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A facet of recent ice sciences

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Abstract

Of prime interest in the numerous studies on water, an important substance to mankind and all other living systems, may be its chemical, physical, biological or geological characteristics but underlying all these is a basic structural problem. One of the important questions that still remains unanswered in this field is: why ordinary ice keep its proton-disordered state down to the lowest temperature. We found that the slowing down of water re-orientational motion at low temperatures leads to freezing of the disordered state in the ice crystal at around 110 K. This was the origin of the deviation of the crystal from the third law of thermodynamics. Doping by a particular kind of impurity recovered the mobility of the molecule to exhibit a long-awaited ordering transition at 72 K. The dopant dramatically accelerated the motion of water molecules to change the crystal from a non-equilibrium frozen-in disordered state to the equilibrium one within our experimental time. New steps in ice sciences and procedures used in these experiments are reviewed briefly. The structure and some properties of the low-temperature ordered phase, designated as ice XI, are described. © 1997 Elsevier Science B.V.

Keywords: Disordered crystals; Doping chemistry; Ice; Lattice defects; Relaxation

1. Introduction

Water is the most abundant liquid compound found on the surface of our earth. The ocean is estimated to contain $\sim 10^{21}$ kg of water, the principal ingredient of all living organisms. The solid form of ice, ice Ih at atmospheric pressure, exists mainly in the polar regions. The Antarctic continent alone is covered by $\sim 10^{19}$ kg of ice and snow [1]. If this amount of ice were distributed equally among the 5 billion people each person could build about 4000 swimming pools of 50 m length. One tenth of this huge quantity exists sporadically in Greenland and in various other glaciers all over the world.

The term "crystal" is derived from the Greek *Krystallos* which meant ice. Ice has long been accepted as a typical crystalline substance surrounding us. Meanwhile, ice was found to deviate from the third law of thermodynamics which is obeyed by crystalline substances in most cases [2]. The exception of ice from the law embarrassed many teachers when they talk about the wide validity of thermodynamics. Why is ice unable to form an ordered phase at 0 K? This question haunted me when I was learning thermodynamics at Osaka University. The situation would be familiar to many students and scientists who might be interested in rigorous features of thermodynamics or in ice sciences. Absence of any

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transition phenomena in the ice crystal has puzzled many researchers over more than fifty years. The present article describes how we started to challenge this intriguing problem and how we succeeded in realizing an ordered state of ice.

2. Historical background

Nowadays we know that ice Ih is an ideal three-dimensional hydrogen-bonded system. Each oxygen atom with sp^3 hybridized orbitals uses two of them to combine with two hydrogen atoms and two to provide lone-paired electrons. Thus each oxygen atom can be proton donor, and proton acceptor at the same time. In this way, four neighboring oxygen atoms can form four hydrogen bonds to the central atom, producing an unusually open structure. This is shown schematically in Fig. 1. The neighboring oxygen atoms are surrounded successively by four oxygen atoms to form three-dimensional networks similar to the wurzite structure. The structure of ice is full of hydrogen bonds of the length of ~ 275 pm. Each hydrogen bond provides a double-well potential for accommodating a proton, but an individual water molecule cannot reorient independently among six possible orientations owing to severe constraints imposed by the ice rules which were first proposed by Bernal and Fowler [3]. The rules state that there is one proton placed asymmetrically along each O···O bond and that neutral water molecules are preserved as structural entities. It is this topological network structure and the rules which provide a highly cooperative nature of the reorganization of water orientations in the lattice. Reorientation of one molecule induces the corresponding motions in the neighboring molecules and this kind of successive movement must occur from one to the other end of the crystal. Obviously, this kind of "chain reaction" requires an enormous amount of activation energy. Debye [4] pointed out the difficulty in explaining the large dielectric constant of ice due to orientation polarization of water dipoles, if an ice sample is a perfect crystal.

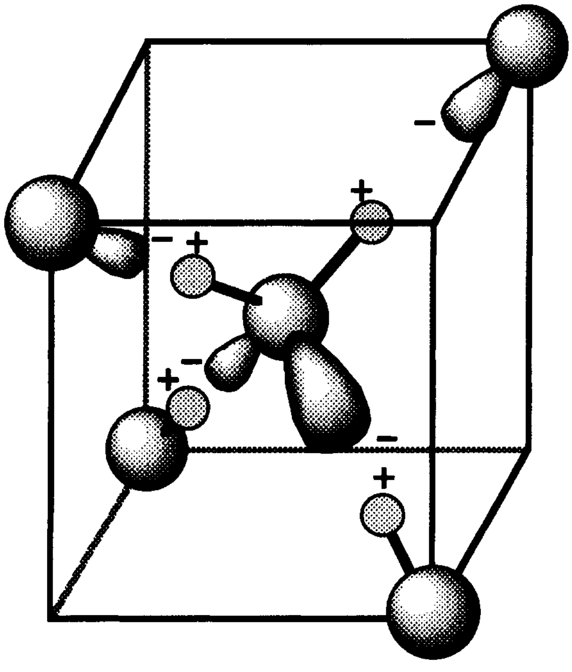

Fig. 1. Local structure of water molecule surrounded by tetrahedrally arranged neighboring molecules.

The story concerning the nature of disorder in ice crystal began in 1936 when Giauque and Stout [5] showed that hexagonal ice possesses a residual entropy of (3.4 ± 0.2) J K^{-1} mol^{-1}. They explained this entropy as arising from random mixing of *ortho* and *para* species of water molecules. Since essentially the same amount of residual entropy was observed in D_2O ice [6] with different nuclear spins, the explanation was replaced by a "half-hydrogen" statistical model proposed by Pauling [7]. Each proton was thought to be located in one of the potential wells with an equal probability of 1/2 under the condition of the ice rules. The calculated residual entropy $R \ln(3/2)$ based on these assumptions agreed well with the observed values. This averaged-structure model was confirmed later by a neutron diffraction experiment [8]. However, no information on the dynamic nature of the disorder was presented.

The dynamical situation of water molecules can be inferred by dielectric spectroscopy. As is well known, ice crystals show a dielectric relaxation [9]. At high temperatures, some of the water dipoles can respond to an external ac electric field with an appropriate frequency. As the temperature is lowered, relaxation time for orientation polarization becomes increasingly longer, until the contribution to the dielectric permittivity completely vanishes, leaving only the contribution from the electronic polarization below a certain temperature range. The temperature dependence of the

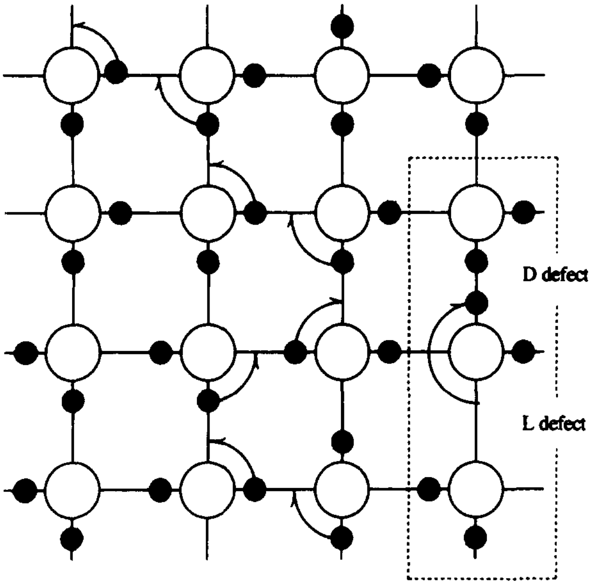

Fig. 2. Proton rearrangement in two-dimensionally presented ice lattice and formation of the orientational defects D and L.

frequency at which the dielectric loss reaches the maximum value gives an activation energy for the motion. Extrapolation of these data to 1 mHz suggests that actual immobilization of the motion will take place at around 110 K. The reciprocal of this frequency corresponds to the time required for a single heat-capacity measurement which has been used traditionally for the detection of glass transitions in liquids.

The orientation polarization of the dipoles is believed to occur through a kind of lattice fault called "orientational defect", a concept introduced by Bjerrum [10]. The rotation of a water molecule due to thermal fluctuation around one of the hydrogen bonds by $(2/3)\pi$ radians produces a pair of D (*doppelt* in German) and L (*leer*) defects. The former contains two protons in a hydrogen bond and the latter none, as shown in Fig. 2. This energized state that temporarily breaches the ice rules, returns to the normal state by recombination of both defects through encounter at some places after a step-by-step movement of the defects along the hydrogen bonds. During the travel of both defects, water molecules along the path can change their orientations. This is the most reasonable model to explain the dielectric property of ice. Knowledge concerning the formation and kinetics for the movement of the defects was obtained by doping an ice sample with a particular kind of impurity which preferentially produces the target defect. The number of orientational defects is, however, quite small and decreases exponentially on lowering the temperature resulting in a lack of thermal equilibrium with respect to the cooperative motion below a certain temperature.

The experimental observation of a possible proton ordering in ice was first reported by Dengel et al. [11]. They ascribed a peak observed in thermo-stimulated depolarization (TSD) current around 110 K to the formation of a ferroelectrically ordered phase below this temperature. The report produced heated discussion and stimulated research for further evidence. Onsager [12] pointed out, however, that there is another explanation for the TSD peak as arising from competitive movements of various lattice imperfections including ionic defects. Since they found the peak only in impure samples, Onsager suggested the use of a doped sample for the confirmation of the ordering transition, particularly by a calorimetric method. Several scientists have tried this experiment, but none of them succeeded in finding a heat capacity anomaly that could be regarded as being associated with a phase transition.

3. New approaches

One of our research interests was the relaxation process observed around the glass transition in liquids by using calorimetric techniques [13]. Since adiabatic calorimeters have extremely high temperature stability of the sample cell, any spontaneous changes in the calorimetric temperature observed occasionally can be ascribed unambiguously to a relaxation process that occurs irreversibly in the sample. The changes can be analyzed by using a suitable function to derive the corresponding relaxation time. The time domain covered by this method ranges between 10^2 to 10^6 s [14], depending on quality of the calorimeter and the patience of the experimenter. Thus, the method is complementary to dielectric, NMR and other spectroscopies which give kinetic parameters in shorter time regimes. Nowadays, we know that the glass transition is not a kind of second-order transition but one of kinetic origin [15,16]. The glass transition is essentially a freezing-in process of the configurational disorder possessed by the liquid. Such a freezing-in process causes the liquid to retain a residual entropy associated with the frozen-in disorder which is unable to maintain ergodicity. Thus the glass transition and residual entropy are key thermodynamic properties characterizing any non-crystalline solids in general.

We, however, discovered glass transition phenomena in many crystalline substances. For example, in [17], the high-temperature phase of cyclohexanol belongs to an *fcc* system, indicating an orientationally disordered state of the constituent molecules. The *fcc* phase can easily by-pass the transformation into a low-temperature ordered phase, and the undercooled *fcc* phase shows a significant heat capacity jump at 150 K. The phase was found to retain a residual entropy of 4.7 J K^{-1} mol^{-1}. Enthalpy relaxation, observed calorimetrically around 150 K, was essentially the same as those observed in liquids around their glass transition regions. The name "glassy crystals" was given to this frozen-in orientational state, keeping the translational invariance with respect to centers of mass of the molecules. This is essentially a new state of aggregation of molecules. A lack of observation of glass transitions in crystalline substances in the past experiments will be due to seemingly contradictory concepts between the glasses and the crystals. In this way, the glassy state of a liquid turns out to be just a single example of a more widespread condition in which a system cannot maintain equilibrium, at least in one degree of freedom, irrespective of the translational periodicity.

Thus the concept of glass transition described in many textbooks must be modified to indicate a demarcation temperature between the equilibrium dynamical and non-equilibrium frozen-in states in any disordered system. Obviously, the temperature depends on the experimental time scale. The higher the heating rate, the higher the demarcation temperature. The glass transition temperature T_g is defined operationally as the one at which the relaxation time for the motion relevant to the freezing becomes 1 ks [18].

The revision of the concept of the glass transition motivated us to reach for a freezing process of dynamical disorder that a stable, and not an undercooled metastable crystal possesses at high temperatures. Actually, the CO crystal provides another example of deviation from the third law; it exhibits a glass transition at 17 K [19]. This will be associated with the freezing of a flip-flop re-orientational motion of CO molecules. The frozen-in disordered state is due to a prolonged relaxation time for the motion before the crystal reaches a hypothetical ordering transition on cooling. The equilibrium transition temperature of the CO crystal is considered to be 5 K [20]. Stannous chloride dihydrate [$SnCl_2 \cdot 2H_2O$] crystals display a relaxational heat capacity anomaly around 150 K, associated with freezing-out of re-orientational motion of the hydrated water molecules [21]. The crystal undergoes a phase transition at 218.01 K (T_c) with the heat capacity divergence, which has long tails below and above T_c. The freezing process in this crystal occurs on the way to a completely ordered state on cooling.

Hexagonal ice had already been found to have a residual entropy. In order to examine the possible occurrence of the "conjugate" glass transition in ice, a series of new measurements were carried out by using an adiabatic calorimeter as an ultra-low frequency spectrometer. In fact, a glass transition was observed at around 110 K. A small heat capacity jump of a relaxational nature increased in magnitude if the sample was annealed at several temperatures below 110 K [22]. A sample without annealing showed, in the subsequent measurement, a spontaneous exothermic, followed by an endothermic effect during equilibration periods whose temperatures were changed stepwise. A well-annealed sample showed only endothermic effects above the annealing temperature. The spontaneous changes in calorimetric temperature were followed for a sufficiently long time, to allow the time constant to be determined. For example, the observations of the temperature change were continued for about one month at 94 K. The relaxation time was determined by using an exponential approach toward an equilibrium value with a single relaxation time.

The enthalpy relaxation time thus determined correlated well with the dielectric relaxation times in an Arrhenius plot. Both data, with different time domains, could be joined by the same straight line indicating that the enthalpic and dielectric relaxations have a common origin. The slope of the line gave an activation energy of 22 kJ mol^{-1} which corresponded roughly of that for the movement of *L* defect. Pitzer and Polissar [23] calculated the equilibrium transition temperature of ice to be 60 K by using a molecular field approximation. If the relaxation time data are extrapolated to 60 K, it turns out that several thousand years are required for the realization of the hypothetically ordered ice. This is far beyond the span of our human life.

Many dielectric studies are on record on doped ice in relation to the clarification of the nature of various lattice defects. Ida, one of my teachers at Kanazawa Normal High School, and his co-workers [24] pointed out that some impurities doped into the ice lattice significantly lowered the temperature at which the dielectric loss in pure ice occurred. In particular, the effects of alkali hydroxides on the shifting effect were noticeable. These reports encouraged us because the shortening of the dielectric relaxation time would come up to the enthalpy relaxation time. Thus, we prepared three ice samples doped with KOH of mole fractions $x = 1.8 \times 10^{-3}$, 1.8×10^{-4}, and 1.8×10^{-5}, respectively. Each sample was cooled down to 12 K, and the first measurement was undertaken. To our regret, the dopant increased only the amount of the heat capacity anomaly at around 110 K. However, a small exothermic effect was noticed at around 65 K during the measurements. We regarded it as an indication of an onset of the transition into an ordered phase. Then the calorimeter was kept at 65 K in order to examine the real significance. In fact, an increased rate of the exothermic effect with time was observed during the annealing process. The effect continued for at least 3 days. Sometimes the calorimetric temperature was maintained between 64 and 68 K in order to accelerate the effect.

The subsequent measurement for the first time showed a first-order phase transition at 72 K [25]. A typical experimental result is shown in Fig. 3. The transition was so sluggish that the equilibration period took longer than normal. The excess heat capacity had a long tail on the high temperature side up to 110 K. It is a part of this tail which was found in pure ice as the heat capacity anomaly with relaxational nature. We can conclude that the re-orientational motion of water molecules was immobilized around 110 K at the initial stage of development of the short-range order, and this freezing caused a peak in the TSD current.

The transition temperature was found to be independent of the amount and nature of the cation used as dopant. The entropy of transition depended, on the other hand, on the dopant amount and the annealing condition. The largest value for the removal of entropy was 2.33 J K^{-1} mol^{-1} which was obtained for the sample with $x = 1.8 \times 10^{-3}$ KOH, annealed for one week. Thus the phase transition removed a substantial fraction of the residual entropy. A neutron diffraction experiment on D_2O ice [26] showed that the transition changed the space group of the lattice from $P6_3/mmc$ (hexagonal) to $Cmc2_1$ (orthorhombic). This structure had already been theoretically predicted by Minagawa [27]. An anomalously broad peak assigned to (131) that appeared in the ordered phase can be interpreted either by a partial ordering of deuterons or by the coexistence of hexagonal and orthorhombic phases. The latter model would be plausible, in view of the first-order of the transition. The domain size of the ordered region estimated by line-profile of the peak was ~ 40 nm. Most probably, one dopant entity acted as a catalytic particle in the ice lattice by inducing the transition in 10^4 of the surrounding water molecules. The low-temperature ordered phase has a polar arrangement of the water dipoles along the c-axis of

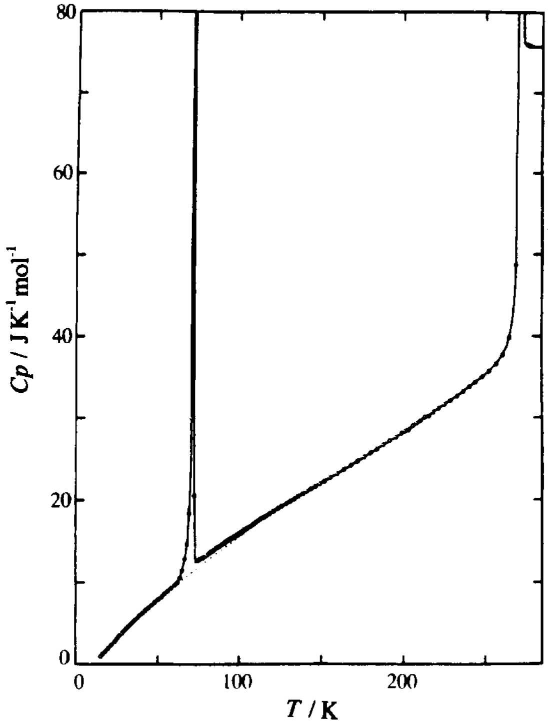

Fig. 3. Molar heat capacity of ice Ih doped with KOH in 1.8×10^{-3} mol fraction plotted as a function of temperature.

the original hexagonal ice and is designated as ice XI, following the discoveries of many ice modifications including high-pressure forms. The proposed structure was later confirmed by another neutron diffraction experiment [28]. The ordering transition was also confirmed by dielectric measurements [29,30].

The important role of the KOH dopant should be briefly mentioned. The hydroxide ion replaces the water molecule in the lattice and creates an ionized vertex together with an orientational *L*-defect. Both the ionic and the *L*-defects introduced artificially can move through the lattice. The negatively charged hydroxide ion attracts neighboring protons more easily, and thus effectively reduces the activation energy for the movement. KOH exhibited the most significant accelerating effect among other alkali hydroxides tested. Therefore the role of the cation cannot be ruled out. The concentration of the defects extrinsically incorporated into the lattice in this way is constant with temperature. This is in good contrast to the intrinsically existing defects. Thus the movement of defects, and hence the reorganization of orientation of the water dipoles in doped ice, can continue down to temperatures much lower than those in pure ice [31].

4. Some properties of ice XI

A high-pressure calorimeter able to work at pressures up to 250 MPa in the temperature range between 20 and 300 K, was used to study the XI → Ih transition [32] in order to determine the phase boundary. Helium gas was used as a pressure-transmitting medium. The applied pressure was automatically kept constant within ±1 kPa by a specially designed control system [33]. The phase diagram of ice determined in this way is shown in Fig. 4. The transition temperature shifted upward by (2.40 ± 0.1) K by the isotropic pressurization of 158.9 MPa. Thus the slope of the boundary was 0.015 K MPa^{-1}. Application of the Clausius–Clapeyron equation to the slope showed that the molar volume change associated with the proton ordering is (0.051 ± 0.003) cm^3 mol^{-1}, corresponding to 0.26% of the total volume at 72 K. The slope of the transition line is similar in magnitude to that between VII and VIII and to that between III and IX. The slopes are almost horizontal in the diagram, reflecting the fact that the volume changes associated with the proton ordering is quite small compared to the corresponding entropy change in each case. The transitions between VII and VIII [34] and between III and IX [35] possess a similar order–disorder nature with respect to protons in differently structured hydrogen-bond networks, and take place rather easily. The extremely sluggish nature of the transition Ih → XI in pure ice turned out to be due to low ordering energy which necessarily induces a kinetic hindrance of the water re-orientational motion at the corresponding low transition temperature.

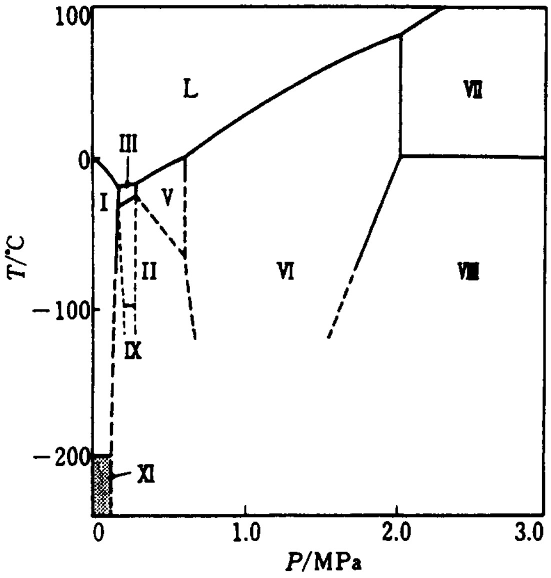

Fig. 4. Phase diagram of H_2O.

The apparent beauty of the ice crystal is marred by the disordered nature of protons at the molecular level. The disorder will surely affect some transport properties of the crystal. There are many data of the thermal conductivity of ice. In view of the interest in examining the relative importance of proton disorder on the heat transportation in ice, the thermal conductivity was measured in the temperature range between 60 and 723 K as a function of pressure, up to 160 MPa. The measurement was performed by using a transient hot-wire method [36] with a Ni wire as probe. The wire was placed horizontally in a ring of constant radius within a temperature-controlled Teflon cell. A KOH aqueous solution with $x = 1.8 \times 10^{-3}$ was introduced into the cell, and the cell was mounted in a pressure vessel. As an example, the thermal conduc-

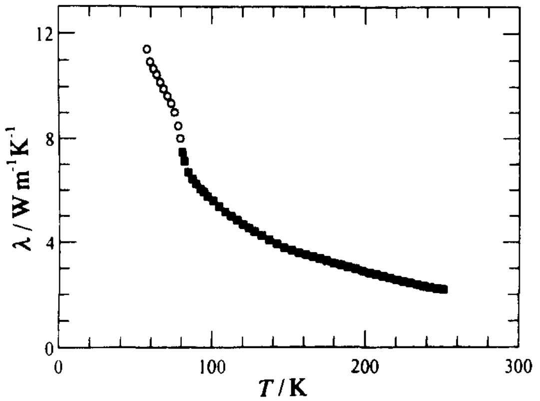

Fig. 5. Thermal conductivity λ of ice measured at 160 MPa as a function of temperature.

tivity λ of KOH-doped ice measured at constant pressure of 160 MPa is plotted in Fig. 5 as a function of temperature. The formation of the low-temperature phase was facilitated by annealing the sample at (65 ± 3) K for 3 days. The temperature dependence of the thermal conductivity for both phases Ih and XI is characteristic of crystals for which the thermal conductivity is inversely proportional to the absolute temperature, arising from an "Umklapp" processes of phonons in the region above the Debye temperature. The effect of proton ordering in ice is reflected as an increase in thermal conductivity by ~ 17% at 72 K. This can be explained by a model in which the decrease in thermal conductivity at the transition on warming is due to an increase in the lattice anharmonicity which might be caused by the disorder in Ih phase.

From the pressure dependence of the thermal conductivity λ of ice, measured at 58 K, it is possible to derive the density dependence of λ by using data on the isothermal compressibility. The quantity is referred to as the Bridgman parameter g and is defined as $g = (\partial \ln\lambda/\partial \ln\rho)_T$, where ρ is the density. Again the effect of proton ordering can be observed in the value of g. The g value for phase XI is 0.2, in contrast to −2.8 for Ih determined at the same temperature. The experimental g value for ice Ih is in good agreement with −2.6, determined at 248 K [37]. In general, crystalline substances exhibit g values greater than 6 [38]. Both phases Ih and XI are exceptional in view of the density dependences of thermal conductivity, as also on many other physical properties.

As to the structure of phase XI, there are still controversial discussions. Howe first showed that a total of 17 orthorhombic symmetry-independent structures can be considered with eight molecules per unit cell [39]. One of them, whose space group is $Pna2_1$ (an antiferroelectrically ordered structure and is designated as P ice), has been the subject of special attention, in addition to that of $Cmc2_1$ (a ferroelectrically ordered structure, C ice). In particular, Davidson and Morokuma [40] selected this structure as the simplest ordered form where protons in neighboring molecules are arranged so as to maximize the distance between them. A three-body potential parameterized on the basis of *ab* initio calculations predicted P ice to be more stable than C ice by ~ 8 kJ mol^{-1}. This is a surprisingly large energy difference. Recently, a quantum-mechanical computation on the two possible structures was carried out by Pisani et al. [41]. The equilibrium geometry and relative stability of the two structures were studied by performing periodic Hartree–Fock calculations. The difference in stability between the two phases was reported to be within the estimated computational uncertainty, and they may be considered to be iso-energetic. Interestingly, the role of KOH is such that the dopant not only enhances the orientational mobility but also stabilizes the C ice by an amount exceeding the computational uncertainty. The significant energy difference supports the hypothesis that microcrystals of ice XI are formed around individual dopant entities.

While summarizing, the following picture can be drawn for the ordering process in ice Ih. The dopant does not act as a catalyst, for uniformly affecting the whole crystal but acts to induce local orderings of the water molecules, in a small region surrounding the dopant. The range of order would then be dictated by a competition between enthalpic advantage and decrease in configurational entropy. Difficulty in realization of a fully ordered ice crystal would partly be due to the limited solubility of KOH dopant in the ice lattice and partly due to the frustration of water dipoles existing among small-sized domains with various polarizations.

5. Cubic ice

There exists another modification of ice, called cubic ice (Ic), which is metastable with respect to ice Ih at atmospheric pressure. The energy difference between them is quite small but Ic is not usually drawn in the phase diagram of ice owing to its metastability. It can appear in the upper atmosphere. The evidence of natural occurrence is Scheiner's halo which occurs rarely at the angle of 28° around the sun or the moon [42], and the observation that dendritic snow flakes often have their c-axes at ~ 70° to one another [43,44]. The structure of the hydrogen-bonded network in Ic is the diamond type with essentially the same O···O distance as Ih. The similarities in dielectric constant and other properties show that protons in Ic should be disordered, as in Ih. Minagawa has calculated the interaction energy among dipolar water molecules and estimated the hypothetical transition temperature for the proton ordering in Ic to be 59 K [45].

There are many ways for producing the metastable Ic: water vapor deposition onto a cold substrate [46]; rapid quenching of aqueous aerosol on a cryoplate [47]; depressurization of any high-pressure modifications of ice at 77 K followed by warming to ~ 160 K [48]; and so on. All the cubic ice thus produced exhibits an irreversible transition to Ih on heating at an extremely slow rate in the temperature 170 ~ 220 K, accompanied by heat evolution of ~ 40 J mol^{-1} [49]. The depressurization method is the most suitable way to prepare Ic in a quantity large enough to be subjected to accurate calorimetry. This motivated us to undertake a thermodynamic investigation of ice by using the high-pressure adiabatic calorimeter [33] already mentioned.

The measurement [50] was first carried out on pure Ic. A purified water sample was crystallized at 265 K and the crystalline Ih was pressurized by using He gas up to 250 MPa to produce ice III. The sample was cooled to 77 K and the pressure was released. Formation of cube ice was found to occur at temperatures around 155 K during warming, as revealed by a large heat effect. The sample was well annealed at 160 K, cooled down to 13 K, and the heat capacity measurement was initiated. The heat capacity of cubic ice was similar in magnitude to that of Ih within ±0.08 J K^{-1} mol^{-1} in the 13–100 K range. As expected, a freezing process was observed at temperatures around 150 K. A quantity called "encraty" (heat capacity divided by temperature) and spontaneous drift rate observed at each measuring point are plotted in Fig. 6 as a function of temperature, respectively. Also plotted in the figure are the corresponding quantities of Ih for comparison. The encraty is convenient in the sense that it can magnify any observed small heat capacity anomaly in the temperature range where the heat capacity changes rapidly with temperature. The glass transition temperature 150 K is 40 K higher than that of pure Ih.

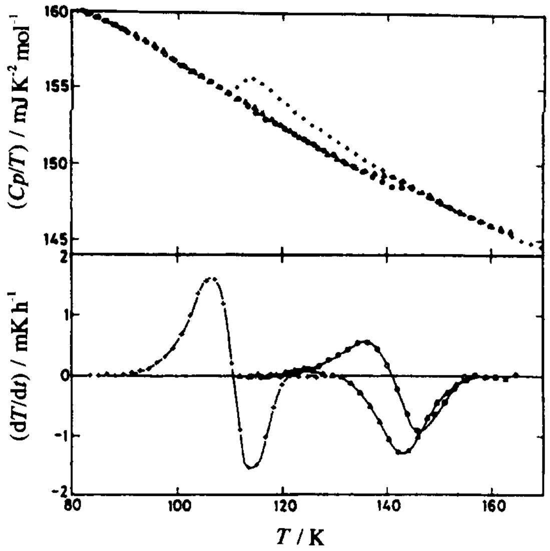

Fig. 6. Encraty (C_p/T) and spontaneous temperature drift rate plotted as a function of temperature: ○,△ – ice Ic, – +ice Ih.

In order to test the effectiveness of the same dopant on Ic, a KOH aqueous solution with $x = 1.8 \times 10^{-3}$ was used as a sample. The corresponding glass transition was found to be lower by 30 K. No heat capacity anomaly ascribable to a transition into the hypothetical ordered phase was observed. It is well known that any high-pressure forms of ice reject their ionic impurities from the specimen [51]. Even under such conditions, a residual portion escaped from segregation and acted to enhance the mobility of water molecules. The rate of spontaneous temperature change was analyzed to derive the relaxation time governing the freezing process. The activation energy was found to be lowered from 38.0 kJ mol^{-1} in pure Ic to 14.9 kJ mol^{-1} in doped Ic sample. In order to realize the hypothetical ordered phase of Ic, the deposition method of atomized aerosol from a KOH aqueous solution will be worthy of trial.

6. Conclusions

During the preparation of this article, the following sentences haunted me. "**Scientific knowledge is based on our limited observation of experiment carried out in laboratory time. Practically all the thermodynamic equilibria are pseudo-equilibria in the sense that they do not correspond to the absolute minima of Gibbs energy with respect to all possible processes but only with respect to processes which can take place within reasonable time** [52]." Obviously the statement can apply not only to chemical reactions but also to various physical processes.

Ice itself does not undergo the ordering transition during any experiments of a human time scale. Only addition of particular impurities, even in small amount, saved the entropy crisis arising from deviation of the wide validity of the third law of thermodynamics [53]. The role of the dopant is to enhance the orientational mobility of water molecules and to recover the crystal from a frozen non-equilibrium state to reveal the hypothetical ordering transition as an equilibrium property within laboratory time. The dopant will modify the structure and properties of the mother crystal to some extent, but its presence is essential in observing any equilibrium properties in an otherwise frozen-in disordered system. Time cannotbe controlled, but molecular mobility in a system can be affected dramatically by the doping method which partly removes severe constraints imposed on relevant motions in the system. The scope of the present-day materials science will surely be extended if some impurities can convert a system from an equilibrium to a non-equilibrium state or vice versa. If this proves to be so, we shall need a new terminology to denote the process: doping chemistry, perhaps!

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