Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

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John S. Tse[a]; Dennis D. Klug[a]
[a] Steacie Institute for Molecular Sciences, National Research Council of Canada Ottawa, Ontario, Canada

To cite this Article Tse, John S. and Klug, Dennis D.(1995) 'Reversible amorphization and structural memory effect in clathrasil dodecasil-3c', Supramolecular Chemistry, 6: 1, 165 — 170
To link to this Article: DOI: 10.1080/10610279508032532
URL: http://dx.doi.org/10.1080/10610279508032532

SUPRAMOLECULAR CHEMISTRY, Vol. 6, pp. 165–170
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Reversible amorphization and structural memory effect in clathrasil dodecasil-3c

JOHN S. TSE* and DENNIS D. KLUG

Steacie Institute for Molecular Sciences, National Research Council of Canada Ottawa, Ontario, Canada K1A OR6

(Received August 5, 1994)

The mechanism for the novel structural memory effect, where a crystalline solid compressed to an disordered phase is able to revert back to the original crystal structure upon the release of the pressure, is investigated using clathrasil dodecasil as a model system. It was found, through experiments and theoretical molecular dynamics calculations, that the presence of undeformable units, such as the guests, are essential for the reversible process. The transformation of the clathrasil to a high density disordered structure at high pressure is due to a mechanical instability. In the absence of atomic diffusive motions, when the pressure is relieved the encaged guests act as templates and redirect the atoms collapsed around them back into the original structure.

INTRODUCTION

The recent discovery of the direct transformation from a crystalline to a disordered structure by compression is potentially a very important industrial process for the manufacturing of amorphous materials [1]. The search for the mechanism of this novel phenomenon has been a subject of topical interest. It was shown that a mechanical instability in the crystal is responsible for the transformation [2]. In one aspect, the transformation is akin to a *pressure melting* of the crystal [3]. However, it was found later that the compressed disordered phase is structurally anisotropic unlike that of a liquid [3–5]. More surprisingly, it was discovered that some crystals, such as α-berlinite [6], can be pressure amorphized but are able to recover the crystalline structures upon the release of the pressure. Molecular dynamics calculations on α-berlinite reproduced this dramatic effect and further suggested that the presence of the PO_4 units in the structure, which are not deformable under high pressure, is the main contributing factor for the reversible transformation [7]. This hypothesis, however, has not yet been examined by experiment.

An ideal experiment would be to observe the behaviour of a crystal towards pressure with and without the presence of the undeformable groups. Therefore, the challenge is to synthesize a solid where nondeformable groups or molecules can be removed or inserted in the structure. Supramolecular compounds with open channels or closed cavities are ideal for this purpose. Clathrasil dodecasil-3C (D3C), a new type of tectosilicate with cage-like voids in which guest species can be enclathrated, is a suitable candidate [8]. In this article, the effects of pressure on the structure of empty and enclathrated D3C are investigated. To help the understanding of the transformation mechanism, molecular dynamics (MD) calculations were also performed. In the next paragraph the experimental and theoretical details are presented. The structural transformation induced by compression is studied by in-situ infrared spectroscopy and synchrotron x-ray diffraction. The experimental results are compared with theoretical simulations and finally the role of non-deformable units in pressure-induced reversible amorphization are discussed.

EXPERIMENTAL AND THEORETICAL PROCEDURE

Samples of dodecasil-3C with enclathrated tetrahydrofuran (D3C/THF) were synthesized according to the published method [8]. The empty D3C structure was prepared by calcination of a D3C/THF sample at 900°C for 24 hours. No organic residual was observed from the solid-state ^{13}C NMR spectrum. The high pressure experiments were performed in a diamond anvil under quasi-hydrostatic conditions. For the infrared measurements, sodium bromide was used as the hydrostatic medium with a small amount of sodium nitrite and nitrate acting as pressure calibrants. A Nicolet 7199 FTIR spectrometer was used. Angle dispersive x-ray diffraction was performed at National Synchrotron Light Source (NSLS), Brookhaven National Laboratory on beamline X-7A and

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*To whom correspondence should be addressed.

the energy dispersive diffraction experiment at the high-pressure beamline at the Cornell High Energy Synchrotron Source (CHESS). In both experiments, sodium chloride was used as the pressure transmission medium as well as the pressure calibrant.

Molecular dynamics calculations were performed in the constant-pressure constant enthalpy (NPH) ensemble [9] at 300 K. 136 SiO_2 units were used in the calculations. The initial coordinates for the atoms were taken from the experimental x-ray structure [8]. The interatomic potential for silica is taken from the work of van Beest et.al. [10] This potential function has been demonstrated to give excellent static structure and dynamics for silica polymorphs even under high pressure [11]. The guest species are assumed to be spherical having interaction parameters that mimic the interactions between two THF molecules. The guest interaction potential is represented in a simple Buckingham form ($Ae^{-Br} - C/r^6$) where A = 7370 kcal mol^{-1}, B = 1.71 $Å^{-1}$ and C = 16281 kcal mol^{-1} $Å^{-6}$. The usual combination rules were employed to construct the guest-SiO_2 interaction parameters.

RESULTS AND DISCUSSION

The infrared spectra for empty and enclathrated D3C with THF at several selected pressures are shown in Fig. 1. At ambient pressure, the vibrational spectra in the region 450 to 1200 cm^{-1} are characterized by three intense bands at around 1070, 800 and 460 cm^{-1} with a distinct peak/shoulder at 550 cm^{-1}. These bands can be approximately assigned to the Si-O stretching, Si-O-Si bending and O-Si-O bending vibrations. For both samples there is little change in the spectral features with initial increase in pressure. At about 4.5 GPa the sharp feature at 550 cm^{-1} vanishes suddenly and the 800 cm^{-1} band shifts to higher frequency. The abrupt change in the infrared pattern indicates a change in the short range structure and suggest a phase transition for both the enclathrated and empty D3C at ~4.5 GPa. Upon the release of pressure, the spectral features for the empty clathrasil are very similar to the high pressure phase apart from a shift to lower energy for the Si-O stretching and Si-O-Si bending modes. In contrast, there is a remarkable change in the infrared spectrum of D3C/THF when the pressure is lowered from 11.7 GPa. The sharp feature at 550 cm^{-1} has reappeared and, moreover, the positions and profile of the major vibrational bands are identical to those of the starting material. These observations strongly suggest that the empty D3C samples retain a structure similar to that of the compressed phase after release of the pressure and the structure of the compressed phase of D3C/THF has reverted back to the original crystal structure.

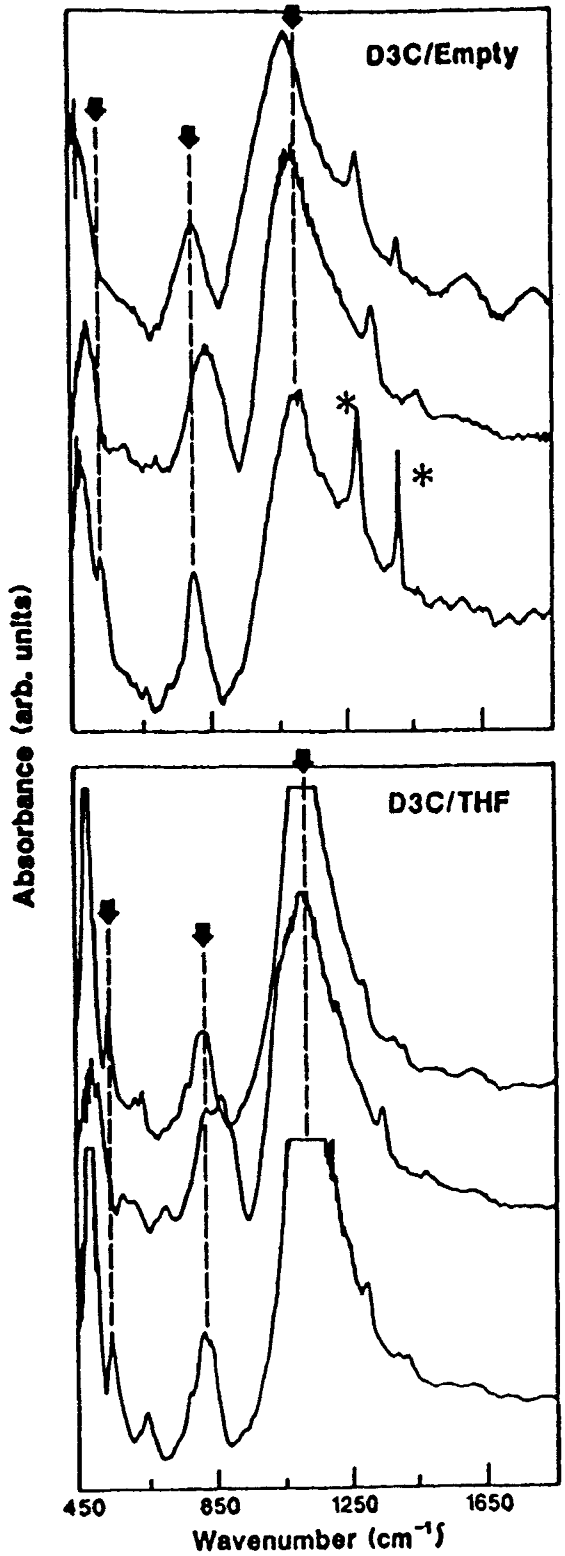


Figure 1 Infrared spectra of clathrasil D3C measured in a diamond anvil. The medium was a dilute solution of a sodium nitrite and nitrate in sodium bromide which also was the pressure calibrant. The pressures for the measurements (top frame) are 1 GPa (lower trace) 12.8 GPa (middle) and after lowering pressure to 0.7 GPa (bottom). For the lower frame the pressures are 2.0 GPa (lower), 11.7 GPa (middle), and 0.8 GPa (upper).

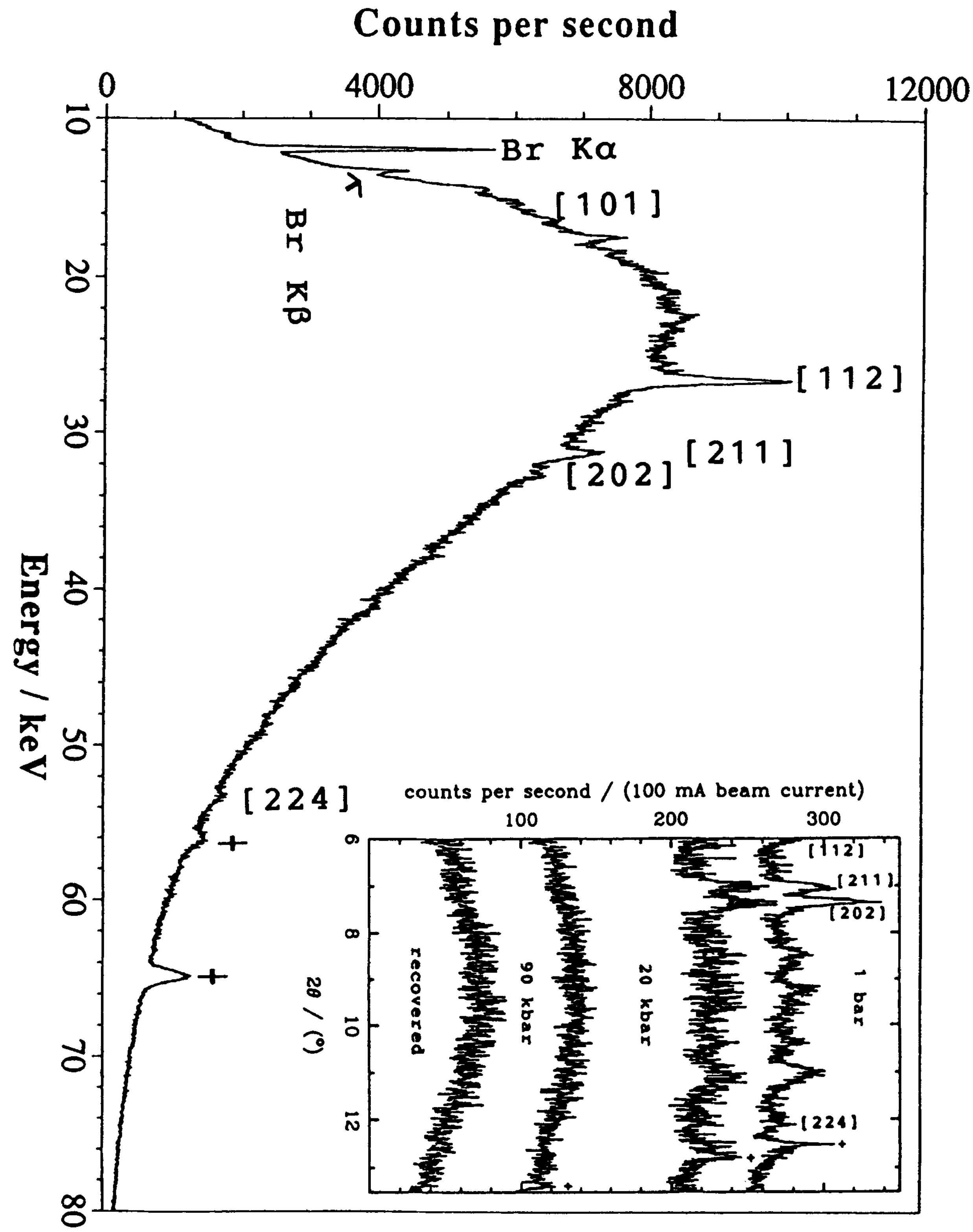


Figure 2 Angle dispersive x-ray diffraction pattern of D3C/THF on compression (inset) and energy dispersive diffraction on a recovered sample at 1 bar after being compressed to 10.5 GPa and allowed to relax for two weeks (main figure).

The observation made from the infrared study is corroborated by the X-ray diffraction experiments. As shown in Fig. 2, the absence of distinct Bragg reflection indicafes that the D3C/THF sample has lost its crystallinity and transformed into a high density disordered (amorphous) phase at pressures above 6 GPa (60 kbar). It is striking to observe that the D3C/THF sample recovers its crystallinity, as shown in the energy dispersive x-ray pattern, when the pressure is removed and the recovered sample is allowed to relax for two weeks in the diamond anvil. In contrast, the x-ray pattern for empty D3C shows that the sample transformed into a high density disordered structure and remained in this structure even after the removal of the pressure.

As demonstrated from the infrared and x-ray diffraction experiments, enclathrated and empty D3C show remarkably different behaviour after the pressure is removed from the pressure-amorphized phases. The presence of THF in the clathrasil structure *must* play a unique role in redirecting the distorted high pressure structure back to the original crystal structure. To further investigate this point, molecular dynamics calculations were performed on the empty structure and the structure with eight guests occupying the empty voids (D3C/X_8). The volume-compression curves for these systems are shown in Fig. 3. The results show that both structures can be compressed to high density phases with a transition pressure approximately 5 GPa in reasonable agreement with experimental observation (*infra supra*). The density of the densified phase is about twice that of the starting material. The volume change from the ambient pressure structure to the high density structure is about 10% larger for the empty D3C than D3C/X_8. When the pressure is relieved gradually, the molar volume of D3C/X_8 recovers to that of the original value at 1 bar. In contrast, there is only a small change in the volume of the empty D3C indicating the structure recovered at 1 bar is still highly densified. The structural relaxation is best illustrated from snapshots of the structure as a function of pressure in Fig. 4 and 5. It is interesting to observe that even though D3C/X_8 can be compressed to a high density disordered phase, reminants of the original crystalline structure are still very strong at 10 GPa. The loss in long range order arises from the dislocation of the Si-O linkages around the guests. When the pressure is relieved, the repulsive interactions between the guest and the network atoms force the Si and O atoms back to the original positions. The overall effect is that the guests act as rigid "reorganizing centers" for the reversible transformation. For empty D3C, the structural changes induced by compression are quite different from that of D3C/X_8. In this case the crystal framework collapses under pressure and fills the voids. This explains the larger volume change observed in the calculations for empty D3C. Furthermore, upon the release of the pressure, the densified structure is maintained even after the sample is recovered at 1 bar. In the absence of "reorganizing centers", no reversible amorphous → crystalline transformation can occur in empty D3C.

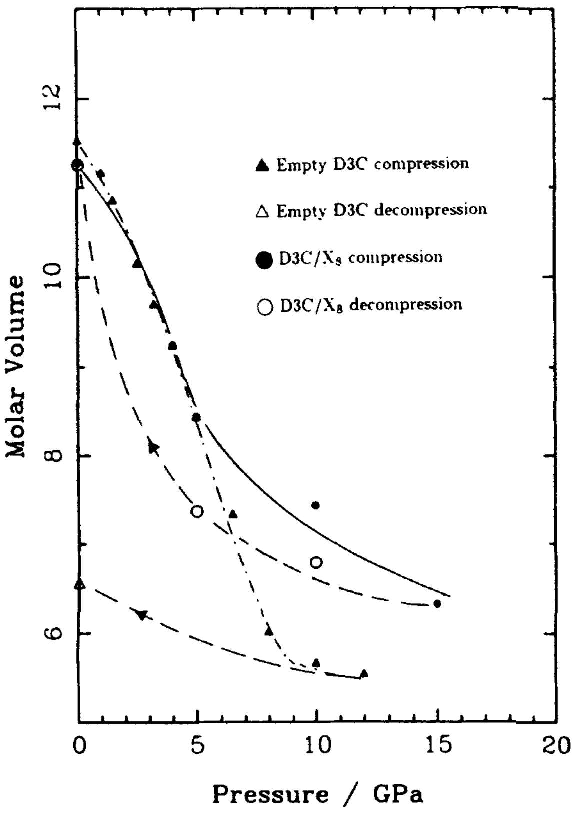


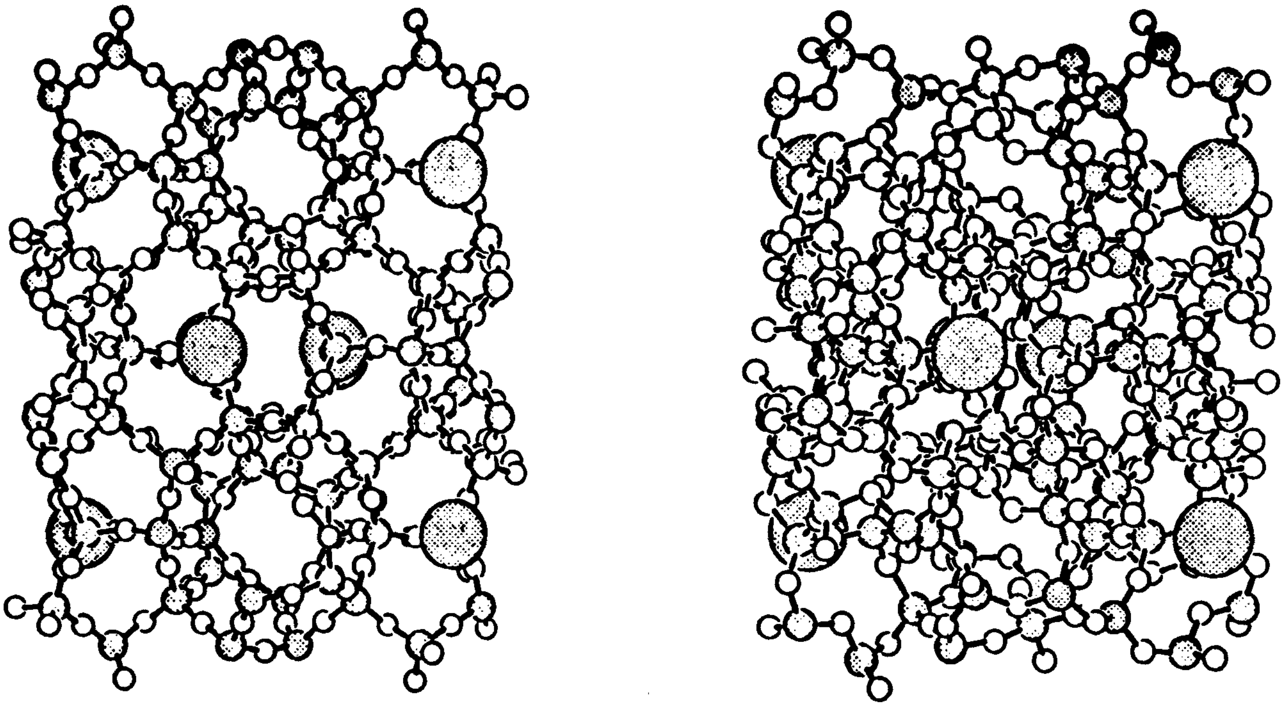
Figure 3 Calculated molar volume versus pressure upon compression and decompression for empty D3C lattice and for lattice with guest atoms occupying the empty voids in the lattice.

CONCLUSION

The presence of nondeformable molecular units in a crystal structure is an essential ingredient for pressure-induced amorphization transformations. At high pressure, the weaker linkages of the crystals structure will be severely distorted. If the diffusion of the atoms is prohibited and the nondeformable units are strategically positioned, the unfavourable repulsive interactions between the undeformable units with the other atoms in the structure are the primary guiding forces for restoring the original structure once the pressure is relieved [12]. Therefore, it is reasonable to speculate that the novel structural memory effect will occur in crystal systems where the ambient structure is relatively open and there are strong molecular groups as constituents. For example, reversible pressure-induced amorphization has been observed in SnI_4 [13] and $LiKSO_4$ [14].

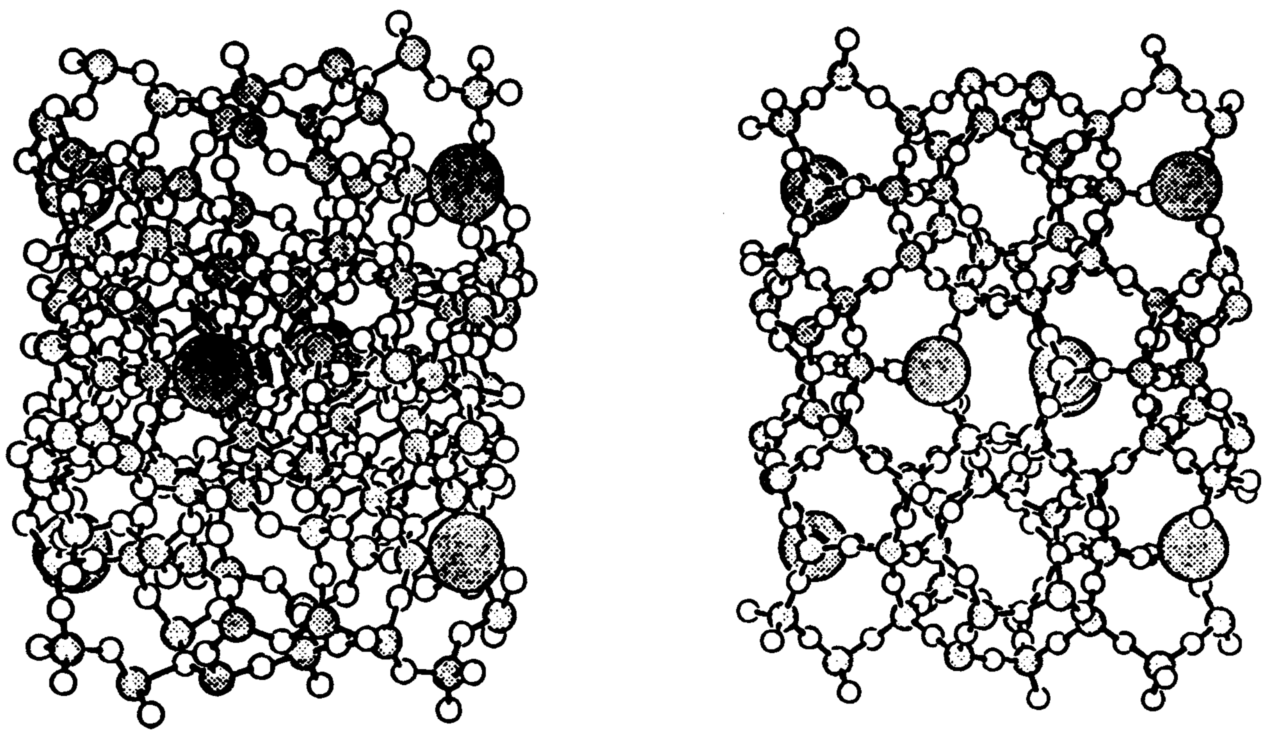
ACKNOWLEDGEMENTS

The authors wish to thank Dr. J.A. Ripmeester for the clathrasil samples and to Drs. D. Cox, K. Brister, S. Desgreniers and K. Lagarec for assistance in the synchrotron x-ray diffraction experiments.



1 bar

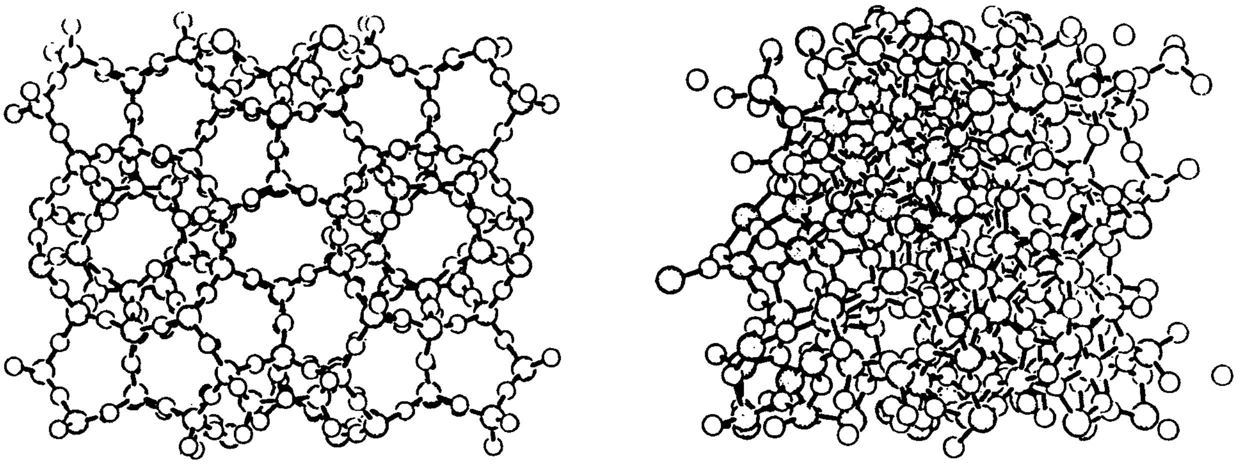
10 GPa



15GPa -> 5 GPa

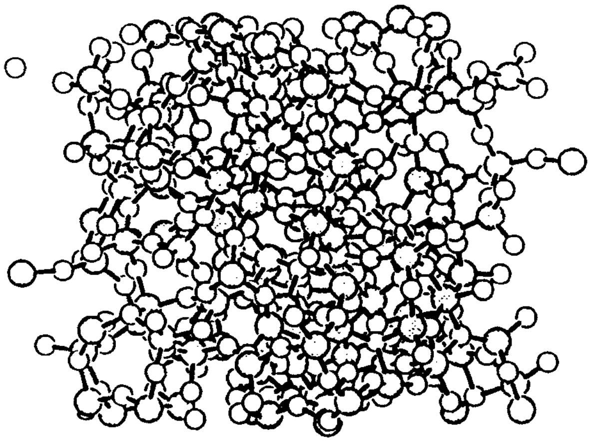
1 bar recovered

Figure 4 The calculated structure of D3C/X_8 upon compression and decompression at various pressures.



Empty D3c 1 bar

Empty D3C at 10 GPa



Empty D3C recovered at 1 bar

Figure 5 The calculated structure of an empty D3C sample at ambient pressure, upon compression, and after releasing the pressure.

REFERENCES

1 S.R. Elliot, "Physics of Amorphous Materials", 2nd Ed., Longman Scientific and Technical, London, **1990.**
2 J.S. Tse and D.D. Klug, *Phys. Rev. Lett.*, *67*, 3559 **1991.**
3 J.S. Tse, *J. Chem. Phys.*, *96*, 5482 **1992.**
4 J.S. Tse and D.D. Klug, *Phys. Rev. Lett.*, *70*, 174 **1993.**
5 L.E. McNeil and M. Grimsditch, *Phys. Rev. Lett.*, *68*, 83 **1992.**
6 M. Kruger and R. Jeanloz, *Science*, *249*, 647 **1990.**
7 J.S. Tse and D.D. Klug, *Science*, *255*, 1559 **1992.**
8 H. Gies, Z. Kristallogr., *175*, 93 **1986.**
9 S. Nosé and M.L. Klein, *Mol. Phys.*, *50*, 1055 **1983.**
10 B.W.H. van Beest, G.J. Kramer and R.A. van Santen, *Phys. Rev. Lett.*, *64*, 1955 **1990.**
11 J.S. Tse and D.D. Klug, *J. Chem. Phys.*, *95*, 9176 **1991.**
12 Y. Fuji, M. Kowaka and A. Onodera, *J. Phys. C18*, 789 **1985.**
13 F.E.A. Melo, V. Lemos, F. Cediera and F. Mendes, *Phys. Rev.*, *B35*, 3633 **1987.**