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Abstract

Low-temperature thermal properties of crystalline $[\text{Co}(\text{H}_2\text{bim})_3](\text{TMA})\cdot 20\text{H}_2\text{O}$ were studied by adiabatic calorimetry, where H_2bim is 2,2'-biimidazole, TMA is 1,3,5-benzene tricarboxylic acid, and $20\text{H}_2\text{O}$ represents the water forming nano-channel in the crystal. A glass transition was observed at $T_g = 107$ K. It was discussed as a freezing-in phenomenon of a small number of water molecules remaining partially disordered in their positional arrangement. The possibility that some defects really remain in the hydrogen-bond network of channel water was mentioned. Two subsequent phase transitions were observed at 54.8 and 59 K. These were interpreted as being of a (super-structural commensurate)–incommensurate–(normal commensurate) type in the heating direction with respect to the hydrogen-atom positions as referred to the periodicity of the hydrogen-bond network. The transition entropy was evaluated to be $0.65 \text{ J K}^{-1} (\text{H}_2\text{O}\text{-mol})^{-1}$ as a total of the two, indicating that the disorder of the hydrogen atoms is present only in part of the water molecules of the channel. Based on the fact that the excess heat capacity due to the equilibrium phase transition is observed down to 35–40 K, the relaxation time for the rearrangement of the hydrogen-atom positions was assumed at the longest to be 1 ks at 35 K. This indicates that the activation energy of the rearrangement amounts to at most 13 kJ mol^{-1} and that the transfer of Bjerrum defects is attributed to the rearrangement.

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1. Introduction

It is well known that water molecules at low temperatures tend to be arrayed tetrahedrally and construct a three-dimensionally extended hydrogen-bond network [1]. The strong directionality of the bond results in large voids surrounded by the network frame. Hexagonal ice is the most typical one formed as such in atmosphere. It is also well known that the hydrogen atoms in the network are in the disordered state and that the freezing-in, namely the glass transition, of the rearrangement of the atoms occurs at $T_g \approx 105$ K [2], at which the characteristic time of the rearrangement becomes 1 ks. No phase transition due to the ordering of the hydrogen-atom positions is found below T_g because of the immobility of the atoms. The phase transition was realized at 72 K only after introducing hydroxide ions in place of water molecules in the network [3, 4]; namely, doping some Bjerrum defects of L type into ice.

The realization of such a hydrogen-bond network, as in hexagonal ice, is based on the fact that the hydrogen bond stabilizes it energetically by an order of magnitude more than the van der Waals interaction, which favours all the constituent molecules aggregating close together without a spatial opening [5]. In nature, however, there are many situations where the space for the water molecules is restricted one-, two-, or three-dimensionally [6, 7], and water as such in reality plays important roles in geological [8], chemical [9], and biological processes [10]. In restricted spaces, such a hexagonal-ice network cannot always be realized, even at low temperatures. The hydrogen-bond network formed, and thus the arrangement of the hydrogen-atom positions and the rearrangement rate, should be different from those of bulk ice, depending on the size and circumstances of the space.

A channel with a nanometre-scale diameter is a typical space subjected to a two-dimensional restriction. Recently, such channel water has been made in self-assembled supra-molecular crystalline complexes where the channel water is contained as an important constituent in the formation of the crystals: Choi *et al* [11] reported the synthesis and crystal structure of $[\text{Ni}(\text{cyclam})(\text{H}_2\text{O})_2]_3(\text{TMA})_2 \cdot 24\text{H}_2\text{O}$ (abbreviated hereafter as crystal **1**), where cyclam is 1,4,8,11-tetraazacyclotetradecane, TMA is 1,3,5-benzene tricarboxylic acid, and $24\text{H}_2\text{O}$ represents channel water with a diameter of 1.03 nm. Tadokoro *et al* [12] reported the synthesis and crystal structure of $[\text{Co}(\text{H}_2\text{bim})_3](\text{TMA}) \cdot 20\text{H}_2\text{O}$ (abbreviated as crystal **2**), where H_2bim denotes 2,2'-biimidazole. $20\text{H}_2\text{O}$, determined by single-crystal x-ray diffractometry at 198 K, corresponds to channel water with a diameter of 1.5–1.6 nm. On the basis of differential scanning calorimetry (DSC), they reported that a phase transition due to reconstruction of the network occurred at 244.8 K [12]. In both crystals, the atoms located at the pore wall possess a long-range periodicity in their positions [11, 12].

We have worked on the structural ordering and dynamics of the channel water of crystal **1** by adiabatic calorimetry, as reported elsewhere [13]. The channel water revealed a phase transition at 196.9 K due to ordering of the hydrogen-bond network to a more stable one. Taking the result of an x-ray diffraction experiment at 293 K by Choi *et al* [11] into account as well, it was concluded [13] that the channel water is in the crystalline state with long-range order as an average structure even at room temperature. The structural ordering was interpreted as being brought about essentially by the formation of the hydrogen bonds between the interfacial water molecules and the oxygen atoms of the channel wall. The water molecules located rather in the central portion of the channel are not necessarily taken into the network on making the hydrogen bonds in the most energetically stable way. This could be the reason why the phase transition accompanying reconstruction of the network occurs at a low temperature such as 196.9 K [13]. A glass transition due to the freezing-in of the rearrangement of the hydrogen-atom positions in the network was found at 87 K [13], which is lower by about 18 K than in hexagonal ice [2]. The hydrogen atoms are interpreted as being frozen in a disordered state.

Crystal **2** [12] contains channel water with a larger diameter than crystal **1** [11]. Therefore it is expected that the hydrogen-bond network and the arrangement of hydrogen atoms are quite different from those of crystal **1**. In the present work, the phase transition and glass transition behaviours of the channel water in crystal **2** were studied by adiabatic calorimetry [14, 15]. Heat capacities were measured by repeating thermometry, the energy supply yielding a temperature rise of 1.0–2.5 K, and again thermometry under adiabatic conditions. When the sample undergoes heat release or absorption due to phase/glass transitions, it can be monitored as a spontaneous temperature rise or fall, respectively, of the calorimeter cell as a function of time. The enthalpy relaxation rates can be calculated from the temperature drift rates. Therefore, calorimetry enables the study of dynamic properties regarding the structural change [16] as well as static properties such as the entropy of the equilibrium phase transition [14]. In this respect, adiabatic calorimetry is quite appropriate for the study of the ordering behaviour of the hydrogen atoms on the hydrogen-bond network.

2. Experiment

Powdered crystal $[\text{Co}(\text{H}_2\text{bim})_3](\text{TMA})\cdot n\text{H}_2\text{O}$ was prepared in aqueous solution according to the procedure described previously [12]. Two samples were used for heat capacity measurements, utilizing an adiabatic calorimeter reported previously [15]. First, the hydrate sample was loaded into a calorimeter cell, together with extra bulk water for fear of dehydration of the hydrate. The heat capacities of the sample were determined in a temperature range from 30 to 200 K. After the measurements were finished, the sample was dehydrated under vacuum at 297 K until the mass of the calorimeter cell loaded with the sample would have reached a constant value. The weight loss equals the quantity of water, as the sum of channel water (corresponding to $n\text{H}_2\text{O}$ in the above formula) and the extra bulk water. After the calorimeter cell loaded with the dehydrated sample was sealed vacuum-tight and installed in the cryostat again, the heat capacities of the sample were measured in a temperature range from 30 to 200 K. The mass of the hydrate sample including the bulk water was 1.249 g, the anhydride sample was 0.491 g, and the water as the sum in the hydrate sample was evaluated to be 0.758 g. The quantity of bulk water was estimated to be 0.494 g, assuming $n = 20$ in the above formula. The heat capacity values are thus derived below, assuming $n = 20$. The inaccuracy and imprecision of the heat capacities obtained have been estimated previously to be $\pm 0.3\%$ and $\pm 0.06\%$, respectively [15]. Considering that about 10 cm^3 of benzoic acid crystal was used in the calibration experiment [15], however, the inaccuracy and imprecision of the heat capacities derived presently are expected to be around $\pm 3\%$ and $\pm 0.6\%$, respectively.

3. Results and discussion

3.1. Heat capacities

Figure 1 shows the heat capacity results. Open circles represent the data per gram of the hydrate sample, which includes extra bulk ice, and open diamonds represent those of the anhydride sample contained in the 1 g hydrate sample. A dashed line in the figure stands for those of bulk ice contained in the 1 g hydrate sample, taken from the literature [2]. While the anhydride sample showed no anomaly over the entire temperature range measured, the hydrate sample revealed two peaks in the range 50–60 K. Heat capacities of the channel water were estimated by subtracting the contributions of the bulk ice and the anhydride sample from the experimental values of the hydrate sample, as shown by open circles in figure 2 as the molar values. A dashed line in the figure represents the literature data of bulk ice [2]. The heat capacity peaks in the range 50–60 K are judged as indicating the presence of equilibrium

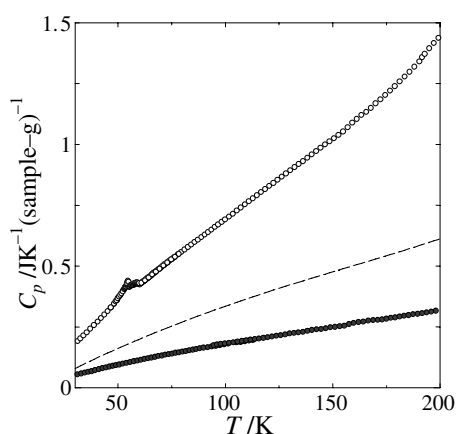


Figure 1. Heat capacities per gram of hydrate sample with excess bulk ice: open circle, hydrate sample with bulk ice; closed circle, anhydride sample contained in the 1 g hydrate sample. A dashed line represents those of bulk ice contained in the 1 g hydrate sample [2].

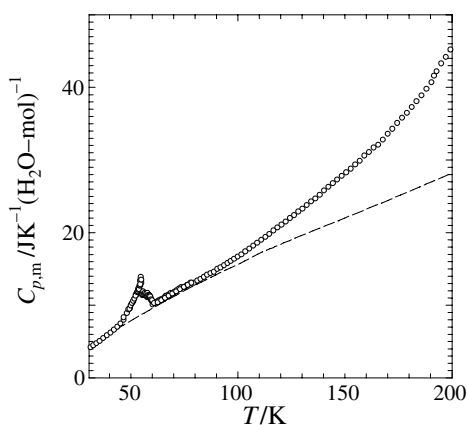


Figure 2. Molar heat capacities of the water of the hydrate. The values were estimated by subtracting the contributions of the bulk ice and the anhydride from the experimental data of the hydrate with extra bulk ice. A dashed line represents molar heat capacities of bulk ice, taken from [2].

phase transitions. Considering that the water molecules (except one of the 60 molecules) were presumed by Tadokoro *et al* to be ordered by forming a hydrogen-bond network even at 198 K [12], the phase transitions occurring at such low temperatures are interpreted as being due to the ordering/disordering processes of the hydrogen-atom positions.

3.2. Glass transition

Spontaneous heat release and absorption phenomena were observed, as shown in figure 3(b), where open and closed circles represent the results for the samples cooled rapidly at 2 K min^{-1} and slowly at 20 mK min^{-1} , respectively, prior to the measurements. On heating the rapidly pre-cooled sample at an average rate of 0.1 K min^{-1} for the measurements, heat release, namely positive $-(dH_m/dt)$, and then heat absorption, namely negative $-(dH_m/dt)$, were

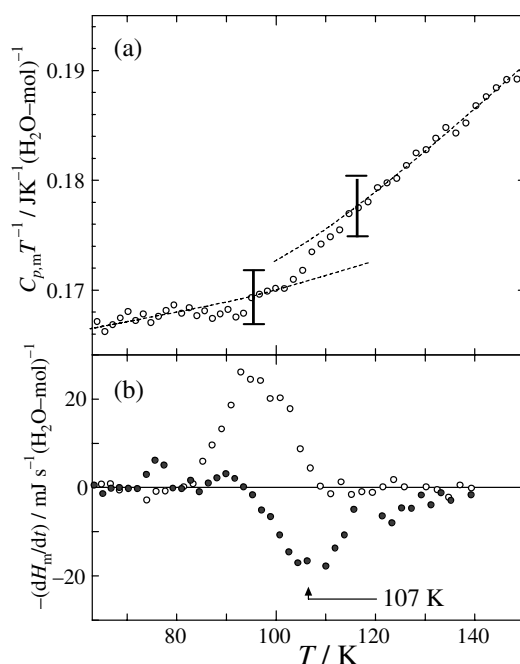


Figure 3. Molar entropies (heat capacities divided by the respective temperatures) of the hydrate water (a) and spontaneous enthalpy-drift rates (b) on an enlarged scale at 70–150 K. Upper and lower dotted lines in (a) represent the temperature dependences of the heat capacities under equilibrium and frozen-in states, respectively, expected at around a glass transition temperature of 107 K. The error bars stand for the magnitude of the imprecision in the data. Open and closed circles in (b) represent the data for the samples cooled rapidly at 2 K min^{-1} and slowly at 20 mK min^{-1} , respectively, before the measurements.

observed. On heating the slowly pre-cooled sample, on the other hand, small heat release and then large absorption effects were observed. The temperature drift after the energy supply for heat-capacity measurements returned to normal at around 115 K for both the samples. These behaviours are characteristic of a glass transition [16, 17]. Regarding the enthalpy relaxation in a glass transition, an empirical relation has been found between the relaxation time τ and the heat release/absorption rates observed by adiabatic calorimetry [15, 17]: the relation is that, at around the temperature at which the τ becomes 1 ks, the slowly pre-cooled sample exhibits the maximum absorption rate, while the rapidly pre-cooled sample shows the sharpest change in drift rate versus temperature. According to this relation, the glass transition temperature where $\tau = 1 \text{ ks}$ was tentatively determined to be $(107 \pm 2) \text{ K}$ in the present case.

Figure 3(a) shows the heat capacities in the glass transition region: the values are plotted as the entropies, $C_{p,m}/T$, to show the temperature dependence more clearly. The relaxation time reaches the calorimetric timescale of 1 ks–100 s in the region 105–115 K, as indicated by the fact that the spontaneous enthalpy drift observed disappears at around 115 K, as shown in figure 3(b), and therefore the equilibrium heat-capacity contribution due to the rearrangement process relevant to the glass transition is expected to be, and not to be, involved in the experimental values above and below the temperature range 105–115 K, respectively. This consideration suggests the presence of a heat capacity jump as another characteristic of the glass transition. The two dotted lines in figure 3(a) indicate the probable temperature dependence of heat capacities below and above the glass transition. The error bars represent the imprecision in

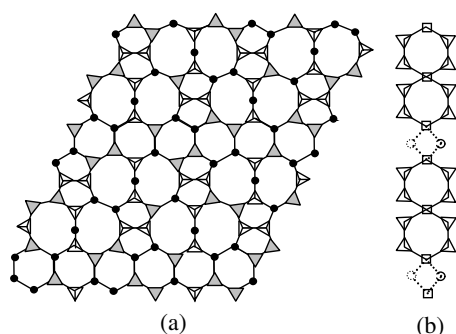


Figure 4. Hydrogen-bond network model given by Tadokoro *et al* [12], depicted as a two-dimensional representation for clarity: (a) primary hydration water; (b) secondary and tertiary (innermost) hydration water; ● in (a), water molecule which forms a hydrogen bond with an oxygen atom on the wall; grey Δ in (a), water molecule which potentially forms a hydrogen bond with imidazole π electrons; Δ in (a), water molecule which forms a hydrogen bond with an internal secondary-water molecule Δ in (b); Δ in (b), water molecule which forms a hydrogen bond with a water molecule represented by Δ in (a); \square in (b), water molecule which forms hydrogen bonds with molecules depicted in (b); open circle in (b), the tertiary water molecule which takes either position, forming hydrogen bonds shown with dotted or dashed lines; solid lines connecting marks, hydrogen bonds. 120 water molecules corresponding to six formula units are drawn in the figure.

the data. The heat-capacity jump is recognized from the two curves to be present and, further, the contribution from the configurational degree of freedom related to the glass transition is implied to increase with temperature. But the jump is almost of the same magnitude as the error bars, so it is difficult for more detailed information to be derived from the jump. Considering that the enthalpy relaxation effect due to the freezing-in of the positional rearrangement of hydrogen atoms in bulk ice was observed in the range from 90 to 115 K [2], conclusive interpretation of the mechanism also requires more precise calorimetry.

Assuming that the glass transition occurred on the development of a hydrogen-bond network in the nano-channel ice of the present crystal, some disorder should remain in the network even at 107 K. Figure 4 shows the hydrogen-bond network model given by Tadokoro *et al* [12] as a two-dimensional representation. The primary water is depicted in (a), and the secondary and innermost, tertiary water in (b). Solid segments connecting marks denote hydrogen bonds. Closed circles in (a) represent the water molecules that form hydrogen bonds with the oxygen atoms of the channel wall. The molecules represented by open triangles in (a) form hydrogen bonds with those represented by open triangles in (b). Grey triangles in (a) and open triangles in (b) apparently form only three hydrogen bonds. Open circles in (b) stand for half a water molecule forming hydrogen bonds represented by either dotted or dashed lines even at 198 K. There are 120 water molecules depicted, namely 240 hydrogen atoms, while there are 220 hydrogen bonds including those with the oxygen atoms of the channel wall. The imbalance between the numbers of hydrogen atoms and bonds as well as the presence of water molecules that are undetermined in position, constituting the tertiary water and represented by the open circles in (b), suggest that some disorder is potentially responsible for the glass transition remaining in the network.

3.3. Sequential phase transitions at 50–60 K

Figures 5(a) and (b) show the molar heat capacities of water on an enlarged scale in 30–80 K and the spontaneous heat-absorption effect observed in the temperature range, respectively. A

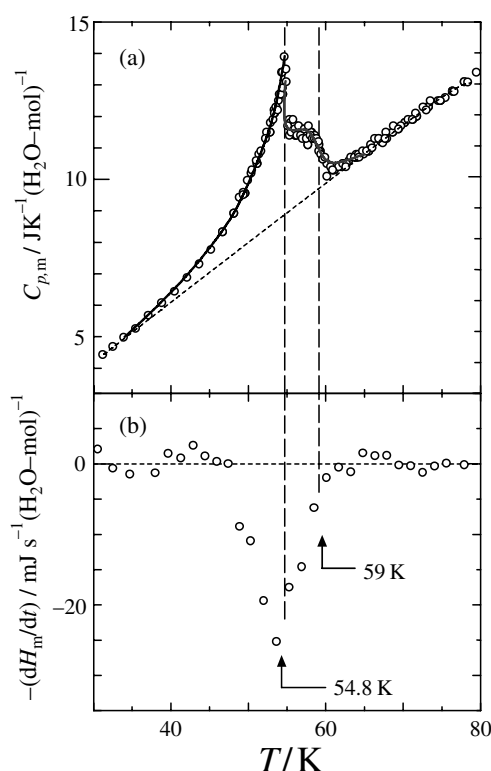


Figure 5. Molar heat capacities of the hydrate water (a) on an enlarged scale at 30–80 K and spontaneous enthalpy-drift rates (b) associated with phase transitions. The dotted line in figure (a) represents the baseline drawn for deriving the contribution of the phase transitions. The presence of heat absorption, negative $-(dH_m/dt)$, peak at 54.8 K and the gradual disappearance of the drifts on heating towards 59 K, in addition to the typical curve of the excess heat capacities, indicate that the 54.8 and 59 K phase transitions are of the first order and the second order, respectively, and of a (super-structural commensurate)–incommensurate–(normal commensurate) type in the heating direction [22–24].

sharp peak and a heat-capacity jump are found in figure 5(a) at 54.8 and 59 K, respectively, indicating the presence of equilibrium phase transitions. A dotted line represents a baseline drawn for estimating the excess heat capacities due to the phase transitions.

In association with the heat-capacity anomalies of the sharp peak at 54.8 K and the jump at 59 K, a heat absorption peak was detected at 54.8 K, and the effect decreases on heating, disappearing at 59 K. Such characters have been found to be of phase transitions of a (super-structural commensurate)–incommensurate–(normal commensurate) type [18–20]: according to this interpretation, the heat absorption at 54.8 K is due to a lock-in transition accompanied by a jump in the wavelength of the modulation vector of the ordering of the hydrogen-atom positions, referred to the periodicity of hydrogen-bond network. Periodicity of the order of the hydrogen-atom positions below 54.8 K is characterized essentially as a super-structure of that of the water–oxygen atoms forming the hydrogen-bond network above 59 K. The periodicity in between 54.8 and 59 K is incommensurate with respect to that of the network, and the amplitude of the modulation wave becomes zero at 59 K, giving a second-order phase transition there. The heat absorption effect observed in between 54.8 and 59 K is recognized as being due to a pinning effect of the wave, for example caused by defects in the network. The presence of

the defects can be recognized as being related to the glass transition observed at 107 K: the disorder, remaining frozen in the positions of water molecules, provides the network with the defects, as does the ordering of hydrogen atoms with the pinning effect. The appearance of the incommensurability is potentially related to the fact that the hydrogen-bond network itself is characterized as the super-structure, referred to the atomic arrangement of the channel wall.

The thermodynamic quantities of the phase transitions were derived from the excess heat capacities estimated as the contributions above the dotted line in figure 5(a). The enthalpy and entropy were evaluated to be $\Delta_{\text{trs}}H = 32 \text{ J (H}_2\text{O-mol)}^{-1}$ and $\Delta_{\text{trs}}S = 0.65 \text{ J K}^{-1} \text{ (H}_2\text{O-mol)}^{-1}$, respectively, in the total of the two transitions. It is noticed that the characteristics of the phase transitions are quite different from those in hexagonal ice [3] and tetrahydrofuran (THF) gas hydrate [21] doped with KOH: the heat capacity anomaly was observed with a sharp peak at 72 K with $\Delta_{\text{trs}}S = 2.41 \text{ J K}^{-1} \text{ (H}_2\text{O-mol)}^{-1}$ for ice [3] and at 61.9 K with $\Delta_{\text{trs}}S = 2.36 \text{ J K}^{-1} \text{ (H}_2\text{O-mol)}^{-1}$ for THF gas hydrate [20]. Therefore, the difference is found in the smallness of the present $\Delta_{\text{trs}}S$, as well as in the way of ordering the hydrogen-atom positions. In ice and gas hydrate, the hydrogen-bond network is extended three-dimensionally and many configurations are permitted in the disordered state of the hydrogen-atom positions, resulting in the large entropy in the degree of freedom. Further, since the configurations are rather close in microscopic energies, a gradual decrease in entropy is observed with decreasing temperature, as is observed in the high-temperature heat-capacity skirt of the peak [3, 21]. The smallness of the entropy in the present system is then considered as being correlated with the two-dimensional restriction: the channel wall attends the hydrogen-bond network only as an acceptor of hydrogen atoms [12]. This means that the primary channel-water molecule always supplies a hydrogen atom to the wall so as to contribute to the stabilization of the organic/inorganic hybrid crystal structure and that the configurational degree of freedom of the primary-water molecules is much restricted compared to those in ice and gas hydrate. In view of no heat-capacity skirt being found on the high-temperature side above 59 K, the restriction in the orientation of the molecules is potentially imposed already at the stage where the crystal was formed at higher temperatures.

3.4. Consideration of the mechanism of hydrogen-atom position rearrangement

No glass transition due to freezing-in of the rearrangement of hydrogen-atom positions was detected in the present work. It is noticed, however, that the excess heat capacity due to the equilibrium phase transitions at 50–60 K is found to tail down to 35–40 K. Considering that the heat-capacity contribution due to the phase transition is observable calorimetrically only for the condition where the relaxation time for the rearrangement of hydrogen-atom positions is shorter than 100 s–1 ks [15, 16], this indicates that the relaxation time becomes, only below 35 K, 1 ks, which is ordinarily assigned as a characteristic time of the calorimetric glass-transition temperature. In general, the relaxation time τ for the reorientation of molecules is expressed by an Arrhenius equation $\tau = \tau_0 \exp(\Delta\varepsilon_a/RT)$, where the pre-exponential factor τ_0 is given as 10^{-13} – 10^{-16} s in many crystalline systems [22, 23] and as 10^{-6} – 10^{-8} s in ice [2, 24]. The 10^{-13} – 10^{-16} s corresponds roughly to the frequency range of infrared rays and is reasonable on account of the frequency of the torsional vibration of water molecules, which leads to the rearrangement of hydrogen-atom positions. Substituting $\tau_0 \geq 10^{-16}$ s and $\tau = 10^3$ s only below $T = 35$ K into the Arrhenius equation, the activation energy for the reorientation is evaluated to be at largest 13 kJ mol^{-1} . This value is close to the energy of an O–H···O hydrogen bond found in the crystalline state [17], and suggests that the rearrangement proceeds with the breaking of only one hydrogen bond. Considering that the hydrogen-bond network is composed of rings of five or more water molecules (except one in the internal portion, as shown

in figure 4), the transfer of a Bjerrum defect in the network is recognized as being responsible for the rearrangement [24, 25]. As described above, in figure 4, there are 120 water molecules, namely 240 hydrogen atoms, and 220 hydrogen bonds, including those with the oxygen atoms of the wall. This implies that 20 hydrogen atoms do not form hydrogen bonds or bonds with, for example, imidazole π electrons. Such a situation would be relevant to yielding some Bjerrum defects in the present system.

4. Concluding remarks

The thermal properties of crystal **2** with channel water of 1.5–1.6 nm in diameter were studied by adiabatic calorimetry. These are different from those of crystal **1** with channel water of 1.03 nm in diameter [11, 13]. A glass transition due to freezing-in of the water molecules on the way to hydrogen-bond network development was found to be potentially present in crystal **2** but not in **1** [13]. This suggests that there is some defect in the network in crystal **2**, while a rather regular and neat network is formed in crystal **1**. On the other hand, a glass transition due to freezing-in of the hydrogen-atom positions was found in crystal **1** [13] but not in crystal **2**. The glass transition in **2** is expected, if any, to occur below 35 K. This is understood as the concentration of Bjerrum defects being small in the hydrogen-bond network in **1** but relatively large in **2**. These differences appear to reveal quite a contrast in the structures and properties of channel water between crystals **1** and **2**. The presence of the channel water is essential for synthesis of both crystals; that is, the formation of the hydrogen bonds between the channel water molecules and the oxygen atoms of the wall is indispensable for synthesis. However, the hydrogen-bond network formed at room temperature is not complete, with some disorder indicated by the occurrence of a phase transition due to the ordering of water molecules, and shows quite different behaviours at low temperatures from channel to channel. As the diameter of the channel increases at least up to 1.6 nm, more defects are potentially produced in the network, although the presence of the defects might enhance the rearrangement rate of the hydrogen-atom positions within the network at lower temperatures.

Comparison between the properties of crystal **2** and hexagonal ice is intriguing too. It is well known that ice forms a three-dimensionally extended, regular and neat hydrogen-bond network without any spatial restriction. A glass transition due to water molecules is not found, but that due to hydrogen atoms is found, just as in crystal **1**, with channel water of smaller diameter. This would reflect the fact that the network structure formed within channel water is different from that of ice without any interaction with the pore wall.

The phase sequence of a (super-structural commensurate)–incommensurate–(normal commensurate) type was proposed in the present work to occur in crystal **2** with respect to the ordering of hydrogen-atom positions. Confirmation using, for example, a neutron diffraction experiment and determination of the real arrangement of hydrogen atoms are interesting subjects to be challenged in the future.

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