

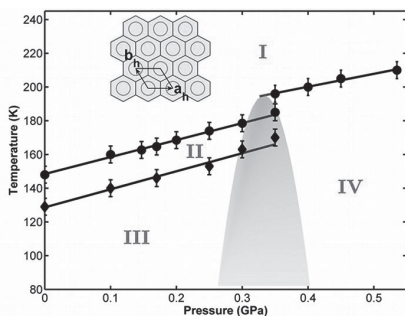
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Acta Cryst. (2011) A67, C502**Pressure induced phase transitions in aperiodic composites**

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Aperiodicity in composite materials may appear rather naturally due to the possible misfit of host and guest parameters along their crystallographic directions. A huge simplification exists in one dimensional (1D) composite aperiodic crystals since the co-linearity of the incommensurate vectors is always maintained allowing a definite assignment of all the diffraction Bragg peaks [1,2]. Urea inclusion compounds (UIC) constitute such a family of molecular composite structures, where long-chain guest molecules are embedded in parallel channels of the host urea sublattice and among them, most of the n-alkane UIC are incommensurate. A large amount of work has been dedicated to the phase transitions in this prototype family but almost all experimental works were described considering conventional three-dimensional crystallography, ignoring their aperiodic feature [3]. Then, a unique phase transition was reported in almost all of these crystals, independently of the n-alkane guest. The same phase transition was assumed to occur under pressure and its evolution was established up to 0.2 GPa [4].

Aperiodicity actually offers many new degrees of freedom which create totally unexpected sequences of phases with long-range order well described within the crystallographic superspace approach [5]. This will be illustrated by the neutron diffraction determination of the (P,T) phase diagram of nonadecane-urea [6] and by the evidence of selective compressibility and pressure induced lock-in in heptane-urea [7,8]



(P,T) Phase diagram of nonadecane-urea : all phases are described within crystallographic superspaces.

[1] T. Janssen, G. Chapuis, M. de Boissieu, *Aperiodic Crystals: From Modulated Phases to Quasicrystals*, Oxford Univ. Press, Oxford, **2007**. [2] S. Van Smaalen, K.D.M. Harris *Proc. Roy. Soc. London Ser. A* **1996**, 452, 677. [3] R. Forst *et al.*, *Acta Crystallogr. B* **1990**, 46, 70. [4] K. Fukao, *J. Chem. Phys.* **1990**, 92, 6867. [5] K. Fukao *et al.*, *Mol. Cryst. Liq. Cryst.* **1990**, 180, 405. [6] B. Toudic *et al.*, *Science* **2008**, 319, 69. [7] B. Toudic *et al.*, *Europhys. Lett.* **2011**, 93, 16003. [8] L. Bourgeois *et al.*, *Phys. Rev. Lett.* **2003**, 91, 025504. [9] B. Toudic *et al.*, *Phys. Rev. Lett.* **2006**, 96, 145503

Keywords: aperiodic, pressure, host guest crystals

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Acta Cryst. (2011) A67, C502**Pair Distribution Function Studies of the Pressure-Induced Amorphisation of Zeolites**

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Zeolites are framework materials with porosity at the molecular scale formed by the complete corner sharing of tetrahedral aluminosilicate groups. The aluminosilicate framework is negatively charged and there are charge-balancing cations inside the pores bonded to the oxygen atoms of the tetrahedra. Like many framework materials, the structures are very flexible and are known to undergo pressure-induced amorphisation at relatively low (< 10 GPa pressures). The amorphisation should not involve significant (Si,Al)-O bond breaking at these pressures but loss of long-range order due to severe and non-correlated distortions of the (Si,Al)-O-(Si,Al) bonds to form network glasses. We [1] and others [2,3] have recently started to use Pair Distribution Function analysis of total scattering data to study the quenched glasses. The goals of our work are both to understand the mechanism of amorphisation and nature of the glass, in particular to determine to what extent it might still have some of the secondary structural building units and porosity of the crystalline precursor.

All work published to date is based on *ex situ* studies of quenched glasses. We have now collected *in situ* high pressure total scattering data on several samples of zeolite A with different charge balancing cations as well as the pure silica polymorph ITQ-29. The analysis from this series allows us to determine the effects that the cations inside the pores have on the amorphisation mechanism and also, by comparing the glasses at pressure and then quenched back to room pressure, to study the reversibility of the process.

[1] J.E. Readman, P.M. Forster, K.W. Chapman, P.J. Chupas, J.B. Parise, J.A. Hriljac *Chem. Comm.* **2009**, 3383-85. [2] A. Isambert, E. Angot, P. Hebert, J. Haines, C. Levelut, R. Le Parc, Y. Ohishi, S. Kohara, D.A. Keen, *J. Mater. Chem.* **2008**, 18, 5746-42. [3] J. Haines, C. Levelut, A. Isambert, P. Hebert, S. Kohara, D.A. Keen, T. Hammouda, D. Andrault *J. Am. Chem. Soc.* **2009**, 131, 12333-38.

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Acta Cryst. (2011) A67, C502-C503**Accurate thermodynamics in the quasiharmonic approximation**

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Is it possible to calculate the thermodynamic properties of a solid with accuracy that rivals that of the experimental measurements for a wide range of pressures and temperatures? We discuss in this report the three main elements that can drive systematically to that result: (i) The density functional perturbation theory (DFPT) by Baroni *et al* [1] and its implementation in codes like Quantum Espresso [2] has made possible the *ab initio* calculation of thermodynamic properties of solids under the quasi harmonic approximation (QHA); (ii) The average of strain polynomials [3] is used to fit faithful and systematically the energy versus volume data, providing the best derivatives available and a statistically relevant estimation of the errors; (iii) The systematic error of the calculations due to the approximate nature of the exchange and correlation functional is repaired through an empirical energy correction scheme (EEC) based only in two experimental data (the equilibrium volume and bulk modulus). Several examples of the extraordinary success of this recipe are discussed.