STRUCTURE-ENERGY RELATIONSHIPS OF WERNER CLATHRATES

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We have synthesised and determined the structures of a series of compounds of general formula: \( \text{Ni}[(\text{NCS})_2(\text{C}_6\text{H}_4\text{NR})_2(\text{C}_6\text{H}_4\text{NR'})_2] \cdot n \text{Si}_4\text{H}_8\text{SiO}_4\) where \( \text{R} \) and \( \text{R'} \) is an organic guest molecule.

\[ \begin{array}{cccc}
\text{Compd} & n & 
\text{R} = 4-\text{Me}, R'_1 = 4-\text{Ph} & 1 \\
2 & R = R'_1 = 4-\text{Me} & 1 \\
5 & R = R'_1 = 4-\text{Ph} & 4 \\
R = R'_1 = 3-\text{Me} & 1 \\
5 & R = R'_1 = 4-\text{Et} & 1 \\
R = R'_1 = 4-\text{Et} & 1 \\
7 & R = R'_1 = 3-\text{Me} & - \\
8 & R = R'_1 = 3,5-\text{Me} & - \\
\end{array} \]

Stoichiometric characterisation of the clathrates was determined by various techniques, including N.M.R., D.T.A. and T.G.A. Host-guest non bonded interactions were studied using atom-pair potentials and the movement of the guest molecules through channels was simulated.

04.5-4 COMPUTATIONAL MODELING OF THE HIGH-PRESSURE STRUCTURE AND THE ELASTIC CONSTANTS OF \( \beta-\text{Mg}_2\text{SiO}_4 \).

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Busing and Matsui (Acta Cryst. (1984) submitted) have recently developed a model for simulating crystal structures under hydrostatic pressures or normal and shearing stresses and a way of calculating elastic constants and their pressure derivatives. They have successfully applied the method to \( \alpha- \) and \( \gamma-\text{Mg}_2\text{SiO}_4 \) and succeeded in reproducing both the experimental structures and the observed elastic properties reasonably well (Phys. Chem. Minerals (1984) submitted). In this paper we present the results for \( \beta-\text{Mg}_2\text{SiO}_4 \), which is an intermediate phase in the high-pressure transformation of \( \alpha-\text{Mg}_2\text{SiO}_4 \) to \( \gamma-\text{Mg}_2\text{SiO}_4 \).

\( \beta-\text{Mg}_2\text{SiO}_4 \) is orthorhombic, space group 14/mma, consisting of \( \text{Mg}^{2+} \) \( 0^2- \) and separate \( \text{Si}_4^2^+ \) ions. The potential energy for our model includes Coulomb and repulsive interactions between non-bonded atoms and bond angle bending and bond distance straining energy terms for the \( \text{Si}_4^2^+ \) ions. The repulsive potentials used were the same as those for \( \alpha- \) and \( \gamma-\text{Mg}_2\text{SiO}_4 \). The net charges on the Si and O atoms in the \( \text{Si}_4^2^+ \) ions and the covalent bond potentials were adjusted so as to reproduce both the experimental atmospheric-pressure structure and elastic constants well.