$Bi_2Mn_{4/3}Ni_{2/3}O_6$: 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 to "commensurate" transition above 410 K, which shows hysteresis. We have previously described the room temperature phase in 3+2 dimensional space group Ibmm(0-p0,q00)mm.ss ($\sqrt{2}a_p$ x $2a_p$ x $\sqrt{2}a_p$ ; p,q ~ ½).[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.

$Bi_2Mn_{2/3}Ti_{2/3}Ni_{2/3}O_6$: This phases also crystallizes in the same superspace group as the manganese nickel analogue, in 3+2 dimensional space group Ibmm(0-p0,q00)mm.ss ($\sqrt{2}a_p$ x $2a_p$ x $\sqrt{2}a_p$ ; p,q ~ ½). It's room temperature structure based combined synchrotron X-ray and time of flight neutron diffraction will be discussed.

$Bi_2CoTiO_6$: 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 I2cm(0p0)000 (p ~ -2/3).

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**Keywords: incommensurate modulated structures, rietveld refinement**

## MS88.P04

**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: $\gamma$= $c_{host}$./ $c_{guest}$ $\cong$ 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.
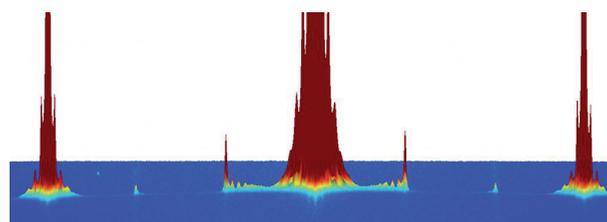


Tetracosane-urea superstructure line (90K) along the incommensurate channel direction in the q–range [-1.2, 1.2] in urea reciprocal units.

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**Keywords: aperiodic, composite, host guest crystal**

## MS88.P05

**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 **k**, which belongs to the sphere of a radius $k_0(T,c)$ about **k** = **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, $\tilde{V}^{vv}(\mathbf{k})$ , of the strain-induced vacancy–vacancy-interaction energies. Within the finite region near $_k$ = **0** [2, 3], the $\tilde{V}^{vv}(\mathbf{k})$ dependence is represented in a following form: $\tilde{V}^{vv}(\mathbf{k}) \cong A(\mathbf{n}) + B(\mathbf{n})|\mathbf{k}|^2 + Q$ ($\mathbf{n} = \mathbf{k}/|\mathbf{k}|$). 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 $|\mathbf{k}_c| \cong \{-(A(\mathbf{n}_c) + Q + \tilde{\varphi}_{el.chem}(\mathbf{0}) + k_B T/[c(1-c)])/[2(B(\mathbf{n}_c) + \gamma)]\}^{1/2}$; $\tilde{\varphi}_{el.chem}(\mathbf{k})$ 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 wave-length approximation, $\tilde{\varphi}_{el.chem}(\mathbf{k}) \cong \tilde{\varphi}_{el.chem}(\mathbf{0}) + \gamma|\mathbf{k}|^2$.

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], $B[100] \cong 9K^2 a_0^5 (L^v)^2 C_{44}/(32C_{11}^2)$, where $K = (C_{11} + 2C_{12})/3$—the crystal-compression modulus, $a_0$—an f.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], [½10] directions in reciprocal space for f.c.c. crystals with anisotropy factor $\xi \equiv (C_{11} - C_{12} - 2C_{44})/C_{44} < 0$. If $\xi < 0$, $\tilde{V}^{vv}(\mathbf{k}_{\|\overline{X\Gamma}} \to \mathbf{0})$ has a one-sided minimum along the [100] direction, but it greater than $\tilde{V}^{vv}(\mathbf{0})$ as a result of the long-range character of strain-induced interaction. Besides, there are inequalities as follow:

$$\tilde{V}^{vv}(\mathbf{k}_{\parallel \overline{X}\Gamma} \to \mathbf{0}) < \tilde{V}^{vv}(\mathbf{k}_{\parallel \overline{W}\Gamma} \to \mathbf{0}) < \tilde{V}^{vv}(\mathbf{k}_{\parallel \overline{K}\Gamma} \to \mathbf{0}) < \tilde{V}^{vv}(\mathbf{k}_{\parallel \overline{L}\Gamma} \to \mathbf{0}).$$

If $(A[100] + Q + \tilde{\varphi}_{\text{el chem}}(\mathbf{0}) + k_B T / [c(1-c)])/[2(B[100] + \gamma)] < 0$,

where, *e.g.*, within the scope of the Debye approximation,

$$Q \cong 9K^2(L^v)^2(a_0^3/4)\langle(1 + 2\xi X + 3\xi^2 Y)/D(\mathbf{n})\rangle_{\mathbf{n}},$$

$$D(\mathbf{n}) = C_{11} + \xi(C_{11} + C_{12})X + \xi^2(C_{11} + 2C_{12} + C_{44})Y,$$

$X = n_x^2 n_y^2 + n_x^2 n_z^2 + n_z^2 n_y^2$, $Y = n_x^2 n_y^2 n_z^2$, the modulated structure can appear along the [100] direction.

Dependence of the modulated-structure period on $T$ is plotted.

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## MS88.P06

**Misfit structure determination of a multication Ce, Nd, (Bi) Cr, V, (Ta) Sulphide**

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In the last 30 years, the synthesis and structure determination of over a hundred synthetic metal chalcogenides presenting misfit layer structure (a subclass of composite modulated structure) has been reported [1], [2], [3], [4]. Their complex stoichiometries are represented by $(MX)_{1+\delta}(T_{1+\varepsilon}X_2)_n$ (M = Rare Earth, Sn, Pb, Sb, Bi; T = Ti, V, Cr, Nb, Ta; X = S, Se).

Here we report the structural determination by electron microscopy/diffraction and associated techniques of a new misfit layer compound (MLC) ~ $[(Bi_{0.04}Ce_{0.66}Nd_{0.30})S]_{1.21}[(Ta_{0.08}V_{0.52}Cr_{0.39})S_2]$.

SAED patterns (JEOL 2000FX) were taken along the three major zone-axes of the MLC. The SAED patterns taken along the [001] axis consist of two basic sublattices of reflections (Q and H). In addition, the splitting of the misfit satellite reflections reveals the incommensurate mutual modulation of the two sublattices. The [010] zone axis SAED patterns provide evidence of the divergence of the *a\** axes of the two sublattices. HRTEM images (JEOL JEM 3000F, $C_s$ = 0.6 mm) taken along $[001]_Q$ show the basic Q substructure with superimposed modulation fringes. The HAADF STEM images (JEOL JEM 3000F) taken along the [100] zone axis show the alternating stacking of the two substructures. In addition, the line-scan profiles (JEOL JEM 3000F, Gatan Enfina), confirm the presence of Ce and Nd in the Q sublattice and V and Cr in the H sublattice. The microanalyses of the crystals by XEDS (LINK ISIS 300) yield a composition $M_{1.1}TS_{3.2}$, in good agreement with the composition $(MS)_{1.21}TS_2$ that it is calculated from the misfit ratio measured in the SAED patterns; both data can be combined into a stoichiometry $[(Bi_{0.04}Ce_{0.55}Nd_{0.25})S]_{1.21}[(Ta_{0.08}V_{0.52}Cr_{0.39})S_2]$. The unit cell parameters of the two sublattices (measured by SAED) are: $a$ = 3.5 Å; $b$ = 5.9 Å; $c$ = 11.3 Å; $\alpha$ = 95.4º; $\beta$ = 95.5º; $\gamma$ = 89.7º for the H Subcell and $a$ = 5.8 Å; $b$ = 5.9 Å; $c$ = 11.3 Å; $\alpha$ = 95.4º; $\beta$ = 90.7º; $\gamma$ = 90.1º for the Q Subcell. No intralayer cation ordering has been observed.

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## MS88.P07

**Transmission electron microscopy study of low Mo-content Bi-Mo-O phases**

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The Bi-Mo-O system presents a wide variety of crystalline phases which have great interest because of their catalytic and ionic conductivity properties. Transmission electron microscopy has probed to be a paramount technique for the crystallographic characterization of many phases in this system and even for the elucidation of their atomic structure [1-3]. In this system we have characterized a whole new homologous series of $Bi_{2(n+2)}Mo_nO_{6(n+1)}$ phases, with n = 3, 4, 5 and 6, ($xBi_2O_3$: $MoO_3$, $1<x<2$) which were isolated at low temperature by the n-butylamine wet synthesis method.

Using the same low temperature methods we have isolated additional low temperature phases at higher values of x ($xBi_2O_3$:$MoO_3$, x = 3, 3.5). The powder nature of the new obtained phases hinders a deep characterization of the structure by traditional crystallographic methods like X-ray diffraction. Therefore, we have studied their structure mainly by means of transmission electron microscopy.

Selected area electron diffraction patterns are very complex but can be interpreted as a basic lattice of fluorite-type structure which gives rise to the basic lattice reflections, plus weaker satellite reflections produced by a structural modulation. Although in general, modulation satellites are very weak, in the present case they exhibit a very high intensity and at least nine harmonics. This modulation is incommensurate with the basic fluorite-type lattice and it is related to the fluorite commensurate superstructure observed in $Bi_{38}Mo_7O_{78}$ [4], [5].

The modulation vector differs clearly from the commensurate one reported in [4], [5] changing in amplitude and direction. The HRTEM micrographs reveal the wave-like nature of the modulation superimposed on the basic fluorite lattice and allows its comparison with the commensurate fluorite superstructures found at the high-temperature phase.

These incommensurate modulations suggest the presence of non-stoichiometry ranges at low temperature phases which can vary the structure and in a very subtle way depending on the synthesis conditions.

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P.MS.88