Anomalies on the heat capacity just below the triple points of e-H_2 and e-D_2 with catalysts

T. Nakano, O. Tamura and H. Sakurai

National Metrology Institute of Japan, AIST central 3, Tsukuba 305-8563, Japan

Molecular hydrogen and deuterium occur in two modifications, ortho- and para-molecules, which differ in the nuclear spin arrangement. The equilibrium fraction of each modification is a function of the temperature but the equilibrium is only slowly established for both hydrogen and deuterium [1-3]. Since the triple point temperature is dependent on the composition of ortho- and para-molecules, a catalyst is required to establish the equilibrium before accurate measurements of each triple point [1-4]. Recently, it has been confirmed using open cells that there is a problem associated with the catalyst for nuclear-spin-equilibration of hydrogen; large anomalous increases exist in the heat capacity at temperatures just below the triple point, which are caused by some kind of interaction between hydrogen and the catalyst, and the anomaly disturbs the measurements of the triple point of nuclear-spin-equilibrated hydrogen (e-H_2) [3 ,5]. To clarify how the anomaly in the heat capacity changes with varying the amount of the catalyst has been expected to give a clue to understand the origin of the anomaly and a best way to realize the triple point temperature of e-H_2 at highest-level accuracy.

The heat capacity of e-H_2 was investigated at temperatures around the triple point using three sealed cells including different amounts of powder of ferric oxy-hydroxide (FeO(OH)) as the catalyst. It is confirmed by precise calorimetric measurements that a significant double anomalous peak exists at temperatures just below the triple point in the heat capacity of an e-H_2 cell including about 90 mmol of H_2 and 0.53 g of FeO(OH). It is also found that there is a strong correlation between the amount of catalyst and the size of the anomaly, and the reduction of the amount of catalyst allows one to obtain more reliable melting curves for e-H_2. We also examined the heat capacity of nuclear-spin-equilibrated deuterium (e-D_2) using a sealed cell fabricated at IMGC. A similar anomaly is also discovered in the heat capacity of e-D_2. The design of NMIJ sealed cells, the experimental setup and the measurement results have been already published [6, 7]. This document gives a short overview.

Figure 1 shows the temperature dependence of the heat capacities of e-H_2 cells, NMIJ H-1, NMIJ H-2 and NMIJ H-5, near the triple point. The cells contain about 90 mmol of H_2 with 0.53 g, 0.12 g and 0.015 g of FeO(OH) as the catalyst for the ortho-para equilibration, respectively. A double anomalous peak is observed at temperatures just below the tripe point, and the total heat of the anomalies (Q_a) is proportional to the amount of the catalyst in each cell. This correlation between the amount of the catalyst and the size of Q_a indicates that the catalyst causes the anomalies, as reported previously [3, 5, 8, 9]. The sum of Q_a and the total heat due to the divergence part of heat capacity at the triple point (Q_o) is about 10 J for each cell. It is expected from the amount of hydrogen in each cell that the total heat of fusion will be about 10 J, which accords with Q_a+Q_o. This accordance strongly suggests that the anomalous peaks come from a depression of the melting temperature of a part of hydrogen due to an interaction between hydrogen and the catalyst.

The reduction of the catalyst amount down to 0.015 g in 90 mmol of hydrogen decreased the anomaly and enabled one to obtain a linear dependence of the temperature on the inverse of fraction of melt ($1/F$) and the width of melting curve less than 0.1 mK in the range up to $1/F$ = 10, as seen in Fig. 2.

Figure 3 shows the heat capacity of an e-D_2 cell including 0.25 g of Gd_2O_3 as a catalyst with 26 mmol of deuterium [10]. Large anomalous increases are discovered about 10 mK below the triple point on heat capacity curves, similarly to that observed for e-H_2. This apparently indicates that the existence of the anomalies in the heat capacity is a universal property for the molecular hydrogen with powder of the catalyst independently of its isotope. The melting curves of e-D_2 are markedly distorted and the width of melting curve spreads over 4 mK in the range up to $1/F = 10$, as seen in Fig. 4. It needs more studies on the triple point temperature of e-D_2 by reducing the amount of the catalyst to realize the triple point of e-D_2 at highest-level accuracy.

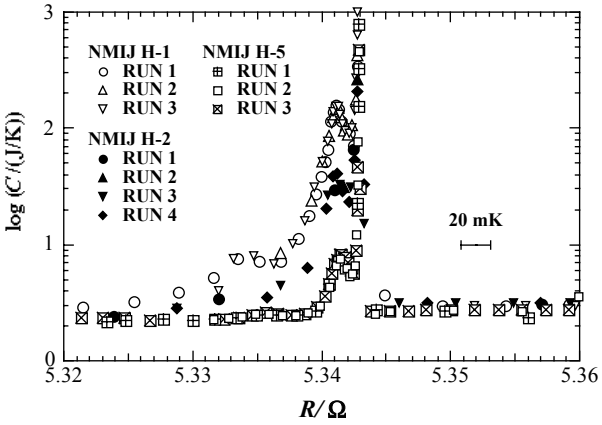

FIGURE 1. Heat capacities of hydrogen cells, NMIJ H-1, NMIJ H-2 and NMIJ H-5 [7].

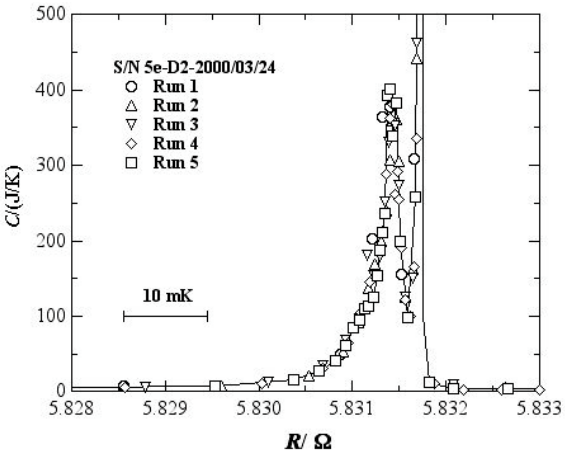

FIGURE 3. Heat capacity of a deuterium cell fabricated at IMGC [6].

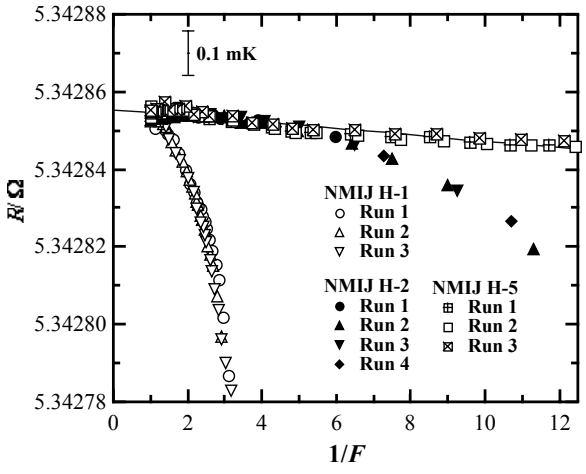

FIGURE 2 Melting curves for hydrogen cells, NMIJ H-1, NMIJ H-2 and NMIJ H-5, against 1/ *F* [7].

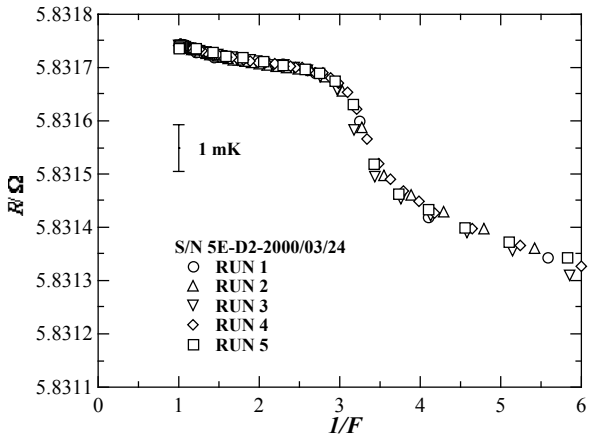

FIGURE 4. Melting curves for a deuterium cell fabricated at IMGC against 1/ *F* [6].

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