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PHASE TRANSITIONS OF ICE V AND VI

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Résumé - Les transitions de phase de la glace V et VI dans le domaine 90-175 K ont été étudiées par calorimétrie. Les transitions dans le domaine 105-140 K qui sont semblables à des transitions ordre-désordre, ont été identifiées. Les variations d'enthalpie de celles-ci ainsi que les transformations des glaces V et VI en glace Ic à plus hautes températures ont été déterminées.

Abstract - Phase transitions of ice V and VI in the range 90-175 K have been investigated by heat-flow calorimetry. Transitions in the range 105-140 K, which are likely order-disorder, have been identified and enthalpy changes of these and the transformations of ice V and VI to ice Ic at higher temperatures have been determined.

Introduction

All known crystalline phases of ice stable below ~ 0.5 Mbar consist of hydrogen-bonded networks of distinct water molecules. Each water molecule is hydrogen bonded to four neighboring water molecules in tetrahedral geometry. At high temperatures all phases except ice II are orientationally disordered and the maximum number of configurations per molecule, as implied by the well known ice rules, is ~ 1.5 . Upon cooling, ice Ih [1] doped with potassium hydroxide, III [2,3], and VII [4] undergo order-disorder transitions to acquire partial or nearly complete order. In addition, all phases except ice Ih transform to ice Ic when heated from 77 K at ambient pressure. A reversible order-disorder transformation in ice V in the range 105 - 130 K has been reported in an abstract [5] and partly ordered ice V and VI have been recognized by neutron diffraction at 110 K [6,7]. Diffraction methods will, of course tell the structure of a particular sample, but not the course of the ordering unless extensive measurements are made. The course of the ordering can be readily followed by calorimetry, and so this paper reports the calorimetry of ice V and VI in the region of the order-disorder transitions and of the transformation to ice Ic. The ordering transitions are sometimes very slow, and so, following Tajima et al. [1,8], samples of ice V and VI doped with potassium hydroxide also have been studied.

Experimental Methods

Samples of ~ 2.4 g of either distilled water or a 0.1 mol dm^{-3} potassium hydroxide solution prepared from potassium hydroxide free of carbon dioxide (J.T. Baker Chemical Co.) were held in closed indium cups. Each sample was frozen in its cup at one bar in about 10 min in a freezer held at 240 K, transferred to a piston-cylinder device, cooled with an alcohol bath, and pressurized to prepare ice V while monitoring the piston displacement with a dial gauge [9,10]. Each sample was held in the region of stability of ice V for 30 min, quenched under pressure in ~ 10 min to 77 K with liquid nitrogen, and recovered in its indium cup.

Pure and potassium-hydroxide-doped samples of ice VI were prepared from ice V by pressurizing to 7.5 kbar [11]. They were held in the region of stability of ice VI for 30 min and quenched and recovered at 77 K.

Each sample in its indium cup was transferred to an automated Tian-Calvet heat-flow calorimeter (Setaram model BT) [12] which had previously been cooled to 77 K, and was annealed at various temperatures in the range 103 - 120 K. Each sample was then cooled to 77 K and heated at the rate of 10 K h^{-1} through the phase transitions described below. The heat capacity and the transition enthalpies were obtained as previously described [12]. To calculate the transition enthalpies, the baselines were drawn parallel to the heat capacity of ice I and passing through the experimental points outside the high- or low-temperature ends of the transitions, as shown in Figs. 1 and 3.

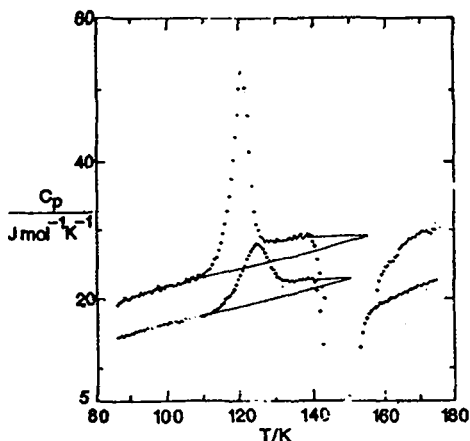


Figure 1. Heat capacity of ice V in the range 85 - 175 K when doped with potassium hydroxide (upper curve) and undoped (lower curve). The upper curve has been translated parallel to the C_p axis by $+5 \text{ J mol}^{-1} \text{ K}^{-1}$. The baselines are drawn parallel to the heat capacity of ice I.

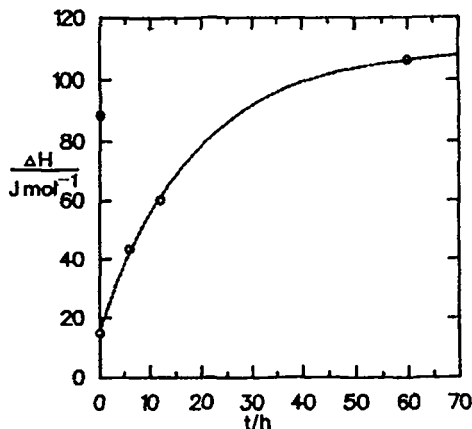


Figure 2. Transition enthalpy, ΔH , for undoped samples (open circles) and a doped sample (closed circle) of ice V as a function of annealing time. "Zero-time" results are for samples cooled in the calorimeter from 132 K to 78 K in 3 h.

Transition entropies, ΔS , were obtained from the integral over the transition region,

$$\Delta S = \int \frac{\Delta C_p}{T} dT,$$

where T is the sample temperature and ΔC_p is the heat capacity increment above the baseline.

Results

Two phase transitions occurred in ice V in the range 106 - 160 K. Typical plots of the heat capacity versus sample temperature are shown in Fig. 1. There is an endothermic transition in the range 106 - 132 K, which has been identified calorimetrically for the first time. The transition occurs in two regions, a principal peak in which most of the heat is absorbed, and a tail, possibly caused by a slower process, in which the rest of the heat is absorbed.

The effect of potassium hydroxide is to decrease the width and to increase the height of the 106 - 132 K peak. The transition is not first order as is indicated

by the width of the transition region and by the fact that the transition was observed regardless of the annealing temperature. The large exothermic transition in the range 140 - 156 K is from ice V to ice Ic [10]. An undoped sample of ice V was annealed for various times in the range 0 - 60 h at 111 K and was heated from 77 K through the first transition. The heat absorbed, ΔH , is plotted versus the annealing time in Fig. 2. It fits well a first-order kinetic relation of the form

$$\Delta H = \Delta H_{\infty} (1 - e^{-(t+t_0)/\tau})$$

with a relaxation time, τ , of 18 h, and an asymptotic ΔH at $t = \infty$, denoted by ΔH_{∞} , of 110 J mol⁻¹. t_0 is the effective annealing time of a sample cooled in the calorimeter through the transition region in 3 h. This yields a ΔH_0 at $t = 0$ of 15 J mol⁻¹, as shown in Fig. 2.

Potassium-hydroxide-doped ice V yielded $\Delta H = 89$ J mol⁻¹ after the sample was cooled in 3 h from 132 K to 77 K in the calorimeter. This is only ~20 percent less than the ΔH of 106 J mol⁻¹ obtained after annealing an undoped sample for 60 h, which demonstrates that doping greatly increases the transition rate. The transition enthalpy obtained after annealing a doped sample for 30 h at 108 K was 229 J mol⁻¹, which is 2.2 times larger than obtained for the undoped sample annealed for 60 h and 2.1 times larger than the apparent asymptotic value of 110 J mol⁻¹ for the undoped sample in Fig. 2. The kinetics varied from sample to sample for undoped samples in a manner similar to that reported for ice Ih [8] and the ΔH obtained after long annealing times also varied by ~20 percent. The error of the enthalpies and entropies of the endothermic transitions is estimated as $\pm 5\%$. In addition, an error could occur due to the placement of the baseline or to variation in kinetics from sample to sample [8].

The enthalpy change of the large exothermic transition that occurred over the temperature range 130 - 158 K was -915 ± 5 J mol⁻¹ and was independent of sample doping, and is in general agreement with the somewhat less precise value of -1100 ± 200 J mol⁻¹ [10] reported previously.

There were two phase transitions in ice VI in the range 120 - 153 K, as is shown in Fig. 3. The enthalpy change for the weak endothermic transition in the range 120 - 141 K was 115 J mol⁻¹ and did not change when the annealing time was doubled from 6 to 12 h or when the sample was doped with potassium hydroxide. The transition in the range 141 - 153 K is from ice VI to ice Ic [11] and the transition enthalpy is -1404 ± 20 J mol⁻¹, in agreement with the value reported earlier of 1200 ± 200 J mol⁻¹ [11] and about an order of magnitude more precise.

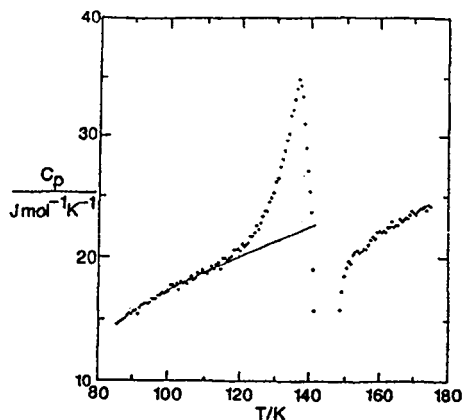


Figure 3. Heat capacity of ice VI in the range 85 - 175 K. The baseline is drawn parallel to the heat capacity of ice I.

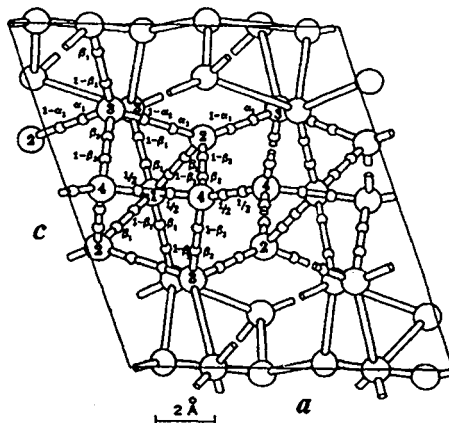


Figure 4. Structure of ice V shown in projection along the b axis. The occupation parameters are consistent with A2/a symmetry and the ice rules.

Discussion

Orientationally disordered ice V belongs to the space group $A2/a$ [13] and its structure is drawn in Fig. 4. A large amount of proton order is allowed under this space group and the neutron-diffraction results at 110 K of Hamilton et al. [6] indicate that the $O2 - O3 - O2$ chains are almost totally ordered, and the $O4 - O4$ chains are totally disordered. The other oxygen-oxygen bonds are slightly ordered. The order can be described by a set of parameters which is determined by the symmetry [in preparation] and are shown in Fig. 4. The ice rules require that $\alpha_1 - \alpha_2 = \beta_1 - \beta_2$, and the reported occupancies [6] require that $\alpha_1 = \alpha_2$ and $\beta_1 = \beta_2$ within the experimental uncertainties. It is very likely that the endothermic transition we observed is due to proton disordering. The transition entropy for an undoped sample annealed for 60 h at 110 K was $0.84 \text{ J mol}^{-1} \text{ K}^{-1}$. The transition entropy for the sample investigated by neutron diffraction [6], as calculated using the relation proposed by Nagle [14], is $0.8 \pm 0.1 \text{ J mol}^{-1} \text{ K}^{-1}$ if it is assumed that ice V at high temperatures is fully disordered within the ice rules. This suggests that our undoped sample has undergone the same ordering process as reported by Hamilton et al., where the $O2 - O3 - O2$ chains are almost fully ordered and the other oxygen-oxygen chains are only slightly ordered or remain fully disordered. On doping, ΔS increases to $1.9 \pm 0.1 \text{ J mol}^{-1} \text{ K}^{-1}$, which is 56 % of the maximum configurational entropy change allowed. Doping thus increases ΔS by 126 % and implies there is additional ordering along the oxygen-oxygen chains. Kamb and La Placa [5] have claimed that ice V transforms to the space group $P2_1/a$, but all configurational entropy can be lost in the space group $A2/a$, and so calorimetry cannot confirm the ordering to $P2_1/a$. This follows since if β_2 in Fig. 4 is either zero or one, which could occur under $A2/a$ symmetry, then each $O4 - O4$ chain would be polarized randomly in either of two directions. This would contribute infinitesimally to the configurational entropy and would not be detected calorimetrically (unpublished).

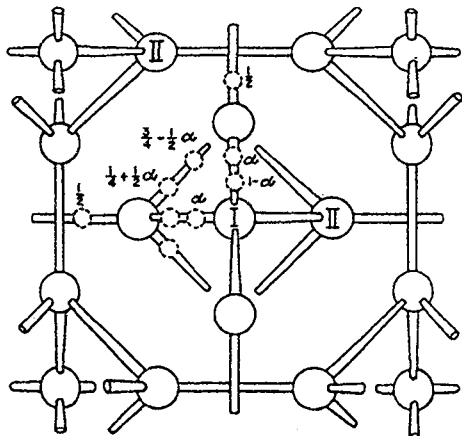


Figure 5. Structure of ice VI shown in projection along the c axis. The proton-occupation parameters are for the space group $Pm\bar{m}n$. For the space group $P4_2/nmc$, $\alpha = 1/2$.

Ice VI belongs to the space group $P4_2/nmc$ [15], which implies full proton disorder. Its structure is shown in Fig. 5. Partial proton order was found in samples studied at 110 K by neutron diffraction [7], and the space group consistent with these results is $Pm\bar{m}n$. The proton occupancies along hydrogen bonds can be described by a single parameter, α , as shown in Fig. 5. For the space group $P4_2/nmc$, $\alpha = 1/2$, and for $Pm\bar{m}n$, α can take any value between 0 and 1.

The transition entropy for ice VI is $0.86 \text{ J mol}^{-1} \text{ K}^{-1}$ and the corresponding order parameter, α , for proton occupancy derived from Nagle's equation [14] is 0.11 which is the same as the value obtained from the proton occupancies reported by Kamb. Doping has no effect because reorientation in ice VI is fast enough that maximum orientational order is probably achieved. The rate of orientational relaxation under pressure is consistent with this suggestion [16].

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COMMENTS

J.P. DEVLIN

Did you use KOH exclusively and if so, can you or someone else give a reasonable explanation why KOH is the dopant of choice (over acids, for example).

Answer :

We have used KOH exclusively for the reason described in the publications of H. Suga and coworkers and to be described again in the talk by T. Matsuo this afternoon.

Remark of J. DUPUY :

With electrolytic glasses by annealing or changing the ions we can produce and control endothermal event on DSC near the glass transition. The neutron diffraction

in connection with this phenomena, could be explained as a formation of a desordered phase appearing before the ice crystallization.

J. DUPUY

Behaviour of DSC ? The relative importance of exothermic peaks is surprising.

Answer :

We have used a Tian-Calvet heat-flow calorimeter (Setaram Model/Bf) with isoperibol operating conditions. The exothermic transitions for ice V and VI to ice I_c have rather large transition enthalpies of $- 915 \pm 5 \text{ J mol}^{-1}$ and $- 1404 \pm 20 \text{ J mol}^{-1}$ respectively.

T. MATSUO

Is the order-disorder change reversible ?

Answer :

Yes. The exothermic transition which is shown for ice V and VI when an annealed sample is warmed are seen on exothermic transition on cooling. We have also seen the transformation on the same sample after cycling through the 77 - 132 K region at least five times.