The effect of proton ordering in thermal conductivity of clathrate tetrahydrofuran hydrate

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The effect of proton ordering in tetrahydrofuran hydrate has been detected using a technique based on measurement of thermal conductivity. The thermal conductivity of tetrahydrofuran hydrate was measured by the steady-state potentiometric method in an interval of 2–150 K. Two regimes were selected to observe the effect: (i) slow cooling of the hydrate sample and (ii) doping the hydrate with a small quantity of KOH alkali to a concentration of 10^{-4}. Proton ordering affects the temperature dependence of the thermal conductivity changing its glass-like behavior to crystal-like below 150 K. The phonon maximum that appears in the temperature dependence of the thermal conductivity at $T = 17$ K is attributed to the cooperative process of local proton ordering stimulated by orientational and ionic defects.

1. Introduction

Clathrate hydrates [1] are ice-like solids formed from a nonstoichiometric mixture of water and low-molecular gases or liquids. In clathrate hydrates the water molecules bound by hydrogen bonds form an open cage with numerous polyhedral voids capable of housing guest molecules of other chemically low-active or inactive substances, including inert gases, O_2, CH_4, CO_2, Cl_2, etc. Most gases (Ar, Kr, Xe, O_2, N_2, CO_2, CH_4, H_2S and so on) can form hydrates under moderate excess pressures at room temperature. Crystalline hydrates with relatively large guest molecules (e.g. tetrahydrofuran (THF) and ethylene oxide) can be synthesized easily from a liquid solution.

In most cases clathrate hydrates are cubic-symmetry crystals that may be considered as glassy crystals in which the water molecules execute rotational motion, $T_g = 85$ K [2]. The dynamic and static proton disorder in the hydrogen-bond subsystem typically observed in most polymorphous crystalline forms of ice is caused by delocalization of the protons between two neighboring oxygen atoms [3]. The cooperative process of orientational proton ordering at the O–H...O — hydrogen bonds in the

vicinity of $T = 100$ K is the most interesting feature of these systems [4].

The processes of ordering in molecular solids affect significantly their thermal properties, the thermal conductivity in particular. Normally, at temperature decreasing below the melting point the thermal conductivity of dielectric crystals increases first by the $1/T$ law, then exponentially with temperature up to a phonon maximum and thereafter starts to decrease [5]. In disordered (amorphous, orientationally-disordered crystalline and other) systems the thermal conductivity behaves in an absolutely different glass-like way. At temperature lowering below the melting point the thermal conductivity is weakly dependent on temperature: it decreases slowly, passes through a plateau and decreases again as a quadratic function of temperature [5]. The thermal conductivity of ice Ih has a crystal-like behavior [3], while in clathrate compounds [6–10] it behaves like in amorphous (glassy) solids. It is however intriguing that both the substances are crystals. The clathrate hydrate is a crystal with proton disorder, just like ice under atmospheric pressure. The introduced guest molecules, on the one hand, stabilize the

clathrate hydrate, but, on the other hand, they cause additional lattice distortions in its polyhedral cage-like structure bound by flexible hydrogen bonds [11].

The transition to the proton-ordered state was observed in clathrate hydrates of only a few substances, namely, acetone, tetrahydrofuran and trimethylene oxide clathrate hydrates. It was similar to the transition of ice Ih to the ordered proton state of ice XI at $T_t = 72$ K [3].

The evidence for the proton-ordering transition in ice Ih and clathrate hydrates was obtained by different experimental methods. The origin of this ordering is being discussed in literature. The data on the heat capacity [12–14], the dielectric susceptibility [15–18], the structure [19,20] and other properties [4,21] of ice Ih and acetone, tetrahydrofuran, and trimethylene oxide clathrate hydrates [22,23] show a certain correlation between the proton-ordering transition and the orientational mobility of the water molecules in the presence of structural defects in the crystalline substance. Structural defects, like the Bjerrum D- and L-defects or the ionic OH$^-$ and H$^+$ defects, stimulate the orientational mobility of molecules. The lack of a proton or the presence of two protons between the oxygen atoms are the so-called Bjerrum L- and D-defects, respectively. These defects possess high thermoactivated mobility in the clathrate cage. The theoretical calculation for ice Ih [24] predict a transition to a low-temperature ordered phase at $T = 92$ K. The phase transformation leading to proton ordering is a first-order phase transition. As a consequence of it, a considerable amount of a proton-ordered state is formed within the proton-disordered phase of the hydrate with a small content of impurity [12,14,26–28]. The alkali hydroxide dopants are very efficient in catalyzing the transition to the proton-ordered phase. There are no direct methods of determining the mixed order-disorder state in hydrates, but the presently available neutron diffraction data for ice XI can be quite helpful. According to neutron diffraction measurements [20], the fraction of the ordered phase is small in ice XI, and most of the obtained structure data refer to the disordered phase. The transition is not much affected by deuteration [19]. Inhomogeneous phases were also revealed in KOH-doped ice below 72 K in the investigations of the dielectric properties of doped ice single crystals [29]. The first results of the theoretical analysis of proton ordering in a frustrated model of gas hydrate frameworks has been presented at Ref. 30. Frustration is a qualitative characteristic distinguishing gas hydrate frameworks from other widespread regular structures of water molecules and stimulating research into such systems.

The first measurement of the thermal conductivity of clathrate hydrates dates back to 1981 [31]. The authors found that the thermal conductivity of the clathrates differed drastically from that of ice in magnitude and temperature dependence. Later on, different research groups [6,32,33] investigated the thermal conductivity of clathrate hydrates prepared from a solution of water and low-molecular liquid in temperature range 55–250 K. The thermal conductivity of CH$_4$ hydrate was measured at rather high temperatures [34,35] ($T > 235$ K). The investigation of the thermal conductivity of THF hydrate was performed at 15–100 K [36], but these results were underestimated and showed rather poor agreement with other data on the thermal conductivity of hydrates. Nevertheless, the authors emphasized a glass-like behavior of the thermal conductivity. Resent surveys [10,37] also mention the unusual temperature T and pressure P behaviors of thermal conductivity for some phases and states, which include glass-like thermal conductivity for crystalline clathrate hydrates and crystal-like thermal conductivity for low-density amorphous ice.

The glass-like behavior of the thermal conductivity was also detected in some thermoelectric clathrates and discussed [38–45].

Recently, the thermal conductivity has been investigated on tetrahydrofuran hydrates and gas hydrates of methane [8] and xenon [9] which have different types of clathrate structure. It is found that in a wide range of temperatures 2–220 K the thermal conductivity $\kappa(T)$ of CH$_4$ and THF hydrates is very little dependent on the type of guest molecules or clathrate structure and exhibits the features typical of amorphous or disordered solids. Two factors may be responsible for this unusual noncrystalline behavior of the thermal conductivity in clathrates — the structural disordering provoked by the proton disorder and the motion of guest molecules strongly influencing the lattice vibrations in the clathrate cage. However, proton ordering did not enjoy much interest of previous researchers whereas its effect on thermal conductivity can be rather significant.

The effect of proton ordering on the thermal and other properties of hydrate structures [4,12,22,24,25] is interesting as a cooperative phenomenon. The heat capacities of pure THF clathrate and THF clathrate doped with a small amount of alkali were investigated [12,22]. It is found that the heat capacity of pure clathrate has a small jump and an extended anomaly at $T \approx 85$ K. The features are attributed to local orientational proton ordering in the proton glass. The doping with alkali enhances the heat capacity anomaly, up to a maximum at $T = 61.9$ K [12], and influences considerably the shape of the thermal conductivity curve. The thermal conductivity of doped normal and deuterated THF has a slight maximum at $T \approx 71$ K [6]. The doping effect in the thermal conductivity of ice [4] is observed below $T \approx 74$ K. As the temperature decreases, the thermal conductivity increases (by ~ 17%) in a narrow interval of temperatures. This grows is due to the transformation of proton glass (ice Ih) into the proton-ordered state (ice XI).

The interpretation proposed for the thermodynamic characteristics of this incomplete phase transition [46] can be applied to the phase transformation in a clathrate hydrate. It is found [46] that the growth of a proton-ordered phase inside the proton-disordered one and vice versa leads to an increase in the elastic energy at the interphase boundary. The elastic energy impedes the phase transformation. The mechanism of the proton disorder — proton order transformation in the polymorphous phases of ice (existing under equilibrium vapor pressure) is not entirely clear because some features of this process are still lacking an adequate explanation.

Why does the amount of the impurity dopant have much effect only on the quantity of the ordered phase and leave the thermodynamic characteristics of the transition unaffected [24,25]? An annealing affect was detected at $T \approx 260$ K [29] in the dielectric relaxation of an Ih-ice sample doped with KOH impurity and prepared by a fast-cooling procedure. The new effect has a direct relationship to structural defects (L Bjerrum defects) that develop in the crystal lattice in the presence of extra OH^- ions. It is noted [17] that a guest molecule can be a source of extra Bjerrum defects in the crystal lattice of clathrate hydrate. OH^- ions catalyze the proton disordering–proton ordering transition [47]. The KOH-doped ice contains two sources accelerating the mobility of protons [28]: L-defects and OH^- ions. At low temperatures these sources act in parallel in the ice lattice [29]. The proton mobility induced by L-defects leads to reorientation of the water molecules.

Recent dielectric and calorimetric experiments [18,48] show that the alkali hydroxide dopant causes polarization of the nearest water molecules and promotes orientational ordering at low temperatures. This polarization can be responsible for the weak concentration dependence of the ordered phase content produced by phase transformation.

The introduction of small quantities of KOH alkali to a clathrate hydrate speeds up the orientational motion of the water molecules, thus removing them from the immobilized state and stimulating their ordering. A phase transition occurred at 61.9 K for THF hydrate, 46.6 K for acetone hydrate, and 34.5 K for trimethylene oxide hydrate, respectively. The change in the entropy during the phase transition is about 2.4 J·K^{-1}· mol^{-1}. This value is similar to that typical for dopant-induced transition in ordinary ice Ih [49]. In KOH-doped Ar hydrate no proton ordering-related phase transition occurred in the interval 12–130 K, but was detected a glass transition at $T \approx 55$ K [50]. This means that guest molecules have a certain effect on the thermodynamic properties of proton ordering in the host lattice. The reason may be that the Ar coupling with a hydrogen-bonded system is much weaker than in the THF-molecule.

It should be noted that the proton ordering stimulated by structural defects in both a clathrate and ice Ih occurs at temperatures considerably higher than the phase transition point. The proton-disordered phase becomes dynamically inhomogeneous since it includes some regions with relating and immobile water molecules that exist in the temperature interval preceding the proton-ordering transition.

Here we describe a special investigation of the thermal conductivity of clathrate THF hydrate. The samples were obtained under different growing and cooling conditions to stimulate the effect of proton ordering at the O–H...O hydrogen bonds. Earlier, the effect was observed in the thermal and structural properties and in dielectric susceptibility. It is found that the thermal conductivity is dependent on the temperature prehistory of the sample (for 1,3-dioxolane) [33]. However, most of the previous studies of the thermal conductivity of THF hydrate have paid little attention to the cooling rate applied to samples.

In this study we measured the thermal conductivity on samples that were cooled slowly after growing and on samples doped with KOH impurity which stimulates proton mobility. In both cases, the thermal conductivity demonstrated a crystal-like behavior at low temperatures.

2. Experimental technique

THF hydrate (a pentagonal ring-like molecule, chemical formula C_4H_8O) was prepared by dissolving THF of different chemical purities and bidistilled water in the proportion 1:16.9. Mixture 1 was the same water — THF solution as in Ref. 7. The purity of THF (Across Organics) was 99.9%. The solution was kept at room temperature for about a year. Mixture 2 was prepared just before measurement. The purity of THF (Sigma Aldrich) was 99.9%. Mixture 3 was solution 2 to which KOH alkali was added ($\sim 10^{-4}$). The purity of THF (Lab-Scan) for mixture 4 was 99.8%. The thermal conductivity of the sample prepared from Mixture 4 was identical to that of disperse ice, i.e. no hydrate was formed in it. It is likely that the THF used for this sample could contain a small quantity of impurity which inhibited the growth of hydrate [51]. pH of initial materials of tetrahydrofuran was 7 (considerate neutral).

Crystalline clathrate THF hydrate was grown in a hermetic cell for thermal conductivity measurements [7,52] just before starting the measurement.

Six different polycrystals were grown from three mixtures at different rates of solidification and cooling (see Table 1). Samples 3, 5 were cooled extremely fast (~ 100 K/min). To achieve this rate, the measuring cell was immersed into liquid nitrogen and then transferred rapidly into the cryostat. The rise of the temperature was no more than 140 K. The mounting is detailed elsewhere [9,52]. In contrast, the growing of other samples was

slow. The growth rate was 30 μm/s for sample 1 and 1–3 μm/s for samples 2, 4 and 6. The measuring cell was cooled at the bottom from $T = 280$ K to $T = 220$ K at the growing.

Table 1. Growth parameters of THF hydrate samples.

Sample	Growth rate, μm/s	Cooling rate, K/min	Mixture
1	30	5	1
2	3	0.9	1
3	200	100	2
4	1	0.02	2
5	200	100	3
6	1	0.02	3

According to Ref. 51, the formation of the crystalline structure in clathrate THF hydrate is dependent on the growth rate. At low rates (up to 10 μm/s) an octahedral structure develops while high rates (10–100 μm/s) are favorable for a dendritic structure. Correspondingly, our samples 2, 4 and 6 grown at low rates ($\approx$ 1–3 μm/s) had the octahedral polycrystalline structure. Samples 1, 3 and 5 were dendritic crystals. We can expect that our THF hydrate samples have a structure identical to that in Ref. 51. On a slow growth the flat front of crystallization was moving from the bottom upwards. Under these conditions of crystallization of the liquid solution, small inclusions of ice and pure THF were only possible near the ends of the sample (in its lower and upper parts) and outside the region where the temperature gradient was measured. Recall that the temperature sensors were far from the ends of the container. Recent thermodynamic measurements [53] show that the supercooled aqueous solutions containing close to stoichiometric amounts of THF explosively crystallize in the supercooled liquid state and form the THF clathrate hydrate. This occurs without the formation of ice as an intermediate phase. Since the temperature sensors were fixed with copper wires running inside the measuring container, these were sources of structural defects in the growing sample. The details of the measuring cell and the sample growth are described in Refs. 7,52.

3. Results and discussion

The thermal conductivity of the THF hydrate samples was measured in the interval 2–150 K by the steady-state potentiometric method [52]. Note that the measurement results on the thermal conductivity of each sample were reproducible when the temperature was cycled.

The measured thermal conductivities of four samples grown from mixtures 1 and 2 (see Table 1) are shown in Fig. 1 on the semilogarithmic scale. Their temperature dependences $\kappa(T)$ differ considerably. The thermal con-
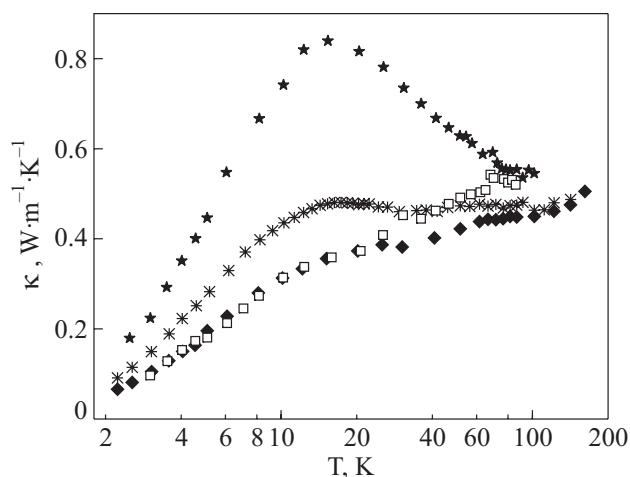

Fig. 1. Temperature dependence of the thermal conductivity of THF hydrate: sample 1 ($\square$), sample 2 ($\star$), sample 3 ($\blacklozenge$), sample 4 ($*$) (see Table 1).

ductivities of samples 1 and 3 (fast cooling) have a glasslike behavior typical of disordered solids: the curve $\kappa(T)$ shows a nearly quadratic dependence at low temperatures, a smeared plateau at rising temperature and then a further growth of the thermal conductivity. The new results are in good agreement with literature data for $\kappa(T)$ [7]. However, $\kappa(T)$ behaves quite differently in the case of slow cooling (samples 2 and 4). It is described by the curve typical of crystalline solids: $\kappa(T)$ increases when the temperature lowers, reaches a maximum and then starts to decrease. The $\kappa(T)$ — maximum at $T = 17$ K is particularly distinct for sample 2. The qualitatively dissimilar behaviors of $\kappa(T)$ for samples cooled at different rates from $T = 280$ K to $T = 220$ K suggest that the thermal conductivity is sensitive to the cooperative processes in the hydrogen-bond subsystem of the clathrate hydrate. The proton transport in the clathrate hydrate plays an important role in proton ordering [3,12,22]. The difference in the cooling rates has no effect on the crystalline clathrate cubic structure of hydrates. It is noted [17] that a guest molecule can be a source of extra Bjerrum defects in the crystalline hydrate lattice. When the cooling rate is high, structural defects such as Bjerrum D and L or ionic OH^- and H^+ can appear in the sample. It is appropriate to consider the orientational disordering of the molecules in hydrates and its possible influence on heat transfer. Normally, two types of orientational disorder can exist in THF hydrates. One is connected with the spatial distribution of protons (hydrogen bonds) in the clathrate cage of the water molecules. The other is determined directly by the THF molecules occupying only the largest 16-hedral voids. The double disorder is a specific feature of the THF hydrate. In such systems, the proton-ordered configuration is most energy-advantageous when the tempera-

ture decreases slowly. In contrast, on fast cooling the hydrogen atoms localize more quickly leaving little time for the protons to order. As a result, the protons appear to be «frozen» in random positions and form a proton-disordered phase (proton glass). Naturally, proton disorder affects a crystal field inside clathrate cavities, including those in which are arranged guest molecules. In this case, the thermal conductivity can have a glass-like temperature dependence [32].

At present the nature of heat transfer in clathrate compounds has been discussed actively [38–42,54]. Several mechanisms have been proposed to describe the weak temperature dependence of the lattice thermal conductivity of clathrates: (i) tunneling [33,44], which may be significant only at low temperatures; (ii) a change in the phonon scattering at charge carriers [38] which may depend on the sample state and (iii) a symmetry-breaking off-center mass defect along with enhanced phonon-rattler coupling for the off-center atoms [39]. We can consider the anomalous glass-like thermal conductivity of a crystalline clathrate as a result of scattering of the thermal phonons belonging to the framework by the «rattling» vibrations of the guest in the clathrate cages. The low glass conductivity was attributed to the strong coupling between the «rattling» vibrations of the guests and the phonons [39,43,54]. This coupling is depended on many factors. It is the coupling strength that is responsible for a crystalline or glass-like behavior of the thermal conductivity in thermoelectric clathrates. The phonon conductivity $\kappa_L(T)$ of thermoelectric clathrate is strongly dependent on the type of charges and their concentration [40,42]. $\kappa_L(T)$ of the n-type $Ba_8Ga_{16}Ge_{30}$ has a sharp crystalline maximum, while $\kappa_L(T)$ of a p-type sample exhibits a glass-like dependence [40,45]. The transition from a glass-like dependence $\kappa_L(T)$ to a crystalline one in n-type Sr-, Eu-based thermoelectric clathrates was not connected with a change of the charge. The transition occurred due to a physical or chemical decrease in the size of the clathrate cage, which suppresses the off-center motion of the guest particles [45]. The Sr and Eu ions of the type I Ge clathrates are obviously off-centered and execute more intensive «rattling» vibrations leading to rather strong coupling to the framework of the n-type clathrate.

As a result, there is a change to a glass-like dependence of $\kappa(T)$. The off-center position of the quest particles enhance the above-mentioned phonon-rattler coupling. The guest that holds an off-center position contributes a large symmetry-breaking mass-defect. None of these models can account for the fundamental distinction in the thermal conductivities of n- and p-type thermoelectric clathrate. Defects and nonstoichiometry are normally features arising from n-type semiconducting state. The type (n- or p-type) of change carriers and their concentration

are dependent on deviation from the perfect stoichiometry and random distribution of Ga and Ge [41].

The factor responsible for the coupling between the local modes of the guest molecule and acoustic phonons is dependent both on the off-center motion of the guest and on the arrangement of the protons between the oxygen atoms, forming the clathrate cages. It is reasonable to assume that the glass-crystal transition in the clathrate THF hydrate occurs because the coupling between local modes of the guest THF molecule and the acoustic phonons becomes weaker due to the change from proton disorder to proton order.

According to heat capacity data [12,22], the transformation from the proton-disordered phase into the energy-advantageous ordered state occurs in THF hydrate at the characteristic temperature 85 K. But in actual practice this transition is not necessarily determined by the weak thermoactivated proton diffusion (or its absence) between the neighboring atoms. It can be stimulated by adding a small amount of hydroxide or by generating proton defects. We assumed that very slow cooling could also trigger the process of proton ordering. For this purpose samples 4 and 2 were cooled at the possibly lowest rates. Their thermal conductivities were drastically different from those measured on the fast-cooled samples. Below 100 K the thermal conductivity of sample 2 increases in a crystal-like manner. The thermal conductivity of sample 4 also has a maximum but it is less pronounced than for sample 2.

Proton ordering was also stimulated by another known method — addition of a small amount of hydroxide to the clathrate sample. The KOH impurity produces an excess of negative OH^- ions and increases the number of orientational point defects (Bjerrum proton L- and D-defects) [3]. Orientational defects develop when the regular arrangement of protons around the oxygen atom is disturbed. Each oxygen atom is bonded covalently to two protons. Normally, there is one proton between two neighboring oxygen atoms.

The alkali concentration in samples 5 and 6 was 10^{-4}. The thermal conductivity was measured, as before, on fast- and slowly-cooled samples. The fast-cooled sample had a glass-type thermal conductivity with a small smeared peak (see Fig. 2) whose position coincided with the one found for doped THF hydrate [6] and attributed to the transition from the proton-disordered phase to the proton-ordered state. Sample 6 was prepared combining two techniques — slow cooling and doping with alkali. The thermal conductivity of this sample is of the crystal-type and has a very interesting feature. As the temperature decreases from 80 K, the thermal conductivity grows, has a kink at $T = 61.9$ K and then continues to increase. Since this feature is observed only for the slow-cooled doped sample, it can be interpreted as the sign of
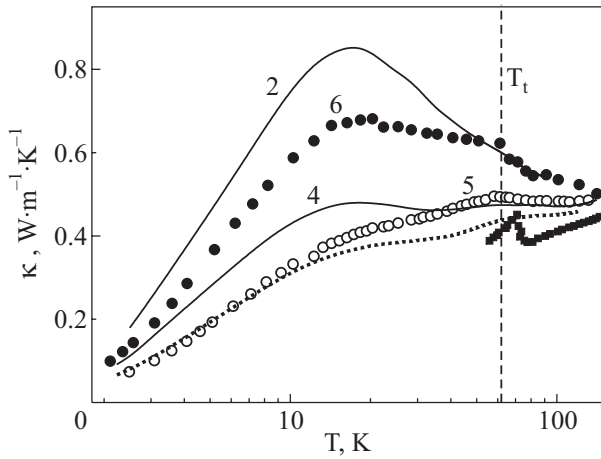
Fig. 2. Thermal conductivities of doped KOH samples of THF hydrate: sample 5 (O), sample 6 (●), smooth thermal conductivities of samples 2 and 4 (——), smooth thermal conductivity of sample 3 (· · ·) (see Fig. 1), [6] (■). $T_t = 61.9$ K is the transition temperature from proton disordered high temperature phase to proton ordered low temperature phase [6].

the impurity effect on the process of ordering in the crystal. Neutron-diffraction studies of THF hydrate were been performed with the high-resolution power diffractometer at ISIS [19]. In their neutron diffraction study Yamamuro *et al.* [19] observed broadening of the diffraction peaks of fully deuterated THF clathrate hydrate in the low temperature region. The indices of the broadened peaks corresponded to a tetragonal structure. The formation of the tetragonal structure in the hydrate suggests that both the water molecules and the guest THF molecules are involved in ordering. However, following ice rules [3], protons in the given tetragonal structure cannot be ordered. It was therefore assumed [19] that below 80 K some orthorhombic domains could form in the hydrate around the KOH impurity, and the impurity molecules stimulated proton ordering in the nearby local domains. As the temperature decreases, the process is progressing and the local domains expand forming a quasi-tetragonal structure. On the dependence of $\kappa(T)$ for sample 6, growth of the thermal conductivity below 80 K and the kink on the curve $\kappa(T)$ are connected most likely with a formation of proton ordered local areas and transition of this areas in quasi-tetragonal structure.

At $T \approx 20$ K the thermal conductivity of sample 6 has a significant maximum $\kappa_{max} = 0.68$ W·m^{-1}·K^{-1} which is about 29% higher than of slowly-cooled alkali-free sample 4 and almost 23% lower than the maximum for sample 2. The highest and most distinct maximum was observed for sample 2 grown from the solution that had been kept in a closed clear bulb under the normal conditions for about a year. We assume that positive and negative ions were formed during the light exposure, which,

like the KOH impurity, enhanced the proton diffusion in the process of slow cooling of the sample.

It is known that even small amounts of impurity added to high-purity top-quality dielectric crystals can suppress the maximum of thermal conductivity. We have a reverse effect in THF hydrate: the thermal conductivity is observed to increase when a small quantity of KOH is introduced into the hydrate. As was mentioned above, the introduced impurity can change the structure of the hydrate into the quasi-tetragonal one [19]. As a result, the crystal develops a mixed state consisting of regions with ordered and disordered protons. In this case the measured thermal conductivity is actually the effective thermal conductivity $\kappa_{eff}(T)$ determined by the relation between the thermal conductivities of the two phases. $\kappa_{eff}(T)$ can be influenced by the complex spatial structure of the mixed state, which varies with the concentrations of the proton-ordered and proton-disordered phases. $\kappa_{eff}(T)$ can be described as [9,10]

$$\kappa_{eff}(T) = (1 - \chi)\kappa_g(T) + \chi\kappa_{cryst}(T), \qquad (1)$$

where χ is a variable parameter of the concentration of the proton-ordered phase, κ_g and κ_{cryst} are the thermal conductivities of the THF hydrate in the proton-disordered (glass-like) and proton-ordered phases, respectively. Since κ_{cryst} is unknown in our case, in our estimation we took it equal to the thermal conductivity of disperse ice [8] because the ordering in ice causes only a minor (17%) increase in the thermal conductivity and does not affect its crystal-like temperature dependence. The thermal conductivity of sample 3 was taken for κ_g because it has a strictly glass-like behavior. The temperature dependences of the calculated concentration χ of the proton-ordered phase in samples 2, 4, 5 and 6 are shown in Fig. 3. It is seen that the ordered phase concentration in samples 2 and 4 (slow growth, no KOH) increases when the temperature lowers. This means that the process of ordering is spread in temperature. In slowly-grown KOH-doped sample 6 the concentration of the ordered phase is not influenced by the phase transition below $T = 62$ K and has a plateau at $\chi = 7\%$. The estimated χ of the ordered phase agrees with the concentration obtained from the anomalous heat capacity of a KOH-doped sample [2]. The concentration of the ordered phase is much lower (< 2%) when a KOH-doped sample (sample 5) is cooled extremely fast. In Fig. 3 χ of sample 5 is observed to decrease slighly at $T < 50$ K. This can be attributed to a certain inadequacy of the model in the low temperature region, since the calculation by Eq.(1) assumes κ_{cryst} to be equal to the thermal conductivity of fine-disperse ice.

It is found [7] that the thermal conductivity of pure THF hydrate is independent of the growth and cooling conditions, if the velocity of the crystallization front varies within 0.2–2 mm/min and the rate of cooling to the
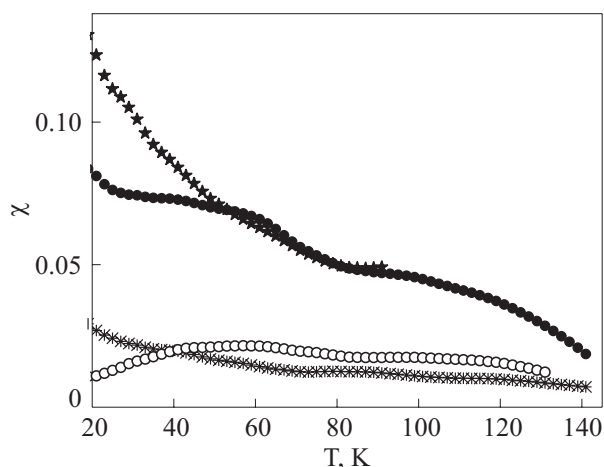
Fig. 3. Calculated concentration of the proton-ordered phase as a function of temperature: sample 2 (★), sample 6 (●), sample 4 (✳), sample 5 (○) (see Table 1).

working temperature is 5–10 K/min. In this case we observe the thermal conductivity typical of amorphous substances. However, if a good-quality sample is cooled slowly enough to develop the proton-ordered state, the thermal conductivity changes and has a crystal-like behavior.

The crystalline and glass behavior of the dependences $\kappa(T)$ of the clathrate THF hydrate and the nonstoichiometric thermoelectric $Eu_8Ga_{16-x}Ge_{30+x}$ clathrate is shown in Fig. 4 [40].

The thermal conductivity of α-$Eu_8Ga_{16-x}Ge_{30+x}$ ($0.28 \leq x \leq 0.48$) [40] has a glass-like dependence on temperature, which is also observed for fast-cooled THF hydrate (sample 3 in this study). Slowly-cooled THF
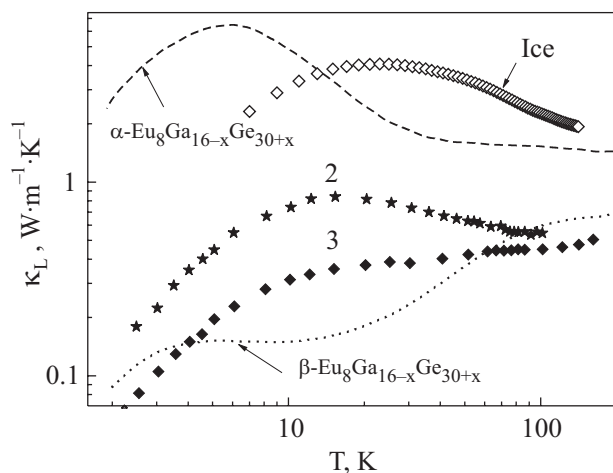
hydrate (sample 2 in this study) and thermoelectric β-$Eu_8Ga_{16-x}Ge_{30+x}$ ($0.49 \leq x \leq 1.01$) [40] exhibit a $\kappa(T)$-dependence that is typical of crystalline substances: the thermal conductivity grows with temperature, reaches a maximum and then decreases at further increasing temperature. The lattice thermal conductivity (κ_L) of α- and β-$Eu_8Ga_{16-x}Ge_{30+x}$ can be described by phonon-charge-carrier scattering at low temperatures and resonant scattering at higher temperatures [40].

This special investigation of the thermal conductivity of clathrate THF hydrate has provided an additional evidence in favor of the effect of proton ordering. We used samples prepared under different growth and cooling conditions and thus could observe the effect on one substance. The two methods employed to observe the effect-prolonged cooling and doping the hydrate with a small quantity of alkali-produce, jointly and individually, strong influence on proton ordering at O–H...O hydrogen bonds. It is found that thermal conductivity is dependent on the temperature prehistory of the sample. The samples that were cooled slowly after their growth and doped with KOH impurity stimulating proton mobility had the crystal-type thermal conductivity in the interval 10–130 K with a smeared phonon maximum at 17 K. The effect may be a consequence of the cooperative process of local proton ordering stimulated by orientational and ionic defects. It is found that the thermal conductivity curve has a kink at $T = 61.9$ K when the cubic $\rightarrow$ quasitetragonal structure transformation occurs in the hydrate.

Fig. 4. Distinctions in the behavior of the thermal conductivity of hydrate and thermoelectric clathrate compounds. Tetrahydrofuran hydrate: sample 2 (crystal behaviour) (★) and sample 3 (glass behaviour) (◆), this work; $Eu_8Ga_{16-x}Ge_{30+x}$ clathrate: dash line shows crystal behavior, dot line — glass behavior [40]. Thermal conductivity of the fine-dispersed ice [8] (◇).

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