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THE DEPENDENCE OF THE COMPRESSION MODULUS OF ICE-SIX AND THE COEFFICIENT OF VOLUME EXPANSION ON PRESSURE AND TEMPERATURE

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Abstract

This pioneering study investigated the partial derivatives of the dependence of the compression modulus of ice-six on pressure and temperature, and the coefficient of volume expansion on the temperature at high pressure and low temperature. Ice six is documented on the phase diagram between the pressures 600 and 2000 MPa and between the temperatures 110 and 330 K. The pressure and temperature dependence of the all-round compression module was practically implemented in a multilayer cylinder-piston vessel. The change in the relative volume of the sample was measured using a transducer which converts linear translational motion into electrical pulses. The pressure of the sample was measured by measuring the electrical resistance of tin and gallium conductors and phase transition points of polymorphic ice modifications.

The temperature of this ice-six modification was determined by a graduated copper-constantan thermocouple. Moreover, in this paper, the Debye characteristic temperatures of ice-six and the Gruneisen constant are estimated.

Keywords: partial derivatives, temperature, pressure, coefficient of compressibility, thermal volume expansion coefficient.

Аңдатпа

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VI-ШЫ МҰЗ ТҮРІНІҢ СЕРПІМДІЛІК МОДУЛІНІҢ ДЕРБЕС ТУЫНДЫЛАРЫНЫҢ ЖӘНЕ КӨЛЕМДІК ҰЛҒАЮ КОЭФФИЦИЕНТІНІҢ ҚЫСЫМ МЕН ТЕМПЕРАТУРАҒА ТӘУЕЛДІЛІГІ

Мақалада алғаш рет жоғары қысым мен төменгі температурада пайда болатын VI–шы мұз модификациясның жан-жақты сығылу модулінің температура және қысымға алынған дербес туындыларының қысымға және температураға, жылулық көлемдік ұлғаю коэффициентінің температураға тәуелділіктері зерттелген. Мұздың VI–шы модификациясы фазалық диаграммада 600 – 2000 МПа қысым мен 110 – 330 К температура аймағында орналасқан. Жан-жақты сығылу модулінің қысым мен температураға тәуелділігі тәжірибе жүзінде көпқабатты цилиндр-поршень типтес ыдыста іске асырылды. Зерттелетін үлгінің салыстырмалы көлемінің өзгерісі сызықты ілгерілемелі қозғалысты электр импульстеріне айналдыратын түрлендіргіш арқылы өлшенді. Үлгідегі қысым, онда орналасқан қалайы, галий өткізгіштерінің электр кедергісін өлшеу және полиморфты мұз модификацияларының фазалық өту нүктелері арқылы өлшенді. Зерттеліп отырғанVI-шы мұз модификациясының температурасы градуирленген мыс-константан терможұбымен анықталып отырды.

Сонымен қатар, мақалада VI–шы мұз үшін Дебай температуралары мен Грюнайзен тұрақтысы шамамен бағаланған.

Түйін сөздер:дербес туынды, температура, қысым, сығылу коэффициенті, көлемдік жылулық ұлғаю коэффициенті.

Аннотация

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ЗАВИСИМОСТЬ МОДУЛЯ ЭЛАСТИЧНОСТИ ШЕСТОГО ТИПА ЛЬДА И КОЭФФИЦИЕНТА РАСШИРЕНИЯ ОБЪЕМА ОТ ДАВЛЕНИЯ И ТЕМПЕРАТУРЫ

В этой статье были исследованы частные производные зависимости модуля сжатия модификации льда-VI от давления и температуры, а также коэффициента объемного теплового расширения от температуры при высоком давлении и низкой температуре.На фазовой диаграмме показана модификация льда-VIмежду давлениями 600 и 2000 МПа и при температурах 110 и 330 К. Зависимость давления и температуры универсального компрессионного модуля была практически реализована в многослойном цилиндропоршневом сосуде. Изменение относительного объема образца измерялось с помощью преобразователя, который преобразует линейное поступательное движение в электрические импульсы. Давление в образце измеряли путем измерения электрического сопротивления проводников олова и галлия и точек фазовых переходов полиморфных модификаций льда. Температура исследуемой модификации льда-VI определялась градуированной термопарой медь-константан.

Кроме того, в этой статье оценены температуры Дебая для льда-VI и константа Грюнайзена.

Ключевые слова:частная производная, температура, давление, коэффициент сжимаемости, коэффициент объемного теплового расширения.

In this research paper, we investigated the partial derivatives of the dependence of the modulus of ice-six elasticity on pressure and temperature, and the coefficient of volume expansion on the temperature at high pressure and low temperature. Ice six is documented on the phase diagram [1] between the pressures 600 and 2000 MPa and between the temperatures 110 and 330 K.

Water plays a unique role as a substance, it is the source of living organism formation and minerals which are found in atmosphere, earth at gas, liquid and solid state. 71% of the Earth surface is surrounded by water.However, it affects the environmental climate and the physical, chemical, and biological phenomena occurring in it. Although a person affects the growth and development of all living organisms, the physical properties of the water and its solid state are not fully researched. Therefore, it is of practical importance to know the dependence of the elastic properties of ice-six on temperature and pressure,and the phase of the ice changes at low temperature and at high pressure.

The concept of high pressure and low temperature are firmly established in modern technology. The problem of the influence of low temperatures and high pressures on the solids covers a wide range of issues – from fundamental problems of stability and phase transformation to the technical material science applications. During the studying the phase change theory there were needed studies, in which the temperature and hydrostatic pressure were used as an additional thermodynamic parameter. By using it, it became possible to explain the relationship between the direction of the phase change point and its mechanism [2].

Another wide area of the pressure and temperature application is the natural science, first of all, physics and earth science. It should be noted here that the work on the study of diagrams of systems, starting from hydrogen, simple metals and other elements, ending with complex combinations of oxides or sulfates, which model the state of matter in the earth's crust. In all of these cases pressure acts as an important parameter of the phase state of the system along with temperature.

The research was carried out in a speciallymolded and automated device[3], in which an ice sample placed in a thin fluoroplastic bag, and housed in a multilayered cylindrical vessel, measured comparative changes in the in the specific volume, temperature and pressure.

There are widely discussed methods for measuring temperature, pressure, and volume changes in a monograph [4].

There are shown dates (table 1, Figure1, and 2) the dependencies on the constant temperature of $\frac{\partial K}{\partial T}$ on the pressure and $\frac{\partial K}{\partial p}$ to the temperature.

Table 1. The dependencies on the constant temperature of $\frac{\partial K}{\partial T}$ *on the pressure and* $\frac{\partial K}{\partial p}$ *to the temperature*

Phase	*T, K*	*P, MPa*	$-\frac{\partial K}{\partial T}$	*P, MPa*	*T, K*	$\frac{\partial K}{\partial p}$
VI	*155*	*1150*	*0,220*	*1400*	*248*	*0,080*
VI	*155*	*1250*	*0,231*		*233*	*0,078*
		1350	*0,264*		*213*	*0,077*
		1450	*0,275*		*193*	*0,076*
		1550	*0,300*		*173*	*0,075*
		1650	*0,322*		*153*	*0,074*
		1750	*0,331*		*133*	*0,074*

From tables and graphs, it can be seen that as the pressure increases the partial derivative of the temperature of the coefficient of elasticity of the ice-six will increase.

As the temperature increases, the partial derivative $\frac{\partial K}{\partial p}$ will increase in an isobaric process.

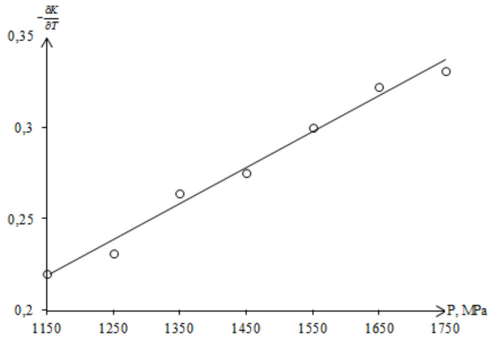

Figure 1. The dependence of $-\frac{\partial K}{\partial T}$ *ice-six on the pressure at a temperature of 155 K.*

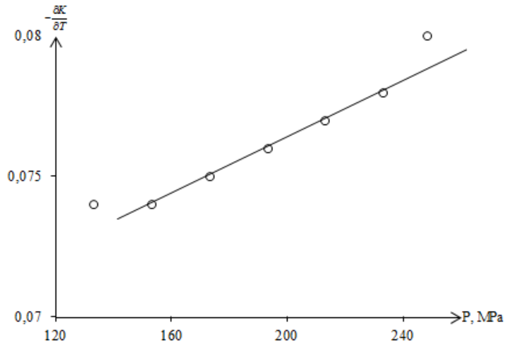

Figure 2. The temperature dependence of the ice-six at a pressure of 1400 MPa.

Table 2 shows the temperature dependence of the coefficient of thermal volume expansion β of ice-six calculated using the formula $\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$ [4] at constant pressure. The negative values are tabled to reveal a positive linear relationship.

Table 2. The temperature dependence of the coefficient of thermal volume expansion β

Phase	*p, MPa*	*T, K*	$-\beta \times 10^{-4}$
VI	*1400*	*180*	*1,00*
		160	*0,97*
		140	*0,95*
		120	*0,93*
	1700	*240*	*0,95*
		220	*0,90*
		200	*0,87*
		180	*0,85*
		160	*0,83*
		140	*0,80*
		120	*0,77*
	2150	*240*	*0,82*
		220	*0,80*
		200	*0,78*
		180	*0,77*
		160	*0,75*
		140	*0,74*
	2300	*240*	*0,78*
		220	*0,76*
		200	*0,75*
		180	*0,73*
		160	*0,70*
		140	*0,68*

Figure3,4,5, 6 show the temperature dependence of the thermal volume expansion coefficients of ice-six at the constant pressures 1400 MPa, 1700 MPa, 2150 MPa, 2300 MPa.

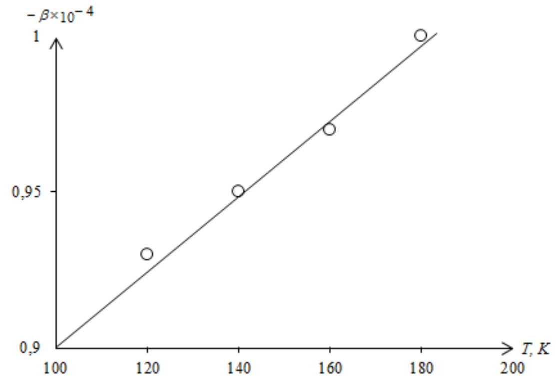

Figure 3. The temperature dependence of the thermal volume expansion coefficients of ice-six at 1400 МПа

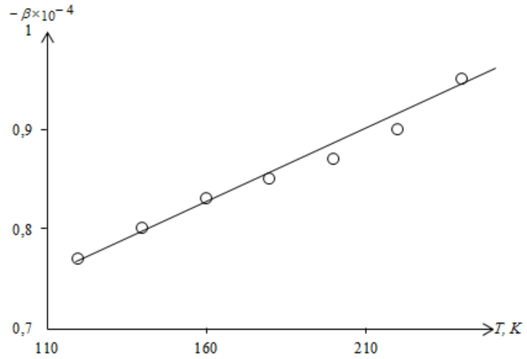

Figure 4. The temperature dependence of the thermal volume expansion coefficients of ice-sixat 1700 МПа

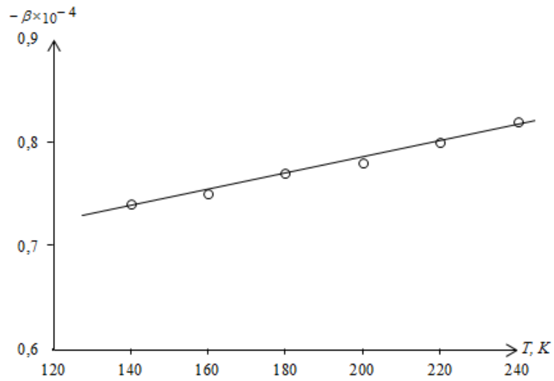

Figure 5. The temperature dependence of the thermal volume expansion coefficients of ice-six at 2150 МПа

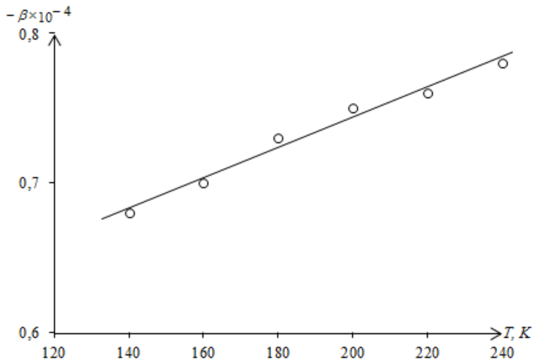

Figure 6. The temperature dependence of the thermal volume expansion coefficients of ice-six at 2300 МПа

According to the definition of compressibility:

$$\chi = -\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_T, \frac{1}{K} = \frac{\partial \ln V}{\partial P}.$$

Denoting$\frac{\partial K}{\partial P} = \varphi$ and considering that $\frac{\partial K}{\partial P}$is a low-varying quantity, we can assume that

$$\frac{d\ln K}{d\ln V} = -\frac{dK}{dP} \approx -\varphi$$

In a first approximation, the Debye characteristic temperature is proportional to$\theta_D = \frac{h}{2\pi K}\sqrt{\frac{K}{\rho}}$, where ρ is the density of ice. Somewhat more accurately, in the approximation of the Debye theory of heat capacity [5]:

$$\theta_D = \left(\frac{9N}{4\pi V}\right)^{1/3} f(\mu)\frac{h}{K}\sqrt{\frac{KV}{M}}$$

or$\ln\theta_D = \frac{1}{2}\ln K + \frac{1}{6}\ln V + \ln\left[\left(\frac{9N}{4\pi}\right)^{\frac{1}{3}}\frac{h\cdot f(\mu)}{MK}\right]$

where μ - Poisson's ratio, N - Avogadro's constant, $\rho = \frac{m}{V}$ – the density of ice, M – the molar mass. The function $f(\mu)$ depends weakly on the changein the Poisson's ratio. This follows from Table 3.

Table 3. The dependence of the function $f(\mu)$ on the change in the Poisson's ratio

μ	$f(\mu)$	$f(\mu)^{\frac{1}{3}}$	$f(\mu)^{-\frac{1}{3}}$	$\mu f(\mu)^{-\frac{1}{3}}$
0,25	4,73	1,68	0,60	0,1575
0,30	6,87	1,90	0,53	0,1590
0,35	11,10	2,23	0,45	0,1575

Therefore, the obtained value of K and $\frac{\partial K}{\partial P}$ allows one to approximately estimate the Debye characteristic temperatures of modification ice-six and the Gruneisen constants.

From the above expression for $\theta_D$neglecting the last term of the right-hand side of the equation, we obtain

$$\frac{d\ln\theta_D}{d\ln V}\sim-\frac{1}{2}\left[\frac{d\ln K}{d\ln V}+\frac{1}{6}\right]\approx\left[\frac{1}{2}\varphi+\frac{1}{6}\right]\approx\frac{1}{6}[3\varphi+1]$$

Substituting the values$\frac{d\ln K}{d\ln V}=\varphi$and assuming that the Grüneisen constant is$\gamma\approx\frac{\partial\ln\theta_D}{\partial\ln V}$, we find:

$$\gamma'\approx\frac{1}{6}[3\varphi+1]$$

As you can see from the result, for the first time, the dependence on pressure and temperature *K(P)*, *K(T)* of the partial derivatives$\left(\frac{\partial K}{\partial T}\right)_P$,$\left(\frac{\partial K}{\partial P}\right)_T$of the experimentally measured universal compression modulus of polymorphic ice-six modification by differentiating the graphs were determined.

With increasing temperature $\left(\frac{\partial K}{\partial P}\right)_T$increases, and with increasing pressure $\left(\frac{\partial K}{\partial T}\right)_P$decreases. Measurement of changes in temperature and pressure in the volume of this sample made it possible to calculate the coefficient of volume thermal expansion of ice-six.

Using the experimentally measured values of the change in the relative volume of the test sample, differentiating the graphs$V(T)_P$, $V(P)_T$ the temperature dependence $\beta=\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$of the ice-six modification in isobaric processes was studied.

The explanations of the dependence between the influence of external factors and parameters measured in practice and calculated using the laws and formulas of physics are given.

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