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Structural ordering and ice-like glass transition on cooling the nano-channel water formed within a crystalline framework

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Abstract

Heat capacities and enthalpy relaxation rates were measured for crystalline $[Ni(cyclam)(H_2O)_2]_3(TMA)_2{\cdot}24H_2O$, where cyclam is 1,4,8,11-tetraazacyclotetradecane, TMA is 1,3,5-benzene tricarboxylic acid, and $24H_2O$ represents the water forming a nano-channel. A phase transition was found to occur at 196.9 K, and a glass transition at 87 K. A potential picture is given for the progress of the ordering of water molecules and hydrogen atoms in the channel. At room temperature, interfacial water molecules form hydrogen bonds with the oxygen atoms of the channel wall, and the aggregation of water molecules is recognized, as the average structure, to be in a crystalline state with a long-range order. The bond formation plays important role in the stabilization of the crystalline framework with a channel structure. The aggregate transforms to a more stable crystalline state at 196.9 K. All the water molecules should be fixed completely there. The positions of the hydrogen atoms on the network are, however, essentially in the disordered state while keeping an ice rule, and freeze at 87 K only with a short-range order in the arrangement. The progress of such ordering of channel water reveals a striking contrast to the behaviour of the water within meso-porous silicas, in which the molecules in the interface are always in the non-crystalline state and those in the pore centre tend to crystallize only when the pore diameter is greater than 2 or 3 nm.

1. Introduction

Bulk water shows strange properties especially at low temperatures [1]. The density exhibits a maximum at 3.98 °C, and the heat capacity increases with decreasing temperature in a

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sub-zero temperature region. Such anomalous behaviours have been understood as attributed to development of a tetrahedrally extended hydrogen-bond network at low temperatures [2]. The bonds formed by the molecules possess a strong directionality so that a lot of voids are produced in the structure of the aggregate [3], and, at ambient pressure, hexagonal ice or cubic ice is formed, depending on the size and temperature.

Water exists in diversely confined spaces as well as the bulk. A channel with nanometre-scale diameter is a typical one subjected to confinement. Channel water is found in many places, such as in minerals and cell membranes. The static and dynamic behaviours of the water are of great interest scientifically, and clarification is indispensable further to understanding the geological and biological phenomena and their mechanisms. What ordering proceeds on cooling and whether or not the ordered structure and dynamics are similar to those of bulk ice have not been disclosed enough so far. Channel water of nanometre scale has been prepared recently so that scientific pursuits can be applied. Silica gel and meso-porous silica such as MCM-41 provide the space for the water. In these materials, silanol groups are arranged on the pore wall rather randomly. The wall is therefore hydrophilic and water is introduced and accommodated to fill the whole space. The water is known to be divided into two types within the pores [4]. The interfacial water is known to be in the non-crystalline state even at very low temperature of 80 K, irrespective of the pore size, and to consist of only a layer of molecules neighbouring the wall [5]. The internal water, located in the central portion of the pore, crystallizes into cubic or hexagonal ice in the cases with diameter above about 3 nm, and remains in the non-crystalline state below about 2 nm [6, 7].

Another new type of nano-channel water has been reported. Organic and inorganic compounds are reacted in aqueous solution, and a kind of hybrid compound with nano-channel water is synthesized as an example of crystal engineering [8, 9]. The points are that the pore-wall framework providing the channel space has a crystalline periodicity of a long range and that the new compound itself including the wall framework is constructed probably only in the situation where the channel pores are filled with water molecules. The water molecules interacting with the atoms of the wall are expected to play some role in the formation of the new compound. The structural ordering of the water on cooling is also expected to be different from that within the meso-porous silicas stated above. The clarification is intriguing in that some knowledge is obtained regarding the role of the water in the compound formation and regarding what difference the presence/absence of the crystalline periodicity of the pore–wall structure bring to the structural ordering of nano-channel water on cooling.

Adiabatic calorimetry is a powerful technique to investigate the change of state of molecular aggregation such as structural ordering and its dynamics [10]. In this technique, heat capacities are measured by repeating energy supply and thermometry under adiabatic conditions [11]. Since heat leak is absent in principle, the heat capacity value derived is the most accurate among many calorimetric methods. Spontaneous heat release and absorption effects due to phase or glass transitions can be detected in the thermometry periods. Since the calorimetry detects the relaxation with a characteristic timescale of 10^6–10^2 s, it works as a kind of low-frequency spectroscopy [10]. This is important, as the smaller (longer) the frequency (timescale), the more clearly the modes of motion of molecules are separated if multiple modes are present.

In the present work, the structural ordering and slow dynamics of the channel water in crystalline $[\mathrm{Ni(cyclam)(H_2O)_2}]_3\mathrm{(TMA)_2}\cdot 24\mathrm{H_2O}$ were studied by using an adiabatic calorimeter [12]. Cyclam is 1,4,8,11-tetraazacyclotetradecane and TMA is 1,3,5-benzene tricarboxylic acid. The synthesis of the compound and the determination of the crystal structure at room temperature were reported by Choi *et al* [8]. According to the report, the compound possesses channels running along the c axis, and the diameter of the channel pores is 1.03 nm as

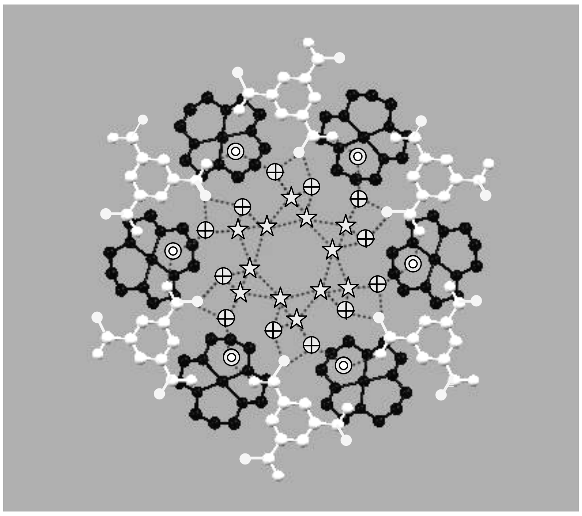

Figure 1. Schematic diagram showing the arrangement of water molecules in a channel and their surroundings [8], seen along the *c* axis, in $[Ni(cyclam)(H_2O)_2]_3(TMA)_2 \cdot 24H_2O$: white balls and sticks, TMA; black balls and sticks, cobalt complex coordinated by cyclam; double circles, coordinated water; crossed circles, water forming a hydrogen bond with the oxygen atom of TMA; stars, water forming hydrogen bonds with other water molecules; dotted lines, hydrogen bonds.

measured between the wall atoms assigned the respective van der Waals radii. Figure 1 shows schematically the arrangement of the water molecules in the channel and the surroundings of the water molecules (seen along the *c* axis). White balls and sticks represent TMA, and black ones the cobalt complex coordinated by cyclam. The double circles is the water molecule coordinating to the cobalt ion and it forms a hydrogen bond with the TMA oxygen atom. Crossed circles represent the water molecules forming hydrogen bonds with the TMA oxygen atoms and coordinated water, and they would be classified as the interfacial water molecules within the channel. Stars represent the water molecules forming hydrogen bonds with other water molecules, and they would be classified as the internal ones. The numbers of interfacial and internal water molecules are equal. The pore–wall atoms constituting the crystal are arranged with a long-range periodicity, and the water molecules are located so as to conform to the periodicity as the average structure. However, there has been no work reported on the structural ordering of the water molecules at low temperatures so far, and it is unknown how rigid/loose a hydrogen-bond network is developed at room temperature. In the case of silicas with pore diameter of 1 nm, the water within the channel always remains in the non-crystalline state [4–6].

2. Experiment

Powdered crystal $[Ni(cyclam)(H_2O)_2]_3(TMA)_2 \cdot nH_20$ was prepared in aqueous solution according to the procedure reported by Choi *et al* [8]. Two samples were used for the present calorimetry [12]. One, named hydrate sample, included excess, bulk water. The other, named anhydride sample, was obtained by dehydrating, under vacuum at 297 K, the hydrate sample which had been used for the measurements of hydrate sample. The weight loss equals the quantity of water as the sum of channel water (corresponding to nH_2O in the above formula), coordinated water ($(H_2O)_2$ in the above formula), and extra bulk water. The mass of the hydrate sample including the bulk water was 1.658 g, the anhydride sample was 0.507 g, and therefore the water as the sum in the hydrate sample was calculated to be 1.152 g. The quantity of the bulk water was estimated to be 0.922 g calorimetrically from the enthalpy of fusion ($\Delta_{\text{fus}}H$) taking place in the hydrate sample. The quantity of channel water was determined to be 0.184 g experimentally; namely $n = 24.0 \pm 0.3$ in the above formula.

The adiabatic calorimetry was carried out with an apparatus reported previously [12]. The sample was loaded into a calorimeter cell under an atmosphere of helium gas. The cell was sealed vacuum-tight with an indium wire and installed in a cryostat. The helium gas served as an energy-exchange gas within the cell. Adiabatic conditions were achieved by keeping the adiabatic shields, surrounding the cell, always at the same temperature as the cell and by evacuating the space within the cryostat to 10^{-4} Pa. An intermittent heating method was utilized for the measurements [11]. The former equilibrium temperature T_f of the cell was determined by following it as a function of time for 8 min, a specified quantity of electrical energy (ΔE) corresponding to the temperature increase of 1.8–2.4 K was supplied into the cell usually for a duration of 5 min at very low temperatures and 50 min at around 290 K, and then the latter equilibrium temperature T_l was determined by following it again for 8 min. The latter thermometry served as the former thermometry in the next set of heat capacity measurement. Without any anomaly due to the sample, the equilibration of the temperature of the cell was attained within 3 min after each heating. The gross heat capacity (C) of the cell was calculated as ΔE divided by ΔT ($=T_\text{l} - T_\text{f}$). The spontaneous enthalpy change, namely heat release or absorption, of the sample due to glass or phase transitions could be observed as the appearance of spontaneous temperature drift of the cell. The rate of change of molar enthalpy, $-\text{d}\Delta H_\text{m}/\text{d}t$, due to for example the channel water, of quantity n_w, is related to the spontaneous temperature-drift rate, $\text{d}T/\text{d}t$, and the gross heat capacity of the cell as follows:

$$-\text{d}\Delta H_\text{m}/\text{d}t = C(\text{d}T/\text{d}t)/n_\text{w}.$$

The inaccuracy and imprecision of the heat capacities obtained were estimated previously to be ±0.3% and ±0.06%, respectively [12]. In view of the situation that only samples of about 1 cm^3 were utilized presently while a benzoic acid crystal of about 10 cm^3 was employed in the calibration experiment [12], however, they are expected to be around ±3% and ±0.6%, respectively, for the hydrate sample and around ±5% and ±1%, respectively, for the water.

3. Results and discussion

3.1. Phase transition

Open circles and diamonds in figure 2 represent the heat capacities per gram of the hydrate sample and the anhydride sample contained in a hydrate sample of 1 g, respectively. Dashed lines in the figure stand for those of bulk water/ice contained in a hydrate sample of 1 g, taken from the literature [13]. While the anhydride sample showed no anomaly over the entire temperature range measured, the hydrate sample revealed three anomalies at 197, 236, and 273.09 K. Assuming that the 273.09 K anomaly only is ascribed to the fusion of bulk ice, the above n was evaluated to be 29.8. Provided that, in addition to the 273.09 K anomaly, the 236 K one originates from the eutectic melting of bulk ice, n was calculated to be 24. While $n = 30$ is considered to be inappropriately large on account of the channel size, $n = 24$ agrees well with the result of previous x-ray diffraction experiment by Choi *et al* [8]. Thus the present results were analysed below assuming $n = 24$. The appearance of a heat-capacity jump associated with the 236 K anomaly is consistent with this interpretation.

The heat capacities as the sum of channel water and coordinated water were estimated by subtracting the contributions of the bulk water/ice and the anhydride sample from the

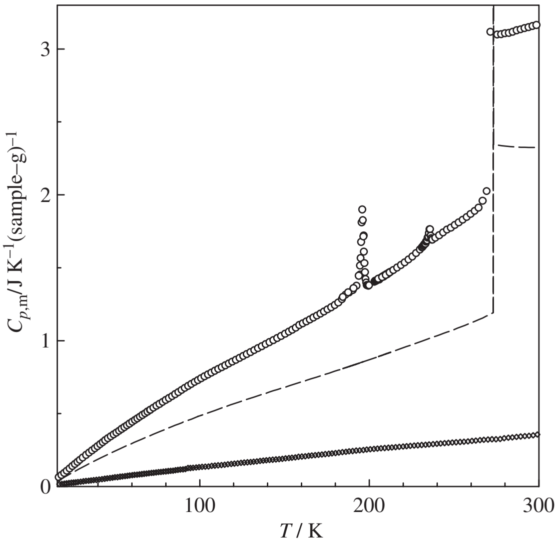

Figure 2. Heat capacities per gram of hydrate sample with excess bulk water/ice: Open circle, hydrate sample with bulk water/ice; open diamond, anhydride sample contained in a hydrate sample of 1 g. Dashed lines represent those of bulk water/ice contained in a hydrate sample of 1 g [13].

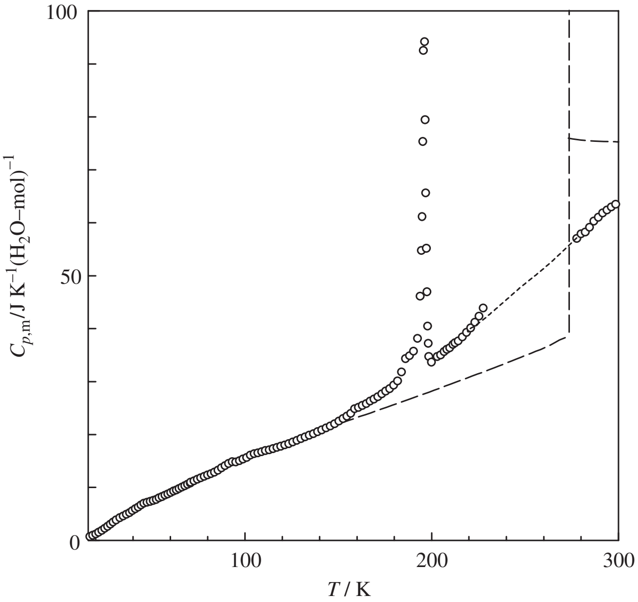

Figure 3. Molar heat capacities of both channel and coordinated water. The values were derived by subtracting the contributions of the bulk water/ice and the anhydride from the experimental data of the hydrate with extra bulk water/ice. The dotted line indicates the temperature dependence of heat capacities of the hydrate water in the high-temperature phase. Dashed lines represent molar heat capacities of bulk water/ice, taken from [13].

experimental values of the hydrate sample, and are shown in figure 3 as the molar values. The values below about 120 K agree with those of bulk ice; dashed lines there represent the

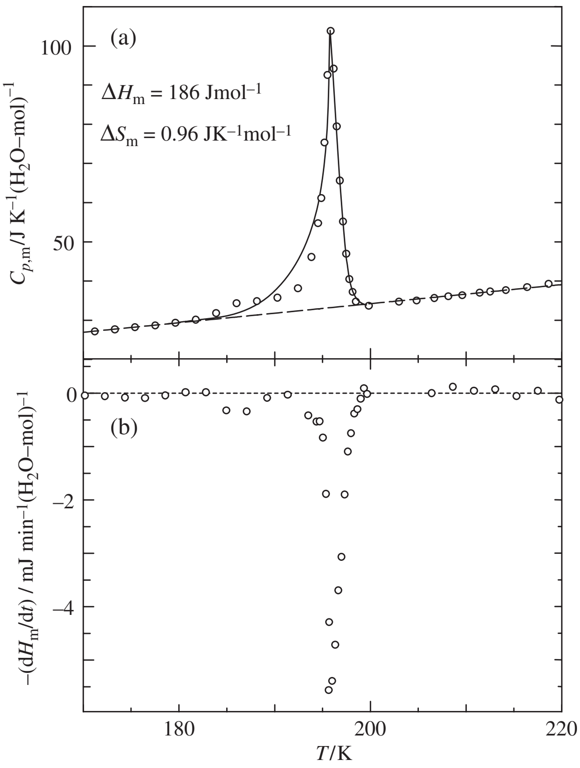

Figure 4. Molar heat capacities (a) of hydrate water in 170–220 K and spontaneous enthalpy-drift rates (b) associated with a phase transition at 196.9 K. The dashed line in (a) represents the baseline to the excess heat capacities due to the phase transition.

literature data of bulk ice and water [13]. The heat capacity peak at 196.9 K is judged as a phase transition; probably, the ordering process of water molecules within channels proceeds on cooling. The transition enthalpy and entropy were determined, assuming a baseline as drawn with a dashed line in figure 4(a), to be $\Delta_{trs}H = 186$ J (H_2O-mol)$^{-1}$ and $\Delta_{trs}S =$ 0.96 J K^{-1} (H_2O-mol)$^{-1}$, respectively. Figure 4(b) shows the rates of the enthalpy relaxation observed in association with the anomaly. The existence of negative rates in $-(dH_m/dt)$ in the transition region indicates that the phase transition is of the first order with a jump in the structure of molecular arrangement. Since the transition appears as related with the ordering of the water molecules, it follows that the jump occurs in the hydrogen-bond network structure.

Based on the x-ray diffraction data at 293 K, Choi *et al* proposed a potential model of the hydrogen-bond network formed among the channel-water molecules and the oxygen atoms of the channel wall as shown in figure 1 [8]. Given that the water molecules can go into and come out of the channel at room temperature and that the heat capacities of water as shown in figure 3 are larger in the high-temperature phase by 30–40% than those of bulk ice, it is reasonable to assume that the channel-water molecules are bound somewhat loosely. That the water molecules are bound by the oxygen atoms of the wall in the high-temperature phase would be consistent with the phase transition taking place at a lower temperature (196.9 K) than the fusion temperature of bulk ice (273 K). In addition, the entropy of the phase transition is much smaller than that of bulk water, 22 J K^{-1} mol^{-1}. The smallness indicates that the number of the hydrogen bonds present does not differ through the phase transition so much. This would

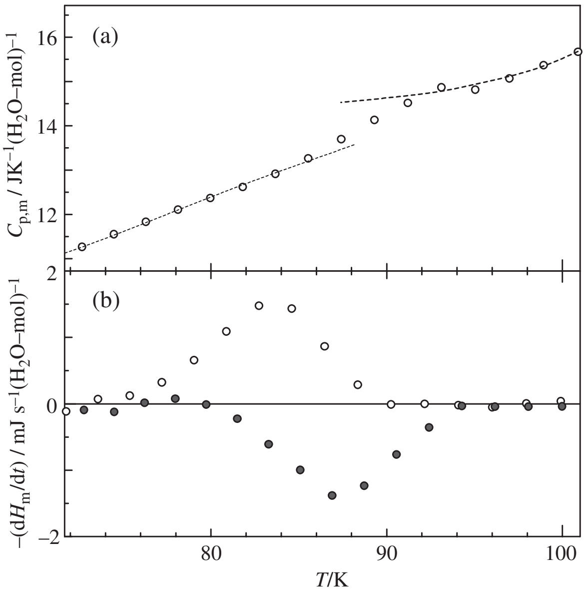

Figure 5. Molar heat capacities (a) of hydrate water on an enlarged scale in 72–100 K and temperature dependence of spontaneous enthalpy-drift rates (b) due to a glass transition. Dotted lines in (a) represent the probable dependences of heat capacities below and above the glass transition temperature. 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.

also reflect that the water molecules are restricted two-dimensionally within the channel even in the high-temperature phase and form hydrogen bonds with the fixed oxygen atoms of the pore wall. It is understood that a long-range order as a character of crystalline aggregation is present even in the high-temperature phase as proposed by Choi *et al* [8]. The presence of long-range order is reasonable as well from the experimental fact that there appears no heat-capacity jump associated with the phase transition at 196.9 K.

3.2. Glass transition

Spontaneous heat release and absorption phenomena were observed in a temperature range 74–94 K as shown in figure 5(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 the average rate of 0.1 K min^{-1} for the measurements, first heat release, namely positive $-(\mathrm{d}H_\mathrm{m}/\mathrm{d}t)$, and then heat absorption, namely negative $-(\mathrm{d}H_\mathrm{m}/\mathrm{d}t)$, were observed. On heating the slowly pre-cooled sample, on the other hand, only a small heat release effect around 78 K and then a large heat absorption effect were observed. The temperature drift after the energy supply for heat-capacity measurements returned to the normal one at around 94 K for both the samples. These behaviours are characteristic of a glass transition [10]. Regarding the enthalpy relaxation, an empirical relation has been reported to hold between the relaxation times and the temperature dependence of spontaneous enthalpy-relaxation rates observed [12, 14]; the slowly pre-cooled sample exhibits the maximum absorption rate at the temperature at which the relaxation time becomes 1 ks. According to the relation, the glass-transition temperature T_g was determined in the present case to be 87 K. In addition to the appearance of the enthalpy relaxation effects, a heat-capacity jump was found as another character of a glass transition, as shown in figure 5(a), in the region 87–91 K where the relaxation time becomes 1 ks–100 s. One might consider that the glass transition is due to the freezing-in of the positional rearrangement of hydrogen atoms in bulk ice involved in the sample [13]. However, while the enthalpy relaxation effect in bulk ice should be observed in the range from 90 to 115 K [13], no appreciable effect was detected above 94 K in the present case. From this, the glass transition observed here is realized as of the present crystal with channel water. Here it is noticed that the relaxation effect was observed in a temperature range of only 20 K, from 74 to 94 K. The temperature width is judged as narrow enough so that the enthalpy relaxation could be characterized as essentially of a single relaxation time without a distribution in the activation energy. The character of a single relaxation-time process indicates that the freezing-in phenomenon takes place in the crystalline state. In view that the phase transition due to the development of the hydrogen-bond network takes place at 196.9 K which is higher by over 100 K than the T_g and that no freezing-in phenomenon due to the rearrangement of the water molecules is observed in the heat-capacity skirt on the low-temperature side of the phase transition, the network seems to have been completed at above the $T_g = 87$ K. Taking further into account that the extra heat-capacity above the T_g appears to decrease with increasing temperature as shown in figure 5(a) and therefore to be a high-temperature skirt of the heat-capacity peak of another phase transition expected below the T_g [15], the glass transition is concluded to originate from freezing-in of the positional ordering of hydrogen atoms within the hydrogen-bond network. The hydrogen atoms are understood as frozen in the disordered state/phase just as in ice [13]. T_g is lower by 15–20 K than that in ice. The reason would be that, since the rearrangement rate of hydrogen atoms in hydrogen-bond networks depends, as is well known, on the number of Bjerrum defects [16], more defects in the concentration could be produced in the network of the confined channel water than in the three-dimensionally extended network of bulk ice.

3.3. Striking contrast to the structural-ordering behaviour of the nano-channel water confined within silica pores

Water molecules aggregate together forming hydrogen bonds. This is attributed to the fact that the hydrogen-bond energy is stronger by about an order of magnitude than the van der Waals interaction. Then, oxygen atoms take use of the sp^3 hybrid electron-orbitals for bond formation according to the valence bond theory. Ideally, four water molecules are arranged tetrahedrally around each molecule as realized in hexagonal or cubic ice. In the real situation restricted in spaces such as channels, the interfacial interaction between the water molecules and the wall atoms affects the detail of the aggregation of water molecules. Since the interfacial interaction favours the formation of hydrogen bonds, the water molecules within the pores cannot be arrayed in the regular way of tetrahedral arrangement. For this reason, the structure of the channel water realized depends on the pore size and on the arrangement of the hydrophilic groups of the pore wall. In this respect, it is intriguing to compare the structure and properties of the water within silica pores and the present channel pores.

Many works have been done on the structural ordering and dynamic properties of the water within meso-porous silicas [4–7, 17]. There, silanol groups are located in a random way on the pore wall resulting in the hydrophilic nature of the wall. Water molecules are introduced easily and fill the pore space [18]. The molecules are divided into two types with respect to the dynamic properties. The interfacial water, being close to the wall, is in a non-crystalline state irrespective of the pore size and temperature [4, 5]. The internal water, being in the central portion within the pores, tends to develop the hydrogen-bond network intrinsic to water molecules. Therefore the crystalline–structural ordering begins to develop in the centre of the pore. The structure formed would be somehow similar to that of bulk liquid water (amorphous ice) and then bulk crystalline ice on increasing the pore size. Above about 3 nm in diameter, the water crystallizes into hexagonal or cubic ice [7]. According to the present results, the circumstance differs in the crystal formed with channel water in the aqueous solution. The pore–wall structure possesses a long-range periodicity as a condition indispensable to the crystal [8]. Based on the presence of the wall atoms fixed in their positions with a long-range periodicity, the interfacial-water molecules tend to develop a hydrogen-bond network conforming to the wall structure [8]. In reality, the hydrogen-bond formation at room temperature between the interfacial-water molecules and the wall atoms must have played an important role for realization of the crystal itself. The water molecules accordingly show, as an average, a periodic structure with the same period as the pore wall. However, the ideal tetrahedral arrangement of water molecules is not necessarily realized and there might exist some configurational disorder in the central portion of the pores. This would originate from the fact that, at room temperature, the interfacial water molecules can change their orientations by forming a hydrogen bond with the wall atoms just as the internal ones can change their positions and orientations. Then the interfacial and internal molecules get more ordered at low temperatures so as to develop the hydrogen-bond network in an associated way. The progress of structural ordering of channel water is thus understood as showing quite a contrast between silicas [4–6] and the crystals such as the present one.

4. Concluding remarks

The present organic/inorganic hybrid crystal was realized with including the channel water in it [8]. In this sense, the details of the structural ordering of the channel water on cooling are intriguing in clarification of the role which the channel water plays in the formation of the crystal. The present adiabatic calorimetry disclosed a progress of the hydrogen-bond network of the channel water in crystalline $[\mathrm{Ni(cyclam)(H_2O)_2}]_3\mathrm{(TMA)_2}\cdot 24\mathrm{H_2O}$; a first-order phase transition appeared at 196.9 K. Such a phase transition has never been found in the channel water, below 2 nm in diameter, of meso-porous silicas [4–6, 19]. This contrast reveals the important role played by the channel water in the realization of the present crystal. Hydrogen bonds should be formed even at room temperature between the water molecules and the oxygen atoms constituting the pore wall, and they must have enhanced the stabilization of the crystal. The appearance of the phase transition would indicate that the water molecules are hydrogen-bonded somewhat loosely in the central portion of the channel at room temperature. However, the transition entropy is much smaller than the fusion entropy of bulk ice. This is connected with the fact that the water molecules are restricted two-dimensionally within the channel, and are considered as bound by the hydrogen bonds with a long-range order along the channel even at room temperature.

The achievement of a completely ordered hydrogen-bond network of the channel water at low temperatures is noticed. Even though the water molecules are arranged with a long-range order as the average, the molecules in the centre of the channel possess some looseness in the hydrogen bond and possibly a disorder in the positions. In such situations, there occurs a phase transition accompanied with reconstruction of the hydrogen-bond network of the channel water at some low temperature. One might also consider a possibility that both the crystalline framework and the channel water change their structure in a coupled way through the phase transition. The structure determination of the low-temperature phase is attractive and necessary in future in these respects.

The appearance of a glass transition at 87 K should be noticed as well. The situation resembles that of bulk ice [13]. The glass transition is considered as due to the freezing in the positions of hydrogen atoms in the disordered arrangement on the completely ordered hydrogen-bond network; in reality, the freezing concerns the reorientation of water molecules proceeding with breaking hydrogen bond(s) [16]. The value of T_g is a little lower than that, $T_g = 105$ K [13], of ice. The low T_g is understood as indicating the presence of more Bjerrum defects contained in the network. The question of why more defects can be introduced and stabilized in the network indeed provides more interest in the clarification of the network structure.

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