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THERMAL CONDUCTIVITY OF NORMAL AND DEUTERATED TETRAHYDROFURAN CLATHRATE HYDRATES

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Abstract—The thermal conductivity λ of normal and deuterated tetrahydrofuran (THF) clathrate hydrates has been measured at temperatures in the range 55–250 K and at pressures up to 0.16 GPa. The normal and deuterated samples exhibited the same values of λ to within 5%. At isobaric heating, the transition from the proton ordered low temperature (LT) phase to the proton disordered high temperature (HT) phase was detected as a discontinuous decrease of λ by about 15% for both the normal and the deuterated samples. The magnitude is nearly the same as that found previously for the related transition phase XI$\longrightarrow$phase Ih of ice and might be due to a change in the lattice anharmonicity. The thermal conductivity of the LT and HT phases increased slightly with increasing temperature and, hence, these *crystalline* phases exhibited both a glass-like $\lambda(T)$. These results can be described using the resonance scattering model in which the phonons are scattered against THF vibrations. The LT phase of both samples exhibited a slight increase of λ with increasing pressure whereas that of the HT phases was roughly independent of pressure, showing that λ does not depend on density.

Keywords: C. high pressure, D. defects, D. phase transition, D. thermal conductivity.

1. INTRODUCTION

Ordered crystals and glassy liquids are the two extremes in our conception of structural regularity in the solid state. Solid states other than these exhibit a variety of structures which are intermediate or partially disordered [1]. It is quite common that a liquid crystallises into this type of mesophase before a subsequent transition to an ordered crystal phase takes place on further cooling. This partial ordering in discrete steps makes it convenient to study the effect of structural disorder on physical properties such as the thermal conductivity λ. The behaviour of λ in monatomic crystals is well understood [2,3] whereas the knowledge of λ in glassy liquids and other disordered states can be improved. In this paper, we shall present results for λ of normal and deuterated tetrahydrofuran (THF) clathrate hydrates and discuss how λ is affected by structural disorder. Clathrate hydrates of hydrocarbons, such as CH_4 and C_2H_6, exist in large quantities in nature. Since these systems have a potential as an energy source in the future, the properties of clathrate hydrates are of particular interest.

Clathrates constitute one class of inclusion compounds in which the cages in the host structure can accommodate various types of guest molecules with suitable sizes and shapes [4]. One type of clathrate compound is clathrate hydrates where the host is H_2O molecules forming several kinds of Archimedes' polyhedral cages through hydrogen bonds. THF can be enclathrated in the type II clathrate hydrates classified by von Stackelberg and Müller [5].

At least two different types of structural disorder can occur in THF clathrate hydrate crystals. One is associated with the H_2O molecules and the other with the THF molecules. In the host lattice, each oxygen is hydrogen-bonded to four other oxygens. Between two adjacent hydrogen-bonded oxygen atoms is a double-minimum potential for accommodating protons. Since the local structure of the hydrogen-bond network is similar to that of phase Ih of ice (ice Ih), the location of the protons in the potential wells will be governed by the ice rules proposed by Bernal and Fowler [6]. These rules state that each of the four hydrogen bonds to an oxygen must be occupied by one proton. That is, only one of the two wells in a bond is occupied by a proton. In addition, two of the four protons in the bonds must be in potential wells close to the oxygen. It follows that structural disorder associated with the proton positions can arise. This disorder can also be described in terms of orientational disorder of the H_2O molecules.

The degrees of freedom for the position of a proton in a clathrate hydrate are essentially the same as that of a proton in ice Ih. It is known that an ordinary ice

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crystal exhibits residual entropy [7] arising from freezing of proton disorder. Therefore, it is reasonable to assume that proton disorder in clathrate hydrates should be present to approximately the same extent as in ice Ih. In fact, data from dielectric spectroscopy [8,9], nuclear magnetic resonance (NMR) [10] and adiabatic calorimetry [11] can be interpreted well in terms of proton disorder in THF clathrate hydrate.

The other type of structural disorder that can arise in THF clathrate hydrate is associated with the orientation of the guest molecules. Since the interaction between the THF and H_2O molecules is considered to be weak and the THF molecules are located inside almost spherical 16-hedral H_2O-cages, they exhibit a large degree of orientational disorder, at least at high temperatures. Results from dielectric spectroscopy [8,9], NMR [10] and adiabatic calorimetry [11] support such a picture. For instance, data for dielectric loss [8,9] exhibit two dispersion regions which can be attributed with confidence to the relaxation of the orientation polarisation of the H_2O and the THF molecules, respectively.

In the case of ice Ih, it is apparent from the existence of residual entropy that the proton motions essentially freeze out at a temperature which is higher than the temperature for a possible transition to an ordered proton state. This is probably due to the fact that the constraints imposed by the ice rules make the motion of a proton strongly correlated with those of other protons and therefore severely restricted. Tajima *et al.* [12] have shown that a small amount of KOH doped into the ice lattice induced a first-order phase transition from the proton disordered phase Ih to the proton ordered phase XI at 72 K. It is reasonable to assume that the KOH dopant incorporated in the ice lattice relaxes the constraints imposed by the ice rules, by creating a kind of orientational defect [13], and therefore accelerates drastically the proton motions. This increase in the proton mobility makes it possible to realise the ordering transition within the time of an experiment.

In analogy with the transition found in ice, it has been shown that THF clathrate hydrate doped with KOH exhibits a transition at 62 K [13,14]. This transition has been associated with the ordering of protons [13,14], as that in ice at 72 K. It was, furthermore, suggested that the guest molecules become ordered at this transition. This suggestion was based on the fact that no dielectric dispersion has been observed below this transition, indicating that the reorientational motions of the THF molecules have stopped.

The thermal conductivity of THF clathrate hydrate (undoped) has been studied previously by several investigators [15–19]. Ross *et al.* [15] were the first to report data for λ of THF clathrate hydrate in the temperature range 100–260 K. They found an unusual temperature dependence of λ which resembles those of glassy liquids [2,3]. That is, λ increased slightly with increasing temperature. As is well-known, λ for ordered crystals decreases with increasing temperature in this range (100–260 K). In general, λ varies roughly as T^{-1} for ordered crystals above the Debye temperature.

A glass-like λ appears to be a general feature of clathrate hydrates [20]. In one work, however, the result for a clathrate hydrate (1,3-dioxolane) was found to depend on the thermal history [21]. A rapidly cooled sample (8 K min^{-1}) yielded a glass-like λ whereas a slowly cooled sample (0.8 K min^{-1}) yielded a crystal-like λ. Such dependence of thermal history has not been observed in any other of the numerous investigations on λ of clathrate hydrates and, as pointed out previously [20], can therefore not be regarded as substantiated.

The generally observed glassy behaviour of λ for clathrate hydrates must, most likely, be due to the same reason. Initially the orientational disorder of the THF molecules was considered as a possible source for the glassy behaviour [15,19]. It is well established that ordinary orientationally disordered phases like plastic crystal phases commonly exhibit a glass-like λ [22]. If the THF molecules were alone in the lattice and exhibited reorientational motion among several preferred orientations then the phase would be regarded as a plastic crystal phase [1]. (It should be noted that the ice can be regarded as an orientationally disordered crystal but not a plastic crystal.) The situation for a clathrate hydrate is more complicated since we must consider both the host lattice and the guest molecules. One expects that the strongly bonded ice lattice should provide the main path for the heat flow whereas the THF molecules could possibly be regarded as lattice defects that scatter the phonons. However, since there is only a weak interaction between the ice lattice and a THF molecule it has been argued that the THF molecules could not provide the strong phonon scattering necessary to obtain the glass-like λ [21,23]. Furthermore, the clathrate hydrate of the monatomic guest xenon also shows glass-like behaviour which obviously cannot be due to guest orientational disorder [24]. Another model in which the vibrational motions of the guest interact with the host lattice has been proposed [24–26]. It has been argued that a strong resonance scattering mechanism can result from this interaction, which would then explain the glassy behaviour [25,26]. This model can describe the data for λ of all clathrate hydrates but is in conflict with earlier arguments of weak interactions between the host lattice and the guests [21,23]. Data for a clathrate which can be synthesised both with and without a guest (Dianin's compound) [27] show that λ is glass-like irrespective of the presence or absence of the guest species, which raises questions about the model. A third way to explain the results has been concerned with the large unit cell of clathrate hydrates [23]. Dharma-wardana [23] showed that λ could become glassy as the number of vibrating units in the unit cell becomes large. This result was based on a finding that $\lambda \propto n^{-2/3}$, where n is the number of atoms in the unit cell [28]. (The number of 'atoms' was considered to be the same as the number of H_2O molecules [23].) In order to obtain this dependence, however, it was assumed that the atoms in each unit cell have masses or bonds which differ substantially [28]. The application of the formula ($\lambda \propto n^{-2/3}$) in the case of clathrate hydrates might therefore be questioned.

The thermal conductivity of the low-temperature phase, which is stable at temperatures below 62 K, has not been investigated previously. As described above, both the H_2O and the THF molecules probably become orientationally ordered in this phase. Consequently, the change in λ at the transition should reflect the extent to which this disorder affects λ and, therefore, provide information about the glass-like behaviour for λ of the high-temperature phase.

2. EXPERIMENTAL

We used the transient hot-wire method [29] to measure the thermal conductivity λ. The hot-wire probe used was a Ni-wire (0.1 mm diameter) placed horizontally in a ring of constant radius within a Teflon cell. The probe, surrounded by the medium under investigation, was heated by a 1.4 s pulse of about constant power and the wire resistance was measured versus time. This enabled the temperature rise of the wire to be determined. A theoretical expression for the temperature rise was fitted to the data points, thereby yielding λ. For temperatures above 100 K, the inaccuracy was estimated as $\pm 2\%$ [29]. Owing to the decreased sensitivity of the hot-wire, the inaccuracy in λ increases with decreasing temperature and was $\pm 4\%$ at 40 K. The standard deviation was an order of magnitude smaller than the inaccuracy.

The Teflon cell was mounted in a piston-cylinder type of pressure vessel of 45 mm internal diameter and the load was applied using a 5 MN hydraulic press. Temperature was varied by cooling or warming the whole pressure vessel and was measured using an internal Chromel versus Alumel thermocouple which had been calibrated against a commercially available silicon-diode thermometer. Pressure was determined from load/area with an empirical correction for friction which had been established using the pressure dependence of the resistance of a manganin wire. The vessel was cooled with a built-in refrigerator using a closed helium gas cycle. The apparatus has been described in detail elsewhere [30].

Commercial reagent of THF purchased from Kishida Chem. Co. was dried using molecular sieves (4 Å), first by coexistence for five days and then by refluxing overnight. Subsequently, THF was purified by fractional distillation with a spinning-band rectifier. An analysis of the sample using gas chromatography revealed an insignificant content of organic impurities. The water content in the purified THF was determined by the Karl–Fisher method to be less than 0.01% in mole fraction. A standard aqueous solution of KOH with a concentration of 0.01 mol dm^{-3}, which corresponds to a mole fraction of 1.8×10^{-4} of KOH against H_2O, was used for the formation of the doped clathrate hydrate.

For the deuterated samples, THF-d_8 (deuteration level > 99.5 %) and KOD in D_2O solution purchased from Wako Pure Chemicals were used without further purification. For both the normal and the deuterated specimens, two sample solutions with different compositions were prepared gravimetrically by mixing the component liquids in a dry atmosphere of N_2 gas. One composition was chosen with a slight excess of the guest compared with the ideally stoichiometric one which is THF·17 H_2O under equilibrium conditions. The other composition was chosen to be close to the stoichiometric ideal one. The compositions of the produced samples THF·nH_2O were in the range $n = 16.7$–17.1. It was found that excess ice occurred in a sample of stoichiometric composition. This made it possible to quantify the effect on λ of excess ice in the sample. Using the Maxwell formula [3], the data were transformed to a composition of THF·16.9 H_2O which seems to be the 'best' composition if we consider that excess ice otherwise occurs under experimental conditions.

3. RESULTS AND COMPARISON WITH PREVIOUS WORK

Figure 1 shows the results for $\lambda(T)$ of both the normal and the deuterated samples. The decrease of λ at about 70 K for both samples are due to the order-disorder transition described in the introduction. As can be seen in Fig. 1, the temperature dependence of λ is glass-like for both the low temperature (LT) phase and the high temperature (HT) phase. That is, λ increases slightly with increasing temperature, which is a completely different behaviour from that normally found for crystals ($\lambda \propto T^{-1}$). These results indicate that there is a strong phonon scattering mechanism present in both phases.

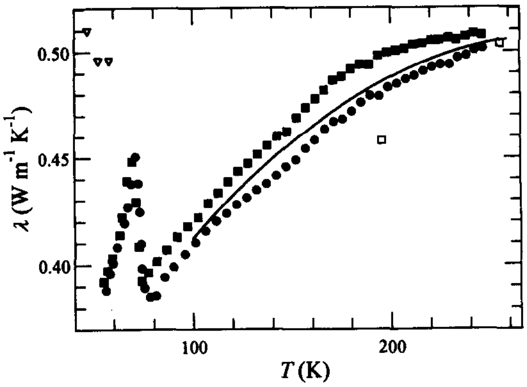

Fig. 1. Thermal conductivity plotted against temperature for: (■) THF·16.9 D_2O, (●) THF·16.9 H_2O, (—) THF·16.5 H_2O [16], (▽) THF·16 H_2O [17], (□) THF·17 H_2O [18].

As shown in Fig. 1, the results for λ of the HT phase of THF clathrate hydrate agree fairly well with the majority of previous results [15–18]. The data presented in Fig. 1 were obtained after the sample had been cooled from the crystallisation temperature at a rate of roughly 1 K min^{-1}. Furthermore, the sample had been annealed at the crystallisation temperature for about 20 min in order to complete the crystallisation.

One earlier work [19] yielded results for λ which were 30% lower at 180 K than those obtained previously [15–18]. This discrepancy was explained in terms of excess ice in the samples of previous workers. It is true that excess ice can increase λ, due to a much larger λ for ice than for THF clathrate hydrate. However, in our case with a KOH-doped sample, any excess ice would yield an extra transition: ice XI⟶ice Ih. Such a transition was indeed detected (not shown) for a sample of almost ideal composition (see Experimental Section). Samples of compositions with a slight excess of THF from the ideal composition did not yield the ice XI⟶ice Ih transition and the data agreed approximately with previous results [15–18].

As can be seen in Fig. 1, the values of λ for the normal and the deuterated samples differ less than 5%, which is almost within experimental inaccuracy. Absence of any significant isotope effect between normal and deuterated samples has been found in ice Ih as well as in many high pressure modifications of ice [31].

As shown in Figs 2 and 3, λ depends only weakly on pressure, especially for the HT phase which exhibits an almost pressure independent λ. This result for the HT phase of the normal THF clathrate hydrate has been noted before [16]. In general, λ for crystalline phases shows a notable increase with increasing pressure [22]. There are a few exceptions, such as ordinary ice Ih [32], phase I of NH_4F [33] and phase II of CuCl [34] which all exhibit a decreasing λ with increasing pressure. In the case of ice Ih, this behaviour has been explained as being a result of softening of the transverse lattice modes with pressure [35]. As is well-known, ice Ih has a negative derivative $\mathrm{d}P/\mathrm{d}T$ for the melting curve, which results in melting when ice Ih is isothermally pressurised above 250 K. Like ice Ih, the substances NH_4F [36] and THF clathrate hydrate [37] also exhibit a negative $\mathrm{d}P/\mathrm{d}T$ for the melting curve. In the case of phase II of CuCl, the phase boundary line to the high pressure modification has a negative slope [38]. It probably follows that a negative $\mathrm{d}P/\mathrm{d}T$ for a phase line, especially the melting curve, provides an indication for a weak or even negative pressure dependence for λ of the low pressure modification.

4. DISCUSSION

In this section, we shall discuss our results by using the theories which have been put forward to explain the glassy behaviour for λ. Since deuterated THF clathrate hydrate exhibits behaviour of λ similar to that for normal THF clathrate hydrate, we will discuss only λ for the latter.

A first important observation is that the glassy behaviour for λ is not affected by the HT→LT phase transition. Since it is unusual for crystals to exhibit glass-like λ, a reasonable conclusion is that the same mechanism causes the glassy behaviour in both phases. In the case that the mechanism is strong phonon scattering, it should be almost equally strong in both phases. This rules out molecular orientational disorder as the scattering source since the LT phase is most likely in orientational order whereas the HT phase is orientationally disordered. Our results support therefore the previous findings that guest orientational disorder is not a very significant source of phonon scattering [24].

The resonance scattering model [25-27] can be investigated using the normal relaxation-time theory for λ given by [2,3]

$$\lambda = \frac{k_B^4 T^3}{2\, v\, \pi^2 \hbar^3} \int_0^{\theta_D/T} \tau(x) \frac{x^4 e^x}{(e^x - 1)^2} \mathrm{d}x \qquad (1)$$

where θ_D is the Debye temperature, v is the phonon velocity, $\tau(x)$ is the resultant relaxation time, $x = \hbar\omega / k_B T$ where ω is the phonon angular frequency and the other symbols have their usual meanings. The formula was originally derived for a monatomic simple crystal but has been successfully used to describe $\lambda(T)$ of polyatomic crystals [2,3].

The theory described by eqn (1) does not take into account changes in λ arising from thermal expansion. It follows that in order to make the best comparison

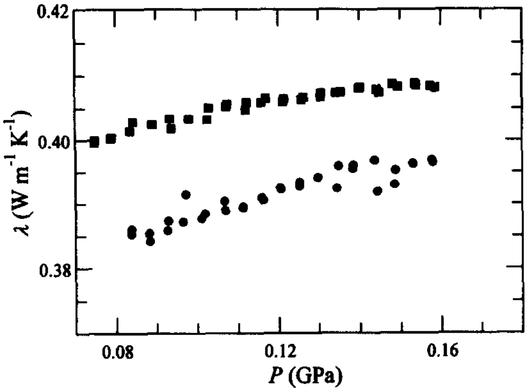

Fig. 2. Thermal conductivity plotted against pressure for THF·16.9 H_2O: (■) high temperature phase at 100 K, (●) low temperature phase at 58 K.

with theory, the measured isobaric data should be transformed to isochoric conditions. However, as seen in Fig. 2, λ is almost independent of pressure. Consequently, λ is almost independent of density and it follows that there is no significant difference between the isobaric and the isochoric data for λ of THF clathrate hydrate.

The resonance scattering model is based on the assumption that the acoustic phonons interact with the guest vibrations to yield phonon scattering. It is, furthermore, assumed that the relaxation time for this scattering [39] can be written as

$$\tau_s^{-1} = A\frac{\omega^2}{(\omega_0^2 - \omega^2)^2} \qquad (2)$$

where A is a scattering constant which depends on the number of scattering sources (guest molecules) as well as a coupling coefficient between the water lattice vibrations and the guest vibrations [25], ω is the phonon angular frequency and ω_0 is a resonance angular frequency.

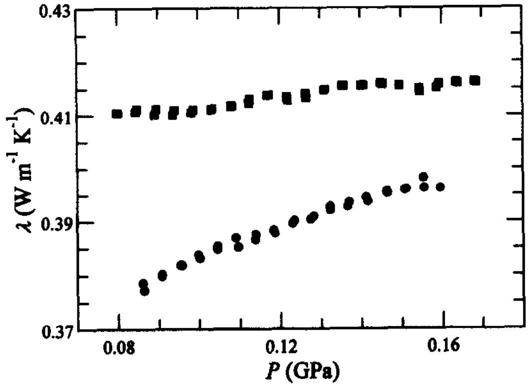

Fig. 3. Thermal conductivity plotted against pressure for THF·16.9 D_2O: (■) high temperature phase at 100 K, (●) low temperature phase at 58 K.

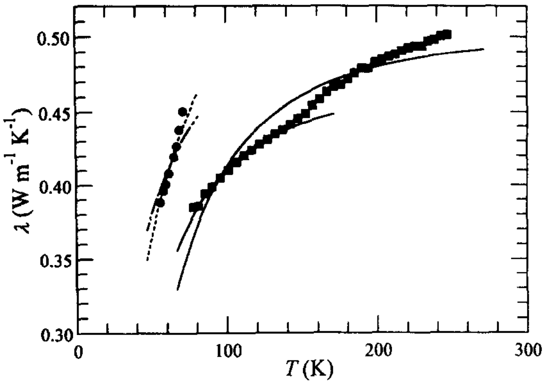

Fig. 4. Thermal conductivity plotted against temperature for: (■) high temperature phase of THF·16.9 H_2O, (●) low temperature phase of THF·16.9 H_2O, (—) resonance model for λ of the high temperature phase for $T < 150$ K and $T < 260$ K. Resonance model for λ of the low temperature phase assuming that only: (···) the resonance frequency changes at the transition, (- - -) the scattering constant changes at the transition.

The resultant relaxation time involves, in general, many different terms arising from for umklapp and phonon-structural scattering point defects, grain boundaries and dislocations. In this case, however, τ is different from that normally found for crystals which, in the temperature range considered here, is dominated by that for three phonon umklapp processes leading to $\lambda \propto T^{-1}$. Since the experimental data for $\lambda(T)$ deviate strongly from this dependence, three phonon umklapp processes must have little significance in phonon scattering and we can, to a first approximation, neglect this scattering. Moreover, if we assume that the THF clathrate hydrate crystals are not of poor quality then phonon-structural scattering can also be neglected. Consequently, in the resonance model, λ can be calculated from eqn (1) with the resulting τ given approximately by eqn (2). Using this approximation, curves were fitted to our experimental data for the HT phase and the results are shown in Fig. 4. In the fits, we used $v = 1871$ m s^{-1} and $\theta_D = 198$ K [25] whereas A and ω_0 were left as adjustable parameters. As shown, the experimental data cannot be reproduced exactly but the weak increasing tendency of λ with increasing temperature can be reproduced. In these rather crude calculations one cannot expect satisfactory agreement and we can conclude that resonance scattering can explain the results for $\lambda(T)$ of the HT phase. In the temperature range investigated here ($T > 50$ K), the fits were not very sensitive to the value of ω_0. The best one for temperatures less than 150 K yielded $\omega_0 = 1.6 \cdot 10^{13}$ s^{-1} and $A = 8.3 \cdot 10^{38}$ s^{-3}, but the experimental data can be described almost equally well with significantly different values for ω_0 by using different values for the scattering constant A.

Since the resonance model can describe qualitatively the glassy $\lambda(T)$ of the HT phase it is also able to explain that for the LT phase. We have also investigated if the small increase of λ at the HT⟶LT phase transition can be explained within the model. One possibility is that the slightly modified guest environment associated with the ordering transition will change the resonance frequency and, consequently, the scattering rate. A fit using the same scattering constant in the LT phase as that of the HT phase but allowing the resonance frequency to change, yielded $\omega_0 = 1.7 \cdot 10^{13}\ \mathrm{s}^{-1}$ (chain curve in Fig. 4). The phonon velocity and the Debye temperature were assumed to be the same in both phases. The latter assumption has been shown to be valid for the related transition: phase Ih⟶phase XI of ice [40]. Another possibility is that the scattering constant changes at the transition whereas the resonance frequency remains essentially constant through the transition. A fit assuming the same resonance frequency in the two phases yielded $A = 6.9 \cdot 10^{38}\ \mathrm{s}^{-3}$ (dashed curve in Fig. 4). As shown in Fig. 4, a slightly better fit was obtained using the latter assumption but the difference is probably within the inaccuracy of the model and the experimental data. Consequently, the change in λ at the transition can be described by the resonance model but, judging from the agreement in our fits, we cannot find a significant difference between the two extreme ways of describing the change (change of ω_0 or A).

An interesting comparison can be made between the change in λ at the transition of THF clathrate hydrate with that at the transition ice Ih⟶ice XI. As mentioned, these transitions are closely related to each other and the change in λ at the transitions could therefore be correlated. In the investigation of ice [40], it was found that the transition from the proton ordered phase XI to the disordered phase Ih induced a 17% decrease of λ, which is, in fact, the same magnitude as that we find here for the transition in THF clathrate hydrate. The decrease of λ at the transition in ice could be interpreted well in terms of an increase of the lattice anharmonicity, described by the absolute magnitude of the Grüneisen parameter $|\gamma|$, which was ascribed to the order⟶disorder transition of the protons. The host ice lattice of THF clathrate hydrate is similar in local oxygen-atoms arrangement to the ordinary ice lattice. Furthermore, the transition in THF clathrate hydrate is associated with the proton positions as that in ice. It is therefore probable to consider that the step in λ of THF clathrate hydrate could be explained by a change in the lattice anharmonicity with equal magnitude. In the case of ice, the fit of a model for λ yielded the result of 10% increase in $|\gamma|$ at the phase XI⟶phase Ih transition. If this model is valid then γ for the ice lattice of THF clathrate hydrate should also change roughly 10% at the transition. It is, however, not straightforward to anticipate how such a change would affect the values of ω_0 and A. If we consider phonon scattering in general then it commonly depends on γ. The larger the anharmonicity of a lattice, the stronger the phonon scattering. For instance, for phonon scattering from strain fields of dislocations varies as γ^{-2} [2,3]. Scattering from three phonon umklapp processes exhibits the same dependence [2,3]. If the strength of the resonance scattering is assumed to exhibit this dependence, then $A \propto \gamma^2$. If only the scattering strength is affected by the transition then we can calculate λ of the LT phase using the fitted parameters of the HT phase. Based on the assumptions that $A \propto \gamma^2$ and that $|\gamma|$ increases by 10% at the transition from the LT to the HT phase, the calculation yields $A_{\mathrm{LT}} = A_{\mathrm{HT}}/1.2$. The curve calculated using eqns (1) and (2) with A given by this method is described to within 1% by the curve where A was fitted (dashed curve in Fig. 4). In view of the fact that no adjustable parameter was used in the calculation, the good agreement between the model and the measured data provides support for the validity of the model. Consequently, if our assumptions are correct, a change in γ can account for the change in λ at the transition in ice as well as in THF clathrate hydrate, despite the fact that the magnitude and temperature dependence for λ are significantly different in the two substances. It should be noted that this result does not provide further evidence for the resonance scattering model. Any scattering processes which can describe the temperature dependence of the HT phase and have a scattering strength which varies as γ^2 would do equally well.

The resonance model has also been applied in another way different from the one described above. If a scattering source is strong enough then the phonon mean free path becomes of the order of the intermolecular spacing and λ reaches its minimum possible value [41]. That is, addition (or subtraction) of other scattering sources does not affect λ since the phonon mean free path cannot become shorter (or longer if the scattering is very strong). Under this condition, a simple formula for λ can be derived [42,26] and used to calculate λ of various clathrate hydrates. As a result, it can be shown that the magnitude for λ of different clathrate hydrates should not differ much. This finding provides evidence that the mean free path in clathrate hydrates takes the minimum possible value since, in fact, all investigations of the type II clathrate hydrates have yielded about the same magnitude of λ. However, if in our case the LT phase should be described by this model then the decrease of λ at the LT⟶HT phase transition cannot occur since the phonon scattering should be saturated already and additional scattering sources would not affect λ anymore. It follows that any model which leads to the smallest possible phonon mean free path cannot describe the change in λ at the transition. This includes the model of Dharma-wardana [23] which also results in the minimum phonon mean free path.

Finally, it should be mentioned that results for neutron diffraction of the LT phase of deuterated THF clathrate hydrate [13] show very broad Bragg peaks contrary to the HT phase. This indicates that the size of individual crystallites in the LT phase might be extremely small which, consequently, can lead to a glass-like λ. We can therefore not rule out the possibility that the glassy behaviour of the two phases has different origins.

5. CONCLUDING REMARKS

The results for λ of normal and deuterated THF clathrate hydrate were shown to be glass-like. That is, λ increases slightly with increasing temperature. This glass-like behaviour was found for both the LT and HT phases of THF clathrate hydrate, in which the LT phase is believed to be an ordered state. Since the HT phase exhibits guest (THF) orientational disorder whereas the low temperature phase is probably orientationally ordered, the orientation of the guest molecules must be insignificant in phonon scattering. The glassy behaviour of λ can instead be due to resonance scattering against the guest vibrations, which is a model that has been proposed earlier [25,26]. However, the scattering cannot be strong enough to yield the minimum possible λ for the LT phase since λ decreases at the LT⟶HT phase transition.

The relative difference $\Delta\lambda/\lambda$ between the two phases of THF clathrate hydrate was shown to be essentially the same as that between ice Ih and ice XI [40]. Since both the transitions are associated with proton ordering it is possible that this can be the reason for the equal relative change in λ at the transitions. In the case of ice, this change was found to be well described by a model assuming a change in the lattice anharmonicity [40]. In this investigation, it was found that the change in λ at the transition of THF clathrate hydrate can be described by a model assuming a change in the lattice anharmonicity of the same size as that for ice. This correlation is found under the assumption that the scattering strength of the scattering source which causes the glassy behaviour (possibly resonance scattering) depends on the lattice anharmonicity.

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REFERENCES

1. Parsonage N. G. and Staveley L. A. K., *Disorder in Crystals.* Clarendon Press, Oxford (1978).
2. Berman R., *Thermal Conduction in Solids.* Clarendon Press, Oxford (1976).
3. Parrott J. E. and Stuckes A. D., *Thermal Conductivity of Solids*, Pion, (1975).
4. Yamamuro O. and Suga H., *J. Therm. Anal.* **35,** 2025 (1989).
5. von Stackelberg M. and Müller H. R., *Z. Electrochem.* **58,** 25 (1954).
6. Bernal J. D. and Fowler R. H., *J. Chem. Phys.* **1,** 515 (1933).
7. Giauque W. F. and Stout J. W., *J. Am. Chem. Soc.* **58,** 1144 (1936).
8. Davidson D. W., In *Water: A Comprehensive Treatise* (Edited by F. Franks), Vol. 2, p. 115. Plenum Press, New York (1973).
9. Yamamuro O., Matsuo T. and Suga H., *J. Incl. Phenom.* **8,** 33 (1990).
10. Garg S. K., Davidson D. W. and Ripmeester J. A., *J. Magn. Reson.* **15,** 295 (1974).
11. Yamamuro O., Oguni M., Matsuo T. and Suga H., *J. Phys. Chem. Solids* **49,** 425 (1988).
12. Tajima Y., Matsuo T. and Suga H., *Nature* **299,** 810 (1982).
13. Suga H., Matsuo T. and Yamamuro O., *Pure Appl. Chem.* **64,** 17 (1992); *Supramolecular Chem.* **1,** 221 (1993).
14. Yamamuro O., Oguni M., Matsuo T. and Suga H., *Solid State Commun.* **62,** 289 (1987).
15. Ross R. G., Andersson P. and Bäckström G., *Nature* **290,** 322 (1981).
16. Ross R. G. and Andersson P., *Can. J. Chem.* **60,** 881 (1982).
17. Ashworth T., Johnson L. R. and Lai L.-P., *High Temp. High Pressures* **17,** 413 (1985).
18. Cook J. G. and Laubitz M. J., *Thermal Conductivity* (Edited by J. G. Hust), Vol. 17, p. 745. Plenum Press, New York (1983).
19. White M. A., *J. de Physique (Paris), Colloq. C1* **48,** 565 (1987).
20. Ross R. G., *Phys. Chem. Liq.* **23,** 189 (1991).
21. Ahmad N. and Phillips W. A., *Solid State Commun.* **63,** 167 (1987).
22. Ross R. G., Andersson P., Sundqvist B. and Bäckström G., *Rep. Prog. Phys.* **47,** 1347 (1984).
23. Dharma-wardana M. W. C., *J. Phys. Chem.* **87,** 4185 (1983).
24. Handa Y. P. and Cook J. G., *J. Phys. Chem.* **91,** 6327 (1987).
25. Tse J. S. and White M. A., *J. Phys. Chem.* **92,** 5006 (1988).
26. Tse J. S., *J. Incl. Phenom.* **17,** 259 (1994).
27. Zakrzewski M. and White M. A., *Phys. Rev. B* **45,** 2809 (1992).
28. Roufosse M. and Klemens P. G., *Phys. Rev. B* **7,** 5379 (1973).
29. Håkansson B., Andersson P. and Bäckström G., *Rev. Sci. Instrum.* **59,** 2269 (1988).
30. Andersson O., Sundqvist B. and Bäckström G., *High Pressure Res.* **10,** 599 (1992).
31. Ross R. G., Andersson P. and Bäckström G., *J. Chem. Phys.* **68,** 3967 (1978).

32. Ross R. G., Andersson P. and Bäckström G., *High Temp. High Pressures* **9,** 87 (1977).
33. Ross R. G. and Sandberg O., *J. Phys. C* **11,** 667 (1978).
34. Slack G. A. and Andersson P., *Phys Rev. B* **26,** 1873 (1982).
35. Slack G. A., *Phys. Rev. B* **22,** 3065 (1980).
36. Kuriakose A. K. and Whalley E., *J. Chem. Phys.* **48,** 2025 (1968).
37. Dyadin Yu. A., Kuznetsov P. N., Yakovlev I. I. and Pyrinova A. V., *Dokl. Chem.* **208,** 9 (1973).
38. Pistorius C. W. F. T., *Prog. Solid State Chem.* **11,** 1 (1976).
39. Pohl R. O., *Phys. Rev. Lett.* **8,** 481 (1962).
40. Andersson O. and Suga H., *Phys. Rev. B.* **50,** 6583 (1994).
41. Slack G. A., In *Solid State Physics* (Edited by H. Ehrenreich, F. Seitz and D. Turnbull), Vol. 34, p. 1. Academic Press, New York (1979).
42. Cahill D. G., Watson S. K. and Pohl R. O., *Phys. Rev. B* **46,** 6131 (1992).