

## Thermal Conductivity of the Urea–Hexadecane Inclusion Compound

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**Abstract.** The thermal conductivity  $\lambda$  and the heat capacity per unit volume  $\rho c_p$  have been measured for the urea–hexadecane inclusion compound using the transient hot-wire method. Measurements were made under isobaric conditions at a pressure of 0.1 GPa and in the temperature range of 100–300 K. There

was evidence for a phase transition at a temperature of about 160 K, in reasonable agreement with previous work. For the high-temperature phase  $\lambda$  was independent of temperature within  $\pm 1\%$ . The low-temperature phase showed a weak temperature dependence, with  $(d \ln \lambda / d \ln T)_p = -0.13$ . It was inferred that interaction between acoustic phonons and low-frequency vibrational excitations of the guest molecules made a major contribution to the thermal resistivity. For the quantity  $\rho c_p$  a weak maximum was observed in the region of the phase transition temperature.

**Key words.** Thermal conductivity, heat capacity, channel compound, urea adduct, phase transition.

### 1. Introduction

The thermal conductivity  $\lambda$  of nonmetallic solids is a property which has been much studied over many years and numerous data are available [1]. Most investigations in this area have been concerned with structurally ordered substances, typified by the alkali halides, or with topologically disordered substances, typified by silica glass. It is only comparatively recently [2] that investigations of  $\lambda$  have been extended to substances having phases which are intermediate in terms of structural disorder, within which category inclusion compounds may be included. Amongst inclusion compounds, the present work is the first report of the thermal conductivity of a channel compound, specifically the urea–hexadecane adduct. The data presented here are a brief report of how  $\lambda$  varies with the temperature  $T$  under isobaric conditions.

It is assumed that readers of this Journal are broadly familiar with the general features of inclusion compounds but it does seem appropriate to provide here a concise description of salient points in connection with  $\lambda(T)$  for nonmetallic solids [2, 3]. The description is restricted to temperatures which are sufficiently high that the vibrational spectrum of the solid may be regarded as fairly fully excited. The temperatures referred to are therefore of the order of or greater than some characteristic temperature for the solid such as the Debye temperature  $\theta$ . On the other hand, temperatures are not so high that heat transport by radiation is

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significant. Within these limits, it is found to a reasonable approximation for ordered solids such as the alkali halides that  $\lambda \propto T^{-1}$ , or in terms of the thermal resistivity  $W (= \lambda^{-1})$  that  $W \propto T$ , with such behaviour being attributed to three-phonon interaction processes. It is worth remarking at this point that the most illuminating analysis of  $\lambda(T)$  may be undertaken for data which refer to isochoric (constant volume) conditions, in order to eliminate any effect which thermal expansion may have on  $\lambda$ , and to point out that the theoretical prediction  $\lambda \propto T^{-1}$  for three-phonon processes strictly refers to isochoric conditions. However, in the present work the distinction between isobaric and isochoric conditions will (necessarily) be ignored because data to enable transformation from isobaric to isochoric conditions are not available. Returning to the description of  $\lambda(T)$  for nonmetallic solids, it is found that topologically disordered substances such as glasses exhibit behaviour which strongly contrasts with that found for ordered solids. Whereas  $\lambda$  increases with decreasing temperature for an ordered solid it is found that  $\lambda$  decreases with decreasing temperature for a glass. The latter behaviour may be understood on the basis of the Debye formula,  $\lambda \sim Cvl$ , where  $C$  is the heat capacity per unit volume,  $v$  is the phonon velocity and  $l$  is the phonon mean free path. In analysing the observed behaviour, it is assumed that topological disorder in the glass fixes  $l$  at some small value which is perhaps about the intermolecular spacing, and that the temperature dependence of  $\lambda$  arises mainly from the temperature dependence of  $C$  which can be described approximately by a Debye model.

The features and analysis of  $\lambda(T)$  given above may be regarded as reasonably well-established. They refer, in fact, to two extreme situations: an ordered crystal and a topologically disordered glass. Our present interest is in solids exhibiting some intermediate degree of structural disorder [4]. Amongst inclusion compounds, the first intermediately-disordered phase for which  $\lambda(T)$  was investigated was the (zero pressure) clathrate hydrate incorporating tetrahydrofuran as the guest species [2, 5]. Although it is well known [4] that clathrate hydrates have long-range translational periodicity in the  $H_2O$  lattice structure it was found that  $\lambda(T)$  for this phase was similar to that for a glass, in the sense that  $\lambda$  decreased with decreasing  $T$ . It appears that such behaviour for  $\lambda(T)$  is characteristic for clathrate hydrates. It is probably due to interaction between acoustic phonons and low-frequency vibrational excitations of the guest molecules [6]. The recent suggestion [7] that the sign of  $d\lambda/dT$  for a clathrate hydrate may depend on cooling rate history during sample preparation is not substantiated by other investigations [6].

The present work extends the investigation of  $\lambda(T)$  for intermediately-disordered phases to channel compounds. As we shall see, it appears that the behaviour of  $\lambda(T)$  for a channel compound falls between that for an ordered crystal and a clathrate hydrate in the sense that  $\lambda$  was found to be almost independent of  $T$  over a substantial range of temperature.

## 2. Experimental Details

Measurements were made using the transient hot-wire method which has been described in detail elsewhere [8]. Very briefly, in this method it is arranged that a fine metal wire (0.1 mm diameter Ni) is surrounded by the substance under investigation. Electrical power dissipation in the wire over a short (1 s) period

results in a temperature rise of the wire, varying with time and up to about 4 K in magnitude. The temperature rise of the wire is determined by treating the wire as a resistance thermometer. Fitting a suitable theoretical expression to the data for temperature rise of the wire yields values for two properties of the substance under investigation: the thermal conductivity  $\lambda$  and the heat capacity per unit volume  $\rho c_p$ , where  $\rho$  is the mass density and  $c_p$  is the specific heat capacity at constant pressure. Experimental inaccuracies are  $\pm 3\%$  in  $\lambda$  and  $\pm 10\%$  in  $\rho c_p$ . In the present work, the Ni wire was located between two discs of the urea adduct, each disc being about 40 mm in diameter and 8 mm thick. These discs, which were polycrystalline, were prepared by compacting powdered adduct material in a die under a pressure of about 0.1 GPa. The disc assembly was placed in a Teflon cup within a piston-cylinder type of pressure vessel having an internal diameter of 45 mm. Pressure (see also below) was generated using a 5 MN hydraulic ram and measured using a load/area relation which had been established using known phase transitions. The temperature of the substance under investigation was measured using a Chromel–Alumel thermocouple.

Use of high pressure is closely connected with measurement of  $\lambda$  of solids using the transient hot-wire method. Initially, and before serious measurements begin, the hot-wire is simply situated between the discs of the substance under investigation. In order that the substance should entirely surround the hot-wire a preliminary conditioning is needed and this is done by applying high pressure. In the present work the conditioning pressure was 1 GPa, applied at room temperature. Thereafter, a modest (minimum) pressure (here 0.1 GPa) is used to ensure that substance and hot-wire remain in good thermal contact. Thus, data reported here refer to isobaric conditions at a pressure of 0.1 GPa. Data for the pressure dependence of  $\lambda$  for channel compounds is expected to be the subject of a report elsewhere.

The urea adduct material was prepared following the procedure described by Fieser and Williamson [9]. Analytic grade urea was dissolved in boiling methanol to form a saturated solution and synthetic grade hexadecane in the molar ratio urea/hexadecane = 12.3/1 was added. Crystals of the adduct precipitated during cooling with continuous stirring and were recovered by filtration. After filtration, the adduct material was dried in air at room temperature for several days in order to ensure that all traces of the solvent had evaporated. There is no reported evidence to suggest that the solvent (methanol) could have formed an adduct with urea.

### 3. Results and Discussion

Results for  $\lambda(T)$  for the urea–hexadecane adduct under isobaric conditions at a pressure of 0.1 GPa are shown in Figure 1. There are no previous measurements with which present results may be compared. Over the temperature range 160–300 K  $\lambda$  remained roughly constant at a value of  $0.50 \text{ W m}^{-1} \text{ K}^{-1}$  within about  $\pm 1\%$ . In the temperature range 100–160 K  $\lambda$  showed a slight variation with temperature, with  $(d \ln \lambda / d \ln T)_p \approx -0.13$ . The corresponding value of this quantity for an ordered crystal would be about  $-1$ . The change in the value of  $(d \ln \lambda / d \ln T)_p$  from zero to about  $-0.1$  which occurred in the region of 160 K (with about 10 K hysteresis between heating and cooling conditions) was almost

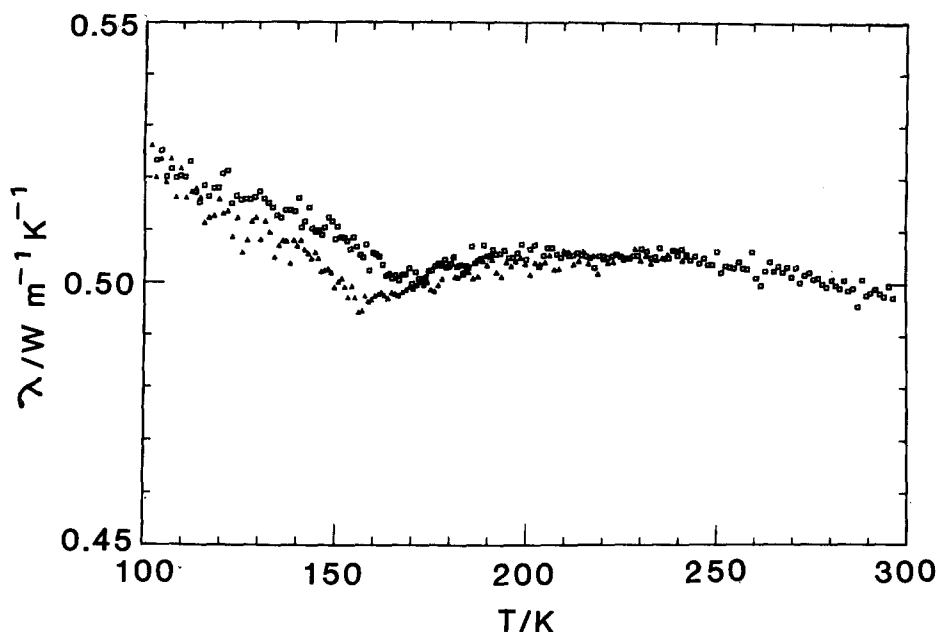


Fig. 1. Thermal conductivity  $\lambda$  plotted against temperature  $T$  under isobaric conditions for the urea-hexadecane adduct at a pressure of 0.1 GPa. Cooling ( $\Delta$ ); heating ( $\square$ ).

certainly due to a phase transition which a recent structural investigation [10] indicates is associated with a lateral orientational ordering of hexadecane guest molecules in adjacent channels and a simultaneous orthorhombic distortion of the urea host lattice. Such a phase transition was first detected in the heat capacity measurements of Pemberton and Parsonage [11] where  $c_p$  for the urea-hexadecane adduct showed a pronounced maximum in the temperature range 150–155 K. In the present work, results for the related but not identical quantity  $\rho c_p$  are shown in Figure 2, from which it can be seen that a very weak maximum was observed in the region of the phase transition. Why were the strengths of the maxima in heat capacity so different in present and previous work? It seems unlikely that such a difference is the result of an inherent limitation in use of the hot-wire method for measurement of heat capacity, although the hot-wire temperature rise of a few K does smear out any actual divergence which may occur. Evidence for this assertion is provided by the work of Ross and Sandberg [12] where a quite pronounced maximum in  $\rho c_p$  was detected through the order-disorder transition in  $\text{NH}_4\text{Cl}$ . Another possibility is that  $\rho c_p$  has a less pronounced maximum than  $c_p$  because of a sharp minimum in  $\rho$  at the phase transition, but this seems unlikely. A further possibility, perhaps the most probable, is that the difference in observed heat capacity is connected with the difference in time scales on which the measurements were made. Heating rates in the measurements of Pemberton and Parsonage [11], although not stated explicitly, were probably  $\sim 1 \text{ K min}^{-1}$  [13]. On the other hand, in the present work the entire heating event of about 4 K took place over a period of 1 s, and detailed consideration of the fitting procedure shows that the value for

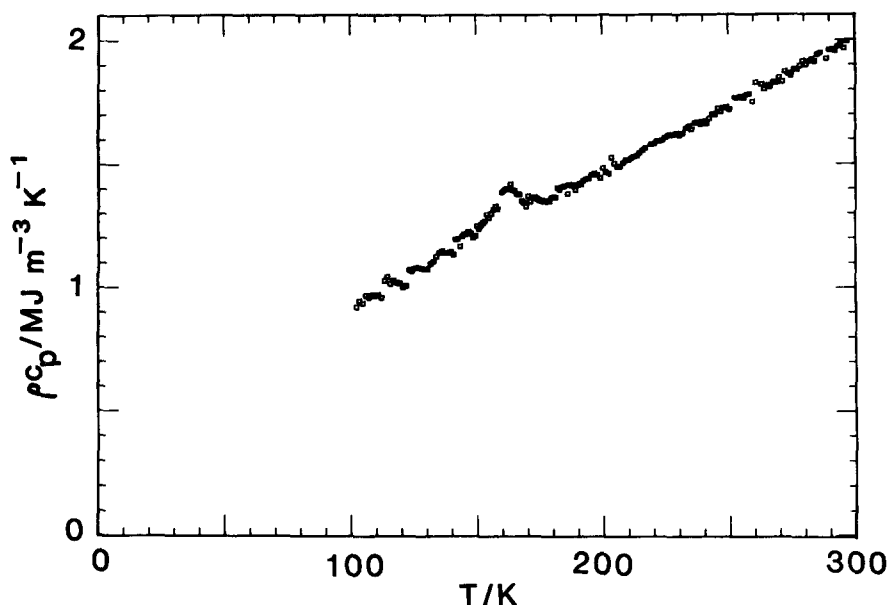


Fig. 2. Heat capacity per unit volume  $\rho c_p$  plotted against temperature  $T$  under isobaric conditions for the urea-hexadecane adduct at a pressure of 0.1 GPa. In the interests of clarity, only data for heating conditions are shown. Data for cooling were similar, including a weak maximum occurring about 10 K lower in temperature than on heating.

$\rho c_p$  is determined predominantly by about the first 10% of the heating event. If the phase transition is indeed associated with an orientational ordering of hexadecane guest molecules in adjacent channels then it is possible that this is a sufficiently slow process (at 150 K) that it would not be probed to a very significant extent during the (effective) measurement time of about 0.1 s which pertains to the hot-wire method.

The magnitude of  $\rho c_p$  in the present work at a temperature of 300 K was 5% higher than that calculated from the results of Pemberton and Parsonage [11], assuming a mass density for the adduct of  $1.156 \text{ g cm}^{-3}$ . This value for density was calculated using crystallographic data for the hexagonal unit cell of the adduct [14]. Agreement for  $\rho c_p$  is within experimental inaccuracy.

A thermal conductivity which is almost constant over a considerable range of temperature, as found here for the urea-hexadecane adduct, is unusual but not previously unknown. Kamilov [15] observed such behaviour for zinc ferrite ( $\text{ZnFe}_2\text{O}_4$ ). For the adduct, it seems likely by analogy with clathrate hydrates [6] that interaction between acoustic phonons and low-frequency excitations of the guest molecules has a dominant effect on the heat conduction process. It is presumably simply accidental if such an interaction should result in  $\lambda$  being almost independent of  $T$  for the room-temperature phase of this substance. For the low-temperature phase (designed III in the notation of Forst *et al.* [10]) the observed value of  $(d \ln \lambda / d \ln T)_p$  indicates that so far as heat transport is concerned this

phase is far from behaving like an ordered crystal. Although the guest molecules may be ordered structurally [10], the present results suggest that their low-frequency excitations can still make an important contribution to the thermal resistivity.

In the case of clathrate hydrates, a notable feature of the results for  $\lambda$  [6] is that the host material ( $\text{H}_2\text{O}$ ), in its normal polymorphic modification (ice  $\text{I}_h$ ), has a thermal conductivity which is 5–20 times that of a typical clathrate hydrate. At room temperature, the urea–hexadecane adduct and a typical clathrate hydrate have about the same value of  $\lambda$  ( $0.5 \text{ W m}^{-1} \text{ K}^{-1}$ ). By analogy between channel compounds and clathrate hydrates, one might expect that the host material of the former (urea), in its normal polymorphic modification, might have a relatively high thermal conductivity. This conjecture cannot be tested at present because there are no data available, but it is expected to be the subject of a future investigation in our laboratory.

#### 4. Concluding Remarks

From the preliminary results reported here it may be concluded that  $\lambda(T)$  for both low-pressure phases of the urea–hexadecane adduct are quite different from the behaviour expected for an ordered crystal. In particular, the temperature dependence of  $\lambda$  is much weaker than the variation  $\lambda \sim T^{-1}$  which is found for a typical ordered crystal. The closest analogy would appear to be another class of inclusion compound, that of clathrate hydrates. Evidence is accumulating for clathrate hydrates [6] that a dominant contribution to the thermal resistivity arises from interaction between acoustic phonons of the host lattice and the low-frequency (localised) vibrational excitations of the guest molecules. A similar, but less pronounced, effect seems to be occurring in the urea–hexadecane channel compound. It may be the case that appropriate low-frequency vibrations are less easily excited in a spatially-extended linear guest species such as hexadecane than in a spatially-localised guest species in a typical clathrate hydrate, yielding behaviour for the channel compound which falls between an ordered crystal and a clathrate hydrate.

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#### Dedication

This report is dedicated to the late Don Davidson. It was at his suggestion that we first undertook measurements of the thermal conductivity of clathrate hydrates, as reported in reference [5]. The present report is also dedicated to my friend and colleague Per Andersson. It was intended that Per should participate in the present work but he was prevented from doing so by a serious illness.

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