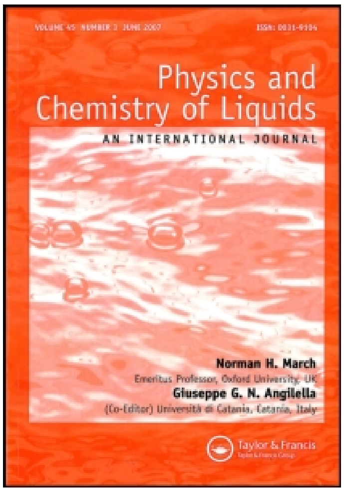

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Calculation of the compressibility and heat capacity of ice I in the pre-melting region

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The isothermal compressibility and the heat capacity are calculated here using the experimental data for the heat expansion of ice I in the pre-melting region. By analysing the data at various pressures, compressibility and the heat capacity are predicted as functions of temperature and pressure near the melting point ($p_m = 202.4$ MPa, $T_m = 252.3$ K) in ice I. Our predicted compressibility and heat capacity exhibit anomalous behaviour as the heat expansion in the pre-melting region of ice I.

Keywords: compressibility; heat capacity; melting point; ice

1. Introduction

Various physical properties of ice and its phase diagram have been studied extensively in the literature [1–4]. Water freezes as ice I_h (hexagonal) and it transforms into ice I_C (cubic) at about −80°C at atmospheric pressure. The I_h structure has hexagonal symmetry and I_C has the cubic symmetry [5,6]. Ice I_C has two molecules in the unit cell, whereas ice I_h has four molecules, and both ice I_c and I_h are disordered phases. Ordered ice I is orthorhombic with a space group C_{mc2_1} [7], and it has been studied in relation to ice I_h [8].

Regarding the experimental studies on the hexagonal ice, measurements using various techniques have been reported recently in the literature. Among those, calorimetric measurements for amorphous ices [9,10], the thermal expansivity for hexagonal and cubic ices [11], lattice parameters in ice I_h [12], neutron diffraction [13,14] and the Brillouin scattering [15] have been given.

It has been shown experimentally that ice I exhibits a second-order phase transition prior to melting [16]. Close to the melting point, the heat expansion α_P shows anomalous behaviour, which can be described by a power-law formula in ice I, and it has been indicated that this is of a λ-type transition [16]. Measurements of the heat expansion α_P along the isotherm 252.3 K from 192 MPa to the melting pressure ($p_m = 202.4$ MPa) have been analysed according to a power-law formula with the critical exponent γ for ice I [16]. For those systems exhibiting λ-type phase transitions such as ice I considered in this study, it is not only the heat expansion α_P that diverges, but also the specific heat C_p and the isothermal compressibility κ_T are expected to diverge as the melting point is approached.

In this study we calculate those thermodynamic quantities, α_P, κ_T and C_p, as functions of temperature and pressure in the pre-melting region of ice I. By analysing the

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experimental data for the heat expansion α_P measured at various pressures in the pre-melting region for a constant temperature of 252.3 K [16], we calculate the heat expansion α_P as a function of temperature, and the isothermal compressibility κ_T and the heat capacity C_p as functions of temperature and pressure in the pre-melting region of ice I.

Below, we give an outline of the theory used for our calculations in Section 2. Our calculations and results are given in Section 3. We discuss our results in Section 4. Finally, conclusions are given in Section 5.

2. Theory

The critical behaviour of the heat capacity C_p, heat expansion α_P and the isothermal compressibility κ_T can be described by a power-law formula for ice I in the pre-melting region. Thus, the temperature and pressure dependence of the C_p, α_P and κ_T can be calculated in the vicinity of the melting point in this crystal. Here, we study the critical behaviour of C_p, α_P and κ_T in the pre-melting region of ice I.

Starting with the pressure dependence of the heat expansion α_P described by a power-law formula

$$\alpha_p = A_1(p - p_m)^{-\gamma} \tag{1}$$

as given previously [16], we can obtain the temperature dependence of α_P, using an approximate relation

$$\partial p_m/\partial T = [p - p_m(T)]/[T_m(p) - T] \tag{2}$$

near the melting point, which can be expressed as

$$\alpha_p = A_1(\partial p_m/\partial T)^{-\gamma}(T_m - T)^{-\gamma} \tag{3}$$

in the pre-melting region of ice I. In Equation (2), the melting pressure p_m is a function of temperature and the melting temperature T_m is a function of pressure.

The pressure and temperature dependence of the isothermal compressibility κ_T and the heat capacity C_p can also be obtained from that dependence of α_P (Equations (1) and (3)). The pressure dependence of κ_T can be expressed as

$$\kappa_T = A_1(\partial p_m/\partial T)^{-1}(p - p_m)^{-\gamma}, \tag{4}$$

using the thermodynamic relation

$$\alpha_p/\kappa_T = \partial p_m/\partial T \tag{5}$$

through Equation (1) close to the melting point in the pre-melting region of ice I. Also, the temperature dependence of the isothermal compressibility κ_T can be derived using the approximate relation (Equation (2)) in Equation (4), which gives

$$\kappa_T = A_1(\partial p_m/\partial T)^{-\gamma-1}(T_m - T)^{-\gamma} \tag{6}$$

in the pre-melting region of ice I.

Similarly, we can derive the pressure and temperature dependence of the heat capacity C_p using the thermodynamic relation

$$C_p = TV\alpha_p^2\kappa_T^{-1}. \tag{7}$$

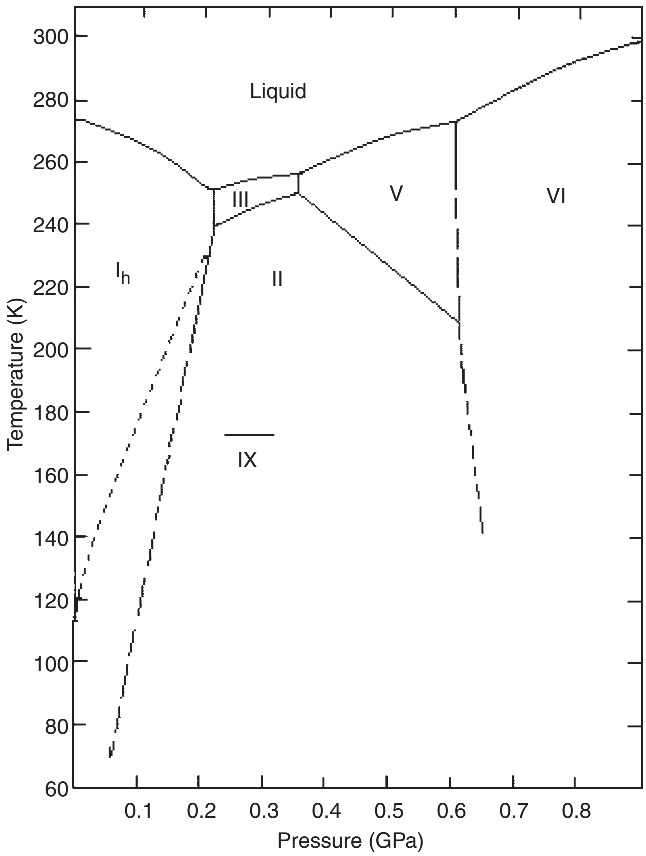

Figure 1. Experimental phase diagram of ice. Dashed lines represent extrapolations [1,17].

In Equation (7) the pressure dependence of α_P (Equation (1)) and κ_T (Equation (4)) can be used, which then expresses the pressure dependence of C_p as

$$C_p = A_1 TV\left(\frac{\partial p_m}{\partial T}\right) \cdot (p - p_m)^{-\gamma}. \tag{8}$$

Also, in Equation (7) the temperature dependence of α_P (Equation (3)) and κ_T (Equation (6)) can be used to give C_p as a function of temperature,

$$C_p = A_1 TV(\partial p_m/\partial T)^{1-\gamma}(T_m - T)^{-\gamma}, \tag{9}$$

in the pre-melting region of ice I.

3. Calculations and results

An observed *T–P* phase diagram of ice including various phases [1,17] is given in Figure 1. On the basis of the volume measurements [18], a *P–T* phase diagram of ice has been obtained [19], as given in Figure 2. In Figure 2, curves 1 and 2 represent melting of I_h ice and III ice, and curve 3 is the phase equilibrium of I_h ice-III ice, with the triple point *P* that

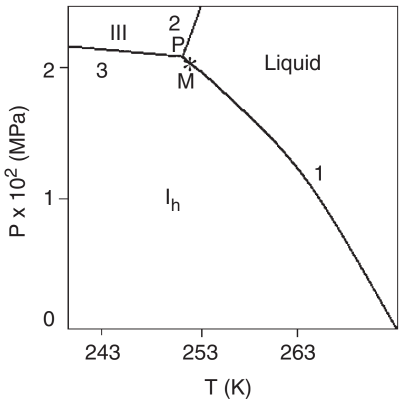

Figure 2. Phase diagram of ice for the phases of I_h, III and liquid [19] which have been obtained using the volume measurements [18]. P denotes the triple point ($P_t = 207$ MPa, $T_t = 251.15$ K) and M indicates the melting point ($p_m = 202.4$ MPa, $T_m = 252.3$ K).

has coordinates of $P_t = 207$ MPa and $T_t = 251.15$ K [19]. The experimental data for the heat expansion α_P, which we analysed in this study, has been obtained as a function of pressure from 192 MPa to melting along the isotherm 252.3 K on the melting curve of I_h (curve 1) in Figure 2. Our calculations for the heat expansion α_P, isothermal compressibility κ_T and the heat capacity C_p were conducted here for the temperature range of 251.6 and 252.3 K along the isobar 202.4 MPa on curve 1 in Figure 2. Also, our calculations for the κ_T and C_p were conducted for the pressure range of 201.6 and 202.3 MPa prior to melting along the isotherm 252.3 K on curve 1 in Figure 2. All our calculations for α_P, κ_T and C_p were carried out in the pre-melting region close to the melting point M with the coordinates $p_m = 202.4$ MPa and $T_m = 252.3$ K, as shown on curve 1 in Figure 2. For our calculations, we first analysed the experimental data [16] for the pressure dependence of the heat expansion α_P in the pre-melting region of ice I according to a power-law formula (Equation (1)). From our analysis of α_P at a constant temperature of $T = 252.3$ K within the interval of the reduced pressure ($p_m = 202.4$ MPa), we extracted the value of the critical exponent $\gamma = 1.14$ and the amplitude value, as given in Table 1. We then evaluated the heat expansion α_P as a function of temperature by Equation (3), where we used the experimental value of the slope $\partial p_m/\partial T = 50\,\mathrm{MPa\,K^{-1}}$ [16] within the interval of the reduced temperature (Table 1) for a constant pressure of $p = 202.4$ MPa in the pre-melting region of ice I. We give our plot of the heat expansion α_P as a function of temperature ($p = 202.4$ MPa) for ice I in Figure 3. From the calculation of α_P, we then calculated the pressure and temperature dependence of the isothermal compressibility κ_T using Equtions (4) and (6), respectively, in the pre-melting region of this crystal. Figures 4 and 5 give the isothermal compressibility κ_T calculated as functions of pressure ($T = 252.3$ K) and temperature ($p = 202.4$ MPa), respectively. Finally, we were able to evaluate the pressure and temperature dependence of the heat capacity C_p according to Equations (8) and (9), respectively, in the pre-melting region of ice I. In Equations (8) and (9), we used the volume value of $V = 19.03\,\mathrm{cm^3\,mol^{-1}}$ at 196.2 MPa and $T = 252.85$ K [19] along the melting curve (curve 1 in Figure 2) as given in Table 1. We have plotted the heat capacity C_p at various pressures ($T = 252.3$ K) and temperatures ($p = 202.4$ MPa) in Figures 6 and 7, respectively, for ice I.

Table 1. Within the regions of the reduced pressure ($p_m = 202.4$ MPa) and the reduced temperature ($T_m = 252.3$ K), the values of the critical exponent γ and the amplitude A_1 according to Equation (1) in the pre-melting region of ice I.

$T = 252.3$ K $p_m = 202.4$ MPa	Reduced pressure $\varepsilon = (p - p_m)/p_m$	$p = 202.4$ MPa $T_m = 252.3$ K	Reduced temperature $\varepsilon = (T_m - T)/T_m$	γ	A_1 (MPa K^{-1})	V $\times 10^{-6}$ (m^3 mol^{-1})	$\partial p_m/\partial T$ (Mpa K^{-1})
$p > p_m$	$3.95 \times 10^{-3} < \varepsilon < 6.42 \times 10^{-3}$	$T < T_m$	$7.9 \times 10^{-5} < \varepsilon < 2.8 \times 10^{-3}$	1.14	1.218	19.03	50

Note: The values of the volume at 252.85 K (196.2 MPa) [19] and of the slope $\partial p_m/\partial T$ [16] are also given here.

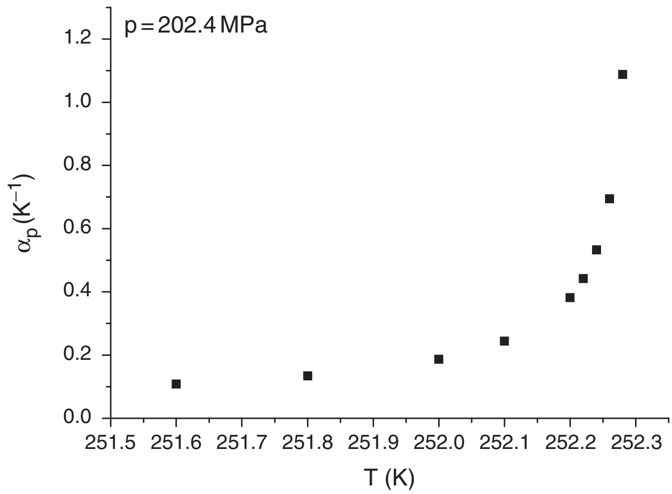

Figure 3. Heat expansion α_P calculated as a function of temperature for a constant pressure of 202.4 MPa according to Equation (3) in the pre-melting region of ice I.

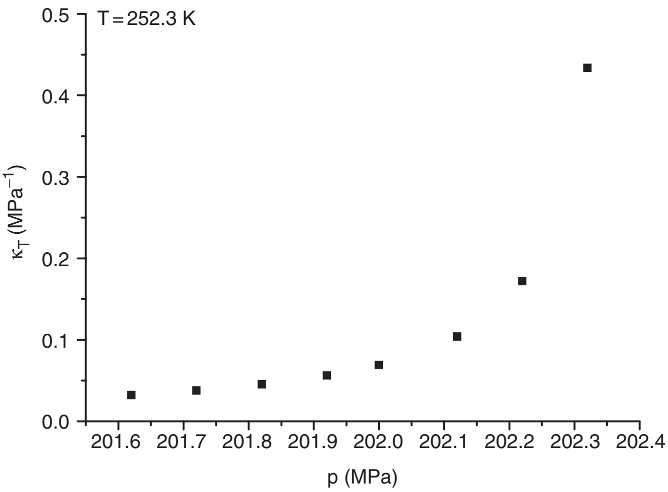

Figure 4. Compressibility κ_T calculated as a function of pressure for a constant temperature of 252.3 K according to Equation (4) in the pre-melting region of ice I.

4. Discussion

Calculations of heat expansion α_P, isothermal compressibility κ_T and heat capacity C_p were carried out by analysing α_P at various pressures for a constant temperature of 252.3 K using the experimental data [16] for the pre-melting region of ice I, as we noted earlier. From our analysis, we extracted the value of $\gamma = 1.14$ for the critical exponent of the heat expansion α_P. This value of the critical exponent was restricted to the interval of the reduced pressure and the reduced temperature (Table 1) when we calculated α_P, κ_T and

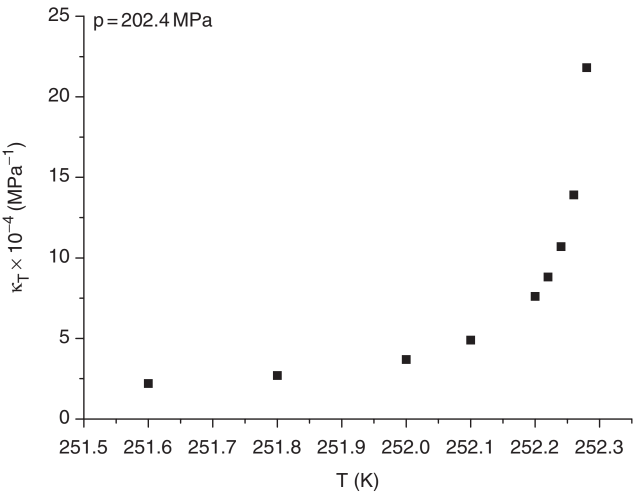

Figure 5. Compressibility κ_T calculated as a function of temperature for a constant pressure of 202.4 MPa according to Equation (6) in the pre-melting region of ice I.

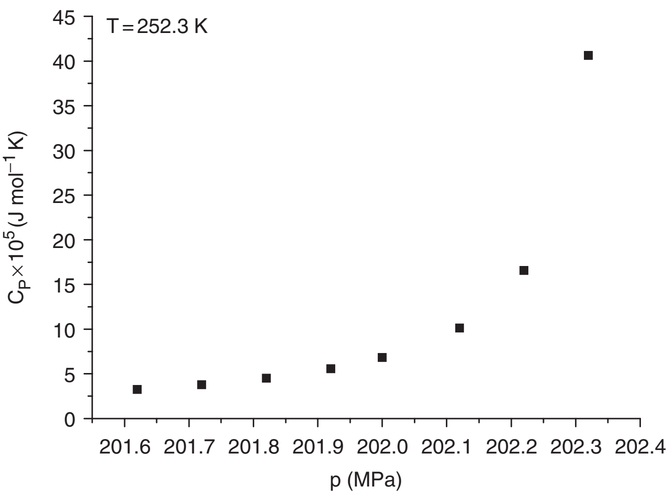

Figure 6. Heat capacity calculated as a function of pressure for a constant temperature of 252.3 K according to Equation (8) in the pre-melting region of ice I.

C_p as functions of pressure and temperature in the pre-melting region of ice I near the melting point.

Regarding the temperature and pressure dependencies of α_P, κ_T and C_p which we calculated here, they were all based on the experimental measurements of α_P at various pressures for a constant temperature of 252.3 K [16]. As shown in Figure 3, our calculated α_P increases with the increasing temperature at 202.4 MPa, when the observed α_P decreases with the increasing pressure just above the melting pressure ($p > p_m$) at 252.3 K in the pre-melting region of ice I [16]. This is due to the fact that the volume decreases as the

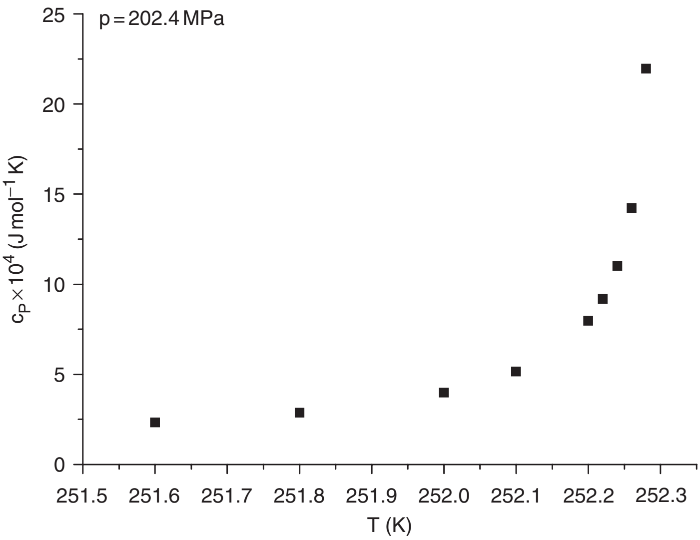

Figure 7. Heat capacity calculated as a function of temperature for a constant pressure of 202.4 MPa according to Equation (9) in the pre-melting region of ice I.

temperature decreases or the pressure increases [19]. Different from the other forms of ice, for I_h ice the melting point decreases with an increase in the pressure (curve 1 in Figure 2), as noted previously [19]. For the same reason, the isothermal compressibility κ_T decreases as the pressure increases above the melting pressure ($p > p_m$, $T = 252.3$ K). Below the melting pressure ($p < p_m$), the isothermal compressibility κ_T increases as the pressure increases ($T = 252.3$ K) and it will also increase with increasing temperature ($p = 202.4$ MPa), as plotted in Figures 4 and 5, respectively.

As the heat expansion α_P [16] and the isothermal compressibility κ_T (Figure 4) decrease, the heat capacity C_p is also expected to decrease with increasing pressure, just above the melting pressure ($p > p_m$) for a constant temperature of 252.3 K in the pre-melting region of ice I. On the other hand, just below the melting pressure ($p < p_m$), the heat capacity C_p should increase as the isothermal compressibility κ_T increases (Figure 4) with increasing pressures ($T = 252.3$ K), which is plotted in Figure 6. Furthermore, anomalous behaviour of α_P (Figure 3) and κ_T (Figure 5), both of which increase with increasing temperature, should be expected from the C_p, as shown in Figure 7 for a constant pressure of 202.4 MPa in the pre-melting region of ice I. This is due to the fact that the pressure dependencies of α_P, κ_T and C_p were described by the power-law formulae, Equations (1), (4) and (8), respectively, with the same critical exponent γ. Also, the temperature dependencies of the α_P, κ_T and C_p were described by Equations (3), (6) and (9), respectively, with the same exponent γ. This assumes that the heat expansion α_P, isothermal compressibility κ_T and the heat capacity C_p exhibit similar critical behaviour, as formulated by Pippard [20] for λ-phase transitions. Since the isothermal compressibility and heat capacity can be obtained as linear functions of heat expansion in the pre-melting region of ice I, as studied here, on the basis of the Pippard relations, it is indicated that ice I exhibits λ-type phase transition in the pre-melting region.

Our calculations of the heat expansion α_P, isothermal compressibility κ_T and the heat capacity C_p can be examined experimentally in the pre-melting region of ice I. Since we started in this study with the analysis of the experimental data for the heat expansion α_P at various pressures for a constant temperature of 252.3 K, the temperature dependence of α_P (Equation (3)) at 202.4 MPa can be examined experimentally. Also, the pressure dependence of the isothermal compressibility κ_T (Equation (4)) and the heat capacity C_p (Equation (8)) can be examined by the measurements at 252.3 K in the pre-melting region of ice I. Additionally, experimental measurements can be performed for κ_T and C_p as a function of temperature at a constant pressure of 202.4 K to test our relations, Equations (6) and (9), respectively, close to the melting point ($T_m = 252.3$ K) in the pre-melting region of ice I.

5. Conclusions

We calculated here, using the experimental data for the heat expansion α_P at various pressures ($T = 252.3$ K), the temperature dependence of α_P, the isothermal compressibility κ_T and the heat capacity C_p at a constant pressure of $p = 202.4$ MPa close to the melting temperature ($T_m = 252.3$ K) in the pre-melting region of ice I. We also calculated the pressure dependence of κ_T and C_p at a constant temperature of 252.3 K in the pre-melting region of ice I, close to the melting pressure ($p_m = 202.4$ MPa).

Our calculations show that the heat expansion α_P, isothermal compressibility κ_T and the heat capacity C_p exhibit similar anomalous behaviour close to the melting point in the pre-melting region of ice I. This indicates that ice I exhibits λ-phase transition prior to melting. The experimental measurements for α_P, κ_T and C_p as functions of temperature and pressure can be carried out to examine our calculations given in this study.

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