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The α–β Transition of Nitrogen

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Abstract It is well-known that, aside from its triple point, nitrogen exhibits a solid-to-solid transition at about 35 K that is of some interest as a secondary reference temperature. During the recently published highly accurate measurements of the triple point of nitrogen (*Metrologia* **43**, 435 (2006)), an extensive study was made also of the solid α–β transition of nitrogen, using both the continuous heating method and the pulse-heating method. This transition is of significantly lower quality than the triple point of nitrogen. A very high thermal resistance and a large time constant characterize the transition. Therefore, even the determination of the self-heating of the thermometer requires a very long time. A value of $T_{90} = 35.620\,\text{K}$ with an expanded uncertainty $U = 8\,\text{mK}$ for the coverage factor $k = 2$ was found, differing by +6 mK from the published CCT-recommended value. The reproducibility of the value was better than ±5 mK. In addition to the temperature value found for the transition, a comparison is made with previous measurements on this point, and an overview is given of the available information about it.

Keywords α–β Transition · Nitrogen · Solid thermometry

1 Introduction

In 1996, the Consultative Committee for Thermometry (CCT) published an updated list of recommended values of temperature on the International Temperature Scale

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of 1990 (ITS-90) for a selected set of secondary reference points [1]. The numerical value of most of these points was obtained by converting values on the IPTS-68 (the International Practical Temperature Scale of 1968) to the ITS-90. This is generally the reason that the uncertainty in these values is larger than would be expected from the original data presented on the IPTS-68. Only a small number of the fixed-point temperatures were revised by experiments performed with thermometers calibrated on the ITS-90.

Some low-temperature secondary fixed-point temperatures have been checked at the Institute of Low Temperature and Structure Research (INTiBS) in Poland, such as the solid oxygen phase transitions [2,3]. Recently the temperatures of the triple point of nitrogen and the α–β transition in solid nitrogen were determined for the first time on the ITS-90. Nitrogen was chosen because previous measurements of its triple point demonstrated its good thermometric properties [4–7]. The results for the triple point were published in [8], and results for the solid α–β transition are presented here.

2 Nitrogen Cell

The measurements were performed on the sealed-cell 3N2 manufactured at the Istituto di Metrologia "G.Colonnetti" (IMGC, now INRIM) in Italy. The construction of the cell is typical of other IMGC single-substance thermometric cells as described in [5]. The total mass of the cell was measured in 1986 at IMGC as 175.3210 g, as 175.3200 g in 1999, and in 2004 at INTiBS as 175.3164 g. The very small differences in mass could arise from cleanliness (traces of silicon grease, abrasion), differences in measurement accuracy at both institutes, or (very unlikely) from a real leakage of gas, but the thermometric properties of the cell, as well as its fixed-point temperature, remain unaffected. At the time of filling, 4.230 g of gas was sealed inside. On the basis of the most recent weighing, now 4.225 g of gas is present. The cell, then, contains 0.151 mol of nitrogen leading to a value for the total heat of melting, at the triple point, of 108.7 J. The nominal purity of the gas is 99.9995%, while the certificate of analysis gives $\mathrm{Ar} + \mathrm{O}_2 = 1.6$ ppm. The remaining impurities are assumed to be negligible.

3 Scale Realization

The capsule standard platinum resistance thermometer (CSPRT) Leeds and Northrup No. 1866336 was used for the temperature measurements. The thermometer was chosen from a group of six CSPRTs—Tinsley (3), VNIIFTRI (2), and Leeds and Northrup (1)—because it shows the best reproducibility. For several years, its reproducibility at the water triple point has been checked two to three times per year. The thermometer was calibrated at INTiBS, for the range above 24.6 K, at the six low-temperature fixed points defined by the ITS-90. The CSPRT was also used to determine the thermometric properties of a new generation of multi-compartment cells within the framework of the EU project MULTICELLS[1] [9].

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[1] Improvement of European traceability in temperature measurements below 0°C using permanently-sealed transportable multicell standards.

The water triple point is realized in cells made by the National Physical Laboratory of the UK (NPL) and the Ulusal Metroloji Enstitüsü of Turkey (UME). Cell UME No. 51 was compared with the Główny Urząd Miar[2] (GUM) standard cell (Tinsley No. 782), which participated in EUROMET Project No 549, and a difference between the GUM and INTiBS cells of 3 μK was found with an expanded uncertainty $U = 85\,\mu$K. [10]. This cell was used to calibrate thermometer No. 1866336. Propagating this uncertainty to 35 K, where the α–β transition of nitrogen occurs, results in a negligible contribution to the measurement uncertainty.

The mercury triple point is realized in a miniature cell made at INTiBS [11] and compared with a traditional mercury cell at IMGC [12]. Several miniature cells (the size of a SPRT) were sealed at INTiBS with mercury from different sources: NIST (99.99999%), Rône Alpes (99.9999%), and Goodfellow (99.9999%). All melts were within 0.1 mK, i.e., comparable to the realization uncertainty [11,12]. The fixed points of hydrogen, neon, oxygen, and argon were realized in sealed cells, all produced by IMGC. These cryogenic fixed-point cells participated in the international star comparisons of low-temperature fixed points carried out under the auspices of EUROMET Project No. 377[3] [13].

Impurity data for the fixed-point cells 3Ar and 2O2 were already given in [8]. The impurity levels of the other two fixed-point cells, 7Ne and 14eH2, are omitted here for lack of space, but they are of comparable quality. The uncertainty budget for the realization of the various fixed points is given in Table 1. Considering the modest quality of the α–β transition, these uncertainties hardly influence the assigned temperature.

All these cells together constitute at INTiBS the national temperature standard for the low temperature range between 24.5561 and 273.16 K.

4 Cryostat

The cryostat fabricated at INTiBS and used for the measurements was already described in [11]. In order to improve the adiabatic conditions, an additional gold-plated copper shield was mounted around the cell. The temperature of the two shields is controlled by a Lake Shore Cryotronic controller Model 340. The temperature of the shields is measured by two small rhodium–iron thermometers from Oxford Instruments. The thermal resistance R_S between the nitrogen cell and an adiabatic shield in the cryostat was equal to 51,000 $\mathrm{K \cdot W^{-1}}$ at a temperature of about 35 K. With these conditions, the parasitic heat to the cell amounted to less than 10 μW.

5 The α–β Transition in Nitrogen

In solid nitrogen, two solid-to-solid phase transitions appear but only one—the α–β transition—is on the vapor pressure curve, at a temperature of about 35 K. A γ-phase

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[2] Central Office of Measures in Warsaw.

[3] Intercomparison of Low-Temperature Fixed Points using Sealed Triple Point Cells.

Table 1 Uncertainty budget for calibration of resistance thermometers at the low-temperature fixed points

	Uncertainty u (mK)					
Uncertainty components	H_2O	Hg	Ar	O_2	Ne	H_2
Long-term stability of the standard resistor	0.03	0.00	0.00	0.00	0.00	0.00
Temperature dependence of the standard resistor	0.02	0.01	0.00	0.00	0.00	0.00
Readings of standard resistance value	0.01	0.00	0.00	0.00	0.00	0.00
Bridge readings at the triple point of reference substances	0.00	0.04	0.03	0.03	0.10	0.45
Bridge readings at the water triple point	0.03	0.02	0.01	0.00	0.00	0.00
Influence of impurities and isotopic composition of substances	0.06	0.06	0.03	0.13	0.16	0.13
Hydrostatic pressure correction for reference substances	0.00	0.02	0.05	0.02	0.03	0.01
Adiabatic conditions in cryostat	0.05	0.00	0.00	0.00	0.00	0.00
Thermometer self-heating correction	0.01	0.04	0.02	0.03	0.07	0.00
Measurement of resistance using AC bridge	0.02	0.02	0.02	0.02	0.07	0.34
Propagation of uncertainty from the water triple point	0.00	0.10	0.02	0.01	0.01	0.00
Definition of T_{tp} (including fitting)	0.00	0.02	0.02	0.02	0.06	0.06
Standard combined uncertainty	*0.09*	*0.14*	*0.08*	*0.14*	*0.22*	*0.58*
Expanded combined uncertainty; $k=2$	*0.18*	*0.28*	*0.15*	*0.29*	*0.44*	*1.16*

exists in pure nitrogen, but at pressures higher than 3.5 kbar. At a slightly higher pressure, a triple point exists between the α, β, and this new γ-phase at about 40 K (E. Szczepaniec-Cieciak, Private communication). Then the γ-phase-limit pressure continues to increase with temperature until another triple point of phases β, γ, and a new δ-phase appears at about 50 kbar and 65 K; then a δ-phase exists above about 50 kbar, while a triple point between the β, δ, and liquid phase occurs at about 70 K (E. Szczepaniec-Cieciak, Private communication). An approximate temperature value for the α–β transition, which is of the order(fcc)–disorder(hcp) type, was given by Brookeman and Scott [14] as 35.6 K. The initial slope is 207 bar·K^{-1} (with a standard uncertainty $u = 17$ bar·K^{-1}). Investigations of the thermometric properties of the α–β transition were only carried out in 1979 by Kemp and Kemp [15]. They noticed that the transition plateau observed by continuously heating the sample had a most peculiar shape unlike any previously observed for other phase transitions. The α–β nitrogen transition temperature rises to a peak before falling to a long, shallow minimum and increasing in temperature toward the end of the transition. In view of this shape, it is not obvious how to associate a temperature with the transition. For thermometric purposes, the central and flattest part of the transition is the most suitable and, to this region, Kemp and Kemp assigned a temperature value of 35.621 K ($u = 3$ mK) on IPTS-68, equivalent to 35.614 K on ITS-90, the current CCT-recommended value. At the time, the heat-pulse method was not used for studies of the transition because of the very long recovery time.

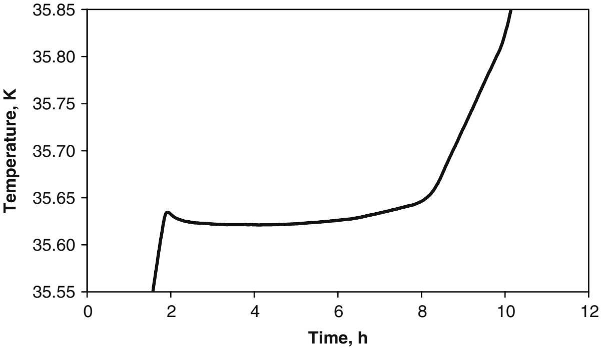

Fig. 1 Shape of the α–β transition in nitrogen

The α–β nitrogen transition was also investigated at INTiBS. It is a first-order transition, as demonstrated by its volumetric change, see Manzhelii and Freiman [16], Heberlein [17], and Brookeman and Scott ($0.311\,\mathrm{cm}^3\cdot\mathrm{mol}^{-1}$, with $u = 0.025\,\mathrm{cm}^3\cdot\mathrm{mol}^{-1}$) [14]. According to the same source, hysteresis (observed at INTiBS) is to be attributed to the transition, being of first order. The heat of transition for the tested cell was measured as being $Q_{\alpha-\beta} = 32.4\,\mathrm{J}$, leading to a ratio of $Q_{\alpha-\beta}/Q_{\mathrm{melt}} = 0.312$. This compares favorably with the molar ratio of $Q_{\alpha-\beta}/Q_{\mathrm{melt}} = 0.318$, calculated from the experimental values of Giauque and Clayton [18], as given by Manzhelii and Freiman [16], $\Delta H_{\mathrm{tr}} = 721.4\ \mathrm{J}\cdot\mathrm{mol}^{-1}(u = 2.1\,\mathrm{J}\cdot\mathrm{mol}^{-1})$ and $\Delta H_{\alpha-\beta} = 229.1\,\mathrm{J}\cdot\mathrm{mol}^{-1}(u = 0.4\,\mathrm{J}\cdot\mathrm{mol}^{-1})$.

The shape of the transition plateau—presented in Fig. 1—was similar to that observed by Kemp and Kemp. A maximum in temperature is seen at the beginning of the transition before an almost flat plateau, and the temperature then increases quickly toward the end of the transition—yet before the full transformation of the α-phase to the β-phase appears, a rare case of overheating of the lower solid, here probably apparent and prompted by the very long thermal equilibration time. The slope of the curve between 8 and 10 h is different from that when only the β-phase exists. The measurements were carried out a few times with different rates—where the total time of transformation varied between 5 and 15 h. In each run, the sample was cooled below 30 K and kept there for a few hours. The curve shapes obtained were similar, independent of the heating rate and "annealing" time. The temperature of the flat part of the plateau in the α–β transition of nitrogen is equal to $T_{90} = 35.620\,\mathrm{K}$, with an expanded uncertainty $U = 8\,\mathrm{mK}$. The reproducibility of the temperature was better than ±5 mK.

The sample was also cooled from the β-phase to the α-phase at a specified rate by properly controlling the temperature of the adiabatic shield surrounding the cell. An apparent hysteresis effect was observed for the transitions. The β–α transition temperature is lower and equal to $T_{90} = 35.550\,\mathrm{K}$ as shown in Fig. 2.

Considering the modest quality of this transition, details of the SPRT calibration down to 24.5 K and possible effects on the calibration from isotopic influences at the hydrogen and neon fixed points have negligible influence on the total uncertainty, see Table 1. As can be seen in Fig. 2, the shapes of the heating and cooling curves

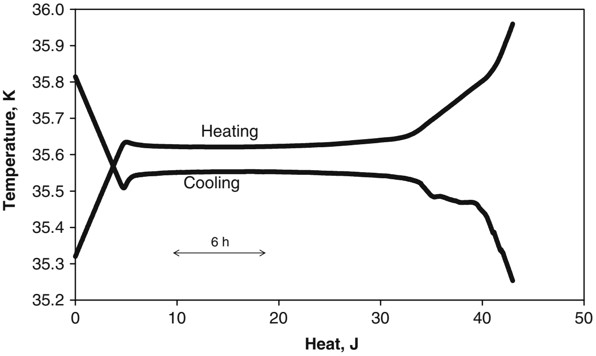

Fig. 2 Hysteresis effect in the α–β and β–α transitions in solid nitrogen

are almost a mirror image, and the minimum temperature difference between the two curves is 69 mK on the plateau. This temperature difference almost certainly arises from the very long thermal equilibration time of the transition.

To define the transition (α–β) temperature, the heating process is adopted because realization of the cooling (β–α) transition with sufficient reproducibility is almost impossible.

An attempt was made to determine the α–β transition using the heatpulse method. The test confirmed the very large recovery time of the transition. Figure 3 shows a heat pulse and the recovery after switching off the power. As can be seen, equilibrium was not fully reached even after 20 h. The measurements were repeated a few times, with similar results. To estimate the self-heating of the thermometer in a quasi-stable state, the measuring current I was changed from 1 to 2 mA, showing clearly the effect of the relatively high thermal resistance between the thermometer-as-a-heat-source and the substance undergoing the phase transition, with a consequently long equilibration time. With an estimated temperature change of about 3 mK, the thermal resistance becomes about 300 K·W^{-1} or more. The temperature started to increase continuously, as shown in Fig. 4. The calculated time constant of the curve is about 80 min. This value depends on the fraction of the sample in the α phase. Returning to the value I = 1 mA causes a slow decrease of the sample temperature to almost the same value as before the current increase—see Fig. 5. Assuming asymptotic behavior on top of the initial linear decrease, an asymptotic value of 2.852 mK is found to within 2 μK after about 40 h (!).

The same change in thermometer current was also applied away from the phase transition, see Fig. 6, where the thermal resistance is found to be smaller than during the transition. With an average temperature change of about 0.8 mK, the thermal resistance is estimated to be less than 80 K·W^{-1}. At a current $I = 1$ mA, a small temperature drift of the cell is observed from the Joule heat generated by the thermometer but, unlike during the transition, the increase of the current to $I = 2$ mA causes a prompt increase in the drift. By reducing the current again to $I = 1$ mA, the drift quickly returns to the previous value.

The high thermal resistance during the transition is also exemplified by the fact that the plateau temperature obtained with continuous heating, 35.620 K, is higher than the

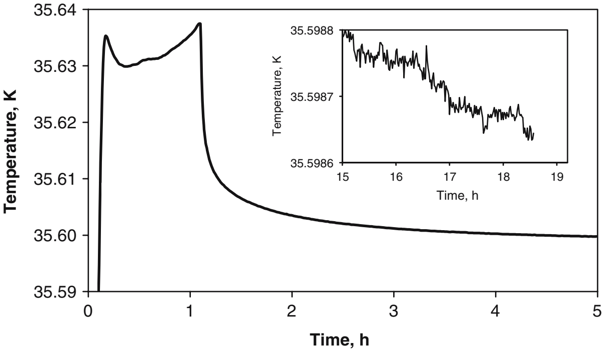

Fig. 3 Behavior of the nitrogen sample after a heat pulse in the α–β transition region

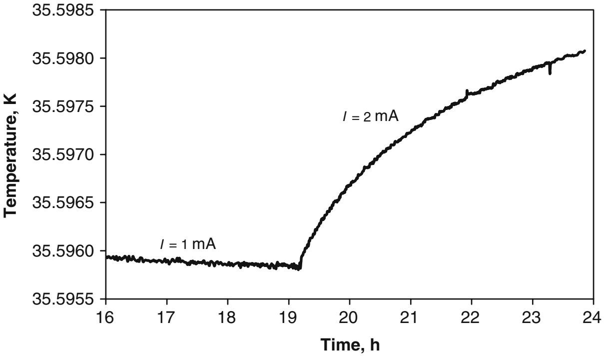

Fig. 4 Change in sample temperature after increasing the thermometer current

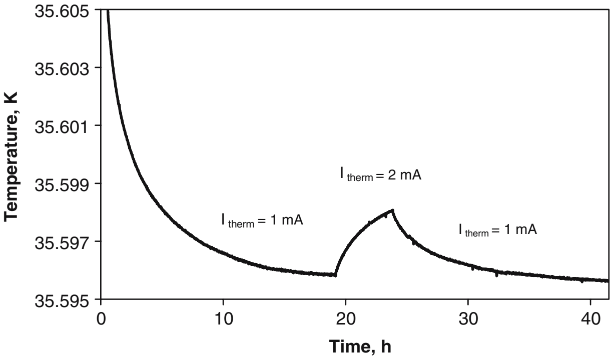

Fig. 5 Dependence of the nitrogen temperature on the thermometer current during the α–β transition

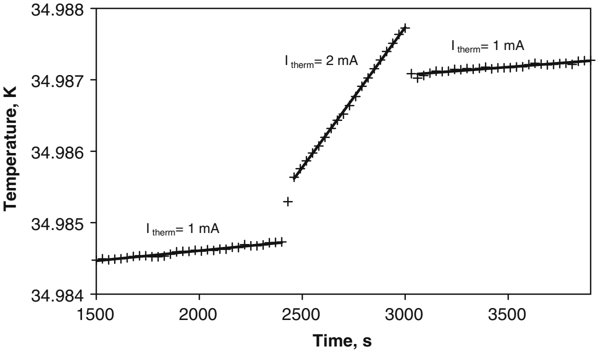

Fig. 6 Temperature drift at different thermometer currents, outside the α–β transition

temperature value obtained with the pulse method, 35.596 K, even though equilibrium is not fully reached.

6 Conclusion

The temperature of the α–β solid–solid transition in nitrogen was found to be $T_{90} = 35.620\,\mathrm{K}$, at mid-plateau, with an expanded uncertainty of $U = 8\,\mathrm{mK}$ for a coverage factor $k = 2$. This value, obtained by the continuous heating method, is in agreement with the CCT recommended value of $T_{90} = 35.614\,\mathrm{K}$ with a standard uncertainty of 6 mK ($k = 1$). The heat of the α–β transition was found to be $215\,\mathrm{J{\cdot}mol^{-1}}$, and the ratio between the total latent heat for this transition (32.4 J) and that for the triple point (108.7 J) is 0.312, in good agreement with a value of 0.318 dating from 1933. It is clear that this transition is of inferior quality compared to the triple point. Due to the high thermal resistance and very large time constant, thermal equilibrium at the millikelvin level cannot be reached after a heat pulse, even on a time scale of 10–20 h, leaving only the continuous heating method for its realization. The high thermal resistance is exemplified by the temperature difference of about 24 mK between the values obtained with the two different methods (continuous heating or pulse method). These factors do not support the use of this transition for precision thermometric purposes.

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