JOURNAL OF SOLID STATE CHEMISTRY **106**, 83–98 (1993)

Investigating the Structure and Dynamics of a Family of Organic Solids: The Alkane/Urea Inclusion Compounds

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Received December 4, 1992; accepted December 23, 1992

IN HONOR OF SIR JOHN MEURIG THOMAS ON HIS 60TH BIRTHDAY

Crystalline organic inclusion compounds are currently of considerable interest to solid state chemists and physicists in view of the wide range of important physicochemical properties associated with them. The urea inclusion compounds represent one classic example of such solids, and this article is focused on the urea inclusion compounds containing alkane guest molecules. Structural and dynamic properties of these solids have been probed using a wide range of experimental and computational techniques, and the aim of the article is to assess the current level of understanding of these properties. The importance of adopting a multidisciplinary experimental and computational approach towards investigating the properties of these solids is emphasized.

1. Introduction

One of the many important aspects of the philosophy of scientific research that I learned from Professor Thomas during my period of time working in his laboratory is the necessity of adopting a multidisciplinary approach in tackling problems in solid state chemistry. There is now a very wide and diverse range of experimental and computational techniques available for probing the properties of solids, each with its own inherent strengths and limitations, and each becoming of increasing power and widening scope with the evolution of scientific instrumentation. The prerogative of the solid state chemist, in attempting to answer to the best of his ability the important questions of the day, is to identify the combination of techniques, and the experimental strategy, which can best elucidate the information that he seeks. The synergistic benefits of pursuing a multidisciplinary approach of this type in attempting to derive a detailed fundamental understanding of a family of organic solids are illustrated here by discussing recent results on the alkane/urea inclusion compounds, obtained both in my own laboratory and in others. The aim of the article is twofold; first, to weave together many of the available strands of experimental evidence on these solids in order to describe their structural and dynamic properties in as complete a manner as presently possible, and second, to emphasize that the level of understanding that has now been acquired for these systems has arisen only through the combined use, and exploitation, of a wide range of experimental, computational, and mathematical approaches. Nevertheless, it is clear that many important fundamental issues relating to these solids remain to be fully understood, and the article also aims to identify some of these key areas for future investigation.

It is interesting to reflect that Professor Thomas's own work on urea inclusion compounds represents, in some respects, an in-

0022-4596/93 $5.00

terface between two of the major themes of his research over the years—organic solid state chemistry (*1*) on the one hand, and microporous inorganic solids (*2*) on the other. Indeed, the impetus behind our own initial studies of urea inclusion compounds was to compare and contrast the photoreactivity of diacyl peroxides within urea inclusion compounds and within the topologically similar inorganic host materials silicalite and ferrierite (*3*). A detailed discussion of the similarities and differences between organic tunnel-containing host structures (such as those in the urea and thiourea inclusion compounds) and microporous inorganic solids (such as zeolites and aluminophosphates) has been given elsewhere (*4, 5*), and the present article will focus entirely upon the alkane/urea family of inclusion compounds. It is now known that urea inclusion compounds exhibit a wide diversity of fundamental physicochemical phenomena seldom found occurring together in one particular class of material, and the article will highlight some of the properties of the alkane/urea inclusion compounds which demonstrate this fact.

2. General Structural Description

Within the conventional urea inclusion compounds (*6, 7*), the urea molecules pack in an extensively hydrogen-bonded arrangement containing linear, parallel, nonintersecting tunnels as shown in Fig. 1. Guest molecules based on a sufficiently long alkane chain and possessing a sufficiently low degree of substitution can be accommodated within these tunnels (*8, 9*), and here we focus upon the urea inclusion compounds containing alkane ($CH_3(CH_2)_nCH_3$) guest molecules. The good size and shape compatibility between such guest molecules and the urea tunnel is illustrated in Fig. 2; indeed, such structural compatibility between host and guest components is a general feature of molecular inclusion phenomena, and underlies many of their wide-ranging applications. Thus, it is for this reason that urea inclusion compound formation can serve as an efficient method for separating linear and branched alkanes, and comparisons can be made here with the shape-selective catalytic properties of zeolites and other inorganic molecular sieves (*10*). However, it is important to stress that, in contrast to many microporous inorganic hosts, the urea tunnel structure is stable *only* when the tunnels are packed densely with guest molecules—removal of the guest molecules results in collapse of the tunnel structure (a fact demonstrated both experimentally (*11, 12*) and via computer simulation (*13*)), with the urea recrystallizing in the tetragonal phase of "pure" urea (*14*) (which does *not* contain empty tunnels). Thus, the host/guest molar ratio in the inclusion compound formed between urea and a particular type of guest is a well-defined parameter and, at least at a given temperature and pressure, it is not under the control of the experimenter. A method for assessing, *ab initio*, the optimal host/guest molar ratio in the urea inclusion compound containing any particular guest is discussed elsewhere (*15*).

At room temperature, the symmetry of the urea tunnel structure (*6, 7*) is described by the chiral space group $P6_122$; essentially, the urea molecules forming the walls of the tunnel are arranged in a spiral, and within a given single crystal a homochiral collection of such spirals is present. Clearly this fact presents considerable prospects for host–guest chiral recognition, a fact first recognized and demonstrated (via studies of the 2-chloroctane/urea inclusion compound) by Schlenk (*16*).

At sufficiently low temperature (e.g., $T_t \approx 150$ K for hexadecane/urea), the alkane/urea inclusion compounds undergo a phase transition which is associated, *inter alia*, with a change in symmetry of the host tunnel structure (hexagonal in the high-temperature phase to orthorhombic in the low-temperature phase). This structural change in the host has been investigated via single-crystal (*17, 18*) and powder (*19*) X-ray diffraction (Fig. 3), and has been shown to

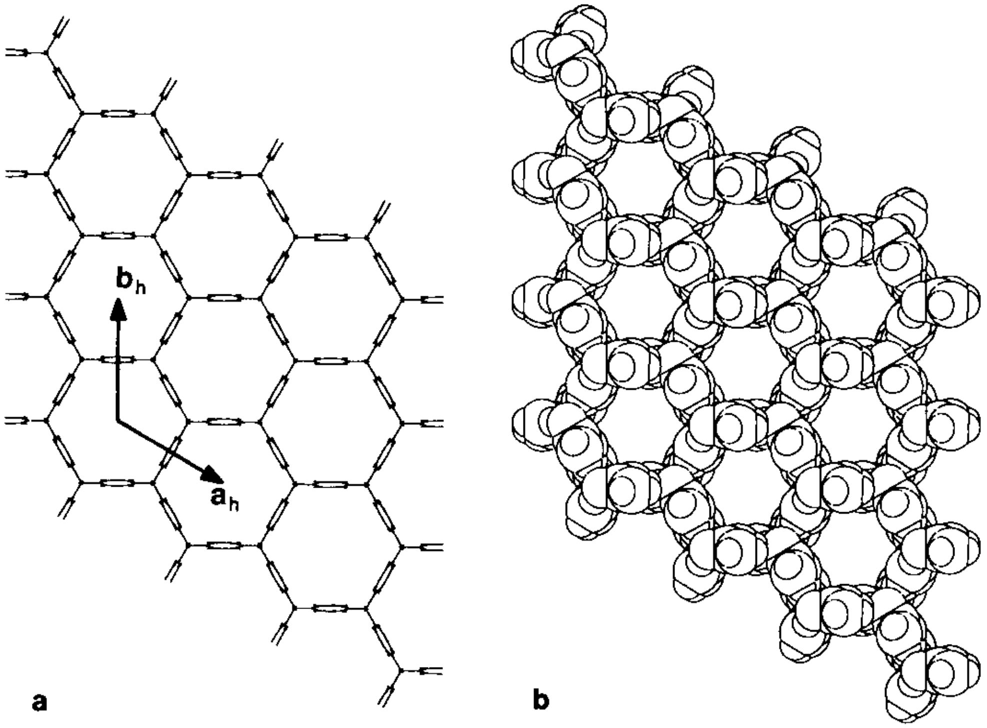

FIG. 1. Two representations (showing nine complete tunnels) of the host structure in the alkane/urea inclusion compounds (7), viewed along the tunnel axis ($\mathbf{c}_h$) [Note: $|\mathbf{a}_h| = |\mathbf{b}_h| \approx 8.23$ Å; $|\mathbf{c}_h| \approx 11.02$ Å]. The atomic radii are zero in (a) whereas conventional van der Waals radii are used in (b). Note that in the real inclusion compounds, the tunnels of this host structure are filled with a dense packing of guest molecules (not shown).

involve only a minor structural distortion of the host to a symmetry much closer to that of the alkane guest molecule. However, no entirely satisfactory determination of the host structure within the low-temperature phase has been reported, partly as a result of the fact that multiple crystal twinning accompanies the phase transition on passing from the high-temperature phase to the low-temperature phase. Various other aspects of this phase transition are discussed in Sections 4 and 5.

We now consider structural properties of the guest structure within the alkane/urea inclusion compounds at room temperature. The guest molecules generally exhibit sufficient positional ordering for an average three-dimensional lattice to be defined; however, in addition to discrete X-ray scattering, the X-ray diffraction pattern generally also contains diffuse scattering, and the nature of this diffuse scattering indicates that there are some regions of the crystal in which the guest molecules are ordered *only* along the tunnel direction (7). This structural heterogeneity of the alkane guest molecules is also found for other classes of guest molecule in urea inclusion compounds. In both the one-dimensionally and three-dimensionally ordered regions of the guest structure, the alkane molecules have a well-defined periodic repeat distance (c_g) along the tunnel, and we now consider how this relates to the periodic repeat distance (c_h) of the host structure along the tunnel. For all the alkane/urea inclusion compounds so far investigated experimentally, there is believed to be an incommensurate structural

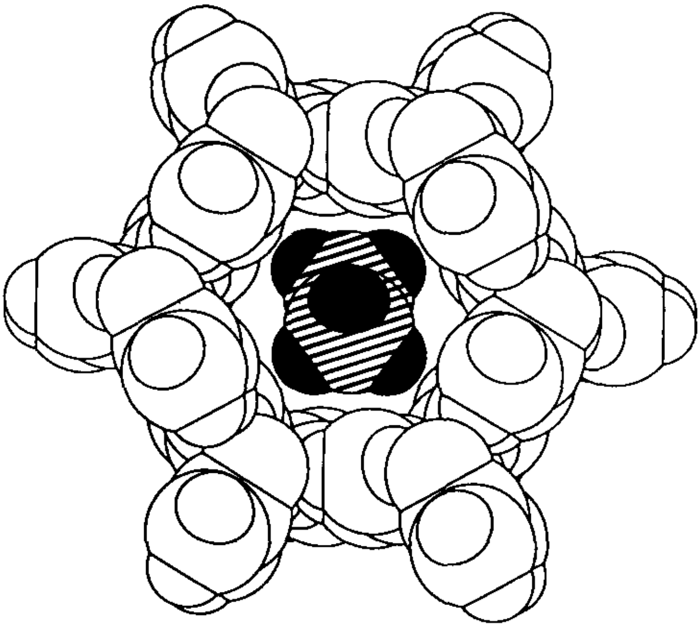

FIG. 2. Structural representation (with van der Waals radii) of a single tunnel within the hexadecane/urea inclusion compound, viewed along the tunnel axis. Note that the real inclusion compound does *not* consist of single, isolated tunnels, but comprises a regular array (see Fig. 1) of tunnels of the type shown.

relationship between the host and guest structures along the tunnel direction; in simple terms, this means that sufficiently small integers m and n can *not* be found for which $mc_g \approx nc_h$ (within experimental error in the determination of c_g and c_h). This incommensurate relationship between the host and guest structures has some important implications, including the fact that, within any individual tunnel, each alkane molecule will, in principle, be in a slightly different environment relative to the host. A detailed discussion of commensurate versus incommensurate behavior in one-dimensional inclusion compounds (exemplified by the urea inclusion compounds) has been published recently (*20*).

The periodic repeat distance (c_g) of the guest molecules along the tunnel has been determined for a wide range of alkane guests (*21, 22*), and it is found that c_g is generally ca. $\frac{1}{2}$ Å shorter than the predicted "van der Waals length" of the alkane molecule in the type of extended, linear conformation that it must adopt in order to fit within the confined space available to it inside the urea tunnel. Three possible reasons can be suggested to account for this apparent "shortening": (a) coiling of the alkane molecule (i.e., deviation from the planar, "all-trans" conformation assumed in the calculation of the van der Waals length); (b) tilting of the axis of the alkane molecule from the tunnel axis; (c) van der Waals overlap of neighboring alkane molecules in the tunnel (leading to a repulsive intratunnel guest–guest interaction). Although factor (a) may occur to some extent (*vide infra*), factor (b) will have a negligible "shortening" effect due to the fact that only comparatively small maximum angles of tilt are possible within the urea tunnel. Recently, a mathematical model has been developed (*20*) which allows various structural properties of one-dimensional inclusion compounds to be predicted and rationalized (*15, 23*) from computed po-

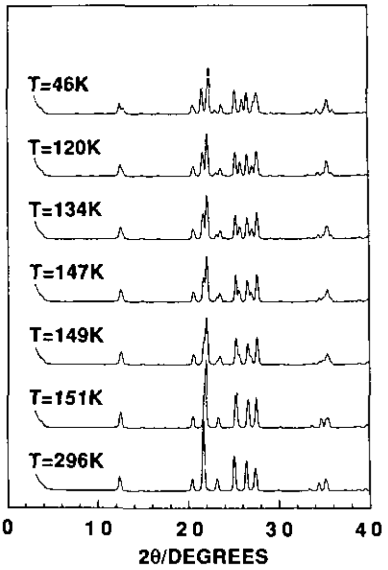

FIG. 3. Powder X-ray diffractograms recorded (Cu$K\alpha$ radiation) for hexadecane/urea as a function of temperature (*19*). Note the significant change in the diffractogram between 151 and 149 K, resulting from a change in symmetry of the host structure at the phase transition ($T_t \approx$ 150 K).

tential energy functions for the inclusion compound. Application of this approach to the alkane/urea inclusion compounds (*15*) has confirmed the importance of factor (*c*), and the discrepancy between the experimental c_g and the value of c_g predicted on the basis of van der Waals length can be accounted for entirely by a repulsive interaction between adjacent guest molecules within the tunnel. As an illustration, application of this model to hexadecane/urea has predicted that the optimal c_g (determined via the use of computed host–guest and guest–guest potential energy functions) is in the range 22.6 ± 0.1 Å, in excellent agreement with recent experimental results (*22, 24*). In contrast, the minimum guest–guest interaction energy, for a pair of hexadecane molecules approaching each other in the trajectory in which they are constrained to approach each other inside the urea tunnel, corresponds to $c_g \approx$ 23.1 Å (note the "shortening" of ca. $\frac{1}{2}$ Å discussed above). Furthermore, application of the mathematical model (*15*) has shown that the optimal c_g for hexadecane/urea will correspond to incommensurate behavior of the inclusion compound (some early literature (*6*) erroneously assigned this inclusion compound as commensurate).

We now consider the three-dimensional structural properties of the guest molecules in alkane/urea inclusion compounds. It has been shown, via photographic single crystal X-ray diffraction (*22, 25*), that, within the three-dimensionally ordered regions of the guest structure, the alkane molecules in a given tunnel are located at the same set of "positions" (*z*-coordinates) as the alkane molecules in the neighboring tunnels (see Fig. 4). The crystal symmetry of the guest structure is hexagonal (in contrast with the situation for urea inclusion compounds containing some other types of guest molecule (*26, 27*)); as discussed in Section 4, this hexagonal symmetry arises as a consequence of dynamic disorder within the guest structure (in the high-temperature phase).

As a consequence of the incommensurate structural relationship between the host and guest components, it is convenient to consider each single crystal of the inclusion compound to be composed of distinguishable, although not independent, host and guest substructures. Each substructure is best considered in terms of an incommensurately modulated "basic structure." Each basic structure (Fig. 1 shows the basic host structure) has three-dimensional periodicity and, although the concept of the basic structure is somewhat hypothetical, the value of invoking this concept is that the structural properties of the basic structure can be understood via conventional crystallographic principles. The incommensurate modulations to each basic structure describe structural perturbations that arise from host–guest interaction. Thus, the incommensurate modulation within the host substructure has the same periodicity as the basic guest structure, and, conversely, the incommensurate modulation within the

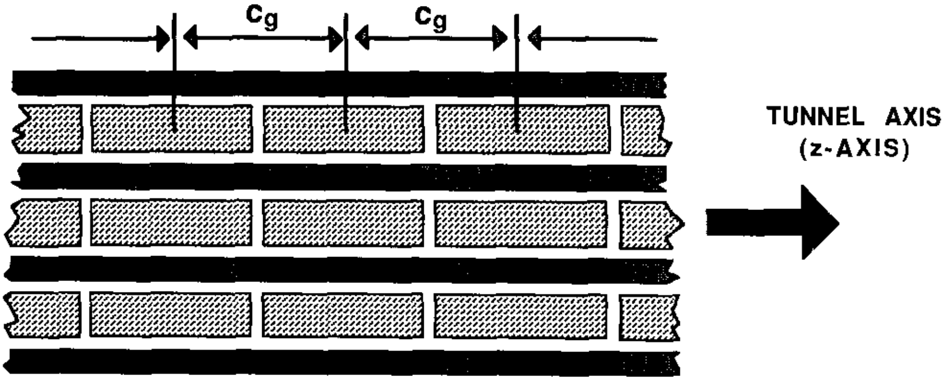

FIG. 4. Schematic two-dimensional representation of an alkane/urea inclusion compound, viewed perpendicular to the tunnel axis and showing three tunnels (horizontal). Note that the guest molecules in a given tunnel sit at the same set of positions (z-coordinates) as the guest molecules in the neighboring tunnels. The periodic repeat distance c_g is also defined.

guest substructure has the same periodicity as the basic host structure. A detailed discussion of these structural concepts, and the way in which they relate to the complex and interesting diffraction phenomena associated with the alkane/urea inclusion compounds, has been given elsewhere (*7*). Considering both the host and guest components implicitly together, it is clear that the composite inclusion compound does *not* possess conventional three-dimensional lattice periodicity (this fact arises from the incommensurate relationship between the host and guest substructures), and its symmetry cannot be described by a conventional three-dimensional space group (the symmetries of the basic host structure and the basic guest structure are described by *different* three-dimensional space groups). However, it *is* possible to rationalize the crystallographic properties of the composite inclusion compound in a four-dimensional superspace; the composite inclusion compound *does* have lattice periodicity in this four-dimensional superspace, and its symmetry is described by a four-dimensional superspace group. The methodology for determining the superspace description of incommensurate solids of this type has been developed elsewhere (*28*).

The ordering of the alkane molecules in the low-temperature phase is an interesting and important question which is currently being investigated via photographic single crystal X-ray diffraction techniques (*22*). Preliminary results suggest that the mode of intertunnel ordering of the alkane molecules remains unaltered (i.e., alkane molecules in neighboring tunnels located at the same set of z-coordinates) upon entering the low-temperature phase. The low-temperature structural properties of the guest molecules in the hexadecane/urea inclusion compound have been the subject of a detailed, although somewhat controversial, study by Boysen and co-workers (*24, 29, 30*); the room-temperature X-ray diffraction pattern obtained by these workers differs substantially, particularly in terms of features of the X-ray scattering from the guest structure, from that obtained by others, and we make no further comment here on the results reported by these authors until the source of these discrepancies has been fully established. In this regard, it is pertinent to note that, from our own experience, the precise nature and quality of the X-ray diffraction patterns of urea inclusion compounds depend critically upon the method of preparation of the inclusion compound; in part, this is due to the fact that coinclusion of solvent molecules in addition to the intended guest molecule is a potential problem during crystal growth, and can seriously disrupt ordering within the guest structure.

3. Local Structural Properties

Section 2 was focused upon the *periodic* structural properties of the alkane/urea inclusion compounds, as determined from diffraction-based investigations. It is important to emphasize that any local (spatial and/or temporal) deviations from this perfectly periodic description are implicitly averaged (over space and time) in deriving structural information from the diffraction results. To investigate the true *distribution* of structural features about this average description it is essential to use other experimental techniques. In this section we consider selected local structural properties of the alkane/urea inclusion compounds, whereas local temporal fluctuations in the structural properties (i.e., the dynamic behavior) are discussed in Section 4.

Monte Carlo (MC) simulation studies of the hexane/urea and octane/urea inclusion compounds have been completed recently (*31*). This technique can provide detailed local structural information, at the molecular level, and although these simulations were carried out using a fixed host framework and rigid guest molecules in the "all-trans" conformation (which is known from Raman spectroscopy and other techniques to be the major conformation for alkane guests), they nevertheless reveal important insights regarding the behavior of the true system beyond the level of information that diffraction-based approaches can provide. A wide range of energetic properties and structural distribution functions (particularly concerning orientational and positional relationships between neighboring guest molecules and between the guest molecules and the host tunnel) have been determined, and two illustrative examples of structural distribution functions are shown in Fig. 5. It is pertinent to recall here that a timescale cannot be attached to the evolution of the structure during the MC simulation, and this technique is therefore not appropriate for probing dynamic properties; molecular dynamics (MD) simulation techniques, however, can furnish information of this type. Two previous MD studies of alkane/urea inclusion compounds have been reported (*32, 33*), although neither can provide a satisfactory improvement in our understanding of these solids in view of the fact that both have considered the hypothetical situation in which only a single tunnel of the inclusion compound is occupied by the guest (the latter paper, furthermore, has considered only a single guest molecule within this tunnel).

The conformational properties of alkane guest molecules within the urea tunnel structure have been investigated extensively, although this has so far proved to be a controversial subject, with substantial disagreements between the results reported by different authors. The two main issues are first the conformation of the main $(CH_2)_n$ portion of the alkane molecule, and second whether there are conformational defects at the ends of the molecule. The opinions of different authors on these issues differ markedly, many proposing that the main portion of the alkane molecule exists essentially only in the "all-trans" conformation (*34*) (which has led to the proposal that the alkane/urea inclusion compounds can be used as model systems for the characterization of alkanes in this conformation); others believe that an appreciable concentration of conformational defects can exist in the main portion of the alkane molecule (*32*). Clearly the existence of such defects can have an important bearing upon the properties of the inclusion compound. Similar disagreements exist in reports of the extent of conformational defects at the ends of the alkane molecule (*32–36*); while it is now widely agreed that both gauche and trans end-groups exist for alkanes included within the urea tunnel structure, the reported percentage of gauche

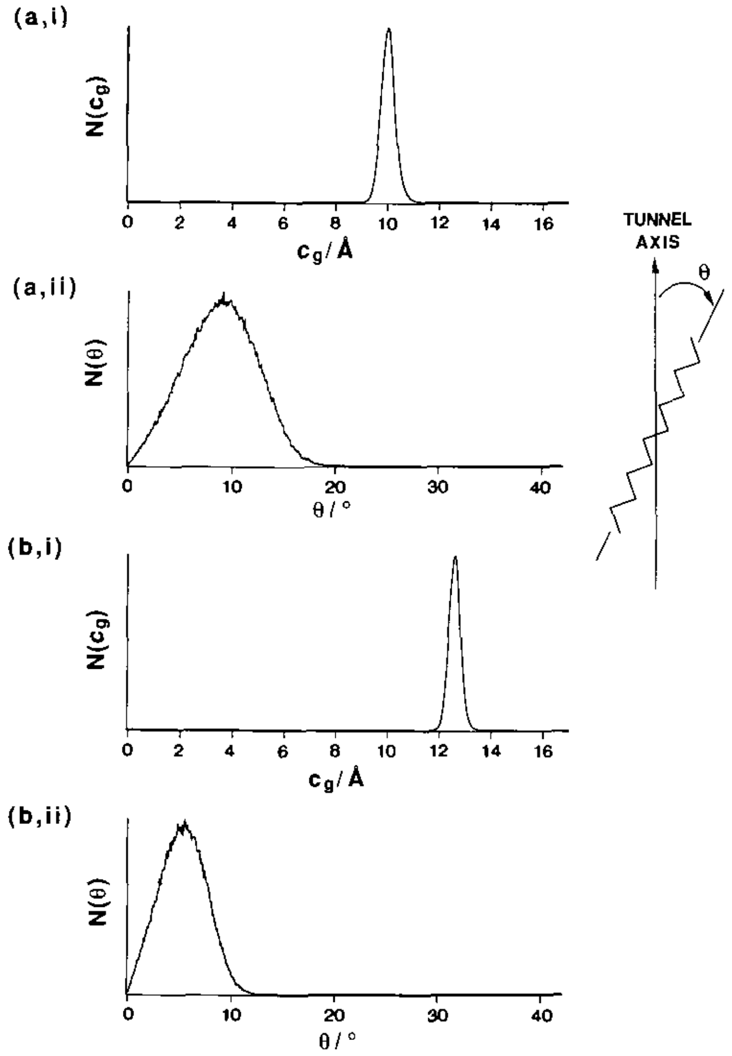

FIG. 5. Structural distribution functions determined (*31*) from Monte Carlo simulation (in the isothermal–isobaric ensemble at $T = 300$ K, $p = 10^5$ Pa) for: (a) hexane/urea, and (b) octane/urea. The distribution functions shown are for: (i) the parameter c_g (the distance between the centers of mass of adjacent alkane molecules in the same tunnel); and (ii) the angle θ (the angle (defined in the inset) between the axis of the alkane molecule and the tunnel axis).

end-groups at room temperature has ranged from under 3% to around 40%. Notwithstanding the fact that a range of different experimental (primarily NMR, Raman, and IR spectroscopies) and computer simulation techniques have been used to derive this information, it is clear that many major issues in this area remain to be resolved. (Importantly, it should be emphasized that some of the techniques used have different characteristic timescales and some are better suited than others to the unambiguous and quantitative assignment of the different conformations; furthermore, the conformational properties will almost certainly depend on the number of methylene groups in the alkane, and therefore results reported on different alkane guests should not, per se, be compared directly). The crystallographic quality of the samples used by different authors might also be an important consideration here.

4. Dynamic Properties

We focus here on the use of solid state NMR and neutron scattering techniques to probe the dynamic properties of alkane/urea inclusion compounds. The existence of substantial motion of the guest molecules in alkane/urea inclusion compounds at ambient temperature has been known for many years, but attention has also been devoted recently to the question of the dynamic properties of the urea molecules.

Early studies of guest motion in alkane/urea inclusion compounds by solid state NMR focused on ^1H linewidth and second moment measurements (*37*, *38*) and measurement of ^1H spin lattice relaxation times (*39*). While these methods yielded considerable insights into the guest mobility and its temperature dependence, as well as enabling an assessment of parameters such as activation energies, it is difficult from these techniques to derive well-defined and unambiguous information relating to the mechanism for the motion. For this reason, attention in this article is devoted to the more detailed mechanistic information that has since been obtained by means of conventional (quadrupole echo) ^2H NMR spectroscopy of urea inclusion compounds containing fully deuterated, or selectively deuterated, alkane guests (essentially, these experiments probe the ^2H quadrupole interaction parameters, and the technique is particularly appropriate for the investigation of motions occurring with characteristic timescales in the range ca. 10^{-3}–10^{-7} sec).

Variable-temperature ^2H NMR investigations of the $CD_3(CD_2)_{14}CD_3$/urea-h_4 inclusion compound (*40*) are now summarized. Motional information has been deduced over a wide temperature range, and at room temperature the following dynamic properties of the guest molecule have been elucidated: (i) rapid ($\kappa \gtrsim 10^7\ \mathrm{sec}^{-1}$) reorientation of the whole molecule about its long molecular axis (which is, on average, coincident with the tunnel axis) (Fig. 6a); (ii) rapid torsional libration (with approximate amplitude ± 25°) about the penultimate C–C bond (Fig. 6b); (iii) rapid rotation of the CD_3 group about the C–CD_3 bond (Fig. 6c). There is a dramatic change in the ^2H NMR spectrum on crossing the phase transition temperature, suggesting that the phase transition is associated with an abrupt discontinuity in the motional freedom of the alkane molecule; nevertheless, there is evidence for some amount of motion even below the phase transition temperature. Similar conclusions have also been reached from an independent ^2H NMR investigation (*41*) of

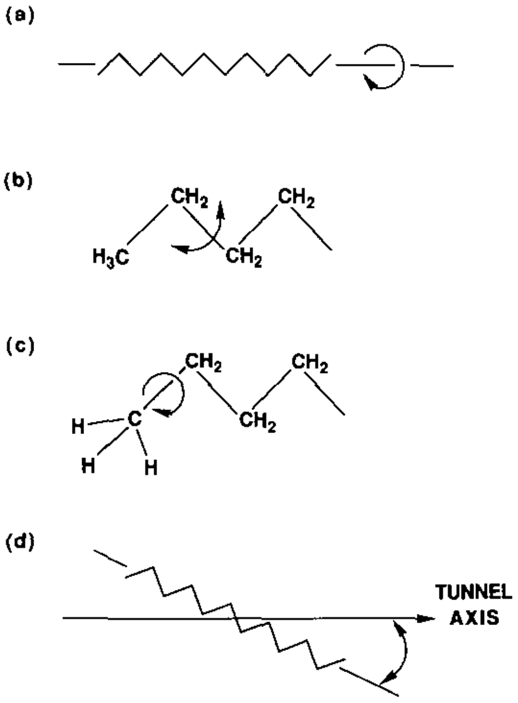

FIG. 6. Dynamic processes for alkane guest molecules in urea inclusion compounds: (a) reorientation about the main molecular axis; (b) torsional libration about the penultimate C–C bond; (c) reorientation of the CH_3 group about its local threefold symmetry axis; (d) libration involving tilting of the molecule away from the tunnel axis.

the $CD_3(CD_2)_{17}CD_3$/urea-h_4 inclusion compound.

Another NMR study (*42*), on a single crystal of $CD_3(CD_2)_{17}CD_3$/urea-h_4, considered the dependence of ^2H spin-lattice relaxation times on temperature and on crystal orientation. From these results, the motion of the CD_2 groups in the central portion of the alkane molecule was assigned as: (i) unrestricted diffusion of the alkane about its long axis (Fig. 6a); and (ii) restricted libration (with amplitude ca. 20–24°) in a plane parallel to the long axis such that the C–D bond is brought out of the plane perpendicular to the tunnel axis (Fig. 6d). However, while a libration of this type must almost certainly occur (thus implying that, over a period of time, a given alkane molecule will sample all regions of the types of angular distribution function shown in Figs. 5a,ii and 5b,ii), the libration amplitude derived from these NMR studies appears unreasonably large given the constraints imposed by the host tunnel structure on an alkane as long as nonadecane. The rate (ca. 10^{10}–10^{11} sec^{-1}) of the rotational diffusion (type (i) motion) derived from these studies is in good agreement with that determined from neutron scattering experiments discussed below.

It is important to stress that the NMR techniques discussed above provide information on motions involving reorientation of the guest molecule (specifically the ^2H nucleus in the guest molecule) relative to the applied magnetic field, and do not yield direct information on translational motions of the guest. Considerable progress has been made recently in understanding translational motions of alkane molecules within urea inclusion compounds from the results of neutron scattering experiments. It should also be stressed that these neutron scattering techniques, now discussed, generally probe motions occurring with characteristic timescales in the range ca. 10^{-10}–10^{-12} sec.

Incoherent quasielastic neutron scattering (IQNS) studies of guest molecule dynamics in urea inclusion compounds containing urea-d_4 and the undeuterated guest $CH_3(CH_2)_{17}CH_3$ have been reported recently (*43, 44*). As a consequence of the large incoherent neutron scattering cross-section for ^1H, deuteration of the host in these samples ensures that the incoherent neutron scattering arises predominantly from the guest molecules. In these experiments, semioriented polycrystalline samples were used in which the tunnel axes of all crystals were aligned parallel to each other, but with random orientation of the crystals with respect to rotation about this axis. Such semioriented samples allow separate IQNS experiments to be performed in which the momentum transfer vector $\mathbf{Q}$ is either parallel ($Q_\parallel$ spectra) or perpendicular ($Q_\perp$ spectra) to the urea tunnel axes. Thus, experiments in $Q_\parallel$ geometry allow translational motions of the guest molecules along the tunnel to be investigated selectively, whereas experiments in $Q_\perp$ geometry allow reorientational motions of the guest molecules about the tunnel axis to be investigated selectively.

The $Q_\perp$ spectra exhibit only elastic scattering within the instrumental resolution in the low-temperature phase, indicating that no reorientational motions of the guest molecules are effective on the instrumental timescale. In the high-temperature phase, quasielastic broadening is evident in the $Q_\perp$ spectra (Fig. 7a) implying that rapid reorientational motions occur. It has been shown directly that this reorientational motion is *not* in the form of discrete jumps (60° jumps might be expected naively from the fact that the host–guest interaction energy profile for reorientation of the guest molecule contains six potential minima separated by approximately 60°). Instead, this reorientational motion is diffusive in character, and has been modelled successfully as uniaxial rotational diffusion in a onefold cosine potential, from which rotational diffusion coefficients (ca. 0.3 $psec^{-1}$ at ambient temperature) and other parameters relating to this dynamic process have been elucidated as a detailed function of temperature.

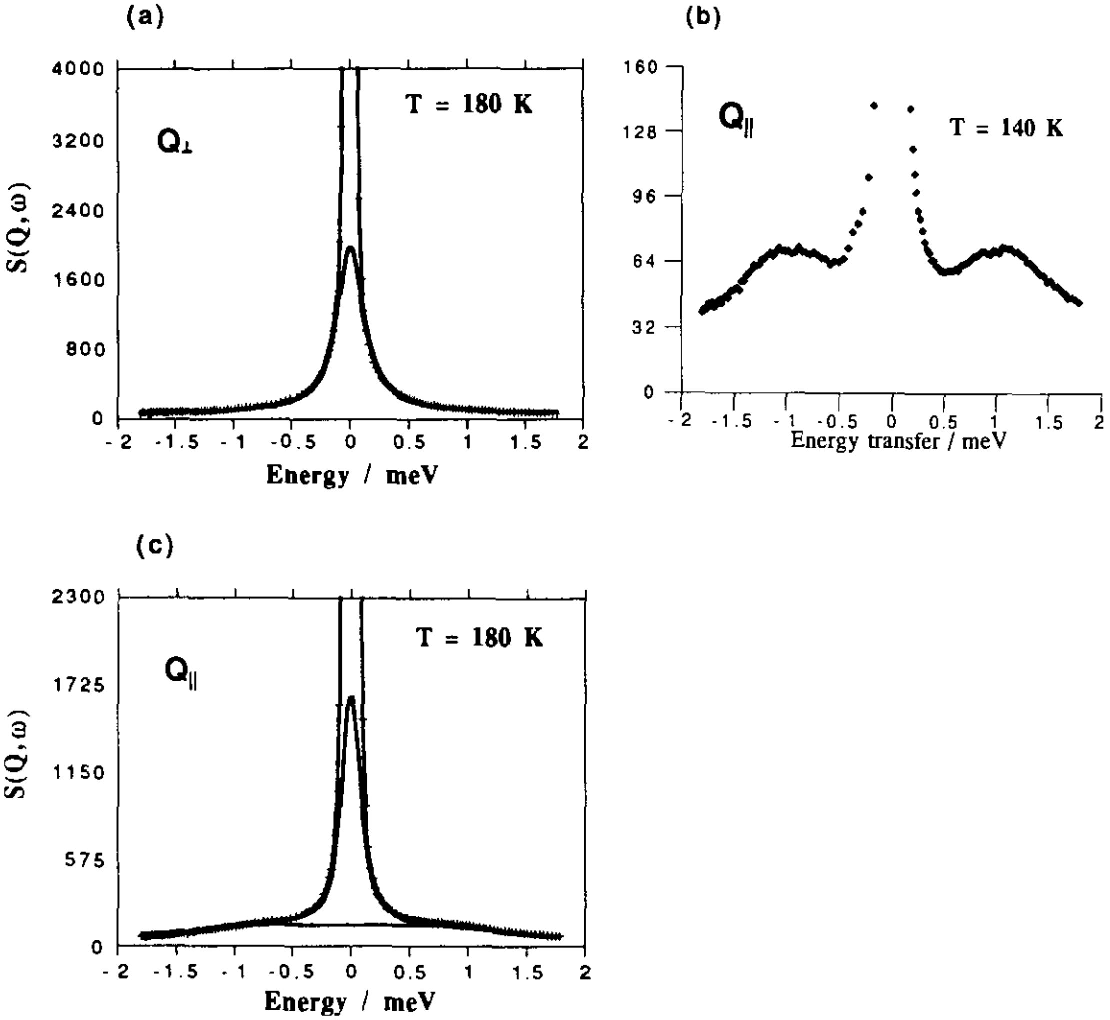

FIG. 7. Incoherent quasielastic neutron scattering spectra recorded (*44*) for semioriented polycrystalline samples of the $CH_3(CH_2)_{17}CH_3$/urea-d_4 inclusion compound: (a) in $Q_\perp$ geometry for the high-temperature phase; (b) in $Q_\parallel$ geometry for the low-temperature phase; (c) in $Q_\parallel$ geometry for the high-temperature phase. The full lines in (a) and (c) show the fits to the spectra obtained using the dynamic models discussed in the text. Note the presence of low-frequency side-peaks in (b), see text for discussion.

The $Q_\parallel$ spectra in the low-temperature phase (Fig. 7b) show inelastic peaks at about ±1 meV which are assigned to an acoustic type mode involving displacements of the hydrogen atoms of the alkane molecule along the tunnel direction; this oscillatory motion becomes overdamped above the phase transition temperature. At present, however, the exact nature of this motion has not yet been assigned. In the high-temperature phase there is substantial quasielastic broadening in the $Q_\parallel$ spectra (Fig. 7c), assigned to translational motion of the alkane molecules along the tunnel. It is important to note that these oscillatory and translatory motions of the hydrogen atoms of the alkane molecule along the tunnel are not coupled in time; the frequency of the oscillatory motion is between one and two orders of magnitude larger. The translatory motion has been modelled successfully as translational diffusion between rigid impermeable boundaries (separated by distance *L*), and diffusion coefficients and translation lengths (*L*) have been determined as a detailed function of temperature. The translation length is ca. 2.7 Å at ambient temperature and ca. 1.1 Å just above the phase transition temperature; the translational diffusion coefficient at ambient temperature is ca. 1.5×10^{-5} cm^2 sec^{-1}. Quantitative details relating to this translational motion are in good agreement with information on longitudinal motions of alkane guests determined from analysis of X-ray diffraction intensities (*25*) (*vide infra*), and results from Monte Carlo simulations of hexane/urea and octane/urea (*31*) are also in broad agreement with the values of the translation length derived experimentally. It is perhaps remarkable that, despite these appreciable translation lengths at ambient temperature, X-ray diffraction patterns of the alkane/urea inclusion compounds nevertheless indicate long-range ordering of the alkane molecules along the tunnel; it thus seems very likely that the translational motions of adjacent guest molecules in a given tunnel are highly correlated.

Since the translational diffusion and rotational diffusion processes of the alkane molecule occur on the same timescale, it is plausible to suggest that these motions are coupled and represent an overall screw motion (indeed, in view of the known spiral nature of the host tunnel, a dynamic process of this type might appear very likely). However, the separate results from the two experimental geometries ($Q_{\|}$ and $Q_{\perp}$) have been analyzed independently, and have not required coupling between the translational and reorientational motions to be invoked; thus, while the dynamics of the guest molecule may indeed be described correctly as a screw motion (at least at a sufficiently local level), the present level of interpretation and understanding of the IQNS results does not indicate definitively whether such a description is appropriate.

Fukao *et al.* (*25*) have carried out a detailed analysis of the temperature-dependence of the intensities of X-ray diffraction maxima from several alkane/urea inclusion compounds, and from these results detailed information relating to the guest dynamics has been deduced. Specifically, it has been proposed that the alkane molecules undergo large amplitude vibrations, in an anharmonic potential field, along the tunnel axis, with an average displacement of over 2 Å for hexadecane at ambient temperature. Again, the occurrence of correlated motions of the guest molecules within a given tunnel has been inferred, and interesting suggestions regarding the collective motions of guest molecules in different tunnels have also been proposed.

The majority of previous investigations of the dynamic properties of urea inclusion compounds have focused upon the motion of the guest molecules, with little attention given to the possibility that the host molecules may also undergo interesting dynamic processes. Recent ^{2}H NMR studies (*45*, *46*) of the $CH_3(CH_2)_{17}CH_3$/urea-d_4 inclusion compound have addressed this issue and have led to the proposal that the urea molecules undergo 180° jumps about their C=O axis, with a jump frequency of ca. 2.0×10^6 sec^{-1} at 303 K (*45*). There was no evidence, from these ^{2}H NMR investigations, for rotation of the NH_2 groups about the C–N bond. Host molecular motion in alkane/urea inclusion compounds has also been investigated by incoherent quasielastic neutron scattering (*47*)—specifically, studies of the $CD_3(CD_2)_{14}CD_3$/urea-h_4 inclusion compound at 300 K have shown that the lower limit (τ_L) for the motional timescale of the urea molecules at this temperature is $\tau_L \gtrsim 50 \times 10^{-12}$ sec. This is substantially longer than the known timescale for motion of the guest molecules at the same temperature (*vide supra*), confirming that the reorientational motions of the host molecules and the reorientational and translational motions of the guest molecules are uncorrelated (at least in the high-temperature phase). It is interesting to note that the possibility that the urea molecules might exhibit interesting dynamic properties was suggested from one of the earliest NMR studies of alkane/urea inclusion compounds (*39*), but this issue apparently remained ignored for 20 years.

5. The Phase Transition

Calorimetric measurements (*48, 49*) gave the first indication that alkane/urea inclusion compounds undergo a phase transition at a temperature which depends upon the length of the guest molecule. As discussed in Sections 2 and 4, this phase transition is now known to be associated with alterations in the structural characteristics of the host as well as changes in the motional behavior of the guest molecules. There have been many attempts to draw analogies between this phase transition and the extensively studied "rotator phase" transitions in the pure crystalline alkanes (*50*), and it is interesting to note that the phase transition temperature for an alkane in its urea inclusion compound is substantially lower than the rotator phase transition temperature for the same alkane in its pure crystalline phase. On the basis of limited data, it was originally believed that there was an odd–even alternation in the phase transition temperature for the alkane/urea inclusion compounds (considering alkanes $CH_3(CH_2)_nCH_3$ with odd and even n); however, more recent results have clouded this issue. A detailed study of the pressure-dependence of the transition temperature has been reported (*51*).

There have been various attempts to rationalize the phase transition in the alkane/urea inclusion compounds, and three will be highlighted here. The earliest attempt, by Parsonage and Pemberton (*52*), considered the phase transition as a strongly cooperative reorientational process, and a statistical mechanical approach invoking an Ising model for longitudinal (intratunnel) guest–guest interactions and a Bragg–Williams treatment of lateral (intertunnel) guest–guest interactions was developed. The orienting effect arising from host–guest interaction was also taken into consideration. It was shown that the interactions between guest molecules in adjacent tunnels, although significantly weaker than the intratunnel guest–guest interaction, are nevertheless sufficiently strong to explain the transition temperatures (as a function of the length of the alkane). Furthermore, it was suggested that the longitudinal interactions cause the alkane molecules within a given tunnel to be strongly correlated; indeed, this work also led to the suggestion, discussed in more detail above, that there is a repulsive interaction between adjacent guest molecules in the same tunnel. In spite of these successes, some of the assumptions embodied within the model are now known, from subsequent experimental results, to be inappropriate (such as the assumption that the host structure is the same in both the high-temperature and low-temperature phases) or to represent severe oversimplifications (such as the assumption that only two orientations of the guest molecule can exist in the high-temperature phase).

A contrasting approach has been developed by Fukao (*53*), based on the assumption that the alkane molecules exist exclusively in the "all-trans" conformation in the low-temperature phase, but contain conformational defects in the high-temperature phase (the important defect is described as a 60° twist, which can also be expressed as a soliton). Implicit within this model is the assumption that there is negligible interaction between guest molecules in neighboring tunnels (in contradiction with one of the main conclusions of Parsonage and Pemberton). Despite the simple level of several of the assumptions made, some of which are again in apparent conflict with experimental evidence, the model has nevertheless achieved remarkable success in correctly predicting several aspects of the phase transition behavior. The approach of Fukao has pursued a strong analogy between the phase transitions in the alkane/urea inclusion compounds and the rotator phase transitions in the pure crystalline alkanes.

A third approach, proposed recently by Lynden-Bell (*54*), has instead drawn an analogy between the phase transition in alkane/urea inclusion compounds and the order–disorder phase transitions in alkali cyanide crystals. Specifically, it has been proposed that, in the alkane/urea inclusion compounds, coupling between transverse acoustic phonons of the host structure and the orientational order of the guest molecules provides an indirect mechanism for orientational ordering of the guest molecules in the low-temperature phase (it being suggested that the intertunnel guest–guest interaction is too weak to provide a direct mechanism for orientational ordering of the guest molecules at the experimentally observed transition temperatures). While there is currently no available experimental evidence to assess the importance of the proposed translation-rotation coupling mechanism for the alkane/urea inclusion compounds (single crystal neutron spectroscopy on a triple axis spectrometer being required to address this question (as well as many other issues relating to urea inclusion compounds)), it has nevertheless been shown that such a mechanism can explain successfully some known features of the phase transition in these systems.

The development of a fundamental understanding of the mechanism for the phase transition in the alkane/urea inclusion compounds clearly remains one of the major challenges in this field.

6. Concluding Remarks

It is clear that the alkane/urea inclusion compounds do indeed exhibit a wide range of interesting and important fundamental physicochemical phenomena, and that the application of a wide range of experimental and computational techniques has been an essential approach in the endeavour to investigate these properties. However, in spite of this recent progress, there nevertheless remain several contentious issues and conflicting opinions on several aspects of these materials. At best, we are only at the preliminary stages of developing a unified description of their fundamental nature, and many crucial issues remain to be properly understood. For example, how are the changes in the dynamic properties of the guest molecules at the phase transition linked with the changes in the structural properties of the host at the transition? What are the consequences of the dynamic properties of the host molecules? What is the exact nature of the low-frequency oscillatory motion evident from the IQNS results? Are the motions of guest molecules in the same tunnel correlated with each other and, indeed, are the motions of the guest molecules in different tunnels correlated with each other? Does the incommensurate structural relationship between the average host and guest structures confer any special properties upon the dynamic behavior? What factors control and dictate the mode of intertunnel ordering of the guest molecules in the three-dimensionally ordered regions of the guest structure? What are the consequences of the existence of conformational defects in the guest molecules? Although experimental information has been obtained that may allow some aspects of these questions to be understood, none of these issues has yet been resolved in a satisfactory manner, and it is clear that there are several major and well-defined challenges still facing solid state chemists in understanding the many-faceted properties of these materials.

As discussed elsewhere (*5*), urea inclusion compounds containing other families of guest molecules (primarily functionalized alkanes) are known, and many of these materials possess structural, dynamic, and chemical properties that contrast markedly with those found for the alkane/urea inclusion compounds. In view of the large body of information now acquired for the alkane/urea systems, the prospects for understanding the properties of this family of urea inclusion compounds are, at present, the most promising. It is the view of the author that the fundamental differences between the urea inclusion compounds containing alkane guests and those containing functionalized alkane guests may be far more profound than was originally thought, despite the fact that, in the majority of cases, they possess ostensibly the same urea tunnel structure. For this reason, each family of urea inclusion compounds, containing a particular type of guest molecule, should be considered as a separate system; the properties of the complete set of all urea inclusion compounds cannot, and should not, be rationalized on a single basis.

Acknowledgments

It is a particular pleasure to take this opportunity to thank Professor Thomas for the many facets of his help over the years. His boundless enthusiasm for all scientific matters, and his considerable knowledge across a wide range of scientific disciplines, have served as a tremendous inspiration to me and to many others. I would also like to thank many of my other collaborators, particularly Dr. F. Guillaume and Professor M. D. Hollingsworth, for many stimulating discussions in the areas of solid state chemistry covered by this article.

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