The Comparison of MTDATA with the Melting/Freezing Point Curves of ITS-90 Metal Fixed Points

D. I. Head · H. Davies · J. Gray · P. Quested

Abstract   The International Temperature Scale (ITS-90) is defined in part by a series of metal freezing points between 156 °C and 1,084 °C. These freezing-point cells provide reference temperatures with an uncertainty of realization claimed to be in the range of several tenths of a millikelvin. The impurities in the nominally 99.9999 % pure metals make a major contribution to the uncertainty of realization of the fixed-point temperature. Recently, a new method to correct for the influence of the impurities by summing the individual contributions of each impurity has been suggested. This method is referred to as the "sum of individual estimates" (SIE). NPL is a partner in a Euromet project to improve the realization of ITS-90 metal fixed points. As part of this project, NPL is particularly interested in the fixed-point cells of tin (231.928 °C) and aluminum (660.323 °C). This article describes the use of a thermodynamic model, embodied in NPL's MTDATA software, to estimate the initial drop in the freezing temperature and the temperature decrease during freezing using both equilibrium and "Scheil" approaches. Calculations of this type establish the effect of single elements, and with the chemical analysis of the metal, enable an estimation of the whole freezing curve. This has been done for a sample of tin from this laboratory, and thereafter, the theoretical curves are compared with previously published experimental data on impurity-doped aluminum, with good agreement, e.g., better than 1 mK over most of the curve for $76\,\mu\mathrm{g}\cdot\mathrm{g}^{-1}$ Ag in Al.

Keywords   Fixed points · ITS-90 · MTDATA · Purity

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1 Introduction

In the range from 0 °C to 962 °C, the International Temperature Scale of 1990 (ITS-90) specifies a series of metal fixed points that can be used to calibrate standard platinum resistance thermometers. In order to calibrate the thermometers with uncertainties of ± 1 mK ($k = 2$) or less, the fixed points need to be realized with an uncertainty measured in tenths of a millikelvin. Inspection of a fixed-point uncertainty budget shows that impurities in the metal and the thermal environment are presently the biggest factors. The latter is discussed elsewhere [1] and here we deal with calculating a correction for the impurities in the metal. (The alternative is to use highly-purified metal, e.g., 7N to 8N, in which case the associated uncertainty becomes a small part of the overall budget, but such materials can be difficult, or at best expensive, to obtain and then the metal must be kept pure throughout its use.) Using nominally 6N (99.9999 %) metal, one might attempt to correct for the presence of impurities, but in this paper we only calculate and compare with "known" doped samples. Potentially, samples could be taken from the fixed-point ingot [2] during its lifetime to check, and correct for, any change in impurity concentration. This assumes the ability to measure impurities at the sub-part-per-million level. At present, this is difficult with assured traceability, though there are a few laboratories in the world that have a good reputation for measuring the relative levels of impurities at this level using a technique referred to as "GDMS" (glow discharge mass spectrometry) and we understand some work is underway to put this on a more quantitative level [3]. Uncertainty in the impurity effects on the initial freezing temperature has historically been assessed using Raoult's law. More recently, a method using the addition of the contributions of the individual effects of each impurity has been suggested (this assumes no cross-impurity effects, which is reasonable for fixed-point materials). This method is referred to as the "sum of individual estimates" (SIE) [2].

2 Thermodynamic Model

This article describes the thermodynamic modeling used—in particular, the application of "MTDATA" [4]—to determine the drop (or rise) in the initial freezing temperature, and the temperature decrease during freezing. Corrections for not only the effect of single elements but, with a chemical analysis of the metal, corrections for most impurities can be made to estimate the difference from the ideal freeze. MTDATA itself calculates the equilibrium thermodynamic curve and can incorporate non-equilibrium effects via the internal "Scheil" simulation or more explicitly via user programming. We have applied these models to two systems relevant to ITS-90 fixed points, viz., tin and aluminum.

The equilibrium state of a chemical system at a fixed temperature (T), pressure (P), and overall composition can be calculated by minimizing its Gibbs free energy with respect to the proportions of individual species that could possibly form. The most stable phase or combination of phases at chemical equilibrium can then be predicted for a chosen T and P as that with the lowest Gibbs energy. When impurities are

present, then additional terms representing the interactions between them and the bulk materials must be included in the model of the Gibbs energy.

This article describes the application of the MTDATA thermodynamic model to determine the drop in the freezing temperature and the temperature decrease during freezing, using both equilibrium and "Scheil" approaches. In order to work with the low $\mu g \cdot g^{-1}$ impurity levels of ITS-90 fixed points, the mode of use of commercial MTDATA has had to be adapted, compared to its use with "normal" alloying concentrations significantly above $\mu g \cdot g^{-1}$ levels. As this is an interpolation between zero and larger impurities, we believe uncertainties remain dominated by the experimental input data.

3 Tin

The above concepts can be applied to the impurities present in one of our fixed-point metals. However, to do the calculation, one needs the relevant thermodynamic data for all the measured (or suspected) impurities. For tin, the relevant databases are dominated by work done on solders. We took a real sample of tin and had it analyzed by GDMS at the National Research Council of Canada (NRC). The conclusion of the analysis is shown in Table 1. Data are available for many of the significant impurities, although not all, but we presently expect that these deficiencies would not normally have a gross effect on the overall result (based on comparison with analogues for missing elements or, at least, at the Raoult's law level). However, the table does show that the GDMS detection limits for some elements are still relatively high and so limit our ability to accurately specify the conditions to model these impurities that may or may not be present (see later).

Firstly, working with those impurities for which we have thermodynamic data, we can plot the affect of impurities on the melt/freeze curve depression and shape. These are shown as graphs of fraction melted against temperature depression for various concentrations of impurities in Figs. 1–3. (The MTDATA curves initially

Table 1 Impurity elements detected by glow discharge mass spectrometry analysis of a tin sample performed at NRC, Canada, compared with those for which thermodynamic data are available

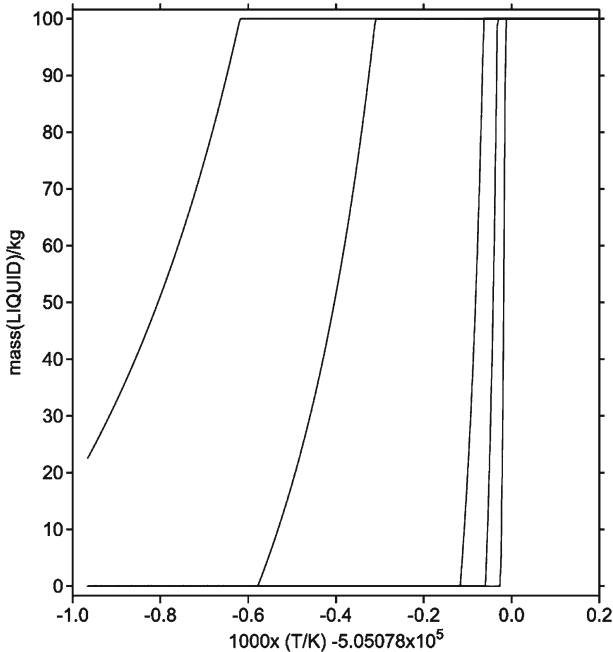| Elements	C	N	O	Na	Al	Si	S	Cl	Tl	Cu	Ag	Pb	Co	In	Sb
Present above detection limits	X	X	X	X	X	X	X	X	X	X	X	X			
Not found but with detection limits >50 ng·g⁻¹													X	X	X
Available for thermodynamic modeling					X	X				X	X	X	X^a	X	X

^{a} Data for Ni are used to model Co

Fig. 1 Simulation of the effects on the freezing curve (melted fraction against temperature) of various levels of aluminum impurities in tin (Sn-Al (20, 50, 100, 500, and 1,000) ng·g^{-1} curves with impurity concentration increasing right to left)

appear strange to thermometerists, who are used to seeing the temperature on the y-axis, as MTDATA normally plots temperature on the x-axis, but a mental rotation by 90 degrees produces the familiar shape of a freeze curve. Note that the "zero" of the x-axis is the ITS-90 freezing temperature of Sn, 505.078 K; the temperature axis is effectively the "mK offset" from the phase-transition temperature). These figures show not only different initial "depressions" in freeze temperature, but also the subsequent shape of the freezing curve, which can be very different for different species; see Figs. 1 and 2 which show the different effects of aluminum and copper impurities on the freezing curve. Note that most impurities depress the freezing curve but there are some elements (e.g., Sb in Sn) that rather elevate it (see Fig. 3).

It is possible to calculate the combined effect of the impurities, and this has been done for the measured impurities in Fig. 4. However, there are presently some limitations of the GDMS detection levels for some elements, and where there is thermodynamic data, one can include a component for such, but to what level? Should it be 50 % of the minimum detection level (as used in [2]); see Fig. 5, or the worst case (i.e., the whole limit of detection amount), or is there some level that would give 95 % coverage? It seems unlikely that ALL the undetected impurities would be just below the limit of detection, so, if these items are to be included, it might be better to use the 50 % graph and have an uncertainty component based on the difference between 50 % and 0 % (with μg·g^{-1} impurities one remains in the linear regime; however, it has not yet been shown that 50 % is the best statistical choice). It does, however, show the need
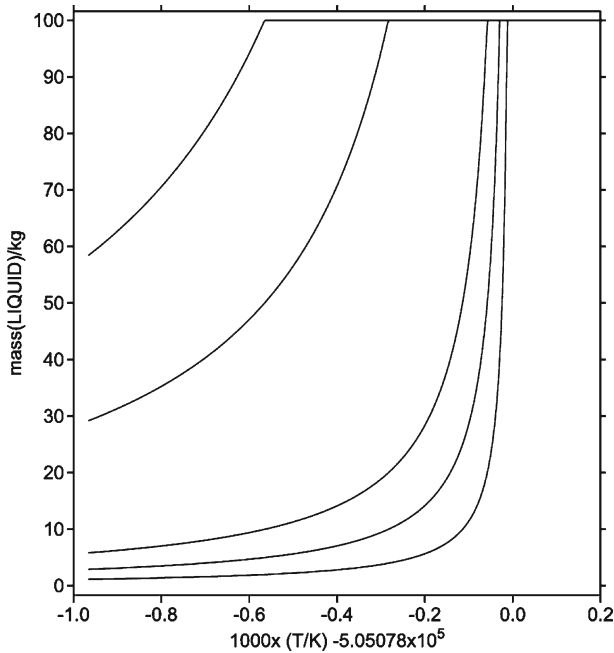
Fig. 2 Simulation of the effects on the freezing curve (melted fraction against temperature) of various levels of copper impurities in tin (Sn-Cu (20, 50, 100, 500, and 1,000) $ng \cdot g^{-1}$ curves with impurity concentration increasing right to left)

for better analysis if the power of this modeling technique is to be fully realized. The traditional alternative was to use Raoult's Law, but this tends to overestimate the effect of most impurities and is blind to others (e.g., those with distribution coefficients >1).

MTDATA is normally used to perform equilibrium calculations and assumes no effects due to diffusion within the material, but can also do limiting-case (non-equilibrium) solidification simulations by assuming rapid diffusion in the liquid and none in the solid and, hence, use what materials experts call the Scheil approximation [5,6]. We used this approximation, as this is what is available within MTDATA. However, approximating Scheil-type solidification for low concentrations of impurities in tin has not been possible. An effect can be seen with much higher concentrations, e.g., Fig. 6 shows the effect of $10 \mu g \cdot g^{-1}$ of Pb in Sn and the difference only becomes acute in the latter part of the freeze. Also, work on aluminum (not shown here) indicates that a noticeable difference from the equilibrium calculation is only seen beyond 50 % frozen. Both Sn and Al calculations show that Scheil solidification shows significant lowering of the temperature at higher solid fractions.

4 Comparison of Theory and Experimental Measurables

From the calculated MTDATA equilibrium freezing curves, it is possible to read off the initial temperature drop from the ideal and the drop part way through a freeze—50 %
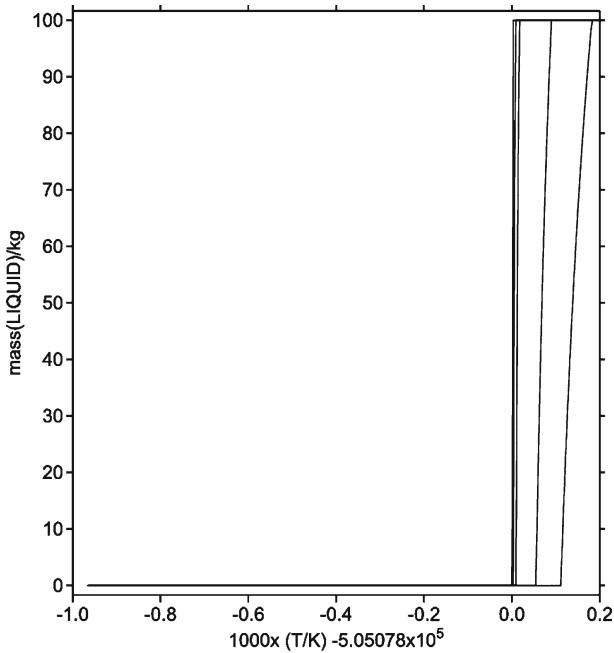
Fig. 3 Simulation of the effects on the freezing curve (melted fraction against temperature) of various levels of antimony impurities in tin (Sn-Sb (20, 50, 100, 500, and 1,000) $ng \cdot g^{-1}$ curves with impurity concentration increasing left to right—opposite to Figs. 1 and 2)

frozen is chosen as a convenient reference point. (Some laboratories arrange their fixed-point systems such that a freeze will last at least 16 h, so that any calibration measurements done during a working day of 8 h occur on the relatively flat part of the freezing curve—i.e., they use the curve to only 50 % frozen). Some examples of the calculated offsets for the impurity cases considered are given in Table 2.

However, in the experimental measurement, there is no way to obtain the initial offset—only the difference between the initial offset point (0 %) and 50 % of the freeze is measurable (and, anecdotally, there appears to be a difference as to whether the calculated 0 % is better represented by the peak of the freeze or its extrapolation back to the time of initiation). However, on inspection of Table 2, we notice that very approximately the initial drop is 1.3 times the measurable drop from 0 % to 50 % in Sn. (We appear to have different values for aluminum, so this figure is not generalizable.) Further work will be needed over a range of elements to see if any approximate theoretical guidance can be given regarding the relationship between the initial drop and the shape of the subsequent freeze curve. Note that the chemical analysis has a claimed uncertainty of a "factor of 2," and though it has been suggested that this is a conservative estimate [2], it dominates any subsequent calculation uncertainty. Furthermore, it must be remembered that MTDATA calculates the equilibrium curve and therefore sees no difference between a melting and a freezing curve; however, in experimental practice, freezing and melting curves usually have different shapes.
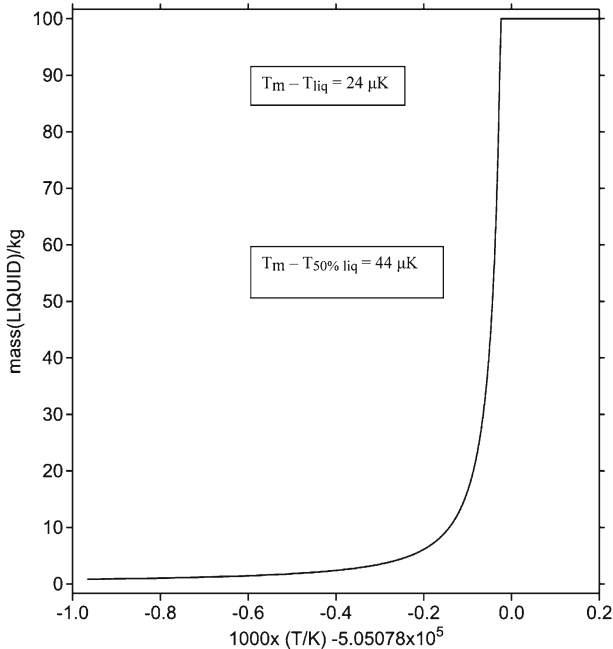
Fig. 4 Simulation of a freezing curve based on the NRC-measured Sn composition; only analyzed levels for Ag, Cu, Pb, and Si are considered. $T_m - T_{liq} = 24\,\mu K$; $T_m - T_{50\%\,liq} = 44\,\mu K$ where T_m is the melting/freezing temperature and T_{liq} is the temperature at freeze start (or 100 % molten). If the Si impurity is excluded, these values become $15\,\mu K$ and $25\,\mu K$, respectively

5 Aluminum

Thermodynamic databases are more extensive for aluminum than tin due to the large amount of commercial work on aluminum alloys. Two interesting items come from the analysis. Firstly, nitrogen has a noticeable theoretical effect even at low concentrations but, as this has not been experimentally reported, it suggests that even if nitrogen is picked up from the air during normal handling, it is then lost during the normal pump-out of the cell/metal at the time of the fixed-point manufacture. Secondly, as aluminum is quite reactive and fixed-point cells are normally made of graphite, we were interested in the affect of aluminum carbide on the phase transition. From the phase diagram, the predicted solubility of carbon in liquid aluminum near the phase transition is $0.3\,ng \cdot g^{-1}$ and, theoretically, should therefore have little effect on the melting transition.

However, due to resource constraints, we have not yet been able to manufacture and test a cell made from an analyzed batch of aluminum. Consequently, to test the MTDATA calculations, we have made use of the previously published aluminum doping experiments of Ancsin [7] where he performed adiabatic measurements on melting plateaux. We calculated the effect of two levels of doping using Ag, Si, and Ti, which respectively represent a "normal" impurity, a dominant impurity, and an impurity that should elevate the phase-transition temperature. Example theory and
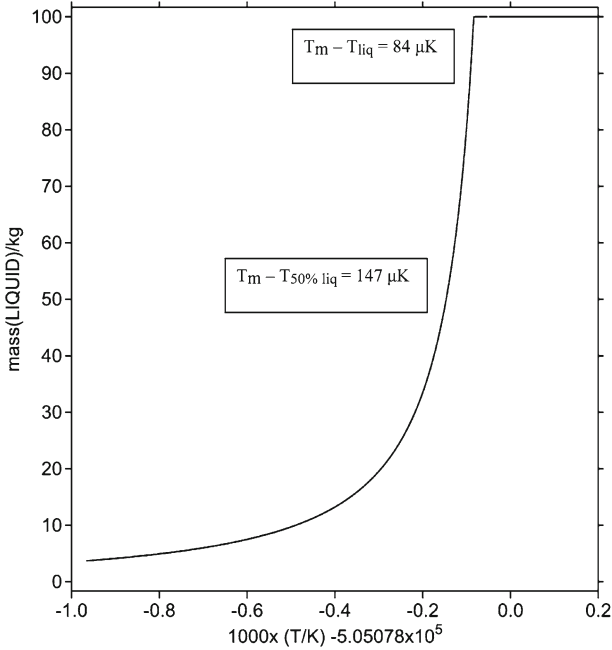
Fig. 5 Simulation of a freezing curve based on the NRC-measured Sn composition; analyzed levels for Ag, Cu, Pb, and Si plus 50 % of the limits of detection for other detectable impurities (T_m, etc. as defined in Fig. 4)
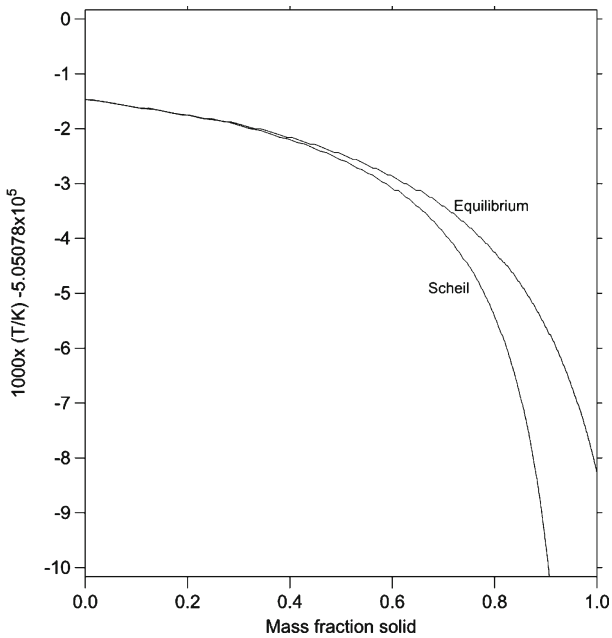

Fig. 6 Comparison of equilibrium vs. non-equilibrium (Scheil) freezing curves using an example of Sn with $10 \mu g \cdot g^{-1}$ Pb impurity

Table 2 Summary of NRC-analyzed Sn composition simulation (Uncertainties are dominated by the uncertainty of the chemical analysis—see text)

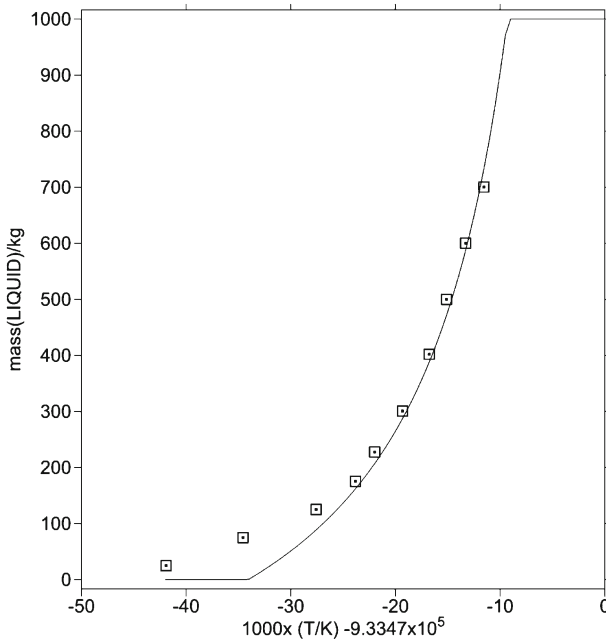| Composition	$(T_m - T_{liq})$ (µK)	$(T_m - T_{50\%\,liq})$ (µK)
Pb only	15	25
Analyzed Cu, Ag, Si, and Pb	24	44
Analyzed excluding Si	15	25
Analyzed + 50 % detection limits	84	147
Analyzed + 100 % detection limits	142	250
Ideal liquid and BCT[a] solid solution	120	214
Ideal liquid and pure BCT solid	180	352

[a] BCT = body cubic tetragonal

Fig. 7 $76\,\mu g \cdot g^{-1}$ Ag impurity in the aluminum point-MTDATA theory (line) compared to experimental points of Ancsin [7]. Temperature scale range is 933.420 K to 933.470 K

experimental results are compared in Figs. 7–9. It can be seen that for Ag (Fig. 7) and Si (Fig. 8) there is reasonable agreement. However, for Ti (Fig. 9) which should elevate the transition temperature and cause more rounding at the liquidus point, the agreement in shape is not so good (though the magnitude does agree). We do not know why this is the case. It may be that thermal effects mask the impurity effects, although the experiments were done in an adiabatic mode.

The diagrams (Figs. 7–9) show a temperature range of 40 mK to 50 mK spanning the pure element melting point; the temperature axis is effectively the "mK offset" from the phase-transition temperature. As the original MTDATA software was designed for commercial situations, the normal output has problems with alignment and over-writing of the axis units and the use of a mass scale (which we have set to a nominal
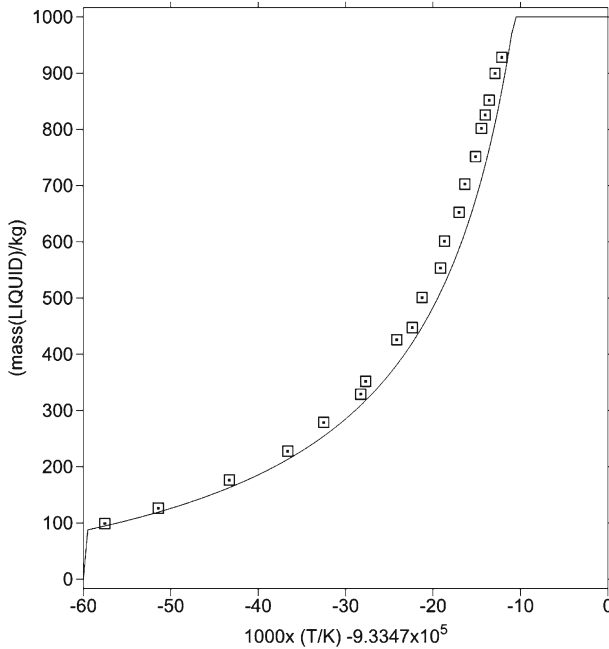
Fig. 8 $18.4\,\mu g \cdot g^{-1}$ Si impurity in the aluminum point-MTDATA theory (line) compared to experimental points of Ancsin [7]. Temperature scale range is 933.410 K to 933.470 K

100 kg for the Sn simulations and to 1000 kg for the Al simulations). Further, some of the values of the fixed-point temperatures are truncated from the full ITS-90 value; e.g., MTDATA uses 933.47 K instead of 933.473 K as the value of the aluminum fixed point. If MTDATA is to be further used for low-level impurities, it will be necessary to adjust the present software for these "extreme" limits. Some work on this has already been done. We are also considering the use of a software tool (called a "virtual measurement system") that would produce a more user-friendly "front end" to the software. This will be dependent on funding sources.

6 Conclusions

Equilibrium thermodynamic and limiting-case non-equilibrium (e.g., Scheil) simulations can help in both extrapolating freezing/melting "plateaux" to true liquidus temperatures and in estimating deviations of observed liquidus temperatures from the true pure element melting points.

There is much more thermodynamic data available for Al-X than for Sn-X (commercial Al-alloys vs. solders) and the experimental study to fill these gaps should be encouraged.

Considering chemical analysis issues, the uncertainty in sample analysis, in terms of the measured concentrations or the chemical state of the elements, is a significant
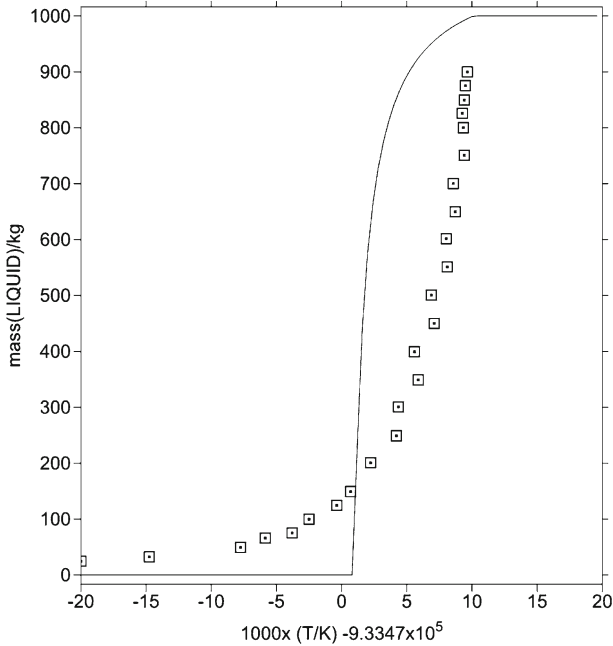
Fig. 9 $2.8\,\mu g \cdot g^{-1}$ Ti impurity in the aluminum point-MTDATA theory (line) compared to experimental points of Ancsin [7]. Temperature scale range is 933.450 K to 933.490 K. Note how the experimental data show the "wrong" curvature

problem possibly introducing more uncertainty than the thermodynamic modeling assumptions.

Results of Scheil simulations only start to significantly deviate from equilibrium above 70 % solid, suggesting equilibrium models are a good first approximation but non-equilibrium modeling should be better at determining the liquidus temperature from sub-liquidus experimental data near the end of solidification.

Equilibrium simulations are in close agreements with NRC doping experiments of melting Al with Ag and Si. The odd curvature of NRC Ti experimental results cannot be explained. With the high carbon levels, indicated by the analysis and use of graphite crucibles, the phase Al4C3 should always be present in Al fixed-point cells, but it does not appear to significantly contribute to deviations in the phase change.

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