibrium melting curves as shown in [3] and the liquidus point cannot be determined. Optimizing thoroughly the temperature distribution in the furnace as well as driving the interface adequately would decrease thermal effects. However, such a quasi-ideal condition is difficult to achieve and maintain routinely. In contrast, careful, preliminary tuning of the furnace is not required to establish the adiabatic condition using the apparatus presented in this paper. The 'almost adiabatic' condition is ensured by the cell-within-cell technique, optimization of the design of the apparatus, and the procedures for its use.

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