[1] Y.H. Wen, X.M. Li, L. Wang, S.S. Zhang, *Acta Cryst.* **2006,** *E62*, o2185u-o2186. [2] J.A. Bortoluzzi, S.E. Andrade, J.R. Nunes. *Acta Cryst.* **2004,** *C60*, o614-o616. [3] A. Thiruvalluvar, Parthasarathi, A. Nagarajan, M. Krishnapillay, *Acta Cryst.* **1994,** *C50*, 1812-1814. [4] M. Pillayd, *Acta Cryst.* **2001,** *E57*, o1240-o1241.

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Modulated *post - simple cubic* structures in compressed P and Ca: electronic origin

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Recent high-pressure x-ray diffraction studies revealed unusual complex structures in phosphorus and calcium that follow the simple cubic structure at pressure above 1 Mbar [1], [2]. These *post - simple cubic* (*post-sc*) phases P-IV and Ca-IV have close structural relation to the simple cubic via orthorhombic or tetragonal distortion of the basic cell and formation of the superlattice in one direction.

For the phase P-IV the basic cell is base-centered orthorhombic, *oC*2, with a incommensurate modulation defined by a wave vector 0.267. We consider a commensurate approximant with a 11-fold supercell along the c-axis and a modulation wave vector equal 3/11. The phase Ca-IV, tP8, has a tetragonally distorted cubic cell with a commensurate 4-fold supercell along the c-axis. P-IV and Ca-IV have some common structural features in the formation of the *post-sc* phases that implies some common physical reasons for such complexity. We consider configurations of Brillouin zones and the Fermi sphere within a nearly-free-electron model in order to analyze the importance of these configurations for the crystal structure energy [3] containing two main contributions: electrostatic (Ewald) and electronic (band structure) energies. The latter can be lowered due to a formation of a Brillouin zone plane and an opening of an energy gap at this plane.

Under pressure, the band structure energy part becomes more important leading to a formation of complex low-symmetry structures [4], [5]. The stability of the *post-sc* phases in P and Ca is attributed to the lowering of the electronic band structure energy due to Brillouin zone – Fermi surface interactions.

[1] H. Fujihisa, Y. Akahama, H. Kawamura et al., *Phys. Rev. Lett*. **2007**, *98*, 175501. [2] H. Fujihisa, Y. Nakamoto, K.Shimizu, T. Yabuuchi, Y. Gotoh, *Phys. Rev. Lett*. **2008**, *101*, 095503. [3] V.F. Degtyareva, I.S. Smirnova, *Z. Kristallogr*. **2007**, *222*, 718-721. [4] V.F. Degtyareva, *Phys. Usp.* **2006**, *49*, 369-388. [5] V.F. Degtyareva, *J. Phys.: Conf. Ser.* **2010**, *226*, 012019.

Keywords: modulated structure, crystal stability, band structure

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Incommensurate electronic motifs in tetramethylpyrene polyiodide crystals

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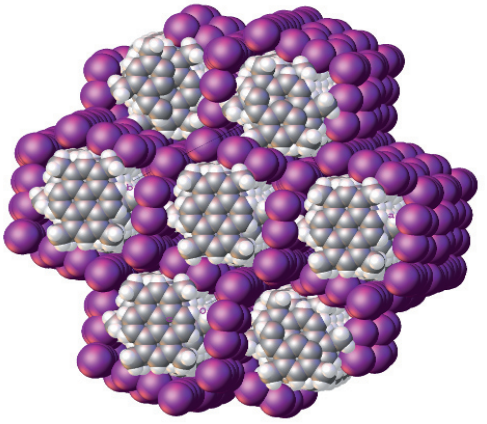
Co-crystallization of neutral tetramehylpyrene (TMP) and elementary iodine yields black needles with metallic shine. The needles produce discrete X-ray diffraction maxima in two dimensions and practically unresolvable quasi-continuous diffraction in third dimension.

After several attempts, a bunch of crystals was isolated that provided discrete diffraction in third dimension but with a very long identity period of c = 86.9 Å. The experimental data were collected using Cu radiation and the structure was successively solved to R=6.0 %.

The structure consists of oxidized TMP molecules forming cation-radical stacks along z direction. The stacks are completely separated from each other being wrapped in rippled two-dimensional anionic polyiodide sheets.



The longest period of the unit cell corresponds to 26 molecular units of TMP with an average separation of 3.34 Å. In the embodying polyiodide substructure, the same period corresponds to 8 tri-iodide ions and 2 di-iodine molecules alternatively forming linear chains along the TMP stacks (these chains are cross-linked by extra di-iodine molecules).

The complex stoichiometry of the structure, corresponding to +0.615 charge per TMP unit and requiring di-iodine "spacers" to commensurate cationic and anionic substructures, exemplify it as a "degenerated" composite crystal.

It is important to point out that TMP cannot be oxidized by elementary iodine in solution. Therefore, the formation of the ion-radical salt is entirely due to the free energy of electronic delocalization in the crystals.

Keywords: incommensurate_structures, composite_crystals, ion-radical_salts

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Incommensurate $BiMO_3$ Perovskites: $Bi_2Mn_{2/3}M_{2/3}Ni_{2/3}O_6$ and $Bi_2M'M''O_6$

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Materials in which dielectric and magnetic properties are coupled are of interest for multiple state memory and information storage applications, and fundamentally in terms of the mechanisms for coupling these properties. Single phase materials which display these properties are important as detailed studies of structural response are possible to permit the identification of the underlying mechanisms for this behaviour. In our search for ferromagnetic ferroelectrics based on Bi^{3+}, we have isolated new phases many of which are incommensurately modulated.