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SOME THERMAL CHARACTERISTICS OF MERCURY NEAR THE EQUILIBRIUM CRYSTALLIZATION TEMPERATURE

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This paper describes the temperature dependences λ, k, c_p of mercury in solid, supercooled and liquid states using the new experimental method of measuring the thermal characteristics of substances. Measured dependences are compared with values, computed from the Wiedemann-Franz law and also with the most accurate measurements of other authors. In the region of achieved undercooling (1.23 °C) in our measurements no anomalities of the temperature dependences of λ, k, c_p were found. On the other hand the melting up to 0.17 °C above equilibrium crystallization temperature (ECT) is not characterized by a significant change of thermal parameters. In the region of crystallization the conclusions following from the fluctuation theory of phase transition of the 1-st order were confirmed.

INTRODUCTION

From the point of view of the investigation of properties of melted metals mercury — the only one which melts at room temperature — is the most ideal experimental material. The electrical properties of mercury (specific resistivity, Hall constant etc.) are well known, but this cannot be said about the thermal characteristics in the liquid state, which varies according to various authors to a surprising extent ($\lambda_{18\,°C} = 7.8-12.5 \times 10^{-2}$ W/cm °C; $c_{18\,°C} = 0.138-0.148$ joule/g °C). These disproportions are even greater in solid state, for example the ratio of the values of thermal conductivity in the solid state to those in the liquid state λ_s/λ_L lies in the interval $\lambda_s/\lambda_L = 2.95-4.05$ [1].

The experiments dealing with the supercooled state of mercury are confined mainly to some general observations (for example the influence of the shape and the volume of samples, the influence of the surrounding medium and of the pressure on the amount of supercooling, its discretion, etc.), on the other hand the supercooled state of some more complicated substances is studied in greater detail because of significant anomalities of some characteristics in the supercooled state.

This paper contributes to the explanation of the thermal properties of mercury at temperatures from 0 °C to — 46 °C by means of a new experimental method of measuring the thermal parameters of solids — the so-called thermal pulse method.

EXPERIMENTAL METHOD

The method of generating thermal pulses by means of light of different wavelengths to generate underheating in a given place [2, 3] is well known. The most simple way to realize it is by the direct passing of the current pulse $I \,.\, \Delta t$ through the resistant wire 4 (Fig. 1) in the form of a straight line [4]. If the current pulse passes through the wire of the length l with the ohm resistance R in the measured material of the specific mass γ, a temperature wave is generated. By using the thermocouple 6 (Fig. 1) it is possible to observe the maximum of the thermovoltage U_m at the time t_m. If we take into account all assumptions of paper [4], it is possible to write the following expressions for the thermal diffusivity k, the thermal conductivity λ and the specific heat c_p:

$$\lambda = 0.24 \frac{nRI^2\Delta t\alpha}{l} \cdot \frac{1}{U_m t_m}; \quad c_p = 0.117 \frac{nRI^2\Delta t\alpha}{la^2\gamma} \cdot \frac{1}{U_m}; \quad k = \frac{a^2}{4t_m};$$

where n is the number of wires (in our measurements $n = 12$), α is the thermoelectric power of the thermocouple 6 (Fig. 1).

It is necessary to isolate perfectly both the resistant wires and the temperature indicator — the thermocouple — in the case when the measured material has a good electrical conductivity. In our case the constantan wire was used as the heating wire of the diameter 0.05 mm, covered with an enamel layer 5 μm thick, applied after previous oxygenation. The enamel layer was heat treated at 350 °C.

In accordance with paper [5] the thermocouple welding was made in order

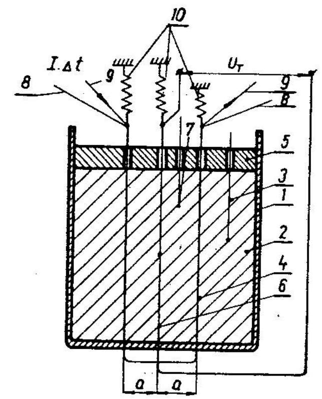

Fig. 1. Scheme of measurement equippment. 1 — teflon vessel; 2 — mercury sample; 3 — screened cable; 4 — heated resistant wire; 5 — distance plate; 6 — Cu-const. thermocouple for measuring; 7 — Cu-const. thermocouple for control; 8 — connection to the compensation measuring of the heated resistant wire; 9 — current-pulse supply; 10 — springs.

to get the smallest response of thermovoltage in connection with conditions inside the measured material. The time response of the used thermocouple was measured directly inside the measured substance, because the values given in literature essentially differ. The thermal pulse was obtained by submerging of thermocouple into mercury at the temperature of − 20 °C approximately. The value of the time response of the used isolated thermocouple $\tau = 26 \times 10^{-3}$ sec was calculated by using the relation $\tau = t_H/\ln 2$, where t_H is the time corresponding to the half-value of the stabilized thermovoltage of the thermal pulse.

A cryogenic equipment was used with the double flask and separated cooling medium. This arrangement makes it possible to achieve the required temperature stabilization within a chosen temperature range. The temperature of the cooling medium was controlled by both the Cu-const. thermocouple and a precise platinum resistance. The temperature of the measured sample was controlled by means of the second Cu-const. thermocouple with the boundary sensitivity of about 1×10^{-2} °C. The corresponding welds of thermocouples were kept at temperatures of 0 °C $\pm 2 \times 10^{-3}$ °C [6]. The given quantities λ, c_p, k are the average values of several measurements. The measurement temperatures in the liquid and solid states were kept near the equilibrium crystallization temperature — ECT (T_f). The solidification of mercury — in order to keep the symmetry of the measuring probe — took place with a simultaneous heating of the wires.

The mercury used for the described measurements was of a polarographic quality with an amount of impurities of 10^{-4} weight percent. In order to improve its quality mercury was vacuum distilled and only then used for further measurements.

EXPERIMENTAL RESULTS

Figure 2 illustrates the measured temperature dependences of the specific heat c_p, the specific mass γ of mercury in accordance with paper [7], including the extrapolation of γ in the nearest vicinity of ECT. For comparison also some other results from the relatively wide range of calorimetric measurements done by other authors [8] are presented.

In Figure 3 there are shown the measured curves of the thermal conductivity λ and the thermal diffusivity k within the observed temperature interval. The values of λ evaluated with the help of the Wiedemann-Franz law are presented, taking into consideration the most accurate values of σ and the values of the Lorentz number $L_s = 2.8 \times 10^{-8}$ WΩ°K^{-2}; $L_L = 2.4 \times 10^{-8}$ WΩ°K^{-2}. The ratio of thermal conductivity in the solid λ_s and liquid λ_L

phases is 4.03 in the present measurements. This value is in good agreement with the last measurement of Powell (4.05) [1]. The present state of experi-

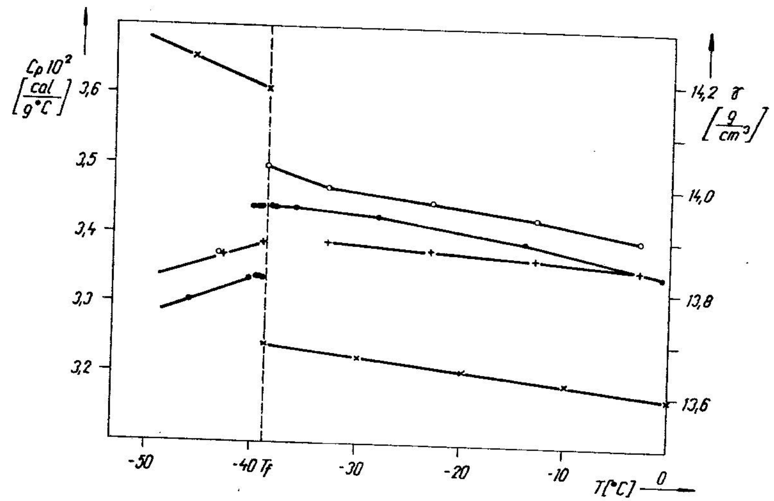

Fig. 2. The temperature dependence of the specific heat of mercury. ● — measured value of c_p; + o — reference values of c_p according to [8]; × — reference values of γ according to [8].

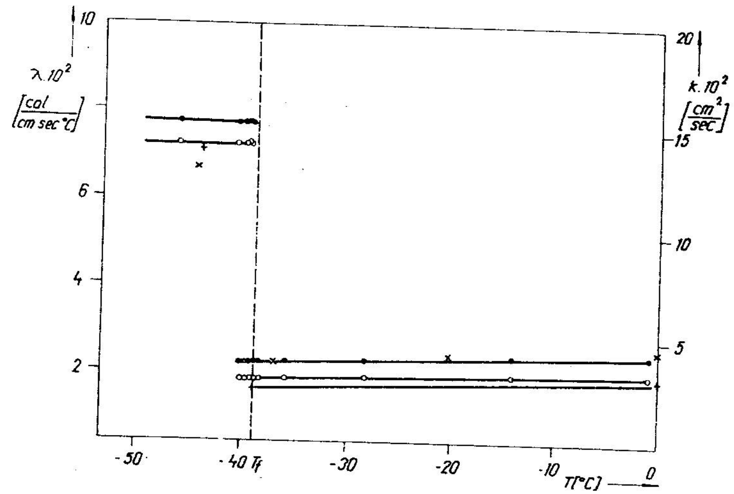

Fig. 3. The temperature dependences of the thermal conductivity and thermal diffusivity of mercury. o — measured value of λ; ● — measured value of k; × — reference values of λ according to [8]; + — evaluated values of λ from the Wiedemann-Franz law.

mental work in this field is characterized by a considerable dispersion of the measured values given by different authors.

Measurements in the solid state near the ECT were accomplished at —39.04 °C due to the necessity of the finite pulse heating in the measured point. Anomalous changes of the temperature dependences of thermal parameters at the temperature of 0.17 °C above the ECT were not observed. The amount of undercooling that the mercury — by the present measuring — will sustain varies up to 1.23 °C in the presence of a small temperature gradient between the cooling medium and the measured sample of a relatively big volume (38 cm³). All measured thermal parameters at supercooling keep their values of the nearest vicinity of the liquid state. No anomalous courses of dependences were observed in the supercooled region. Simultaneously it was observed that the obtained supercooling did not depend on the cooling rate. By passing through the supercooling state a spontaneous balance of temperature takes place and the mercury temperature is stabilized at ECT. The present arrangement of measuring allows to measure the thermal parameters also in this state. The measured values of λ, c_p, k were not reproducible even if the rate of cooling was the same and no connection between the measured values could be established. It is only possible to observe the increase of λ, c_p (by 2—3) and a small decrease of k in this state. The mentioned fact may indicate a possibility of the formation of the first crystal nuclei, confirmed also by ultrasonic measurements in some supercooled substances [9].

The next solidification of mercury takes place unlike that in the mentioned case at a relatively high temperature gradient between the cooling medium and the measured sample (3°C). When we assume that the ECT is characterized by a discontinuity of the measured thermal parameters, we must state that this change takes place at the temperature —39.2 °C, which is 0.33 °C above the ECT. This result is in agreement with conclusions of calorimetric investigations on very pure gallium [10], which leads to discussions about the introduced definition of ECT from the point of view of thermal measurements.

DISCUSSION

Kostrjukov and Strelkov [11] pointed out the possibility of the influence of impurities on the temperature dependence of the effective heat capacity of mercury near the ECT. When the analysis of measured values is made it is necessary to take into consideration the experimental error resulting from the used method of measuring different thermal parameters of metals [12]. From this point of view it is necessary to compare critically the measured results with the theory of Mott [1], according to which:

$$\frac{\lambda_s}{\lambda_L} = \exp\left(80\,\frac{L}{T_f}\right)$$

(where L is the melting heat, T_f is the ECT), which gives the value for mercury equal to 2·4 approximately.

At present the supercooled state and phenomena in the nearest vicinity of ECT become more and more important in explaining the questions of melting and solidification. It is to be noted that a suitable theoretical and experimental solution of this problem does not exist at present.

There are two different opinions as to the course of phase transitions near the ECT. According to the first point of view the disagreements are causeed by heterogenous phase fluctuations in the final temperature region and they are supported by some viscosity measurements, while the second point of view stresses the point changes. If we support the assumption that within the mentioned temperature interval there is valid the relation between the thermal conductivity λ and the viscosity η [8]:

$$\lambda = \frac{15}{4}\,\frac{R}{M} \times 10^{-4}\eta = 1{\cdot}55 \times 10^{-5}\eta \text{ (cal/cm sec °C, poiss)},$$

it is possible to approach the conclusions of viscosity measurements as problems of temperature. We may conclude from the measured values that in the temperature interval above 0·17 °C above the ECT, the conclusions of the fluctuation theory in the solid state are not confirmed, on the other hand the solidification takes place in the definite, final interval of temperatures*.

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