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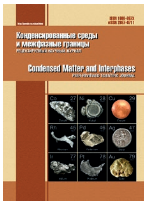

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Influence of pore geometry on the state of bulk pore water in the pressure-temperature phase space

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Abstract

In recent years, the existence of a second critical point of the liquid-liquid transition of water has been proven. In the pressure-temperature phase space, this point is located in the temperature range –50 °C... –100 °C and at pressure ~ 100 MPa. The exact position of this point is not yet known due to experimental difficulties in achieving the deep supercooling of bulk water. The Widom line, the locus of increased fluctuations in entropy and density, is associated with the second critical point. When approaching the Widom line, a sharp increase in a number of physical quantities was established: heat capacity at constant pressure, isothermal compressibility, volume expansion coefficient. However, the practical significance of these features is not clear, since for pressures close to atmospheric, the temperature on it is –45 °C. At the same time, it is known that at temperatures below – 41 °C (homogeneous nucleation temperature), chemically pure supercooled bulk water is unstable due to the very rapid formation of ice crystal nuclei. Nevertheless, supercooling of bulk water to –70 °C in nanometre-sized pores is known.

In the present study, we investigated the possibility of reaching the state on the Widom line at negative pressures, for which, theoretically, the temperature of such a state becomes higher than –45 °C and can reach it positive values at a pressure of –100 MPa. Such a state, in this study, is assumed in the cylindrical hydrophilic pores with a diameter of several nanometres. For the investigation of this possibility and the achievable values of negative pressure (and high temperatures on the Widom line), we measured the low-frequency impedance of a cooled capacitive cell filled with a moistened MCM-41 nanoporous material. In addition, the thermal characteristics were measured in the form of a temperature response of the medium from a pulsed spot heater at a certain distance from it. The position of the Widom line, associated with the second critical point of water, was determined based on the anomalies of the measured physical values in the temperature range –50 °C...+10 °C. For MCM-41 with an average pore diameter of 3.5 nm, dielectric and thermal extrema were found near –18 °C, which corresponds to a pressure of about –65 MPa.

Thus, the performed experiments have shown the possibility of reaching the state on the Widom line at temperatures characteristic of ordinary conditions. Consequently, a significant change in the physicochemical characteristics of dispersed moistened media in various natural and artificial objects is possible. The study of other sorbents with cylindrical pores in order to achieve positive temperatures on the Widom line is of interest.

Keywords: Supercooled water, Second critical point, Widom line, Negative pressure, Nanoporous media

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1. Introduction

Features of the physicochemical characteristics of supercooled bulk metastable water have attracted the attention of researchers in recent decades. Their study allowed a significantly advance in understanding the structure of water. For example, a second critical point of the liquid-liquid transition for water was discovered, which, according to various models, is located in the temperature range (T) –50 °C... –100 °C and at pressure (P) ~ 100 MPa [1, 2]. It is associated with the existence of the Widom line, which is the locus of increased fluctuations in the entropy and density of the liquid. When approaching the Widom line, some thermodynamic quantities of water increase sharply, for example, the heat capacity at a constant pressure (C_p), isothermal compressibility, and coefficient of volumetric expansion [1]. At P ~ 0.1 MPa T on the Widom line is –45 °C.

In recent studies, the behaviour of a number of physical quantities in the region of negative pressures near the Widom line was studied [3, 4]. It turned out that a simple extrapolation of the results, for example, for the speed of sound, obtained at positive P, leads to their strong differences from the experimental results. At the same time, there is a lack of studies dedicated to the clarification of certain models of bulk water.

The phase diagram of the bulk water in the region of positive and negative P according to the results of studies [1, 5, 6] is shown in Fig. 1. An interesting conclusion for research follows from the diagram. The Widom line can reach positive T near –100 MPa. Consequently, anomalies in the physical characteristics of moistened porous media can be observed under normal conditions for media with a special pore geometry and a high degree of hydrophilicity. In this case, an important feature for practical applications can be, for example, the expected acceleration of physicochemical transformations involving water on the Widom line due to an increase in energy fluctuations [7].

The purpose of this study was the search for signs of the state of water located in porous media at temperatures of –25 °C...+10 °C corresponding to the Widom line. The manifestation of this effect is assumed in hydrophilic media with cylindrical filamentous pores of nanometre diameter. In such pores, when concave menisci are formed at both ends of the capillaries, the liquid is stretched, e.g., a negative pressure arises.

Let us estimate the magnitude of the negative pressure in the water of a cylindrical pore. For pores of small diameter, the concave meniscus has a radius (r) close to the pore cross-sectional radius. We assumed that r is 1.75 nm. The pressure in water is calculated using Laplace's formula: $P = 2\sigma/r$, where σ is the coefficient of surface tension. At 0 °C $\sigma = 0.075$ n/m and the calculation provides $P \approx -110$ MPa. Thus, a significant negative pressure near 0 °C for positive T on the Widom line, in accordance with the graph in Fig. 1 it can theoretically be achieved in the pores of existing silicate sorbents (e.g. SBA-15; MCM-41) with cylindrical pores. However, the question about the tensile strength of water in capillaries arises, since it is known to decrease sharply in the temperature range from 5 to 0 °C, when a pressure of –10 MPa is reached [8]. At the same time, the theoretical limit of the onset of cavitation phenomena is estimated at about –140 MPa [9]. On the other hand, when small liquid fragments are formed in a cylindrical pore, the pressure in them must remain negative,

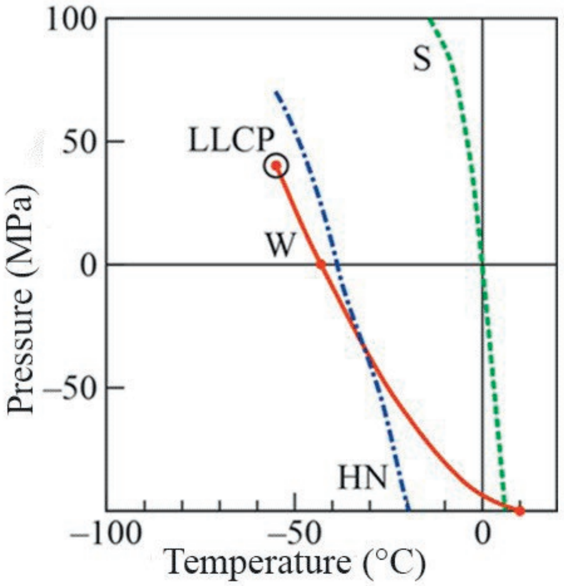

Fig. 1. Phase diagram of water in the region of the Widom line at positive and negative pressures. Adapted from [1, 5, 6]. LLCP (liquid-liquid critical point) is the second critical point, HN is the line of homogeneous nucleation, W is the Widom line, S is the boundary between stable and metastable water

since the concavity of the menisci in them remains even after crushing.

Obviously, the achieved negative pressure will depend on a number of pore characteristics: the degree of their hydrophilic properties, pore geometry, characteristics of water clusters, etc. The solution of this problem seems to be rather complicated [10]. Therefore, in order to determine actually achievable values of negative pressures, it seems appropriate to perform experimental studies of the characteristics of moistened sorbents, which should have special values near the Widom line. In this case, it is necessary to select sorbents, the water in the pores of which has characteristics close to characteristics of bulk water.

For this purpose, temperature measurements of the dielectric and thermal characteristics of the moistened silicate sorbent MCM-41 with cylindrical pores of nanometer diameter were performed.

2. Experimental

2.1. Dielectric measurements

The measurements were performed at frequencies from 25 Hz to 1 MHz. It was assumed that the state on the Widom line can be registered from a change in the electrical response to an alternating electric field, for example, from a change in the real (z') and imaginary (z'') parts of the impedance of the cell with the test material. It is known that the relaxation frequency of water molecules is in the gigahertz range. For silicate materials, it corresponds to the optical frequency range. However, in porous moistened materials, low-frequency relaxation (Maxwell-Wagner) additionally occurs, which has a Debye character and relaxation frequencies much lower than for individual materials. It is important that the effective permittivity at low frequencies is proportional to the same value for the inclusion material [11]. This feature allows an investigation into the nature of the dependence of the dielectric constant of inclusions, e.g. water in pores, on temperature at low frequencies.

The low-frequency impedance of a capacitive cell filled with moistened MCM-41 with a weight humidity of 4–98% in the temperature range from 25 °C to –55 °C was determined. The used material had cylindrical pores with the diameter of 3.5 nm. For such a material, a decrease in the melting temperature of ice in pores (ΔT_m) when they are completely filled, is calculated using the modified Gibbs-Thomson formula: $\Delta T_m = c/(r - t)$, where $c \approx 52$ (K nm), $t \approx 0.38$ nm [12] and the value is approximately –38 °C. In this case, only the first two layers on the contact surface of two media differ in characteristics from bulk water [12, 13]. In the case of incomplete filling of the pores, as well as for the sample cooling mode, the shift of phase transition temperature can additionally increase by tens of degrees. This effect allows reaching the values of the phase transition temperature (liquid water)-ice: –50 °C… –70 °C, which is required to perform the experiment in the area of deep supercooling of water.

The measurements of z' and z'' were performed using an RCL meter. The measuring cell was cooled with cold nitrogen vapour. The results of the determination of z', z'' for a sample with a weight moisture content of 70% are shown in Fig. 2 a, b for some frequencies. On the graphs of dependences of the real and imaginary parts of the impedances, characteristic minima in the temperature range of –25 °C … +20 °C were revealed. Another feature of the graphs shown in Fig. 2 is the absence of frequency dependence for z'

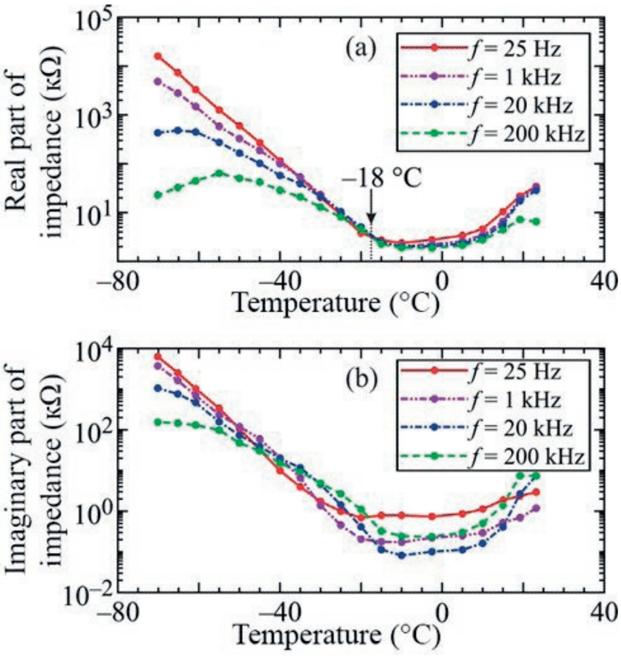

Fig. 2. Dependences of z' (a) and z'' (b) on temperature at four frequencies during sample cooling. The arrow marks is a special temperature point (for z' = const)

at a temperature of –18 °C, at which a coincidence of *z*′ at frequencies from 25 Hz to 200 kHz was observed. These results were also presented as Argand diagrams (relationships between *z*’ and *z*″ at a fixed temperature depending on the frequency), which consisted of two branches - Fig. 3. For the convenience of comparison, the graphs are presented on a double logarithmic scale. One of the branches (LW) corresponded to liquid water, which was determined from temperature changes (this branch disappeared after freezing of water in pores below –40 °C). An analysis of the results showed that the equivalent circuit of the cell cannot be represented as a simple circuit of RC chains (where R is a resistor, C is a capacitor). It is known that Argand diagrams for *z*′ and *z*″ for the group of series-connected chains of parallel-connected R and C for their fixed values have a different form and represent linked fragments of circles [14]. However, in experiments, an unusual change in the nature of the diagrams was observed: the branch associated with water occupied a vertical position for an ambient temperature of –18 °C, i.e. *z*′ did not depend on the frequency.

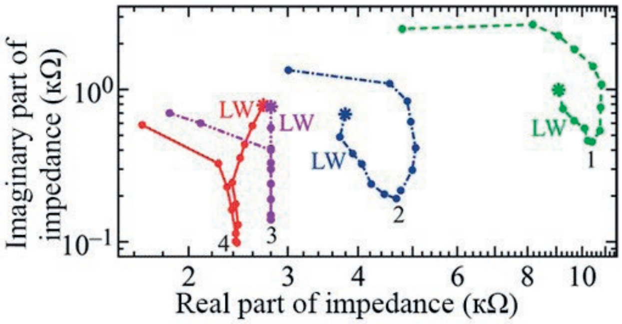

Fig. 3. Argand diagrams of moistened MCM-41 for temperatures 1: –25 °C, 2: –20 °C, 3: –18 °C, 4: –15 °C. Points for a frequency of 25 Hz are marked with an asterisk, the other extreme points of the diagrams correspond to a measurement frequency of 500 kHz and 1 MHz. LW is the branch of the diagram corresponding to liquid water (it disappears when approaching –40 °C)

2.2. Thermal measurements

It is known that the heat capacity C_p increases significantly for water on the Widom line, which takes place at –45 °C at near atmospheric pressure (0.1 MPa). Anomalous behaviour, according to theoretical estimates, should also be observed for the heat capacity at constant volume. In the case of a significant change in pressure, some increase in the volume of the liquid is possible, therefore the thermal response of water in the pores will be a function of two heat capacities. However, in any case, measurements of thermal quantities near the temperature on the Widom line will apparently reveal non monotonic temperature dependences.

For the determination of this special temperature, the measurement of the characteristics of a single pulse of thermal energy propagating in a medium was used [15]. In this method, a short-term heating of the medium was created in a small volume of the sample, followed by recording the temperature at a certain distance from the source of thermal disturbance. It is known that for a flat heat flow front in a homogeneous medium, the thermal conductivity $D = k/\rho C_i$, where k is the coefficient of thermal conductivity, ρ is the density of the material, C_i is the specific effective heat capacity. Near the Widom line, in addition to the heat capacity anomaly, changes in the thermal conductivity coefficient also can be expected. In this case, for a point energy source and a spherical front of a propagating thermal pulse, a diffuse temperature pulse in time will be observed at the points of the medium. In general, the maximum temperature increment (ΔT) will increase with an increase in the coefficient D and decrease with an increase in C_i. Also ΔT will depend in a complex way on the properties of the medium, the geometry of the sample, and the characteristics of the pulse source. However, the purpose of measurements was to determine the temperature range at which an anomaly in the response of the medium will be observed (these can be the temperatures of phase transitions, the critical point, and the area associated with it on the Widom line). For this purpose, it was sufficient to determine only the temperature of the medium for the maximum value of deviations of T caused by the propagation of a thermal pulse in the sample. The scheme of the installation for the measuring the thermal response to an impulse action is shown in Fig. 4.

During measurements, the moistened MCM-41 sorbent was placed in a cylindrical metal container (1), with the diameter of 16 mm and depth of 10 mm, where a filament heater (3) and a thermocouple (4) were located. The heater wire

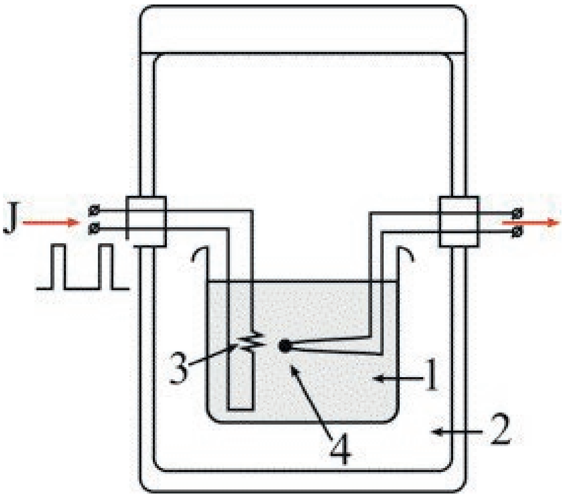

Fig. 4. Scheme of the installation for measuring the temperature increment in the medium caused by the propagation of a thermal pulse, *J* is current form through the heater, (designations are given in the text)

was placed in a volume of 0.4 mm^3, its electrical resistance was 3 Ohm, the distance from the heater to the thermocouple was ~ 7 mm. Thermal waves were created by a sequence of short current pulses of 0.2–0.4 A with a cyclic change in the temperature of the climatic chamber (2) in the range from 25°C to –55°C. The duration of the current pulse, the time between pulses, and the times of cooling and heating of the samples were experimentally chosen in order to obtain a noticeable temperature response during the passage of a thermal pulse with its subsequent relaxation.

The results of one of the measurements at a weight moisture content of 8% are shown in Fig. 5. The graph reveals an extremum of the measured value at temperatures of –14 °C ... –18 °C, indicating a special state of the medium in a certain temperature range and the centre with these values. A similar behaviour with slightly different extremes was also found in measurements with higher humidity MCM-41. Moreover, for a humidity of 98%, the extremum ΔT for the supercooling region of water was not observed.

In addition, the thermometry of the samples was performed during their uniform heating from –55 °C to 10 °C with a relative accuracy of 0.1 °C. For example, for the medium with 70% humidity, a deviation of the time derivative of temperature from a linear dependence in the temperature range of –40 °C ... 0 °C with a non-sharp deviation extremum (a decrease by 10% of the value) at –15 °C ... –20 °C was established. A decrease in the value of the derivative can be attributed to an increase in the heat capacity of water, which takes place near the Widom line [1].

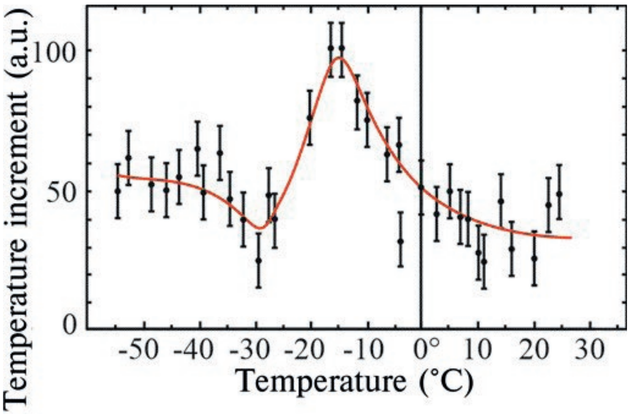

Fig. 5. The maximum value of the medium temperature increment in the thermal wave depending on the temperature of the moistened MCM-41 when the sample is heated from –55 °C (at arbitrary units)

3. Discussion

The performed experiments showed the coincidence of the anomalous behaviour of the dielectric and thermal characteristics of supercooled water located in the cylindrical pores of the MCM-41 silicate sorbent at a temperature significantly exceeding –45 °C. The behaviour of electrical and thermal characteristics revealed in new experiments suggests a special mechanism of susceptibility to external physical influences at certain temperatures. It was associated with the achievement of states of pore water on the Widom line at negative pressures. Anomalous behaviour was observed in the region with the centre near the temperature of –18 °C for experiments with MCM-41 (Fig. 2a), for which the pressure in the pores is approximately equal to –65 MPa as follows from the plot of the Widom line in the pressure-temperature phase space (Fig. 1).

The effect was found for MCM-41 with a weight moisture content below 70% (which corresponded to less than 90% pore volume filling for its pore space parameters). For a medium with a weight moisture content of 98%, according to our measurements, there was no effect. This can be explained by the fact that, for higher humidity, part of the water is located in the space between the granules, which eliminates the menisci and leads to the disappearance of the negative pressure in the pores.

In the case of hydrophobic pores, the pressure in the water should increase due to the convexity of the menisci and the Widom line, in accordance with the graph in Fig. 1 will appear at temperatures below –45 °C. Similar pattern will be observed for completely filled spherical hydrophilic pores. In all cases, the effect will also depend on the features of the filling of the pore space with water, its geometry and defects in the pore structure, moisture values, and possible dissolution of the matrix substance.

As was noted in [1–4, 7], thermal and acoustic indicators change near the Widom line, and the acceleration of thermally activated physicochemical transformations involving liquid water is possible. These features can manifest under natural conditions in various finely dispersed media of complex composition: in atmospheric aerosols, vegetation covers, soils, subsoils, in engineering structures and artificial environments in the case of significant specific volumes of filamentous pores of nanometre diameter.

4. Conclusions

The experimental study of water in a silicate sorbent with filamentous pores revealed anomalous temperature dependences of the low-frequency impedance of the capacitive cell with the sample and the thermal response to pulsed heating of the medium. Extrema of these characteristics were found near –18 °C for the moistened MCM-41 material with a pore diameter of 3.5 nm, which can be explained by the existence of a significant negative pressure in the pores, equal to –65 MPa. These parameters in the pressure-temperature phase space correspond to a point on the Widom line, where there is an increase in fluctuations in the entropy and density of bulk water, which generates anomalies in the physical characteristics of the fluid and its host medium. The study of other similar sorbents for investigation of the possibility of reaching pressures of ~ –100 MPa in pore water, which will correspond to positive temperatures on the Widom line is of interest.

Conflict of interests

The author declares that he has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

1. Anisimov M. A. Cold and super-cooled water: a novel supercritical-fluid solvent. *Russian Journal of Physical Chemistry B*. 2012;6: 861–867. https://doi.org/10.1134/S199079311208009X

2. Shi R., Tanaka H. The anomalies and criticality of liquid water. *Proceeding of National Academy of Science* (USA). 2020;117: 26591–26599. https://doi:org/10.1073/pnas.2008426117

3. Pallares G., Gonzalez M., Abascal I. L. F., Valeriani C., Caupin F. Equation of state for water and its line of density maxima down to −120 MPa. *Physical Chemistry Chemical Physics*. 2016;18: 5896–5900. https://doi.org/10.1039/C5CP07580G

4. Biddle J. W., Singh R. S., Sparano E. M., Ricci F., Gonzalez M. A, Valeriany C., Abascal J. L. F., Debenedetti P. G., Anisimov M. A., Caupin F. Two-structure thermodynamics for the TIP4P/2005 model of water covering supercooled and deeply stretched regions. *Journal of Chemical Physics*. 2017;146(3): 034502. https://doi.org/10.1063/1.4973546

5. Abascal I. L. F., Vega C. Widom line and the liquid-liquid critical point for the TIP4P/2005 water model. *Journal of Chemical Physics*. 2010;133: 234502–234510. https:/doi.org/10.1063/1.3506860

6. Caupin F. Escaping the no man's land: recent experiments on metastable liquid water. *Journal of Non-Crystalline Solids*. 2015;407: 441–448. https://doi.org/10.1016/j.jnoncrysol.2014.09.037

7. Bordonskiy G. S., Gurulev A. A. Regarding physical and chemical transformation with the involvement of water near – 45 °C. *Condensed Matter and Interphases*. 2019;21(4): 478–489. (In Russ., abstract in Eng.). https://doi.org/10.17308/kcmf.2019.21/2359

8. Briggs L. G. Limiting negative pressure of water. *Journal of Applied Physics*. 1950;21: 721–722. https://doi.org/10.1063/1.1699741

9. Alvarenga A. D., Grimsditch M., Bondar R. J. Elastic properties of water under negative pressure. *Journal of Chemical Physics*. 1993;98(11): 8392–8396. https://doi.org/10.1063/1.464497

10. Shi K., Shen Y., Santiso E. E., Gibbins K. E. Microscopic pressure tensor in cylindrical geometry: pressure of water in a carbon nanotube. *Journal of Chemical Theory and Computation*. 2020;16: 5548–5561. https://doi.org/10.1021/acs.jctc.0c00607

11. Artyomenko L. V., Kozhevnicov N. O. Modelling the Maxwell-Wagner effect in frozen unconsolidated

rocks. *Earth's Cryoshere*. 1999;3(1): 60–68. (In Russ., abstract in Eng.). Available at: http://earthcryosphere.ru//archive/1999_1/60-68.pdf

12. Cerveny S., Mallamace F., Swenson J., Vogel M., Xu L. Confined water as model of supercooled water. *Chemical Reviews.* 2016;116(13): 7608–7625. https://doi.org/10.1021/acs.chemrev.5b00609

13. Menshikov L. I., Menshikov P. L., Fedichev P. O. Fenomenological model of hydrophobic and hydrophilic interaction. *Journal of Experimental and Theoretical Physics*. 2017;152(6): 1173–1188. https://doi.org/10.1134/S1063776117120056

14. Barsukov E., Macdonald J. R. (eds). *Impedance Spectroscopy. Theory, experiment and applications.* New Jersey: Wiley; 2005. 595 p.

15. Carballo-Sanchez A. F., Gurevich Y. G., Logvinov G. N., Drogobitskii Y. V., Titov O. Y. Propagation of a heat pulse in a bounded conducting medium: thermoelectric detection. *Physics of the Solid State*. 1999;41(4): 544–549. https://doi.org/10.1134/1.1130821

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