Guide to
the Realization of the ITS-90

Cryogenic Fixed Points

APPENDIX 1: *Suggested Measurements and Measurement Conditions*

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Recommended measurements

It is recommended to perform the following series of measurements for realizing the triple point of a fixed-point sample with the scope of getting the essential data listed below and to reach the state-of-the-art level of uncertainty:

- Measurement of the heat capacity C_c of the entire Sealed Triple-Point Cell (STPC) assembly near to the triple-point temperature. (For hydrogen STPCs, the pre-melting caused by the spin-conversion catalyst may require to measure C_c both in a sufficiently large temperature range below the triple-point temperature T_{TP} and above T_{TP} [Fellmuth *et al.* 2005]).

- Determination of the total thermal isolation resistance R_e between the STPC and its environment (thermal shield) for checking purposes (optimal R_e values lie between 2000 K/W and 10000 K/W [Hermier *et al.* 2003, Pavese *et al.* 2003b]). One method for determining R_e is to observe the change of the STPC-temperature drift due to a jump of the temperature of its environment.

- Heating the sample through the solid-to-liquid phase transition applying two short heat pulses and allowing the STPC to come to thermal equilibrium roughly near the middle of the melting curve. The aims of this first short melt are to determine the heat of fusion Q_{HF} of the fixed-point sample, to perform a first comparison of all thermometers to check the measuring system and to ensure that in the subsequent melts, the sample is properly located in the STPC for maximum thermal contact between the solid-liquid interface and the thermometers. The Q_{HF} values obtained during the subsequent longer melts have to be evaluated as an additional overall check concerning the "parasitic heat load" $P_e + P_m$.

- For the proper realization of the triple-point temperature of equilibrium hydrogen, it has to be checked that the ortho-para conversion of the hydrogen into its equilibrium composition of the two nuclear-spin isomers, often called ortho and para hydrogen, has occurred before the measurements of the final melting curves are made. Several consecutive preliminary melting curves should be measured, allowing various time periods for the conversion to take place (with the sample being maintained in the liquid phase a few 10 mK only above the triple-point temperature during those periods).

- Determination of the relevant thermal resistances of the STPC as discussed in Subsection 3.2 and in more detail in [Wolber and Fellmuth 2013].

- Measurements of at least three melting curves $T_{equ}(F)$ under optimal thermal conditions and determination of mean values for $T_{equ}(F = 50\ \%)$, $T_{equ}(F = 90\ \%)$, and $\Delta T_{80\%} = T_{equ}(F = 90\ \%) - T_{equ}(F = 10\ \%)$ as the most important parameters. ($T_{equ}(F)$ is the equilibrium temperature at fraction F, which may be obtained as the asymptotic value by fitting the thermal recovery by a superposition of exponential components [Wolber and

Fellmuth 2013].) For at least one reference curve, the full melting in the F range from 5 % to 95 % should be investigated using melting steps being not larger than 10 %. The measurement at $F = 5$ % is useful for annealing the sample and for looking for possible pre-melting effects. The equilibrium temperature at $F = 95$ % is measured to check the thermal conditions because the thermal resistance R_{cs} usually has the largest value there. If the evaluation of the melting curves is based on the extrapolation to the liquidus point, the measurement of the complete shape for all three curves is required.

- Estimation of the dynamic temperature-measurement errors: For at least one melting curve, the thermal recovery after the heat pulses should be investigated in detail depending on F. For the investigation of the second part of the recovery of STPCs, it is generally necessary to wait several hours after each heat pulse. The overall necessary recovery times depend primarily on the properties of the fixed-point substance and the design of the STPC.

Desirable measurements

If possible, the following effects should be recorded additionally:

- Slow freezing with the STPC appropriately thermally isolated in vacuum in order to determine the magnitude of supercooling and to investigate the recovery from supercooling. (Since this may drastically change the recovery periods as well as the melting-curve shape [Wolber and Fellmuth 2008 and 2011], full measurement of the shape approaching the asymptotic readings is necessary in this case.)

- Refreezing from a high fraction of sample melted, e.g. $F = 90$ %, which may improve the crystal quality of the solid phase and thus decrease the width of the melting curve.

- Dependence of the thermal recovery and the shapes of the melting curves, especially at their beginning and/or end, on different experimental conditions: heat load determined for instance from the drift of the STPC temperature outside the melting range, temperature and period of the annealing of the solid phase prior to a melt, temperature gradients existing in the STPC after heating (use of heaters located at different parts of the STPC). (An analysis of all effects, which may influence the overall shape of a melting curve, shows that they can be separated only on the basis of results obtained under different experimental conditions. The influence of differing melting-curve shapes will be reduced when extrapolating to the liquidus point.)

Measurement conditions

To enable a direct comparison of the results concerning the thermal properties of STPCs, it is recommended for experimentalists to realize the following conditions for measuring the reference-melting curve:

- Using the R_{cs} data, the drift of the STPC temperature outside the melting range and thus the heat load should be decreased to come below the desired maximum static temperature-measurement error. Generally this condition means that the heat leak to the STPC amounts to, at most, a few microwatt during the measurements of the entire melting curve. The drift should be checked before and after each melting-curve measurement. It must not be towards lower temperatures in order to avoid surface supercooling.

- The determination of the heat load via the drift of the temperature of the STPC should be performed at temperatures, which deviate at least 10 mK from the triple-point temperature

T_{TP}. This ensures that the effective heat capacity is not increased by pre-melting of distorted sample parts having a weakened crystal lattice (below T_{TP}) or by the melting of the last small pieces of solid fixed-point substance (above T_{TP}), respectively. (For hydrogen STPCs, it might be necessary to investigate the temperature dependence of the heat capacity of the STPC in a range of 100 mK (or even more) below T_{TP} because of the pre-melting caused by the spin-conversion catalyst.) An increased effective heat capacity would reduce the drift and, thus, the estimated magnitude of the heat load would be too small. After the first cool-down of the cryostat, one has to wait until steady-state conditions are achieved in the whole measurement system. Otherwise, changing temperature gradients in the system would influence the drift of the STPC temperature, which could not be adjusted as correctly as necessary. Since the settling times are very large especially above 50 K, the first measurement of an oxygen or argon melting curve should start only one day after the first cool-down. (For a possibility to recover deviations from the equilibrium drift see [Wolber and Fellmuth 2013].)

- The heat load should cause at most a melting of only a few percent of the fixed-point sample during the whole melting-curve measurement. As determined from the drift before and after each melting-curve measurement, a correction should be included in the sum of the heat supplied. Otherwise it may not be possible to determine the heat of fusion with the desired uncertainty.

- Considering also the data obtained for the second part of the recovery (to deduce the recovery time $t_{r,x\,\mu K}$), the dynamic temperature-measurement errors caused by an incomplete recovery of the fixed-point sample after the heat pulses should not be larger than the desired level of $x\,\mu K$.

- Prior to the measurement of the melting curve, the solid fixed-point sample should be annealed sufficiently at a temperature which is at most a few 10 mK smaller than the triple-point temperature. True thermal equilibrium is reached during the annealing. Above 50 K, the annealing period should not be shorter than two hours. Below 50 K, a minimum annealing period of half an hour is necessary. For multi-compartment cells, the equalizing periods may be much larger than these values being typical for well designed single-element cells. In any case, a detailed investigation of the thermal equilibration is necessary.

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