

## Thermally Induced Phase Transitions in the Clathrasil Dodecasil-3C (Zeolite ZSM-39)†

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Cross-polarization magic-angle-spinning  $^{29}\text{Si}$  n.m.r., scanning calorimetry, and X-ray diffraction of well-ordered, as-synthesized samples of the clathrasil dodecasil 3-C (Zeolite ZSM-39) show the presence of three thermally induced phase transitions and indicate an important role for the guest molecules in determining the physical properties of this material.

Several papers have appeared recently dealing with silicon ordering in the clathrasil dodecasil-3C<sup>1,2</sup> and the related low Al zeolite ZSM-39.<sup>3-7</sup> For the ideal cubic Fd3 structure expected for these materials<sup>7</sup> there are three types of Si site, T<sub>1</sub>, T<sub>2</sub>, and T<sub>3</sub>, in the ratio 8:32:96, and three lines with intensities reflecting these ratios are expected in the  $^{29}\text{Si}$  n.m.r. spectrum. However, for as-synthesized samples, the T<sub>3</sub> line is either very broad, or a poorly resolved multiplet, whereas calcined clathrasils or de-aluminated ZSM-39 samples show a well-resolved triplet for the T<sub>3</sub> sites indicative of a lower symmetry structure.<sup>1-5</sup> In this communication we show that for several as-synthesized dodecasil-3C samples there exist a number of well-defined phases separated by reversible, thermally induced phase transitions.

Dodecasil-3C samples were synthesized as described by Gies.<sup>7,8</sup> Guest materials were tetrahydrofuran (THF) and N<sub>2</sub> at 25 atm, or THF and Xe at 20 atm. Figure 1 shows a differential calorimetry scan for these two samples. In each case, three weak endothermic peaks were observed with peak values at 245, 269, and 352 K for the THF/N<sub>2</sub> sample, and at 235, 269 and 374 K for the THF/Xe sample. Some peaks show considerable structure, the high temperature peak for THF/Xe sample being a clear doublet.

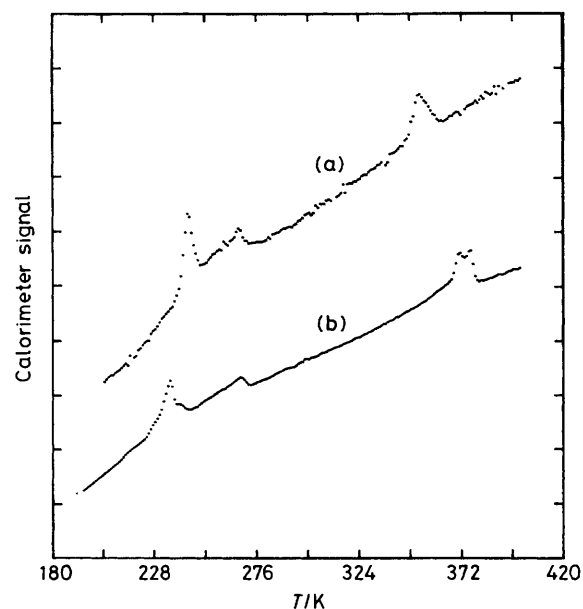
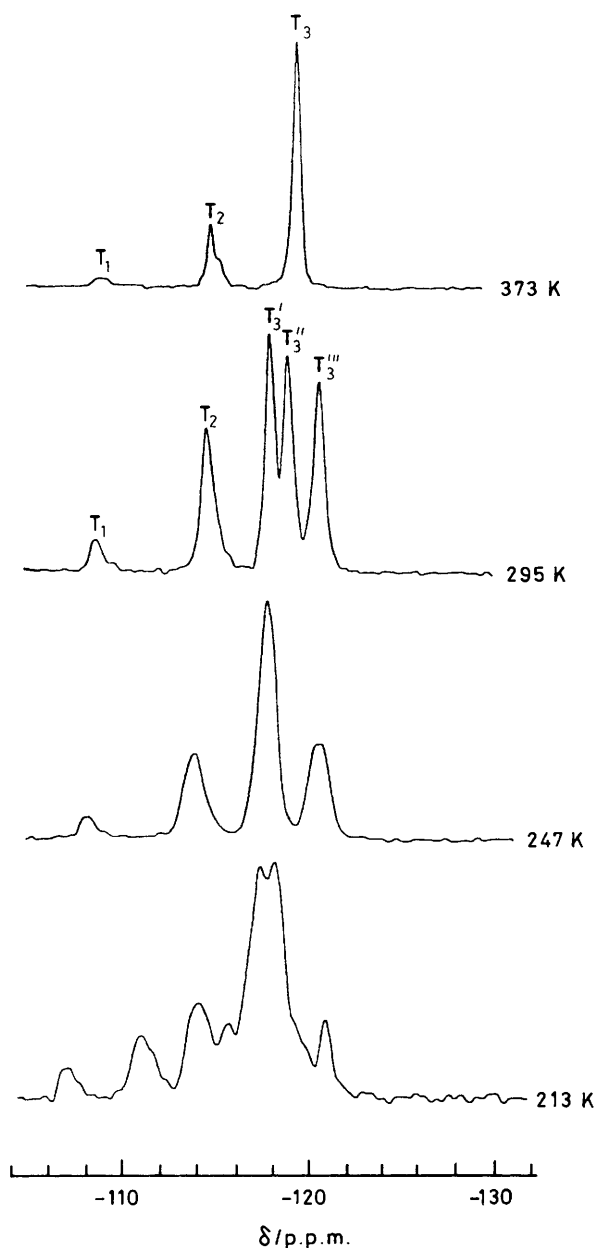


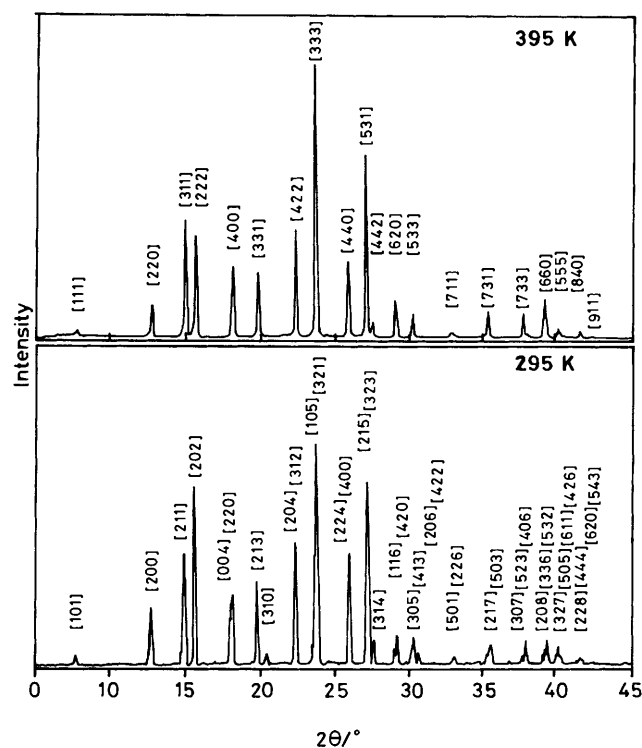
Figure 1. Heat capacity scans for dodecasil-3C sample with (a) THF/N<sub>2</sub> and (b) THF/Xe as guests.

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**Figure 2.** C.p.-m.a.s.  $^{29}\text{Si}$  n.m.r. spectrum of dodecasil-3C with THF and Xe as guests as a function of temperature. Spectra were recorded at 35.8 MHz on a Bruker CXP-180 n.m.r. spectrometer equipped with a Doty Scientific VT/M.A.S. probe.

In order to see if the Si ordering changes in the regions separated by the endothermic peaks, cross-polarization magic-angle-spinning (c.p.-m.a.s.)  $^{29}\text{Si}$  n.m.r. spectra were recorded (Figure 2). In the highest temperature phase, the spectrum corresponds to that expected for the cubic Fd3 structure with the  $T_1$ ,  $T_2$  and  $T_3$  lines in the ratio 8 : 32 : 96.<sup>7</sup> At room temperature, the  $T_3$  line has split into 3 equal components and the spectrum is similar to those observed for calcined dodecasil-3C and de-aluminated ZSM-39 samples.<sup>2-5</sup> Below  $\sim 269$  K two of the  $T_3$  lines again overlap and below the low temperature phase transition at  $\sim 240$  K the Si spectrum becomes a complex pattern not easily analysed in terms of Si ordering without further structural information.

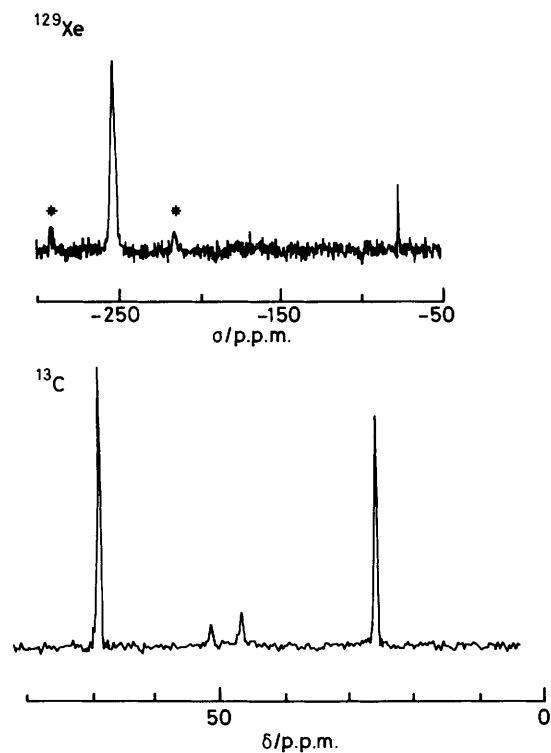


**Figure 3.** X-Ray powder diffraction patterns for dodecasil-3C with THF/ $\text{N}_2$  guests, at 395 and 295 K.

X-Ray diffraction patterns for the high temperature and room temperature phases of the THF/ $\text{N}_2$  sample were obtained (Figure 3) and indexed in terms of the previously reported structures.<sup>7,9</sup> Bragg peaks observed at 395 K were indexed in terms of the cubic system consistent with the space group Fd3. Least-squares refinement on 20 indexed lines gave a unit cell dimension of 1.9370(1) nm, in agreement with other published values.<sup>7,9</sup> The room temperature pattern was indexed in the tetragonal system and least-squares refinement on 41 lines gave parameters  $a = 1.3659(2)$  and  $c = 1.9493(3)$  nm, again in agreement with recently published values.<sup>9</sup>

Although the  $^{29}\text{Si}$  n.m.r. spectra and the powder diffraction data for the THF/ $\text{N}_2$  and THF/Xe samples are virtually identical, the heat capacity plot indicates some role for the guest molecules in determining the exact phase transition temperature. This makes it of some importance to obtain information on the distribution of guest molecules over the two sites, as sometimes it is assumed that the clathrates are essentially stoichiometric compounds with complete filling of each type of cage by a unique guest. The THF/Xe sample lends itself well to this purpose, as both guest materials have spin- $\frac{1}{2}$  nuclei suitable for n.m.r. study. The  $^{129}\text{Xe}$  n.m.r. spectrum, obtained under c.p.-m.a.s. conditions, is shown in Figure 4. The two lines at  $-253$  and  $-81$  p.p.m. can be interpreted as belonging to Xe guests in small and large cages, respectively.<sup>10</sup> The small cage line is relatively broad ( $\sim 140$  Hz) and may reflect the presence of some disorder.  $^{129}\text{Xe}$  Shifts are very sensitive to local surroundings<sup>11</sup> so that, for instance, variation in content of neighbouring cages could cause some distribution in isotropic shift values.

The  $^{13}\text{C}$  n.m.r. spectrum, in addition to the two lines from THF trapped in the large cages at  $\delta$  26 and 69, shows two weak lines at  $\delta$  46.3 and 51.2. The line at  $\delta$  51.2 can be assigned to methanol, a hydrolysis product of  $\text{Si}(\text{OMe})_4$  in the reaction



**Figure 4.**  $^{13}\text{C}$  and  $^{129}\text{Xe}$  C.p.-m.a.s. n.m.r. spectra of dodecasil-3C with THF and Xe guests.

mixture. The line at  $\delta$  46.3 is most likely due to ethylenediamine, the base used in the hydrolysis reaction. Apparently both of these materials can act as guests in the large 16-hedral cage.

The results show that although THF is the main guest, some Xe, methanol, and ethylenediamine are also trapped in the

16-hedral cages. Although Xe is most likely the only small cage guest, there are probably empty cages as well. Therefore, the distribution of guest molecules over the two sites is another potential source of disorder in the clathrasil lattice, as different interactions between distinct guests and the host lattice cages will tend to cause different distortions from ideal symmetry. This may explain some of the relatively poorly resolved  $^{29}\text{Si}$  n.m.r. spectra reported for dodecasil-3C and ZSM-39 samples. Further work on the low temperature structures and the role of guest molecules is in progress.

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