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## THERMAL CONDUCTIVITY OF TETRAHYDROFURAN CLATHRATE HYDRATE

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**RESUME:** On décrit ici la conductivité thermique du clathrate THF·16,94H<sub>2</sub>O dans un intervalle de température allant de 15 à 180 K. Le résultat est sans doute lié à la présence de désordre d'orientation de THF.

**ABSTRACT:** The thermal conductivity of a single crystal of tetrahydrofuran (THF) clathrate hydrate from 15 to 180 K is reported. The results can be explained in terms of disorder of the THF guest molecules.

## I. INTRODUCTION

The physical properties of clathrate hydrates have been of interest since their discovery more than a century ago [1]. The high level of current activity has been influenced by the existence of large deposits of natural gas hydrates in arctic regions [2].

Tetrahydrofuran (THF) is known [3] to form a clathrate hydrate of composition THF·17H<sub>2</sub>O and melting point 277 K. The structure [4] consists of sixteen dodecahedral cages of water molecules (d~5.0 Å) and eight hexakaidecahedral cages of water molecules (d~6.6 Å). The guest (THF) molecules fully occupy the larger cages in this so-called structure II clathrate hydrate. Although there is considerable information concerning many clathrate hydrates (including those with other structures), the greatest amount of information is known about THF clathrate hydrate, primarily because it is prepared easily by freezing an aqueous solution of the appropriate stoichiometry; in contrast, the clathrate hydrates which contain lighter molecules must be prepared with an overpressure of the guest gas.

One of the most interesting unresolved problems in the study of clathrate hydrates is understanding their unusual thermal properties. In contrast with most crystalline solids, in which the thermal conductivity above about 100 K falls as  $T^{-2}$ , the thermal conductivity of clathrate hydrates has been found to increase slightly with increasing temperature [5]. In addition, the thermal conductivity of clathrate hydrates is unusually low, only about 20% of that of ice at temperatures near the melting point and considerably less at lower temperatures.

The objective of the present work was to measure the thermal conductivity of THF clathrate hydrate down to 15 K, in order to shed some light on the mechanisms responsible for the unusually high thermal resistivity. Earlier experiments had been carried out down to 100 K [5-9] and although a recent experiment extended this range to 45 K [10,11], the magnitude of the heat leak in the latter left some uncertainty about those results. Because there is considerable discussion currently about the nature of the conduction-limiting processes in these solids [5-9,12], it was decided to extend the measurements to a lower temperature. In addition, recent low-temperature heat capacity measurements of THF clathrate hydrate [13] now make it possible to calculate the temperature-dependence of the mean free path of the energy carriers.

Because ice impurity would have a substantial effect on these experiments, and this could be minimized with the use of a single crystal of THF clathrate hydrate, and also because the thermal conductivity of the sample is so low that it could be short-circuited by containment of the sample in a cell, we chose to determine the thermal conductivity by the measurement of the temperature gradient along a free-standing single crystal of THF clathrate hydrate under conditions of steady-state heat flow.

## II. EXPERIMENTAL

### a. Sample Preparation:

A large single crystal of tetrahydrofuran clathrate hydrate was grown by gradual solidification of the appropriate proportion of tetrahydrofuran (BDH analytical grade, >99.5%) and doubly-distilled water, overall composition  $\text{THF} \cdot 16.94\text{H}_2\text{O}$ , in a sealed Pyrex ampoule. The ampoule, which had been drawn to a tip at the bottom, was placed in an ice/water/salt bath (as a temperature-gradient thermal contact medium) which was sitting on the cold plate of a StirKool (Thermoelectrics) cooling plate. The entire stage was capped with an unsilvered Dewar, to insulate the system from room air currents. The cooling power of the stage was increased incrementally, allowing controlled growth from the drawn tip at the bottom of the ampoule. The temperature differential along the sample was about 10 K, and the crystal growth was carried out by decreasing the temperature at the bottom of the sample by about 2 K per day. For the thermal conductivity experiments reported here, a 35 mm long (diameter =  $25.6 \pm 0.6$  mm) single crystal (as judged optically) of exceptional clarity was grown during the course of 5 days.

### b. Thermal Conductivity Measurements:

The thermal conductivity measurements were performed by the standard steady-state potentiometric method [14]. For the passage of power  $\dot{q}$  through a single crystal of cross-sectional area  $A$ , the thermal conductivity,  $\kappa$ , is given by:

$$\kappa = \frac{\dot{q}}{A} \frac{d}{\Delta T} \quad (1)$$

where thermocouples placed a distance  $d$  apart are used to measure the temperature difference,  $\Delta T$ .

The thermocouple was 0.08 mm diameter AuFe (0.03 atomic % Fe)/Chromel (Johnson Matthey; supplied and calibrated by Cryogenic Calibrations Ltd., England; accuracy  $\pm 0.05$  K in the temperature range used). This thermocouple wire was chosen for its high sensitivity and low thermal conductivity, as it was necessary to minimize the thermal "short-circuit" along the thermocouple. The length of the AuFe wire between the contacts along the crystal was 106 mm, again chosen to reduce the heat flow along the thermocouple wires. The thermocouple junctions were made by spark welding [15] to reduce thermal noise associated with using dissimilar joining materials. The absolute temperature of the sample was determined by measuring the resistance of a platinum thermometer (PR-100B, CryoCal Inc., St. Paul, Minnesota,  $R(25^\circ\text{C}) \sim 100$  Ohms) in the heat sink. The temperatures thus measured were converted to the temperature of the sample at a point midway between the thermocouple junctions through a knowledge of the temperature gradient along the crystal. The power to the sample heater during the measurements was between 2 and 10 mW, and  $\Delta T$  was maintained at 1 to 1.5 K, chosen to maximize the accuracy of the experiment while minimizing the time required to reach steady state; this time increased from about 3 min at 15 K to 90 min at 150 K. All electrical measurements (heater resistance, heater voltage, thermocouple emf, resistance of Pt thermometer) were automated using a Hewlett-Packard 3456A digital multimeter, interfaced to an IBM PC. The temperature range for this experiment was limited at the low end by the heat leak in the cryostat, and at the high end by radiative heat losses, as is common with this method [16]. Although this loss

could have been reduced with an adiabatic shield, the necessary manipulations were beyond experimental feasibility for use with a crystal with a melting point as low as that of THF clathrate hydrate,  $4^{\circ}\text{C}$ . This thermal conductivity apparatus had been used previously to measure the thermal conductivity of a Harshaw single crystal of NaCl, and gave results within the quoted error in the literature values [17].

The thermocouples and sample heater were frozen into the large single crystal of THF clathrate hydrate, and the crystal was mounted on the copper heat sink with a little silicone grease (Dow Corning) to aid thermal contact. All manipulations, including the installation of the crystal in the cryostat, were carried out under a stream of cold ( $-18^{\circ}\text{C}$ ) dry nitrogen gas, and the sample space of the cryostat was not pumped upon until the temperature was below 250 K due to loss of THF above this temperature (J. Tse, private communication, 1985). All subsequent temperature changes were at rates less than 0.5 K/min, effected by the introduction of  $< 1$  Torr of He exchange gas into the two inner vacuum spaces (cooling mode) or the application of heat to the heat sink (heating mode).

The main sources of error in this experiment were in the determination of the cross-sectional area of the crystal, the thermocouple separation distance, the temperature differential and the power input. Full consideration of these errors gives an overall accuracy in the measurement of  $\pm 30\%$  at the lowest temperatures and  $\pm 12\%$  at the highest temperatures. The error in  $\bar{T}$  is  $\pm 0.05$  K.

### III. RESULTS AND DISCUSSION

The results of the thermal conductivity measurements of tetrahydrofuran clathrate hydrate are illustrated in Figure 1. In the temperature region of overlap, the present results are considerably lower than those of earlier workers [5-11], by about 30% at 180 K. However, it is known from studies of THF clathrate hydrate that the thermal conductivity depends critically on the relative proportions of THF and water - for example,  $\kappa$  of  $\text{THF}\cdot 17.55\text{H}_2\text{O}$  is 10% greater than that of  $\text{THF}\cdot 16.94\text{H}_2\text{O}$  at 100 K [6], due to the very large thermal conductivity of ice. In fact, the difference between the earliest results [5-9] and the present data can

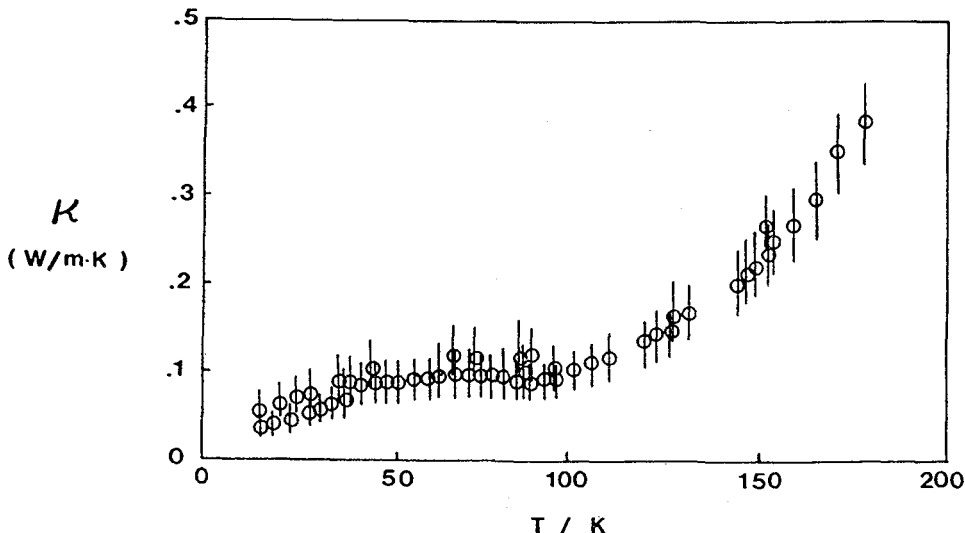


Figure 1. The present measurements of the thermal conductivity of THF clathrate hydrate.

be accounted for by 4% ice impurity, not unreasonable since their solidification procedure was not aimed at producing single crystals. The early experiments also measured  $\rho C$ , the product of the density and the heat capacity at constant pressure, and although these values are a little low (by about 10% at 125 K and 14% at 230 K, in comparison with  $\rho C$  derived from other experiments [13,18,19]), neither the density nor the heat capacity are particularly sensitive to small proportions of ice. The results of the earlier lower-temperature study [10,11], which also are somewhat higher than the present values, have not been corrected for the substantial heat leak due to the use of a cell apparatus. The effect of this correction [10] would bring the earlier data into agreement with ours.

The most striking feature of the thermal conductivity of THF clathrate hydrate is that it continues to decrease as the temperature is lowered. The general shape of the curve is very much like that of a glass such as amorphous  $\text{SiO}_2$  [20]. It is unlikely that the similarity is due to the same physical processes, as it is the absence of long-range order which limits the thermal conduction in glasses [21], and clathrate hydrates are known to be crystalline materials. However, the low thermal conductivity of THF clathrate hydrate may be related to a type of disorder, and we return to this point later.

Another crystalline material which shows very low thermal conductivity and a positive value of  $d\kappa/dT$  is polydiacetylene (PDA) [22]. In PDA it is possible to describe the thermal conductivity as arising from two scattering rates, one independent of frequency and the other dependent on the fourth power of the frequency. The conclusion from such an analysis of PDA is that the temperature-dependence of the thermal conductivity is due to scattering of acoustic phonons by low-lying optical phonons. We have tried such an analysis of our data to determine whether a similar mechanism may be responsible here. Although it is possible to choose scattering rates that reproduce the low-temperature data ( $T < 100$  K), the temperature-dependence of  $\kappa$  for  $T > 100$  K is substantially less than observed experimentally ( $\sim T^{0.2}$  vs  $\sim T^4$ ).

In the context of explaining thermal conductivities near the melting point, Slack [23] has derived expressions for the minimum thermal conductivity of nonmetallic crystals. Evaluation of these equations for THF clathrate hydrate, using an average velocity of sound of 1730 m/s [24], a minimum mean free path of a ( $= 17 \text{ \AA}$  [25]), a high-temperature Debye temperature evaluated from heat capacity measurements [13] ( $= 300$  K), Slack's high- and low-energy optic modes of  $300 \text{ cm}^{-1}$  and  $220 \text{ cm}^{-1}$  [26], we find the sum of the minimum optic and acoustic contributions to the thermal conductivity at 20 and 150 K to be  $5 \times 10^{-6}$  and  $3 \times 10^{-2} \text{ W m}^{-1} \text{ K}^{-1}$  respectively. This result indicates that phonon-phonon scattering in THF clathrate hydrate is at less than maximum effectiveness, although it may tend to approach that at higher temperatures.

An estimate of the mean free path ( $\ell$ ) of the energy carriers can be obtained from the Debye equation for thermal conductivity [27]:

$$\kappa = C v \ell / 3 \quad (2)$$

where  $C$  is the heat capacity per unit volume and  $v$  is the velocity of the energy carriers. Using 1730 m/s as an average sound velocity, and the measured thermal expansion [19] to calculate the heat capacity per unit volume from that per unit mass [13], we find that the mean free path remains essentially constant at a value between 2 and 6  $\text{\AA}$  from 15 to 170 K. Of course the Debye model is too simple to expect these calculations to be exact, but the general conclusion is secure: above about 15 K the mean free path is of the order of one lattice repeat distance.

The constant mean free path can be understood as follows. An analysis of the heat capacity [13] of the THF molecule (i.e. with the heat capacity of the "empty" lattice removed) is shown in Figure 2. (In Ref. [13] we erroneously assumed that intramolecular vibrations would contribute insignificantly at these temperatures. We now find that although each mode contributes but little to the heat capacity,

the multitude of modes makes the total intramolecular vibrational contribution quite substantial, especially at high temperatures, and, we have therefore included these contributions, based on Scott's spectroscopic assignments [28].) It can be seen from Figure 2 that the calculated and experimental values of the heat capacity of the THF molecule are in good agreement, and as before [13], we attribute the slight difference to the use of ice as a model for the "empty" lattice. The conclusion which concerns us here is that even at 20 K the THF molecules appear to be thermally-excited. This is in agreement with results from dielectric measurements [29], and NMR [30], infrared [26,31] and neutron [32] spectroscopies which show that THF molecules can reorient rapidly in THF clathrate hydrate. It seems most likely that this disorder of the THF guest molecules is responsible for the unusually short mean free path in THF clathrate hydrate, and this in turn is responsible for the unusual temperature-dependence of the thermal conductivity.

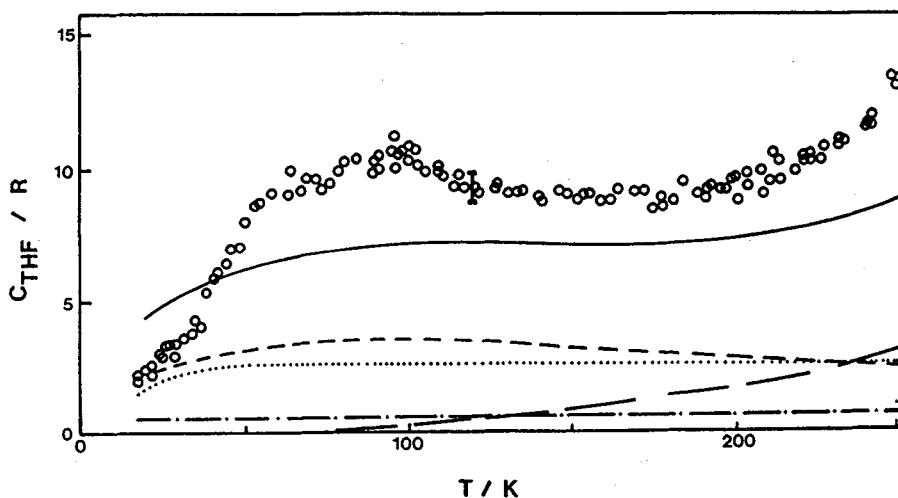


Figure 2. The molar heat capacity of the THF molecule in THF clathrate hydrate.  $\circ$ ,  $C_{\text{THF}}$  derived from the experimental results for  $\text{THF} \cdot 16.83\text{H}_2\text{O}$ ; ———, the calculated pseudorotational contribution [13]; .....<sup>2</sup>, the calculated vibrational rattling contribution [13]; - - - - , the calculated hindered rotational contribution [13]; ———, the calculated intramolecular vibrational contribution; ———, the sum of the calculated contributions to the heat capacity of a THF molecule in THF clathrate hydrate. The error bar at 120 K represents  $\pm 1\%$  in the total measured heat capacity.

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## COMMENTS

J. KLINGER

The decrease of thermal conductivity of amorphous solids is generally explained by the fact the phonon mean free path is constant. As the heat conduction coefficient of clathrates has quite similar values and a similar temperature dependence as amorphous solids I strongly suspect that phonon scattering is controlled by the distortion of the lattice due to the presence of the guest molecules. But in this case the heat conduction coefficient should depend on the occupation of cages by

guest molecules. Do you think that it is feasible to do heat conduction measurements as a function of cage occupation ?

Answer :

Unfortunately, this is not possible for THF clathrate hydrate or for any other clathrate hydrates that are stable enough to grow and handle the large single crystals which we require for this method due to the limited concentration stability range of these materials. However single crystals of other clathrates (i.e. other than hydrates) can be produced with varying composition, and it is likely that these show similar thermal conductivity ; we plan to try these experiments.

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Remark of J.S. TSE :

The rattling motions of the THF molecules in the hydrate cages are mostly optic modes (i.e. they do not show dispersion). At present it is difficult to rationalize the strong scattering of the thermal phonons due to the "rather weak" Van der Waals interactions between the guest molecules with the water lattice.

Answer :

I agree, but everything seems to point to the source of the anharmonic properties of clathrate hydrates (large thermal expansion; low thermal conductivity) being due to the presence of the guest in the lattice, so, although the interaction may be very weak, there must be some coupling between the optic (vibrational rattling) and acoustic (host lattice) modes.