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Apparently complex high-pressure phases of some elements as simple modulated structures

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In the last few years an unexpected series of complex phases have been observed in pure elements when subject to high-pressures. Among them, orthorhombic phases of $C222_1$ symmetry and very large unit cells have been reported for Rb, Cs and Ga (phases Rb-III, Cs-III and Ga-II). The conventional unit cells of these phases have 52, 84 and 104 atoms, respectively, and they have been originally interpreted as complex stacking sequences along the c axis of atomic layers with different atomic densities. We show that in fact these phases can be described as modulated distortions of very simple structures, with one or a few atoms per unit cell, and simple smooth modulations that only require one or two Fourier harmonics. Ga-II is a commensurate modulated structure having an average structure with space group Fddd, Z=8, and a single independent atom with no free parameter. The displacive modulation describing all atomic positions only requires 4 parameters, and evidences a strong correlation of the atomic positions according to a specific superspace group (see Figure below). The modulation is dominated by a sinusoidal component with wave vector (1,1,4/13), at the Brillouin zone border, suggesting an instability of the average structure with respect to this mode as the origin of this phase. The Fddd average structure can be related with a hcp hexagonal structure through a Bürger-like mechanism, with the y-axis of the $C222_1$ being the hcp z-axis. Phases Cs-III and Rb-III are more complex, having two subsystems with different average structures that modulate each other. The subsystems are monoclinic with monoatomic lattices and are related by symmetry operations of an orthorhombic superspace group. The modulations are smooth, simple, and describable by a few parameters. Their amplitudes are much smaller than in Ga-II. Phases Cs-III and Rb-III can be considered as very peculiar examples of commensurate composites with symmetry interrelated subsystems.

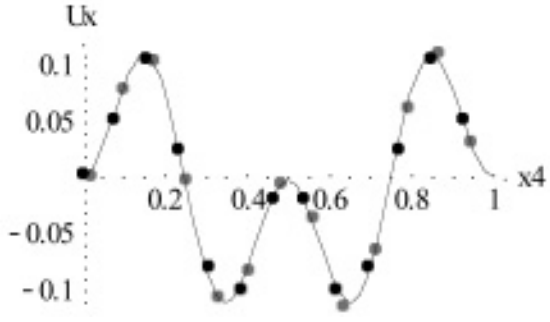

Figure: x-component of the displacive modulation of Ga-II for two rows of atoms along the z-axis lying in layers around y=0 (black points) and y=1/4 (grey points). These two rows of atoms are unrelated by the $C222_1$ symmetry. The fitted function is of the form: Acos[2πx4] + Bcos[6πx4].

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Quantitative explanation for the stacking disorder in tris(bicyclo[2.2.1]hexeno)benzene

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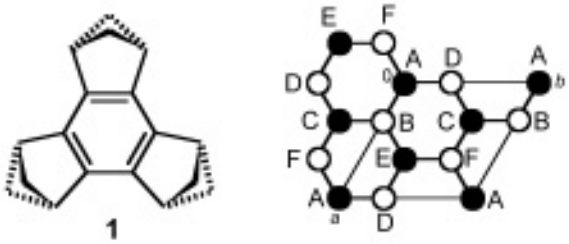
The hexagonal phase of the title compound, $C_{18}H_{18}$ (**1**) shows a strong stacking disorder in [0001] direction. In the first layer, the molecules can be situated on one of the positions A, C, or E; in the second layer the molecules occupy the position B, D, or F.



Bürgi et al. [1] analysed the diffuse scattering and concluded, that there is a local ordering with a given probability for the individual stacking sequencies (see Table below).
We made extensive lattice energy minimizations on this system, using the Dreiding [2] force field. Calculations were done with all 2- and 4-layer sequences (e.g. ABCF), and most 6- and 8-layer sequences. The packings of the molecules were optimized together with the molecular geometries. The optimized structures are very close to the crystal structures determined by X-ray diffraction. The calculated lattice energies correspond very well with the probabilities for the individual layer sequences deduced from the diffuse scattering. Furthermore, the lattice energy calculations give a detailed picture of the local structures, i.e. of the deviation of the local structures from the averaged structure (translation, rotation, and bending of the molecules). The sequence ABCFED (zig-zag) was found to have the lowest energy. This packing was found also experimentally in pure form, as monoclinic polymorph of **1**.

Layer sequence [a]	Probability (from diffuse scattering) [1]	Relative energy (from lattice energy minimization) (*kJ/mol*)
ABAB	9 %	2.38
ABCB	14 %	1.47
ABCD	39 %	0.12 (ABCDEF)
ABCF	39 %	0.00 (ABCFED) 0.04 (1BCFABCF)

a) Including symmetry equivalent sequences.

[1] H.-B. Bürgi, M. Hostettler, H. Birkedal, D. Schwarzenbach, *Z. Krist.* 220 (2005), 1066-1075.
[2] S.L. Mayo, B.D. Olafson, W.A. Goddard III, *J. Phys. Chem.* 94 (1990), 8897-8909.