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M.Koláč, B.S.Neganov, S.Sahling

LOW TEMPERATURE HEAT RELEASE FROM COPPER: ORTHO-PARA CONVERSION OF HYDROGEN

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1. INTRODUCTION

Neganov and Trofimov[1] have built a special calorimeter (sensitivity 10^{-15}W/g at liquid helium temperatures) for studying the discrepancy between theoretical and experimental heat leak to cold parts of the cryostat in the low and very low temperature experiments. In their measurements with polycrystalline copper at the level of 10^{-14}W/g (cosmic rays heating), a large intrinsic heat release after cooling down to 1K was discovered. A more extensive study[1,2] showed that the heat release decreased in time from initial $5\cdot10^{-10}$W/g according to the exponential law with the relaxation time constant τ of about 60 hours; τ is temperature-independent in the region 1-4K. It was also shown that the initial value was two orders smaller after copper was treated at 900°C during 5 hours in vacuo. Relaxation of thermoelastic tensions at the grain boundaries was assumed as a possible origin of this power dissipation. The classical time constant of such relaxation increases rapidly with lowering temperature, being about 100 hours at 300K in copper. To explain experimental results, an assumption about quantum origin of the relaxation at lower temperatures was adopted. In such case, τ would be temperature-independent down to the lowest temperatures, and the heat release might interfere in the nuclear cooling experiments with copper. Indeed, according to Pobell[4] the heat release from copper is the main part of the heat leak to the nuclear stage of the Julich nuclear refrigerator[5].

According to the grain-boundaries model, one may expect a much less heat release in a copper single crystal; but the single-crystal heat release is of the same order.

Schwark et al.[6] studied in the heat release from copper, specially treated at 930°C in the hydrogen atmosphere at different pressures, and cooled down at the rate of 200° per second. Molecular hydrogen precipitates in form of bubbles in copper, treated in such way[7], and low temperature heat release is mainly due to the hydrogen ortho-para conversion. Since the time dependence of this power dissipation seems to be the same as the one in common copper, an idea arose that the heat release in the latter may be due to conversion of the hydrogen admixtures, too.

The aim of our study is to learn this process in greater detail and to choose the right model.

Both models may give very similar data on heat-release relaxation in time, but the temperature dependence of the energy accumulated (the enthalpy of the ortho-para conversion in the hydrogen model) is quite different. Mechanical strains originate mainly in the course of cooling down to nitrogen temperatures because of a small expansion coefficient at lower temperatures. According to this model, after complete relaxation of the system at liquid nitrogen, the total energy dissipated after cooling down to 1.3K is 15 per cent of the energy after fast cooling from the room remperature down to 1.3K.

On the other hand, the enthalpy of hydrogen ortho-para conversion is proportional to the concentration of ortho-hydrogen x_g (see equation (10)) with weak temperature dependence above 80K; after complete relaxation the specimen at liquid nitrogen the enthalpy will drop to 70 per cent of room temperature value only.

For better understanding of the mechanism, the time dependence of heat release was measured more accurately, and temperature dependence of accumulated heat energy with slow dissipation was determined.

2. EXPERIMENTAL

The cryostat is supported by a rigid construction resting on a massive (7000 kg) concrete block which is isolated from the floor by four dampers; natural frequency of the system is less than 2 Hz. Helium vapours are pumped out by Alcatel 12030 H and Leybold-Heraeus WS-2000 which are at a distance of 20 m from the cryostat. The pumping line (150 mm dia.) is fixed at several points in the walls of the building. It is connected to the cryostat by a soft rubber tube.

The cylindrical calorimeter (75 mm dia., 76 mm high), soldered to a stainless steel tube (10/9.7 mm dia., 880 mm long), is suspended as a free pendulum by a rubber damper from the cap of the cryostat.

The cylindrical shaped copper specimen (m = 485 g, 48 mm dia.x30 mm) is suspended in the calorimeter (Fig.1) by 12 kapron threads (~0.13 mm dia., 31 mm long). There are a SI germanium resistor for temperature measurements and a heater (9300 ohm) glued to the specimen.

The thermometer has been calibrated between 1 and 100 K at the Dresden Technical University. Its sensitivity at 1.3 K (5000 ohm) $\partial R/\partial T = 11$ ohm/mK. The Allen-Bradley carbon resistor for measurement of the calorimeter temperature was calibrated against the germanium thermometer with heat switch on at the beginning and at the end of the measurements. The resistivity of both thermometers was measured by the Cryo Bridges S 72A.

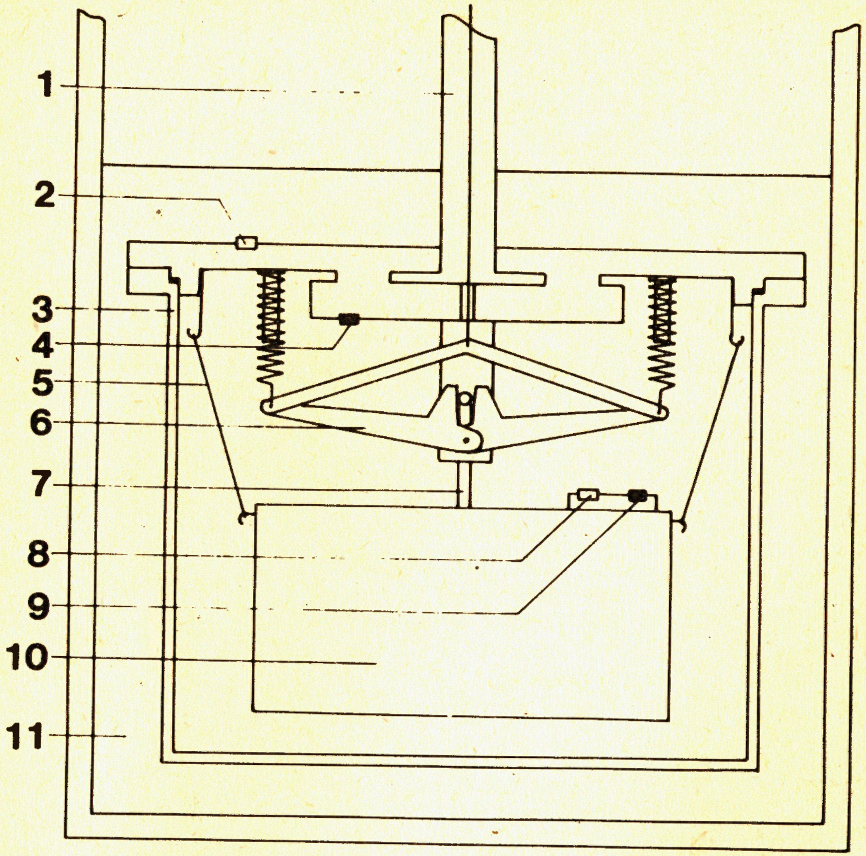

Fig.1. The calorimeter. 1 - stainless steel tube, 2 - heater of the He-bath, 3 - body of the calorimeter, 4 - Allen-Bradley resistor, 5 - kapron thread, 6 - heat switch, 7 - copper heat conductor, 8 - Ge resistor, 9 - specimen heater, 10 - specimen, 11 - liquid He (1.3K).

A scissors-like mechanical heat switch connects the body of the calorimeter with a copper wire (2 mm dia.) soldered into the specimen. For more accurate calibration of the carbon resistor, heat resistivity of the switch was determined as 10^4 K/W at 1.3 K. The switch allows relatively fast cooling of the specimen.(A 479 g sample was cooled from 60K to 1.3K in 1 hour when the calorimeter temperature was 1K).

Heat release was determined from the temperature drift of the specimen with heat switch off. The temperature of the copper sample was chosen very close to the calorimeter temperature which was kept constant (to 10^{-4} K) by a simple electronic circuit.

Power $\dot{Q}$ released inside the specimen was calculated as

$$\dot{Q} = \dot{Q}_S - \dot{Q}_A - \dot{Q}_N , \qquad (1)$$

$$\dot{Q}_S = \dot{R}C/(\partial R/\partial T), \qquad (2)$$

$$\dot{Q}_A = A(T_K - T), \qquad (3)$$

where $\dot{Q}_A$ is the heat leak from the body of the calorimeter to the specimen, A is the coupling constant, determined experimentally for each specimen (for our main specimen A/m = = 0.24 pW/gmK), T is the temperature of the specimen, T_K is the temperature of the body of the calorimeter, $\dot{Q}_S$ is the measured heat release, R is the resistivity drift of Ge-thermometer, C is the specific heat of the specimen, $\partial R/\partial T$ is the sensitivity of the thermometer, $\dot{Q}_N$ is the experimental background power due to the external noise.

At the beginning of the measurements the dependence of $C/(\partial R/\partial T) = \Delta Q/\Delta R$ on T was determined experimentally. Background noise of our apparatus, measured experimentally with the help of a sample with minimum heat release (copper annealed in vacuo at 950°C for 5 hours /2/), $\dot{Q}_N$ = (1.5±0.5) pW/g.

Since $T \simeq T_K$ in most of our experiments, $\dot{Q}_A$ was usually a small correction only.

3. RESULTS

Figure 2 represents the time dependence of the power $\dot{Q}/m$ during 500 hours after the cooling (during 17 hours) from the room temperature to the helium one. The initial heat release $\dot{Q}_1/m$ = 500 pW/g. Since a long time is needed for its measuring, the curve was determined in fully only once, but many further measurements of its various parts (even for powers less than 10^{-11} pW/g) showed its reproducibility: for $\dot{Q}/m \geq 10^{-11}$ pW/g the dispersion of the measured points was no more than 1 per cent.

When the cooling from the room temperature was faster, the initial heat release $\dot{Q}_1/m$ was greater. For example, with cooling time of 6 hours $\dot{Q}_1/m$ = 600 pW/g. In this case, the $\dot{Q}/m$ dependence after the relaxation to 500 pW/g repeated the curve in Fig.2.

All the time when $\dot{Q}/m$ from Fig.2 was being measured, the temperature of the specimen T was close to 1.3K; it rose a little (to 3K) only sometimes during filling the cryostat with liquid helium.

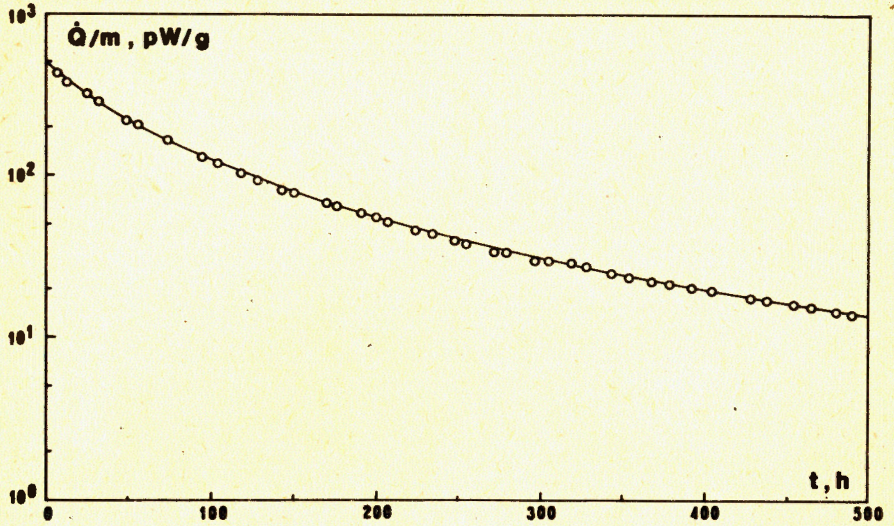

Fig.2. Time dependence of the heat release. The line represents $\dot{Q}/m$ = *410 [pW/g]exp (-t [hours]/55) + + 90 [pW/g] exp (-t [hours]/260).*

Two methods were used to determine the total accumulated heat energy, dissipated at 1.3K after fast cooling down from the equilibrium state at a certain temperature T (the enthalpy of the system at the temperature T in the hydrogen model) (Figs.3,4). The first one consists in keeping the specimen at the temperature $T >$ 1.3K for a long time to reach the full internal equilibrium (the system has relaxed completely at this temperature), fast cooling down to 1.3K and measuring the time dependence of $\dot{Q}/m$.

In the second method, the specimen after partial relaxation is heated up to such a temperature T, where there is neither relaxation, nor excitation; after fast cooling from this temperature to 1.3K the time dependence of $\dot{Q}/m$ is measured again.

Then the total accumulated energy for both cases is

$$H(T) = \int_0^\infty \dot{Q}(t)\,dt . \qquad (4)$$

$H(T)$ in the hydrogen model is the enthalpy of ortho-para conversion at the temperature T if we omit the value of enthalpy at 1.3K (theoretically $H(1.3K)/m < 5\cdot 10^{-8}$ pJ/g /8/).

There is no need to measure always the whole curve $\dot{Q}(t)$ owing to its good reproducibility in various measurements. The first method was used for determination of $H(77K)$. The specimen was kept at liquid nitrogen for 700 hours before measuring $\dot{Q}/m$ at 1.3K (Fig.3).

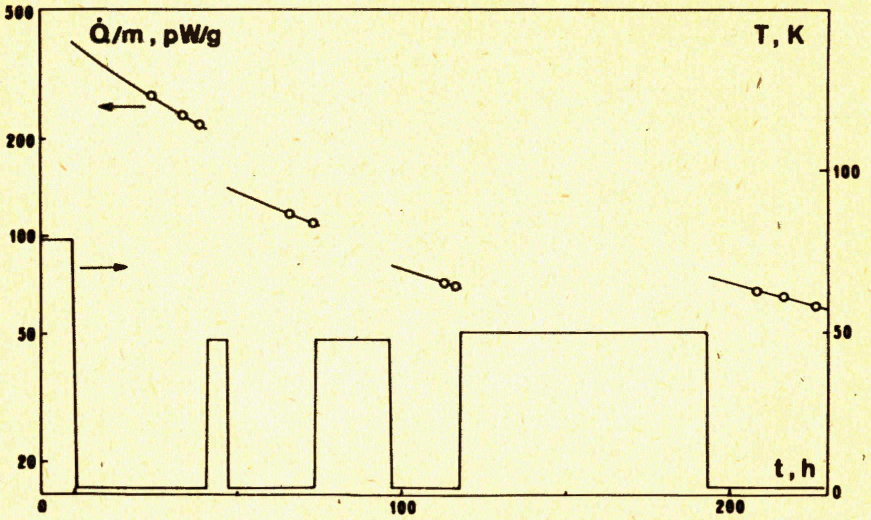

Fig.3. Time dependence of the heat release after the 77K equilibrium and the influence of the temperature variation. Dots and the upper line - heat release per gram per second, the lower line - the temperature. At -700< t < 0 hours the specimen was kept at 77K; at 41 < t < 47 h and 74 < t < 97 h faster relaxation is observed, at 118 < t < 193 h neither relaxation, nor excitation are observed.

The values of H (50K) and H (35.5K) were measured using the second method. According to Figs.3 and 4 at $\dot{Q}/m$ = 78 pW/g (9.1 pW/g) there is neither relaxation, nor excitation at the temperature T = 50K (35.5K).

Two interesting phenomena follow from Figures 3,4:

1. Relaxation at 50K, 35.5K, and 25K goes faster than at 1.3K; it is - in our case - six times faster at 50K than at 1.3K and 19 times faster at 35.5K. (It is to be noted just now that the mechanism of this phenomenon needs more thorough study. It is observed down to 10K according to preliminary measurements. Data for 50K and 35.5K will be used for corrections in calculations of $\dot{Q}_0(T)/m$ and H(T) only.

2. If $\dot{Q}/m$ is measured just after cooling, additional heat release relaxing during several hours is observed (see Fig.4). Both phenomena may be interdependent.

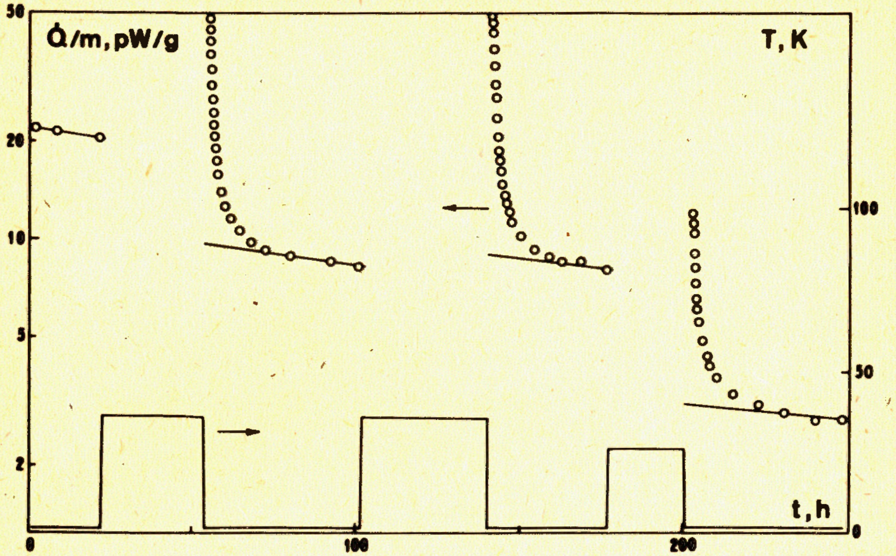

Fig.4. Time dependence of the heat release and influence of temperature variation, $\dot{Q}/m < 30$ pW/g. Dots and the upper lines - heat release per gram per second, the lower line - the temperature. At 22 < t < 53 h and 177 < t < 200 h faster relaxation is observed, at 102 < t < 140 h there is neither relaxation nor excitation; at 54 < t < 64 h, 140 < t < 150 h and 201 < t < 220 h additional heat release is observed.

4. DISCUSSION

The time dependence of the heat power per gram $\dot{Q}/m$ is very similar to the one from earlier measurements /1,2/. The "grain-boundaries" model gives an exponential dependence of the form

$$\dot{Q}/m = \sum_{i=1}^{n} \dot{q}_i e^{-t/\tau_i}. \qquad (5)$$

With $\dot{q}_1$ = 410 pW/g, τ_1 = 55 h, $\dot{q}_2$ = 90 pW/g, τ_2 = 260 h, $\dot{q}_i$ (i > 2) = 0, we can fit the experimental results fairly well (Fig.2).

On the other hand, the results of the experiments may be explained by the model of ortho-para conversion of admixed hydrogen. In this case, the relaxed power is proportional to the change of ortho-concentration x per second:

$$Q = -Nq\,dx/dt, \qquad (6)$$

where N is the number of moles of molecular hydrogen, $q = 1063$ J/mole is the conversion energy, x is the relative concentration of ortho hydrogen, $x = N_{ortho} / (N_{ortho} + N_{para})$.

In free hydrogen the process of setting up the equilibrium concentration x_g at a certain T is a result of pair interactions between the ortho-molecules /8/,

$$dx/dt = -k(x - x_g)^2 , \tag{7}$$

where k is a constant. At 1.3K $x_g \simeq 0$ and

$$x_1/x = 1 + kx_1(t - t_1) , \tag{8}$$

where x_1 is the concentration at the moment t_1. From (6)-(8) we can express x as a function of $\dot{Q}$:

$$x_1/x = (\dot{Q}_1/\dot{Q})^{1/2} = 1 + kx_1(t - t_1) , \tag{9}$$

where $\dot{Q}_1$ is the heat release at the moment t_1.

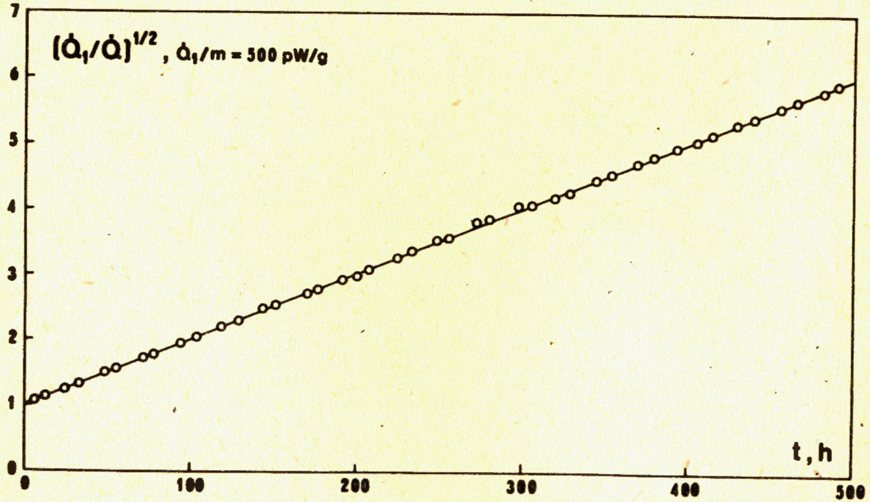

Fig.5. $\dot{Q}^{-1/2}$ *as a function of time. The slope of the straight line is* $kx_1 = (1.04 \pm 0.02) \cdot 10^{-2}\ h^{-1}$.

Experimental values of $(\dot{Q}_1/\dot{Q})^{1/2}$ are plotted in Fig.5 as a function of t (with $\dot{Q}_1/m = 500$ pW/g, $t_1 = 0$). The curve is, according to (9), a straight line with the slope $kx_1 = (1.04 \pm 0.02) \cdot 10^{-2}$ h^{-1}.

If we take $k = 0.019$ h^{-1}, i.e., an experimental value for free solid hydrogen /9/, the initial heat release $\dot{Q}_1/m = 500$ pW/g corresponds to the concentration $x_1 = 0.53$. If the "hydrogen" hypothesis is true, about 30 per cent of ortho-molecules converted during cooling down from room temperature to 1.3K. In what follows corrections for relaxation during the cooling process will be calculated; $x_1 = 0.53$ is shown to be an acceptable value. Therefore, the value for free solid H_2 $k = 0.019$ h^{-1} is also acceptable. From this point of view, in our specimen - according to (6) - there is about 19 at.ppm of admixed molecular hydrogen.

According to (9), heat release of 600 pW/g after faster cooling-down corresponds to the concentration $x_1 = 0.58$; infinitely fast cooling from the room temperature ($x_0 = 0.75$) would lead to the release of $Q_0/m = 1000$ pW/g. According to this simple scheme the initial release after fast cooling from the equilibrium state at 77K ($x_g = 0.50$), 50K ($x_g = 0.23$), and 35.5K ($x_g = 0.07$) would be $\dot{Q}_0(T)/m = 443$ pW/g, 94 pW/g and 8.7 pW/g, respectively.

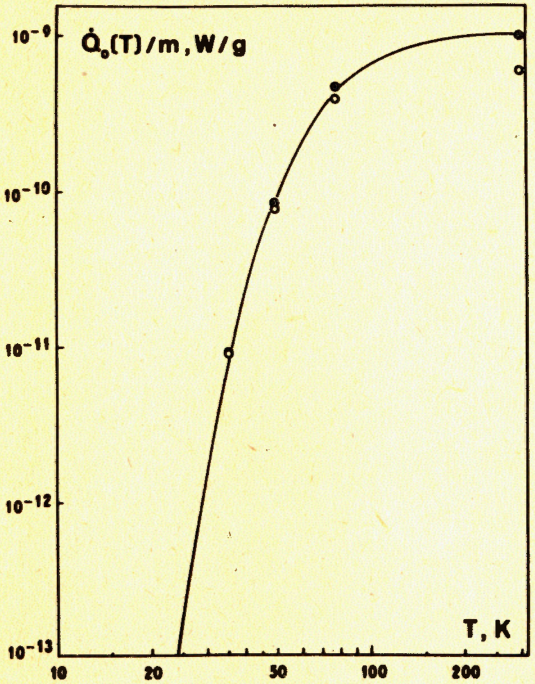

Fig.6. Heat release observed at 1.3K after reaching equilibrium at fixed T *. Dots - experiment* (o - $\dot{Q}_0(T)/m$, ● - $\dot{Q}_0(T)/m + \Delta\dot{Q}/m$), *line - "free solid hydrogen" model with* $\dot{Q}_0/m = 1000$ *pW/g.*

Corresponding experimental results, determined by the methods mentioned above from the measured values, shown in Figs.3,4, are 398 pW/g, 78 pW/g and 9.1 pW/g. They are plotted in Fig.6. The continuous curve in this figure was calculated from

$$\dot{Q}_0(T) = \dot{Q}_0(x_g(T)/x_0)^2 \tag{9'}$$

with $\dot{Q}_0/m = 1000$ pW/g, $x_0 = 0.75$; values of $x_g(T)$ are taken from /8/. Agreement between the theory and the experiment is good. The low-temperature heat release seems to be, indeed, due to the ortho-para conversion of hydrogen, precipitated in copper.

As we mentioned earlier, faster relaxation at temperatures higher than 1.3K was observed (see Figs.3,4). We have not studied this phenomenon in detail so far, but preliminary data may be used to estimate the relaxation rate in the cooling process to explain the reduced heat release of 500 pW/g after the cooling down from the room temperature, to correct the experimental values of $\dot{Q}_0(T)$ and, in this way, to find their accuracy.

In our fastest cooling from the room temperature to the helium one (4 hours from 300K to 90K, 2 hours from 90K to 4K, $\dot{Q}_1/m$ = 600 pW/g) it is possible to neglect the relaxation during the first four hours of the cooling process. According to (7), taking into account "faster" relaxation at elevated temperatures, cooling from 90K to 50K yields a correction of $\Delta_1 x \lesssim 0.005 \cdot 6 = 0.03$, from 50K to 4K $\Delta_2 x \lesssim 0.01 \cdot 19 = 0.19$. Then $x_0 \lesssim x_1 + \Delta_1 x + \Delta_2 x = 0.80$, which is to be compared to $x_0 = 0.75$, the true room temperature value. Per analogiam, corrections $\Delta \dot{Q}$ to the experimental values of $\dot{Q}_0(T)$ at 77, 50 and 35.5K may be calculated. Cooling from the nitrogen temperature to the helium one during an hour yields – according to the same formulas – $\Delta \dot{Q}/m \simeq 80$ pW/g, and as a result of cooling down from 50K (35.5K) the heat release will be 5 pW/g (0.1 pW/g) smaller than the true one. The corrections add to better agreement between the theory and the experiment (see the Table).

The values of H(T) may be calculated by integration of the curve in Fig.2 according to (4), or directly from the corresponding $\dot{Q}_0(T)$ since

$$H(T) = Nqx_g(T), \tag{10}$$

and, according to (6), (7), (9)

$$\dot{Q}(T) = kNqx_g^2(T), \tag{11}$$

$$\dot{Q}_0/x_0^2 = \dot{Q}_0(T)/x_g^2(T). \tag{12}$$

Then

$$H(T) = (1/kx_0) \cdot (\dot{Q}_0 \cdot \dot{Q}_0(T))^{1/2}. \tag{13}$$

Determined in this way, the specific enthalpy H(T)/m is shown in the Table and Fig.7 analog with a theoretical curve, calculated under the assumption that $\dot{Q}_0/m$ = 1000 pW/g.

A practical conclusion follows from the temperature dependence of $\dot{Q}_0(T)$ and H: for removing $\dot{Q}$ when necessary (for instance in ultralow temperature measurements), it is almost of no use to keep copper samples at liquid nitrogen for a long time since the corresponding $\dot{Q}$ drops no more than by half. Samples being kept at the liquid hydrogen temperature the initial heat release may be 10^4 times smaller. In addition, in our specimen the relaxation at 20K was much faster than at helium temperatures.

Table

Temperature dependence of the heat release and the enthalpy

T/K		273	77	50	35.5
x_g		0.75	0.50	0.23	0.07
$\dot{Q}_0(T)/m$ (theor)	pW/g	1000	443	94	8.7
$\dot{Q}_0(T)/m$	pW/g	600	398	78	9.1
$\frac{\dot{Q}_0(T)}{m} + \frac{\Delta \dot{Q}}{m}$	pW/g	1033±100	478±50	83±8	9.2±1
H/m(theor)	pJ/g	19.5	13.0	6.0	1.8
H/m	pJ/g	19.8±2	13.5±1.5	5.6±0.6	1.9±0.2

x_g – equilibrium concentration of ortho-hydrogen/8/ ,
$\dot{Q}_0(T)/m$ (theor) – heat release according to the "free hydrogen" model with $\dot{Q}_0/m$ = 1000 pW/g,
$\dot{Q}_0(T)/m$ – initial heat release measured at 1.3K after cooling down from equilibrium state at the temperature T ,
$\Delta \dot{Q}/m$ – correction due to the relaxation during the cooling process,
H/m(theor) – specific enthalpy of the ortho-para conversion for 19 at. ppm of molecular hydrogen,
H/m – experimental value of total heat released per 1 g of copper.

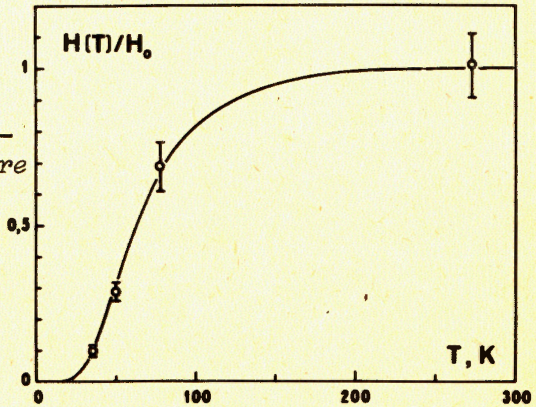

Fig.7. Dependence of total heat released after cooling the system from the equilibrium state at the temperature T to 1.3K. Dots – experiment; line – "free solid hydrogen" model, $\dot{Q}_0/m$ = 1000 pW/g.

Such fast relaxation was not observed in liquid or solid hydrogen/9/. While the time dependence of $\dot{Q}(t)$ and temperature dependence of the enthalpy H(T) of hydrogen in copper seem to be the same as those in free H_2, the observed fast relaxation may be due to an external influence of copper lattice or any admixture.

We also are not able to explain the additional heat release during the first several hours after cooling down the specimen by the model of free H_2. According to our preliminary measurements, this additional heat release is also connected with hydrogen since it depends on ortho concentration.

The study of these two phenomena is going on.

5. CONCLUSIONS

Experimental results on the heat release in copper after cooling down to 1.3K and above all, the dependence of the total heat released on the temperature T of the equilibrium state of copper just before cooling down correspond to the model of the ortho-para conversion in hydrogen bubbles, precipitated in copper and behaving as free molecular hydrogen.

It is shown that it is of no use to try to diminish the heat release essentially by keeping the copper specimen at nitrogen temperature, but after equilibrium is reached at 20K the 1.3K heat release is about 10^4 times smaller.

The relaxation process above 10K was found to be much faster. Moreover, an additional heat release, relaxing with a characteristic time of the order of 1 hour, was observed just after the cooling-down. Both these phenomena cannot be interpreted by "free hydrogen" model.

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Колач М., Неганов Б.С., Салинг С. E8-84-460

Низкотемпературное тепловыделение в меди - результат орто-пара превращения водорода

В калориметре с паразитным теплопритоком около 1,5 пВт/г измерялось тепловыделение в меди /бескислородной, чистота 99,99%/ после охлаждения до 1,3К. Релаксация этого тепловыделения, а также зависимость полного выделенного тепла от температуры, от которой охлаждается медь до 1,3К, хорошо согласуется с предположением об орто-пара превращении молекулярного водорода, находящегося в меди, который ведет себя как свободный водород. Наблюдалась температурная зависимость времени релаксации и добавочное "быстрое" тепловыделение непосредственно после охлаждения.

Работа выполнена в Лаборатории ядерных проблем ОИЯИ.

Препринт Объединенного института ядерных исследований. Дубна 1984

Koláč M., Neganov B.S., Sahling S. E8-84-460

Low Temperature Heat Release from Copper: Ortho-Para Conversion of Hydrogen

Heat release from polycrystalline copper (oxygen free, 4N purity) after cooling down to T = 1.3K was measured in a calorimeter with the parasitic heat leak of about 1.5 pW/g. Its relaxation and the dependence of the total heat released on the temperature of the specimen before cooling down to 1.3K agree well with the hypothesis of the ortho-para conversion of molecular hydrogen, precipitated in copper, which behaves as free hydrogen. Temperature dependence of the relaxation time and additional "fast" heat release just after colling was observed.

The investigation has been performed at the Laboratory of Nuclear Problems, JINR.

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