SHEAR ELASTICITY OF ICE NEAR ITS MELTING POINT

N.L. SHEIKO, O.YU. AKTAN, YU.F. ZABASHTA, T.YU. NIKOLAYENKO

Taras Shevchenko National University of Kyiv
(6, Academician Glushkov Ave., Kyiv 03127, Ukraine; e-mail: portis@univ.kiev.ua)

PACS 64.70.D-, 62.20.de

The values of ice shear modulus in the temperature interval 208–273 K and at frequencies of 0.3–2 Hz have been measured. A considerable decrease of the shear modulus with the temperature growth starting from 258 K has been revealed. The observed anomaly is associated with a premelting process. It has been demonstrated that, of all the hypotheses concerning this phenomenon, only a suggestion that the premelting is connected with the formation of an intermediate structure is in agreement with experiment. Using the experimental data obtained, the dependence of the intermediate structure concentration on the temperature has been calculated.

1. Introduction

When studying the physical properties of ice, the main attention of researchers is paid to the melting point vicinity. In this work, the temperature dependence of the dynamic shear modulus in this temperature interval is studied.

The choice of the shear modulus as a macroscopic characteristic to study was based on the following speculations. The values of this quantity for a crystal and its melt differ by several orders of magnitude (according to various estimations, this difference is about 8 to 9 orders). Therefore, the shear modulus of liquid is adopted to equal zero, whereas other macroscopic characteristics (such as the density, bulk elastic modulus, and so on) of the crystal and its melt have, as a rule, the same order of magnitude.

According to the thermodynamic theory of phase transformations (see, for instance, work [1]), the dependence of the shear modulus G' on the melting temperature in the vicinity of the melting point T_m consists of three sections: a smooth curve ab which corresponds to a reduction of the shear modulus of the crystalline phase with the temperature growth; a jump bc to zero value at the melting point T_m, and a zero section cd which corresponds to the liquid (Fig. 1).

The same figure exhibits experimental values obtained for the shear modulus of ice (black points). One can see that, starting from a certain temperature T_0, a substantial deviation of the experimental dependence $G'(T)$ from the theoretical one is observed.

The observed anomalous experimental behavior of the shear modulus is not at all unexpected. In the vicinity of the melting temperature, the anomalies of other thermodynamic characteristics (the heat capacity, coefficient of thermal expansion, and so on) are also observed. Those anomalies are associated with a premelting process [7]. Therefore, it is logical to admit that the anomaly of the shear modulus, which was found by us, is also induced by it.

In the literature, there are various hypotheses concerning the origin of the premelting phenomenon [7]. In this paper, we have examined them using the obtained

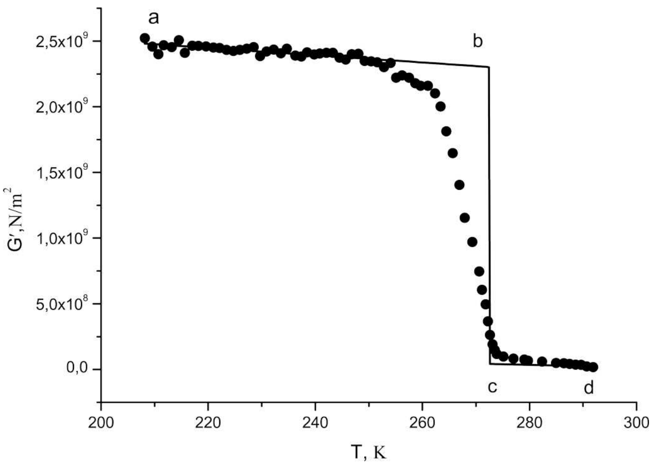

Fig. 1. Theoretical and experimental temperature dependences of the real part of the shear modulus $G'(t)$

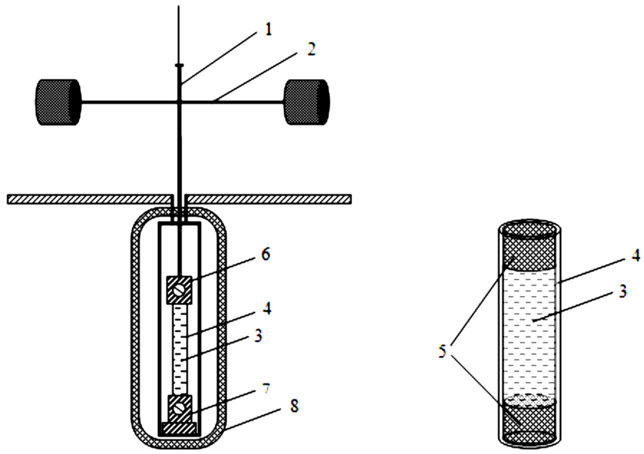

Fig. 2. Schemes of the experimental installation and a cuvette with a liquid to study

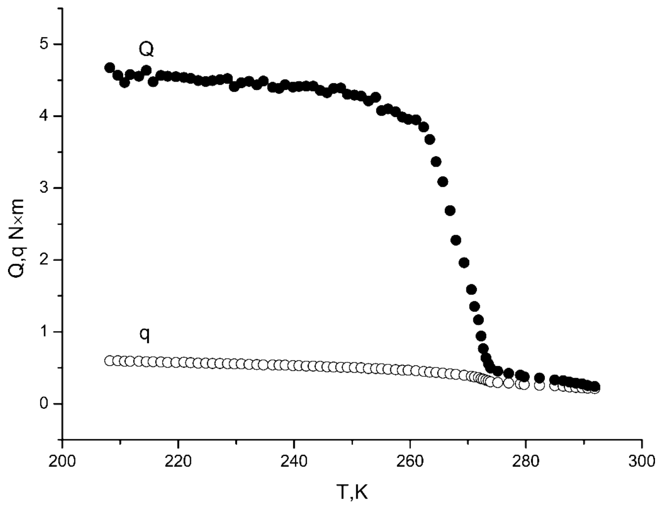

Fig. 3. Temperature dependences of the torsion rigidities of an empty cuvette, q', and the cuvette with a liquid to study, Q'

experimental data and have chosen a hypothesis which is in the closest agreement with our experiment.

2. Technique of Shear Modulus Determination

Measurements were made with the help of a method proposed in works [2, 3]. Its feature consists in a capability of measuring the shear modulus of the same specimen in the permanent heating mode, from temperatures $T < T_m$ to temperatures $T \geq T_m$, irrespective of the aggregate state of the specimen.

The method was realized by means of a torsion pendulum, the scheme of which is exhibited in Fig. 2. The main part of the pendulum was rod *1* suspended by an elastic thread, with beam *2* with counter-balances at its ends. Elastic cylindrical polyethylene cuvette *4* was filled with a substance to study. The cuvette was closed by corks *5* and fixed in clips *6* and *7* of the torsion pendulum: its lower part was attached to a motionless base of the pendulum, and the upper one to the rod with the beam. The cuvette was placed into heat chamber *8*.

The equation of motion for the torsion pendulum looks like [4]:

$$\frac{d^2\varphi}{dt^2} + \omega^2\varphi = 0, \tag{1}$$

where φ is the rotation angle, $\omega = \sqrt{Q/I}$ is the cyclic frequency (complex-valued), I is the moment of inertia of the mobile part of the pendulum, and Q is the torsion rigidity. The solution of this equation is damped oscillations

$$\varphi = \varphi_0 e^{i\omega t}, \tag{2}$$

where

$$\omega = \omega' + i\omega''. \tag{3}$$

After the substitution of expressions (2) and (3) into Eq. (1), we obtain the following expression for the real part Q' of the specimen torsion rigidity:

$$Q' = I((\omega')^2 - (\omega'')^2). \tag{4}$$

In formula (4), the cyclic frequency ω' and the damping coefficient ω'' are determined from experiments. In a similar way, the real part q' of the torsion rigidity of the empty cuvette is determined. The real part of the torsion rigidity of the substance under investigation is determined as a difference between the torsion rigidity Q' of a specimen with the substance and the torsion rigidity of an empty cuvette q':

$$S' = Q' - q'. \tag{5}$$

The temperature dependences of the torsion rigidities Q' and q' are depicted in Fig. 3.

For the calculation of the dynamic shear modulus G' of a researched substance, we used the well-known solution for the problem of twisted elastic round rod [5] which gives rise to the formula

$$G' = \frac{S'l}{I_p}, \tag{6}$$

where, in our case, l is the working length of the cuvette, $I_p = \pi R^4/2$ is the polar moment of inertia, and R is the internal radius of the cylindrical cuvette. The length between cork end faces was taken as the working length.

At measurements, we used polyethylene cuvettes with the internal radius $R = 2.5$ mm and the working length $l = 35$ mm. The cuvette was filled with bidistilled water and cooled down to a temperature of -60 °C by embedding heat chamber *8* into a Dewar vessel with liquid nitrogen. There was no direct contact between the specimen and liquid nitrogen at that. After the ice formation had finished, the process of slow heating was started. At every new temperature value (with a step of 1 °C), the quantities ω' and ω'' were measured, which allowed the modulus G' to be calculated by formulas (4)–(6).

The temperature was measured with the help of a single-crystal temperature-sensitive element of the DS18b20 type (Dallas Semiconductor Corp.), the accuracy of which was ± 0.5 °C.

The temperature was measured in two stages. At the first stage, the temperature-sensitive element was placed into the heat chamber and arranged close to the specimen. As a result, the quantities ω' and ω'' were obtained, and the dependence

$$G' = G'(T_a), \tag{7}$$

where T_a is the air temperature in the heat chamber, was calculated.

At the second stage of measurements, an additional platinum resistance thermometer was placed into the specimen. The specimen was heated up in the same regime, but the quantities ω' and ω'' were not measured; only the readings of an additional temperature-sensitive element T_i were registered simultaneously with the measurements of the air temperature T_a in the heat chamber. That is, the dependence

$$T_a = f(T_i), \tag{8}$$

where T_i is the real temperature of ice, was determined. It is exhibited in Fig. 4.

Such a technique of temperature measurement allowed us to avoid possible distortions of the measurement results for ω' and ω'', which might arise owing to the presence of a strange body (the temperature-sensitive element) in the cuvette. The dependence $T_a = f(T_i)$ at $T_i < T_m$ is linear: the difference between the values of T_a and T_i is constant.

Substituting dependence (8) into expression (7), we obtain the sought experimental dependence $G'(T_i)$ – or simply $G'(T)$ – depicted in Fig. 1.

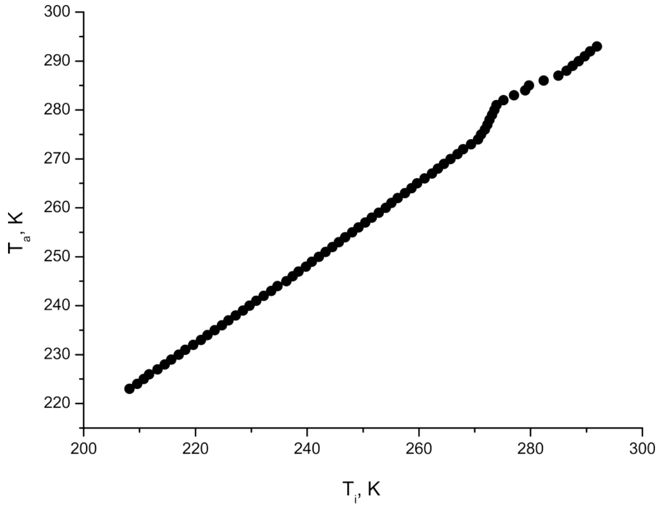

Fig. 4. Experimental dependence $T_a = f(T_i)$

3. Discussion of Experimental Results

For one thing, let us make sure that a noticed decrease of the shear modulus in the vicinity of the melting point is really associated with the premelting, rather than follows from other reasons. The matter is that, when water in the measuring cuvette freezes, it increases its volume. Indeed, at $T = T_m$, the ice density $(0.92 \times 10^3\ \mathrm{kg/m^3})$ is lower than that of water. As a result, strains arise in the cuvette and squeeze the formed ice. The pressure growth is known to induce a decrease of the melting temperature [6, 8].

Let us evaluate, which is a reduction of the melting temperature in our case. For this purpose, let us take advantage of a solution of the Lamé problem [5], where the strained state of a pipe, the internal surface of which is subjected to the action of a pressure p, is considered. For the pipe displacement u on the internal radius, we obtain

$$u = -\frac{pa^3}{a^2 - b^2}\left(a^2\frac{1-\nu}{E} + b^2\frac{1+\nu}{E}\right), \tag{9}$$

where E and ν are the Young modulus and Poisson's ratio, respectively, of the pipe; and a and b are the external and internal pipe radii, respectively.

Let θ denote the relative volume variation at the water–ice transformation. This quantity is connected with the displacement u by the formula

$$\theta = 2u/a. \tag{10}$$

Substituting formula (10) into expression (9), we obtain

$$p = \frac{\theta/2}{\frac{a^2}{b^2-a^2}\left(a^2\frac{1-\nu}{E} + b^2\frac{1+\nu}{E}\right)}. \tag{11}$$

Using the value of ice density at $T = T_m$ given above, we obtain $\theta = -0.08$. From our experiment with the empty pipe, we found that the shear modulus $G_b \approx 20$ MPa. Assuming that $\nu = 0.5$, we obtain the Young modulus $E = 3G \approx 60$ MPa.

Substituting the quoted numerical values to formula (11), we obtain the estimation $p_a \leq 1$ MPa. According to the ice phase diagram [6, 8], such a pressure brings about a reduction of the melting temperature by $\Delta T_m \leq 0.1$ K. This means that a decrease of the modulus was not caused by a reduction of the melting temperature in our case, owing to an increase of the pressure in the pipe.

Another reason for the melting temperature to decrease can be the presence of impurities in water [7]. When the crystal lattice of ice is formed, impurities are pushed out into intergrain boundaries. Therefore, they become non-uniformly arranged over the volume, forming solid solution domains. According to Raoult's law [1], the melting temperature for such domains is lower than that of ice. It is this circumstance that can provoke the premelting process.

In this work, we used bidistilled water. The volume fraction of impurities in such water was less than 10^{-4}%. It is evident that such an amount of impurities cannot stimulate a decrease of the modulus at $T = 258$ K, which was observed in experiment. Hence, the hypothesis that the premelting process occurs owing to the presence of impurities does not agree with the results obtained in this work.

One more hypothesis was proposed in work [9]. Namely, the premelting is associated with heterophase fluctuations. The crystal in the state of thermal equilibrium at $T < T_m$ contains some amount of the liquid phase, the volume concentration v of which is determined by the formula

$$v = \sum_{g=g_0}^{\infty} g \exp\Big(-ag - bg^{2/3}\Big), \tag{12}$$

where g is the number of molecules in a "droplet", and g_0 is the minimal admissible value of g.

The constants a and b are given by the expressions

$$a = \frac{\lambda\,(T_m - T)}{k_{\rm B} T T_m}, \tag{13}$$

$$b = \frac{\alpha}{k_{\rm B} T} = \frac{4\pi r^2 \sigma}{k_{\rm B} T}, \tag{14}$$

where λ is the melting heat per one molecule, σ the coefficient of surface tension at the "crystal–melt" interface, r the molecular radius, and $k_{\rm B}$ the Boltzmann constant.

The temperature dependence of the volume concentration of water in ice, calculated by formula (12), is presented in Fig. 5. The numerical values $\lambda = 10^{-20}$ J and $\sigma = 14.56 \times 10^{-3}$ J/m^2 used at calculations were adopted according to handbook data. The estimation $g_0 = 150$ was taken from work [9].

On the basis of values obtained for v, the shear modulus can be calculated. For this purpose, we use the elasticity theory for microinhomogeneous media [10], in which the system of two components with different shear moduli is considered. In the case of our system, where heterophase fluctuations take place, those components are ice and water. Let the shear modulus of the liquid phase be denoted as G'_l, and that of solid phase as G'_c. For the shear modulus G' of their mixture, the theory gives the formula

$$\frac{v}{1 + \beta\,(G'_l/G' - 1)} + \frac{1 - v}{1 + \beta\,(G'_c/G' - 1)} = 1. \tag{15}$$

The constant β is determined by the formula

$$\beta = \frac{2\,(4 - 5\nu)}{15\,(1 - \nu)}. \tag{16}$$

Poisson's ratio v for the mixture is calculated as follows:

$$\nu = \nu_c(1 - v) + \nu_l v, \tag{17}$$

where ν_c and ν_l are the corresponding parameters for the solid and liquid components, respectively. They are: $\nu_c = 0.34$ and $\nu_l = 0.5$.

In our calculations, the shear modulus of water G'_l was assumed to be zero. For G'_c, the experimental value of the real part of the shear modulus G' at the temperature $T_c = 258$ K was taken, which corresponds to the beginning of its deviation from line ab (Fig. 1).

The dependence $G'(T)$ calculated on the basis of data presented in Fig. 5 and making use of formula (15) is depicted in Fig. 6 as a solid line. The experimental data are also exhibited there. The figure testifies that the experimental data do not agree with the results obtained in the framework of the heterophase fluctuation theory. Hence, this theory turns out incapable of explaining the revealed anomaly of the shear modulus.

One more hypothesis was proposed in works [11–15]. It was suggested that the process of ice premelting is caused by the formation of an intermediate structure, the ordering of which is higher than that of water, but lower than that of ice. This hypothesis seems to be the most plausible one owing to the following reasoning. The fact that the shear modulus substantially decreases in the vicinity of the melting point can be uniquely explained

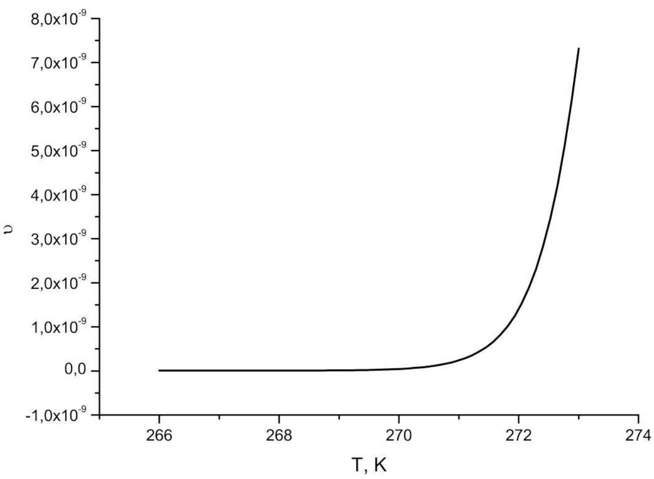

Fig. 5. Temperature dependence of the volume concentration of water in ice, v, calculated in the framework of the heterophase fluctuation theory

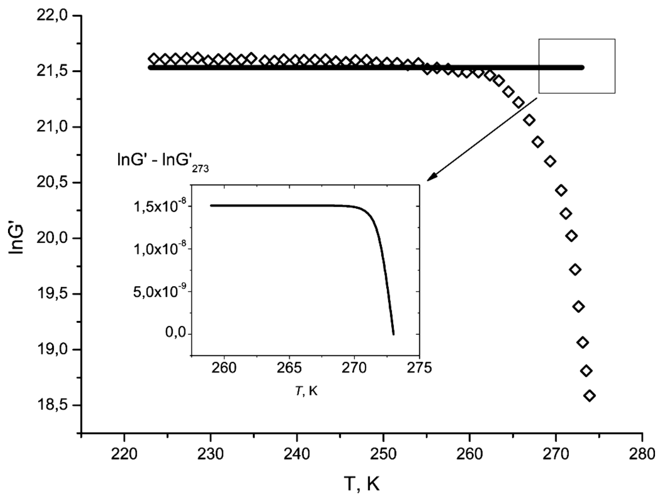

Fig. 6. Comparison of theoretical (calculated in the framework of the heterophase fluctuation theory) and experimental real parts of the shear modulus G'

as the appearance – together with the hard component, i.e. ice – of some soft component, the shear modulus of which is substantially lower than that of ice. Since the temperatures lower than the melting point are considered, classical thermodynamics totally forbids the appearance of the liquid phase in this temperature interval. The unique mechanism for a liquid to appear in this range is thermal fluctuations. Such fluctuations (heterophase) were considered above. However, we showed that they cannot explain the observed decrease of the shear modulus. Therefore, in the framework of the existing hypotheses concerning the nature of premelting phenomenon, we adhere to the hypothesis of the intermediate structure existence.

The issue concerning a specific model of such a structure remains highly disputable. Till now, it has not been established whether such a structure is a certain thermodynamic phase, i.e. whether the formation of an intermediate structure is a phase transition. In such an indefinite situation, the additional experimental material should be gathered to have a ground to speak about that or another macroscopic model of intermediate structure with larger reliability.

The experiment we have carried out allows the dependence of the intermediate structure concentration on the temperature to be determined. To find this dependence, let us once more take advantage of formula (15), but with the shear modulus for the intermediate structure G'_q substituted for the shear modulus of the liquid phase G'_l:

$$\frac{\upsilon}{1+\beta\left(G'_q/G'-1\right)}+\frac{1-\upsilon}{1+\beta\left(G'_c/G'-1\right)}=1. \qquad (18)$$

The quantity G'_q can be determined using the following speculations. By definition, the system is a melt at a temperature of 273 K. The temperature was measured to within ±0.5 K. Therefore, the last experimental temperature, at which the system was in the solid aggregate state, is a temperature of 272 K. According to the model under consideration, the system is a mixture of crystalline and intermediate structures at this temperature. When the temperature grows, the concentration of the intermediate structure increases; it reaches 1, when the total shear modulus of the system becomes equal to the shear modulus of the intermediate structure G'_q. Therefore, the inequality $G'_q < G'_{272\ \mathrm{K}}$ must be obeyed. On the other hand, since the intermediate phase differs from the liquid, the inequality $G'_q > 0$ must be fulfilled. Hence, the following expression is valid:

$$0 < G_q < G'_{272\ \mathrm{K}}. \qquad (19)$$

An exact value of G'_q is unknown. Therefore, we assume G'_q to be a random quantity, with every its value having an identical probability. In this case, the shear modulus of the intermediate structure is a mathematical expectation of the mentioned random quantity, which allows the following equality for the shear modulus to be written down:

$$G_q = \frac{1}{2}G_{272\ \mathrm{K}}. \qquad (20)$$

Figure 7 demonstrates the temperature dependence of the intermediate structure concentration which was calculated using the experimental curve in Fig. 1 and with

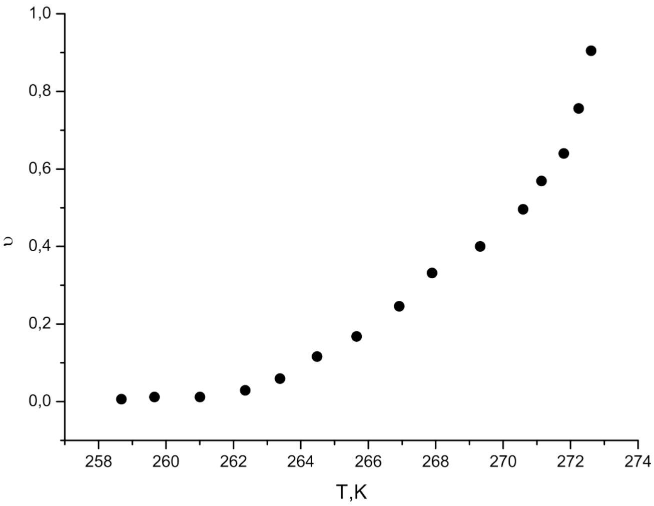

Fig. 7. Temperature dependence of the volume concentration of an intermediate structure in ice, v, calculated on the basis of experimental data

the help of formula (18), in which the shear modulus of the intermediate structure G'_q was determined by equality (20).

Hence, the measurements of the shear modulus in the vicinity of the melting temperature allowed the intermediate structure concentration in this temperature interval to be determined. The authors hope for that the information obtained about the intermediate structure concentration will be useful for finding a specific microscopic model of intermediate structure.

4. Conclusions

The main result of this paper is the experimental discovery of an anomaly in the behavior of the shear modulus of ice in the vicinity of the melting temperature, which consists in that the shear modulus becomes substantially lower even before the melting in the temperature interval 258–273 K has started. In our opinion, considering the modern state of theoretical ideas with respect to the mechanism of ice melting, it cannot be an ultimate answer concerning the nature of the revealed anomaly. Only the more or less agreement between that or another physical model selected from those proposed in the literature and experimental data can be the matter of discussion. The only thing that can now be asserted with a fair degree of confidence is that the observed anomaly is associated with premelting. We have analyzed the existing models proposed for the description of the ice behavior in the vicinity of the melting temperature point. It turned out that only one model agrees with experimental data, including ours. It is a model that admits the formation of an intermediate structure, in which the ordering is higher than that in water, but lower than that in ice. Proceeding from this fact, we assert that the observed anomaly of the shear modulus is induced by the formation of this structure.

1. L.D. Landau and E.M. Lifshitz, *Statistical Physics, Part 1* (Pergamon Press, Oxford, 1980).
2. L.A. Bulavin, Yu.F. Zabashta, O.Yu. Aktan, and T.Yu. Nikolayenko, Patent for invention No. 78094, Ukraine; IPC(2006) G01N11/16 (2007.01) G01N11/10; Bull. N 2 of 15.02.2007.
3. O.Yu. Aktan, O.S. Svechnikova, and T.Yu. Nikolayenko, Funct. Mater. **14**, 146 (2007).
4. L.D. Landau and E.M. Lifshitz, *Mechanics* (Butterworth Heinemann, Oxford, 2001).
5. L.D. Landau and E.M. Lifshitz, *Theory of Elasticity* (Pergamon, New York, 1959).
6. D. Eisenberg and W. Kautzman, *The Structure and Properties of Water* (Oxford University Press, Oxford, 1968).
7. A.R. Ubbelhode, *Melting and Crystal Structure* (Clarendon Press, Oxford, 1965).
8. W. Wagner and R.J. Feistel, Phys. Chem. Ref. Data **35**, 1021 (2006).
9. J. Frenkel, *Kinetic Theory of Liquids* (Dover, New York, 1955).
10. T.D. Shermergor, *Elasticity Theory for Microinhomogeneous Media* (Nauka, Moscow, 1977) (in Russian).
11. N.H. Fletcher, Philos. Mag. **18**, 1287 (1968).
12. A. Lied, H. Dosch, and J.H. Bilgram, Phys. Rev. Lett. **72**, 3554 (1994).
13. H. Bluhm, T. Inoue, and M. Salmeron, Phys. Rev. B **61**, 7760 (2000).
14. X. Wei, P.B. Miranda, and Y.R. Shen, Phys. Rev. Lett. **86**, 1554 (2001).
15. S. Engemann, H. Reichert, H. Dosch, J. Bilgram, V. Honkimaki, and A. Snigirev, Phys. Rev. Lett. **92**, 205701 (2004).

Received 15.02.09.
Translated from Ukrainian by O.I. Voitenko

ЗСУВНА ПРУЖНІСТЬ ЛЬОДУ В ОКОЛІ ТЕМПЕРАТУРИ ПЛАВЛЕННЯ

Н.Л. Шейко, О.Ю. Актан, Ю.Ф. Забашта, Т.Ю. Ніколаєнко

Р е з ю м е

Експериментально отримано значення динамічного модуля зсуву льоду в температурному інтервалі 208–273 К при частотах 0,3–2 Гц. Виявлено значне падіння модуля зсуву зі зростанням температури, починаючи з 258 K. Спостережену аномалію пов'язують з процесом передплавлення. Показано, що з існуючих гіпотез щодо цього процесу, з експериментом узгоджується гіпотеза про зв'язок передплавлення з утворенням проміжної структури. За експериментальними даними розраховано залежність концентрації проміжної структури від температури.