J. Am. Chem. Soc. 1993, 115, 281–284

Thermally Induced Phase Transformations in the Clathrasil Dodecasil-3C: The Role of Guest Molecules[†]

J. S. Tse,[*,‡] M. Desando,[‡] J. A. Ripmeester,[*,‡] and Y. P. Handa[§]

Contribution from the Steacie Institute for Molecular Sciences and Institute for Environmental Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6.

Received May 7, 1992

Abstract: Phase transitions, phase structures, and guest motions in the clathrasil Dodecasil-3C were studied by means of calorimetry, solid-state NMR, dielectric relaxation, and synchrotron powder diffraction. In contrast to the behavior of the empty clathrasil, a gradual lowering in the unit cell symmetry from cubic → tetragonal → orthorhombic → monoclinic is observed in THF D3C as the temperature is lowered. ^{2}H NMR line widths showed that there is a concurrent increase in motional anisotropy as the lattice symmetry is lowered, suggesting that the two phenomena are coupled. THF electric dipole reorientation, with an activation energy of 7.7 ± 0.6 kJ mol^{-1}, is fast at all temperatures greater than 100 K and is not affected by the symmetry lowering.

Introduction

The clathrasil Dodecasil 3-C (D3C)[1,2] is the metal-free variant of the zeolite ZSM-39[3] formed from a three-dimensional network in which guest molecules reside in distinct cavities. If all cavities are occupied, then the ideal composition is $16M_1 \cdot 8M_2 \cdot 136SiO_2$, where M_1 and M_2 are guests in the 12-hedral and 16-hedral voids, respectively.[4] Several structurally distinct phases have been identified for D3C with different guests at room temperature.[2,5–8] Moreover, it was found that certain samples exhibited phase transitions at temperatures which depended on the nature of the guest.[9] These observations strongly suggest that the guest molecules play an important role in determining the struture of the host lattice framework. A possible explanation for the variation in the structure is that the crystal symmetry can be affected by orientational ordering of the guest molecules. For large guests, the molecular motion is likely to be hindered at low temperatures. The guest molecules may then adopt certain preferred orientations, thus removing the host framework symmetries and leading to a slightly distorted unit cell. To further the understanding of this problem, a complementary study on both crystal structure and molecular motion is essential. In this contribution, the structural stabilities of THF D3C clathrasil and an empty clathrasil are studied with scanning calorimetry, solid-state ^{2}H and ^{29}Si NMR, dielectric relaxation, and powder diffraction with synchrotron radiation.

Experimental Section

D3C samples were synthesized hydrothermally in a Teflon-lined Parr pressure vessel from tetramethyl orthosilicate hydrolized in aqueous ethylenediamine, with tetrahydrofuran (THF) or THF-d_8 as guest template.[2] Guest-free material was obtained by calcining the samples. The best results were obtained for samples calcined in oxygen at 600 °C for a prolonged period of time (several days), followed by heating at 900 °C for 24 h. The quality of the samples was checked by X-ray powder diffractometry and ^{29}Si CP/MAS NMR spectroscopy. Phase-transition temperatures were determined by calorimetry on a Tian–Calvet heat-flow calorimeter.[10] Adequate resolution for defining the structure of the different low-temperature phases could not be obtained on a standard powder diffractometer (Cu $K\alpha$, 1.5405 Å), so powder patterns were obtained by using synchrotron radiation[11] (beamline X7A, 1.1997 Å) at the National Synchrotron Light Source, Brookhaven National Laboratory. ^{13}C and ^{29}Si CP/MAS spectra were obtained on a Bruker CXP-180 NMR spectrometer with a variable temperature double airbearing Doty probe. ^{2}H NMR line shapes were obtained by using a quadrupole echo sequence on the same spectrometer equipped with a variable temperature solenoid probe. Dielectric measurements were made at frequencies between 10 kHz and 4 MHz by using a Hewlett-Packard Model 4275A multifrequency LCR meter. Powdered D3C samples were pressed into thin discs. These were placed in a parallel-plate three-terminal cell which was suspended in a liquid He cryostat for temperature variation and control.[12]

Results and Discussion

(A) Phase Transitions and Structures. In general, it was found that samples with a single guest species gave more highly ordered samples, as attested by the sharpness of the calorimetric transitions and the quality of the ^{29}Si NMR spectra. As before,[9] some variation in exact transition temperatures was noted on going from one sample to another. A calorimetry scan for the best THF D3C sample showed three transitions (Figure 1), as before. The transitions at 374 and 228 K are relatively sharp, but the intermediate transition at 268 K is somewhat sluggish. These results suggest the existence of four distinct phases between 80 and 400 K (phases I–IV). In comparison, no phase transitions were detected for the calcined clathrasil sample. These observations were corroborated by both the NMR and diffraction results.

CP/MAS ^{29}Si NMR spectra at selected temperatures (Figure 2) show significant differences in both peak intensities and positions for the different phases. At 373 K (phase I), there are three magnetically distinct Si atoms (T_1, T_2, and T_3) in the structure. At room temperature (300 K, phase II), the T_3 peak splits into a set of three peaks with equal intensities. When the sample cooled to 260 K (phase III), the T_2 peak splits into a doublet, with further unresolved splittings in the three peaks of T_3. When the sample is cooled below 255 K, the ^{29}Si pattern becomes even more complicated, with many overlapping bands (phase IV). On the contrary, the ^{29}Si NMR pattern of the calcined sample shows only three peaks, with chemical shifts very close to those in the high-temperature phase of THF D3C, although the line widths are considerably broader due to poorer crystallinity. The spectral features show no obvious temperature dependence. The thermally induced structural transformations in the THF clathrasil are also

---

[*] Authors to whom correspondence should be addressed.

[†] Issued as NRCC No. 33321.

[‡] Steacie Institute for Molecular Sciences.

[§] Institute for Environmental Chemistry.

(1) Gies, H.; Liebau, F.; Gerke, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 206.

(2) Gies, H. Z. *Kristallografiya* **1984**, *167*, 73.

(3) Schlenker, J. L.; Dwyer, F. G.; Jenkins, E. E.; Rohrbaugh, G.; Kokotailo, G.; Meier, W. M. *Nature* **1981**, *294*, 300.

(4) Jeffrey, G. A. In *Inclusion Compounds*; Ed. Atwood, J. L., Davies, J. E. D., MacNicol, D. D. Eds.; Academic Press: New York, 1984; Vol. I.

(5) Groenen, E. J. J.; Alma, N. C. M.; Bastein, A. G. T. M.; Hays, G. R.; Huis, R.; Kortbeek, A. G. T. G. *J. Chem. Soc., Chem. Commun.* **1983**, 1360.

(6) Long, Y.; He, H.; Zheng, P.; Wu, G.; Wang, B. *J. Inclusion Phenom.* **1987**, *5*, 355.

(7) Higgins, J. B.; Woessner, D. E.; Trewella, J. C.; Schlenker, J. L. *Zeolites* **1984**, *4*, 112.

(8) Kokotailo, G. T.; Fyfe, C. A.; Gobbi, G. C.; Kennedy, G. J.; DeSchutter, C. T. *J. Chem. Soc., Chem. Commun.* **1984**, 1208.

(9) Ripmeester, J. A.; Desando, M.; Handa, Y. P.; Tse, J. S. *J. Chem. Soc., Chem. Commun.* **1988**, *608*.

(10) Handa, Y. P.; Hawkins, R. E.; Murray, J. J. *J. Chem. Thermodyn.* **1984**, *16*, 623.

(11) Cox, D. E.; Hastings, J. B.; Cardoso, L. P.; Finger, L. W. In *High Resolution Powder Diffraction*; Catlow, C. R. A., Ed.; Trans Tech Publications Ltd.: Switzerland, 1986; p 1.

(12) Gough, S. R. *J. Phys. E.: Sci. Instrum.* **1982**, *15*, 530.

0002-7863/93/1515-281$04.00/0 Published 1993 by the American Chemical Society

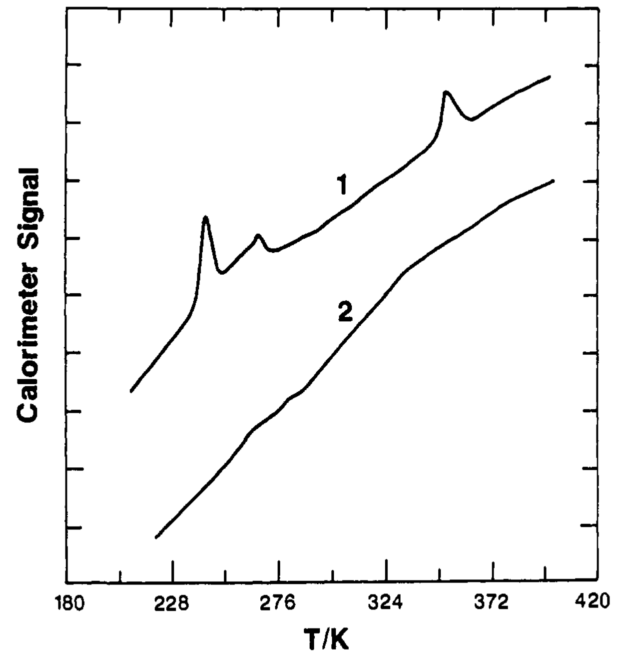

Figure 1. Calorimetry scan for a sample of (1) THF D3C clathrasil and (2) a sample of the calcined empty clathrasil.

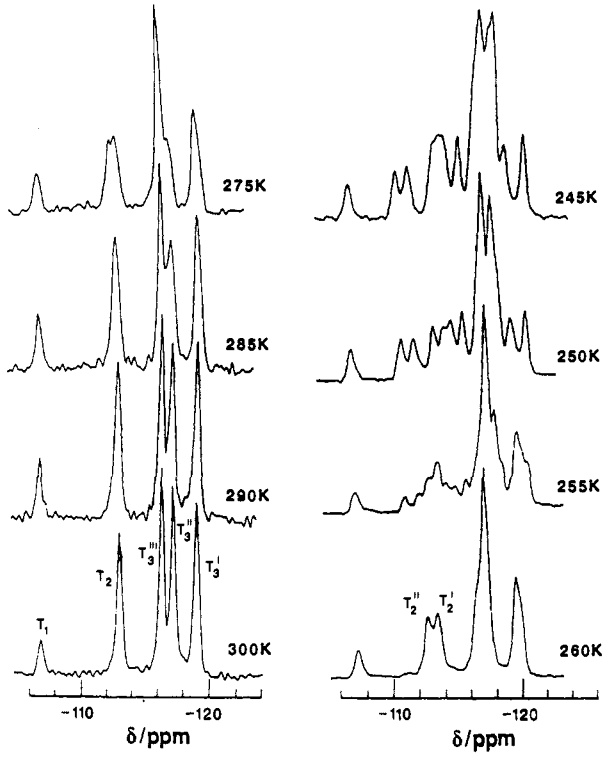

Figure 2. ^{29}Si NMR spectra of THF D3C as a function of temperature.

confirmed by X-ray powder diffraction. The diffraction patterns obtained with synchrotron radiation at 295, 260, and 80 K are shown in Figure 3, and it is clear that the diffration patterns are quite different at these temperatures. In the case of the calcined sample, the diffraction patterns are similar to those of phase I of THF D3C, and no change in structure was observed in the same temperature region.

The powder pattern of the highest temperature phase I of THF D3C is consistent with a face-centered cubic space group with cell constant a = 19.370 (1) Å. Using a trial and error procedure,[13,14] the room temperature phase II can be indexed according to a body-centered tetragonal (I4) structure with a = 13.636 (2) and c = 19.446 (3) Å. The intermediate phase III, which is stable between 245 and 269 K, can be indexed readily in a centrosymmetric orthorhombic space group with a = 13.608 (2), b = 13.622 (3), and c = 19.423 (3) Å. Finally, the powder pattern of phase IV is indexed successfully as a monoclinic C-centered structure with cell parameters a = 13.604 (1), b = 13543 (1), and c = 19.244 (2) Å and β = 90.79 (1)°.

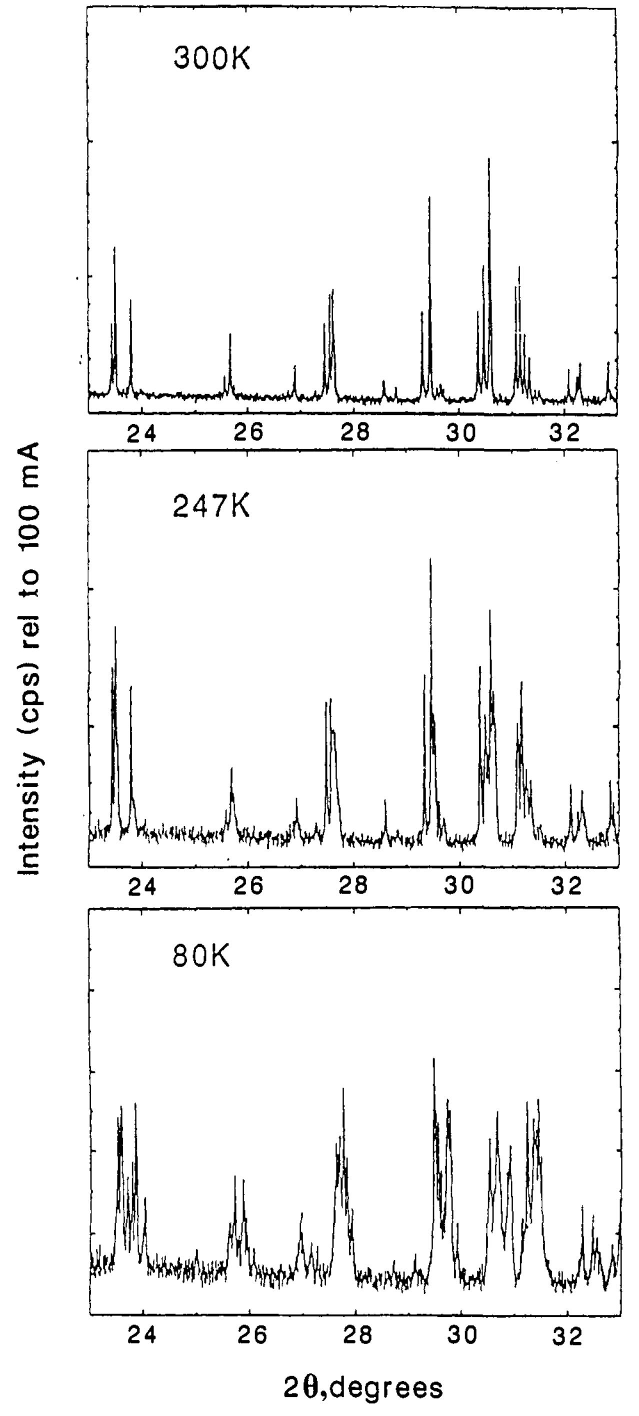

Figure 3. Synchrotron radiation (1.1997 Å) powder diffraction patterns for the tetragonal (300 K), orthorhombic (247 K), and monoclinic phases (80 K) of THF D3C between 23 and 33°.

The space group of phase I of THF D3C cannot be uniquely defined by considering only the powder diffration data. The gradual reduction in crystal symmetry can be rationalized through the group–subgroup relationships.[15] The lower symmetry maximal

---

(13) Visser, J. W.; *J. Appl. Crystallogr.* **1969**, *2*, 89.

(14) Werner, P.-E. *Z. Kristallogr.* **1964**, *120*, 375.

(15) Barnighausen, H. *MATCH* **1980**, *9*, 139.

nonisomorphic subgroup can be generated from that of the higher symmetry by removing appropriate symmetry elements in steps. It is not possible to reduce a $Fd\bar{3}$ cell to a tetragonal structure simply by nondisplacive symmetry lowering. However, removal of the 3-fold axes from the $Fd\bar{3}m$ space group leads to a body-centered tetragonal cell with $I4/amd$ symmetry. Further removal of the 4-fold symmetries from the tetragonal cell results in an orthorhombic cell of Laue symmetry $Imma$. Final removal of the mirror planes leads to a monoclinic $C2/m$ cell. In view of these symmetry relationships, it is likely that the space group of the cubic phase I is $Fd\bar{3}m$. It is significant to point out that the indices of the Bragg reflections given for the low-temperature phases do obey the systematic absence conditions of the space group presented here.

Additional information supporting the space group asssignments can be obtained from the examination of the number of ^{29}Si resonances and their relative intensities. In phase I, the intensity ratios of the three ^{29}Si peaks are consistent with the three crystallographically distinct sites in the $Fd\bar{3}m$ space group. The three unique Si atoms at the symmetry sites $..m$, $.\bar{3}m$, and $\bar{4}3m$ have multiplicities of 96, 32, and 8, respectively. This is in accord with the 12:4:1 intensity ratio of the T_3:T_2:T_1 peaks observed in the ^{29}Si NMR spectrum. Lowering the cubic symmetry to tetragonal by removing the 3-fold axis splits the $..m$ sites (T_3) into three inequivalent sites of equal multiplicities (T_3', T_3'', and T_3''') without affecting the other two sites. The expected five ^{29}Si resonances with intensity ratios 4:4:4:4:1 are observed in the experimental spectrum. The loss of a 4-fold axis from the tetragonal structure leads to the orthorhombic structure. In this case, except for the ^{29}Si atoms with the lowest multiplicity (T_1), the degeneracies of the other Si sites will be lowered and should result in a nine-peak spectrum of intensity ratio 2:2:2:2:2:2:2:2:1. The splitting of T_2 into two peaks (T_2' and T_2'') is clearly visible in the experimental spectrum. The splitting of the other peaks is less obvious due to the very small differences in the chemical shifts. It is apparent that the T_3' and T_3'' peaks have merged into a strong, broad band centered at −118 ppm, with an integrated intensity eight times that of T_1, and a weaker band (T_3''') at −121 ppm, with a total intensity four times stronger than that of T_1. Finally, elimination of the mirror planes in the orthorhombic structure lifts the degeneracy of all the Si sites. As a result, 17 ^{29}Si peaks of equal intensity are expected. The experimental spectrum of the low-temperature phase IV is very complicated and certainly consists of many overlapping bands. At 250 K, nine lines of about intensity = 1 can be observed, with the stronger doublet arising from a number of degenerate lines, in general agreement with the proposed symmetry.

(B) Molecular Motion. The coupling of guest dynamics to lattice distortions can, in principle, be obtained by following the molecular motion of the guests in the different phases. Since ^{2}H NMR has excellent sensitivity to motional anisotropy,[16] a D3C sample prepared with THF-d_8 was examined by ^{2}H NMR spectroscopy. For motionally narrowed lines in the fast motion limit, the residual splitting R is given by

$$R = 0.75(e^2qQ/h)\cdot S \qquad (1)$$

where e^2qQ/h is the quadrupole coupling constant and S is an order parameter, given by

$$S = 0.5|3\cos^2\theta - 1| \qquad (2)$$

Here, θ is the angle between the principal axis of the quadrupole coupling tensor (usually the C–D bond) and the rotation axis.

Unfortunately, there is no temperature region where the ^{2}H NMR line shape is a straightforward powder doublet (Figure 4, inset) interpretable in terms of a detailed motional model. The THF molecule has relatively low symmetry, and most motions will result in the presence of inequivalent C–D bonds and, hence, unresolved ^{2}H NMR splittings. However, there are significant changes in the line width of the resonance line which signal differences in average motional anisotropy and which can be used to reflect changes in lattice symmetry in the different phases. Experimental ^{2}H NMR line widths (full width at half height) are shown in Figure 4. In the cubic phase I, the relatively narrow line of 0.6-kHz width idicates isotropic reorientation and, hence, is in compliance with the tetrahedral ($\bar{4}3m$) site symmetry of the 16-hedral cages. The line width increases significantly in the tetragonal II and orthorhombic III phases (3.1 and 3.6–6.0 kHz, respectively), characteristic of reduced symmetry of the 16-hedral cage. In the monoclinic phase IV, the line width increases rapidly to ca. 20 kHz, and here doublet structure is first resolved, although it is complex. It is clear that the motion of the THF is highly anisotropic and that the symmetry of the 16-hedron has been reduced significantly. Previously,[24] it was found that the 12-hedral cage undergoes symmetry lowering as well. ^{129}Xe NMR showed that the cage's axial symmetry in the cubic phase is lost in the tetragonal and orthorhombic phases and that in the monoclinic phase there are at least two 12-hedral cages of general symmetry.

From the available data, only qualitative information is available on the THF motion in the low-temperature phase. Since there is no significant reduction in integrated intensity of the ^{2}H signal, the motion responsible for the line shape is in the fast motion limit. The 20-kHz average splitting also is reduced considerably from a rigid lattice splitting of 125 kHz, indicating an order parameter of ~0.16 and considerable motional averaging. A separate assessment of the motion of the THF guest dipole was made by using

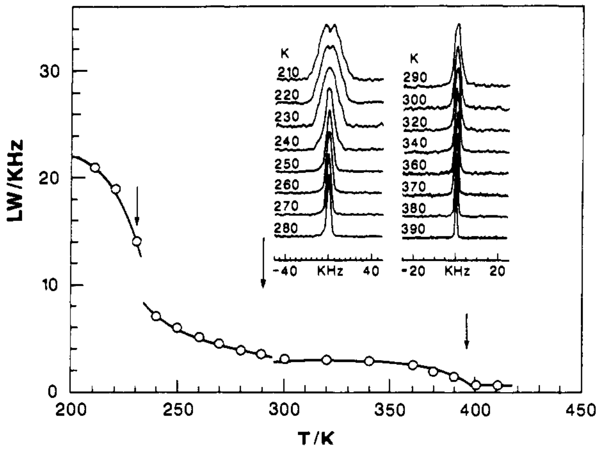

Figure 4. ^{2}H line widths and line shapes (inset) of THF-d_8 D3C as a function of temperature. The solid line is intended only as a guide for the eye. The arrows indicate phase-transition temperatures for this sample.

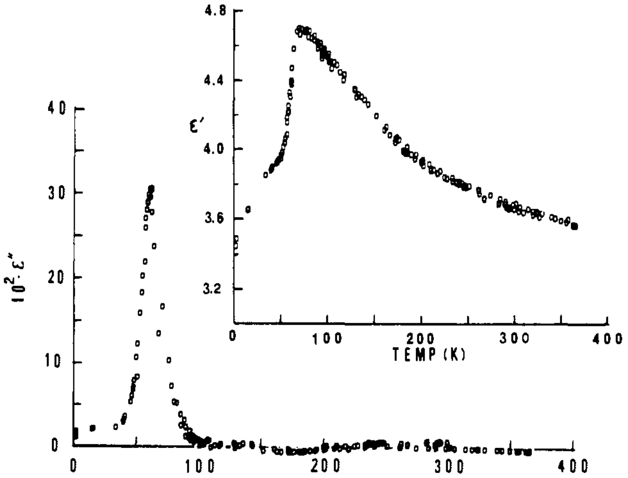

Figure 5. Dielectric permittivity ϵ'' and absorption ϵ' for THF D3C at a frequency of 1 MHz as a function of temperature. Note the Curie behavior above 125 K.

---

(16) Ripmeester, J. A.; Ratcliffe, C. I. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Oxford University Press: Oxford, U.K., 1991.

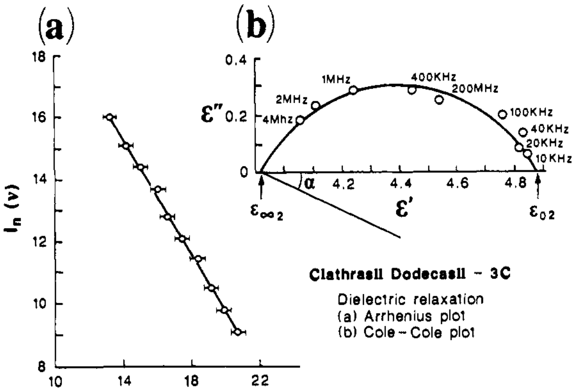

Figure 6. (a) Arrhenius plot of dielectric absorption peak maxima for frequencies between 10 kHz and 4 MHz for THF D3C. (b) Cole–Cole plot of complex permittivities ϵ' and ϵ'' for THF D3C at 60 K. The solid line is calculated according to eq 3 with distribution parameter $\alpha = 0.27$.

dielectric relaxation measurements. Figure 5 shows the permittivity ϵ' and dielectric absorption ϵ'' obtained at a frequency of 1 MHz. At temperatures above 125 K, the static permittivity follows a Curie law. There are no discontinuities in ϵ'' at any of the phase transitions, indicating that dipole reorientation rates are not affected. Straightforward application of the Onsager equation[17] for a polar molecule in dilute solution yields a dipole moment of 1.5 D, which compares with values of 1.65–1.82 D for solutions of THF in nonpolar solvents.[18] This suggests that the motion is isotropic, bearing in mind the different requirements for isotropic averaging in dielectric spectroscopy, in which the averaging involves first-order spherical harmonics, as opposed to NMR, in which the second-order spherical harmonics are involved. For the THF molecule in the presence of ring puckering, the average electric dipole is in the ring plane, so in-plane rotation is all that is required for complete dipole averaging. At lower temperatures, there are significant deviations from Curie behavior in ϵ' until the permittivity goes through a maximum and dispersion occurs. This is characteristic of the slowing down of dipole motions as the motional frequencies become similar to the frequencies of measurement. Complex permittivities associated with the reorientation frequencies at 60 K describe an arc (Figure 6b) which can be described in terms of the Cole–Cole equation[19,20]

$$\epsilon^* = \epsilon_{\infty 2} + [(\epsilon_{\infty 2} - \epsilon_{02})/(1 + (\omega\tau_0)^{1-\alpha})] \qquad (3)$$

where ω is the angular frequency of measurement, τ_0 is a motional correlation time, and α is a distribution width parameter. The solid line in Figure 6b is a fit of the above equation to the data points, which gives the distribution parameter $\alpha = 0.27$. The origin of the distribution may be due to distinct motional modes within each cage or, on the other hand, to motions of guests in cages which are inequivalent due to low crystal symmetry. Frequencies of maximum absorption plotted vs $1/T$ (Figure 6a) give an activation energy of 7.7 ± 0.6 kJ mol^{-1} for the motion, with a correlation time of 9.3 ps at 295 K.

There are some remarkable differences between THF trapped in D3C and the isostructural structure II clathrate hydrate.[20,21] At high temperatures, guest motions are near isotropic in both instances. However, the lowest temperature transition observed for D3C seems to affect the cage symmetry drastically, rendering the motion extremely anisotropic. Moreover, dipole reorientation is much more hindered in case of the clathrasil than in the hydrate, 7.7 vs 3.8 kJ mol^{-1},[20] despite the fact that the undistorted clathrasil cage has a larger free volume than the hydrate cage. Another important difference is the fact that in pure hydrate samples the cubic structure is preserved down to very low temperatures (with one known exception[22]), although again it must be remembered that the high symmetry arises because of proton disorder. When samples have been doped to shorten the host lattice dipole relaxation time, ordering transitions have been observed to take place along with ordering of the guest dipoles.[23]

In summary, the thermally induced structural transformation in THF D3C can be described as follows. Above 370 K, the crystal structure is cubic. Upon the sample cooling to room temperature, the F-centered cubic transforms into an I-centered tetragonal structure. The observed a/c ratio of the tetragonal structure is very close to the ideal cubic ratio of $1/(2)^{1/2}$ (0.7071), indicating that the distortion in the host structure is minimal. The intermediate phase III formed when the sample cools below 269 K is orthorhombic. The nearly equivalent a and b unit cell axes again show that the distortion is small. Further cooling below 250 K lowers the symmetry of THF D3C to monoclinic. Yet in this lowest symmetry structure, the lengths of the a and b axes are very similar and the monoclinic angle β deviates only very little from 90°. The most important observation, however, is that the empty calcined clathrasil does not undergo structural modifications and remains a single phase over the temperature range of study. This strongly suggests that the distortion in the unit cell is strongly coupled to the motion of the guest and that, indeed, the phase transitions may be guest driven, although the guest dipoles do not appear to play a major role.

It is tempting to propose a separation of the freezing of dipolar and quadrupolar order of the guest sublattice, as was proposed for CN$^-$ ions in a mixed KCN/KBr crystal lattice.[25] However, the relatively flexible nature of the THF guest molecule and the lack of a clear motional model at higher termperatures do not allow for such an analysis. Examination of similar clathrasil lattices with a rigid polar guest would be a useful step in defining a more detailed model for the guest motions and their relationship to host lattice phase transitions.

Acknowledgment. We would like to acknowledge the help of D. E. Cox in setting up experiments at the National Synchrotron Light Source, Brookhaven National Laboratory. NSLS is supported by the U.S. Department of Energy, Divisions of Material Sciences and Chemical Sciences.

---

(17) Onsager, L. *J. Am. Chem. Soc.* **1936**, *58*, 1486.

(18) McClellan, A. L. *Tables of Experimental Dipole Moments*; Rahara Enterprises: El Cerrito, CA, 1989; Vol. 2.

(19) Cole, K. S.; Cole, R. H. *J. Chem. Phys.* **1941**, *9*, 341.

(20) Gough, S. R.; Hawkins, R. E.; Morris, B.; Davidson, D. W. *J. Phys. Chem.* **1973**, *77*, 2974.

(21) Garg, S. K.; Davidson, D. W.; Ripmeester, J. A. *J. Magn. Reson.* **1974**, *15*, 295.

(22) Gough, S. R.; Garg, S. K.; Davidson, D. W. *Chem. Phys.* **1974**, *3*, 239.

(23) Yamamuro, O.; Matsuo, T.; Suga, H. *J. Inclusion Phenom.* **1990**, *8*, 33.

(24) Ripmeester, J. A.; Ratcliffe, C. I.; Tse, J. S. *J. Chem. Soc., Faraday Trans.* **1988**, *84*, 3731.

(25) Doverspike, M. A., Wu, M.-C., Conradi, M. S. *Phys. Rev. Lett.* **1986**, *56*, 2284.