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Keywords: crystal , derivative, spectroscopy

MS88.P01

Acta Cryst. (2011) **A67**, C755

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, *oC2*, 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.

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Keywords: modulated structure, crystal stability, band structure

MS88.P02

Acta Cryst. (2011) **A67**, C755

Incommensurate electronic motifs in tetramethylpyrene polyiodide crystals

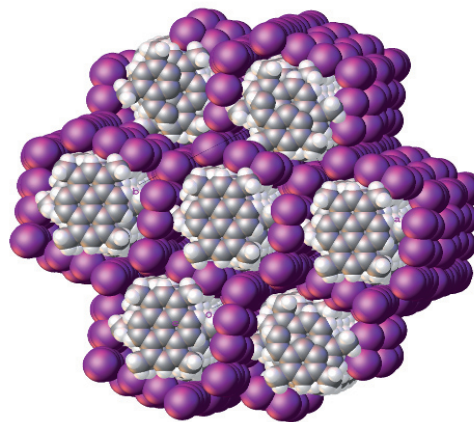
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Co-crystallization of neutral tetramethylpyrene (TMP) and elementary iodine yields black needles with metallic shine. The needles produce discrete X-ray diffraction maxima in two dimensions

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 $c = 86.9 \text{ \AA}$. 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

MS88.P03

Acta Cryst. (2011) **A67**, C755-C756

Incommensurate BiMO₃ Perovskites: Bi₂Mn_{2/3}M_{2/3}Ni_{2/3}O₆ and Bi₂M'M'O₆

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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 Bi³⁺, we have isolated new phases many of which are incommensurately modulated.

$\text{Bi}_2\text{Mn}_{4/3}\text{Ni}_{2/3}\text{O}_6$: This is a very unusual material as it adopts the perovskite structure with Bi^{3+} on the A site – there has only been one previous example of perovskite stable to ambient pressure synthesis, BiFeO_3 . The material is spin-glass-like with a freezing temperature, T_f , of 35K due to competing exchange interactions on the B site of the perovskite structure and undergoes an incommensurate “commensurate” transition above 410 K, which shows hysteresis. We have previously described the room temperature phase in 3+2 dimensional space group $\text{Ibmm}(0\text{-}p0,q00)\text{mm.ss}$ ($\sqrt{2}a_p \times 2a_p \times \sqrt{2}a_p$; $p,q \sim 1/2$). [1] Herein we will describe the temperature variation of the modulation vectors and the persistence of incommensurate cation order into the “commensurate” high temperature phase from combined synchrotron X-ray and time of flight neutron diffraction data.

$\text{Bi}_2\text{Mn}_{2/3}\text{Ti}_{2/3}\text{Ni}_{2/3}\text{O}_6$: This phases also crystallizes in the same superspace group as the manganese nickel analogue, in 3+2 dimensional space group $\text{Ibmm}(0\text{-}p0,q00)\text{mm.ss}$ ($\sqrt{2}a_p \times 2a_p \times \sqrt{2}a_p$; $p,q \sim 1/2$). It’s room temperature structure based combined synchrotron X-ray and time of flight neutron diffraction will be discussed.

$\text{Bi}_2\text{CoTiO}_6$: This metastable high pressure double perovskite unusually shows no cation order but does show an incommensurate modulation, like several other similar phases. The combined refinements show that this material crystallizes in the polar superspace group $\text{I}2\text{cm}(0p0)000$ ($p \sim -2/3$).

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Keywords: incommensurate modulated structures, rietveld refinement

MS88.P04

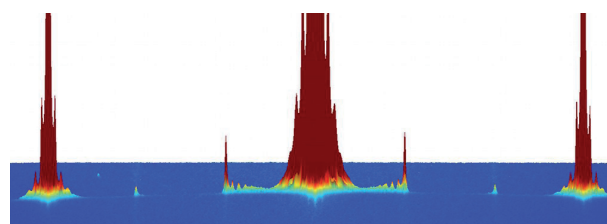
Acta Cryst. (2011) **A67**, C756

Huge period vs aperiodicity in organic host guest systems.

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Supramolecular chemistry and crystal engineering enable very attractive aperiodic host-guest architectures, where guest molecules are confined with their own periodicity into nanochannels [1]. The diffraction patterns of these aperiodic materials exhibit sharp Bragg peaks characteristic of long-range order, although the system is not invariant under a lattice of translations [2]. Short peptides and other organic molecules yield numerous examples of molecular self-assembled systems. The host-guest alkane-urea inclusion compounds typically form such aperiodic crystals, and their structural instabilities have been extensively studied.[3,4 and herein ref.].

Here, we discuss very high resolution synchrotron diffraction studies of the structural instability in n-tetracosane/urea, a compound where competing forces maintains aperiodicity with a misfit parameter very close to a rational number at ambient conditions: $\gamma = c_{\text{host}}/c_{\text{guest}} \cong 1/3$ (0.337±0.002). Below phase transition, a complex crystallographic diffraction pattern is observed with a very dense set of superstructure Bragg peaks along the aperiodic direction (figure). These are interpreted as the appearance of a huge periodicity of about 460Å associated to the host guest intermodulation. Similar results will be discussed considering other compounds of this family.



Tetracosane-urea superstructure line (90K) along the incommensurate channel direction in the q-range [-1.2, 1.2] in urea reciprocal units.

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Keywords: aperiodic, composite, host guest crystal

MS88.P05

Acta Cryst. (2011) **A67**, C756-C757

On the criterion of modulated-structures formation for strain-induced-interacting vacancies in irradiated f.c.c. crystals.

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Within the crystals under irradiation, the modulated structures can be formed [1]. With decreasing temperature (T) or increasing concentration of defects (c), their interaction-caused drift begins to dominate their random motion, and the damping decrement becomes negative for every values of wave vector \mathbf{k} , which belongs to the sphere of a radius $k_0(T,c)$ about $\mathbf{k}=\mathbf{0}$, and the modulated structures appear. For $|\mathbf{k}| > k_0(T,c)$, the damping decrement is positive, and the modulated structures disappear [2].

A given paper is based on overrunning continuous approximation for the Fourier components, $\tilde{V}^{\text{vv}}(\mathbf{k})$, of the strain-induced vacancy–vacancy-interaction energies. Within the finite region near $\mathbf{k}=\mathbf{0}$ [2, 3], the $\tilde{V}^{\text{vv}}(\mathbf{k})$ dependence is represented in a following form: $\tilde{V}^{\text{vv}}(\mathbf{k}) \cong A(\mathbf{n}) + B(\mathbf{n})|\mathbf{k}|^2 + Q(\mathbf{n} = \mathbf{k}/|\mathbf{k}|)$. Here, the well-known first term is based on long-wave-limit approximation [3], the second term is a correction to this approximation, and the third term is a gauge, which eliminates strain-induced self-action of vacancies.

The modulated structure can be formed along those crystallographic direction, which is parallel to $\mathbf{n}_c = \mathbf{k}_c/|\mathbf{k}_c|$ corresponding to the highest growth rate, and has the wave-vector with a magnitude $|\mathbf{k}_c| \cong \{-A(\mathbf{n}_c) + Q + \tilde{\Phi}_{\text{el,chem}}(\mathbf{0}) + k_B T/[c(1-c)]\}/[2(B(\mathbf{n}_c) + \gamma)]^{1/2}$; $\tilde{\Phi}_{\text{el,chem}}(\mathbf{k})$ is the Fourier component of energies of direct electrochemical interaction between vacancies (v), c is their concentration, T is the temperature of a crystal, k_B is the Boltzmann constant. With the wavelength approximation, $\tilde{\Phi}_{\text{el,chem}}(\mathbf{k}) \cong \tilde{\Phi}_{\text{el,chem}}(\mathbf{0}) + \gamma|\mathbf{k}|^2$.

The approximated expansion coefficients for Fourier components of the strain-induced v - v -interaction energies are dependent on the elasticity moduli of f.c.c. crystals, C_{11}, C_{12}, C_{44} ; e.g., $A[100] = -9K^2(L^v)^2 a_0^3/(4C_{11})$ [2, 3], [2, 3], $B[100] \cong 9K^2 a_0^3 (L^v)^2 C_{44}/(32C_{11}^2)$, where $K = (C_{11} + 2C_{12})/3$ —the crystal-compression modulus, a_0 —anf.c.c.-lattice parameter, L^v —the concentration coefficient of f.c.c.-lattice dilatation). As shown, the coefficient $B(\mathbf{n})$ is positive along all the high-symmetry [100], [110], [111], $[\frac{1}{2}10]$ directions in reciprocal space for f.c.c. crystals with anisotropy factor $\xi \equiv (C_{11} - C_{12} - 2C_{44})/C_{44} < 0$. If $\xi < 0$, $\tilde{V}^{\text{vv}}(\mathbf{k}_{|\xi\mathbf{T}}) \rightarrow \mathbf{0}$ has a one-sided minimum along the [100] direction, but it greater than $\tilde{V}^{\text{vv}}(\mathbf{0})$ as a result of the long-range character of strain-induced interaction. Besides, there are inequalities as follow: