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Calorimetric studies of some energy-related materials

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Abstract

Low-temperature heat capacities were measured for two kinds of energy-related materials. The first is a series of OH-substituted neopentane, $C(CH_3)_{4-n}(CH_2OH)_n$ with n=2 and 3. Each of them undergoes a first-order phase transition with a large enthalpy change. The transition occurred at 314.5 K with $\Delta_{trs}H=(12.50\pm0.02)$ kJ mol^{-1} for n=2, at 358.2 K with $\Delta_{trs}H=(21.24\pm0.05)$ kJ mol^{-1} for n=3, respectively. Both of them prove to be useful as an energy reservoir which stores and releases the latent heat while keeping their transition temperatures. The second is the clathrate hydrates. For the type II clathrate hydrates encaging polar guest molecules (tetrahydrofuran THF, acetone Ac and trimethylene oxide TMO), two kinds of dielectric relaxation are observed in relation to the freezing out of reorientational motion of the host water molecules and of the guest dipoles. Doping of a minute amount of KOH into the samples turns out to accelerate dramatically the motion to release the immobilized state and to induce their ordering transitions. A phase transition occurred at 61.9 K for THF hydrate, 46.6 K for Ac hydrate, and 34.5 K for TMO hydrate, respectively. The associated entropy change is of the order of 2.4 J K^{-1}(H_2O mol)$^{-1}$ and similar in magnitude to that of dopant-induced transition in ordinary ice I_h. Nature of dynamic disorder of the host and guest species as studied by dielectric and thermal conductivity measurements are reviewed briefly in relation to the ordering processes. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Heat capacity; Phase transition; Energy reservoir; Ordering process; OH-substituted neopentane; Clathrate hydrate

1. Introduction

A wide variety of substances of organic and inorganic origin are known to form an orientationally disordered crystal (ODC) phase below their fusion temperatures [1]. These phases are soft or waxy and easily deformable, even while they exhibit a highly symmetrical translational long-range order with respect to their centers of masses, being generally f.c.c. or b.c.c. system [2]. On cooling, the crystals undergo phase transitions into ordered phases with low symmetry. The enthalpy change associated with the orientational order–disorder transition is much larger than that of fusion. These compounds have, therefore, a potential use as energy reservoir which stores and releases the latent heats in a solid state while remaining at constant temperature. As one possible candidate, thermodynamic properties of a series of OH-substituted neopentane, $C(CH_3)_{4-n}(CH_2OH)_n$ with n=2 and 3, were measured. Thermodynamic studies of both the end members, neopentane [3] and pentaerythritol [4], have shown the existence of their ODC phases. Low-temperature heat-capacity studies on the $C(CH_3)_{4-n}(CH_2OH)_n$ family will clarify the relation between the formation of ODC phase and molecular properties and the effect of substitution of methylol group on the nature of phase transition [5].

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Other interesting energy-related materials are clathrate hydrates [6] which occur in nature in a large amount. Gas hydrates exist mainly in permafrost and deep oceans. With the huge reserves of natural gas hydrates, concern has been expressed about the release of CH_4, since its greenhouse effect is more serious than that of CO_2. The phase equilibria between ice and gaseous guest species have been formulated by statistical thermodynamics [7,8]. Phase diagrams between water and various guest species have been determined experimentally.

Undoubtedly, one of the driving forces to undertake the research of the clathrate hydrates is the orientational disorder exhibited by both of the host and guest species, in spite of geometrical beauty of the host cages composed of water molecules through the hydrogen bonds. All the clathrate hydrates described in this paper have the type II structure with an ideal composition $G\cdot17H_2O$ (G, guest molecules), which belongs to the cubic system of $Fd\bar{3}m$. This high crystallographic symmetry strongly suggests that the clathrate hydrates form ODC phases at least below their fusion temperatures. For the clathrate hydrates encaging dipolar molecules, two kinds of dielectric relaxation [9] are observed. The one occurring at around 150 K is ascribed to the freezing out of reorientational motion of the host water molecules, and the other occurring at cryogenic temperatures as low as 30 K to that of the guest species. The former relaxation is similar to that of the hexagonal ice and may be accelerated by the special kind of dopant [10]. Dielectric study will clarify the dynamic situation of disorder which the host and guest molecules possess in the lattice. Calorimetric and dielectric studies on some clathrate hydrates are reviewed briefly. Results of the thermal conductivity measurement [11] will be discussed in relation to the molecular disorder.

2. Experimental

Neopentanetriol NPT (2-hydroxymethyl-2-methyl-1,3-propanediol), neopentyl glycol NPG (2,2-dimethyl-1,3-propanediol) and its deuterated analog NPG-d_{12} were donated from Mitsubishi Gas [12]. Partially deuterated sample NPG-d_2 was prepared by repeated recrystallization of NPG from D_2O (99.75% deuteration level). They were purified by recrystallization followed by sublimation and zone refinings. The purity of each sample was determined by fractional-melting method with Perkin-Elmer DSC7 to be 99.99% for NPG, 99.99% for NPG-d_2, 99.48% for NPG-d_{12}, and 99.96% for NPT, respectively. The deuteration level was determined from NMR spectra to be $(98.15\pm0.05)\%$ for NPG-d_2 and $(97\pm2)\%$ for NPG-d_{12}, respectively.

Three kinds of type II clathrate hydrates were prepared. Commercial tetrahydrofuran THF, acetone Ac, and trimethylene oxide TMO were purified by a rectifier possessing theoretical plate number more than 80 [13]. Each of them was mixed with purified water by gravimetric method, respectively. The composition of each hydrate was $THF\cdot16.6H_2O$, $Ac\cdot16.9H_2O$, and $TMO\cdot16.8H_2O$, respectively. The formation of THF hydrate is straightforward by cooling the sample solution because the hydrate crystal exhibits congruent melting. On the contrary, the hydrates of Ac and TMO exhibit incongruent melting. Thus the formation of a sample crystal was carefully done by annealing the sample solution at several temperatures below its peritectic point until exothermic effect due to homogenization of components ceased almost completely. The extent of formation of the clathrate hydrate can be calculated by measuring the enthalpy change associated with the melting at a eutectic point which exists below the peritectic point.

The heat capacities were measured by low-temperature adiabatic calorimeters [14,15] and collected with an on-line data-acquisition system [16]. Adiabatic calorimeter with a high temperature stability can work not only for the determination of the equilibrium heat capacity but also for the study of slow dynamics [17] governing any relaxation processes that a crystal might exhibit over a temperature range at which freezing process occurs. The time domain covered by this method is 10^2–10^6 s [18], and is complementary with the dielectric spectroscopy. Dielectric measurements on clathrate hydrates were carried out by an LCR meter (Yokogawa Hewlett-Packard 4284A) for 100–1 MHz frequency range and a capacitance bridge (General Radio 1615A) for 20–100 Hz. The sample solution was loaded into a home-made dielectric cell by a syringe under a helium atmosphere. For the acceleration of reorientational motion of water molecule, each sample solution was doped with KOH in the mole fraction of 10^{-4}.

Thermal conductivities of ice and THF clathrate hydrate were measured by a transient hot-wire method [19]. The hot-wire probe, a Ni-wire of 0.1 mm diameter, was placed in a ring of a constant radius inside a Teflon cell. The wire surrounded by a sample is heated by a 1.4 s pulse of constant power and the temperature of wire in terms of its resistance is measured as a function of time to derive the thermal conductivity datum.

3. Results and discussion

3.1. Neopentane family

The heat capacities of NPT, $(CH_3)C(CH_2OH)_3$, are reproduced in Fig. 1. The crystal undergoes a first-order transition at (358.2±0.1) K with an associated large enthalpy change. The crystal of NPG, $(CH_3)_2$-$C(CH_2OH)_2$, also exhibits the corresponding first-order transition into an ODC phase. The thermodynamic quantities associated with the transition are as follows:

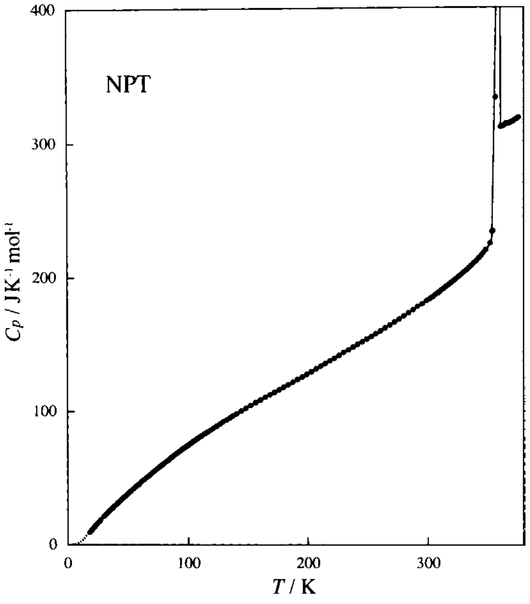

Fig. 1. Molar heat capacity of neopentanetriol $(CH_3)C(CH_2OH)_3$ as a function of temperature.

$$\begin{aligned}\text{NPG}:\ & T_{\text{trs}} = (314.5 \pm 0.1)\,\text{K},\\ & \Delta_{\text{trs}}H = (12.52 \pm 0.02)\,\text{kJ mol}^{-1},\\ & \Delta_{\text{trs}}S = (39.81 \pm 0.08)\,\text{J K}^{-1}\,\text{mol}^{-1}.\end{aligned}$$

$$\begin{aligned}\text{NPT}:\ & T_{\text{trs}} = (358.2 \pm 0.1)\,K,\\ & \Delta_{\text{trs}}H = (21.24 \pm 0.05)\,\text{kJ mol}^{-1},\\ & \Delta_{\text{trs}}S = (59.30 \pm 0.13)\,\text{J K}^{-1}\,\text{mol}^{-1}.\end{aligned}$$

It can be recognized easily from the figures that each transition is accompanied by a rather large heat-capacity jump ΔC_p. The amount of discontinuity between the low-temperature and high-temperature phases in (68.9±0.5) J K^{-1} mol^{-1} for NPG and (79.3±0.5) J K^{-1} mol^{-1} for NPT, respectively. The heat-capacity jump is taken into account when the excess heat capacity due to the transition is extracted from the total value. The temperature, enthalpy and entropy of transition depends systematically on the number of the methylol group in the molecule. The entropy of transition can be written approximately as R In 110 and R In 1250, for NPG and NPT, respectively, in terms of the number of accessible states W referred to as the complexion in the Boltzmann's expression of the entropy. The number W is too large to ascribe it to the disorder of intermolecular origin alone. Molecular conformation associated with the methylol group in each molecule must be excited to give higher entropy and hence higher molecular symmetry on the time average.

The entropy of transition is mush larger than that of fusion. The enthalpy of fusion was determined by DSC in relation to the purity determination. The corresponding entropy change is 9.9 J K^{-1} mol^{-1} for NPG and 9.9 J K^{-1} mol^{-1} for NPT, respectively. These values are comparable in magnitude to 12.7 J K^{-1} mol^{-1} for neopentane [3], and 9.8 J K^{-1} mol^{-1} for pentaerythritol [4]. All the family compounds belong to the category of the "plastic crystals" originally defined by Timmermans [20] for the crystals which have the entropy of fusion less than 20 J K^{-1} mol^{-1}. The phase is optically isotropic and mechanically soft in relation to the highly orientational disorder of the constituent molecules, while keeping the translational invariance with respect to the centers of masses of the constituent molecules. All of the high-temperature phases including the end members are known to belong to the face-centered cubic

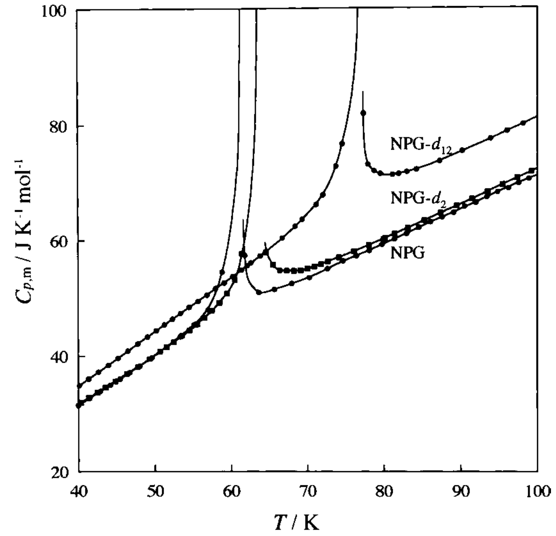

Fig. 2. Molar heat capacity of neopentylglycol $(CH_3)_2C(CH_2OH)_2$ and its deuterated analogs in the lower transition region.

system, being the most efficient structure in packing any pseudo-spherical molecules. Thus the transition entropy may be interpreted on a common basis in terms of the orientational and conformational degrees of freedom each molecule has in the crystalline lattice. At the same time, any proposed model must explain the large amount of heat-capacity discontinuity accompanied by the phase transition.

Another small transition appears at a low temperature only in NPG crystal. The heat capacities of NPG, NPG-d_2 and NPG-d_{12} in the relevant temperature regions are shown in Fig. 2. The transition temperature 60.4 K for NPG shifts to 63.0 K for NPG-d_2 and 76.0 K for NPG-d_{12}, respectively. The isotope effect on the transition temperature is +2.6 K for NPG-d_2 and +15.6 K for NPG-d_{12}. Although the transition is of the first-order nature, the entropy of transition is quite small and almost constant (3.0 ± 0.4) J K^{-1} mol^{-1} for the three compounds. This amount of entropy change reminds us the residual entropy [21] observed in $Na_2SO_4\cdot10H_2O$ crystal in which a four-membered hydrogen-bonded ring is formed per formula unit [22]. There are two possible ways of arranging the hydrogen atoms in each ring, either clockwise or anti-clockwise along the hydrogen-bonded ring. If the disorder remains to exist during cooling the hydrate crystal down to the lowest temperature, the resulting residual entropy amounts to $R\ln 2$. Similarly, there is one such four-membered ring per two molecules in NPG crystal [23]. Thus the observed phase transition seems to be associated with the order–disorder process between the two arrangements. The expected entropy change $(1/2)R\ln 2=2.8$ J K^{-1} mol^{-1} would explain the experimental result. If the phase transition involves the ordering process, however, it is hard to explain the small isotope effect for NPG-d_2 compared to NPG-d_{12}. Both the deuterated compounds should exhibit the same order of the deuteration effect on the transition temperature. Most probably, the hydrogen atoms which are not involved in the hydrogen bonds will play an important role in the transition mechanism. Anyway, structural study on NPG, hopefully by a neutron diffraction technique, is highly desiderant.

The amount of the enthalpy of transition is particularly large for NPG ($\Delta_{trs}H=12.50$ kJ mol^{-1}) and for NPT ($\Delta_{trs}H=21.24$ kJ mol^{-1}). The compounds are suitable as energy reservoir which stores and releases the latent heat while maintaining a constant transition temperature. The compounds can be combined with solar system to form passive solar heating materials. There is no leakage problem which is encountered frequently in a system based on solution materials. The high-temperature phase is mechanically soft and does not damage seriously any kinds of container. Since ODC phases of different substances have mutual solubility, the temperature and energy-storage ability can be modified by adding an appropriate amount of second component [24]. In fact, Font and others [25] have studied thermodynamic features of some alloyed plastic crystals.

3.2. Clathrate hydrates

Natural gases such as methane encaged in the clathrate hydrates can be released easily from the cages by fusing the crystal. The properties of clathrate hydrates are of particular importance, since the systems are the possible natural resources of the fuel for the next generation [26]. The heat capacity of clathrate hydrate enclathrating monatomic molecule, say Ar [27], is a monotonous function of temperature without any indication of anomalous behavior arising from a phase transition or a glass transition. Each guest molecule in the cages of limited space undergoes rattling, which is the motion of intermediate nature between vibration and translation. The total heat capacity can be decomposed approximately into the contribution from the host lattice and from the guest molecules. Since each molecule is located in cavities of almost symmetrical spherical symmetry, the potential function relevant to the motion is the Pöschl-Teller [28] function, which is described in terms of the mass of guest molecule, the inner diameter of cage, and an adjustable parameter reflecting the stiffness of the cage wall. The eigen values have a simple analytical form and the associated partition function can be obtained straightforwardly. Thus the heat capacity of Ar·5.67 H_2O [27] can be well reproduced by adding the terms arising from each contribution. The disorder due to the proton position in the hydrogen-bonded network of the host lattice seems to be frozen-in down to the lowest temperature. The situation does differ, however, for the clathrate hydrates encaging dipolar species.

The low-temperature heat capacity of THF hydrate was measured by MacLean et al. [29] They reported that any heat-capacity anomaly arising from phase transition or glass transition was not observed in the temperature range between 15 and 250 K. This is not accord with the dielectric relaxation experiment which shows disappearance of orientation polarization of the water dipoles at low temperatures. Careful examination of their data shows, however, clear indication of a small anomaly in the heat capacity. In fact, our remeasurement shows a small heat-capacity jump with relaxational nature at around 90 K [30]. This temperature corresponds to the one at which the dielectric relaxation time becomes 10^3 s, being just the timescale of a single heat capacity determination. Spontaneous changes in the calorimetric temperature was followed over a long period to derive the characteristic time for the enthalpy relaxation. The calorimetric relaxation times thus determined can be correlated well with the dielectric relaxation times obtained at higher temperatures [31].

The situation is similar to the case of ordinary ice I_h. The orientational disorder contributing to the dielectric permittivity of ice becomes frozen-in at around 100 K owing to prolonged relaxation time for the water reorientational motion. The disorder can be removed at a first-order phase transition which occurs at 72 K when the ice specimen is doped with alkali hydroxide of the order of 10^{-4} in the mole fraction [32]. This particular kind of impurity dramatically enhances the reorientational mobility by creating a kind of lattice defects which relax the severe constraints for cooperative motion imposed by the "ice rules" [33]. The rules state that each of the four hydrogen bonds to oxygen must be occupied by one proton. In addition, two of the four protons in the bonds must be close to the oxygen so as to form always neutral H_2O species. As a result, there is a strong correlation of the proton movements among the neighbors or equivalently of the reorientational motion of the H_2O molecules.

The same acceleration effect of the dopant on the orientational motion of water molecules can be found in the clathrate hydrates. Fig. 3 shows the heat capacity curves of THF·16.6H_2O crystal with and without addition of KOH. The doped sample exhibits a first-order phase transition at 61.9 K with the entropy change of 2.36 J K^{-1} (H_2O mol)$^{-1}$. As stated earlier, the enthalpy relaxation times determined as a function of temperature can be correlated well with the dielectric relaxation times for the neat sample. Thus the enthalpy relaxation can be confirmed to be ascribable to the freezing out of reorientational motion of the water molecules in the host lattice and the freezing process is released by the catalytic action of the dopant.

Dielectric measurement on the KOH-doped THF clathrate hydrate shows that the dielectric permittivity decreases discontinuously at the transition temperature T_{trs}. The dielectric relaxation observed in the neat sample at temperatures as low as 30 K disappears for the doped sample. The dielectric permittivity below T_{trs} corresponds to that ascribed to the electronic polarization of the crystal. This means that the guest molecules become ordered concomitantly with the host molecules at the transition. Most probably, a strong electric field produced by an ordered arrangement of water dipoles in the host lattice will force the gust molecules in a cavity to align along the field [34]. Unfortunately, structural determination of the ordered phases is not possible. A neutron diffraction experiment [35] for the low-temperature phase of the deuterated THF hydrate shows that the diffraction peaks are very broad contrary to those for the high-temperature phase. This indicates that the size of individual ordered crystallite may be extremely small or the

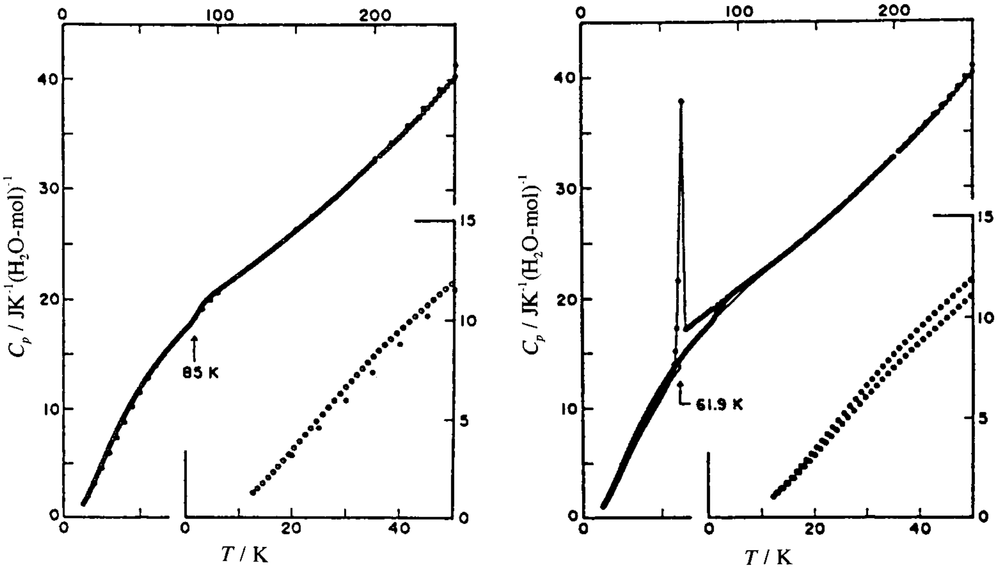

Fig. 3. Molar heat capacity of pure (left) and KOH-doped (right) tetrahydrofuran clathrate hydrate crystals [36].

ordered lattice is highly deformed. The only thing we can draw from the diffraction data is that the low-temperature phase has either orthorhombic or monoclinic structure similar to tetragonal system.

Similar KOH-induced ordering transition is observed at 46.6 K for Ac hydrate, at 34.5 K for TMO hydrate, respectively. Excess heat capacities associated with the ordering transition are summarized in Fig. 4. It is interesting to not that each excess heat-capacity curve has a long tail above respective T_{trs}. The lower the transition temperature, the larger the short-range order effect. The limiting values for the entropy of transition are in the range 2.4–2.5 J K^{-1} (H_2O mol)$^{-1}$ and comparable in magnitude to that of XI→I_h transition in ordinary ice. Although the main ingredient of the phase transition of these clathrate hydrates is the ordering of protons in the host lattice, the transition temperature depends strongly on the guest species. It seems that the guest species with larger molecular size will induce the ordering of the host lattice at higher temperature.

In the clathrate hydrates, the force binding the host molecules together is the hydrogen bond, which is of highly directional character and makes it possible for them to build various cages with open structure. Energetically, the cage structures are less favorable

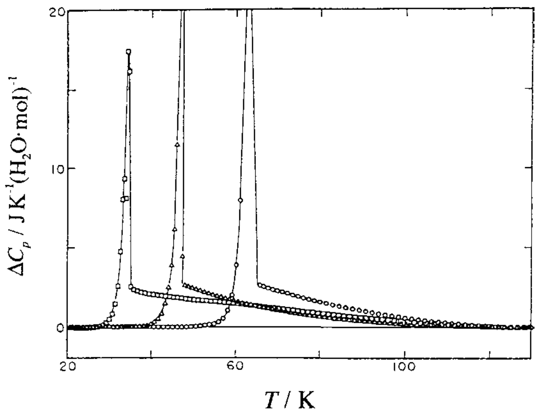

Fig. 4. Excess heat capacities associated with phase transitions of clathrate hydrates encaging tetrahydrofuran THF (○), acetone Ac (●) and trimethylene oxide TMO (□).

compared to the hexagonal ice. The structure is, however, stabilized by van der Waals interaction with appropriate size of the guest molecules enclathrated inside each cage. In the present cases, each guest molecule has negatively charged oxygen atom. The guest molecule reorients inside the cage in addition to the rattling motion. Electrostatic interaction due to close approach of oxygen atom to the cavity wall affects the fluctuation of the water dipoles with respect to the orientation in the lattice to induce local ordering. Dipolar interactions of long range nature among the guest species will also contribute to the ordering process. In this way, the host lattice is considered to control the motion of the guest molecule. At the same time, the guest molecules affect the ordering with respect to the orientation of the water molecules in the host lattice.

For the clathrate hydrate encaging 1,3-dioxolane ($DXL \cdot 17H_2O$), however, only a glass transition due to the freezing out of water motion is observed at 43 K [37] even for a sample doped with KOH. The hypothetical transition temperature would be too low to be observed within a laboratory time. Examination of binary system $DXL_xTHF_{1-x} \cdot 17H_2O$ shows that the estimated transition temperature for DXL clathrate hydrate lies between 20 and 40 K. The acceleration effect of KOH dopant is not enough owing to its limited solubility into the host lattice for the hydrate clathrates which have their ordering transitions at very low temperatures. At the moment, we cannot propose any methods to save the revisited crisis in the third law of thermodynamics. There must be some important factors in determining the ordering process other than the guest property such as dipole moment or van der Waals diameter. Our present knowledge with respect to the relation between the static and dynamic properties of condensed phase is still far from satisfactory.

The thermal conductivity λ of normal and deuterated THF clathrate hydrates [11] are similar in some aspect and dissimilar in another aspect to that of ice I_h [38]. The order–disorder transition with respect to the proton position is manifested as a discontinuous change in thermal conductivity by about 15% for both THF hydrates. The magnitude of discontinuity is nearly the same as that for ice $I_h \rightarrow XI$. The decreases of thermal conductivity at the phase transition can be explained in terms of a change in lattice-vibrational anharmonicity which is caused by the proton disorder in each high-temperature phase.

Both the thermal conductivities of ice I_h and XI [38] are inversely proportional to temperature ($\lambda = A/T$), being typical behavior observed in crystalline substances [39]. On the contrary, the thermal conductivity of THF hydrates increases with temperature below and above the ordering transition. The results are shown in Fig. 5 for the normal and deuterated samples. This glass-like behavior of thermal conductivity appears to be a general features of clathrate hydrates [40]. There must be a strong phonon scattering in determining the rate of heat transportation in these crystals. The important thing is that the glassy behavior in λ is not affected by the ordering transition. Since it is unusual for crystals to exhibit the glass-like thermal conductivity, a reasonable conclusion is that the same mechanism must operate in both of the ordered and disordered phases. The orientational disorder of the guest molecules is not a very important source of phonon scattering [41].

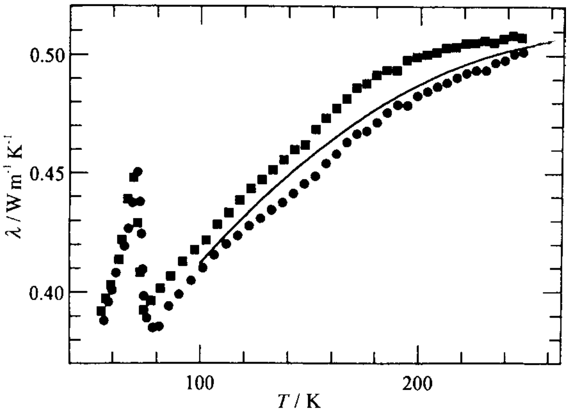

Fig. 5. Thermal conductivity of tetrahydrofuran clathrate hydrate $THF \cdot 16.9H_2O$ (●) and its deuterated analog $THF \cdot 16.9D_2O$ (■).

The resonance scattering model proposed by Tse [42] is used to explain the experimental results. The model is based on the assumption that the acoustic phonons interact with the guest vibrations to yield the phonon scattering. Resonance frequency of the order of 80 cm^{-1} can well reproduce the thermal conductivity data in the high-temperature phase. Thus the long-wavelength acoustic lattice waves help to conduct the heat flux across the crystal. The propagation is scattered periodically through exchange of energy with the localized rotation-vibrational excitations of the guest THF molecules. The loss in thermal energy by the scattering results in higher thermal resistivity, or lower thermal conductivity. Effect of the ordering transition can be taken into account in the model by modifying either the resonance frequency or the scattering constant. The decrease of thermal conductivity at the transition can be explained likely well by the increase of the lattice anharmonicity, as stated above in the case of ice XI→I_h transition. However, we cannot rule out a possibility that the glassy behavior for both phases has different origins in view of the small size of individual crystallite in the low-temperature phase.

4. Concluding remarks

Ordered crystals and glassy liquids are the two extremes in our conception of structural regularity in the solid state. Solid states other than these extreme cases exhibit a variety of structures which are intermediate or partially disordered. It is not uncommon that a liquid crystallize into this type of mesophase before a subsequent transition into an ordered crystalline phase takes place on further cooling. Various properties of the mesophase lie between those of the ordered crystal and disordered liquid. Thus the clarification of relation between the nature of disorder and change in physical property will deepen our understanding of the substance and contribute to enrich the world of materials science.

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