International School on Aperiodic Crystals

26 September - 2 October 2010, Carqueiranne, France

Incommensurate composite crystals

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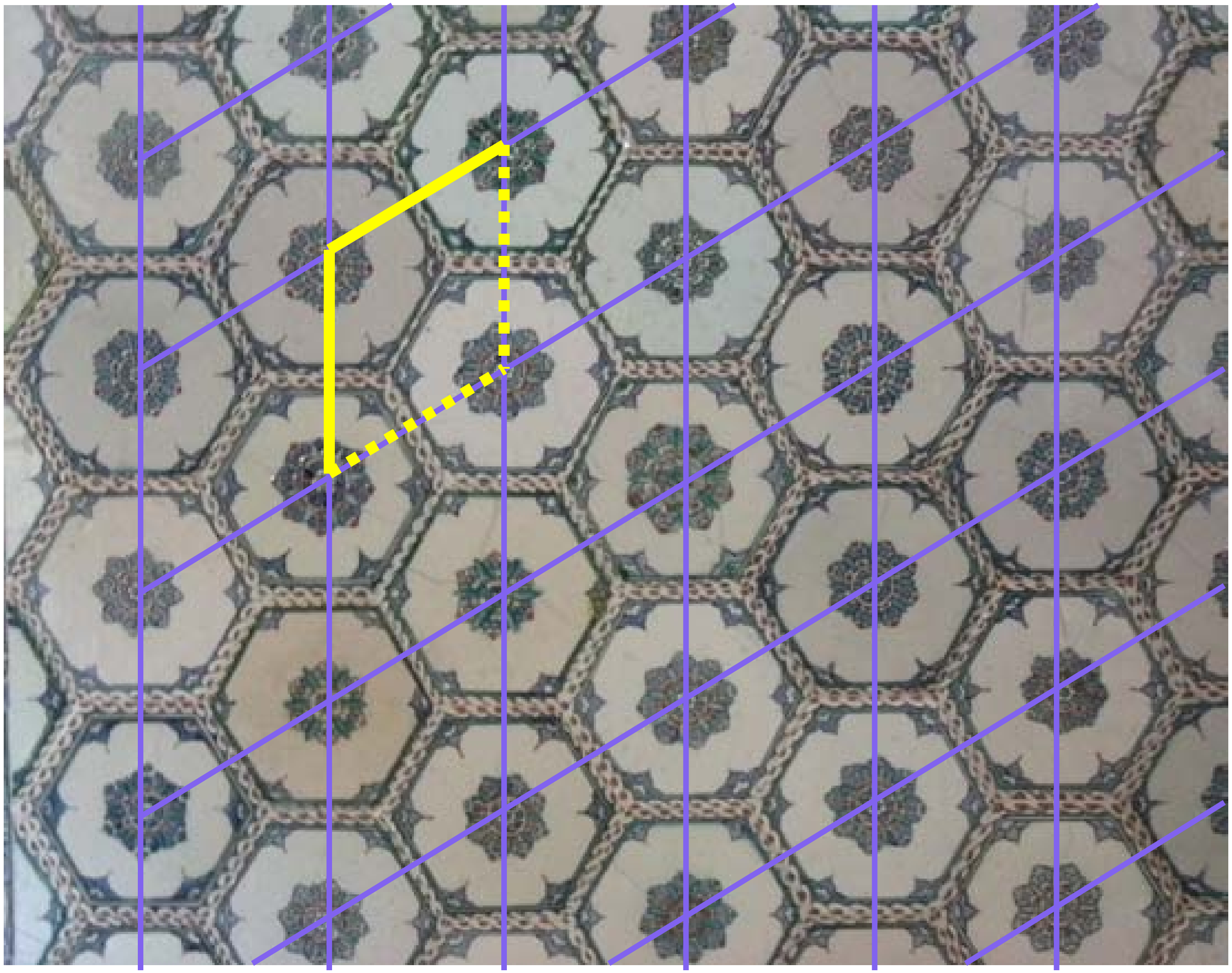
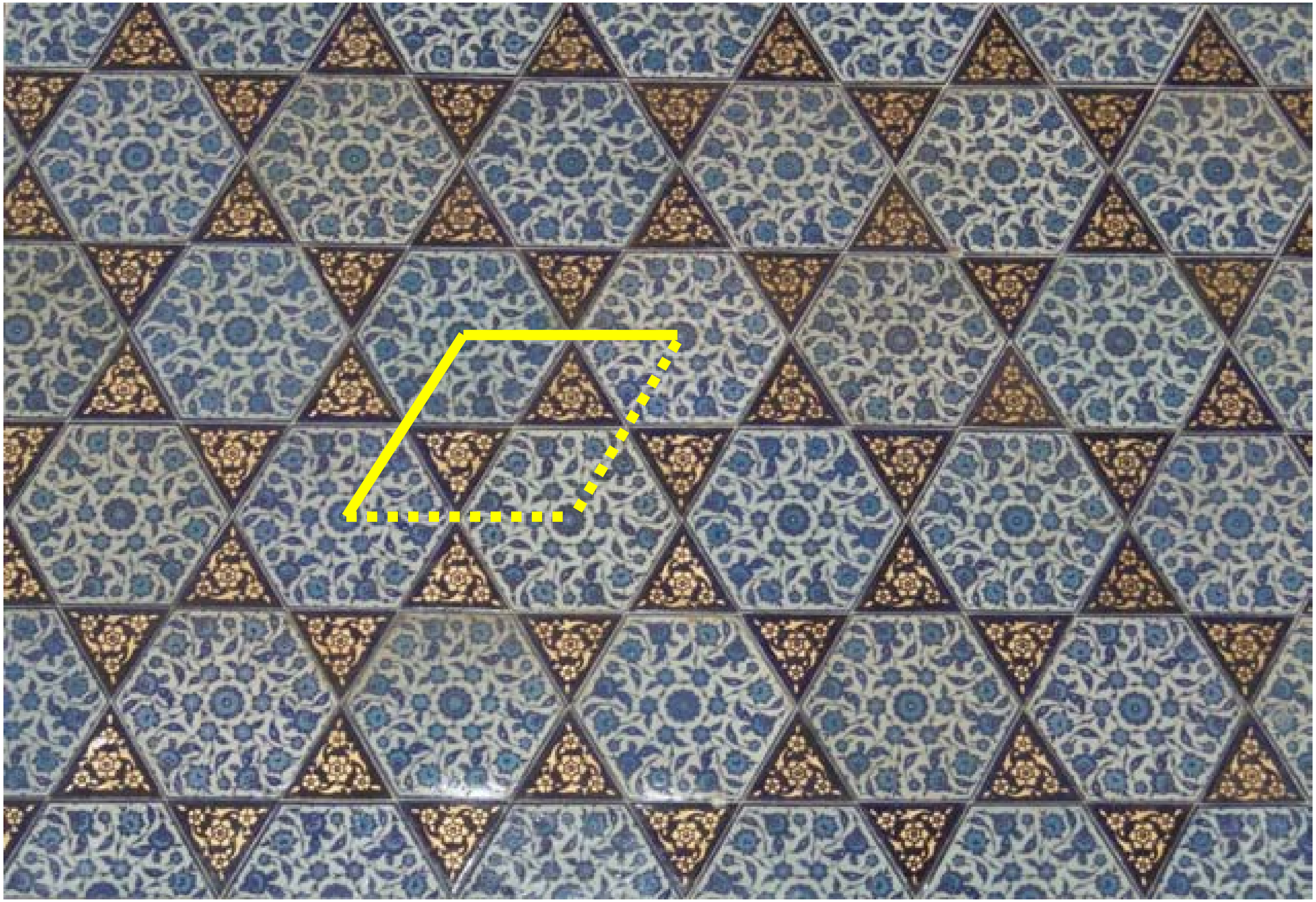
Honeycomb lattice
hexagonal lattice with one tile per unit cell



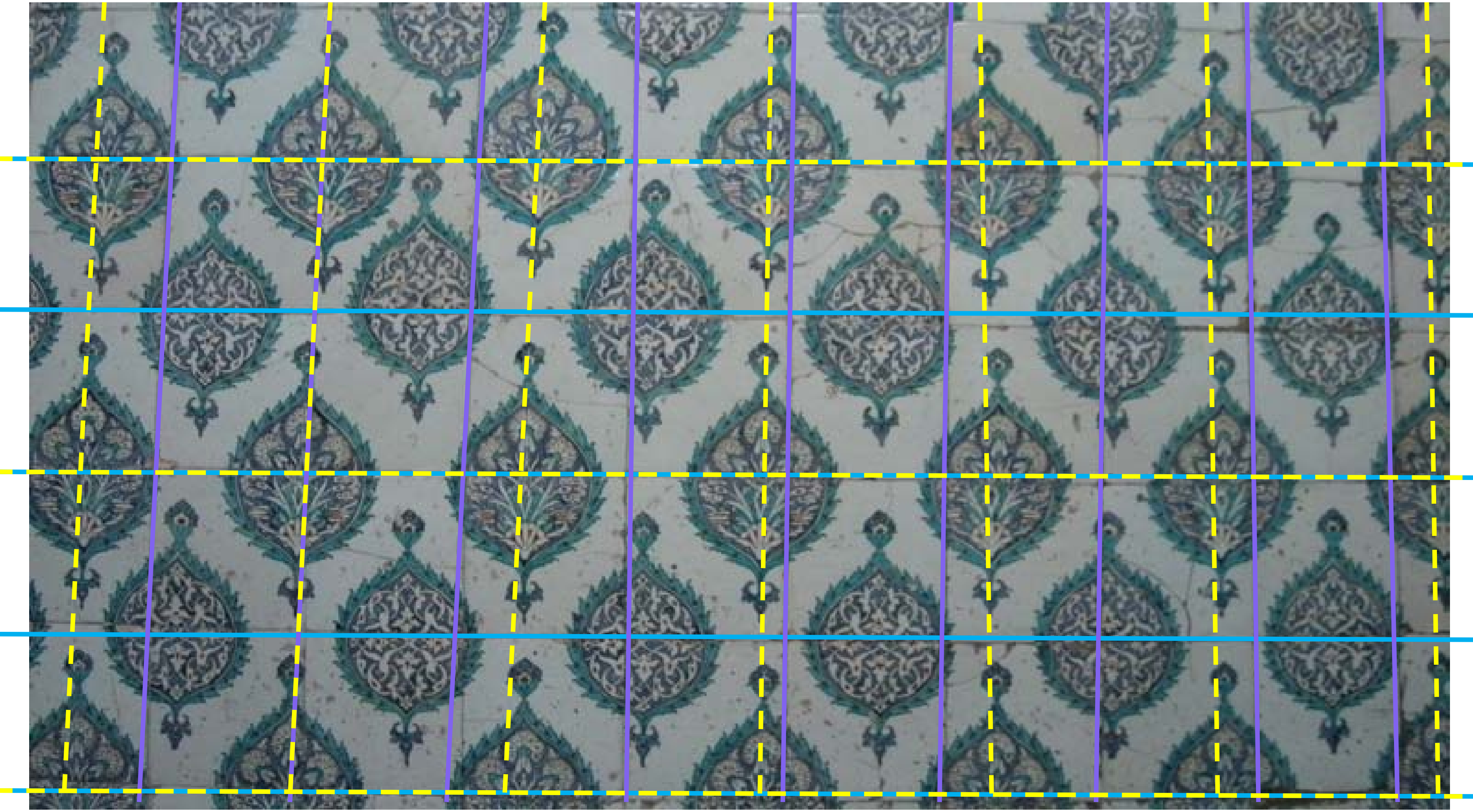
ECM25, Instanbul (2009) harem at topkapi palace

Kagome lattice
One hexagon and two triangles per unit cell



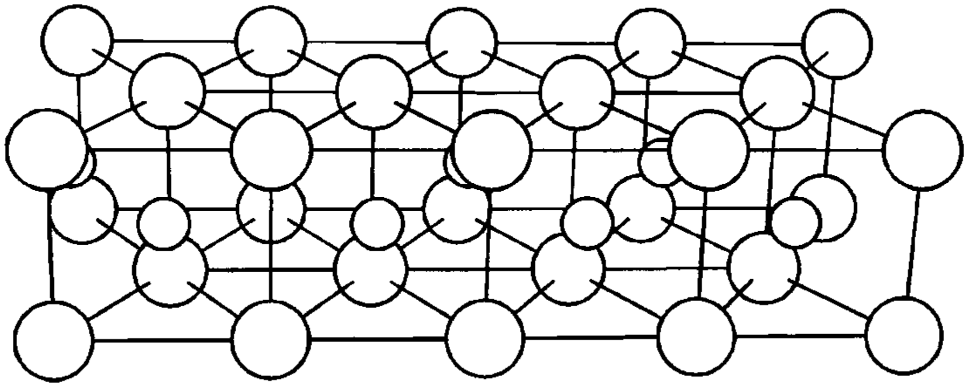
ECM25, Instanbul (2009) harem at topkapi palace

Mutually incommensurate periodicities for tiles and design layers; 2a×1.37··· b supercell



ECM25, Instanbul (2009) harem at topkapi palace

Misfit layer sulfide $[LaS]_{1.13}[TaS_2]$

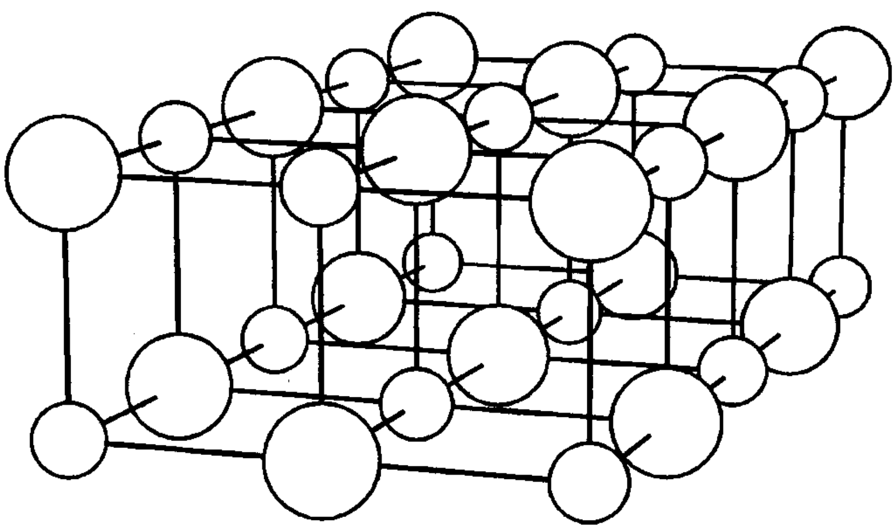


Subsystem $\nu = 2$: TaS_2

$a_2 = 3.295$ Å

$b = 5.775$ Å

$c = 23.06$ Å



Subsystem $\nu = 1$: LaS

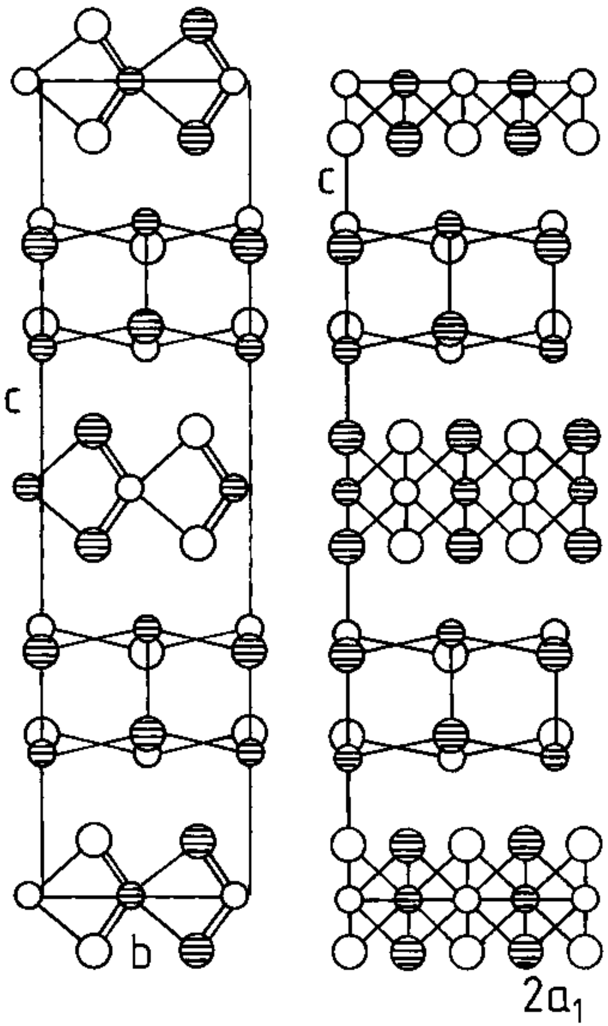
$a_1 = 5.813$ Å

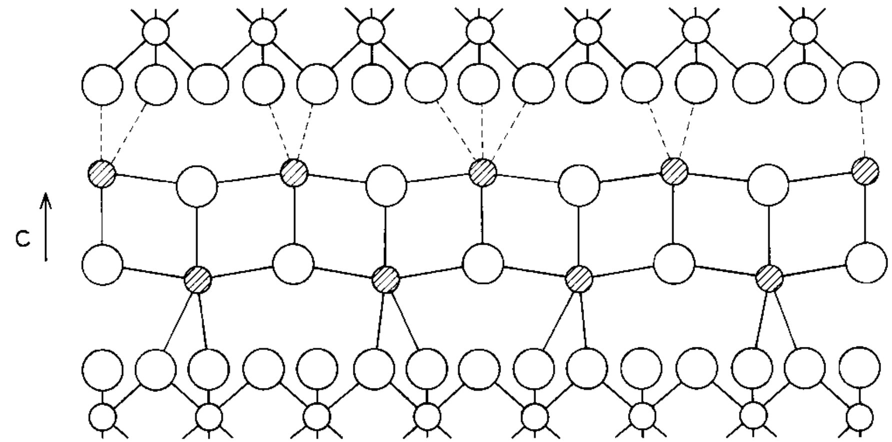
$b = 5.775$ Å

$c = 23.06$ Å

$\alpha = a_1/a_2 = 0.5668\cdots$

Packing principles of composite crystals



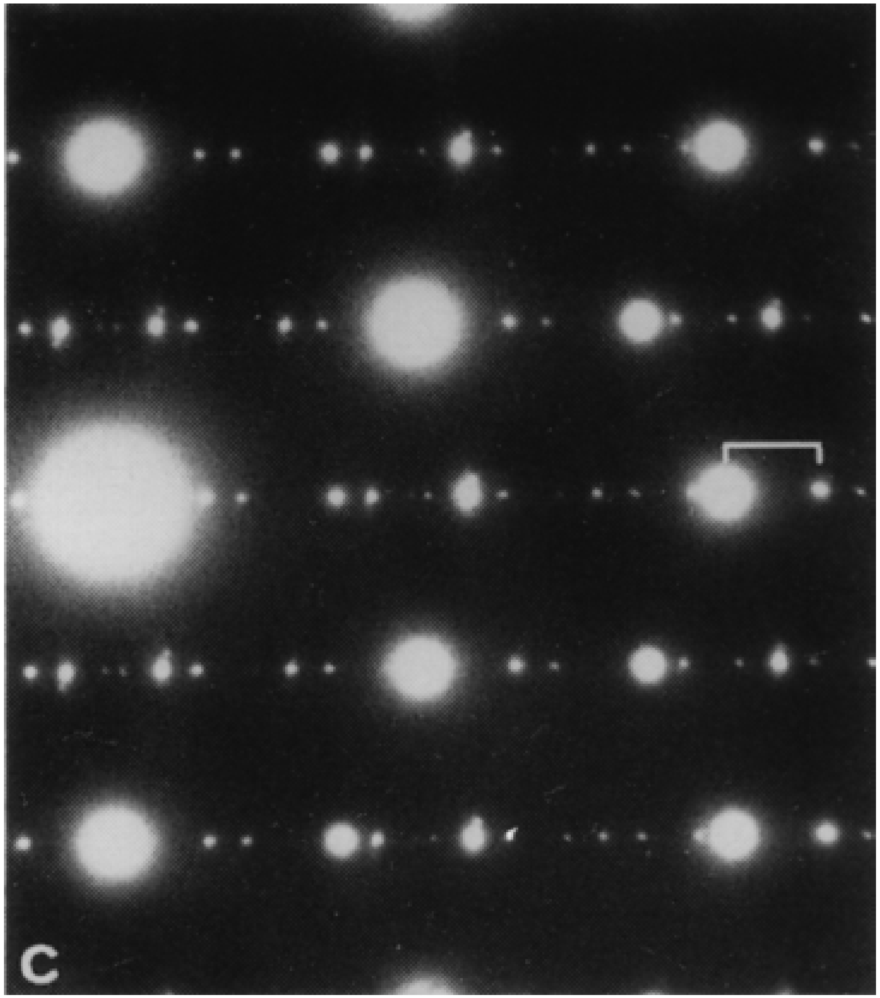


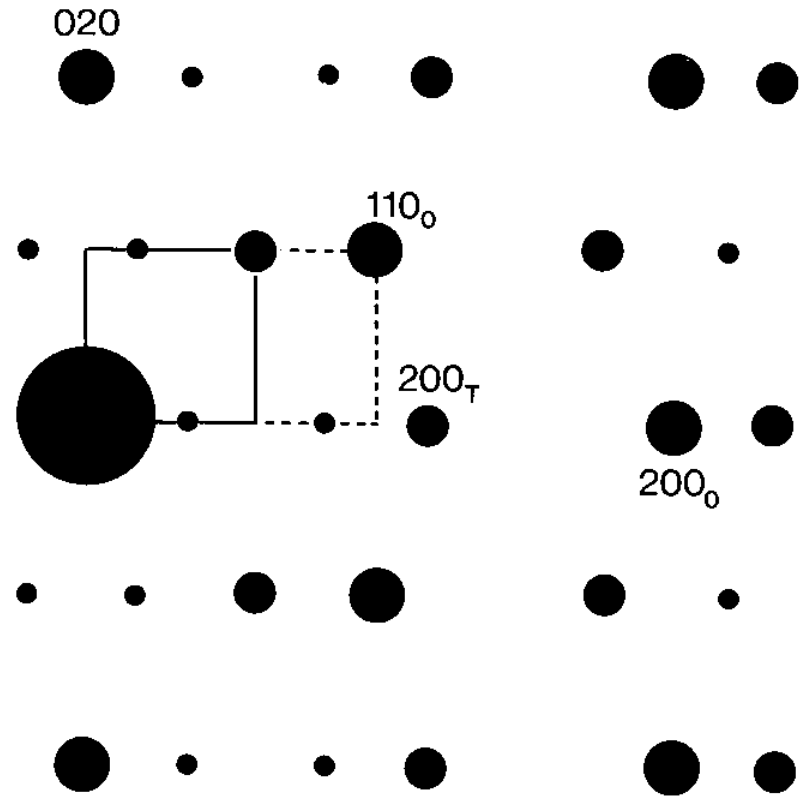
Two unit cells with common **b*** and **c*** axes

Incommensurate structure in (3+1)D Superspace

$a_2 = 1.761\ a_1$

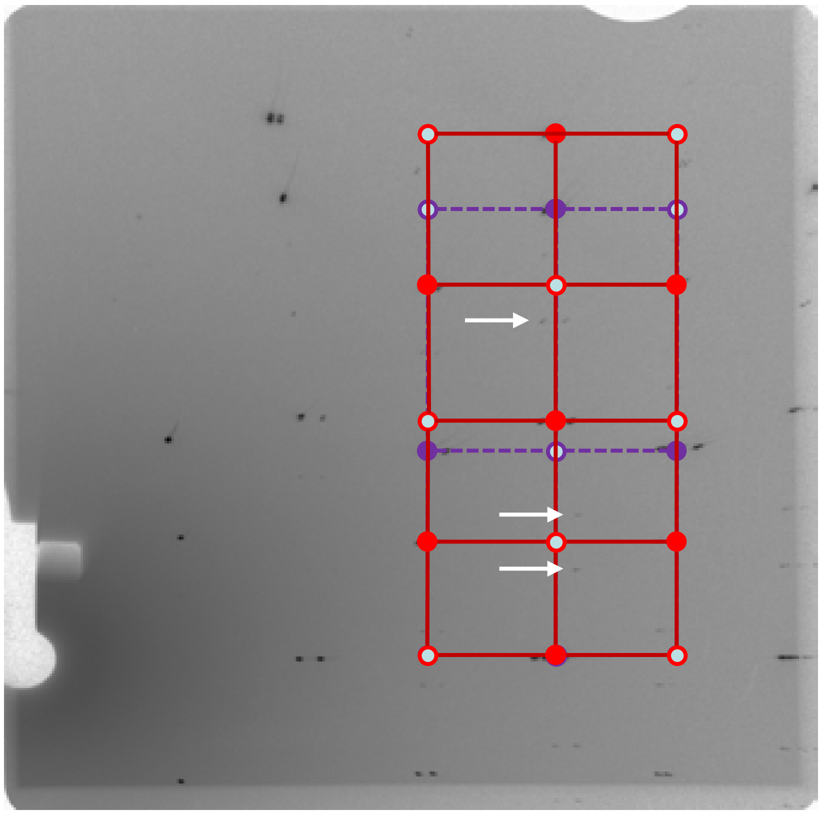
Electron Diffraction by $[SnS]_{1.17}[NbS_2]$





S. Kuypers, J. Van Landuyt and S. Amelinckx, J. Sol. State Chem. **86**, 212-232 (1990)

Diffraction by composite crystals



$h_1 = 2$

$h_2 = 3$

$h_2 = 2$

$h_1 = 1$

$h_2 = 1$

$h = 0$

Rotation Photograph (20 deg.) of $[LaS]_{1.13}[TaS_2]$

Scattering vector:

$h\,\mathbf{a}_1^* + k\,\mathbf{b}^* + l\,\mathbf{c}^* + m\,\mathbf{a}_2^*$

ν=1 LaS: $(h, k, l, 0)$

ν=2 TaS_2: $(0, k, l, m)$

Common: $(0, k, l, 0)$

Satellites: (h, k, l, m)

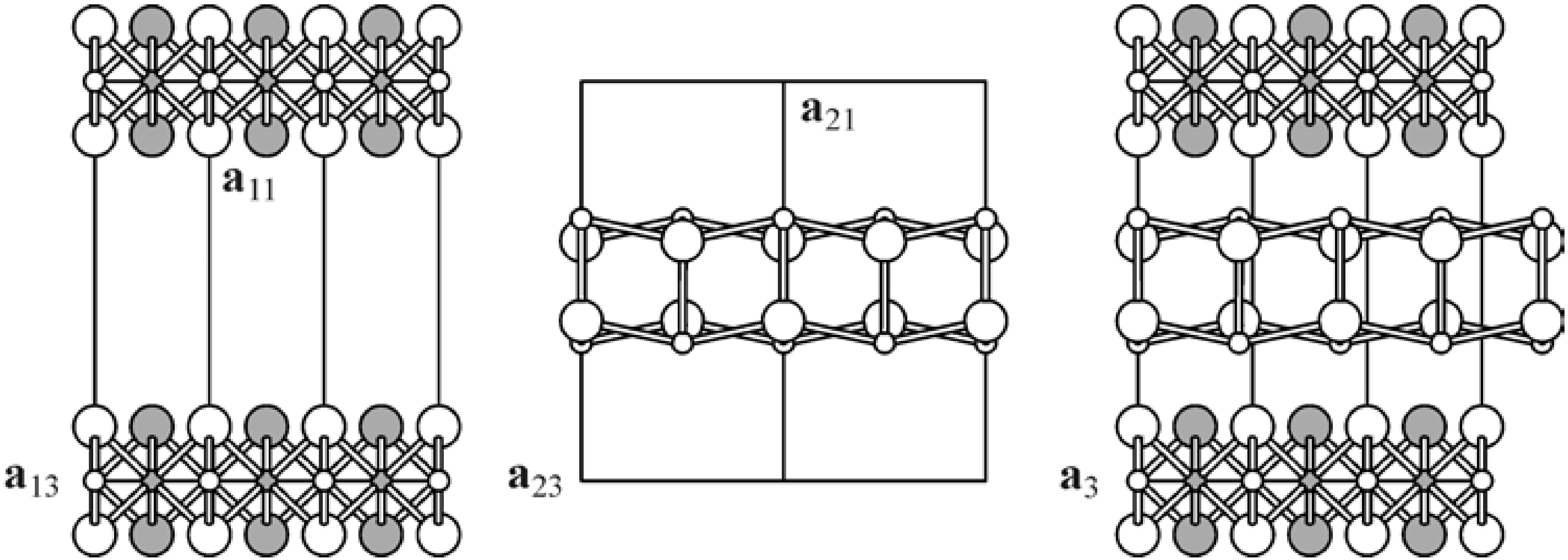
with $h \neq 0$ & $m \neq 0$

Order of satellites:

Minimum[h, m]

A. Jobst and S. van Smaalen, Acta Cryst. B **58**, 179 (2002)

TaS_2 + LaS gives $[LaS]_{1.13}[TaS_2]$



$\mathbf{c}^* = \mathbf{a}_{13}^* = \mathbf{a}_{23}^*$ Perpendicular to layers

$\mathbf{b}^* = \mathbf{a}_{12}^* = \mathbf{a}_{22}^*$ Interactions between layers

$\mathbf{a}_2^* = \mathbf{a}_{21}^* = (a_{11}/a_{21})\, \mathbf{a}_{11}^* = \alpha\, \mathbf{a}_1^*$ Incommensurate

S. van Smaalen: *Incommensurate Crystallography*, Oxford University Press (2007)

The W$^\nu$ matrix defines subsystem ν

$$\begin{pmatrix} \mathbf{a}^*_{\nu 1} \\ \mathbf{a}^*_{\nu 2} \\ \mathbf{a}^*_{\nu 3} \\ \mathbf{q}^\nu \end{pmatrix} = \begin{pmatrix} W^\nu_{11} & W^\nu_{12} & W^\nu_{13} & W^\nu_{14} \\ W^\nu_{21} & W^\nu_{22} & W^\nu_{23} & W^\nu_{24} \\ W^\nu_{31} & W^\nu_{32} & W^\nu_{33} & W^\nu_{34} \\ W^\nu_{41} & W^\nu_{42} & W^\nu_{43} & W^\nu_{44} \end{pmatrix} \begin{pmatrix} \mathbf{a}^*_1 \\ \mathbf{a}^*_2 \\ \mathbf{a}^*_3 \\ \mathbf{a}^*_4 \end{pmatrix}$$

$$W^{\nu=1} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \qquad W^{\nu=2} = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}$$

S. van Smaalen, Phys. Rev. B **43**, 11330 (1991)

The subsystem superspace group

W^{ν} is coordinate transformation in superspace

$$\{R_s \,|\, \mathbf{v}_s\} \in G_s \qquad \begin{cases} R_s^{\nu} = W^{\nu} R_s \left(W^{\nu}\right)^{-1} \\ \mathbf{v}_{\nu s} = W^{\nu} \mathbf{v}_s \end{cases}$$

$\{R_s^{\nu} \,|\, \mathbf{v}_{\nu s}\} \in G_s^{\nu}$ subsystem superspace group

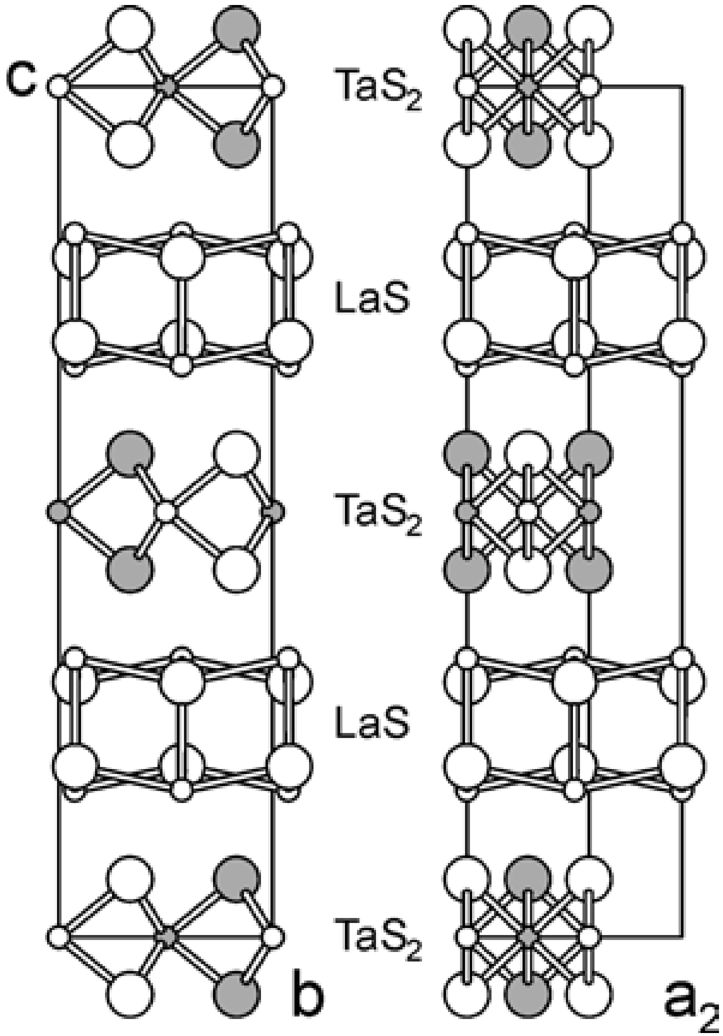
Subsystem superspace group gives symmetry of subsystem ν

Symmetry of the periodic basic structure of subsystem ν by

$\{R^{\nu} \,|\, v_{\nu,1}, v_{\nu,2}, v_{\nu,3}\} \in G^{\nu}$ subsystem spacegroup

S. van Smaalen, Phys. Rev. B **43**, 11330 (1991)

Unit cells of subsystems of $[LaS]_{1.13}[TaS_2]$



Subsystem $\nu = 1$: TaS_2

F-centered

$a_{13} = 23.06$ Å

Subsystem $\nu = 2$: LaS

C-centered

$a_{23} = (1/2)\ 23.06 = 11.58$ Å

$(0, k_1, l_1, 0)$: k_1, l_1 even

$(0, k_2, l_2, 0)$: k_2 even AND

$l_1 = 2l_2$ due to $a_{23}^* = 2a_{13}^*$

A. Jobst and S. van Smaalen, Acta Cryst. B **58**, 179 (2002)

Non-equivalent subsystem superspace groups

$$F'm2m(\alpha,0,0)00s$$

$$\mathbf{W}^1 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \longrightarrow Fm2m(\alpha,0,0)00s$$

$$\mathbf{W}^2 = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 2 & 0 \\ 1 & 0 & 1 & 0 \end{pmatrix} \longrightarrow Cm2a(1/\alpha,0,1/2)$$

S. van Smaalen, Phys. Rev. B **43**, 11330 (1991)

Exercise: Subsystem superspace groups of monoclinic $[PbS]_{1.18}[TiS_2]$

SSG: $C_c2/m(\alpha\ 0\ 0)s0$

$C_c = (1/2, 1/2, 0, 1/2)$

$\alpha = a_{11}/a_{21} = 0.5878$ origin at *i*

Subsystem TiS_2 ($\nu = 1$)

$a_{11} = 3.409$ Å

$a_{12} = 5.880$ Å

$a_{13} = 11.760$ Å

$\alpha_1 = 95.29°$

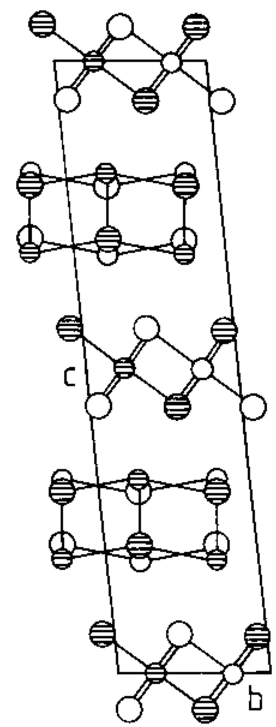
Subsystem PbS ($\nu = 2$)

$a_{21} = 5.800$ Å

$a_{22} = 5.881$ Å

$a_{23} = 11.759$ Å

$\alpha_2 = 95.27°$



$$\mathbf{W}^1 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \qquad \begin{cases} R_s^{\nu} = W^{\nu} R_s \left(W^{\nu}\right)^{-1} \\ \mathbf{v}_{\nu s} = W^{\nu} \mathbf{v}_s \end{cases} \qquad \mathbf{W}^2 = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}$$

S. van Smaalen, A. Meetsma, G.A. Wiegers & J.L. de Boer, Acta Crystallogr. B **47**, 314 (1991)

Solution: Subsystem TiS_2 ($\nu = 1$)

$G_s^1 = G_s = C_c2/m(\alpha\ 0\ 0)s0$ because W^1 = identity matrix

mirror plane has an origin-dependent translation

Subsystem space group

$G_2 = C2/m$

$$\begin{cases} R_s^{\nu} = W^{\nu} R_s \left(W^{\nu}\right)^{-1} \\ \mathbf{v}_{\nu s} = W^{\nu} \mathbf{v}_s \end{cases}$$

$$\begin{cases} (E,0) & \{E,1\,|\,l_1,l_2,l_3,l_4\} \\ \mathbf{ct} & \{E,1\,|\,1/2,1/2,0,1/2\} \\ (2,s) & \{2^x,1\,|\,0,0,0,1/2\} \\ (i,\overline{1}) & \{i,\overline{1}\,|\,0,0,0,0\} \\ (m,\overline{1}) & \{m_x,\overline{1}\,|\,0,0,0,1/2\} \end{cases}$$

S. van Smaalen, A. Meetsma, G.A. Wiegers & J.L. de Boer, Acta Crystallogr. B **47**, 314 (1991)

Solution: Subsystem PbS ($\nu = 2$)

$G_s = C_c2/m(\alpha\ 0\ 0)s0$. Rotation matrices of all four operators are diagonal matrices, so:

$$R_s^\nu = W^\nu R_s \left(W^\nu\right)^{-1} = R_s W^\nu \left(W^\nu\right)^{-1} = R_s$$

$$\mathbf{W}^2 = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}$$

W^2 applied to $\mathbf{v}_s$ interchanges the 1st and 4th coordinates:

$$\mathbf{v}_{2s} = W^2 \mathbf{v}_s = \left(v_{s4}, v_{s2}, v_{s3}, v_{s1}\right)$$

$\mathbf{q}^2 = \mathbf{a}_{11}^* = (1/\alpha)\ \mathbf{a}_{21}^*$

Subsystem superspace group

$G_s^2 = C_c2_1/m(\alpha'\ 0\ 0)00$ with $\alpha' = 1/\alpha$

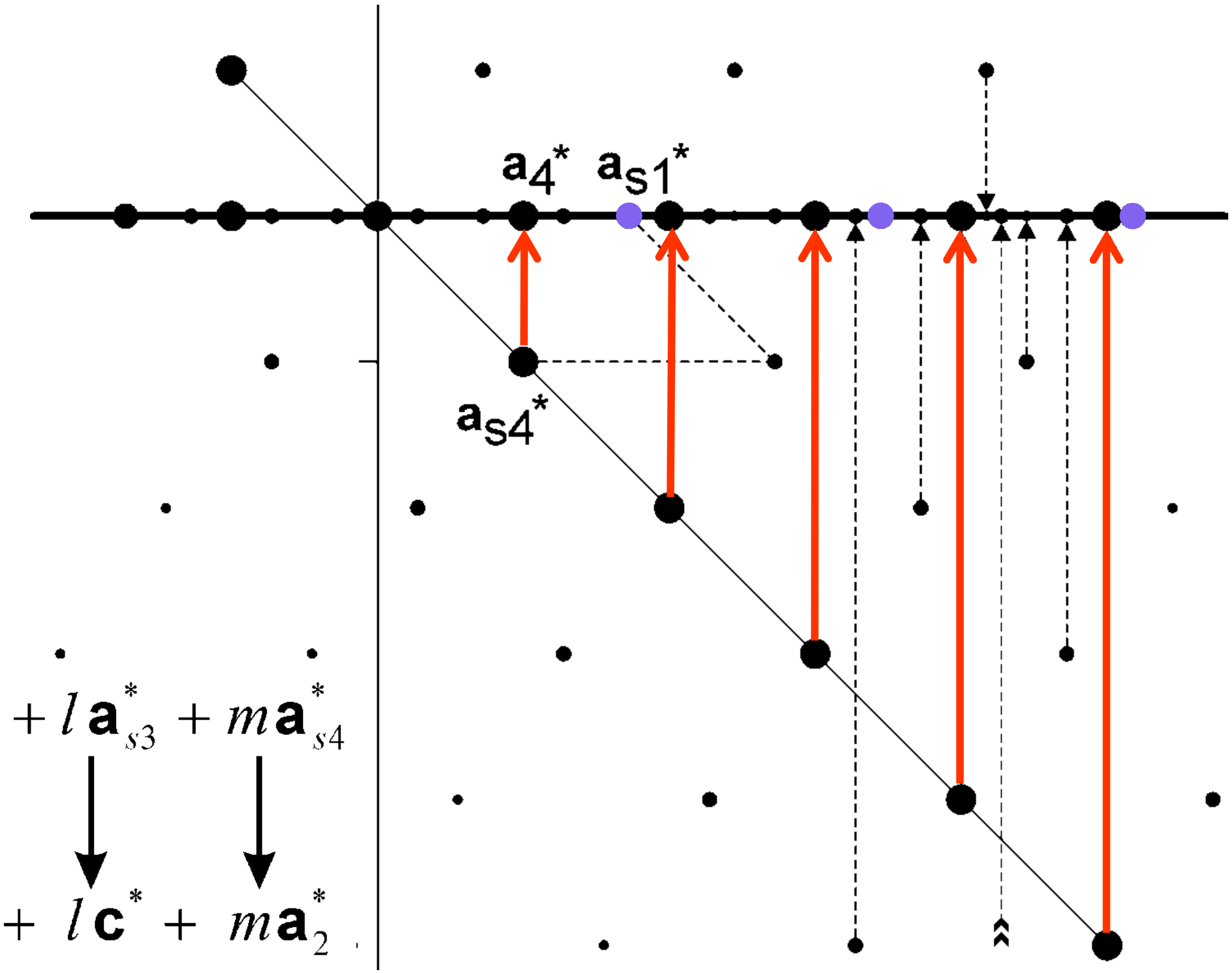
Subsystem space group

$G_2 = C2_1/m$

$$\begin{cases} (E,0) & \{E,1\,|\,l_1,l_2,l_3,l_4\} \\ \mathbf{ct} & \{E,1\,|\,1/2,1/2,0,1/2\} \\ (2_1,0) & \{2^x,1\,|\,1/2,0,0,0\} \\ (i,\bar{1}) & \{i,\bar{1}\,|\,0,0,0,0\} \\ (m,\bar{1}) & \{m_x,\bar{1}\,|\,1/2,0,0,0\} \end{cases}$$

S. van Smaalen, A. Meetsma, G.A. Wiegers & J.L. de Boer, Acta Crystallogr. B **47**, 314 (1991)

Reciprocal superspace of composite crystals



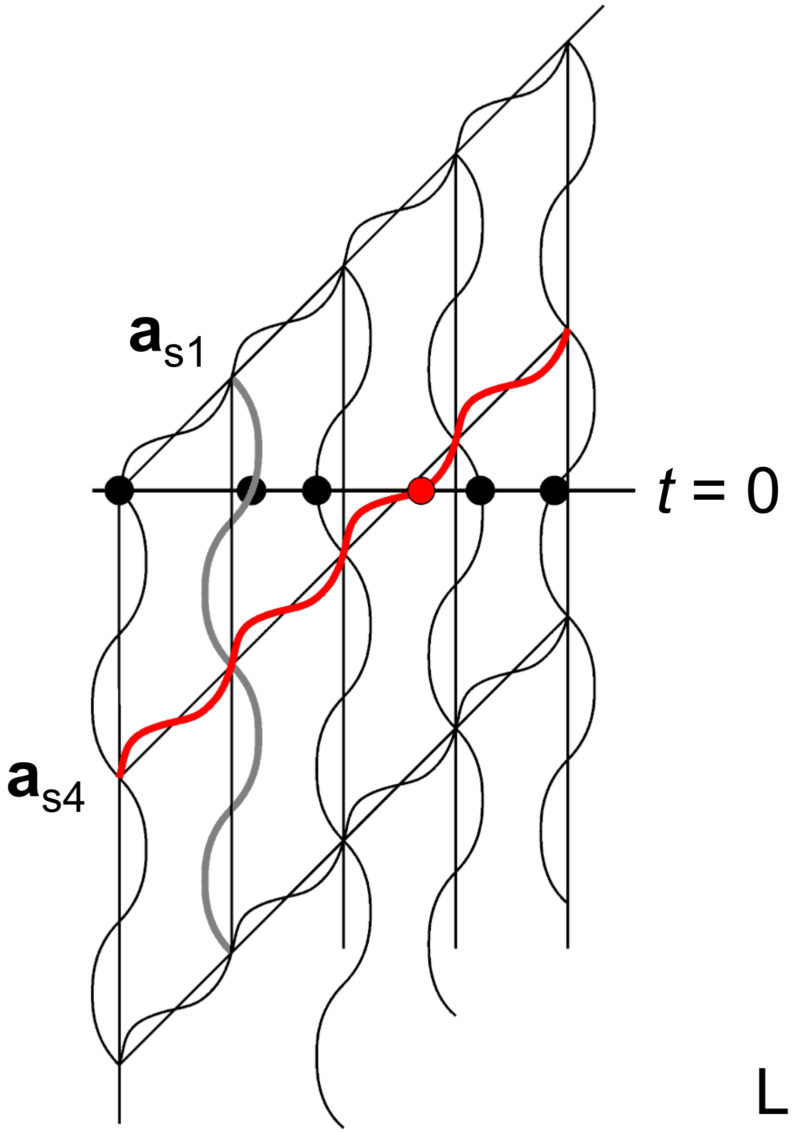
$$\mathbf{S}_s = h\,\mathbf{a}^*_{s1} + k\,\mathbf{a}^*_{s2} + l\,\mathbf{a}^*_{s3} + m\,\mathbf{a}^*_{s4}$$

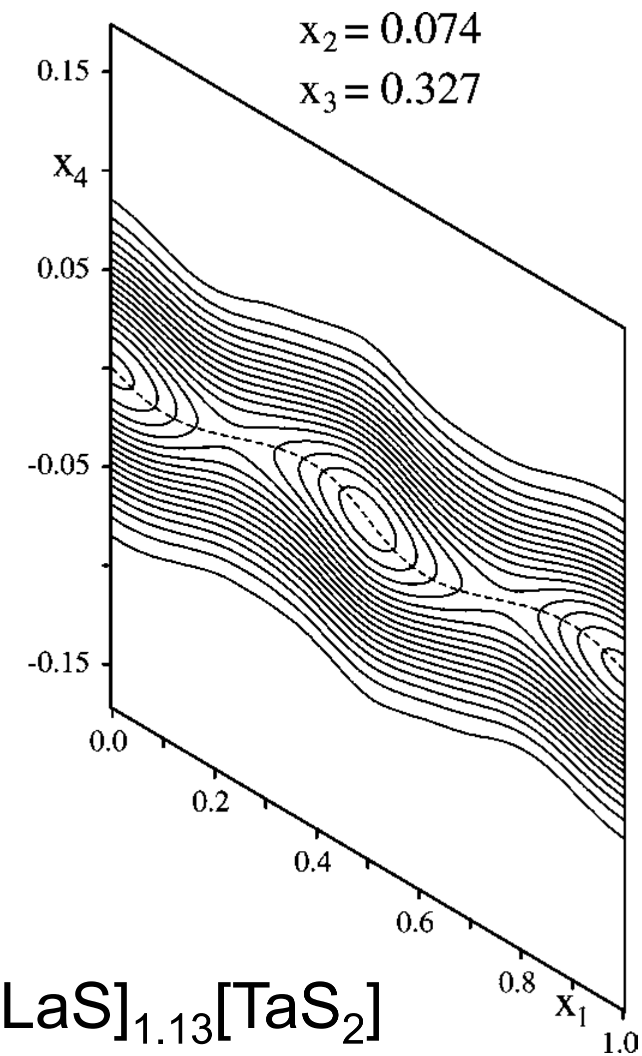
$$\downarrow \quad \downarrow \quad \downarrow \quad \downarrow$$

$$\mathbf{S} = h\,\mathbf{a}^*_1 + k\,\mathbf{b}^* + l\,\mathbf{c}^* + m\,\mathbf{a}^*_2$$

S. van Smaalen: *Incommensurate Crystallography*, Oxford University Press (2007)

Modulation functions in superspace





La atom of $[LaS]_{1.13}[TaS_2]$

Structural parameters for composite crystals

Coordinates are with respect to the subsystem lattices

$$x^{\mu}_{\nu i} = l_{\nu i} + x^{\mu 0}_{\nu i} + u^{\mu}_{\nu i}[t_{\nu} + \mathbf{q}^{\nu} \cdot (\mathbf{L}_{\nu} + \mathbf{x}^{\mu 0}_{\nu})]$$

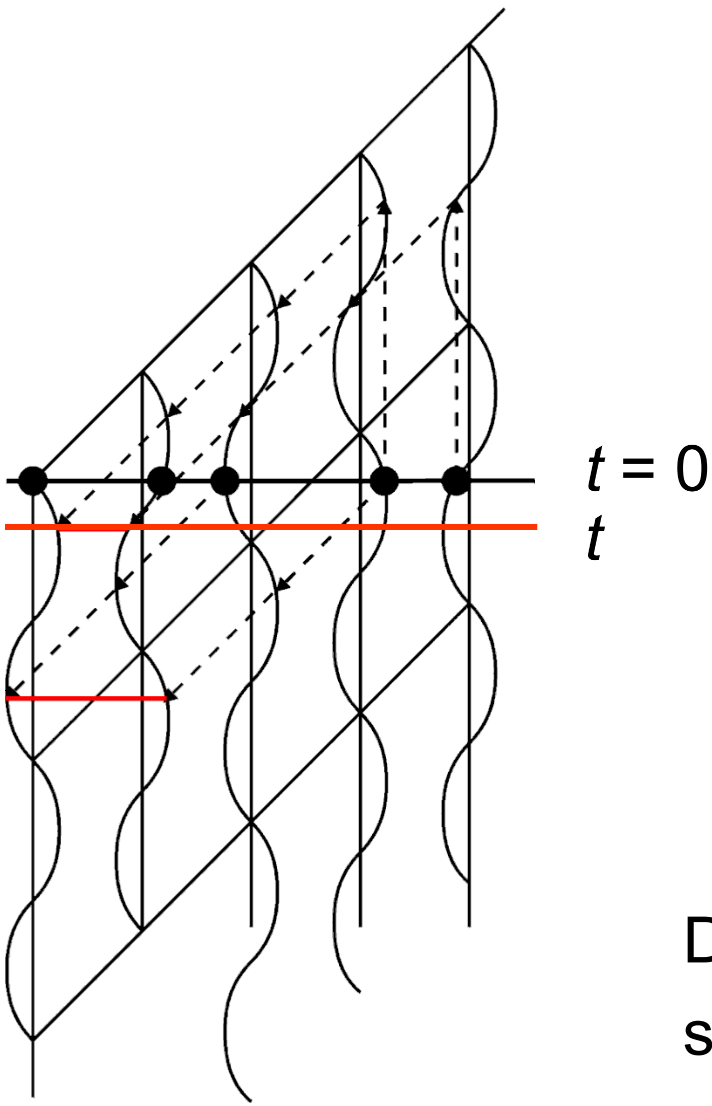
$$u^{\mu}_{\nu i}(\bar{x}_{\nu s4}) = \sum_{n=1}^{\infty} A^{\mu}_{\nu n i} \sin\left(2\pi n \bar{x}_{\nu s4}\right) + B^{\mu}_{\nu n,i} \cos\left(2\pi n \bar{x}_{\nu s4}\right)$$

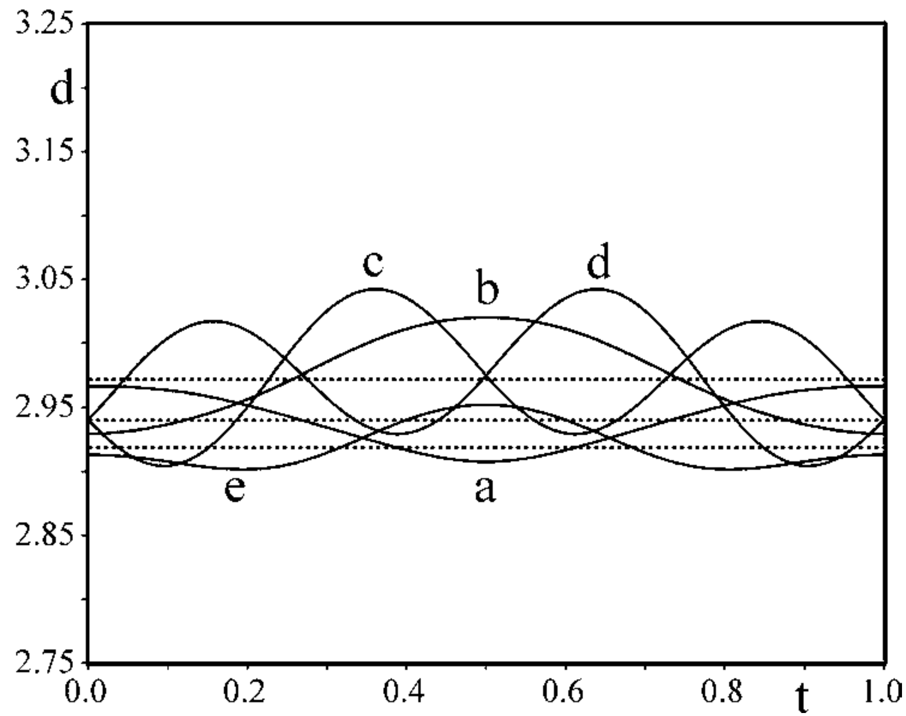
$$\bar{x}_{\nu s4} = t_{\nu} + \mathbf{q}^{\nu} \cdot (\mathbf{L}_{\nu} + \mathbf{x}^{\mu 0}_{\nu})$$

$$\mathbf{q}^{\nu=1} = \mathbf{a}^{*}_{2} = 0.5668\, \mathbf{a}^{*}_{1} \qquad \mathbf{q}^{\nu=2} = \mathbf{a}^{*}_{1} = 1.764\, \mathbf{a}^{*}_{2}$$

Relations between subsystems via $\mathbf{W}^{\nu}$-matrices allows computation of structure factor, distances and others

Superspace and interatomic distances: *t* plots

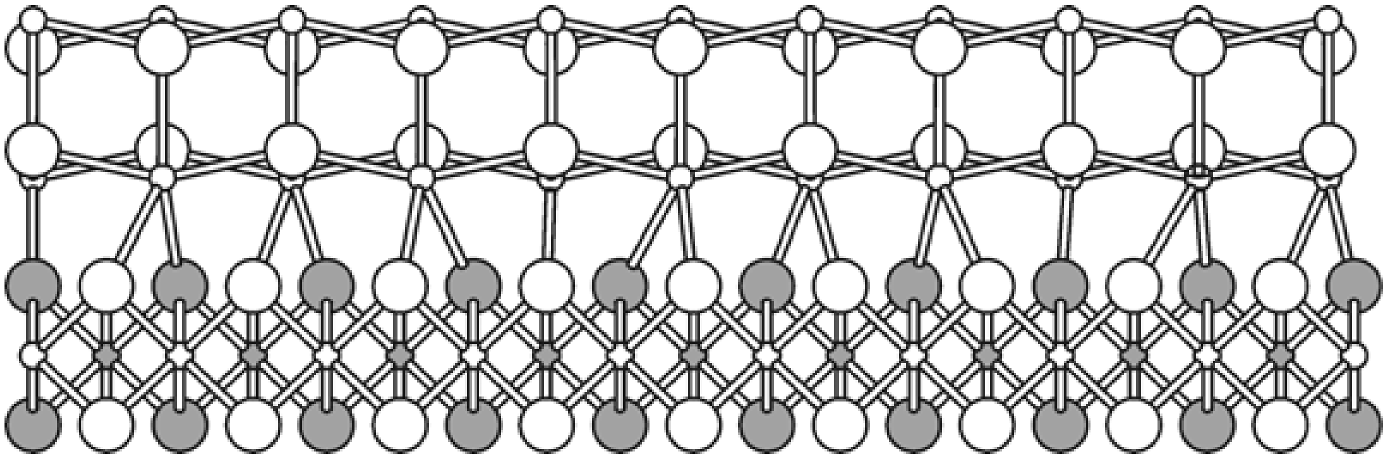


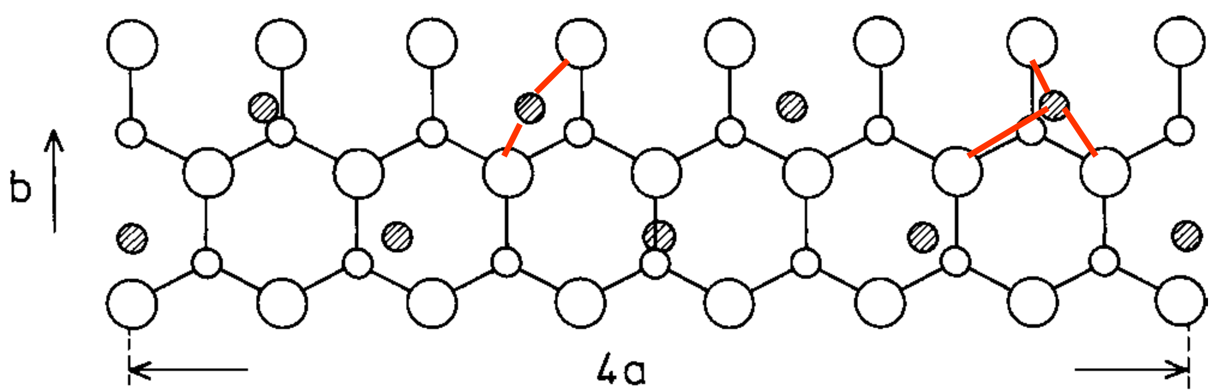


$[LaS]_{1.13}[TaS_2]$

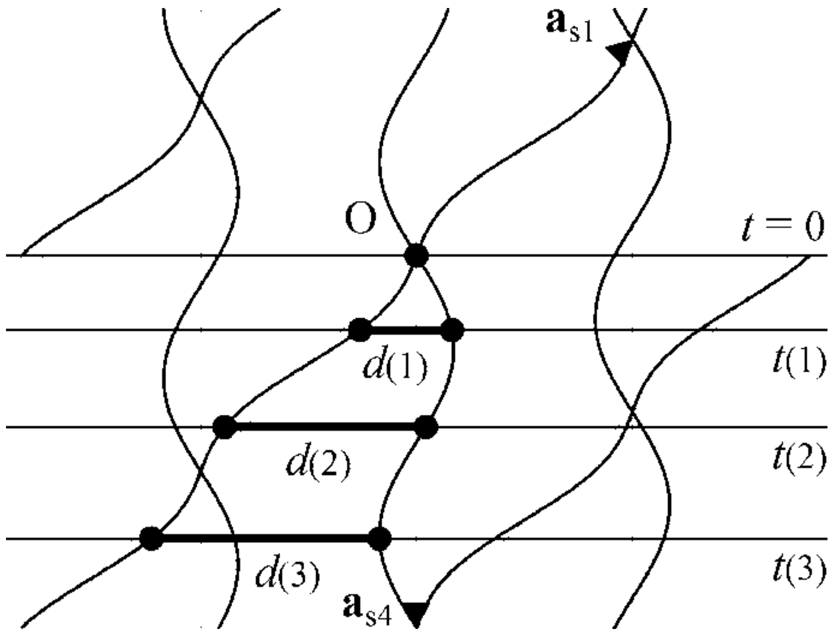
Distances of La towards the five surrounding S of the LaS subsystem

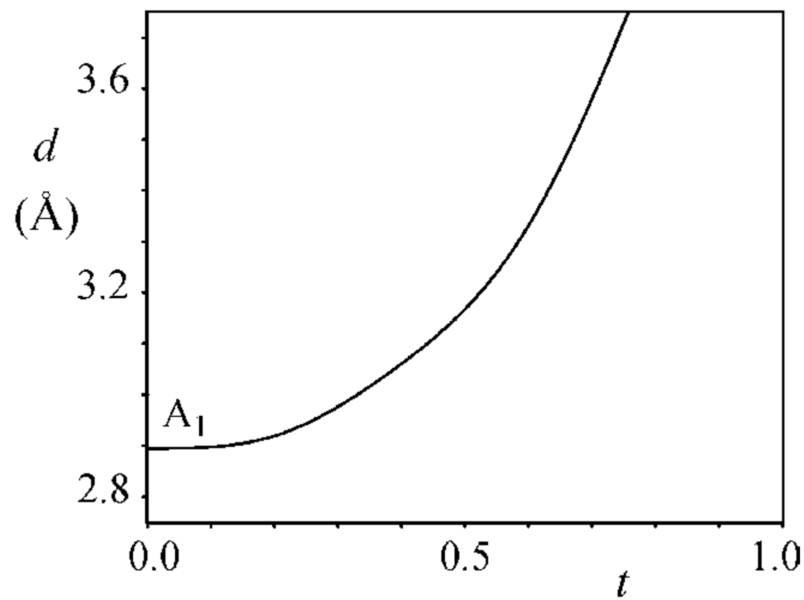
Chemical bonding across the incommensurate gap





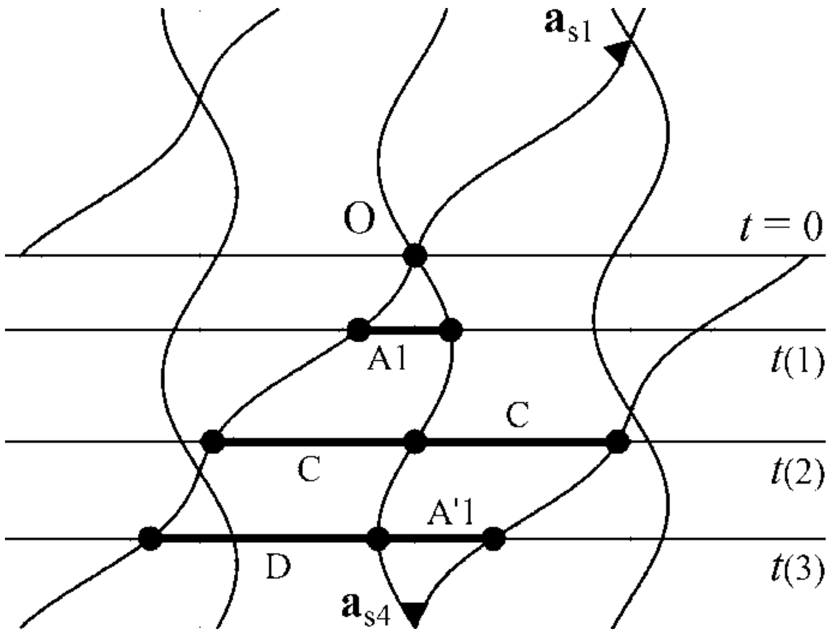
Interatomic distance between one atom of ν = 1 and one atom of ν = 2.

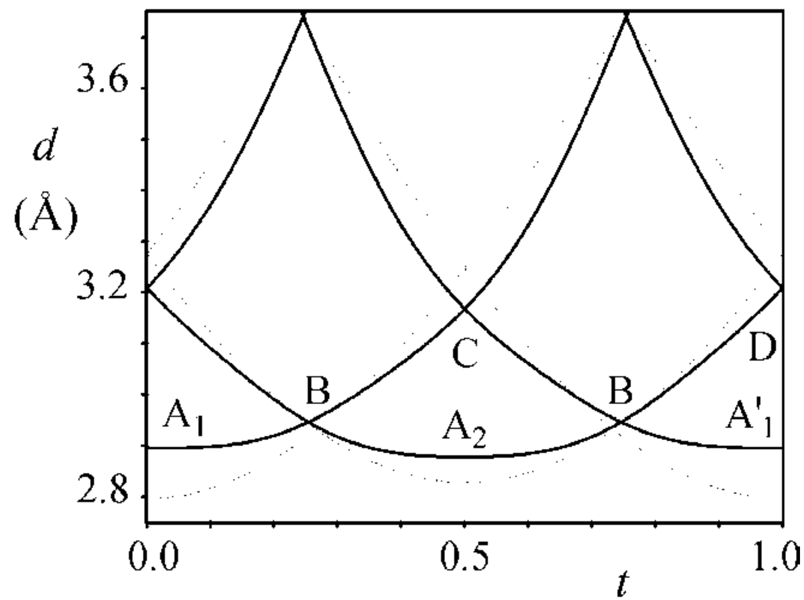




S. van Smaalen: *Incommensurate Crystallography*, Oxford University Press (2007)

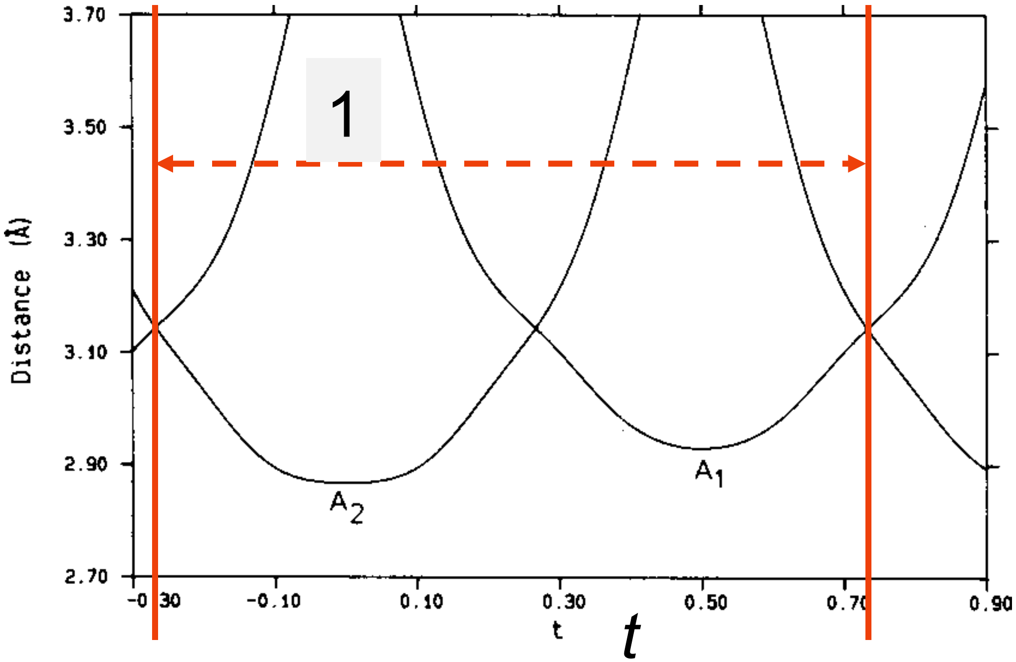
La of $[LaS]_{1.13}[TaS_2]$ as central atom
Distances to all S atoms of ν = 2
gives periodic function in *t*

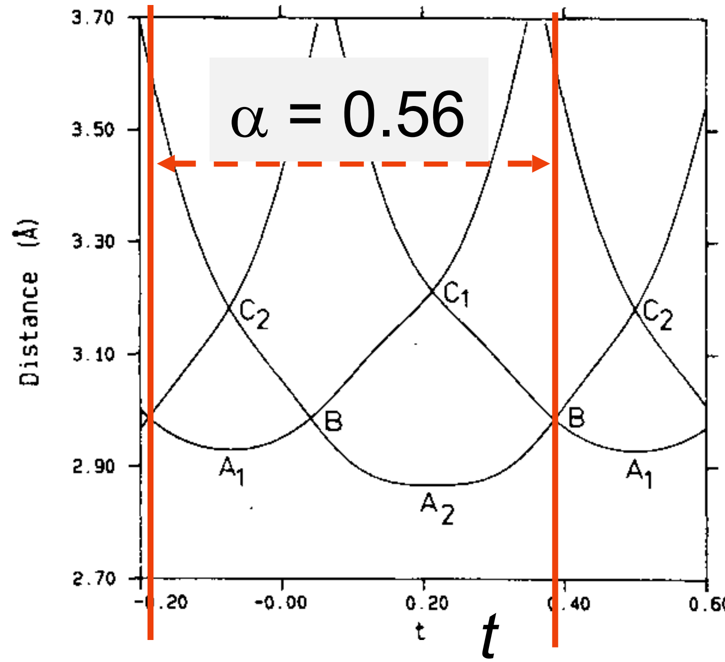




S. van Smaalen: *Incommensurate Crystallography*, Oxford University Press (2007)

$[LaS]_{1.14}[NbS_2]$: distances S1 (ν=1) – La (ν=2)





Central atom S1 (ν = 1)

Periodicity 1 in $t_1 = t$

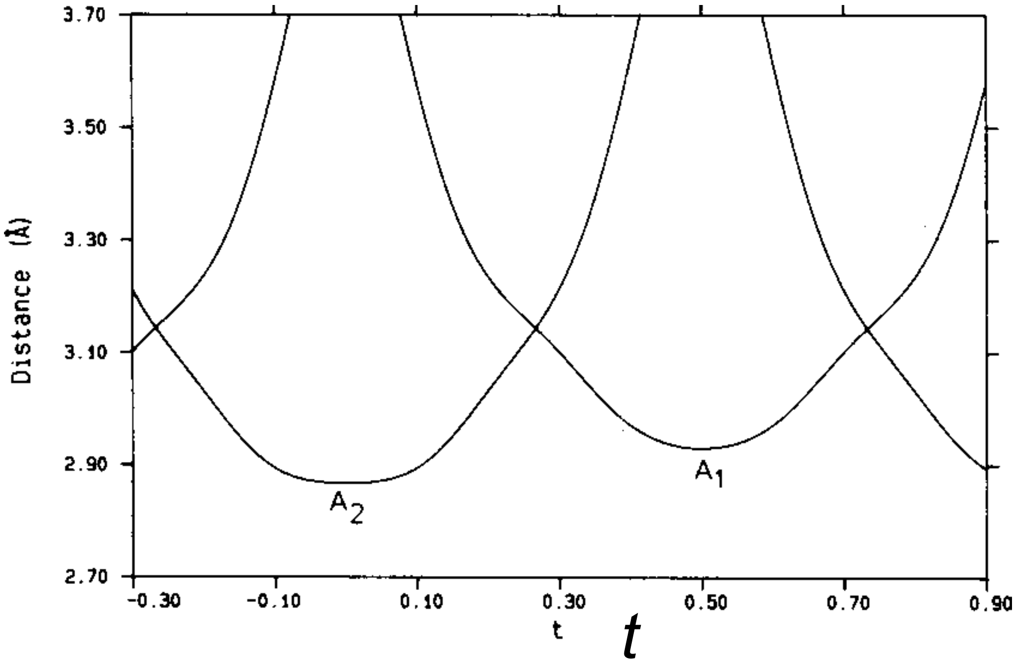
Central atom La (ν = 2)

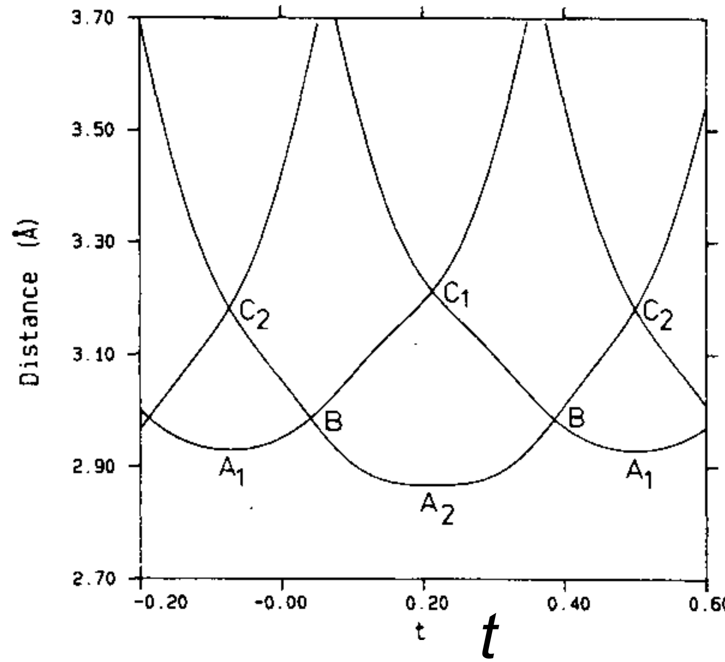
Periodicity 1 in $t_2 = t/\alpha$

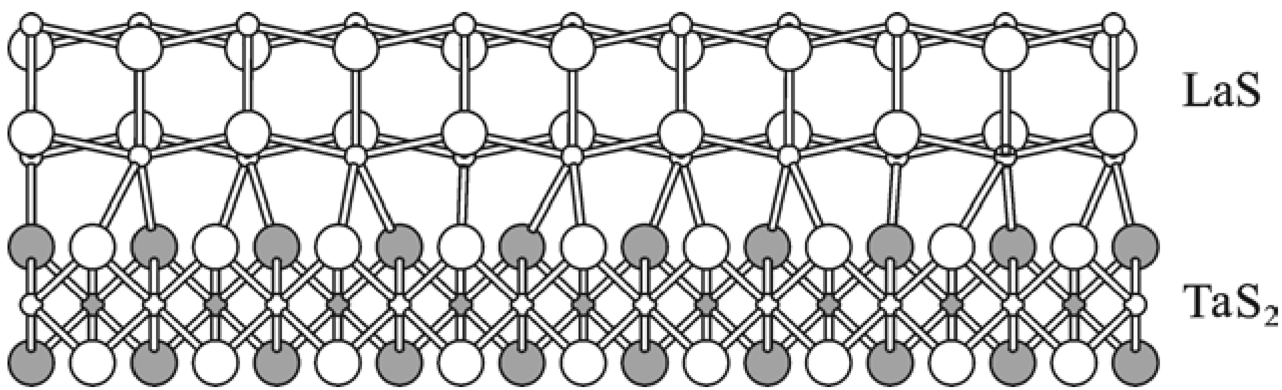
Periodicity α in $t = \alpha\, t_2$

S. van Smaalen, J. Phys.: Condens. Matter **3**, 1247 (1991)

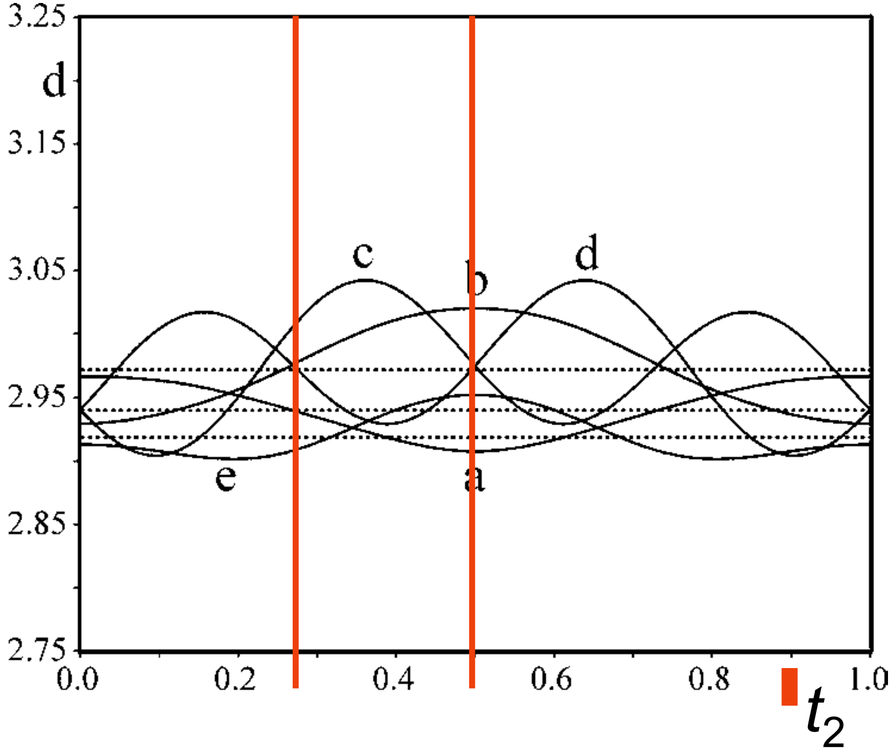
Distance S1 (ν=1)–La (ν=2) in physical space

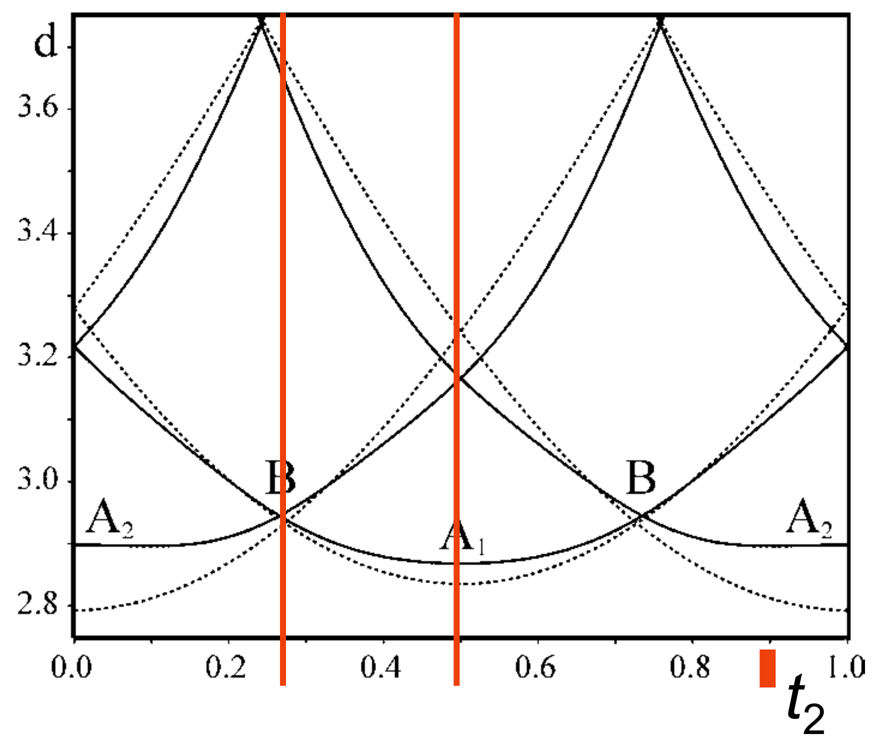






Central atom La of subsystem ν = 2: LaS Distances to atoms S1 (ν = 1) and S2 (ν = 2)

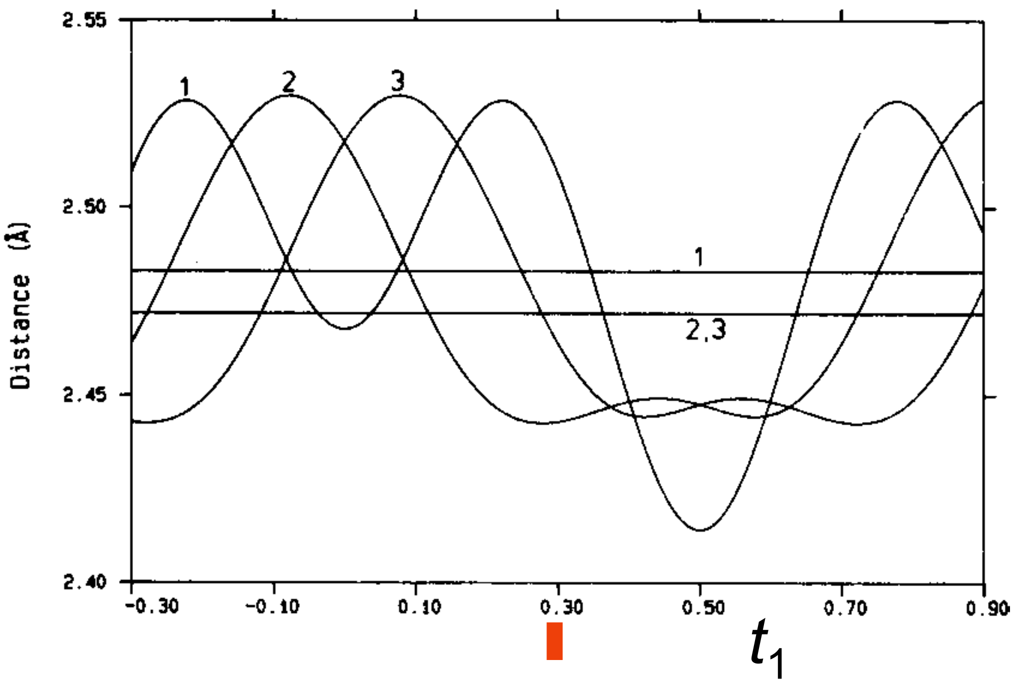


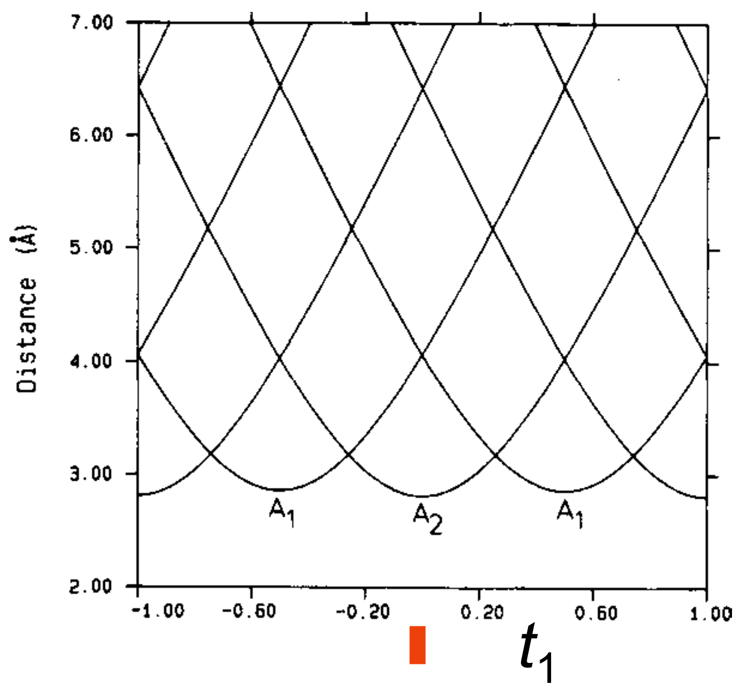


$[LaS]_{1.13}[TaS_2]$

A. Jobst and S. van Smaalen, Acta Cryst. B **58**, 179 (2002)

Central atom S1 of subsystem $\nu = 1$: TaS_2
Distances to atoms La ($\nu = 2$) and Nb ($\nu = 1$)





$[LaS]_{1.14}[NbS_2]$

Summary

Composite crystals are a single thermodynamic phase

Comprise modulated subsystems $\nu = 1,2,...$

Subsystem superspace groups follow by W^ν matrices from the single (3+d)D superspace group

t plots of distances and other structural parameters

International School on Aperiodic Crystals

26 September - 2 October 2010, Carqueiranne, France

Incommensurate composite crystals materials and properties

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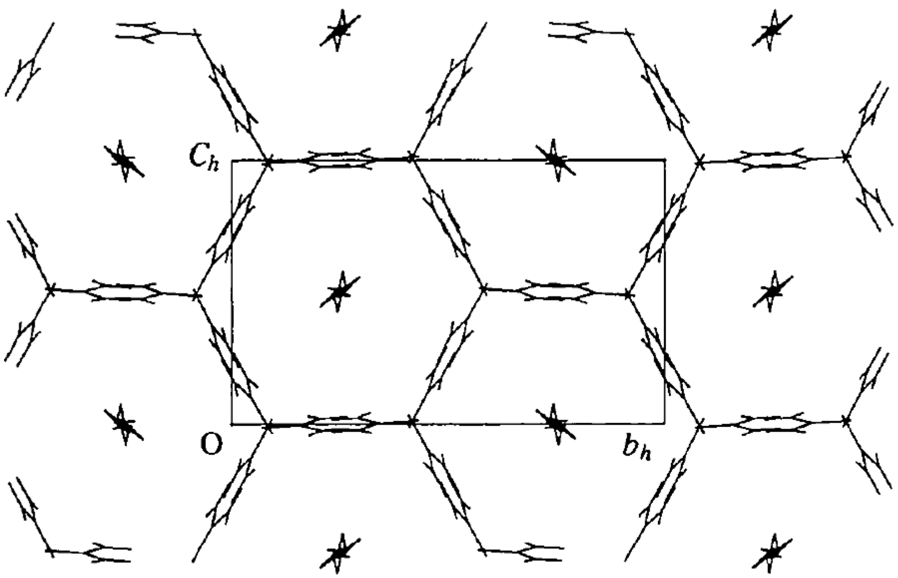
Channel-type incommensurate composite crystals—urea/alkane inclusion compounds



Subsystem 1 urea

$P6_122$

a = 8.24 Å

c = 11.05 Å

Subsystem 2 n-alkane

"disordered"

common (**a***,**b***)-plane

collinear **c**-axes

incommensurability

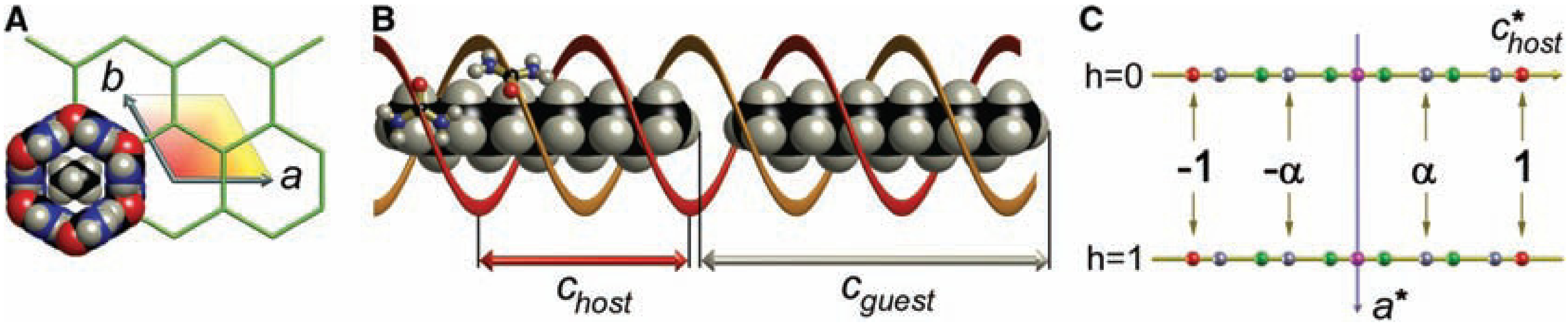
c_{guest}/c_{host} = irrational

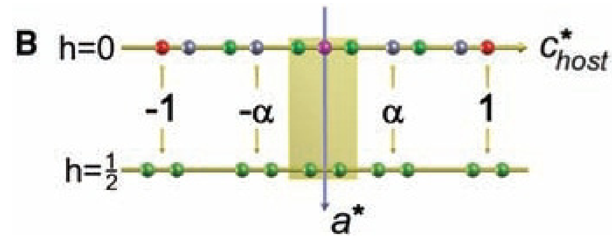
(3+1)D superspace group

$P6_122(00\gamma)000$ — orthorhombic distortion for ordered guest

L. Yeo & K.D.M. Harris, Acta Crystallogr. B **53**, 822 (1997)

Urea/alkane inclusion compounds





HT: hexgonal (3+1)D superspace group

$P6_122(00\gamma)000$

$\mathbf{H} = h\,\mathbf{a}^* + k\,\mathbf{b}^* + l\,\mathbf{c}_{host}{}^* + m\,\mathbf{c}_{guest}{}^*$

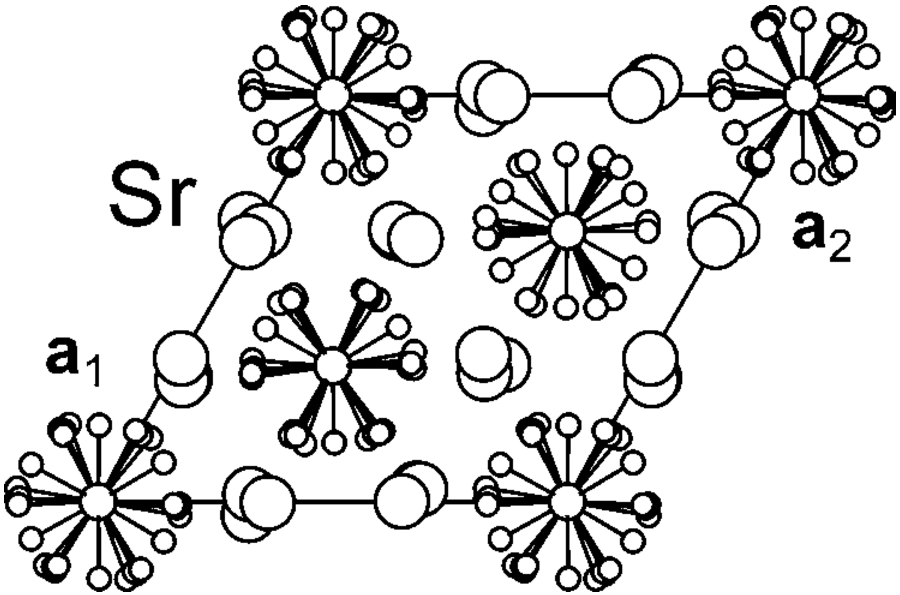
LT: orthohexagonal supercell $C222_1$

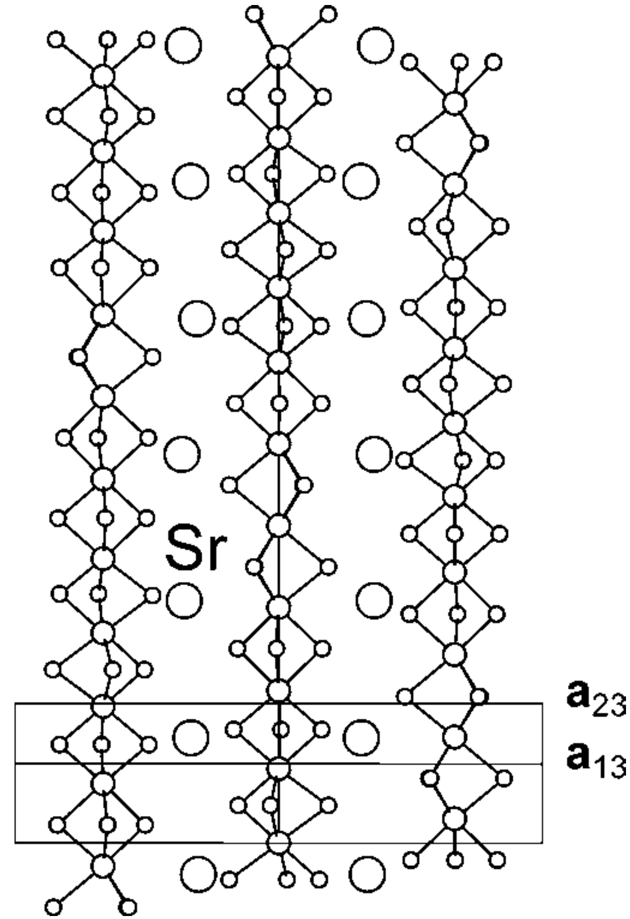
$\mathbf{H} = h\,\mathbf{a}^* + k\,\mathbf{b}^* + l\,\mathbf{c}_{host}{}^* + m_1\,\mathbf{c}_{guest}{}^* + m_2\,\mathbf{q}^2$

$q^2 = (1, 0, \gamma')$

B. Toudic *et al.,* Science **319**, 69-71 (2008)

Columnar type composite crystals—$[Sr]_x[TiS_3]$





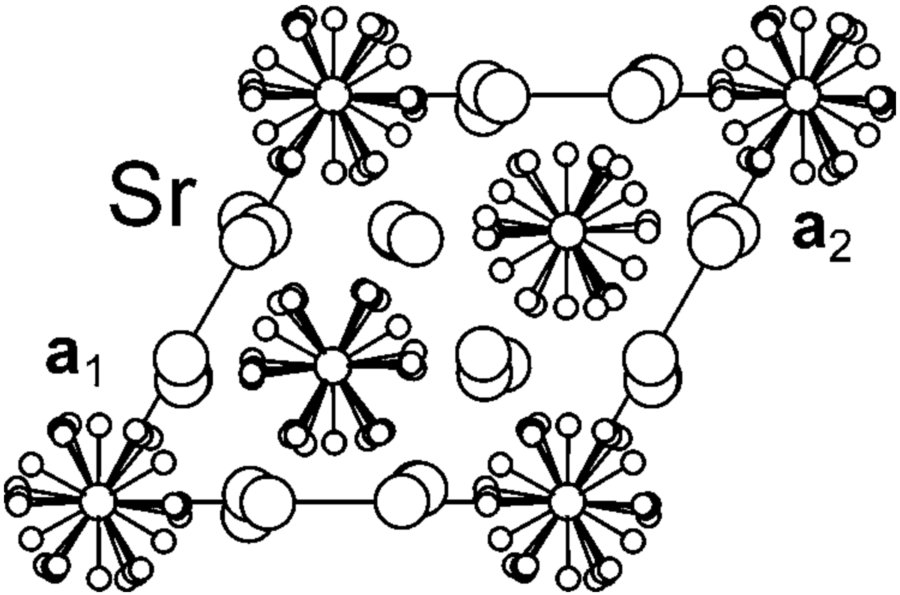
(3+1)D superspace group

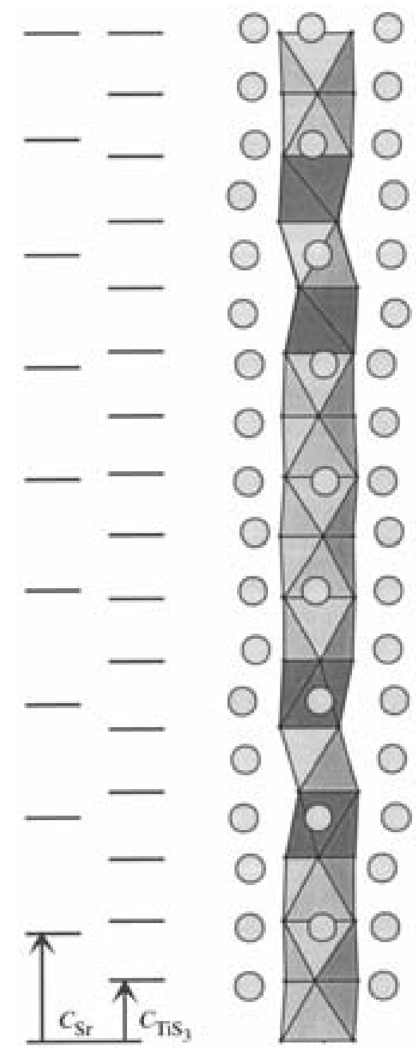
R3m(00γ)0s

$\mathbf{H} = h\,\mathbf{a}^* + k\,\mathbf{b}^* + l\,\mathbf{c}_{host}^* + m\,\mathbf{c}_{guest}^*$

M. Onoda, M. Saeki, A. Yamamoto & K. Kato, Acta Crystallogr. B **49**, 929 (1993)

Atomic modulations in $[Sr]_x[TiS_3]$ ($x \approx 1.12$)





Modulation of Sr atomic positions.

Aperiodic sequence of octahedral (short) and trigonal prismatic (long), face-sharing TiS_6 groups

O. Gourdon, V. Petricek & M. Evain, Acta Crystallogr. B **56**, 409 (2000)

Rhombohedral / trigonal composite crystal $[Sr]_x[TiS_3]$ (x ≈ 1.12)

$$G_s = R\bar{3}m(00\gamma)0s$$

$$(h\ k\ l\ m):\ -h+k+l=3n$$

$$\begin{cases} \mathbf{ct}_1 & \{E,1|2/3,1/3,1/3,0\} \\ \mathbf{ct}_2 & \{E,1|1/3,2/3,2/3,0\} \end{cases}$$

$$(h_2\ k_2\ l_2\ m_2):\ -h_2+k_2+m_2=3n$$

$$\begin{cases} \mathbf{ct}_1 & \{E,1|2/3,1/3,0,1/3\} \\ \mathbf{ct}_2 & \{E,1|1/3,2/3,0,2/3\} \end{cases}$$

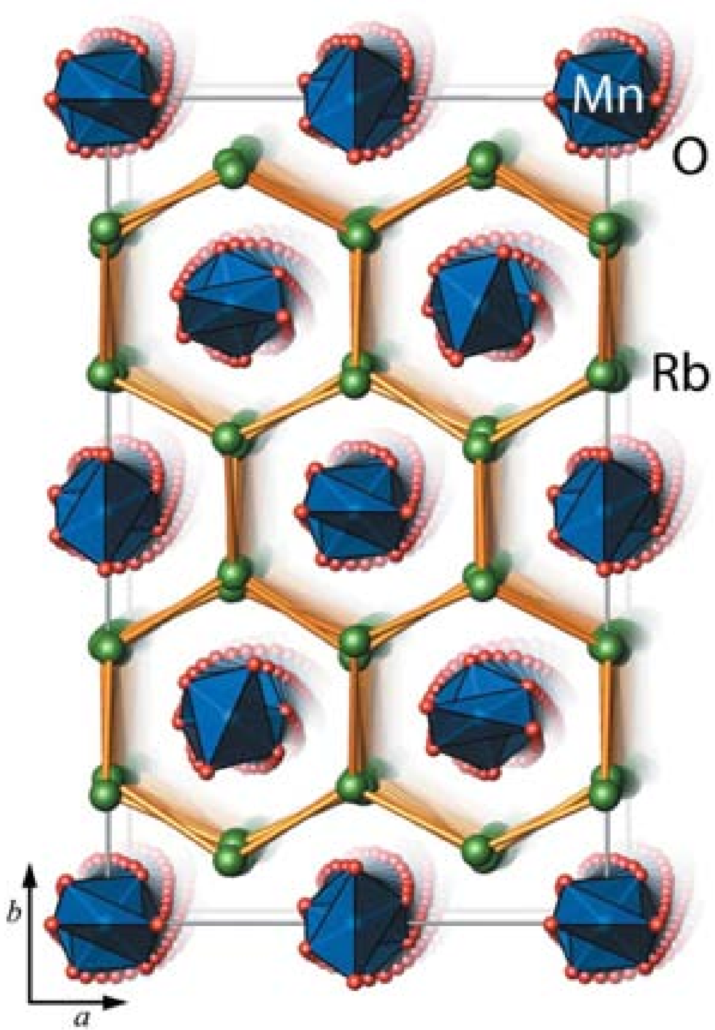
$$\begin{cases} R_s^{\nu} = W^{\nu} R_s \left(W^{\nu}\right)^{-1} \\ \mathbf{v}_{\nu s} = W^{\nu} \mathbf{v}_s \end{cases}$$

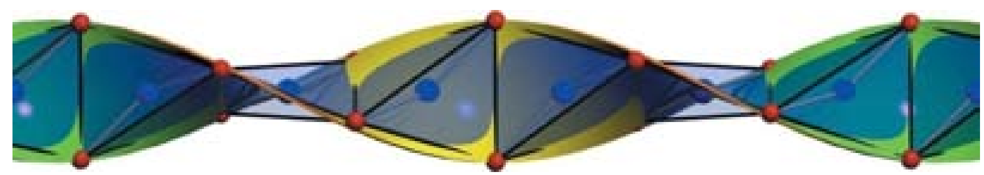
$$\mathbf{W}^2 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}$$

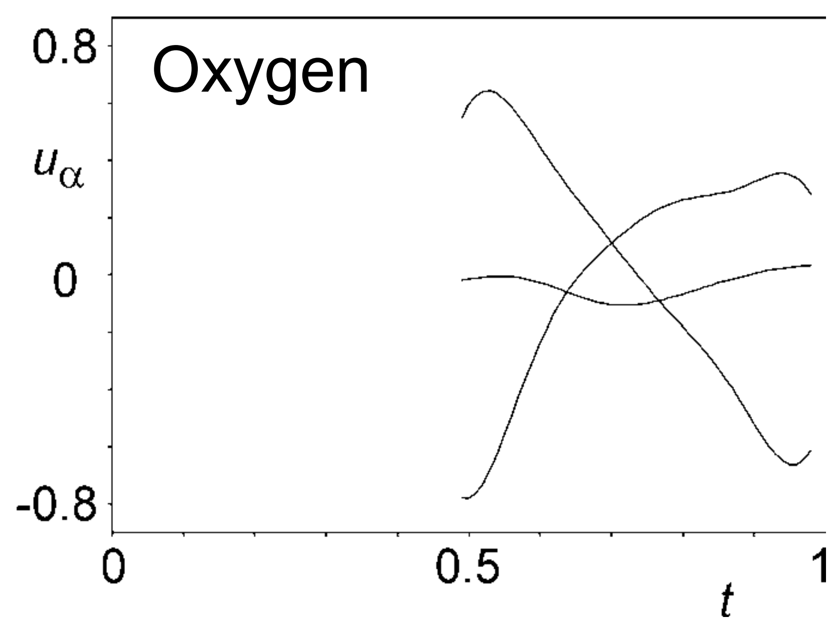
$$G_s^2 = P\bar{3}1c(00\gamma')000$$

$$G_s^2 = H'\bar{3}c1(00\gamma')000$$

Very large modulations in $[Rb]_x[MnO_2]$

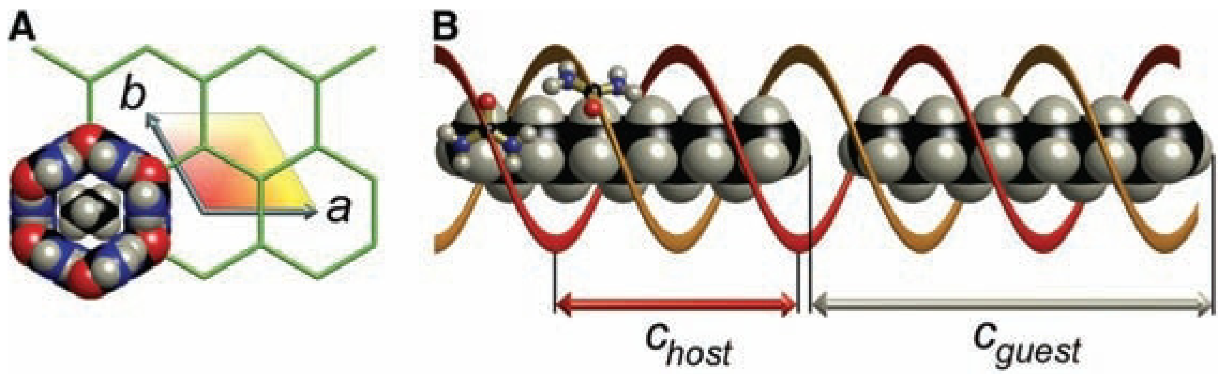






J. Nuss, S. Pfeiffer, S. van Smaalen & M. Jansen, Acta Crystallogr. B **66**, 27–33 (2010)

Sliding mode and phasons



Relative shift of subsystems ⇔ phase shift of modulation (*t*)

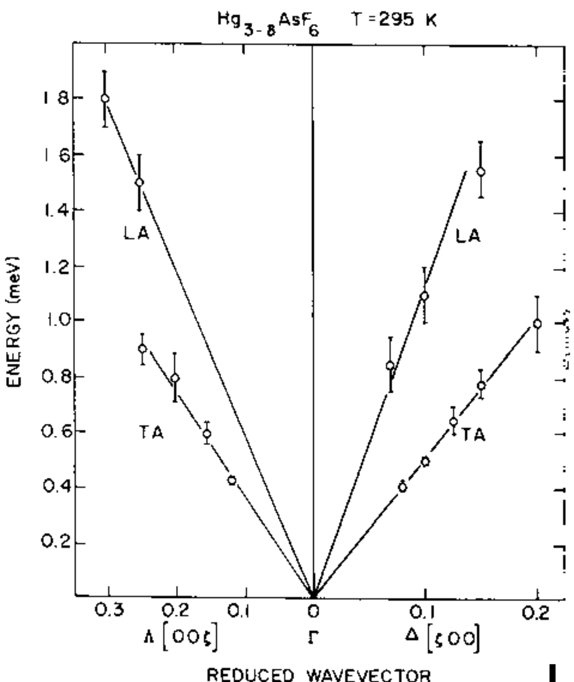
All states have equal energy ⇒ sliding or phason mode

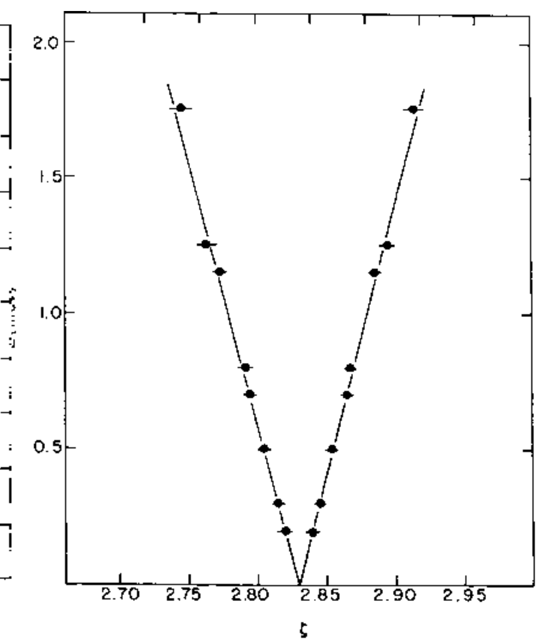
But: Pinning to surfaces and impurities

And: finite damping ⇒ low-energy modes are overdamped

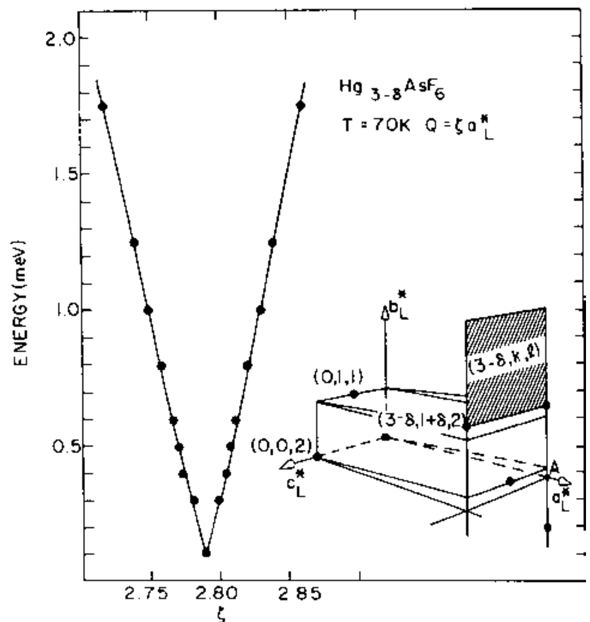
B. Toudic *et al.,* Science **319**, 69-71 (2008)

Sliding mode in $[Hg]_{3-\delta}[AsF_6]$ observed by inelastic neutron scattering





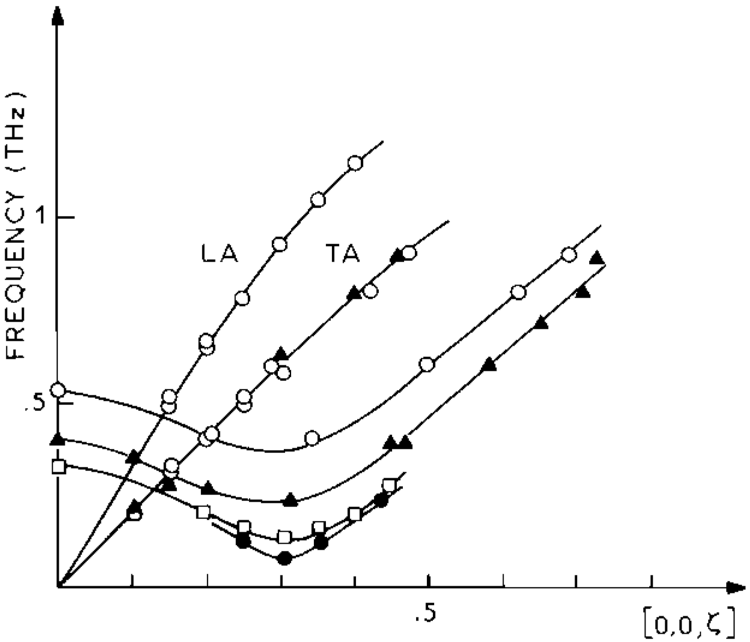
HT

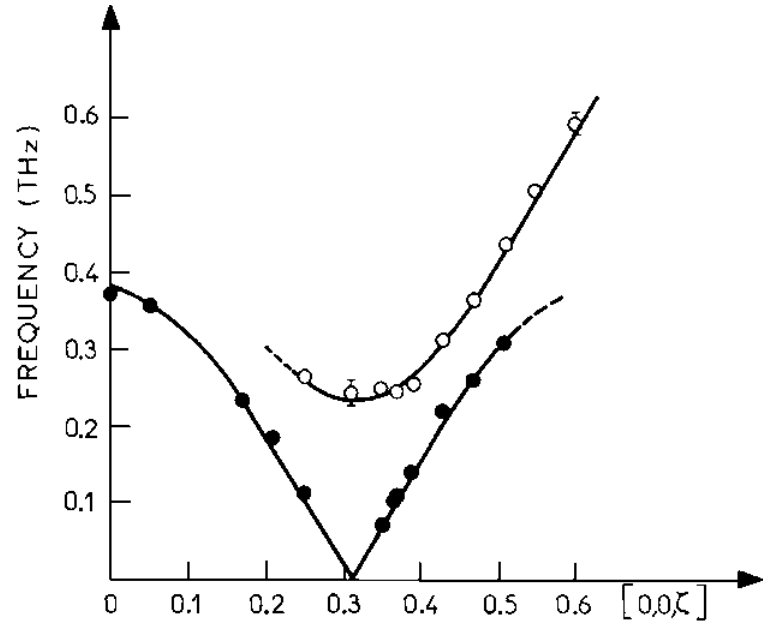


LT

I.U. Heilmann *et al.*, Phys. Rev. B **20**, 751 (1979)

Phason mode in $ThBr_4$



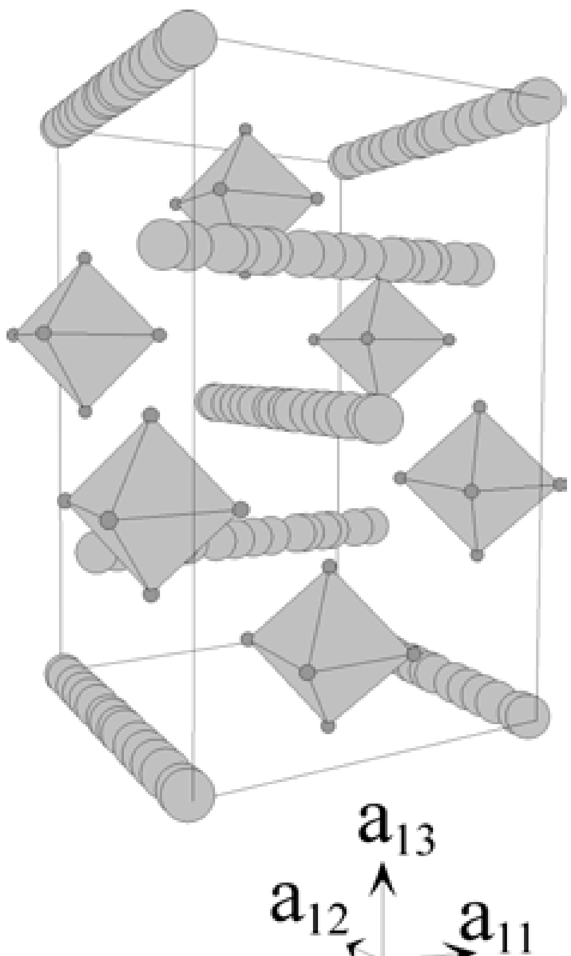


$$\omega_\phi^2 = \eta^2 + v_\phi^2 (\delta q)^2 \qquad \eta = 0 \quad \text{phason}$$

$$\omega_A^2 = \omega_0^2 + v_\phi^2 (\delta q)^2 \qquad \text{amplitudon}$$

R. Currat, L. Bernard & P. Delamoye (1986)

Composite crystal $[Hg]_{3-\delta}[AsF]_6$ ($\delta = 0.18$)



T > 120 K $I4_1/amd$

a=7.5 Å c = 12.4 Å

(2+1)D-order of the Hg chains

$3\times d$(Hg-Hg) = 7.9 Å

T < 120 K

AsF_6 *Fddd*

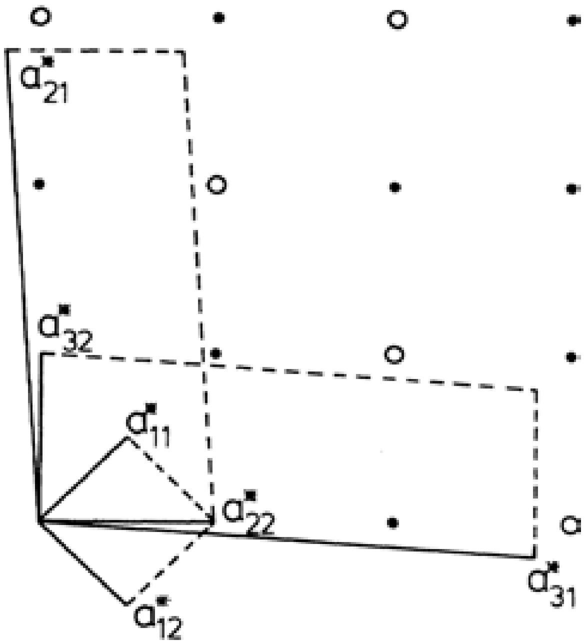
Hg ($\nu = 2$) *I2/m*

Hg ($\nu = 3$) *I2/m*

I. D. Brown *et al.*, Can. J. Chem. **52**, 791 (1974)

Pouget *et al.*, Phys. Rev. B **18**, 3645 (1978)

$[Hg]_{3-\delta}[AsF_6]$ in superspace—*Fddd*(α 0 0)00s



$\mathbf{a}_1^* = \mathbf{a}_{11}^*$

$\mathbf{a}_2^* = \mathbf{a}_{12}^*$

$\mathbf{a}_3^* = \mathbf{a}_{13}^* = \mathbf{a}_{23}^* = \mathbf{a}_{33}^*$

$\mathbf{a}_4^* = -2\delta\, \mathbf{a}_1^*$

$$W^1 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

$\alpha = -2\delta$

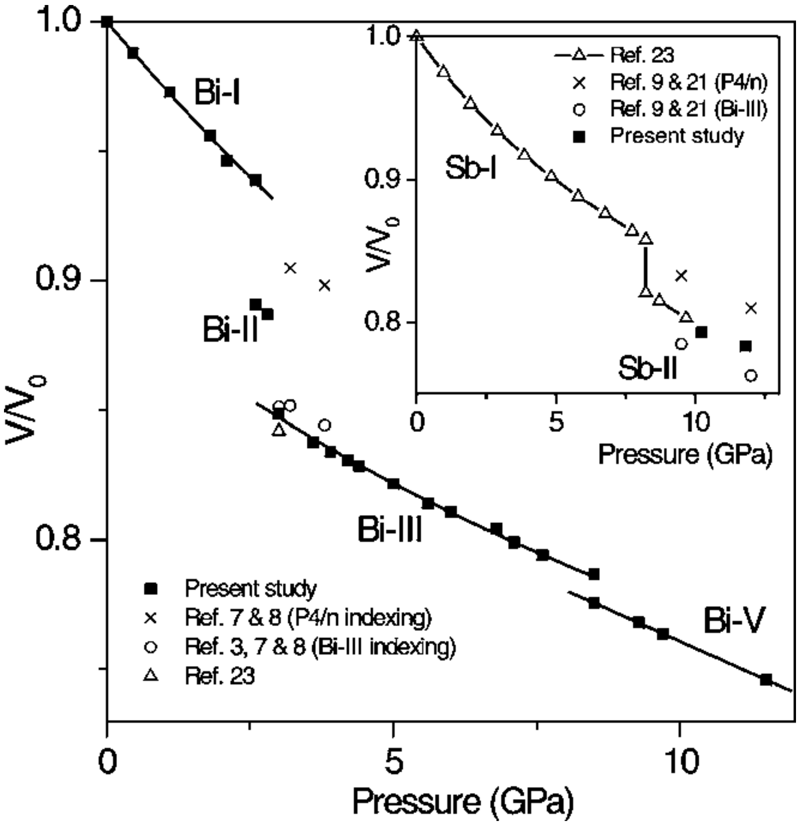
$$W^2 = \begin{pmatrix} 3 & \bar{3} & 0 & 1 \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 2 & 0 & 0 \end{pmatrix} \quad W^2 = \begin{pmatrix} 3 & 3 & 0 & 1 \\ 1 & \bar{1} & 0 & 0 \\ 0 & 0 & \bar{1} & 0 \\ 0 & 2 & 0 & 0 \end{pmatrix}$$

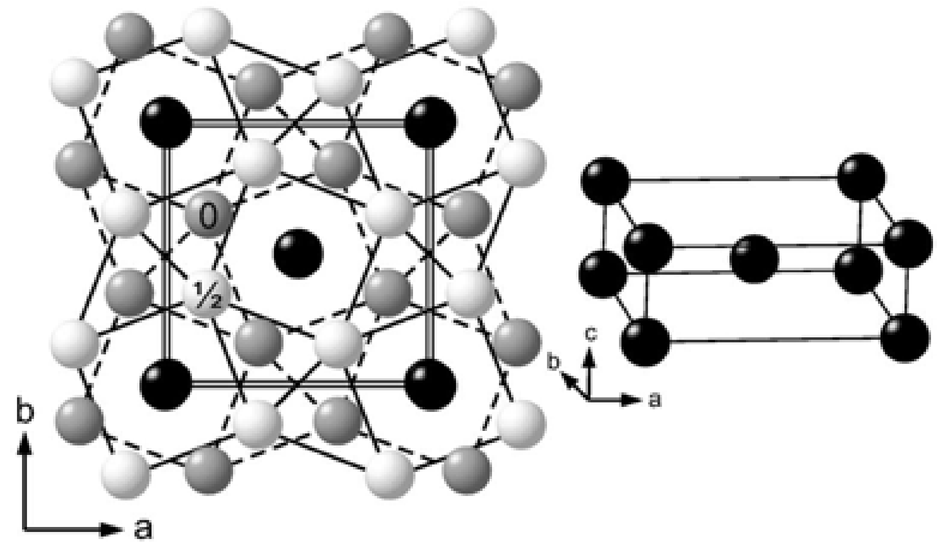
$$G_s^2 = I2/m(\alpha', 2-3\alpha', 0)0s$$

$$\alpha' = 1/(3-\delta)$$

S. van Smaalen, Phys. Rev. B **43**, 11330 (1991)

High-pressure phase III of Bi at p = 5.5 GPa





Tetragonal

I4/mcc

a = 8.56 Å

c_1 = 4.18 Å

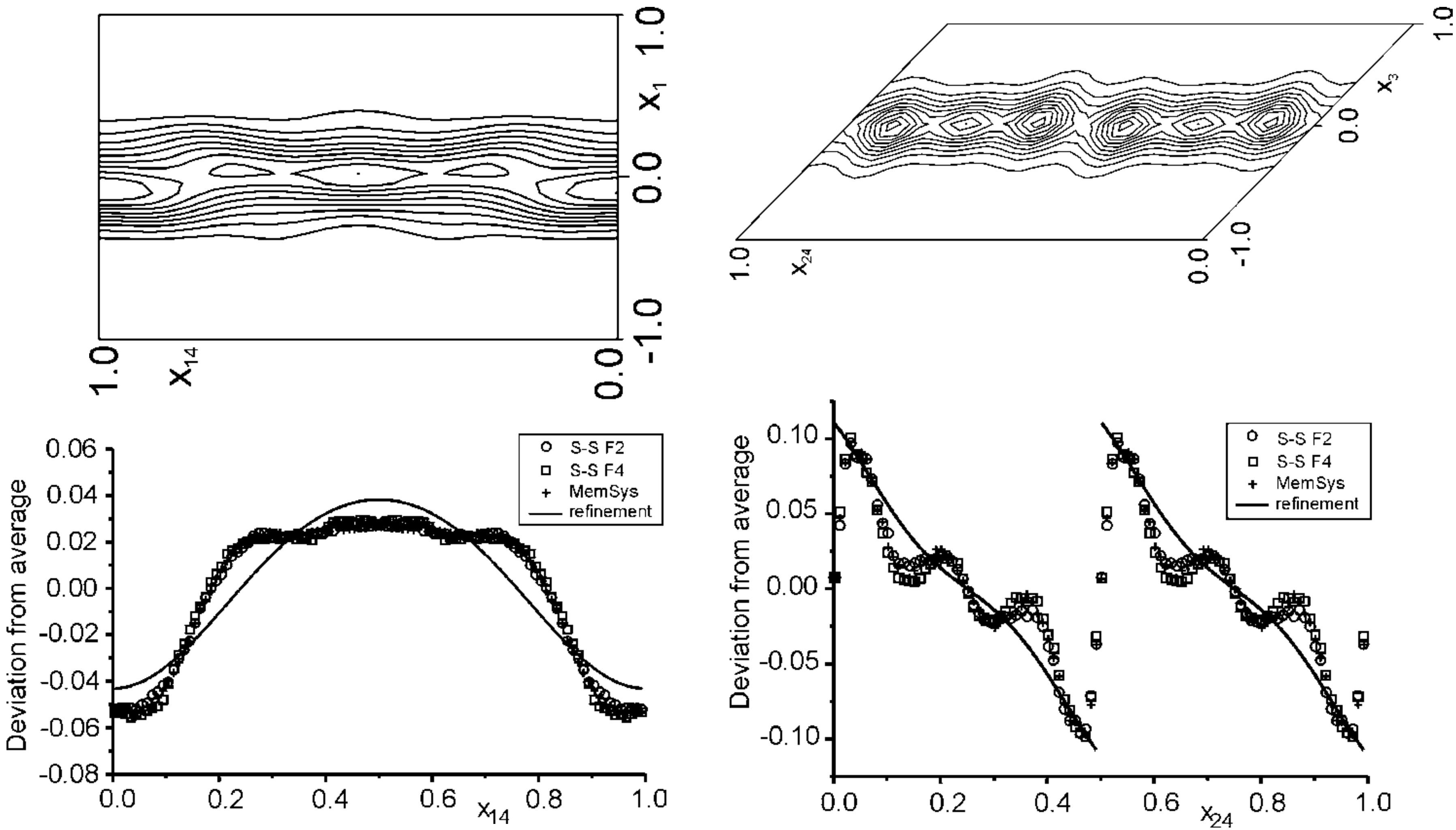
c_2 = 3.19 Å

$[Bi]_x[Bi]$

$x = 4c_2/c_1 = 3.05$

McMahon *et al.* (2000) PRL **85**, 4896

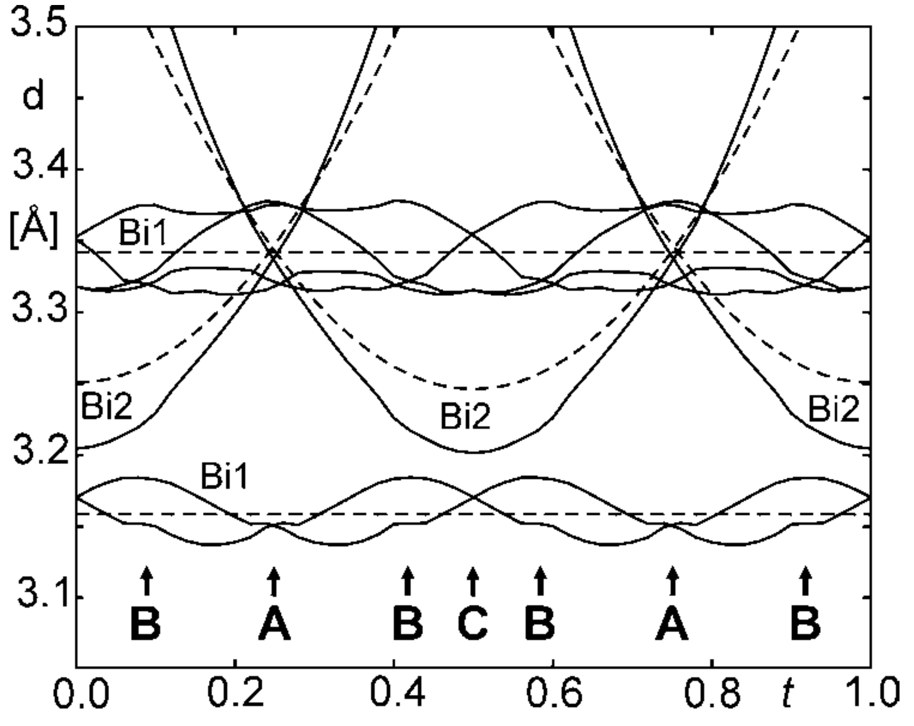
MEM electron density of Bi-III in superspace

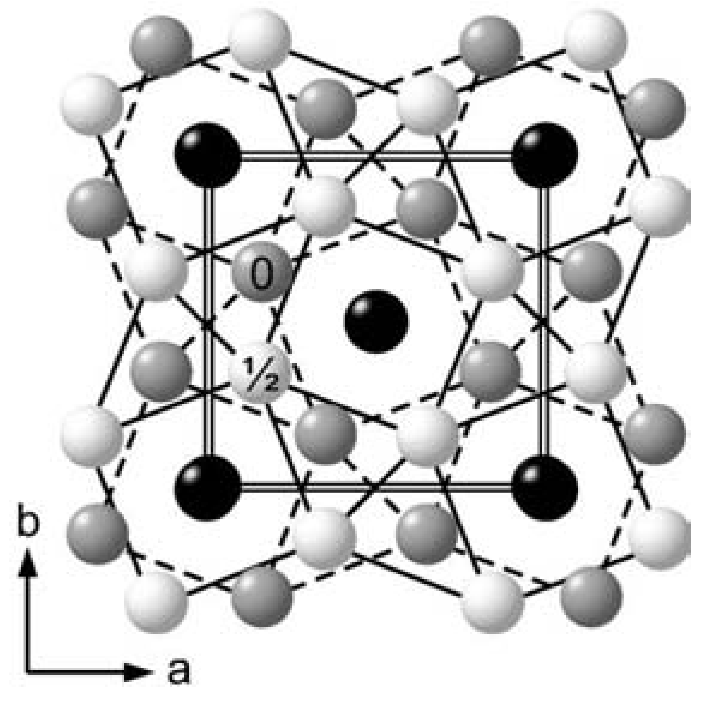


Bi1 Bi2

McMahon, Degtyareva, Nelmes, van Smaalen & Palatinus, Phys. Rev. B **75**, 184114 (2007)

Coordination of Bi1 host atoms in Bi-III



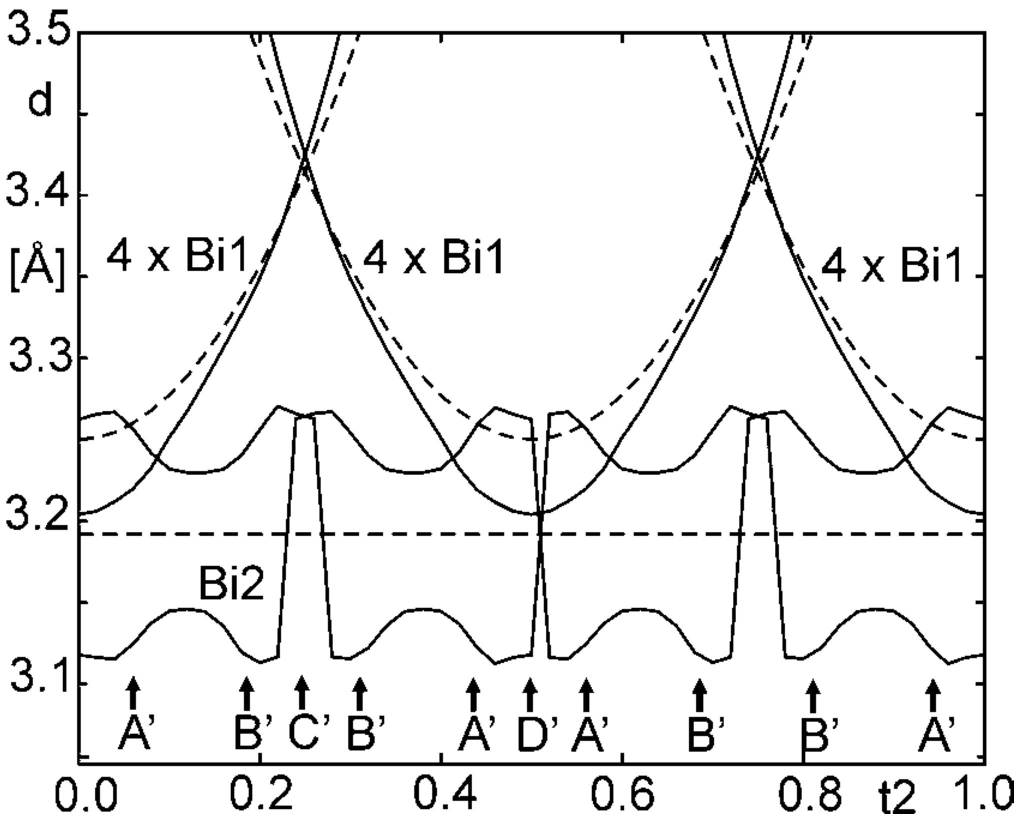


Distances around Bi1

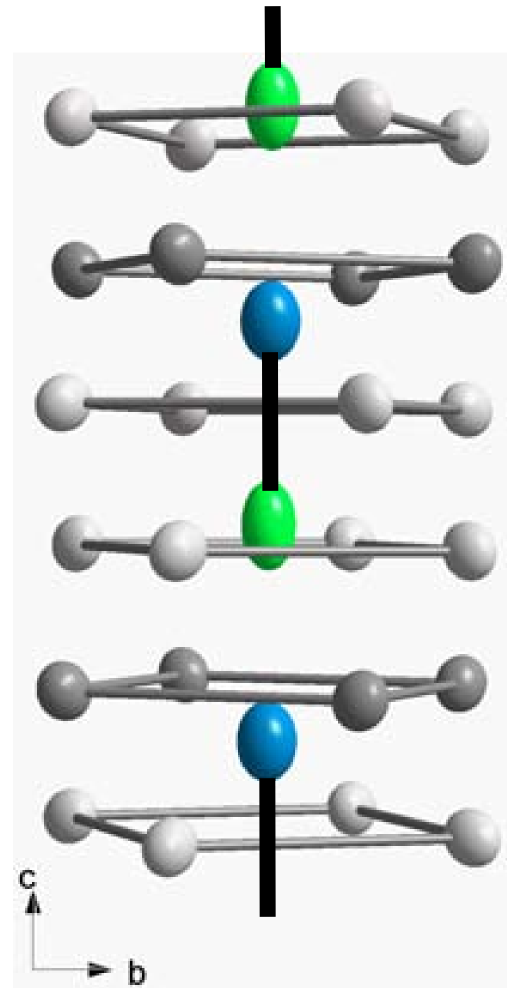
Increased inter-subsystem bonding

McMahon, Degtyareva, Nelmes, van Smaalen & Palatinus, Phys. Rev. B **75**, 184114 (2007)

Quasi dimers of Bi2 guest atoms in Bi-III



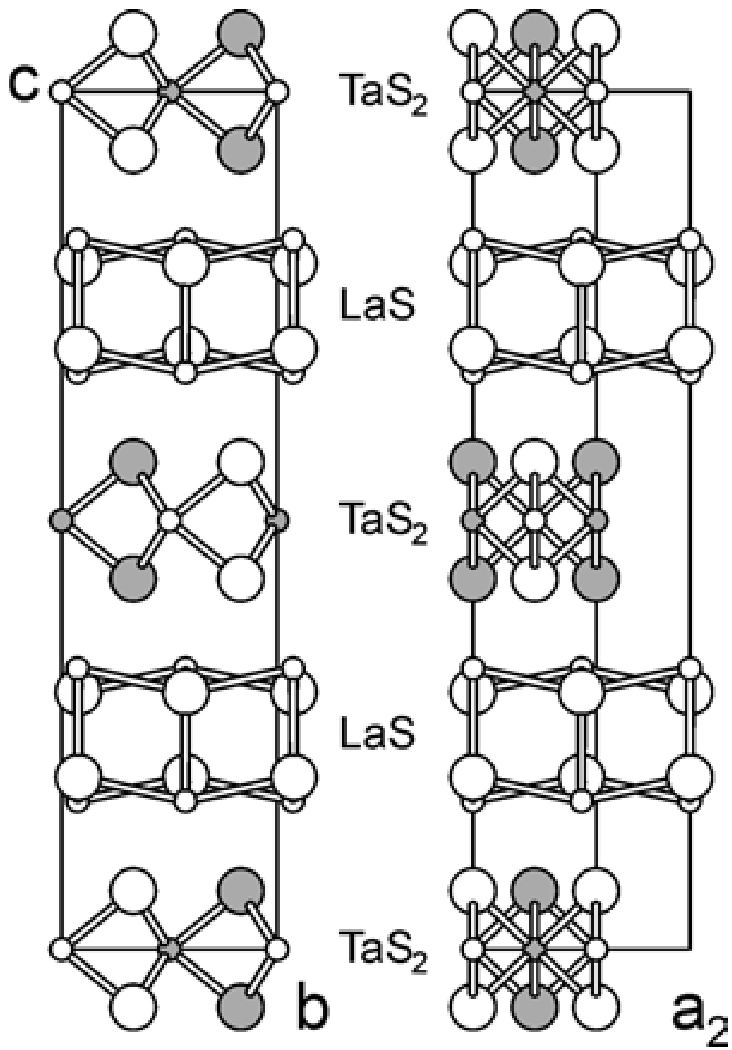
Distances around Bi2



$4c_g/c_h = 3.05$

McMahon, Degtyareva, Nelmes, van Smaalen & Palatinus, Phys. Rev. B **75**, 184114 (2007)

X-ray diffraction data for $[LaS]_{1.13}[TaS_2]$



X-ray diffraction (*h k l m*)

Up to second-order satellites

$[\sin(\theta)/\lambda]_{max} = 1.0$ Å^{-1}

F'm2m(α 0 0)00s

A. Jobst and S. van Smaalen, Acta Cryst. B **58**, 179 (2002)

Structure refinements of $[LaS]_{1.13}[TaS_2]$

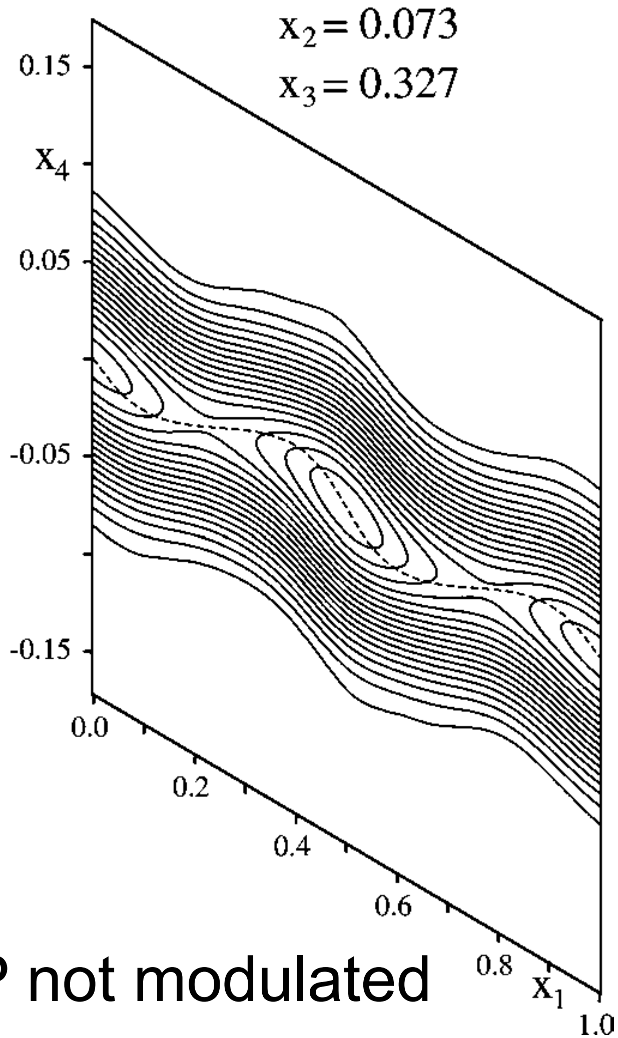
	Displacement modulation	**Modulated ADPs**
Refl. group	**R**	**R**
All	0.062	0.046
Main	0.039	0.034
Sat m=1	0.167	0.103
Sat m=2	0.206	0.128
$(\Delta\rho)_{max}$	73	12

Principal modulation on La: 0.1 Å

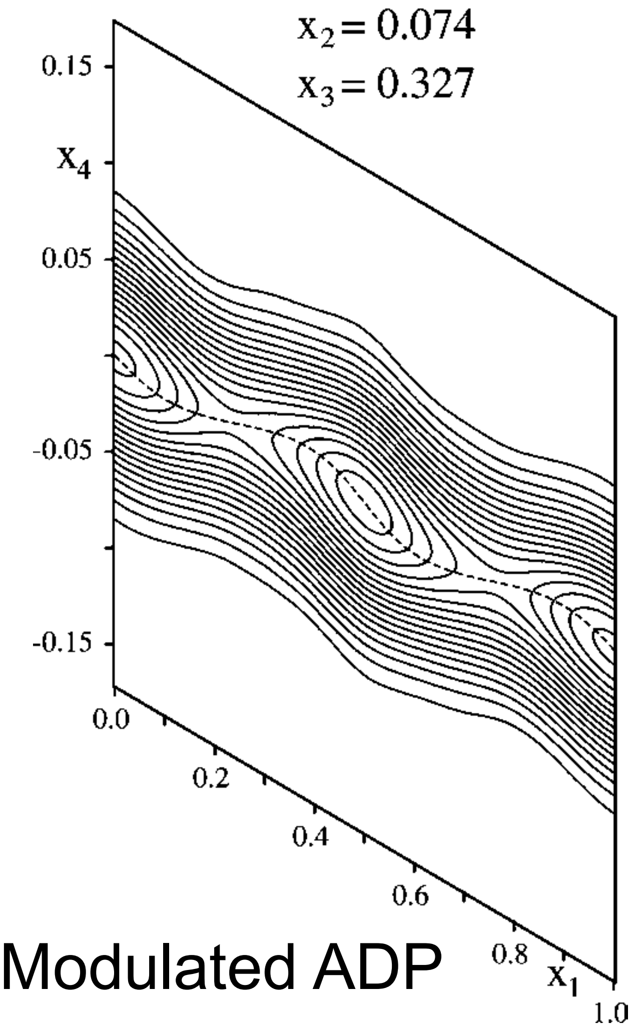
Secondary modulation on S1 and S2 : 0.05 Å

A. Jobst and S. van Smaalen, Acta Cryst. B **58**, 179 (2002)

Fourier map of $[LaS]_{1.13}[TaS_2]$

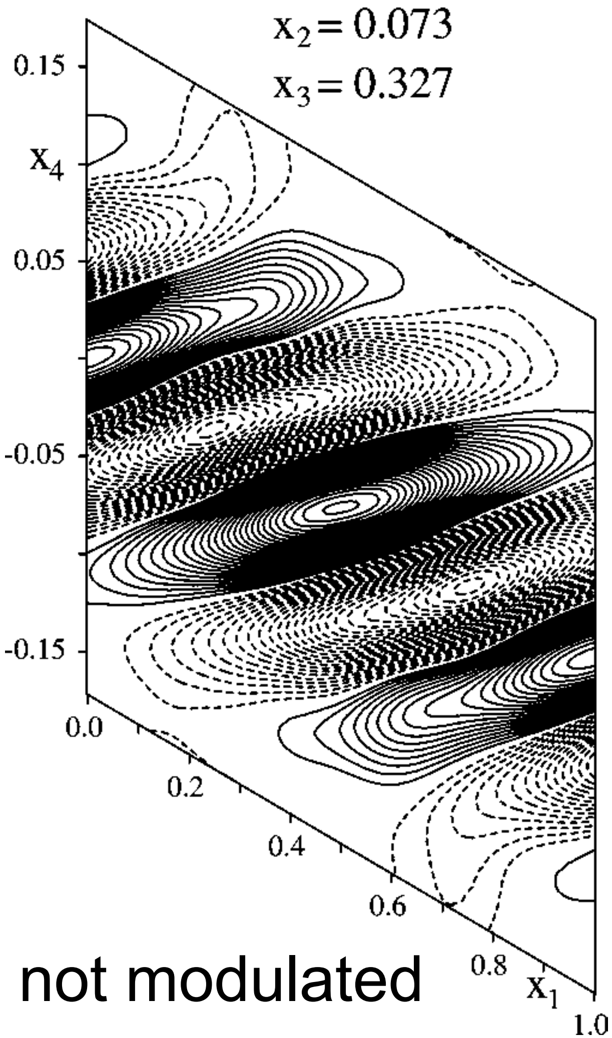


ADP not modulated

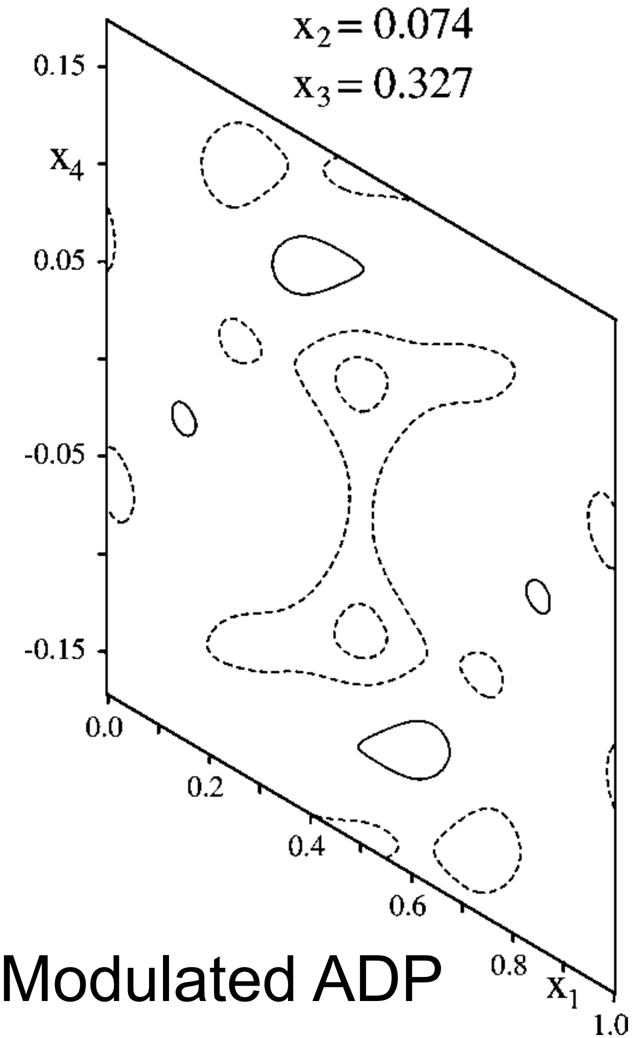


Modulated ADP

Difference Fourier map of $[LaS]_{1.13}[TaS_2]$

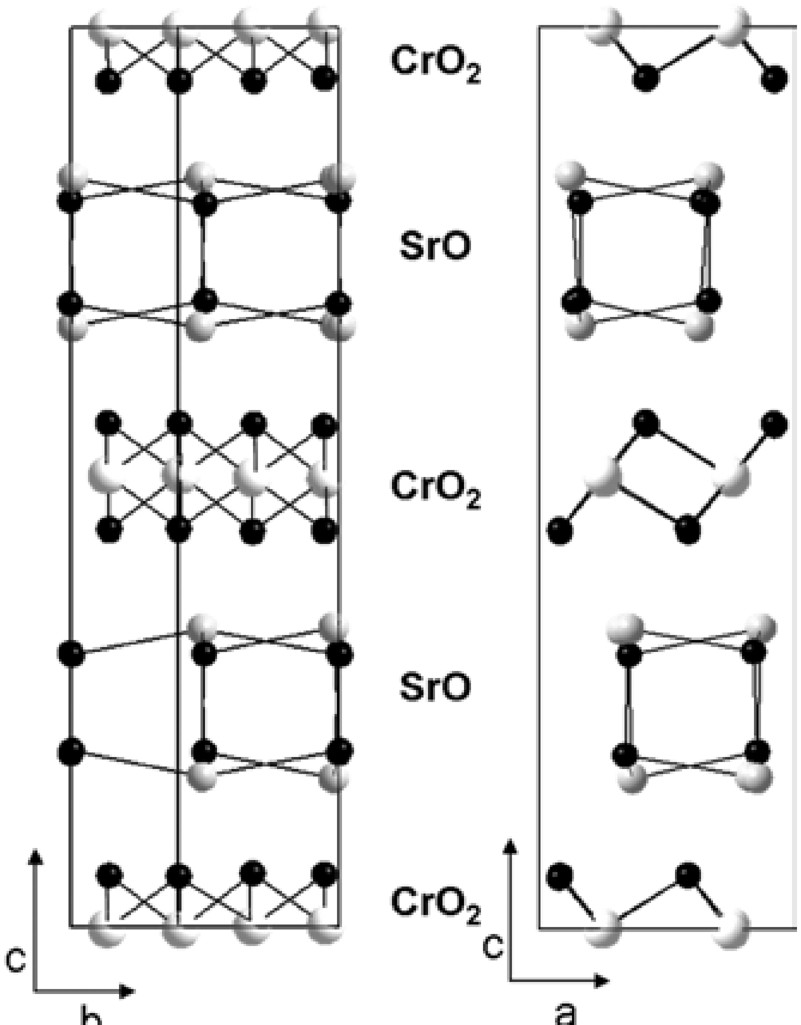


ADP not modulated



Modulated ADP

Misfit layer structure of $[SrO]_2[CrO_2]_{1.85}$



$[SrO]_{1.08}[CrO_2]$

Collaboration with M.A. Alario-Franco (University Complutense, Madrid); PhD-thesis work E. Castillo-Martinez.

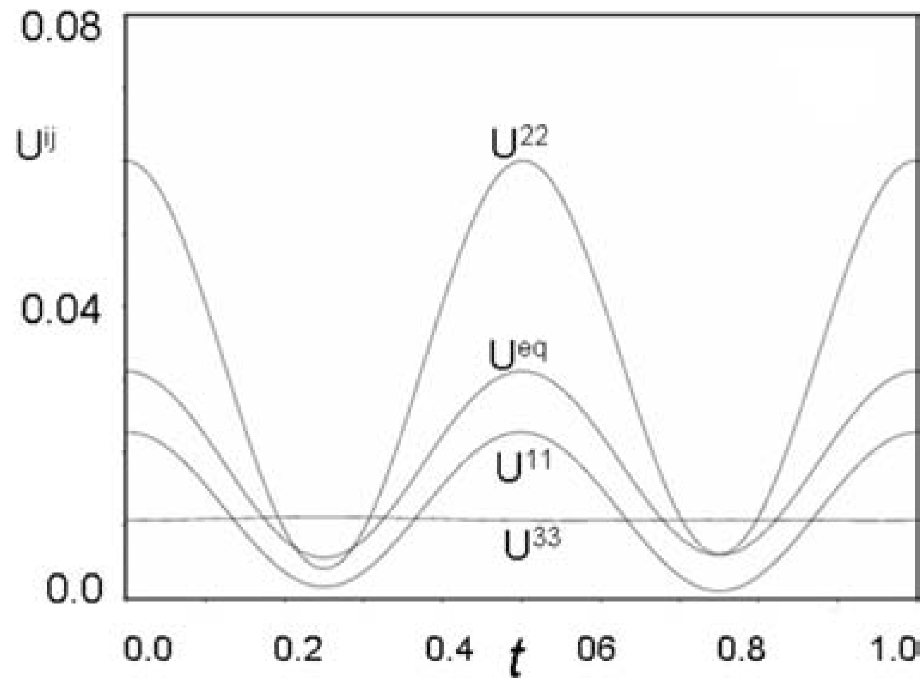
Similar to misfit layer sulfides.

Better crystal quality than misfit layer cobaltites.

E. Castillo-Martinez *et al.*, J. Sol. Stat. Chem. **181**, 1840 (2008)

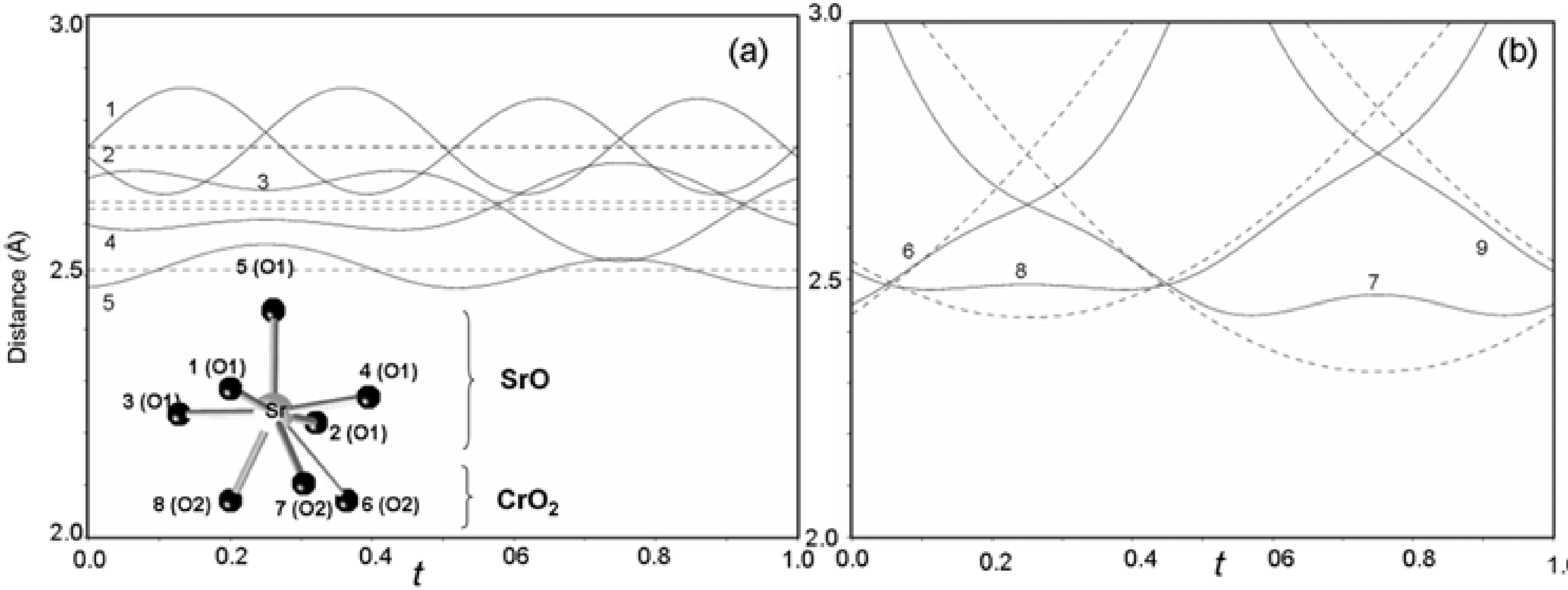
Modulated ADPs of Sr in of $[SrO]_2[CrO_2]_{1.85}$

Refl. group	#Refl.	R_F(obs)
All	778	0.044
Main	473	0.042
SrO–main	271	0.044
CrO2–main	136	0.048
Common	66	0.030
Sat m=1	248	0.044
Sat m=2	57	0.088



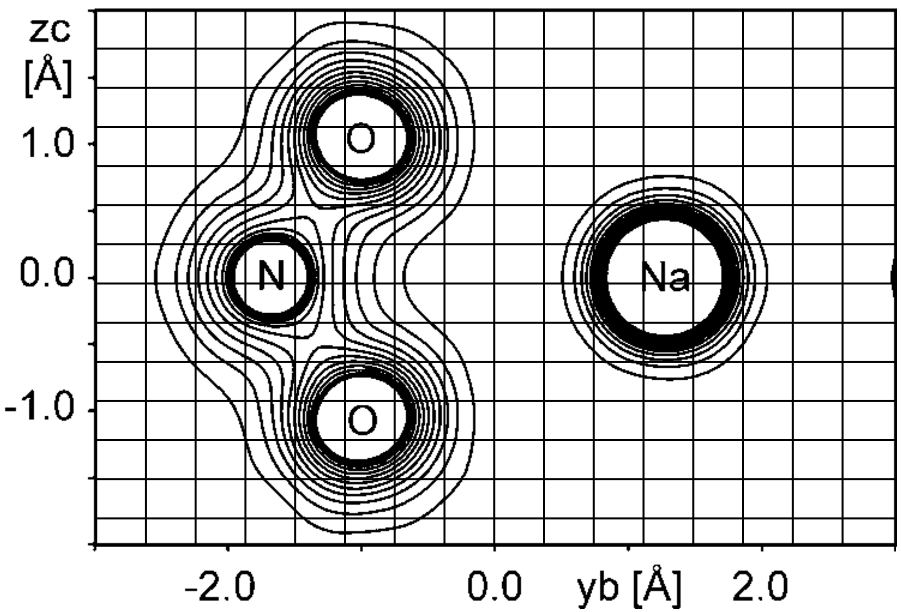
E. Castillo-Martinez *et al.*, J. Sol. Stat. Chem. **181**, 1840 (2008)

Environment of Sr in of $[SrO]_2[CrO_2]_{1.85}$



E. Castillo-Martinez *et al.*, J. Sol. Stat. Chem. **181**, 1840 (2008)

The Maximum Entropy Method (MEM)



ρ_k Electron density

τ_k Prior density

$N_1 \times N_2 \times N_3$ Grid

Entropy: $$S = \sum_{k=1}^{N_{pix}} \rho_k \ln\left(\rho_k / \tau_k\right)$$

Constraint: $$\frac{1}{N_F} \sum_{h,k,l} w_{hkl} \, | F_{MEM}(h,k,l) - F_{obs}(h,k,l) |^2 = 1$$

The computer program BayMEM

Various choices of PRIOR density

Various choices of Constraints

Sakata-Sato and Cambridge algorithms

MEM calculations in (3+*d*) dimensional superspace

$N_{pix} = N_1 \times \ldots \times N_{3+d}$ pixels

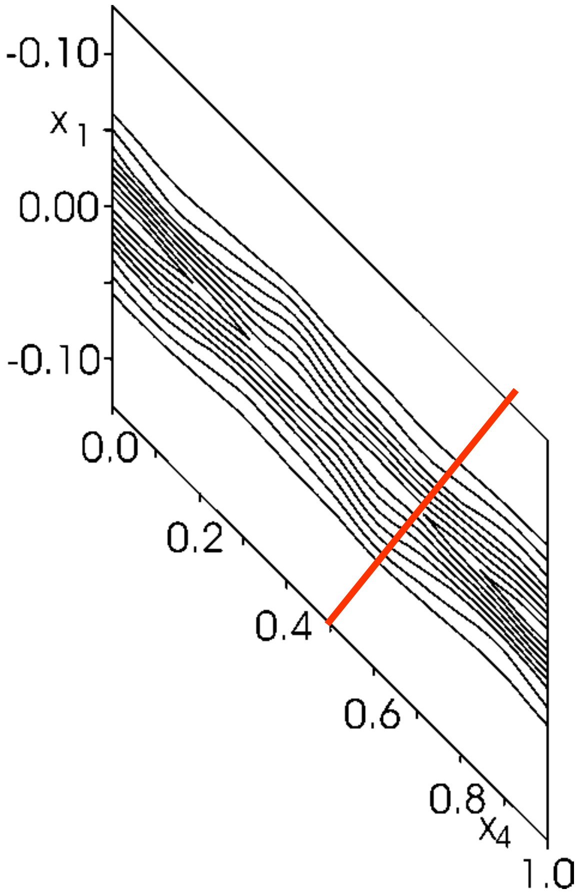
Periodic crystals correspond to $d = 0$

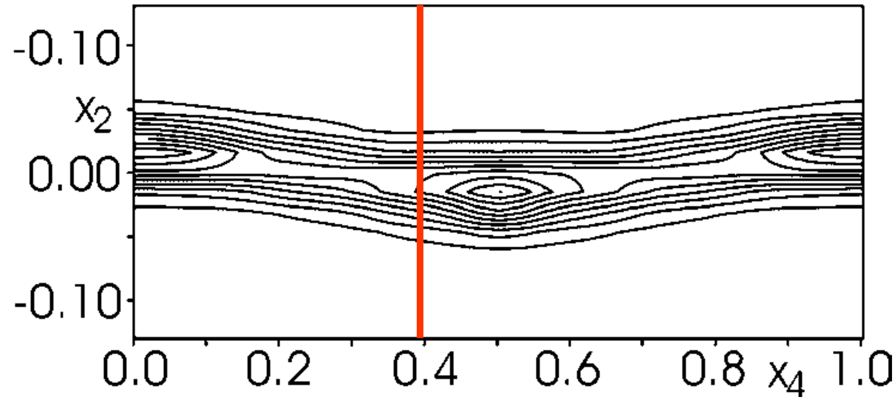
Full (super-)space group symmetry

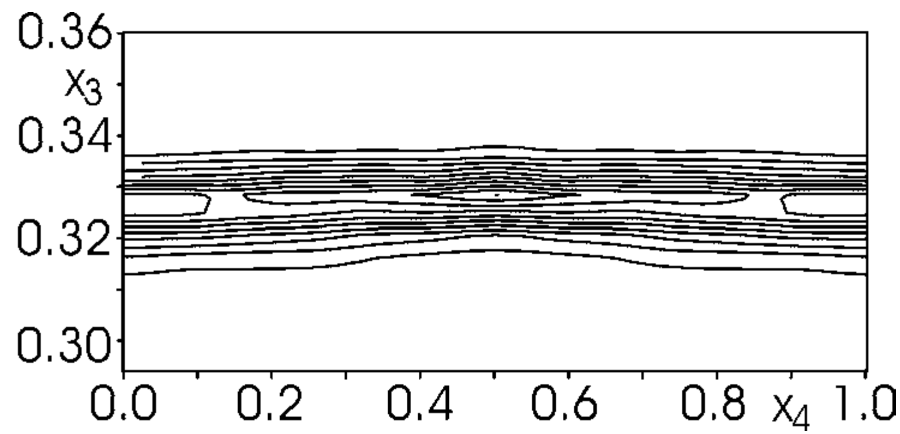
Fast Fourier Transform (FFT) in arbitrary dimensions

S. van Smaalen, L. Palatinus & M. Schneider, Acta Crystallogr. A **59**, 459 (2003)

Maximum Entropy Method on $[LaS]_{1.14}[NbS_2]$



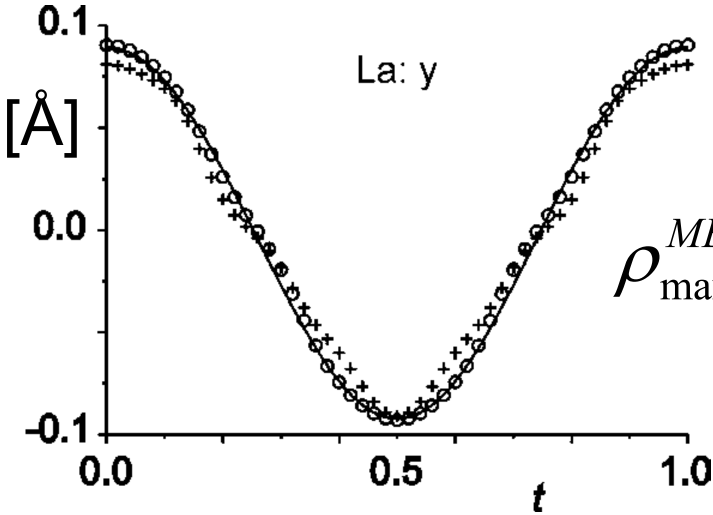




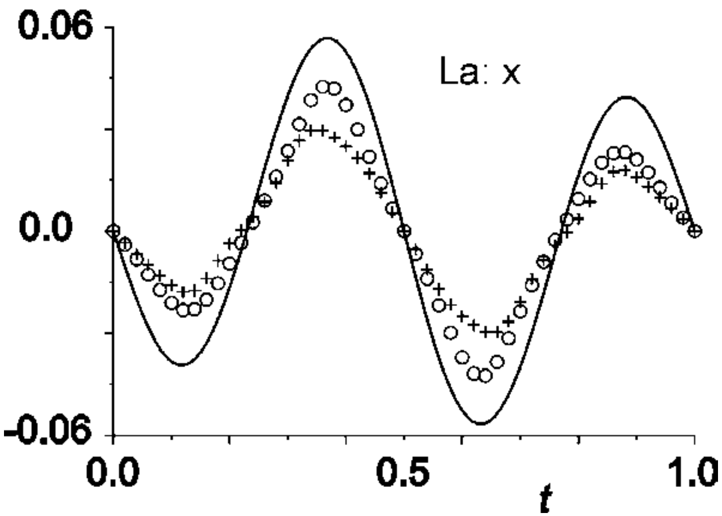
Software BayMEM. Pixels: 32 × 64 × 256 × 32

S. van Smaalen, L. Palatinus & M. Schneider, Acta Crystallogr. A **59**, 459 (2003)

Displacement modulation of $[LaS]_{1.14}[NbS_2]$



$$\rho_{\max}^{MEM}(t)$$



Pixels 32 x 64 x 256 x 32

0.10 x 0.09 x 0.09 x 0.18 $Å^4$

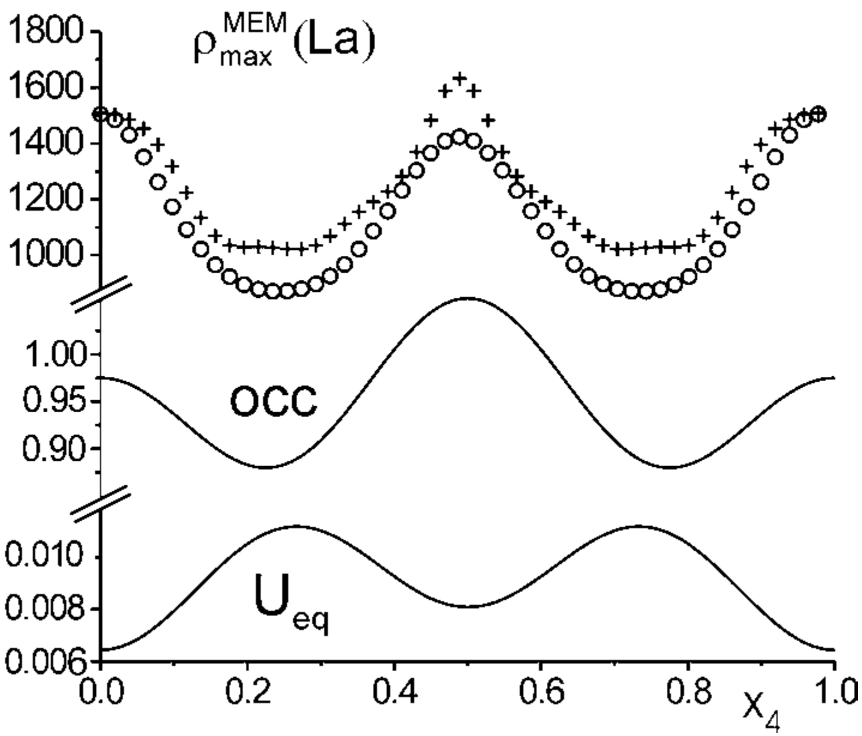
Average difference

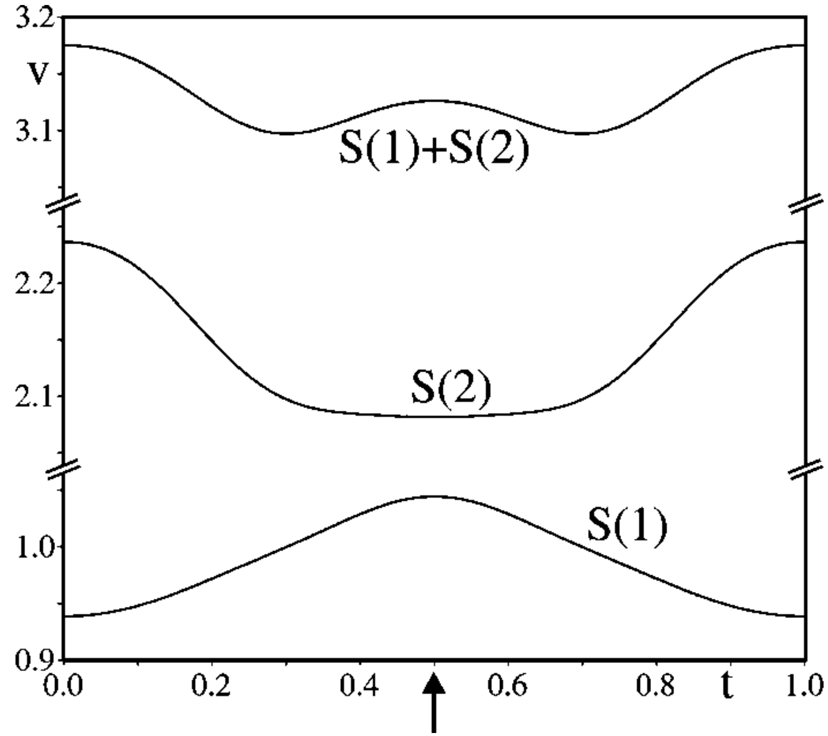
$\Delta U = (u_i - u_i^{MEM})$

	ΔU (Å)	ΔU (%)
u_x	0.012	6.7
u_x'	0.003	2.9
u_y	0.002	2.2
u_z	0.001	1.1

S. van Smaalen, L. Palatinus & M. Schneider, Acta Crystallogr. A **59**, 459 (2003)

Modulation of ADPs of $[LaS]_{1.14}[NbS_2]$





Value [e/Å³] of $\rho_{\max}^{MEM}(t)$

Valence of La

S. van Smaalen, L. Palatinus & M. Schneider, Acta Crystallogr. A **59**, 459 (2003)

Summary

Incommensurate composite crystals:

- layer type
- channel type
- columnar type

Subsystems superspace groups may not be equivalent

Subsystems equivalent by symmetry in $[Hg]_{3-\delta}[AsF_6]$

Phasons & sliding modes due to incommensurability

Modulated ADPs & modulated third-order anharmonic ADPs are an essential part of the modulation