Noise temperature measurements for the determination of the thermodynamic temperature of the melting point of palladium

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Abstract

The thermodynamic temperature of the melting point of palladium in air was measured by noise thermometry. The method is based on comparisons to a reference temperature near room temperature and utilized a two-channel arrangement to eliminate parasitic noises of electronic components by cross correlation. Three miniature fixed points filled with pure palladium (purity: ~99,99 %, mass: ~90 g) were used to realize the melts of the fixed point metal. The measured melting temperature of palladium in air amounted to a value of 1552,95 °C ± 0,21 K (k = 2). This temperature is 0,45 K lower than the temperature of the melting point of palladium measured by radiation thermometry. This is in good agreement with former measurements based on radiation thermometry which gave a mean value of 1553,4 °C ± 0,34 K (k=2) if corrected to temperatures in air.

1.   Introduction

The melting point of palladium is a widely used fixed point, for instance for the calibration of noble metal thermocouples in the temperature range above 1100 °C. According to the International Temperature Scale of 1990 (ITS-90) [1] in that range temperatures are defined by Planck's radiation law. Therefore the value of the temperature of the melting point of palladium of 1554,8 °C ± 0,1 K (k = 1) in an argon atmosphere provided by the Working Group 2 of the Comitè de Consultatif de Thermomètrie (CCT) [2] is based on radiation thermometry. Because thermocouples are contact thermometers it is desirable to determine the temperature of the melting point of palladium also by contact thermometers. In addition such a measurement should be performed in air, i.e. under the specific conditions of thermocouple calibrations.

Steady progress has been made over the last forty years in noise thermometry as a method to measure thermodynamic temperatures. It has been variously applied at both high and low temperatures. The development of two-channel correlation techniques and switching correlators [3] allowed the application of noise thermometry for metrological purposes [4, 5]. Several groups are involved in applying noise thermometers to the determination of thermodynamic temperatures [6]. The advanced improvement of electronic components, especially of the preamplifiers [7, 8] and the improvement of the measuring method now allow noise temperature measurements also at higher temperatures, for instance at the melting point of palladium, within about the same uncertainties that are accessible by radiation thermometry.

The aim of the noise temperature measurements at the melting point of palladium at the Physikalisch-Technische Bundesanstalt (PTB) was to determine the thermodynamic temperature of this fixed point independent on radiation thermometry and measured under the specific conditions of thermocouple calibrations. For this purpose a noise thermometer constructed at Forschungszentrum Jülich GmbH [9] was used.

2.   Noise thermometry

Noise thermometry is quantitatively based on the Nyquist formula which holds for all practical applications:

$$\overline{U^2} = 4kTR\Delta f \tag{2.1}$$

where $\overline{U^2}$ is the mean square noise voltage of any resistor, k the Boltzman constant, T the thermodynamic temperature R the ohmic resistance and Δf the bandwidth over which the noise voltage is measured. Equation 2.1 is the basis equation of noise thermometry, but it is seldom used directly because of practical problems, for instance the presence of other than thermal noise sources in the measuring circuit (amplifiers, leads, switches), the difficulty in measuring the bandwidth of the thermometer and the necessity of the calibration of the gain of the measuring system used. To overcome these problems the unknown temperature T_S is determined by comparing the mean square noise voltage of the measuring resistor R_S with that of a reference resistor R_R at a known reference temperature T_R within the same bandwidth Δf:

$$T_S = \frac{\overline{U_S^2}}{\overline{U_R^2}} \cdot \frac{R_R}{R_S} \cdot T_R \qquad (2.2)$$

Furthermore a correlation technique is applied to eliminate non-thermal, parasitic noise voltages. In the block diagram (figure 2.1) the consistent two-channel arrangement of parallel amplifiers is shown. For the noise signals of the measuring resistor and the reference resistor this arrangement means autocorrelation, for the parasitic noise signals of the amplifiers, leads and switches it means cross correlation. In this way such parasitic noise voltages will be eliminated [10].
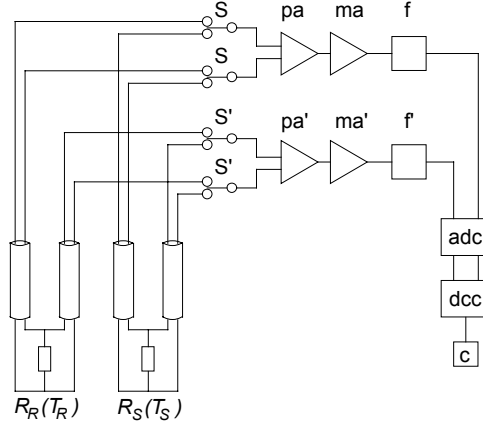

Fig. 2.1: Block diagram of a noise thermometer system (pa, pa': pre amplifiers; ma, ma': main amplifiers; f, f': filters; adc: analog to digital converter; dcc: digital cross correlator; c: computer)

By using equation 2.2 for calculating noise temperatures a linear function of amplification is assumed, but general the amplification is charcterized by a non-linear function $f(RT)$. Therefore two reference resistors are chosen with mean square noise voltages $\overline{U_{R1,2}^2}$ which fulfill the following condition (see figure 2.2):

$$\overline{U_{R1}^2} < \overline{U_S^2} < \overline{U_{R2}^2} \Rightarrow R_{R1}T_R < R_S T_S < R_{R2}T_R \qquad (2.3)$$

In this way only a limited range of the amplification function is used, which should be linear.
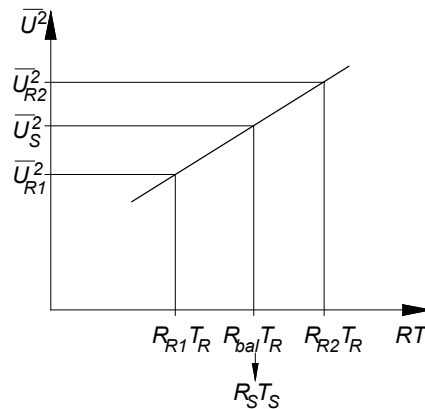

Figure 2.2: Mean square noise voltages $\overline{U^2}$ as function of resistances and absolute temperatures

The unknown temperature T_S can be calculated by equation 2.4 according to the difference-quotient method [4]:

$$T_S = \frac{R_{bal}}{R_S} \cdot T_R \qquad (2.4)$$

where R_{bal} is called balanced resistance. It can be calculated by linear interpolation of the noise voltages and the measured values of the different resistors. From figure 2.2 equation 2.5 can be deduced:

$$(\overline{U_S^2} - \overline{U_{R1}^2}) / [(\overline{U_{R2}^2} - \overline{U_S^2}) + (\overline{U_S^2} - \overline{U_{R1}^2})] = (R_{bal} - R_{R1}) / (R_{R2} - R_{R1}) \qquad (2.5)$$

The mean square noise voltages $\overline{U_S^2}$ and $\overline{U_{R1}^2}$ and $\overline{U_S^2}$ and $\overline{U_{R2}^2}$ will be measured in pairs within an interval of some minutes. Therefore the noise voltages $\overline{U_S^2}$ of the sensor resistor can represent different values $\overline{U_{S1}^2}$ and $\overline{U_{S2}^2}$ due to drift effects. The balanced resistance R_{bal} can be calculated by transforming equation 2.5:

$$R_{bal} = R_{R1} + [(R_{R2} - R_{R1}) \cdot \frac{(\overline{U_{S1}^2} - \overline{U_{R1}^2})}{(\overline{U_{R2}^2} - \overline{U_{S2}^2}) + (\overline{U_{S1}^2} - \overline{U_{R1}^2})}] \qquad (2.6)$$

The measurement process can be performed in cycles of different measuring times. At the beginning of each cycle, a standard resistor (100 Ω) is measured to calibrate the current source and to adjust the measuring current, which is used to calculate the values of the parameters R_S, T_R and R_{R1} (first cycle) from the measured voltages. Then the noise voltages of the measuring resistor R_S and of the first reference resistor R_{R1} are measured. During the next cycle, the same procedure is done for the measuring resistor R_S and the second reference resistor R_{R2}. One cycle lasts about 5-10 minutes so that influences of drift effects of the parameters on the measured noise temperature can be minimized. The measurement of the parameters were performed by current reversal to minimize uncertainties caused by offset voltages of the multimeter.

The accuracy of noise temperature measurements depends on the bandwidth Δf and the measuring time τ due to the stochastic nature of the thermal noise. In spite of the elimination of parasitic noise voltages by cross correlation such noise voltages still influence the statistical measuring uncertainty. The relative uncertainty is given by:

$$\frac{\Delta T}{T} = \sqrt{\frac{2}{\Delta f \cdot \tau}(2 + \frac{B}{A} + \frac{C}{A} + \frac{BC}{A^2})} \qquad (2.7)$$

A is the power spectral density of the measuring resistor ($R_S \cdot T_S$) and B and C are the power spectral densities of the amplifier chain's internal noise of the two channels ($R_{equi} \cdot T_R$) with R_{equi} as the equivalent noise resistance of each channel [11].

The most severe problem at noise temperature measurements is the detection and the avoidance of external electro-magnetic interferences (EMI), which can be superimposed on the useful noise signal. The inspection of the noise voltages for the presence of EMI is done by averaging the signals in the time domain and in the frequency domain. In this way non-random contributions can be detected. Interferences can be eliminated by blanking in the time domain and filtering in the frequency domain.

Another source of measuring uncertainties are the transmission properties of the transmission leads because these are the only parts of the noise thermometer which have not been passed through both by the signals of the measuring resistor and by the signals of the reference resistors. No transmission error occurs if the impedance of the transmission leads Z_W is fitted to the measuring resistor R_S, i.e. if the condition $Z_W = 2 \cdot R_S$ is fulfilled. That is valid for a signal transmission without any losses. In any other case the measured noise temperature depends on the frequency. Therefore this fitting condition can be checked by noise temperature measurements in different frequency intervals, where no differences in the measured noise temperatures should appear.

Furthermore uncertainties at noise temperature measurements can be caused by non-linearity effects of electronic components and by low insulation resistances between the measuring resistor or the transmission leads and the outer shielding tube of the noise sensor. For a detailed discussion of measuring uncertainties at the melting point of palladium see chapter 3.7.

3. Noise temperature measurements at the melting point of palladium
3.1 Performance characteristic of the noise thermometer

Independent on the theoretical consideration of sources of errors in noise thermometry practical noise temperature measurements at known temperatures can give an impression of accessible measuring uncertainties. The performance characteristic of the noise thermometer had been evaluated by measurements at three fixed points of the ITS-90, the triple point of water, the melting point of gallium and the freezing point of silver [5]. It should be noted that melts and freezes were used at silver point to determine its thermodynamic temperature. The measured noise temperatures correspond to the temperatures of these fixed points within their uncertainties based on the thermodynamic temperatures of these fixed points (Table 3.1). Furthermore it is recognizable that especially at higher temperatures the attainable uncertainties of noise temperature measurements will be in the same order of magnitude like the measuring uncertainties on application of other methods for measuring thermodynamic temperatures.

Table 3.1

Fixed points of ITS-90	ITS-90 temperature	Uncertainty of the thermodynamic temperature ($k = 2$)	Noise temperature	Uncertainty of the noise temperature ($k = 2$)
tp water	0,01 °C	-	0,013 °C	16 mK
mp gallium	29,7646 °C	2 mK	29,765 °C	12 mK
fp silver	961,78 °C	80 mK	961,813 °C	79 mK

3.2 High temperature furnace for the melting point of palladium

A vertical high-temperature three-zone furnace was used to form the thermal conditions for the realization of the melting point of palladium. It is designed for temperatures up to 1580 °C. The three separately controllable heating elements were made from powder-metallurgically produced molybdenum disilicide ($MoSi_2$). Each heating element is equipped with a type B control thermocouple.

The entire length of the furnace amounts to 1000 mm, the heated length to 750 mm and the inner diameter of the ceramic working tube amounts to a value of about 50 mm. Temperature gradients over the palladium ingot were determined with thermocouples and found to be within a temperature equivalent of ±0,2 K. Long-term temperature fluctuations (60 h) at fixed parameters of the controller ($T \approx 1550$ °C) did not exceed a value of about ±0,2 K. This indicates a high thermoelectric stability of the control thermocouples which is a precondition for reproducible temperature measurements.

In order to perform noise temperature measurements with relative uncertainties $\Delta T/T$ of about $4 \cdot 10^{-5}$ - $5 \cdot 10^{-5}$, some measures are necessary to optimize the furnace system with respect to electro-magnetic interferences. Instead of an alternating current power supply with phase-controlled thyristor units that is normally used for calibration furnaces, this furnace is equipped with a direct current load control including a three phase transformer and a three phase full-wave bridge-connected rectifier unit. Power control is effected by a current controlled power-FET unit for each heating circuit with water cooling for the power MOSFET's. Nevertheless during the preparation of the noise temperature measurements at the melting point of palladium some electro-magnetic interferences caused by the power supply of the furnace still were found. For their elimination three additional coils each with an inductivity of 7-8 mH have to be installed into the three heating circuits of the high temperature furnace.
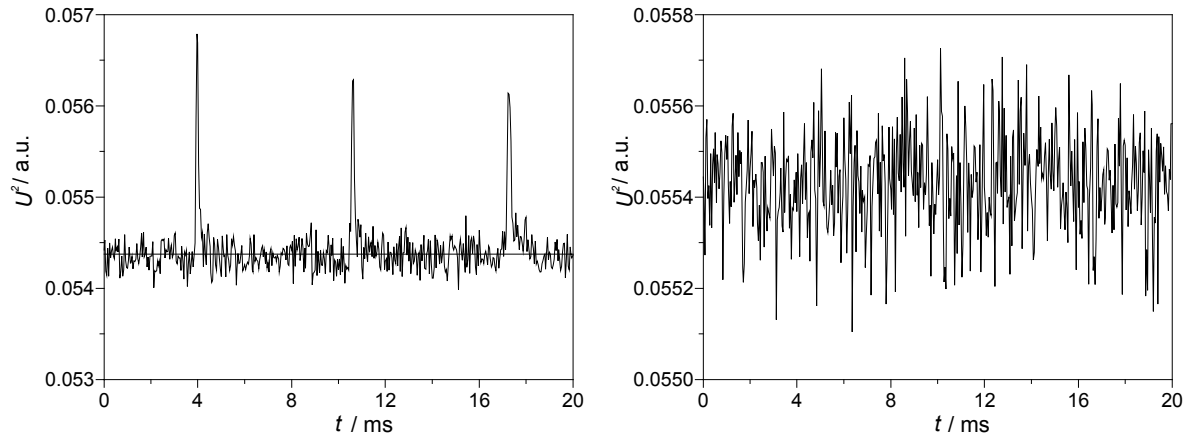
Figure 3.1: Noise signals in the time domain (1550 °C, sensor Pd-E2); left : before elimination of interference; right : after elimination of interference (Note that scale has been enlarged by a factor of 5)

In figure 3.1 the averaged noise voltages of the measuring resistor in the time domain are shown at a temperature of about 1550 °C before and after the elimination of the interferences by the additional coils. In both figures the squared noise voltages during about 2 hours measuring time are plotted (triggering: 50 Hz; time window: 20 ms; frequency interval: 20 kHz – 200 kHz). The three interferences (left graph) at a time distance of 6,67 ms correspond to a relative increase of the mean noise voltage of about $7 \cdot 10^{-4}$. In contrast, remaining EMI's at noise temperature measurements after reducing electro-magnetic interferences (right graph) were found to be lower than a relative temperature equivalent of $\Delta T/T = 2 \cdot 10^{-5}$.

3.3   Noise temperature sensor

The combined thermocouple-noise sensor Pd-E2 used consists of the measuring resistor (9,3 Ω at the melting point of palladium) welded between the measuring junctions of two type B thermocouples (figure 3.2). The four thermocouple wires (diameter 0,5 mm) serve simultaneously as transmission leads for the noise voltages. The measuring resistor is formed by a thin platinum wire (diameter 0,1 mm) that is threaded through the ten parallel holes in the wall of a small ceramic tube (length 15 mm). This tube is mechanically stabilized by a two-hole capillary tube inside of that tube. Two thicker platinum wires (diameter 0,35 mm) are drawn to this capillary tube and welded at their one ends to the thin platinum wire and at the other ends to the measuring junctions of the two type B thermocouples to close the electrical circuit. The four transmission leads run in a four-hole capillary tube on a length of 600 mm. At the upper end of the four-hole tube they are soldered to insulated copper leads which have been twisted in pairs to reduce the impedance Z_W of the transmission leads for a better fitting to the measuring resistance R_S. These copper leads have been connected to the noise thermometer. The noise sensor is sheathed with a thin Pt10%Rh tube (diameter: 6 mm, length: 620 mm) and a flexible copper shield at the cold end.
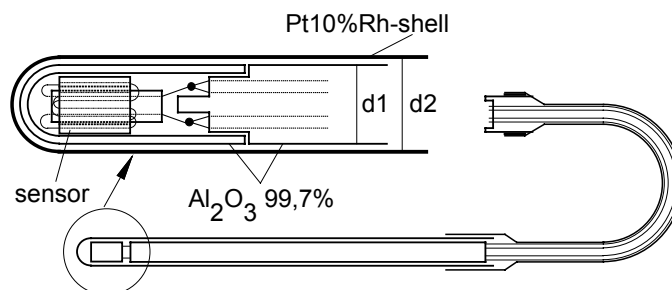

Figure 3.2. Combined thermocouple-noise sensor Pd-E2

3.4   Miniature fixed points for the melting point of palladium

Three miniature fixed point cells were constructed from components of pure alumina (Al_2O_3 99,7%). They were built up like classical fixed points for the realization of phase transitions in thermometry (figure 3.3). The miniature crucibles consist of a outer tube closed at one end with an outer diameter of 25 mm, a length of 90 mm and a wall thickness of 3 mm. The thermometer well (outer diameter: 12 mm, inner diameter: 7,5-8 mm) is located axially and is hold by two spacers at the top and the bottom of the crucible. The miniature fixed point PdRT-1 was filled with nominal 99,9985% pure palladium powder (90 g, Johnson & Matthey) and the two other fixed points were filled with nominal 99,99% pure palladium wire (Heraeus F&F GmbH, PdRT-2: 118 g, PdRT-3: 102 g).

Before the miniature fixed point cells were filled up with the fixed point metal the ceramic components were cleaned with distilled water and alcohol in an ultrasonic bath. Then they were heated in air for about four hours at a temperature of about 1580 °C to remove remaining impurities. To fill the ceramic crucibles with the palladium they were heated together with the starting material to a temperature of about 1560 °C in the same high temperature furnace that was used for the noise temperature measurements. This process was repeated three or four times until the crucibles were filled up to a height of about 60 mm. The filling procedure was performed in air as well as the noise temperature measurements too.
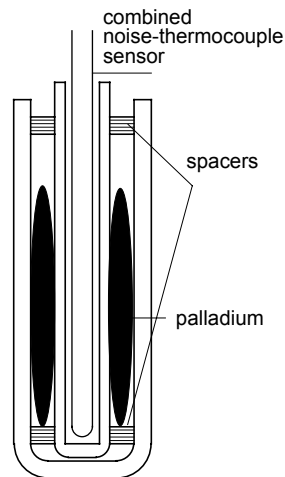

Figure 3.3: Miniature fixed point for the melting point of palladium

A special peculiarity at the phase transition of the palladium must be considered by using crucibles at this fixed point. Because of the expansion of the palladium during freezing and cooling there is a danger of cracking of the ceramic crucibles. At a first counter-measure the temperature of the furnace was left overnight at 1200 °C to reduce thermal strains. Furthermore during the freezing process a temperature gradient was adjusted so that the freezing starts from the bottom to the top of the crucible. This procedure should allow the palladium to expand to the free volume above the liquid phase of the palladium.

Nevertheless at the end of the noise temperature measurements cross cracks were found above the bottom of the fixed point crucible PdRT-3. By that a small amount of the palladium were leaked out of the crucible but no influence on the melting temperature could be detected.

3.5   Determination of the melting temperature of palladium

All experiments were performed in air to meet the specific conditions of thermocouple calibrations. The measuring procedure for the determination of the melting temperature of palladium was characterized by the following steps:

- installation of a miniature fixed point in the working tube of the high temperature furnace,
- adjustment of the furnace temperature to a value of about 1540°C (heating rate: ≈300 K/h),

- stabilizing of the temperature for about two hours to adjust the thermal equilibrium between the furnace temperature and the temperature of the fixed point cell with the palladium,
- increasing of the furnace temperature by a heating rate of 1 K/min up to a value 1-2 K above the melting temperature of palladium and calculating of the melting curve by the measured thermovoltages of the combined thermocouple-noise sensor simultaneously,
- noise temperature measurement during the melting process (chapter 2),
- decreasing of the furnace temperature by about five or six Kelvin to introduce the freezing of the palladium after its undercooling and
- once more stabilizing of the furnace temperature at about 1545 °C for the next melting (or decreasing the furnace temperature to a value of 1200 °C overnight).

3.6   Results

For the determination of the thermodynamic melting temperature of palladium 38 melts with the different miniature fixed points were realized and the accompanying melting plateaus were analysed. The duration of the melting plateaus was usual between three and five hours but only about one or two hours for the miniature fixed point PdRT-3 after its ceramic had been cracked. In figure 3.4 the results of the noise temperature measurements are shown. The noise temperatures of the single measurements correspond within their statistical uncertainties ($k = 2$) (equation 2.7) to the averaged noise temperatures of the single miniature fixed points independent on the measuring mode (time or frequency domain). The calculated mean noise temperatures of the three miniature fixed points also correspond to each other within their statistical uncertainties given for $k = 1$, which indicate a good reproducibility of the measurements (table 3.2).

On the other hand the agreement of the measured noise temperatures indicates that the higher starting purity of the palladium powder in the miniature fixed point cell PdRT-1 did not influenced the value of the melting temperature of the palladium significantly. The reason could be that the surface-to-volume ratio of powder is more unfavourable than that of a wire. In this way the powder is more prone for picking up impurities from the furnace atmosphere, which could diffused into the palladium during the repeated filling procedure. As a result the whole impurity concentration in the palladium of the miniature fixed point PdRT-1 could be increased faster than that of the palladium wire of the miniature fixed points PdRT-2 and PdRT-3. Finally the impurity concentrations of the palladium in the three miniature fixed points could have been attained about the same value.
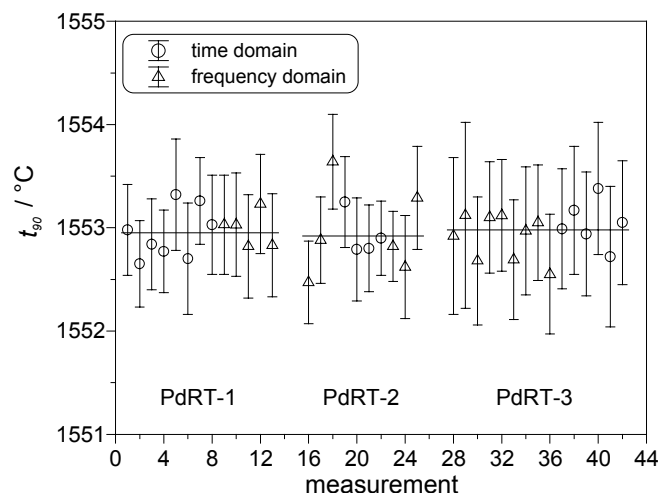

Figure 3.4: Noise temperatures at the melting point of palladium

Table 3.2:

miniature fixed point	t_{90} / °C	statistical uncertainty ($k = 1$)
PdRT-1	1552,95	0,065 K
PdRT-2	1552,92	0,068 K
PdRT-3	1552,98	0,078 K

3.7 Measuring uncertainties

The unknown noise temperature at the melting point of palladium is obtained according to equation 2.4 from:

$$T_{Pd} = (\frac{R_{bal}}{R_S} + \delta \frac{R_{bal}}{R_S}) \cdot (T_R + \delta T_R) + \delta T_{stat} + \delta T_{EMI} + \delta T_{trans} + \delta T_{lin} + \delta T_{flux} + \delta T_{range}, \qquad (3.1)$$

with

T_{Pd}	noise temperature at the melting point of palladium,
$\delta \frac{R_{bal}}{R_S}$	correction due to the uncertainty of the electrical measurement of the resistances,
δT_R	correction due to the uncertainty of the reference temperature,
δT_{stat}	correction due to the statistical uncertainty of the noise temperature (equation 2.7),
δT_{EMI}	correction due to electro-magnetic interferences,
δT_{trans}	correction due to the transmission properties of the noise sensor Pd-E2,
δT_{lin}	correction due to non-linearity effects of electronic components of the noise thermometer,
δT_{flux}	correction due to the heat conduction along the noise sensor and
δT_{range}	correction due to the extension of the melting plateau to a melting range.

The uncertainty budget of the noise temperature measurements at the melting point of palladium is summarized in table 3.3. The specific contributions are qualified below.

The melting temperature of palladium is calculated by equation 2.4 with a resistance ratio $R_{bal}/R_S \approx 6,1$. At a reference temperature of about 300 K and an uncertainty of the electrical measurement of $9,6 \cdot 10^{-6}$ the measuring uncertainty at the melting point of palladium caused by the uncertainty of this resistance ratio corresponds to a temperature equivalent of about 18 mK. The uncertainty of the reference temperature T_R was caused by the measuring uncertainty of the calibration of the used Pt-100 thermometer of 3 mK. This measuring uncertainty lead to an uncertainty of the noise temperature at the melting point of palladium of about 18 mK.

The statistical uncertainty of the mean noise temperature was calculated corresponding equation 2.7. The entire measuring time $\tau \approx 70$ h was determined by adding the measuring times τ of all the single measurements by the miniature fixed points PdRT-1 – PdRT-3. The noise temperature measurements were carried out in the frequency interval Δf between 20 kHz and 140 kHz, so that for Δf a value of 120 kHz was used. A was received by multiplication of the balanced resistance with the reference temperature. The values of B and C could be calculated as the product of the reference temperature and the equivalent noise resistances of the both channels for amplification and signal transmission. The equivalent noise resistances were determined by noise voltage measurements at a short-circuit state of the measuring and the reference resistor. The ratios of the power spectral densities B/A, C/A and BC/A^2 amounted to about 1,6; 1,5 and 2,3 respective.

Before starting a noise temperature measurement the noise signals were checked for electro-magnetic interferences in the time domain and in the frequency domain. All interferences found could be reduced (see chapter 3.2), so that their remaining influences on the measured noise temperature did not exceed a value of about $\Delta T/T = 2 \cdot 10^{-5}$, which corresponds to a temperature of 37 mK at the melting point of palladium. If necessary a correction or rejection of a noise temperature measurement could be performed on basis of the stored noise signals in the time or in the frequency domain (as an example see figure 3.5) during such a measurement.

The uncertainty caused by the non entirely fitted impedance Z_W of the transmission leads and the measuring resistance R_S, limited by the construction of the noise sensor, could be estimated from the recorded averaged temperature spectra within the used frequency interval. In figure 3.5 the averaged temperature spectrum of six noise temperature measurements at the miniature fixed point PdRT-2 in the frequency interval between 20 kHz and 140 kHz is presented. The entire measuring time of these six measurements amounts to a value of 13,5 hours. The mean noise temperature calculated from the noise signals in the frequency interval Δf between 20 kHz and 80 kHz was about 60 mK higher than the temperature calculated from the signals in the frequency interval Δf between 80 kHz and 140 kHz. In this way a slight dependence on the frequency of the noise temperature was detected. The caused uncertainty contribution corresponds to half of that temperature difference, i.e. to a temperature equivalent of about 30 mK at the melting point of palladium. On the other hand

no electro-magnetic interferences appeared, which could be influenced the value of the noise temperature measured significantly.
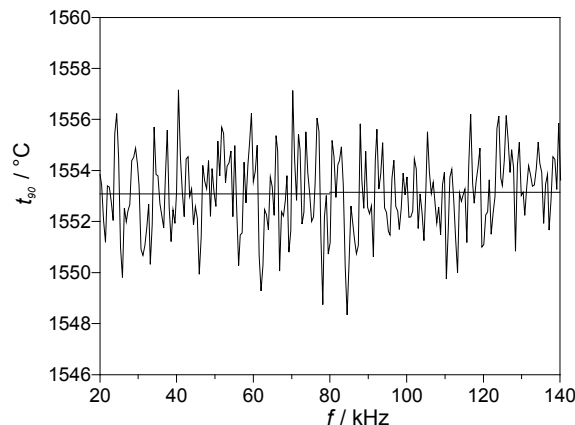

Figure 3.5: Averaged temperature spectrum of six noise temperature measurements at the melting point of palladium

Non-linearities of electronic components of the noise thermometer, especially such of the amplifiers, can cause measuring errors during the measurement of the measuring and reference resistors. That is the case, if the output voltages of the both resistors at the correlator are different and parts of them are in the non-linear amplification range. An indication for the probability of that state is the value of the voltage U_{rms} at the output of the correlator. If this value is lower than 0,1 V influences of non-linearities on the measured noise temperature can be almost neglected [4]. By changing the amplification of the measuring system the voltage at the output of the correlator could be reduced to a value of $U_{rms} < 0,1$ V. In this way the uncertainty contribution caused by non-linearities could be estimated to a value of $\Delta T/T = 1,5 \cdot 10^{-5}$ by considering the results of the extensive investigations of that problem at noise temperature measurements at the triple point of water [4].

The influence on the measured temperature of the heat flux along the noise sensor was estimated on basis of thermovoltage measurements at different immersion depth by the thermocouples of the combined noise sensor Pd-E2 at a temperature of about 1550 °C. The change of the measured thermovoltages by reducing the immersion depth by a value of 5 cm corresponds to temperature equivalent of about 40 mK ($\Delta T/T = 2,2 \cdot 10^{-5}$).

The most important contribution of the combined uncertainty of the noise temperature at the melting point of palladium was the shape of melting plateaus. In contrast to usual phase transitions of fixed point realizations there were found no really flat and temperature constant plateaus at the melting point of palladium. The phase transitions could be described by melting ranges extended over some tenth of a Kelvin. The reason could be the temperature profile of the furnace that promote an axial phase transition in the crucible. The liquid/solid phase boundary moves from the bottom to the top of the crucible passing the measuring resistor. In this way the needed melting heat counteracts only locally restricted against the increase of the temperature in the immediate surrounding of the measuring resistor. In the case of an even movement of the liquid/solid boundary and a central position of the measuring resistor in the miniature fixed point cell the mean temperature of the melting range can be assumed as the value of the melting temperature of palladium. This temperature corresponds to the arithmetic average of all noise temperature values measured during the corresponding melting process. The mean melting range of a palladium melt amounted to about 430 mK. Therefore the uncertainty of the averaged noise temperature corresponds to half of the melting range, i.e. 215 mK.

The measuring results of a single noise temperature measurement at the melting point of palladium are shown in figure 3.6. The temperatures calculated by the thermovoltages of the two thermocouples of the combined noise sensor Pd-E2 allow an unambiguous identification of the melting plateau from the recorded melting curve. The vertical lines mark the beginning and the end of the phase transition and only these noise voltages were used to calculate the noise temperature, which were measured during this melting period.
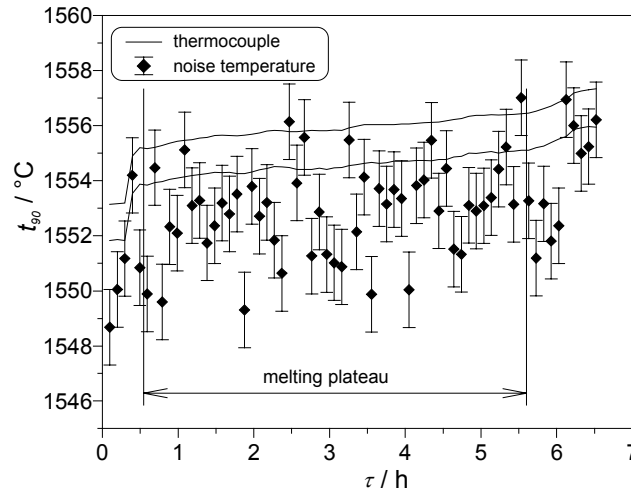
Figure 3.6: Melting curve during a noise temperature measurement at the melting point of palladium

The uncertainty budget of the noise temperature measurements at the melting point of palladium for $k = 1$ is given in table 3.3. The first column contains the different quantities of uncertainty, the second one the estimation of the corresponding corrections, the third column the uncertainties or estimated limits of uncertainties, the fourth one the probability distributions and the last column the individual uncertainty contributions. The combined uncertainty (106 mK) is received by the quadratic addition of the uncertainty contributions. The expanded uncertainty ($k = 2$) of the average measured noise temperature of 1552,95 °C (Table 3.2) amounts to a value of 0,21 K, which corresponds to a relative measuring uncertainty of $\Delta T/T = 1{,}16 \cdot 10^{-4}$.

Table 3.3. Uncertainty budget of the noise temperature measurements at the melting point of palladium ($k = 1$)

quantity	estimation	uncertainty/limit	probability distribution	uncertainty contribution
δT_{stat}	0	40 mK	normal	40 mK
$\delta(R_{bal}/R_S)$	0	18 mK	rectangular	10 mK
δT_R	0	18 mK	normal	18 mK
δT_{EMI}	0	37 mK	rectangular	21 mK
δT_{trans}	0	31 mK	rectangular	18 mK
δT_{lin}	0	27 mK	rectangular	16 mK
δT_{flux}	0	40 mK	rectangular	23 mK
δT_{range}	0	215 mK	triangular	88 mK
T_{Pd}	1552,95 °C	/	/	106 mK

3.8 Discussion

For a direct comparison of the measured noise temperature at the melting point of palladium in air with the temperatures measured by radiation thermometry in argon the last ones must be corrected by the known temperature difference of –1,4 K to the melting temperature in air [12]. The noise temperature measured in air as well as the temperatures measured by radiation thermometry in an argon atmosphere (corrected for the melting temperature in air) are presented in figure 3.4. The mean noise temperature amounted to a value of 1552,95 °C ± 0,21 K, by which the uncertainty given for $k = 2$ of this thermodynamic temperature is in the same order of magnitude as the uncertainty of 0,34 K ($k = 2$) of the mean thermodynamic temperature measured by radiation thermometry and corrected for air. The last uncertainty (0,34 K) can be derived from the three following uncertainty contributions:

- uncertainty of 0,2 K ($k = 2$) of the ITS-90 temperature [2] based on the three independent radiation thermometric measurements at the melting point of palladium,

- uncertainty of the thermodynamic temperature of the melting point of gold propagated to the melting point of palladium $(0,1 \text{ K} \cdot (T_{Pd}/T_{Au})^2 = 0,19 \text{ K})$ and
- uncertainty of 0,2 K $(k = 2)$ of the temperature correction of $-1,4$ K between the melting temperatures of palladium in argon and air, determined by our own measurements [5].
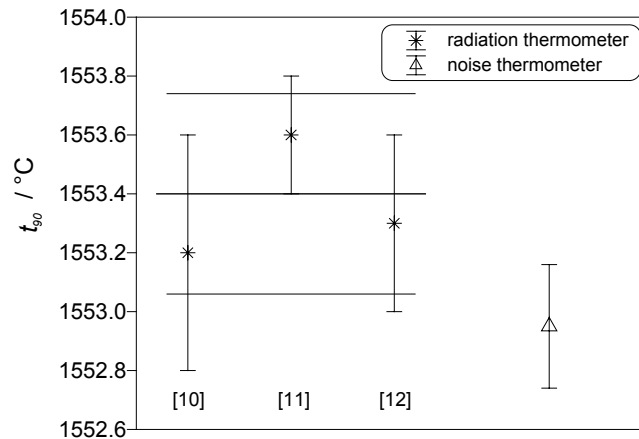

Figure 3.7: Thermodynamic temperatures at the melting point of palladium

It should be mentioned, that the uncertainty of the mean temperature measured by radiation thermometry really amounts to a value of only 0,28 K $(k = 2)$, because the uncertainty contribution of the applied temperature correction of $-1,4$ K is not primarily ascribable to the temperature measured by radiation thermometry. Nevertheless by utilizing this correction of $-1,4$ K and its uncertainty of 0,2 K a value of 1553,4 °C $\pm$ 0,34 K $(k = 2)$ is received for the melting temperature of palladium in air based on the temperature for that fixed point given by WG 2 of CCT [2]. Consequently the temperature difference between the both methods amounted to 0,45 K.

The purity of a metal has an important influence on the value of its melting temperature. Samples of the starting material (palladium wire) and palladium samples of the miniature fixed points after the determination of the melting temperature were investigated by mass spectroscopic methods. The entire impurity concentrations of the palladium from the three miniature fixed points after the noise temperature measurements were about two to three times higher than these found for the starting material. Therefore the purity of the palladium in the miniature fixed points during the noise temperature measurements should be in the range between 99,97% and 99,99%.

For the comparison of the melting temperatures of palladium measured by noise thermometry and radiation thermometry on basis of the purity of the palladium the following specifications can be considered:

- Jones and Hall [12] used palladium with less than 10 ppm impurities, i.e. a purity of 99,999%,
- Coates, Chandler and Andrews [13] corrected their measured melting temperature on a state of pure palladium, i.e. a purity of at least 99,9999% and
- Jones [14] used palladium of 99,99% purity.

The mean purity of the palladium used for the measurements by radiation thermometry amounts to a value of about 99,996%, the mean purity of the palladium for the noise temperature measurements (PdRT-1 – PdRT-3) amounts to a value of about 99,98 %. Most of the proved impurities in the palladium cause a decrease of the melting temperature (exceptions: Pt, Rh, Ir). Because of the lower purity of the palladium for the noise temperature measurements, this temperature should by systematically lower than the melting temperature measured by radiation thermometry. An estimation of the temperature difference caused by the different impurity concentrations in the palladium concludes from the comparison of the measurements by radiation thermometry among themselves. The temperature of Coates, Chandler and Andrews is about 0,3 K – 0,4 K higher due to the higher purity (about one order of magnitude) than the two other temperatures at the melting point of palladium based on radiation thermometry. Therefore the measured noise temperature could be

corrected by about the same order of magnitude (+0,3 K) if one considered the different purity of the palladium used.

4.   Conclusion

The thermodynamic temperature of the melting point of palladium, measured by noise thermometry in air, was found to be 1552,95 °C ± 0,21 K ($k = 2$) and corresponds to about the temperature of that fixed point based on radiation thermometry within the uncertainties. The temperature measured by radiation thermometry corrected to the temperature in air of 1553,4 °C ± 0,34 K ($k = 2$) is systematically higher (+0,45 K) than the thermodynamic temperature based on noise thermometry due to the higher purity of the palladium used. Nevertheless the correspondence of the results of the both different methods for the measurement of thermodynamic temperatures and the similar measuring uncertainties show clearly, that the noise thermometry is an alternative method to the radiation thermometry for the measurement of thermodynamic temperatures in the higher temperature range.

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