GROUP 3: *EX UNITATE VIRES* – THE COMBINATION OF METHODOLOGIES

Thermodynamic and Resonance Studies of Structural Changes in Crystals

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Abstract

When disordered crystalline materials are cooled, they often show phase transitions to more ordered phases which are accompanied by rearrangements in structure and/or changes in the dynamics of the constituent molecules or molecular fragments. It then becomes necessary to study all of these aspects (structure, dynamics and thermodynamics) in order to understand the system more completely. We give examples of (*a*) the naphthalene–tetracyanobenzene system, where a disorder observed in the room-temperature structure led to extensive NMR and heat capacity investigations in order to obtain an understanding of the disordered and ordered phases; (*b*) the *t*-butylcalix[4]arene toluene clathrate, where a disordered room-temperature structure posed a number of problems regarding the symmetry and dynamic state of the system, and where subsequent NMR and heat-capacity measurements led to a reinvestigation of the structure and a better structural model; (*c*) a set of xenon cyclodextrin compounds with different hydration states where no structural information was available, and NMR and thermodynamic measurements were used to constuct a partial phase diagram.

1. Introduction

Structural changes in solids are usually associated with thermodynamic phase changes involving the variables temperature (T), pressure (P) or composition, as indicated by a variable n. The vast majority of studies to date have involved changes in T, and in open systems, also n.

When disordered crystalline materials are cooled, they either exhibit phase changes to more ordered states or the material has residual zero-point entropy. In order to understand the nature of the phase transition one must know the structure and, preferably, also the dynamic state of the components which make up the crystal both above and below the phase transition. In the past, much effort has been directed at understanding the interplay of structure and dynamics in simple molecular solids and in the more complex plastic crystals (Parsonage & Staveley, 1978; Sherwood, 1979). Today there is also considerable interest in guest–host systems, where both structure and dynamics play a role in defining many properties which

depend on molecular recognition. (Davidson & Ripmeester, 1984; Ripmeester & Ratcliffe, 1991, 1992).

For transitions involving changes in composition, there are many examples of crystals which crystallize as solvates, and which may lose solvent in one or more well defined steps. Within the group of guest–host materials, an interesting problem exists in solids where multiple hydration states are possible, such as the cyclodextrins (Saenger, 1982). Although water appears to play a critical role in determining structure and properties, detailed structural studies by single-crystal diffraction methods are difficult or impossible except for the highest hydration state, and a whole realm of structural and phase information remains almost untouched.

Over the years diffraction methods have become increasingly sophisticated and are now capable of handling structural problems involving disorder. Independently, solid-state NMR methods have evolved rapidly from the basic broadline methods, and now a range of techniques is available for the study of solids. Diffraction and NMR together are a powerful and complementary combination to address the often difficult problems of dynamic disorder, where methods sensitive to both long- and short-range order are required.

Alongside the microscopic methods such as diffraction and NMR, thermodynamic measurements give a macroscopic account of the degrees of freedom active in the system. Such measurements in open systems may involve not only heat capacity determinations, but also thermogravimetric, dilatometric and vapour pressure measurements.

The three approaches in combination provide a powerful means of assessing the interplay of structure and dynamics in solid systems and how these change with temperature and composition. However, in many cases information is available from only one or two of the above approaches.

First, we will briefly review salient features of resonance and thermodynamic methods and then present an example involving in-plane motions of planar molecules to illustrate the use of the methods. We will then consider some current challenges to the understanding of structural transitions in host–guest systems.

2. A brief review of the experimental approaches

It is beyond the scope of this article to do more than mention the methods which have proved to be most valuable in giving structural information on phase changes in solids. The NMR methods especially continue to advance at a rapid pace, giving ever more sophisticated methods for solving complex problems. The reader is referred to a number of reviews which document the applications of NMR methods to the study of chemical problems (Fyfe, 1982; Davidson & Ripmeester, 1984; Ripmeester & Ratcliffe, 1991, 1992; Clayden, 1992).

2.1. *Broadline NMR*

The study of molecular motion was one of the earliest applications of classical 'broadline' NMR studies on solids. Much work has been performed on molecular solids with simple melting transitions and also on plastic crystalline solids with much more complicated phase behaviour. These studies used the fact that in solids containing the abundant ^{1}H or ^{19}F nucleus, the line width is governed by the direct dipolar interaction between magnetic nuclei.

Except for isolated cases, the resonance lines are featureless, and resort must be made to moment analysis. The experiment is then reduced to comparing experimentally determined moments with calculated moments M_2, which are relatively rapidly converging lattice sums

$$M_2 \propto \sum_{ij} r_{ij}^{-6}, \tag{1}$$

where r_{ij} is the internuclear vector. When large amplitude motions become sufficiently rapid, *i.e.* when the motional correlation time $\tau_c \sim (\gamma \delta H)^{-1}$, where δH is the line width, the dipolar interactions are averaged, thus causing line narrowing. In the fast motion limit, $\tau_c \ll (\gamma \delta H)^{-1}$, the moments can again be calculated

$$M_2 \propto \sum_{ij} \langle (1 - 3\cos^2 \theta_{ij}) r_{ij}^{-6} \rangle. \tag{2}$$

Here θ_{ij} is the angle between the internuclear vector and the magnetic field. The moment analyses often were combined with spin-lattice relaxation time T_1 measurements to give the motional rate as a function of temperature. Briefly, following a radiofrequency pulse which produces non-equilibrium nuclear-spin populations, the spins are relaxed by the fluctuations in the nuclear dipolar interactions of nearby spins, and this process is most efficient when the motional correlation time is near to the inverse of the Larmor frequency

$$T_1^{-1} \propto \tau_c/(1 + \omega^2 \tau_c^2) + 4\tau_c/(1 + 4\omega^2 \tau_c^2). \tag{3}$$

Assumption of Arrhenius behaviour for the motional correlation time then leads to a V-shaped relaxation minimum with the slopes equal to the activation energy for the motion

$$\tau_c = \tau_0 \exp(E_a/RT). \tag{4}$$

Many motions were detected and characterized in this way. The strong point of the method is that motions are detected quite readily, the weak point being that it is often difficult to distinguish motional models, and when motions become non-random (involving inequivalent sites), the analysis becomes very difficult unless other information is available.

2.2. ^{2}H *NMR*

^{2}H NMR spectroscopy is based on the fact that in hard solids at moderate field strength the resonance line shape is governed almost completely by the interaction of the nuclear quadrupole Q with the electric-field gradient (abbreviated as e.f.g.) q. The interaction is quantified by the quadrupole coupling constant $\chi = e^2 qQ/h$, q_{ii} ($ii = xx, yy, zz$) being the electric-field gradient tensor components in the tensor's principal axis system, and the asymmetry parameter $\eta = (q_{xx} - q_{yy})/q_{zz}$. For most materials this means that the bond containing the ^{2}H atom, including dynamic properties, determines the line shape. This is the main difference compared with broadline ^{1}H studies, for instance, where in principle the lattice sums are carried over all pairs in the sample. The ^{2}H spectrum therefore is able to provide much more specific information. It is still a broadline method, as

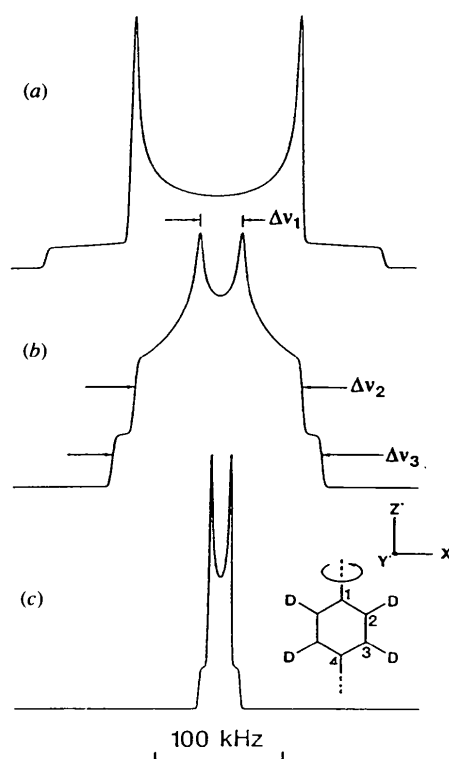Fig. 1. ^{2}H NMR spectra for a *para*-disubstituted benzene ring: (*a*) rigid lattice; (*b*) rapid 180° flips about the C(1)—C(4) axis; (*c*) rapid rotation about the C(1)—C(4) axis, where the order of the axis is greater than or equal to 3.

generally speaking the quadrupole coupling constants are not particularly sensitive to chemical or crystallographic differences (a few per cent, except in cases involving hydrogen bonding). Again, molecular motion causes line narrowing, this time due to averaging of e.f.g. by the motion. The line shape is independent of motional rate in the slow and fast limits, but depends markedly on the rate and detailed geometry of the motion in the intermediate regime. The fast motion limit line shape requires the calculation of the averaged e.f.g. components. For each site j new q'_{ii} must be calculated in a common reference frame according to $q^j_{ii} = R_j^{-1} q_{ii} R_j$, where R are rotation matrices, and the averaged tensor components are given by

$$\overline{q_{ii}} = (1/n) \sum_{j=1,n} q^j_{ii}. \tag{5}$$

Some typical ^2H powder patterns are given in Fig. 1. As the ^2H powder line shape is inhomogeneous, spin-lattice relaxation is anisotropic, and between line shape studies and relaxation a wide range of motional models can be tested. For slow motions, the spin-alignment technique can be used on a timescale limited only by the spin-lattice relaxation time (Fleischer & Fujara, 1994).

2.3. High-resolution NMR in the solid state

The spectroscopy of spin-$\frac{1}{2}$ systems applied to static samples gives rise to broad powder patterns as well, and the theory and applications of line shapes showing chemical shift anisotropy follow those described for spin-1 nuclei.

One of the most powerful methods developed in magnetic resonance spectroscopy is magic angle spinning (MAS), where the sample is spun rapidly at an angle (equal to half the tetrahedral angle) with respect to the magnetic field direction, usually applied in combination with strong decoupling to remove dipolar couplings of protons coupled to 'rare' nuclei. This reduces the broad chemical shift powder pattern to a sharp resonance line at the isotropic chemical shift, in essence equivalent to the resonance seen in solution, plus a set of spinning sidebands separated from the isotropic line by multiples of the spinning frequency. For crystalline materials, the chemical shifts reflect not only chemical inequivalence, but also crystallographic inequivalence, so that in principle the solid-state NMR spectrum should give information on the asymmetric unit in the crystal.

Dynamic information can originate from standard chemical exchange averaging and two-dimensional (2D) exchange spectroscopy (EXSY) NMR (Ernst, Bodenhausen & Wokaun, 1987), much as in solution NMR, or from line-broadening processes which are unique to the solid state. The latter occur due to interference between random motional processes and the coherent averaging processes used to obtain high-resolution spectra, that is dipolar decoupling and MAS. Both of these effects can

be used to study motional rates, although details of the geometry of the motion must be deduced separately.

Although, in general, solution NMR methods cannot be carried over to the solid state, some techniques such as COSY and INADEQUATE can be used to map out connectivities in solid-state lattices (Fyfe, Feng, Grondey, Kokotailo & Gies, 1991). It must always be remembered that the anisotropic interactions (nuclear dipolar, anisotropic chemical shift) do not vanish even if they are not directly visible in the spectrum. Their presence is actually of advantage as these interactions can be manipulated by combining spinning methods with synchronized pulse sequences, so that many new experiments giving new and unique information are possible (Clayden, 1992).

2.4. Thermodynamic measurements

The measurements of relevance to crystal transitions usually involve the determination of the transition temperature, and if possible the enthalpy and entropy of transition. For many years these measurements were made in fine detail by adiabatic calorimetry, but increasingly so by differential scanning calorimetry.

Interpretation of entropies of transition in solids with orientational disorder has involved identifying ΔS with $R \ln N$, where N is an integer or small fraction. The simplest explanation then identifies the disorder with a change in going from a state with N_1 distinguishable orientations to one with N_2, where $N = N_2/N_1$. This assumes that the potential shapes do not change much, and that the crystal transition itself does not contribute.

Another important indicator is, of course, the presence of zero-point entropy, as for ice and the related clathrate hydrates. Dilatometry (dV/dP or dV/dT) can also give useful information, as can thermogravimetry (dm/dT) and vapour pressure measurements (dP/dT).

3. Experimental

Solid-state NMR measurements were carried out on Bruker CXP-180, MSL-200 and AMX-300 NMR spectrometers, as described elsewhere (Facey et al., 1993). Single-crystal X-ray diffraction measurements were made on an Enraf–Nonius CAD-4 diffractometer. Differential scanning calorimetry and thermogravimetry experiments were performed on a Dupont 2100 instrument.

4. Results and discussion

Some of the most definitive and easily demonstrated applications from combined experimental approaches to the study of dynamics and disorder in crystals come from considerations of planar systems such as pyrene and naphthalene and some of their charge-transfer complexes. We discuss one of these systems, which after

some 15 years of study is reasonably well understood. However, there are related systems still unsolved which could benefit from such a combined approach.

4.1. The naphthalene–tetracyanobenzene complex

Quite definitive results have been obtained for the charge-transfer complex between naphthalene and tetracyanobenzene, where alternate donor and acceptor molecules lie in parallel stacks [Fig. 2(a)]. Initial structural studies showed that there were two disordered positions for the naphthalene molecule in the crystal related by an in-plane rotation of 36° (Kumakara, Iwasaki & Saito, 1967). Subsequent ¹H NMR studies above 77 K (Fig. 3) showed that there were two in-plane motions present at high temperatures: a motion corresponding to twofold flips of the entire molecule, and a motion corresponding to a jumping between the disorder sites (Fyfe, 1974; Fyfe, Harold-Smith & Ripmeester, 1976). Consideration of the potential hindering in-plane rotation of the naphthalene molecule [Fig. 2(b) (Shmueli & Goldberg, 1973; Fyfe, Harold-Smith & Ripmeester,

1976)] suggested that the low barrier motion should be assigned to jumping between adjacent disorder sites and the high barrier motion to 180° jumps.

The presence of disorder suggests that a phase transition should be present if the material is to be ordered at 0 K. Such a phase change was indeed found (Boerio-Goates, Westrum & Fyfe, 1978), the maximum in the heat capacity appearing near 72 K. Further low-temperature ¹H broadline and relaxation NMR measurements also detected the phase change [Figs. 3 and 4 (Ripmeester, Dalal & Reddoch, 1981)], signalling changes in dynamic processes that accompany the phase transition. Again, on considering the energy potential for in-plane rotation of the naphthalene molecule, it was concluded that results were in agreement with a model where the two disorder sites become inequivalent in the low-temperature phase (Fig. 3). The analysis of the relaxation time data suggests that the difference in energy between the disorder sites is temperature dependent (Fig. 5). This, combined with the long low-temperature tail on the heat capacity data, suggests that the unit-cell parameters may also depend on temperature as the structure becomes increasingly ordered below the transition. A more sophisticated treatment might try to relate the temperature dependence of a number of measured parameters (ΔE in the potential, lattice parameters) to the temperature below the phase change through an order parameter.

However, the general correctness of the model is easy to check with ²H NMR. The spectrum above 77 K should reflect only the motion between the disorder sites, with the angle between disorder sites directly obtainable from the spectral splittings (Ripmeester, 1982a). The overall 180° in-plane flip does not affect the ²H NMR spectrum (Fig. 3), which confirms the assignment of the ¹H broadline and relaxation data.
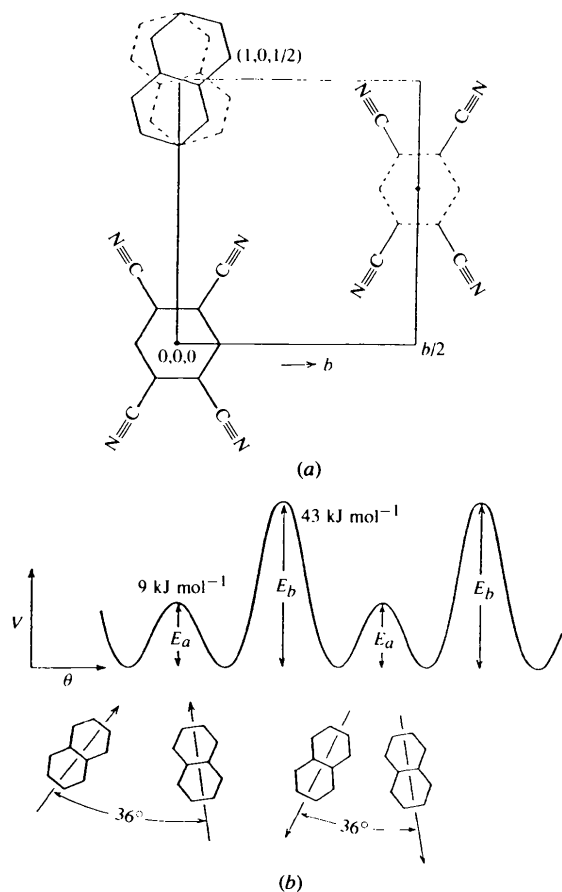

(a)

(b)

Fig. 2. (a) Crystal structure of naphthalene–tetracyanobenzene at room temperature (Kumakura, Iwasaki & Saito, 1967); (b) schematic representation of the potential for reorientation of a naphthalene molecule in its plane (Fyfe, Harold-Smith & Ripmeester, 1976).
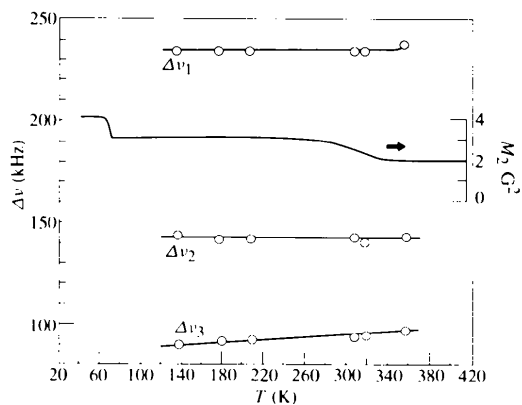

Fig. 3. ¹H second moment (M_2) data for naphthalene–tetracyanobenzene, showing the changes accompanying the phase transition near 70 K (Ripmeester, Dalal & Reddoch, 1981), and the onset of twofold flips at 280 K (Fyfe, 1974). Also shown are the quadrupole splittings for the ²H spectrum, showing that these are insensitive to the twofold flips (Ripmeester, 1982a).
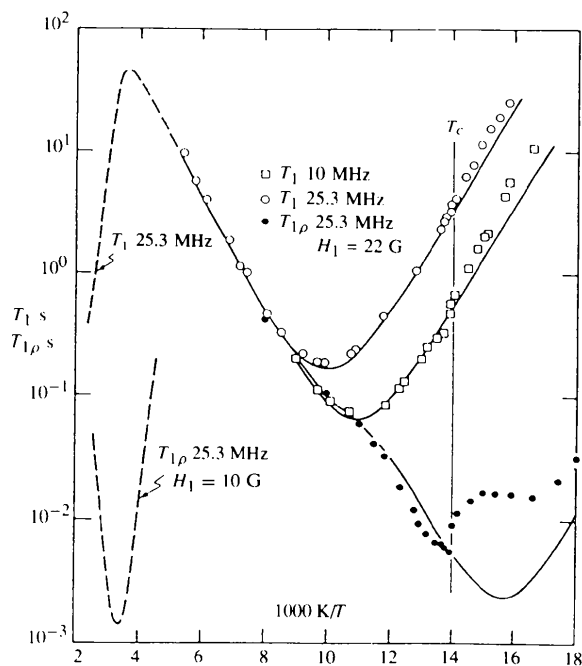
Fig. 4. Static (T_1) and rotating frame $(T_{1\rho})$ ^{1}H spin-lattice relaxation times observed for naphthalene–tetracyanobenzene (Ripmeester, Dalal & Reddoch, 1981); solid lines below the phase-transition temperature are based on extrapolations from higher-temperature data.
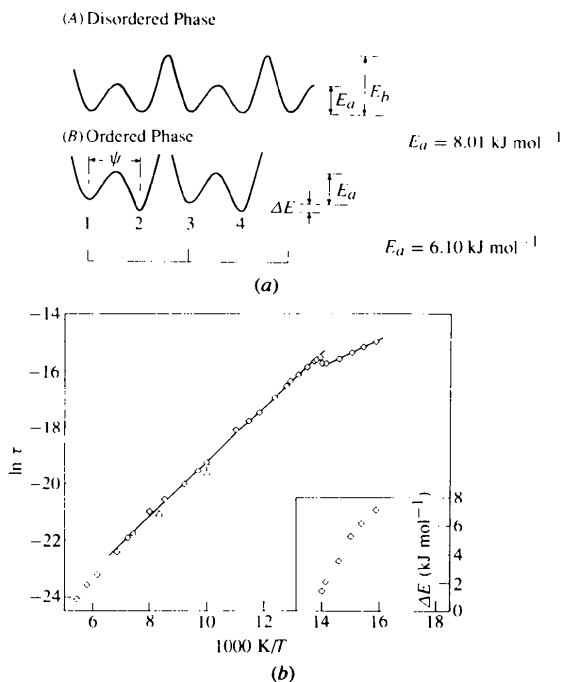
The case of the naphthalene–tetracyanoethylene complex is not as straightforward, but a similar analysis is possible.

4.2. The t-butylcalix[4]arene complex with toluene

The calixarenes are a relatively new group of host materials with many diverse modifications. The earliest calixarene crystal structure determined was that of the toluene complex of t-butylcalix[4]arene (Andreetti, Ungaro & Pochini, 1979). The structure shows fourfold symmetry, which is achieved by the toluene, which fits into the calix, occupying two distinct orientations at right angles to each other. The t-butyl groups were found to be disordered over two sites with a relative occupancy of 1:3. Other studies generally confirmed that t-butyl-calix[4]arene was in a cone conformation with fourfold symmetry (Andreetti, Pochini & Ungaro, 1983; Gutsche & Bauer, 1985; Grootenhuis et al., 1990).

We became interested in this material because the results obtained raised a general question as to why a guest with no more than twofold symmetry might induce fourfold symmetry in the host lattice. If the disorder is static, one might expect the high symmetry to be achieved by space-averaging of individual guest–host units of lower symmetry. On the other hand, if the disorder is dynamic, the high symmetry can be achieved by time averaging of lower symmetry guest–host configurations.
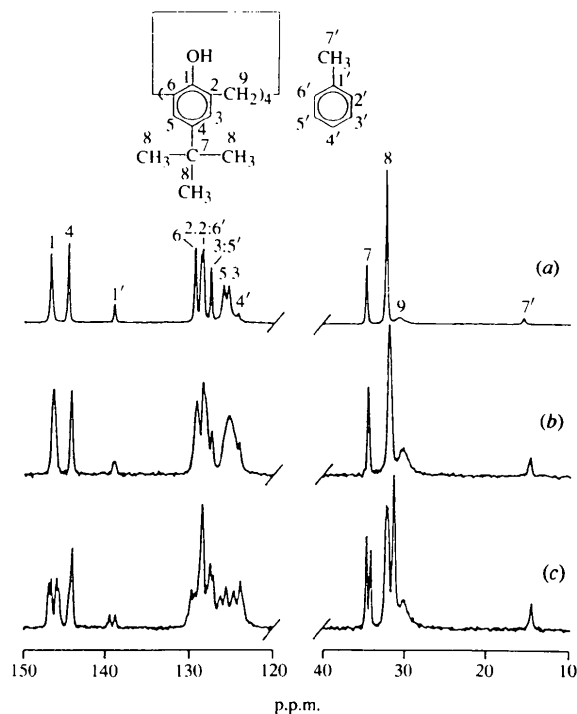

Fig. 5. (a) Potential for in-plane reorientation of naphthalene in the disordered and ordered phases used in the relaxation time and second moment calculations; (b) motional correlation times plotted as a function of inverse temperature for small barrier jumps; inset: change in the energy inequivalence (ΔE) with inverse temperature of the two sites in the ordered phase (Ripmeester, Dalal & Reddoch, 1981).

Fig. 6. ^{13}C CP/MAS NMR spectra of the t-butylcalix[4]arene toluene clathrate obtained at (a) 298, (b) 250 and (c) 230 K.

Application of ^{13}C CP/MAS spectroscopy (Fig. 6) showed a spectrum completely in agreement with the fourfold symmetry of each guest–host unit (Facey *et al.*, 1993). Application of ^{2}H NMR spectroscopy to the toluene-d_8 guest molecule showed that toluene behaves as an axial rotor (Fig. 7), *i.e.* the disorder must be dynamic, and the motion is close to the fast limit at room temperature.

One can also speculate on what may happen at lower temperatures as the fourfold motion slows down. In general, one would expect a symmetry lowering transition, and indeed a phase transition was found by differential scanning calorimetry (250 K, $\Delta H = 0.398\,\mathrm{J\,g^{-1}}$). Examination of the low-temperature phase at 230 K by ^{13}C CP/MAS NMR showed that many of the host lattice lines became multiplets, and that also the C1 carbon line of toluene itself split into a doublet. The implication is that symmetry lowering indeed took place with at least two distinct guest–host units in the new asymmetric unit.

It came as a surprise, then, that examination of the crystal structure in the low-temperature phase at 150 K showed the lattice symmetry to be unchanged at $P4/n$ with only slightly modified lattice parameters. Additional ^{2}H NMR studies were carried out (this time on toluene deuterated only on the aromatic ring) to check on the dynamic state of the guest molecule. At 77 K the line shape indicates a static guest molecule, then going through an intermediate motional rate region, until around 200 K the motion reaches the fast limit. The line shape can be simulated in terms of a twofold flip of the guest, roughly about the C1—C4 molecular axis (Fig. 7). This clearly indicates that although the lattice symmetry is still high, each guest–host unit now has just twofold symmetry. In the low-temperature phase, the high
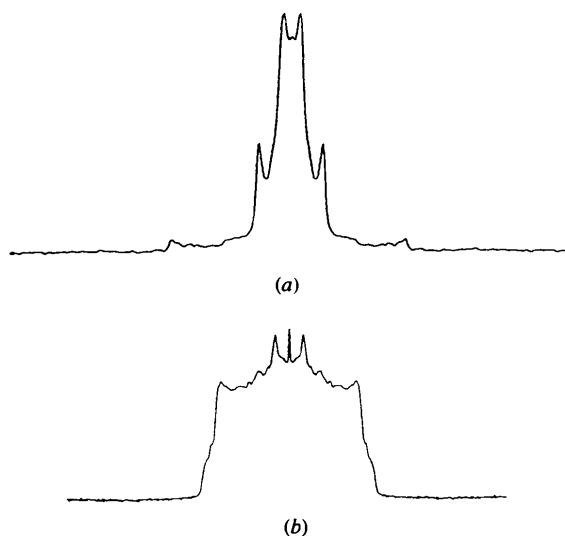
Table 1. *Summary of diffraction results for t-butyl-calix[4]arene–toluene*

	Room temperature	150 K
Space group	$P4/n$	$P4/n$
Z	2	2
Unit cell	$a = 1.2756$ (2)	$a = 1.2554$ (3)
parameters (nm)	$c = 1.3793$ (3)	$c = 1.37665$ (2)
R, Rw	0.092, 0.086	0.061, 0.056
t-Butyl disorder	77/23	50/50

Room-temperature data from Andreetti, Ungaro & Pochini (1979).

apparent symmetry is therefore achieved by space averaging.

The low-temperature structure was then refined in terms of a model with twofold local symmetry (for summary, see Table 1). The disorder of the t-butyl groups was now resolvable as 1:1, and involves not only the t-butyl groups, but also the aromatic ring (Fig. 8). Each of the two disorder sites can be associated with a different orientation of the toluene in the structure. We are currently checking to see if the disorder of the t-butyl groups is dynamic, and if the motion is coupled to the toluene ring rotation. Further points about the multiplicity of the toluene C1 NMR resonance, the appearance and disappearance of superlattice reflections, the remaining site-to-site disorder and the presence of end-for-end disorder of the toluene molecules will be discussed elsewhere in more detail.

4.3. Xenon α-cyclodextrin

Cyclodextrins are another group of versatile host materials for which a number of commercial applications

(a)

(b)

Fig. 7. ^{2}H NMR line shapes for t-butylcalix[4]arene clathrates: (a) toluene-d_8 at room temperature; (b) toluene-d_5 at 205 K.
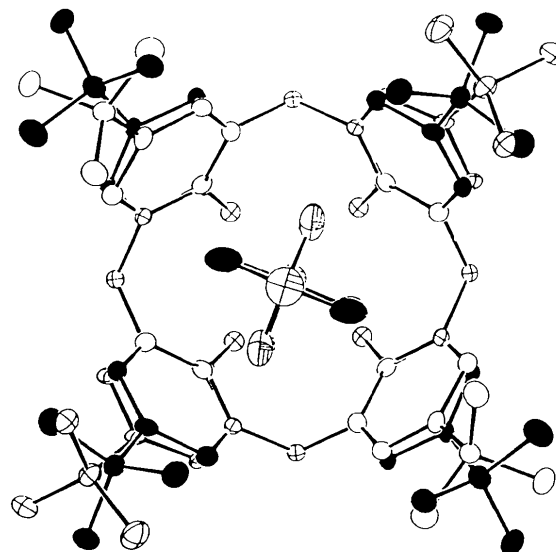

Fig. 8. Structure of t-butylcalix[4]arene toluene clathrate guest–host unit at 150 K, illustrating 50:50 disorder of the t-butyl groups and the attached aromatic rings.

have been realized (Szejtli, 1988). They are cone-shaped oligomers of glucose comprised of six or more anhydroglucose units bonded in a head-to-tail fashion with hydrophilic upper and lower rims and a hydrophobic interior. Almost all cyclodextrin complexes studied to date by diffraction methods were at least three-component systems consisting of guest, host and water, and most complexes were studied in the highest hydration state (Saenger, 1982). Although water plays a critical role both in complex formation and guest release, it is somewhat ironic that most complexes prepared for practical purposes are freeze-dried. There is then a gap in knowledge as the structures of anhydrous or partially hydrated states of cyclodextrin complexes remain essentially unknown. As we will demonstrate, NMR and thermodynamic measurements do offer some possibilities of classifying or fingerprinting structures, and offer a way of rapidly screening samples if powder diffraction methods are to be considered for more complete structure determinations.

A typical high quality ^{13}C CP/MAS NMR spectrum of cyclodextrin hexahydrate is shown in Fig. 9, along with a cyclodextrin molecule. The main point to be made here is that the ^{13}C spectrum reflects the asymmetric unit of the crystal. Since the asymmetric unit contains an entire molecule, each carbon line is split into six, reflecting the inequivalence of the anhydroglucose units.
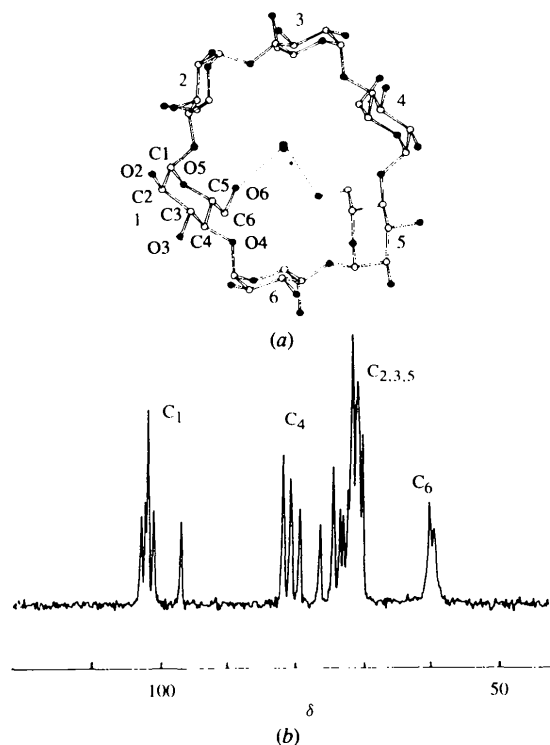
We have chosen the xenon α-cyclodextrin complex as a convenient system for study, as the host lattice can be characterized by ^{13}C CP/MAS NMR, and the guest xenon resonance can be expected to be extremely sensitive to the geometry of the guest site (Ripmeester, 1982b; Ripmeester, Ratcliffe & Tse, 1988).

Figs. 10(a), (b) and (c) show ^{13}C NMR spectra for different hydration states of the xenon α-cyclodextrin complex: (a) fully hydrated, (b) dried over calcium chloride and (c) dried over phosphorus pentoxide. The presence of sharp lines indicates that each material is crystalline, and the relatively simple but distinct splitting patterns show that for each sample the asymmetric unit contains one complete hexameric cyclodextrin molecule. The chemical shifts indicate that for each hydration state the detailed geometry of the molecule is slightly different. The most unusual feature is the C6 resonance at 64 p.p.m. for sample (c), which indicates an unusual geometry of at least some of the primary hydroxyl groups.

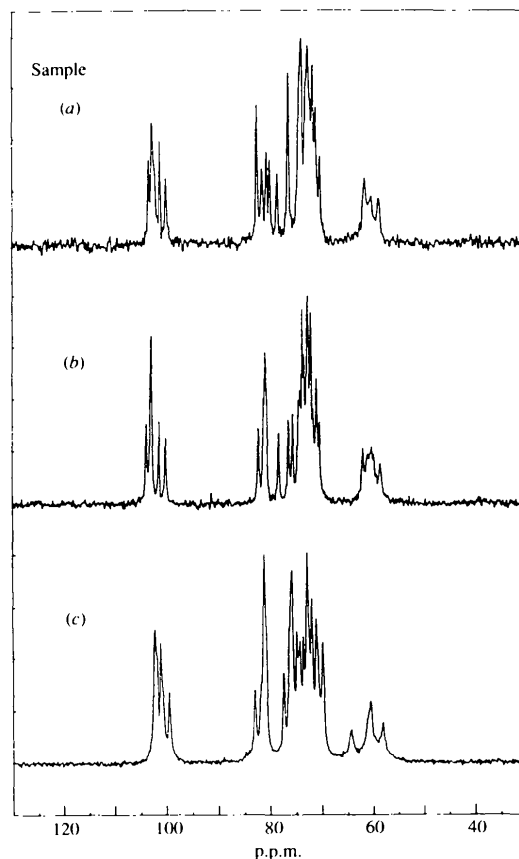Fig. 11 shows xenon guest resonances, both for static and spinning samples. The isotropic chemical shifts

Fig. 9. (a) Structure of the cyclodextrin molecule in α-cyclodextrin hexahydrate; (b) the ^{13}C CP/MAS NMR spectrum.

Fig. 10. ^{13}C CP/MAS NMR spectrum of xenon α-cyclodextrin: (a) fully hydrated sample; (b) sample dried over CaCl₂; (c) sample dried over P₂O₅.

change only slightly on going from sample to sample, however, the chemical shift tensors do change quite markedly. For the fully hydrated sample, the pattern is axially symmetric, the dried sample (b) shows a small shoulder as the symmetry is lowered, and the fully dry sample shows a general pattern of much greater width. Generally speaking, as the sample loses water, the guest site becomes more anisotropic. By using the chemical shift–cage size calibration reported previously (Ripmeester, Ratcliffe & Tse, 1988), one can estimate the size and asymmetry of the xenon trapping sites

Temperature variation of the ^{129}Xe spectrum also reveals some interesting features. For sample (a), the

spinning spectrum broadens as the temperature decreases, and a considerable fine structure develops (Fig. 12). Below 250 K, three distinct resonances are now visible, indicating the presence of three distinct environments for the xenon guest. The best explanation for the observed temperature dependence is that the room-temperature structure is a dynamically averaged structure of relatively high symmetry. As the temperature decreases there is a freezing in of water molecular motion, and the hydrogen-bonding network involving the water and cyclodextrin hydroxyls goes from a dynamic time-averaged state to a static situation where there is considerable disorder. This is confirmed by the low-temperature ^{13}C spectrum which consists of rather broad lines. There is no sign of a phase transition.

The ^{129}Xe CP/MAS NMR spectrum for sample (b) shows an interesting shift in the position of the main resonance line as the temperature drops below 250 K (Fig. 13). The shift is some 20 p.p.m. to low field, and represents a considerable decrease in the amount of space available for the xenon guest. The static xenon powder pattern also shows a large change, indicating a change in the shape of the guest space. The ^{13}C spectrum (Fig. 14) shows a similar sudden change, to a phase which also has a single molecule per asymmetric unit. The suddenness of the spectral shifts signals the presence of a phase change, and indeed, examination of a DSC trace (Fig. 15) shows an exotherm of 3.216 J g^{-1} at 252 K on warming the sample.
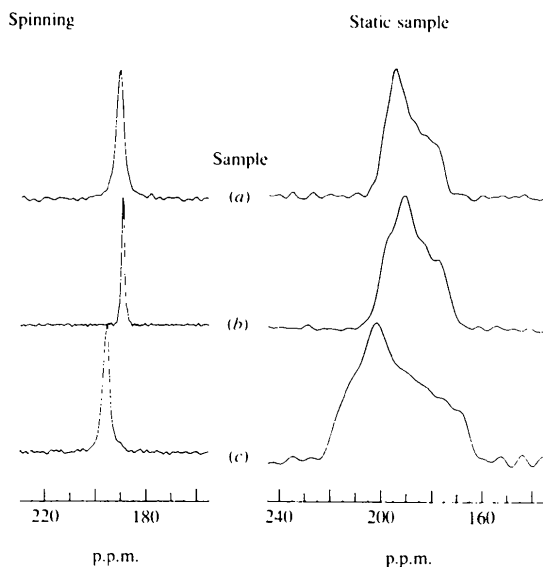
Fig. 11. ^{129}Xe NMR spectra for xenon α-cyclodextrin: (a) fully hydrated; (b) sample dried over CaCl$_2$; (c) sample dried over P$_2$O$_5$.
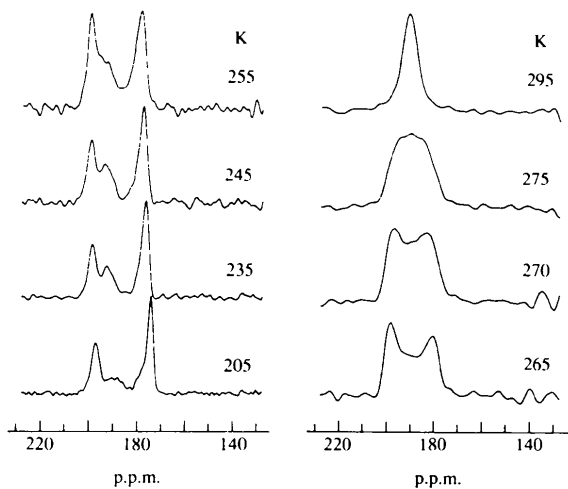
Fig. 12. ^{129}Xe NMR spectra for xenon α-cyclodextrin sample (a), temperature dependence.
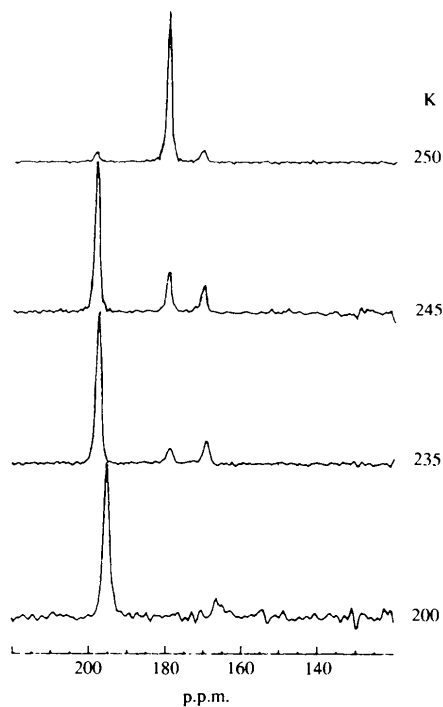
Fig. 13. ^{129}Xe NMR spectra for xenon α-cyclodextrin sample (b), temperature dependence.

Sample (c) showed relatively little change in the ¹³C and ¹²⁹Xe NMR spectra with decrease in temperature. Some additional experiments on higher hydration states of the xenon α-cyclodextrin complex showed that there may well be more distinct structures intermediate between (a) and (b) in water content. As shown below, the ability to retain local as well as crystalline order in crystals with variable water content seems to be a more general property of cyclodextrin structures. Fig. 16 shows a summary of the results obtained for xenon α-cyclodextrin. There is a remarkable complexity which may well be duplicated for many cyclodextrin complexes.

Recently it has been illustrated (Ripmeester, 1983) that for β-cyclodextrin hydrate there is a continuous change in structure as the water content goes from 12.5 to 10 waters per cyclodextrin. This implies that the water which is lost rather easily does not play a strong structural role, and that perhaps its role in the structure is best described as that of a space-filling guest molecule. The observation of ¹³C spectra characteristic of well-
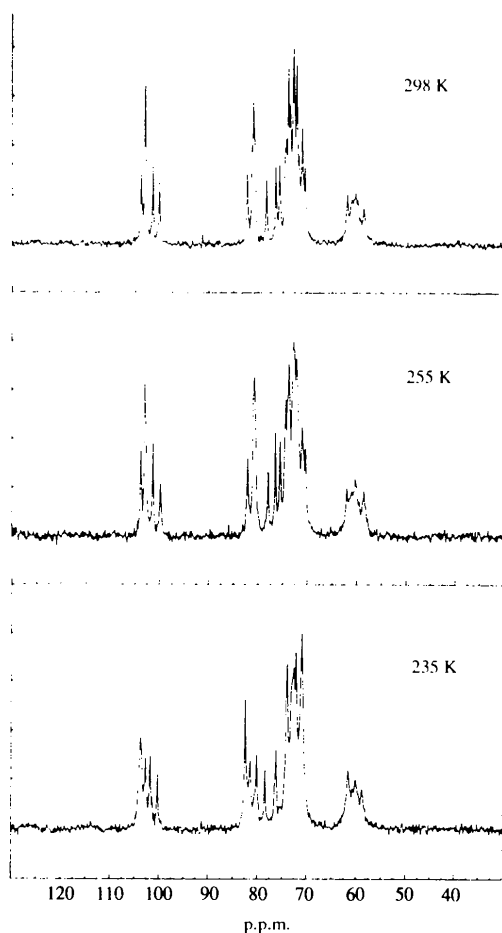
ordered crystalline material with just a single molecule per asymmetric unit then suggests that water molecules are shared by a number of cyclodextrin molecules, i.e. again we have a dynamic structure where water molecules can move rapidly from one cyclodextrin molecule to another on an NMR timescale. Naturally, the structure obtained from diffraction will also be the time-averaged structure.

5. Concluding remarks

From the examples shown it is clear that there is much to be gained by using complementary techniques in order to obtain a better understanding of the structure of crystalline solids which show complex phase behaviour. There will be further advantages in combining detailed structural and dynamic information with modelling calculations. This should allow the testing and refining of potential functions and parameters, and it is hoped that
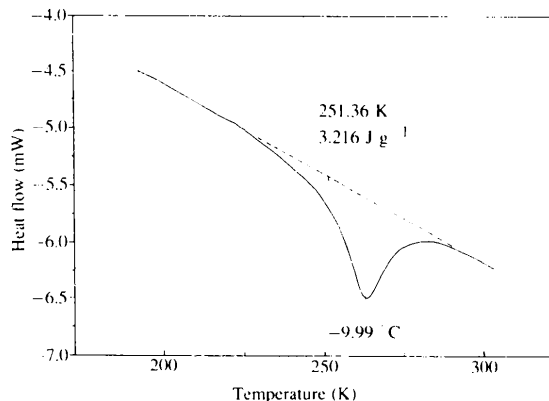

Fig. 15. DSC trace for xenon α-cyclodextrin sample (b) showing the presence of a phase transition.

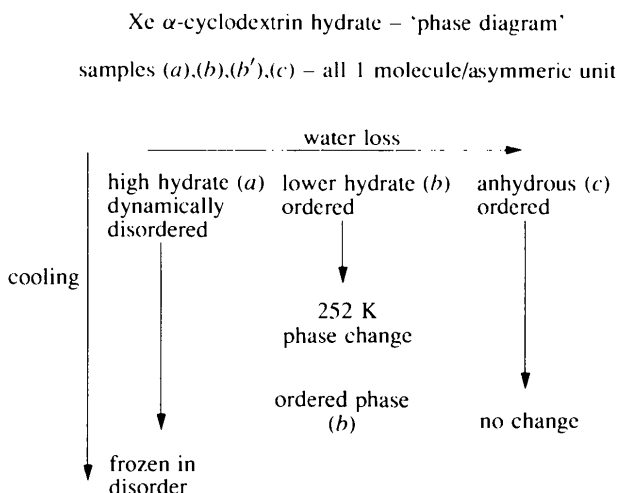Fig. 14. ¹³C NMR CP/MAS NMR spectra for xenon α-cyclodextrin sample (b) at different temperatures.

Fig. 16. A summary of the NMR and calorimetric work on the xenon α-cyclodextrin system.

eventually this approach should lead to the predictive use of modelling in such systems.

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