Thermal Conductivity and Disorder in Nonmetallic Materials

Russell G. Ross[a]

[a] Department of Experimental Physics, University of Umeå, Umeå, Sweden

PLEASE SCROLL DOWN FOR ARTICLE

REVIEW ARTICLE

Thermal Conductivity and Disorder in Nonmetallic Materials

RUSSELL G. ROSS

Department of Experimental Physics,
University of Umeå, S-901 87 Umeå, Sweden.

Experimental results for thermal conductivity λ are presented and discussed for a range of nonmetallic materials. Disorder, involving both static and dynamic aspects, is covered over a range from well-ordered solids to glasses. Amongst intermediately-disordered (ID) solids which are considered the cases of plastic crystal phases, the glassy crystal state, inclusion compounds and chiral substances receive detailed attention. Emphasis is given to relatively-high temperature (T) where results for λ of glasses and ID solids are shown to be similar. It is demonstrated how data for $\lambda(T)$ which have been measured under isobaric conditions can be transformed to isochoric conditions, and this transformation is shown to be important for purposes of analysis of results. Limitations at high temperature of the phonon picture of heat transport are explored using an empirical approach and an alternative picture involving hopping of localized vibrational excitations is also briefly discussed.

KEY WORDS: Thermal conductivity, disordered materials, glasses, high pressure, phonons.

INTRODUCTION

Thermal conductivity λ is a familiar property, even in everyday life, and has been much studied scientifically. For example, data for λ of about 400 solid substances are contained in a compilation[1] which was published in 1970 and investigations have been extended to a significant number of other solids since that date. As a result, there is copious experimental information on which to base a discussion.

We are concerned in this short and selective review with thermal conductivity and its relation to disorder. As is well known, solids can cover a very wide spectrum in terms of order and disorder in their structure. At one extreme the idealization of a perfect crystal is represented to a good approximation by a well-ordered solid such as a pure alkali halide. At the other extreme we have the topologically-disordered glass, such as vitreous SiO_2, which is completely lacking in long-range translational periodicity. However, there are also a number of materials which are neither as ordered as a pure alkali halide nor so disordered as an "ordinary" glass. Such materials we may refer to as *intermediately-disordered* (ID) solids and the thermal conductivity of a number of these will be described later in our discussion.

In order to introduce the general idea of an ID solid we take as a particular example the KBr-KCN system and consider the equimolar composition. It is found

in this case that the structure[2] is essentially crystalline in the sense that there is long-range translational periodicity of the K, Br and CN centres of mass although the Br and CN ions are located randomly on the halide sites of the crystal structure. However, and more importantly, the CN ions are disordered in terms of orientation. This type of ID solid might reasonably be referred to as an orientational glass and it turns out in practice that its low-temperature thermal properties[2] are quite similar to those found for more conventional glasses such as SiO_2. (The presence of long-range translational periodicity is typical for ID solids but the detailed features of the disorder will depend on the specific system being considered.) Aside from their intrinsic interest, ID solids may provide valuable models[3] for the glass state. Because such models avoid the conceptual and computational difficulties associated with topological disorder they have been found useful in the theoretical analysis of low-temperature thermal properties[4].

In this review we consider only nonmetallic solids in which the transport of heat occurs through the vibrational motion of atoms or molecules and we concentrate on the temperature (T) dependence of the thermal conductivity, $\lambda(T)$. After some preliminary remarks on the comparison between theory and experiment we begin our discussion of $\lambda(T)$ with the extreme cases of the well-ordered solid and the glass which will serve to indicate limiting forms of behaviour. We then consider a number of examples of ID solids having various forms and degrees of disorder. We shall place most emphasis on the relatively-high temperature range, e.g. $T > 100$ K, which implies that most heat-transporting vibrational modes of motion will be fairly fully excited. On the other hand, the temperatures to be considered are not so high that heat transport by radiation needs to be taken into account. A relatively wide range of materials will be considered with some emphasis on molecular solids. It will be difficult in our discussion to avoid a bias towards experiment because theory is in general poorly developed over the area of investigation being considered. We take λ to be a scalar quantity, since we shall be discussing polycrystalline solids or glasses.

ON THE COMPARISON BETWEEN THEORY AND EXPERIMENT FOR $\lambda(T)$

It hardly needs emphasizing that a crucial aim in science must be the realistic comparison of theory and experiment. In making such a comparison for $\lambda(T)$ there is an important feature which is not always taken into account. This concerns the possible effect of thermal expansion, which we now consider.

The essence of the situation is simply stated: theories[5-7] for $\lambda(T)$ refer to isochoric (constant volume V) conditions whereas the corresponding experimental measurements are usually made[1] under isobaric conditions. A solid ordinarily expands when its temperature is increased under isobaric conditions and in principle all properties, including λ, will thereby be affected. To put the matter in perspective, we need to estimate how large a change of λ will arise in practice as a result of thermal expansion. We shall find that the size of this effect depends on the type of material and on whether high or low temperatures are being considered. We shall also need to indicate how the results of measurement of $\lambda(T)$ under isobaric conditions can be transformed

to isochoric conditions for purposes of comparison between theory and experiment. In what follows, we shall use the notation $\lambda(T)_P$ for the results of measurements under isobaric conditions and $\lambda(T)_v$ to describe the situation where these data have been transformed to isochoric conditions.

To give a feeling for how much λ is likely to change with thermal expansion we look at two specific examples[8]: KBr and phase I of adamantane. The former is a typical well-ordered solid whereas the latter is a type of ID solid which is known as a plastic crystal phase. In a plastic crystal phase[9] there is long-range translational periodicity of molecular centres of mass but disorder in molecular orientation. Such a phase is most likely to be found for a substance whose molecules are rather "globular", i.e. roughly spherical in external form. To examine the effect of thermal expansion we consider a temperature increase of 100 K. We use data pertaining to about room temperature and modest pressures up to a few hundred MPa. At the temperatures being considered volumetric thermal expansivity α_P $(= (\partial \ln V/\partial T)_P)$ has the values $1.2 \times 10^{-4}\,\mathrm{K}^{-1}$ for KBr[10] and $4.5 \times 10^{-4}\,\mathrm{K}^{-1}$ for phase I of adamantane[11]. Thus, in the region of room temperature an increase of T of 100 K yields a decrease of the density ρ of 1.2% for KBr and 4.5% for adamantane.

To proceed further we need to know how λ varies with ρ which is conventionally expressed using the parameter $g = (\partial \ln \lambda/\partial \ln \rho)_T$. Values for g may be deduced from measurements of λ under high pressure P, which yield $(\partial \lambda/\partial P)_T$, combined with data for isothermal compressibility $\kappa_T = (\partial \ln \rho/\partial P)_T$. It must be emphasized that results for $\lambda(P)$ are rare by comparison with the copious data[1] which are available for $\lambda(T)_P$. Reliable results for $\lambda(P)$ have been mainly obtained only within the past two decades. This situation reflects the experimental difficulties associated with measurement of λ under pressure. Returning to our two specific examples, Ross et al.[12] gave values for g at room temperature of 8.8 for KBr and 6.4 for phase I of adamantane. Putting the results together, we can deduce that following a temperature increase of 100 K the values of λ pertaining to isochoric conditions will exceed those measured under isobaric conditions by 11% for KBr and 29% for phase I of adamantane. These are differences of λ which arise entirely from thermal expansion. (It is easy to deduce that going from isobaric to isochoric conditions will yield an increase of λ. To maintain isochoric conditions whilst increasing T we also need to increase P, and for the examples considered it is known that λ increases with P, as is usually the case[12].)

It is evident that λ is significantly affected by thermal expansion for these examples. It follows in such cases that experimental data for $\lambda(T)$ measured under isobaric conditions will need to be transformed to isochoric conditions for purposes of comparison with any reasonably accurate theory. In principle, such a transformation can easily be carried out[12,13] using results for α_P and g but in practice there is sometimes a lack of the required data. The lack of data refers not only to $\lambda(P)$, which was already mentioned above, but also to α_P and κ_T. Relevant sources of information on what is available in practice are reviews or data compilations for λ under pressure[12], thermal expansivity[10] and isothermal compressibility[14–16].

On the other hand, at rather low temperatures it is usually satisfactory to test a theory for $\lambda(T)$ using only isobaric experimental data, without making the transfor-

mation to isochoric conditions, because α_P becomes vanishingly small as $T \to 0$. For example, the change of density of KBr[10] under isobaric conditions over the temperature range 0 to 100 K is about 0.45%. For this solid, the quantity g has been measured[12] only in the temperature range 100–400 K but a plausible extrapolation provides an estimate $g \approx 6$ at low temperatures. Hence, following a temperature change from 0 to 100 K it is found that the difference in λ at the latter temperature between isochoric and isobaric conditions is only about 3%. Such a difference in λ would probably be within experimental inaccuracy in a typical investigation. However, it may be pointed out that the measurement of λ under pressure at very low temperatures (say, $T \sim 10$ K) is also of interest in itself and such experimental investigations are beginning to be undertaken[17]. Most of the available measurements[12] of $\lambda(P)$ refer to $T > 100$ K.

THERMAL CONDUCTIVITY OF WELL-ORDERED SOLIDS AND OF GLASSES

Well-ordered solids and glasses are the two extremes in our spectrum of structural regularity. These two extremes will be discussed in this section so as to provide a background for our main interest in ID solids.

Well-ordered solids

The alkali halides provide typical examples of well-ordered solids. Our interest here is in the thermal conductivity of these materials for temperatures $T \geq \theta_D$, where θ_D is the Debye temperature. Heat transport is by quantized elastic waves (i.e. phonons) and thermal resistivity $W(= \lambda^{-1})$ arises from phonon–phonon interactions[5–7]. An elementary argument[18] yields the prediction $\lambda \sim T^{-1}$ in the regime of temperature being considered. This prediction has recently been confirmed by one of the rare examples in this area of a numerical calculation using realistic dispersion relations. This is due to Pettersson[19], who solved the Boltzmann equation using a variational method. Pettersson found generally good agreement between his theoretical results and experimental data for $\lambda(T)$ which had been transformed to isochoric conditions. For our purposes, the most important conclusion from this work is the result $\lambda \sim T^{-1}$ for a well-ordered solid under isochoric conditions.

Glasses

Glasses are the subject of much current investigation[20–22], in particular at low temperatures[23]. Such "low temperature" studies refer to $T < 100$ K and as a result they are peripheral to our present discussion. However, the low-temperature thermal conductivity[24] is especially interesting because it exhibits strikingly-different (and "universal") features for glasses (and ID solids) as compared with well-ordered solids. We therefore give a brief summary of the main features of $\lambda(T)$ of glasses by way of background. Our description is arranged, in a way which has become conventional,

on the basis of three temperature regimes: (i) $\lambda \sim T^2$ for $T < 1$ K, (ii) $\lambda \sim$ constant ("plateau") for $T \sim 10$ K and (iii) λ increases monotonically with T for $T > 10$ K, with a variation $\lambda \sim T$ for temperatures immediately above the plateau. At the higher temperatures (≥ 100 K) in regime (iii) it is found that $\lambda(T)$ bends over and becomes concave to the T axis (as is illustrated for SiO_2 glass in Figure 1). The modest increase of λ with T for a glass at relatively-high temperatures has been well-known[6] for some time. If results for crystal and glass are compared for the same chemical substance, e.g. SiO_2[6], and at the same temperature, then it is found that $\lambda_{glass} < \lambda_{crystal}$ and that the two sets of data approach each other near the melting point.

It has already been pointed out that the great majority of measurements of thermal conductivity have been made under isobaric conditions, with such data being indicated by $\lambda(T)_P$ in our notation. Lack of information about $\lambda(P)$, which is required in order to transform to isochoric $\lambda(T)_v$, is especially acute in the case of glasses. As will be clear from our earlier discussion, results for $\lambda(T)_P$ are potentially subject to the effect of thermal expansion, with this effect being most pronounced at high temperatures. With reference to glasses, we can make estimates in this connection for glassy poly(vinyl acetate) (PVA) and an epoxy resin (EP) using results by Sandberg[25]. The epoxy resin he investigated was CIBA-GEIGY Araldite AW 106 plus an equal proportion by volume of hardener HV 953 U, and we take this material to be roughly typical of epoxy resins in general. Sandberg obtained values for g of 1.7 for PVA and 2.7 for EP, at a temperature of 300 K. We use values for α_P of 3×10^{-4} K^{-1} for PVA[26] and 1.5×10^{-4} K^{-1} for EP[27]. Considering as before a temperature increase of 100 K, we find that λ pertaining to isochoric conditions exceeds that measured under isobaric conditions by 5% for PVA and 4% for EP. On the basis of these results we conclude for a glass that the difference in λ between isochoric and isobaric conditions is likely to be small and comparable to typical experimental inaccuracies, even at high temperatures. This result is due mainly to comparatively small values for the parameter g.

A general description of $\lambda(T)$ for glasses is conveniently based on the survey given by Cahill and Pohl[24]. $\lambda(T)$ for all glasses studied is remarkably similar ("universal") in both magnitude and form. In what follows, we restrict our description to $T \geq 100$ K. At these temperatures, it is found that measured values of λ are approximately in the range 0.1–1 W m^{-1} K^{-1}, independent of bonding type. For a specific glass, λ increases modestly with T and appears to approach a constant value at the highest temperatures (Figure 1). This constant value, which is also approached (from higher values) by λ for the crystal[24] in the typical case of SiO_2, has been identified with what is known as the *minimum thermal conductivity*, λ_{min}, which we shall discuss briefly. The concept of a minimum thermal conductivity has been emphasized by Slack[13] but the idea goes back at least to Roufosse and Klemens[28].

As a preamble and as a basis for later discussion, we describe a simple approach to the analysis of data for λ. It is usual in considering thermal conductivity[18] to make use of the familiar expression from kinetic theory

$$\lambda = \tfrac{1}{3}Cv\ell \tag{1}$$

which is commonly associated with the name of Debye. In Eq. (1), C is the heat

capacity per unit volume ($= \rho c_P$, where c_P is the isobaric specific heat capacity), v is the velocity associated with the heat-transporting "particles" and ℓ is the mean free path between scattering events for these "particles". The use of Eq. (1) is well-established in discussions of λ for crystals. In this case the heat-transporting "particles" are identified with phonons (as already noted above), or more precisely with a phonon wave packet[29], and v is then the corresponding group velocity. If ℓ is calculated using Eq. (1), say at a temperature $\sim\theta_D$, we obtain values[18] for ℓ of about 10^2 times the interatomic spacing in a well-ordered solid. However, there is some uncertainty in choosing the value of C to use in Eq. (1) when the solid does not have a monatomic basis. It is well-known for solids of greater than monatomic basis that the optic modes typically have a relatively small slope and corresponding group velocity over at least part of the Brillouin zone. Should one then conclude[28] that the optic modes will make only a small contribution to λ and that one should therefore use for C a value associated only with the acoustic modes which do have a significant group velocity? There is no simple answer to this question, but it does suggest we should be cautious about the uncritical use of Eq. (1). For example, the detailed calculations of Pettersson[19] for the alkali halides (diatomic basis) have shown that the optic modes can make a significant contribution to both heat transport and phonon–phonon interactions, so ignoring the contribution of the optic modes to the quantity C will be an over-simplification.

Difficulties of interpretation become somewhat more severe in attempting to apply Eq. (1) to glasses or 1D solids. As an example, consider a very simple analysis in connection with plastic crystal phase I of adamantane. By using acoustic mode values for C and v, and an experimental value of λ of about $0.2 \text{ W m}^{-1} \text{ K}^{-1}$, we obtain[12] from Eq. (1) a value of ℓ about equal to the distance between molecular centres ($\approx 1.2 \text{ nm}$). A similar calculation for several glasses[24] yields ℓ in the range 0.1–1 nm, and constant for $T > 100$ K. Although values of ℓ are commonly calculated in this way, it seems reasonable to ask whether Eq. (1) is actually valid, even approximately, when the apparent mean free path of the heat-transporting "particles" is as short as the distance between vibrating (molecular) units? Although thermal conductivity in the short mean free path regime has been considered by Roufosse and Klemens[28], the applicability in this regime of the kinetic theory approach in general, and hence the validity of an equation of the form of (1), does not seem to have been addressed theoretically. In any case, to the extent that the concept of a mean free path remains useful it seems clear that ℓ cannot decrease indefinitely. The minimum thermal conductivity, λ_{min}, then arises when ℓ has its smallest possible value ℓ_{min}. A common proposal[13,28] has been $\ell_{min} \sim$ one phonon wavelength, as an alternative to $\ell_{min} \sim$ the intermolecular spacing[28], but both assumptions give about the same calculated value[24] of λ_{min}. Although it is probable that ℓ is quite small for glasses and 1D solids at high temperatures, our doubts about the strict validity of Eq. (1) imply that we should have reservations about the accuracy of the corresponding numerical values of ℓ which have been calculated using this equation. Looked at another way using the picture of a phonon wave packet, we can see that if the phonon wave vector $\mathbf{k}$ is to have a well-defined value then the spatial extent of the wave packet cannot be as small as interatomic dimensions[29]. Evidently, the kinetic theory approach is being

strained to describe the observations since identification of the heat-transporting "particles" is certainly becoming unclear. However, the assumption ℓ = constant and use of Eq. (1) does predict that $\lambda(T)$ for glasses should roughly follow $C(T)$, as was pointed out by Kittel[30], and this prediction is in reasonable agreement with experiment at high temperatures.

As a way to circumvent conceptual difficulties at short mean free path, one recent suggestion by Cahill and Pohl[24] is to recognize explicitly that the concept of elastic waves carrying heat loses its significance when the calculated value of ℓ approaches intermolecular distances, i.e. it is suggested that the phonon picture should be discarded in this situation. Using an idea going back to Einstein, Cahill and Pohl proposed as an alternative that heat should be regarded as being transported by a random walk of localized oscillations. Values of λ calculated on this model are similar to those found experimentally for glasses at $T > 100$ K and also similar to values of λ_{min} as calculated by Slack[13].

In a general way, one perhaps has the intuitive feeling that "disorder" is somehow instrumental in providing the dominant contribution to the thermal resistivity in glasses. Some years ago, Ziman[31] attempted to approach this problem by considering the analogous situation of propagation of radio waves in an irregularly refracting ionosphere and showed that the mean free path tended to a constant value at high frequencies. According to the dominant phonon approximation[24], high frequency waves should be important for λ at high temperatures. In a more direct approach which has been employed very recently, a computer simulation study by Michalski and Erdös[32] has provided a positive indication that glass-like behaviour can arise as a consequence of the introduction of a degree of structural disorder. These workers investigated a classical system in two dimensions, using an array of masses connected by springs, and determined values for λ. For a periodic array they found that λ decreased with increasing T, as for a crystal. On the other hand, the introduction of a slight aperiodicity, by moving 5% of the masses, had the result that λ increased with T, as for a glass, and in this case there was evidence for some localization of vibrational modes. It will be recalled that localization of vibrational modes was a feature of the model for a glass at high temperatures proposed by Cahill and Pohl[24].

Localization of vibrational modes also enters into an alternative analysis of $\lambda(T)$ of glasses and ID solids due to Jagannathan et al.[33]. These workers used a microscopic model in which it was assumed that there was a fractal connectivity for the masses which participate in the vibrational dynamics, with quantized localized vibrations of the fractal network being referred to as "fractons". According to their model, at temperatures above the "plateau" (a "universal" feature at ~ 10 K, see above) the predicted behaviour was $\lambda \sim T$ as a consequence of phonon-induced fracton hopping between localized vibrational excitations. An upper-temperature limit to the linear variation of λ with T was supposed to be provided by the "anharmonic quenching" of hopping conductivity at high T. Despite some reasonable agreement with experimental data, it is fair to say that the basic assumptions of this model have not been widely accepted. Reservations have been expressed[34,35] that the fractal nature of fully-dense glassy systems has not been convincingly argued or demonstrated (although low-density silica aerogels have been shown to have fractal properties[35]).

Another theoretical approach which predicts $\lambda \sim T$ for glasses at temperatures above the (~ 10 K) plateau in λ is due to Karpov and Parshin[36] who used a microscopic model incorporating localized "soft" potentials[37]. They deduced a variation $\lambda \sim T$ at relatively-high temperatures as a consequence of a resonant scattering interaction between phonons of less than thermal energy and two-level states (TLS). The phenomenological model of TLS has been extensively used[23,38,39] in discussions of the low-temperature properties of glasses, especially for $T < 1$ K. TLS are claimed to arise naturally in the soft potential model[37].

THERMAL CONDUCTIVITY OF INTERMEDIATELY-DISORDERED (ID) SOLIDS

An overview of $\lambda(T)$ for a range of ID solids is given in Figure 1, with the well-ordered solid KBr and SiO_2 glass included to indicate limiting behaviour. A number of the solids for which data are shown refer to organic substances. The substances which have been selected for discussion have comparatively small values of λ over the temperature range considered (100–400 K). For some of these it can be seen from the figure that λ is in the range 0.1–1 W m^{-1} K^{-1}, which is the same order of magnitude of λ as for the various glasses of different bonding types described by Cahill and Pohl[24]. In most cases shown in Figure 1 it has been practical to transform the data to isochoric conditions so they are described by $\lambda(T)_v$ in our notation. λ is only weakly dependent on T for many of the results in the figure.

The data[12] shown for KBr pertain to isochoric conditions and can be described by $\lambda(T)_v \propto T^{-1}$. This variation is not obvious from Figure 1 but an alternative procedure is to plot the thermal resistivity $W(= \lambda^{-1})$ against T. If this is done[12] then it is found that an extrapolation of the data passes through the origin of co-ordinates within experimental inaccuracy, which proves $W \propto T$ and hence $\lambda \propto T^{-1}$. We also estimate ℓ for KBr at a temperature of 300 K. We use $\lambda = 3.5$ W m^{-1} K^{-1} (Figure 1), which is the thermal conductivity at 300 K of a crystal having a density equal to that at zero temperature and pressure, and we assume a molar heat capacity of 3R, where R is the gas constant. (This assumption for the molar heat capacity, which has already been used above, takes only the acoustic modes into account, and we shall also make the same assumption in all later estimates of ℓ for ID solids.) The velocity v is taken to be the bulk velocity given by the well-known expression $(v_L^2 - \frac{4}{3}v_T^2)^{1/2}$, where v_L is the longitudinal and v_T the transverse sound velocity. (No claim is being made that the expression for the bulk velocity provides the best average over v_L and v_T and our justification for its use is on practical grounds. We also have that $v = (\rho\kappa_S)^{-1/2}$, where κ_S is the adiabatic compressibility, so that v may be estimated in a consistent way from data for compressibility in those cases where data for sound velocity are not available.) Using data for v_L and v_T from the compilation of Simmons and Wang[40] we obtain $v = 2.27$ km s^{-1}. With $\rho = 2.75$ Mg m^{-3} and using Eq. (1) we obtain $\ell = 8$ nm, which is about 24 times the interionic spacing[41].

The data[1] shown in Figure 1 for SiO_2 glass actually refer to measurements under isobaric conditions, $\lambda(T)_P$. However, it turns out for this substance that these data
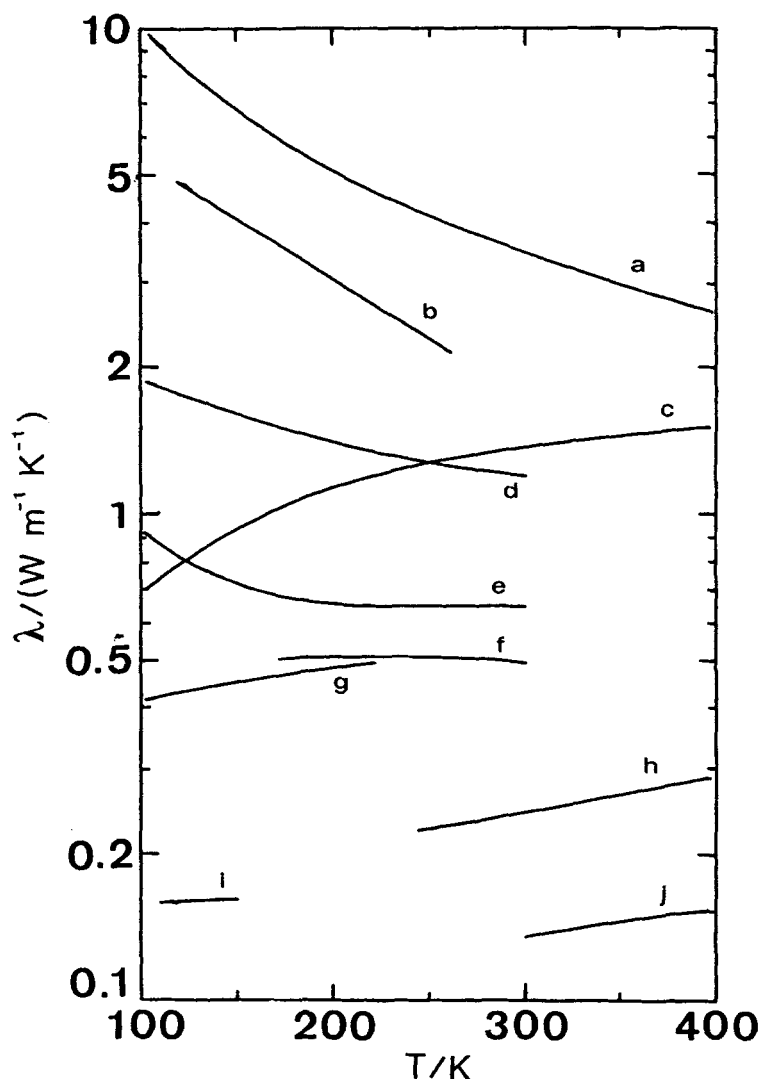
Figure 1 Thermal conductivity λ plotted against temperature T for nonmetallic solids: (a) KBr[12], (b) ice Ih[12], (c) SiO$_2$ glass[1], (d) equimolar KBr–KCl alloy[12,42], (e) phase I of benzene[12], (f) urea-hexadecane channel compound[75], (g) tetrahydrofuran clathrate hydrate[63], (h) plastic crystal phase I of adamantane[12], (i) glassy crystal state derived from plastic crystal phase I of cyclohexanol[54], and (j) plastic crystal phase II of (+)-camphor and (indistinguishable results for) plastic crystal phase II' of (±)-camphor[79]. Data are isochoric $\lambda(T)_v$ except for (f) and (i) which are isobaric $\lambda(T)_P$ at low pressure.

are effectively the same as $\lambda(T)_v$ (within $\sim 10^{-2}\%$). This situation arises because g is small[13], and α_P is very small[10], for SiO$_2$ glass.

The remaining solids included in Figure 1 will now be considered, roughly in the sequence of increasing "disorder". As a crude indicator of "glassy" behaviour, we shall take note of the slope $d\lambda/dT$, which ranges from $(\partial \ln \lambda/\partial \ln T)_v = -1$ for the well-ordered solid KBr to $d\lambda/dT > 0$ for SiO$_2$ glass.

Alkali-halide alloys

Data[12] for λ of the equimolar alkali-halide alloy KBr-KCl which are shown in Figure 1 pertain to isochoric conditions[42]. It can be seen from the figure that the magnitudes of both λ and its temperature dependence have been reduced on going from KBr to the alloy. It can also be seen from the figure that $\lambda_{alloy}/\lambda_{KBr} \approx 0.2 - 0.3$ and detailed analysis shows that $(\partial \ln \lambda/\partial \ln T)_v$ for the alloy is about -0.4 compared with the value -1 for KBr. Alternatively, when the thermal resistivity W is plotted against T it turns out that the results can be described to a reasonable approximation by an expression of the form $W = A + BT$. (The plot of isochoric $W(T)$ is not shown here but corresponding isobaric data are displayed in Figure 4 of Ref. 12. The forms of $W(T)$ are effectively the same for this alloy under both isochoric and isobaric conditions.) By using this analysis, it is found that the terms "A" and "BT" each make up about one half the total W at a temperature of 300 K. A straightforward interpretation of the results would then be to regard the constant A as a "disorder" term arising from mass and strain fluctuations associated with the random arrangement of Br and Cl ions on the halide sites of the crystal, and to regard BT as a "thermal" term associated with phonon-phonon interactions. On this picture of the alloy, disorder and thermal contributions to W are independent, additive and of about the same magnitude near room temperature. In principle, mass and strain fluctuation contributions to the thermal resistivity of an alloy are taken into account in the phenomenological model due to Abeles[43].

Simple molecular solids, benzene and ice Ih

Results for λ of the atmospheric-pressure solid modification of benzene (C_6H_6) presented in Figure 1 indicate an even greater deviation from the behaviour of a well-ordered solid than was found for the alkali-halide alloy. Measurements under low-pressure isobaric conditions[44] yielded a variation $\lambda(T)_P \sim T^{-1}$ but when these data are transformed[12] to isochoric conditions we find $\lambda(T)_v \approx$ constant in the temperature range 180-290 K, as shown in Figure 1. Evidently, thermal expansion has a significant effect on λ for this phase of benzene and transformation to isochoric conditions is a crucial step in the analysis of data.

Unfortunately, no explicit theoretical calculation of λ has yet been attempted for a molecular solid like benzene so our approach must be empirical. For a start, we may ask whether the result $\lambda(T)_v \approx$ constant is in fact always found as a characteristic feature of simple molecular solids. We can show that this is not the case by examining results for another simple molecular solid, ice Ih. It can be seen from Figure 1 that $\lambda(T)_v$ for ice Ih is not at all constant and in fact has a pronounced negative slope. It turns out that if we consider the quantity $(\partial \ln \lambda/\partial \ln T)_v = -n$ for this solid then we find $n \geq 1$, according to the analysis by Slack[45].

We can also estimate ℓ for these solids. In the case of benzene, there do not appear to have been any measurements of sound velocity, so we use an indirect procedure. From isothermal compression measurements by Bridgman[46] we estimate the adiabatic compressibility $\kappa_S \approx 0.20$ GPa^{-1}. Using $\rho \approx 1$ Mg m^{-3} and calculating v from

the expression $(\rho\kappa_S)^{-1/2}$ we obtain a value of 2.2 km s^{-1}. We use the value 3R for the molar heat capacity and take $\lambda = 0.6$ W m^{-1} K^{-1} (Figure 1). Using Eq. (1), we obtain $\ell = 2.6$ nm, which is about 5 times the cube root of the volume per molecule[47]. In the corresponding calculation for ice Ih at a temperature of about 250 K we take $\lambda = 2.5$ W m^{-1} K^{-1} (Figure 1), a molar heat capacity of 3R and density[48] $\rho = 0.93$ Mg m^{-3}. We substitute measured values[49] of v_L and v_T in the expression for bulk velocity to obtain $v = 3.1$ km s^{-1}. Using these values, Eq. (1) yields $\ell = 1.9$ nm, which is only about 7 times the nearest neighbour distance between oxygen atoms[48]. (Slack[45] obtained the value $\ell = 9.5$ nm for ice Ih at a temperature of 273 K. The difference between this result and the value we have estimated is due mainly to Slack's assumption of a molar heat capacity of 3R/4, which is about 17% of the experimental value[48].) As a multiple of the intermolecular spacing, our estimated values of ℓ, although somewhat uncertain, are apparently quite similar in benzene and ice Ih, even though the temperature dependence of λ is very different for these two solids. On the evidence presented here, it is clear that we cannot always expect to find that a relatively short calculated mean free path is associated with a deviation from the variation $\lambda \sim T^{-1}$ which is characteristic of a well-ordered solid.

Some further insight into the results for benzene may be gained using an approach due to Roufosse and Klemens[28] who discussed λ for complex crystals. They included consideration of the situation where the mean free path was limited by anharmonicities and they took the frequency dependence of ℓ explicitly into account. They assumed that, at low frequencies, the frequency (ω)-dependent mean free path $\ell(\omega)$ was given by $\ell(\omega) \propto \omega^{-2}$. For high frequencies they made the crucial assumption that the mean free path was given by a constant value $\ell_0 = \alpha a$, where a is the interatomic spacing. The constant α was assumed to be of order unity but was not otherwise evaluated. The development of a constant value of ℓ, as the temperature was increased, was attributed by these workers to a progressive deterioration of the first-order perturbation approximation in a situation of increasing strength of anharmonic interactions. Thermal conductivity calculated according to this model showed a gradual transition from $\lambda \sim T^{-1}$ at low temperatures to $\lambda \sim$ constant at high temperatures. The results for $\lambda(T)$ of benzene in Figure 1 are broadly consistent with such predicted behaviour.

There is even an independent indication of an exceptional degree of anharmonicity in solid benzene. Andrew and Eades[50], in their nuclear magnetic resonance (NMR) investigation of this solid, observed a narrow and constant line width for $T > 120$ K. The narrowing was interpreted as indicating reorientational motion of the benzene molecule about its hexad axis between structurally indistinguishable orientations. The estimated reorientational frequency was ~ 0.1 THz near melting. It seems plausible that the intermolecular potential function could be strongly anharmonic in a solid which exhibited such reorientational motion. It is worth remarking that narrowing of the NMR line width has also been observed[51] to be essentially unchanged at the pressures required to maintain isochoric conditions in the data for λ of benzene in Figure 1.

If these semi-quantitative ideas are roughly correct, then the weak temperature dependence of λ in solid benzene may be connected with anharmonicity and

molecular motion. In this situation, the term "dynamic disorder" might usefully be employed in association with the reorientational motion which was inferred for the benzene molecule. There is no evidence for such motion in the case of ice Ih^{45} where $(\partial \ln \lambda / \partial \ln T)_v$ is about the same as for a well-ordered solid.

Plastic crystal phases and glassy crystal states

Plastic crystal phases[9,52] have already been mentioned above and many are known, mainly for organic substances. In such phases, rather globular (i.e. roughly-spherical) molecules exhibit long-range translational periodicity in typically highly-symmetric lattices which are often cubic and, characteristically, there is disorder in the orientation of molecules. Clearly, it is of the essence for such phases that the effective structural unit should have a specifiable orientation, a feature which restricts them to the province of *molecular substances*. A given substance may possess more than one plastic crystal phase over different ranges of temperature and pressure.

Under equilibrium conditions, a plastic crystal (PC) phase (when it exists) will form on isobaric cooling from the liquid phase, and an additional PC phase (or phases) could exist at lower temperatures. However, when the temperature is reduced sufficiently we can expect the substance to transform to a phase which is not plastic and which we may refer to as a normal crystal (NC) phase. This expectation is to some extent based on a simple thermodynamic argument. As already described, it is characteristic of a PC phase to exhibit disorder in the orientation of molecules and such disorder implies a contribution to the configurational entropy S_{config}. If the third law of thermodynamics is to be satisfied then disorder must disappear and $S_{config} \rightarrow 0$ as $T \rightarrow 0$. Although there seems to be nothing in principle to prevent a PC phase becoming orientationally ordered in a continuous manner as $T \rightarrow 0$, in practice it is found that the PC phase undergoes a first-order transition to an NC phase having very much reduced orientational disorder. This change in the degree of disorder is reflected in a substantial measured change of entropy[9] through the PC–NC transition.

However, equilibrium conditions need not always apply. In particular, we can imagine a PC phase being cooled in such a way that the equilibrium PC $\rightarrow$ NC transition does not take place and that the molecular orientational disorder which is characteristic of a PC phase becomes "frozen in" at low temperatures. This possibility seems to have first been recognized in an investigation of cyclohexanol by Adachi et al.[53], who also invented the term "glassy crystal" to describe the state which exhibits this frozen-in orientational disorder. In addition, these workers provided evidence that the transition from the supercooled PC phase to the glassy crystal (GC) state showed features (e.g. in the heat capacity) which were correspondingly similar to those for the transition from a supercooled liquid phase to a glass state. The GC state is not generally difficult to obtain, a cooling rate of about 3 K min^{-1} being sufficiently rapid to achieve it in cyclohexanol, for example.

Although λ under pressure has been measured for a number of PC phases[12] the corresponding data for α_P and κ_T are not generally available. One exception in this respect is adamantane ($C_{10}H_{16}$) and results for $\lambda(T)$ under isochoric conditions[12] for PC phase I of this substance are included in Figure 1. Measurements of $\lambda(T, P)$

for adamantane were made by Wigren and Andersson[11]. They found the result $(\partial\lambda/\partial T)_P < 0$ for phase I under low-pressure isobaric conditions but when the data are transformed to isochoric conditions we obtain $(\partial\lambda/\partial T)_v > 0$, as can be seen in Figure 1. For this phase, the effect of thermal expansion is sufficiently great to change the sign of $d\lambda/dT$, so transformation to isochoric conditions is important to the analysis. (Recently, the thermal conductivity of PC phase I of cyclohexanol was investigated by Andersson et al.[54] who found that $(\partial\lambda/\partial T)_v$ was clearly positive and $(\partial\lambda/\partial T)_P$ was slightly positive for this phase.)

For the PC phase of adamantane, it can be seen from Figure 1 that λ has a small value, 0.25–0.30 W m^{-1} K^{-1}, and a positive $(\partial\lambda/\partial T)_v$ which is similar in magnitude to that for SiO$_2$ glass. As described above, the value $\ell \approx 1.2$ nm which was estimated using Eq. (1) is about the same as the intermolecular distance. All these features are consistent with regarding this PC phase as significantly "glass-like" in terms of heat transport despite the fact that the molecular positions exhibit long-range translational periodicity[9].

No theory has yet been produced which attempts to predict λ for a PC phase but we might speculate as to the physical features which will probably need to be taken into account. A microscopic model for the PC phase of adamantane[55,56] is that the molecules are probably distributed at random over two distinguishable preferred orientations separated by a 90° rotation. Abrupt reorientational motion between preferred orientations takes place over a range of frequencies ~ 0.1 THz. PC adamantane and benzene[50] (described above) appear to be analogous in terms of dynamic disorder associated with reorientational motion of molecules. In adamantane, however, there is the additional structural feature that the solid, at any instant, exhibits semi-static disorder in molecular orientation over the set of preferred orientations. On the basis of the microscopic models which have been described, it seems plausible, although speculative, that heat transport properties should be expected to be somewhat more "glass-like" in PC adamantane than in benzene. Very simply, in terms of molecular orientation, adamantane exhibits both dynamic and semi-static disorder whereas only dynamic disorder has been detected in benzene. In terms of the value of $d\lambda/dT$, PC adamantane is closer to SiO$_2$ glass than is benzene, as can be seen from Figure 1. These remarks suggest that a model to predict λ for a PC phase will need to take into account both the consequences of strong anharmonicities[28] (which might be associated with reorientational freedom) and the known existence of semi-static molecular orientational disorder.

The thermal conductivity of the GC state has so far been little investigated. Figure 1 shows results by Andersson et al.[54] for $\lambda(T)$ of the GC state associated with PC phase I of cyclohexanol. The results are for isobaric $\lambda(T)_P$ because data are not available to enable transformation to isochoric conditions. Measurements were made only up to a temperature of 120 K because the GC state could not be maintained at higher temperatures. The small magnitude of λ (<0.2 W m^{-1} K^{-1}) and the slightly positive value of $(\partial\lambda/\partial T)_P$ which can be seen in Figure 1 provide an indication that heat transport properties for the GC state resemble those of a glass like SiO$_2$. This indication is further substantiated using results by Bonjour et al.[57] for $\lambda(T)$ (and heat capacity) of the GC state of cyclohexanol at lower temperatures (1–20 K). Their

results also showed that this ID solid had thermal properties which are similar to those of glasses.

Results closely resembling those for cyclohexanol were obtained in recent measurements of λ for cyclooctanol[58]. GC states arising from three different PC phases of cyclooctanol each showed a small magnitude of λ (≈ 0.2 W m^{-1} K^{-1}) and a small or slightly positive value of $(\partial\lambda/\partial T)_P$.

As regards theory for λ, future developments[3,4,24,38,39] are likely to feature a close connection between glasses and ID solids (including the GC state).

Inclusion compounds

For our purposes, solid-state inclusion compounds[9] (also known as adducts) contain two distinct chemical species that are only loosely bound to each other. The major (host) species is arranged in a crystal structure incorporating molecular-sized voids, or cages, wherein the molecules of the minor (guest) species are located. Host-guest bonding is weak; the geometry of the host structure encapsulates the guest. Vibrational and/or rotation-like motion of the guest molecules can readily occur.

Clathrate hydrates

Clathrates constitute one class of inclusion compound in which the voids in the host structure are roughly spherical. In these voids, guest molecules of similar shape and up to a certain size can be accommodated. A sub-class of clathrates is that of clathrate hydrates[59] where the host species is H_2O. In clathrate hydrates, localized excitations due to translation and/or rotation-like motion of the guest molecules are known to exist at very low frequencies[59,60].

Since the host structure is "ice-like" in clathrate hydrates there is, not surprisingly, a good deal of similarity[59] between some properties of clathrate hydrates and the corresponding properties of ice. However, the thermal conductivity is an exception in this respect. The first indication of such exceptional behaviour was found in measurements of λ by Stoll and Bryan[61] for clathrate hydrates in which methane or propane was the guest species. In both cases, these workers found $\lambda \approx 0.4$ W m^{-1} K^{-1} near melting. This value of λ is about the same as that for liquid water and only about 1/5 the value for ordinary ice (Ih) at similar temperatures. The temperature dependence of λ was not determined by Stoll and Bryan. Shortly thereafter, the results of experiments in our laboratory[62,63] showed a similar magnitude of λ for a tetrahydrofuran (THF) clathrate hydrate but with the additional, and surprising, feature that there was a positive, "glass-like", value of $(\partial\lambda/\partial T)_p$ over our entire range of measurement of 100–260 K.

Our data[63] for $\lambda(T)_v$ of the THF clathrate hydrate are included in Figure 1. In fact, results for $\lambda(T)_v$ and $\lambda(T)_p$ are nearly the same for this solid. This near-equality is mainly due to the very small value $(\partial \ln \lambda/\partial P)_T = 0.058$ GPa^{-1} which we found in our experiments[63]. Using $\kappa_T = 0.126$ GPa^{-1} which Bathe et al.[64] deduced from their measurements of sound velocity, we obtain $g = 0.46$ which is very small by comparison with the values $g \approx 5$–12 which are typical for well-ordered solids[12].

Combining the value $g = 0.46$ with a measured value[65] of $\alpha_P = 1.85 \times 10^{-4}\,\mathrm{K}^{-1}$ we find that an increase of temperature of 100 K yields a difference between isobaric and isochoric values of λ of $<1\%$. From the results shown in Figure 1, we can see that $\lambda(T)$ for the THF clathrate hydrate is similar to that for SiO_2 glass.

It should be mentioned that $\lambda(T)$ under isobaric conditions for the THF clathrate hydrate has also been measured by other workers. In some cases[66,67] there was agreement within experimental inaccuracy with the results of Ross and Andersson[63] (Figure 1). However, this was not the case for the measurements of Tse and White[60]. Their results for λ at a temperature of 100 K were only about 1/4 the values[63,66,67] which had been obtained in previous work. Although Tse and White[60] tried to maintain that their results could be reconciled with those of other workers within experimental inaccuracy their arguments are not convincing. The reason for this disagreement in results is unknown.

In order to help analyse the results, we can estimate ℓ for the THF clathrate hydrate which is well-known to have the composition $THF \cdot 17H_2O$. We assume for the specific heat capacity the expression $18 \times 3R/(M_{THF} + 17 \times M_{H_2O})$ where M_{THF} and M_{H_2O} are the molar masses of THF and H_2O respectively. This gives $c_P = 1.19\,\mathrm{J\,K^{-1}\,g^{-1}}$ which is about 60% of the experimental value[68]. From the work of Bathe et al.[64] we obtain $\rho = 0.954\,\mathrm{Mg\,m^{-3}}$ and a bulk velocity $v = 2.94\,\mathrm{km\,s^{-1}}$. Taking $\lambda = 0.5\,\mathrm{W\,m^{-1}\,K^{-1}}$ (Figure 1) and using Eq. (1) we obtain $\ell = 0.45$ nm. This relatively-short distance is in fact about equal to the cage diameter in clathrate hydrates[69]. When we consider the small values of ℓ and λ, together with the positive sign of $d\lambda/dT$, we can conclude that the THF clathrate hydrate strongly resembles a glass in terms of heat transport properties.

Tse and White[60] showed that their results for $\lambda(T)$ of the THF clathrate hydrate could be fitted by a resonant scattering model involving interactions between localized low-frequency vibrations of the guest molecules and the acoustic phonons of the host lattice. Such a model, if it is valid for the THF clathrate hydrate, may also pertain to clathrate hydrates generally because they all have very similar thermal properties. Measurements of λ of clathrate hydrates with guest species 1,3-dioxolane[70,71], cyclobutanone[70], ethylene oxide[66], methane[61,72], propane[61] and Xe[73] all yielded values in the range 0.3–$0.5\,\mathrm{W\,m^{-1}\,K^{-1}}$ and, where the temperature dependence of λ was determined, the result was always $d\lambda/dT > 0$. The thermal conductivity of clathrate hydrates therefore appears to be "universal"[60] in the same sense as was described earlier in connection with glasses[24]. The "universal" behaviour of λ for clathrate hydrates has been found to be insensitive to a change of structure of the host lattice over the two structure types (I and II)[59,69] which have been investigated[73]. The magnitude of λ may depend to a relatively small extent on the guest species[70,73].

There is a point in connection with experimental data that should be mentioned for the 1,3-dioxolane clathrate hydrate. Ahmad and Phillips[71] presented evidence that a "glass-like" $\lambda(T)$ for this clathrate hydrate (i.e. $d\lambda/dT > 0$) could be obtained for a specimen subjected to a rapid cooling rate of $8\,\mathrm{K\,min^{-1}}$ but their measured values of λ were different when they used a slower cooling rate of $0.8\,\mathrm{K\,min^{-1}}$. In particular, as a consequence of the latter slow cooling rate, they obtained the result

$d\lambda/dT < 0$ at a temperature of 100 K, which is the same sign of this derivative as is found for a well-ordered solid. However, no dependence of $\lambda(T)$ on cooling rate history has ever been observed in any other investigation of heat transport in clathrate hydrates[60,62,63,66,67,70,72,73] and such history-dependent behaviour therefore cannot be regarded as substantiated. By way of a direct comparison, Andersson and Ross[70] employed a cooling rate of about 0.3 K min^{-1} in their measurements of λ for the 1,3-dioxolane clathrate hydrate (although this experimental detail was not in fact stated in Ref. 70), which is even slower than the slowest cooling rate employed by Ahmad and Phillips[71].

Attempts to account in general terms for the "glass-like" $\lambda(T)$ observed for clathrate hydrates have commonly concentrated on motional excitations of the guest molecules[60,63,70] but alternative interpretations have also been advanced. Ahmad and Phillips[71] employed a model which incorporated tunnelling states associated with proton disorder together with point defect scattering. In their analysis, the effect of the guest species was ignored on the grounds of weak guest-host interaction. The guest species was also ignored in another analysis of $\lambda(T)$ for clathrate hydrates (and ice polymorphs) due to Dharma-wardana[74]. He assumed that ℓ was scaled according to the number of oxygen atoms per primitive cell, with ℓ being "quenched" at a minimum and constant value $\sim$ the lattice parameter in the clathrate hydrates. The observed positive $d\lambda/dT$ was not predicted by this model.

It will be clear from the foregoing discussion that no theoretical model for $\lambda(T)$ of clathrate hydrates has yet been firmly established, similar to the case for glasses and other ID solids. In this situation, it might be worth re-examining a feature which Ross and Andersson[63] observed for the THF clathrate hydrate. They obtained the empirical result that their isobaric data for $\lambda(T)$ (which are close to isochoric, see above) could be described within experimental inaccuracy by the expression $\lambda \sim \exp(-T_0/T)$, with $T_0 = 37$ K. This functional form suggests the possibility of thermally-activated hopping of heat-transporting excitations, in the same spirit as in some other recent proposals[24,33] for heat transport in solids having a small estimated value of ℓ.

Channel compounds

Channel compounds[9] are another class of inclusion compound. In this case the guest molecules have a linear external shape and the voids in the host lattice are in the form of tubes, or channels. Typical guest species are n-alkanes, and urea or thiourea can act as host species.

The only measurements of thermal conductivity for a channel compound are for a specimen in which urea was the host and hexadecane was the guest. Results[75] for $\lambda(T)_P$ of this solid, measured under low-pressure isobaric conditions, are included in Figure 1. Values of λ which were obtained are constant to within $\pm 1\%$ over a range of temperature of about 120 K and they are similar in magnitude to those for the THF clathrate hydrate.

Structural investigations[76] for the room-temperature phase of the channel compound have shown that the hexadecane guest molecules are distributed statistically

over a set of orientations which are separated by rotations of 60° about the long axis of the molecule. Furthermore, recent NMR measurements[77] have been interpreted as indicating substantial dynamic disorder of the guest molecules. The motion which was inferred included low-frequency jump reorientation between these 60° positions.

Since guest molecule dynamics apparently have some similarity in channel compounds[77] and in clathrate hydrates[60], the observed similarity in λ (Figure 1) is perhaps not surprising if host-guest interactions are indeed a significant contributing factor to the total thermal resistivity.

It is known that the urea-hexadecane channel compound undergoes a phase transition[76,77] which was also detected in measurements of λ. Results[75] for $\lambda(T)_P$ of low-temperature phase III of this compound under low-pressure isobaric conditions (not shown in Figure 1) exhibited a weak temperature dependence with $(\partial \ln \lambda / \partial \ln T)_P \approx -0.13$, which is about an order of magnitude different from what is expected for a well-ordered solid. The inference from NMR measurements[77] was that there is an appreciable degree of guest-molecule motion in phase III of the adduct (as well as in phase II). Thus, the results suggest that freedom of motion of the guest species may have a significant effect on $d\lambda/dT$ in both phases II and III of this channel compound.

Chiral substances

As is well-known, a chiral substance is one having constituent molecules which cannot be superimposed on their own mirror image. In other words, the molecules of such a substance may exist as either of two distinguishable enantiomers which are mirror images of each other. These two enantiomers are commonly designated (+) and (−). A given specimen of a chiral substance may consist entirely of molecules which are all the same enantiomer (either (+) or (−)), or it may contain a mixture of the two enantiomers in some proportion. A general description of a chiral substance in a thermodynamic sense is provided by the *compositional phase diagram*. Such a diagram has as axes the temperature T and the mole fraction X of one of the enantiomers, and it refers to isobaric conditions, usually at atmospheric pressure. Compositional phase diagrams and other properties of chiral substances have been discussed in detail by Jacques *et al.*[78], and in what follows we use their terminology.

A specimen of equimolar composition (i.e. for $X = 0.5$ and hence with (+)- and (−)-enantiomers present in equal proportions) whose physical state is not specified is referred to as a racemate and designated by the symbol (±). Further specialized terminology pertaining to this value of X is used with reference to solids. A solid phase in which the enantiomers occupy a crystal lattice in a well-defined (and hence ordered) structural arrangement is referred to as a racemic compound. The ordered arrangement of structural units implies that an ideal racemic compound will have a vanishingly-small range of solid solubility. On the other hand, if the phase is a solid solution which exists over some range of X then the enantiomers must occupy the crystal lattice in an unordered way if a continuous variation of X is to be accommodated. Such a solid solution at the special composition $X = 0.5$ is referred to as a pseudoracemate.

The only chiral substance whose thermal conductivity has been measured is camphor (1,7,7-trimethyl-bicyclo[2.2.1]heptan-2-one). Andersson et al.[79] measured $\lambda(T, P)$ for a number of solid phases of both (+)- and (±)-camphor. Structural data for the camphor molecule[9,80] show that it is both chiral and globular. The pure enantiomer (+)-camphor has three solid phases, I, II and III, at atmospheric pressure. Data for entropy[9] and dielectric permittivity[81] indicate that phases I and II are PC phases. The compositional phase diagram of camphor determined by Schäfer and Wagner[82] shows that these PC phases each form the terminus of a continuous solid solution. Because of continuity of crystal structure, such solid solutions will also be PC phases and will moreover be disordered in terms of occupation of lattice sites by the two enantiomers, as noted above. At the composition $X = 0.5$, we use the designations I' and II' for the pseudoracemates corresponding to phases I and II, respectively, of the pure enantiomer. At the same composition, a phase transition II'–III' takes place at a temperature[82] of 208 K (at atmospheric pressure). It may be inferred[79] that phase III' will be a racemic compound (i.e. the enantiomers will be arranged in an ordered way in the structure) under equilibrium conditions.

For use in our discussion, we introduce the term configuration[83] which refers to the way in which the atoms of a molecule are connected spatially. A change of configuration can only take place by breaking and reforming chemical bonds. Inspection of the structure of the camphor molecule[9,80] shows that (+)- and (−)-camphor correspond to different configurations which, as noted in earlier discussion, are also enantiomers. The results of Andersson et al.[79] enable us to explore how configuration can affect heat transport in a solid. As an example, we describe the situation for phase II of (+)-camphor and II' of (±)-camphor. Both phases have the same crystalline symmetry[84,85] and the same[84] or nearly the same[85] lattice parameter. Both are PC phases, which implies disorder in molecular orientation (although the details are not known). The main difference between these phases is therefore that all of the molecules have the same configuration in phase II whereas in pseudoracemate phase II' there are two configurations which are arranged at random on the lattice sites (see above). Another way of making a distinction between these two phases is to describe the disorder in phase II as "orientational" and in phase II' as "orientational + configurational". However, it turns out that this distinction has no detectable consequences for heat transport. When results for $\lambda(T, P)$ of phases II and II' were compared at the same values of T and P it was found[79] that λ had the same value for both phases with experimental inaccuracy (±2%). The same general result was obtained for all (+) − (±) PC phase-pairs of camphor for which measurements[79] of $\lambda(T, P)$ were made.

Some results for $\lambda(T)$ of camphor are included in Figure 1. The data[79] which are shown in the figure refer to both of the phases II and II', since, as just emphasized, the measured values of $\lambda(T, P)$ of these two phases were indistinguishable at the same values of T and P. The results which are presented are for isochoric $\lambda(T)_v$. The data in the figure indicate that these ID solids were glass-like, with $(\partial\lambda/\partial T)_V > 0$. We may also estimate the value of ℓ for these phases. As has been our usual practice, we assume a molar heat capacity of 3R (which is about 10% of the experimental value[86]). We

use the density[87] $\rho = 1.00\ \mathrm{Mg\ m^{-3}}$ and estimate bulk velocity v from the expression $(\rho\kappa_T)^{-1/2}$. Using an average value[79] $\kappa_T = 0.27\ \mathrm{GPa^{-1}}$ we obtain $v = 1.9\ \mathrm{km\ s^{-1}}$. We take $\lambda = 0.136\ \mathrm{W\ m^{-1}\ K^{-1}}$ at a temperature of 300 K (Figure 1). The result using Eq. (1) is $\ell = 1.3$ nm compared with the cube root of the volume per molecule[85] of 0.6 nm. For phases II and II' of camphor, a relatively-small value of ℓ, a small magnitude of λ and a positive value of $(\partial\lambda/\partial T)_V$ (Figure 1) all give a clear indication of glass-like heat transport properties, similar to other PC phases which were discussed above.

We now consider the observation[79] that λ was the same for both phases II and II' of camphor and explore two possible interpretations. One possibility is simply that heat transport is in general insensitive to molecular configuration. This seems improbable, since molecular interaction and hence vibrational motion should depend, at least to some extent, on configuration. More data are needed in order to assess this possibility, not only in relation to the situation considered here of con-figurationally-disordered solids but also in connection with the related (and similarly little-developed) area of conformationally-disordered solids[88]. (The term conforma-tion[83] refers to the way in which the atoms of a molecule of a given configuration are arranged in space. A change of conformation takes place without the breaking of chemical bonds.)

Another possible interpretation of the observations for λ of the PC phases of camphor implicitly involves the concept of a minimum thermal conductivity. If $\lambda_{\min}$ has already been reached in these phases as a consequence of orientational disorder then we might suppose that λ could not be reduced still further by any additional disorder such as that associated with a mixture of molecules having different configurations. This seems a probable qualitative interpretation of the observations, but attempts to derive a serious theoretical model are clearly required.

The influence of a mixture of configurations[86] may be greater, and more subtle, in connection with phase III' of $(\pm)$-camphor. Suppose that phase III' is formed in the usual way by cooling phase II' under isobaric conditions. Recall that in phase II' the molecules are disordered both orientationally and configurationally whereas phase III' should be structurally ordered. As a consequence of the II' $\to$ III' transition we expect the orientational disorder to disappear, substantially or entirely, since phase III' is not a PC phase. A change of crystal symmetry also probably occurs but no details in this connection are known at present. These two changes are likely to take place fairly readily in a slowly-cooled specimen. However, there is a third change on a microscopic scale which should also take place if phase III' is to be ordered in every respect and this concerns the positional arrangement of molecules of different configurations. The two enantiomers were located randomly on the lattice sites of phase II' but should exhibit a regularly-ordered arrangement on the lattice sites of phase III'. The corresponding positional re-arrangement which needs to take place across this phase transition can only occur as the result of a diffusion process, which may be slow. Equilibrium conditions will only be attained in phase III' (to yield a true racemic compound) for a structure in which the two configurations exhibit a spatially (i.e. positionally) ordered arrangement.

Nagumo et al.[86] were the first to draw attention to the considerations just described

in connection with the II' → III' transition in camphor. They interpreted some of their calorimetric measurements as indicating that ordering with respect to the positions occupied by molecules of different configurations was not achieved in practice in phase III' except as the result of a prolonged annealing procedure. In other words, they proposed that equilibrium conditions were not attained in an unannealed specimen because of disorder associated with the positions occupied by molecules of different configurations. Nagumo *et al.* considered such a state to be a new form of glassy crystal.

Turning briefly to a consideration of thermal conductivity, Andersson *et al.*[79] reported data for $\lambda(T)$ of an unannealed specimen of phase III' which indicated the possibility of glassy crystal behaviour for this phase. These results were preliminary, and this topic is presently the subject of further investigation.

CONCLUDING REMARKS

The present review has tried to illustrate the continuing interest and activity in the field of thermal conductivity and disorder. For the range of substances considered, which were usually under isochoric conditions, it was found that experimental results for $\lambda(T)$ could be analysed fairly consistently using a simple empirical approach. Even on an empirical basis, it seems clear that the phonon picture of heat transport is at the limit or beyond its useful range of applicability in connection with ID solids at high temperatures. In this situation, a picture of heat transport which involves hopping of localized vibrational excitations shows promise as an alternative but the corresponding models are rudimentary or controversial at present. Heat transport in ID solids at high temperatures remains a difficult theoretical problem.

References

1. Y. S. Touloukian, R. W. Powell, C. Y. Ho and P. G. Klemens (ed), *Thermophysical Properties of Matter* vol 2 *Thermal Conductivity, Nonmetallic Solids* (Plenum, New York, 1970).
2. J. J. De Yoreo, W. Knaak, M. Meissner and R. O. Pohl, *Phys. Rev.*, **B34**, 8828 (1986).
3. A. M. de Goër, *Phonon Scattering in Condensed Matter V* (Springer Series in Solid-State Sciences 68), ed A. C. Anderson and J. P. Wolfe (Springer-Verlag, Berlin, 1986), pp. 6–14.
4. E. R. Grannan, M. Randeria and J. P. Sethna, *Phys. Rev.*, **B41**, 7799 (1990).
5. J. E. Parrott and A. D. Stuckes, *Thermal Conductivity of Solids* (Pion, London, 1975).
6. R. Berman, *Thermal Conduction in Solids* (Clarendon, Oxford, 1976).
7. G. P. Srivastava, *The Physics of Phonons* (Adam Hilger, Bristol, 1990).
8. R. G. Ross, *High Temp.-High Press.*, **21**, 261 (1989).
9. N. G. Parsonage and L. A. K. Staveley, *Disorder in Crystals* (Clarendon, Oxford, 1978).
10. Y. S. Touloukian, R. K. Kirby, R. E. Taylor and T. Y. R. Lee (ed), *Thermophysical Properties of Matter* vol 13 *Thermal Expansion, Nonmetallic Solids* (Plenum, New York, 1977).
11. J. Wigren and P. Andersson, *Mol. Cryst. Liq. Cryst.*, **59**, 137 (1980).
12. R. G. Ross, P. Andersson, B. Sundqvist and G. Bäckström, *Rep. Prog. Phys.*, **47**, 1347 (1984).

13. G. A. Slack, *Solid State Physics* vol 34, ed H. Ehrenreich, F. Seitz and D. Turnbull (Academic, New York, 1979), pp 1–71.
14. G. Beggerow, *High-Pressure Properties of Matter, Landolt-Börnstein (New Series) Group IV* vol. 4 (Springer-Verlag, Berlin, 1980).
15. S. K. Bhateja and K. D. Pae, *Reviews in Macromolecular Chemistry* vol 14A, ed G. B. Butler, K. F. O'Driscoll and M. Shen (Marcel Dekker, New York, 1975) pp 77–133.
16. T. Ito, *Polymer*, **23**, 1412 (1982).
17. J. M. Grace and A. C. Anderson, *Phys. Rev.*, **B40**, 1901 (1989).
18. C. Kittel, *Introduction to Solid State Physics* 6th ed (Wiley, New York, 1986).
19. S. Pettersson, *J. Phys. C: Solid State Phys.*, **20**, 1047 (1987).
20. S. R. Elliott, *Physics of Amorphous Materials* (Longman, London, 1983).
21. N. E. Cusack, *The Physics of Structurally Disordered Matter: An Introduction* (Adam Hilger, Bristol, 1987).
22. A. Loidl, *Ann. Rev. Phys. Chem.*, **40**, 29 (1989).
23. W. A. Phillips (ed), *Amorphous Solids, Low-Temperature Properties* (Springer-Verlag, Berlin, 1981).
24. D. G. Cahill and R. O. Pohl, *Ann. Rev. Phys. Chem.*, **39**, 93 (1988).
25. O. Sandberg, *Ph.D. Thesis*, University of Umeå, Sweden (1980).
26. J. E. McKinney and M. Goldstein, *J. Res. NBS* A, **78**, 331 (1974).
27. F. A. Khayyat and P. Stanley, *J. Phys. D: Appl. Phys.*, **11**, 1237 (1978).
28. M. C. Roufosse and P. G. Klemens, *J. Geophys. Res.*, **79**, 703 (1974).
29. N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt, Reinhart and Winston, New York, 1976).
30. C. Kittel, *Phys. Rev.*, **75**, 972 (1949).
31. J. M. Ziman, *Electrons and Phonons* (Clarendon, Oxford, 1960).
32. J. Michalski and P. Erdös, *Solid State Commun.*, **72**, 967 (1989).
33. A. Jagannathan, R. Orbach and O. Entin-Wohlman, *Phys. Rev.*, **B39**, 13465 (1989).
34. E. Courtens, R. Vacher and E. Stoll, *Physica*, **D38**, 41 (1989).
35. E. Courtens, R. Vacher and J. Pelous, *Fractals' Physical Origin and Properties*, ed L. Pietronero, (Plenum, New York, 1990), pp. 285–294.
36. V. G. Karpov and D. A. Parshin, *Sov. Phys.-JETP*, **61**, 1308 (1985).
37. Yu. M. Galperin, V. G. Karpov and V. I. Kozub, *Adv. Phys.*, **38**, 669 (1989).
38. S. Hunklinger and A. K. Raychaudhuri, *Prog. Low Temp. Phys.*, **9**, ed D. F. Brewer (North-Holland, Amsterdam, 1986) pp. 265–344.
39. W. A. Phillips, *Rep. Prog. Phys.*, **50**, 1657 (1987).
40. G. Simmons and H. Wang, *Single Crystal Elastic Constants and Calculated Aggregate Properties: A Handbook*, 2nd ed, (MIT Press, Cambridge, Mass., 1971).
41. R. W. G. Wyckoff, *Crystal Structures*, 2nd ed, vol. 1 (Wiley, New York, 1963).
42. P. Andersson and R. G. Ross, unpublished work.
43. B. Abeles, *Phys. Rev.*, **131**, 1906 (1963).
44. R. G. Ross, P. Andersson and G. Bäckström, *Mol. Phys.*, **38**, 377 (1979).
45. G. A. Slack, *Phys. Rev.*, **B22**, 3065 (1980).
46. P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **77**, 129 (1949).
47. E. G. Cox, D. W. J. Cruickshank and J. A. S. Smith, *Proc. R. Soc. London Ser. A*, **247**, 1 (1958).
48. P. V. Hobbs, *Ice Physics* (Clarendon, Oxford, 1974).
49. R. E. Gagnon, H. Kiefte, M. J. Clouter and E. Whalley, *J. Chem. Phys.*, **92**, 1909 (1990).
50. E. R. Andrew and R. G. Eades, *Proc. R. Soc. London Ser. A*, **218**, 537 (1953).
51. B. I. Obmoin, N. K. Moroz and S. P. Gabuda, *Sov. Phys.-Solid State*, **16**, 1167 (1974).
52. J. N. Sherwood (ed), *The Plastically Crystalline State* (Wiley, Chichester, 1979).
53. K. Adachi, H. Suga and S. Seki, *Bull. Chem. Soc. Japan*, **41**, 1073 (1968).
54. O. Andersson, R. G. Ross and G. Bäckström, *Mol. Phys.*, **66**, 619 (1989).
55. M. Bée, J. P. Amoureux and R. E. Lechner, *Mol. Phys.*, **40**, 617 (1980).
56. R. E. Lechner and A. Heidemann, *Commun. Phys.*, **1**, 213 (1976).
57. E. Bonjour, R. Calemczuk, R. Lagnier and B. Salce, *J. Phys. Paris*, **42**, C6, 63 (1981).
58. O. Andersson and R. G. Ross, *Mol. Phys.*, **71**, 523 (1990).
59. D. W. Davidson, *Water: A Comprehensive Treatise*, vol. 2, ed F. Franks (Plenum, New York, 1973), pp 115–234.
60. J. S. Tse and M. A. White, *J. Phys. Chem.*, **92**, 5006 (1988).
61. R. D. Stoll and G. M. Bryan, *J. Geophys. Res.*, **84**, 1629 (1979).
62. R. G. Ross, P. Andersson and G. Bäckström, *Nature*, **290**, 322 (1981).
63. R. G. Ross and P. Andersson, *Can. J. Chem.*, **60**, 881 (1982).
64. M. Bathe, S. Vagle, G. A. Saunders and E. F. Lambson, *J. Mater. Sci. Lett.*, **3**, 904 (1984).

65. J. S. Tse, *J. Phys. Paris*, **48**, C1, 543 (1987).
66. J. G. Cook and M. J. Laubitz, *Thermal Conductivity 17*, ed J. G. Hust (Plenum, New York, 1983) pp. 745–751.
67. T. Ashworth, L. R. Johnson and L-P. Lai, *High Temp.-High Press.*, **17**, 413 (1985).
68. M. A. White and M. T. MacLean, *J. Phys. Chem.*, **89**, 1380 (1985).
69. D. W. Davidson and J. A. Ripmeester, *J. Glaciol.*, **21**, 33 (1978).
70. P. Andersson and R. G. Ross, *J. Phys. C: Solid State Phys.*, **16**, 1423 (1983).
71. N. Ahmad and W. A. Phillips, *Solid State Commun.*, **63**, 167 (1987).
72. J. G. Cook and D. G. Leaist, *Geophys. Res. Lett.*, **10**, 397 (1983).
73. Y. P. Handa and J. G. Cook, *J. Phys. Chem.*, **91**, 6327 (1987).
74. M. C. W. Dharma-wardana, *J. Phys. Chem.*, **87**, 4185 (1983).
75. R. G. Ross, *J. Inclusion Phenom. Mol. Recognit. Chem.*, **8**, 227 (1990).
76. R. Forst, H. Boysen, F. Frey, H. Jagodzinski and C. Zeyen, *J. Phys. Chem. Solids*, **47**, 1089 (1986).
77. K. D. M. Harris and P. Jonsen, *Chem. Phys. Lett.*, **154**, 593 (1989).
78. J. Jacques, A. Collet and S. H. Wilen, *Enantiomers, Racemates and Resolutions* (Wiley, New York, 1981).
79. O. Andersson, R. G. Ross and A. Jezowski, *Mol. Phys.*, **70**, 1065 (1990).
80. F. H. Allen and D. Rogers, *J. Chem. Soc. (B)*, 632 (1971).
81. V. Rossiter, *J. Phys. C: Solid State Phys.*, **5**, 1969 (1972).
82. K. Schäfer and U. Wagner, *Z. Elektrochem.*, **62**, 328 (1958).
83. J. Dale, *Stereochemistry and Conformational Analysis*, (Universitetsforlaget, Oslo, 1978).
84. J. E. Anderson and W. P. Slichter, *J. Chem. Phys.*, **41**, 1922 (1964).
85. C. C. Mjojo, *J. Chem. Soc. Faraday Trans. II*, **75**, 692 (1979).
86. T. Nagumo, T. Matsuo and H. Suga, *Thermochim. Acta*, **139**, 121 (1989).
87. K. Schäfer and O. Frey, *Z. Elektrochem.*, **56**, 882 (1952).
88. B. Wunderlich and J. Grebowicz, *Polym. Sci. Technol.*, **28**, 145 (1985).