Struktura Mg_2Al_3, układu o gigantycznej komórce elementarnej

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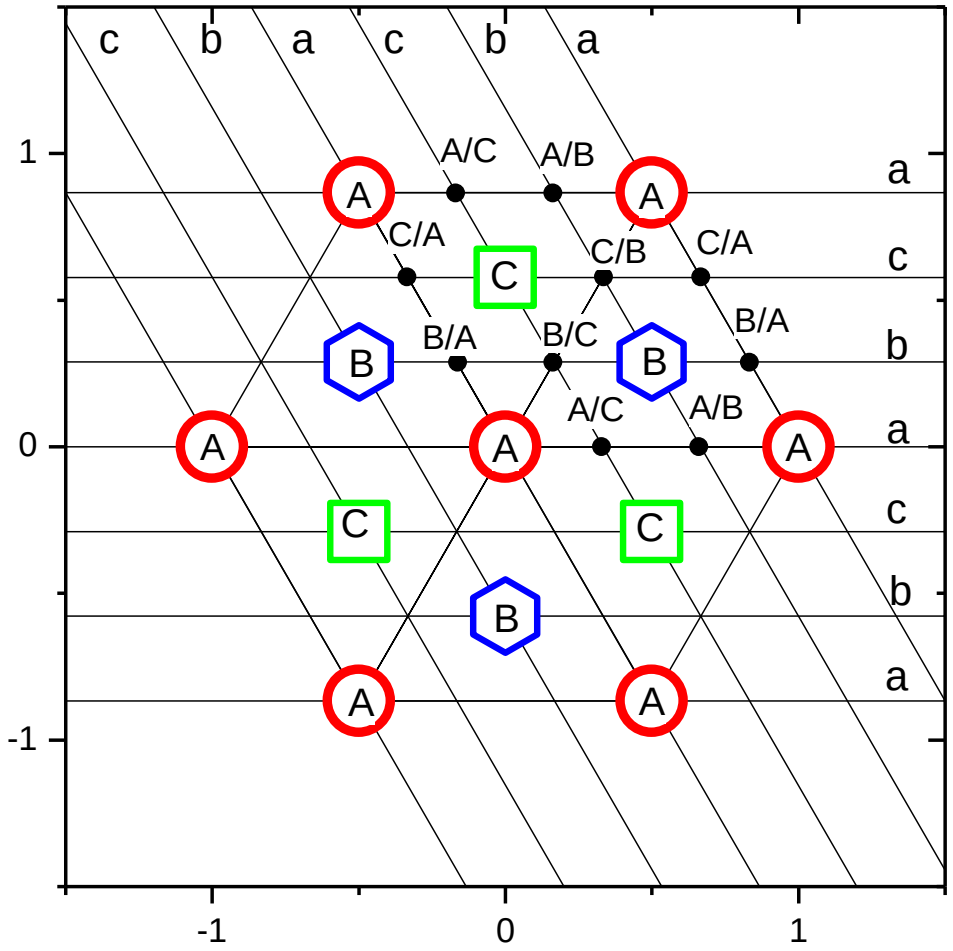
Współpraca z siecią CMA
M. Duda (doktorat), B. Kozakowski - struktura
W. Sikora, A. Bartyzel – analiza symetryczna
L. Pytlik, J. Adamowski, B. Łabno – stabilność klastrów
K. Wierzbanowski + zespół – naprężenia

Wstęp:

Jakie struktury mogą tworzyć stabilne konfiguracje dla izotropowych oddziaływań między atomami?

Struktury gęsto upakowane w D2 - warstwa heksagonalna



Struktury gęsto upakowane w D3

Możemy wyróżnić następujące sekwencje warstw:

- **AB** – struktura HCP,

  na heksagonalną komórkę elementarną przypadają dwa węzły w pozycjach (0,0,0) oraz (2/3,1/3,1/2); c/a = 1.633, np. struktura Mg …..
  Inwersja nie jest elementem symetrii węzłów sieci.

- **ABC** – struktura FCC,

  na kubiczną komórkę elementarną przypadają cztery węzły sieci: (0,0,0) oraz (0,0,1/2) ….., np. struktura Cu …..
  Inwersja jest elementem symetrii każdego węzła sieci.

•**ABAC** – struktura DHCP,

na heksagonalną komórkę elementarną przypadają cztery węzły sieci. Dla dwóch węzłów lokalna symetria zawiera inwersję (są to tzw. węzły kubiczne) a dla pozostałych dwóch węzłów inwersja nie jest elementem symetrii lokalnej (są to tzw. węzły heksagonalne). Rozróżnienie symetrii lokalnej węzłów ma zasadnicze znaczenie w przypadku pojawienia się uporządkowania magnetycznego, co zostało zaobserwowane dla neodymu i prazeodymu.

•Bardziej skomplikowane sekwencje warstw (mogą być periodyczne lub aperiodyczne) – politypy.

Do opisu struktur z układu regularnego, heksagonalnego i romboedrycznego stosujemy współrzędne heksagonalne.

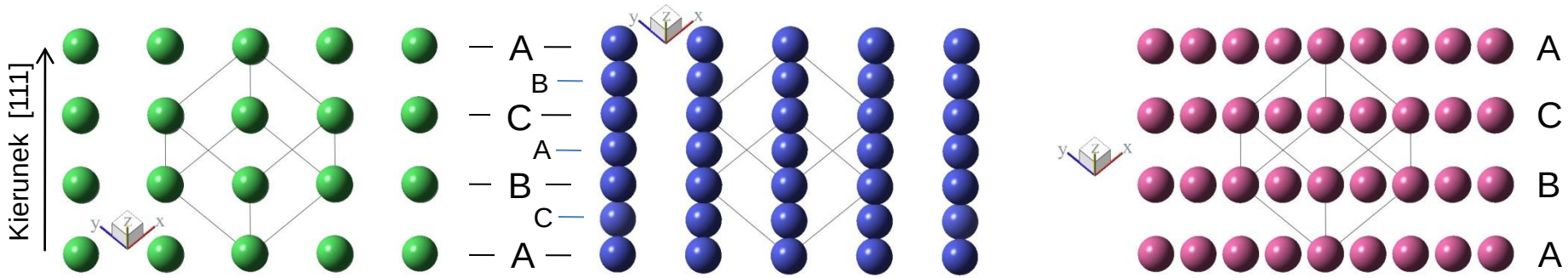
Przeliczniki:

$$a_{\mathrm{h}} = \frac{a_{\mathrm{FCC}}}{\sqrt{2}} \qquad c_{\mathrm{h}} = a_{\mathrm{FCC}}\sqrt{3} \qquad d_{\mathrm{h}} = \frac{a_{\mathrm{FCC}}}{\sqrt{3}} \qquad \frac{d_{\mathrm{h}}}{a_{\mathrm{h}}} = \sqrt{\frac{2}{3}}$$

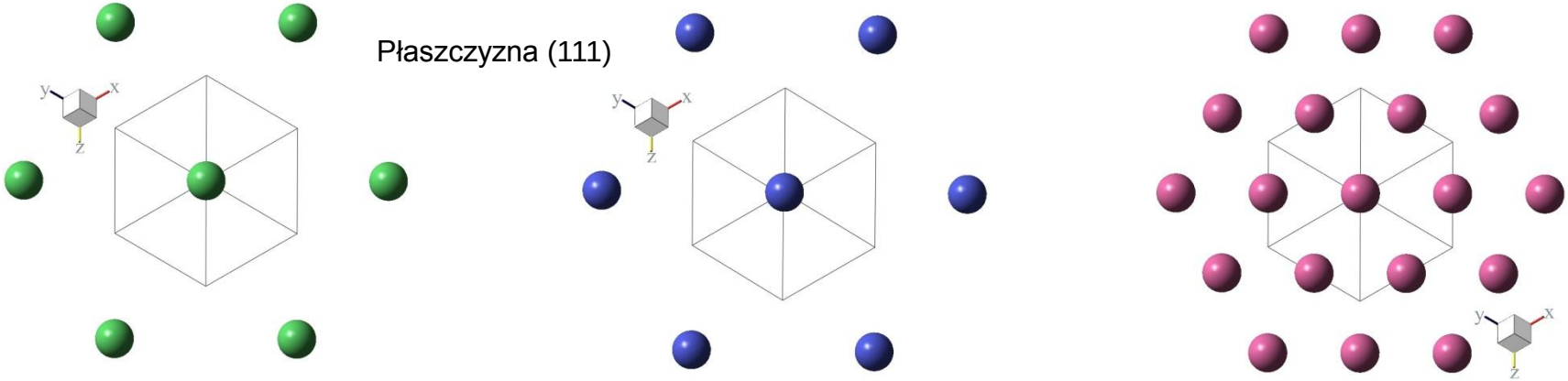
$$a_{\mathrm{h}} = \sqrt{2}a_{\mathrm{sc}} \qquad c_{\mathrm{h}} = a_{\mathrm{sc}}\sqrt{3} \qquad d_{\mathrm{h}} = \frac{a_{\mathrm{sc}}}{\sqrt{3}} \qquad \frac{d_{\mathrm{h}}}{a_{\mathrm{h}}} = \sqrt{\frac{1}{6}}$$

$$a_{\mathrm{h}} = \sqrt{2}a_{\mathrm{BCC}} \qquad c_{\mathrm{h}} = a_{\mathrm{BCC}}\sqrt{3} \qquad d_{\mathrm{h}} = \frac{a_{\mathrm{BCC}}}{2\sqrt{3}} \qquad \frac{d_{\mathrm{h}}}{a_{\mathrm{h}}} = \sqrt{\frac{1}{24}}$$

Każda sieć regularna składa się z warstw heksagonalnych: ABC



SC **BCC** **FCC**

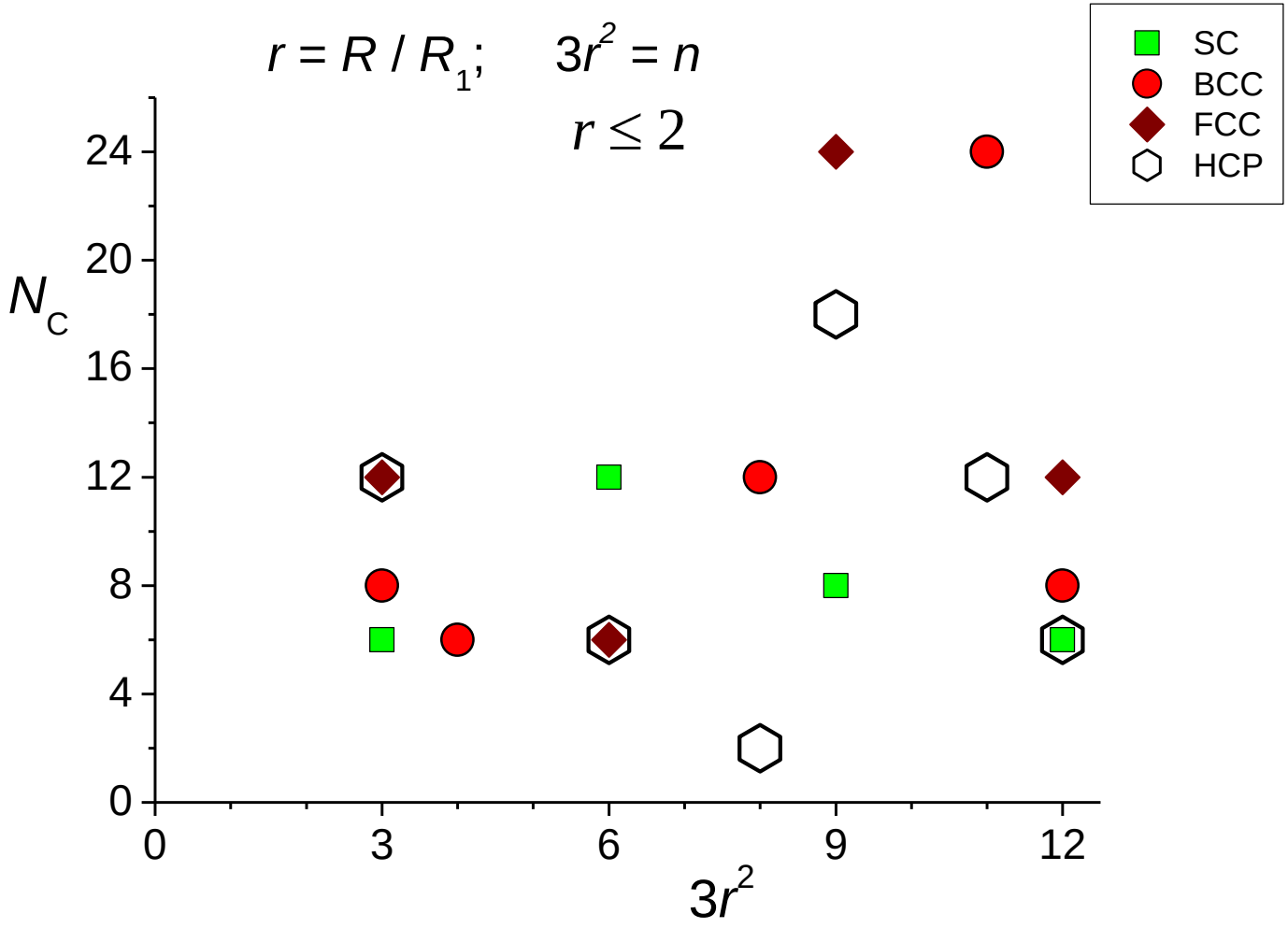


(52%, może być stabilna, np. Polon)

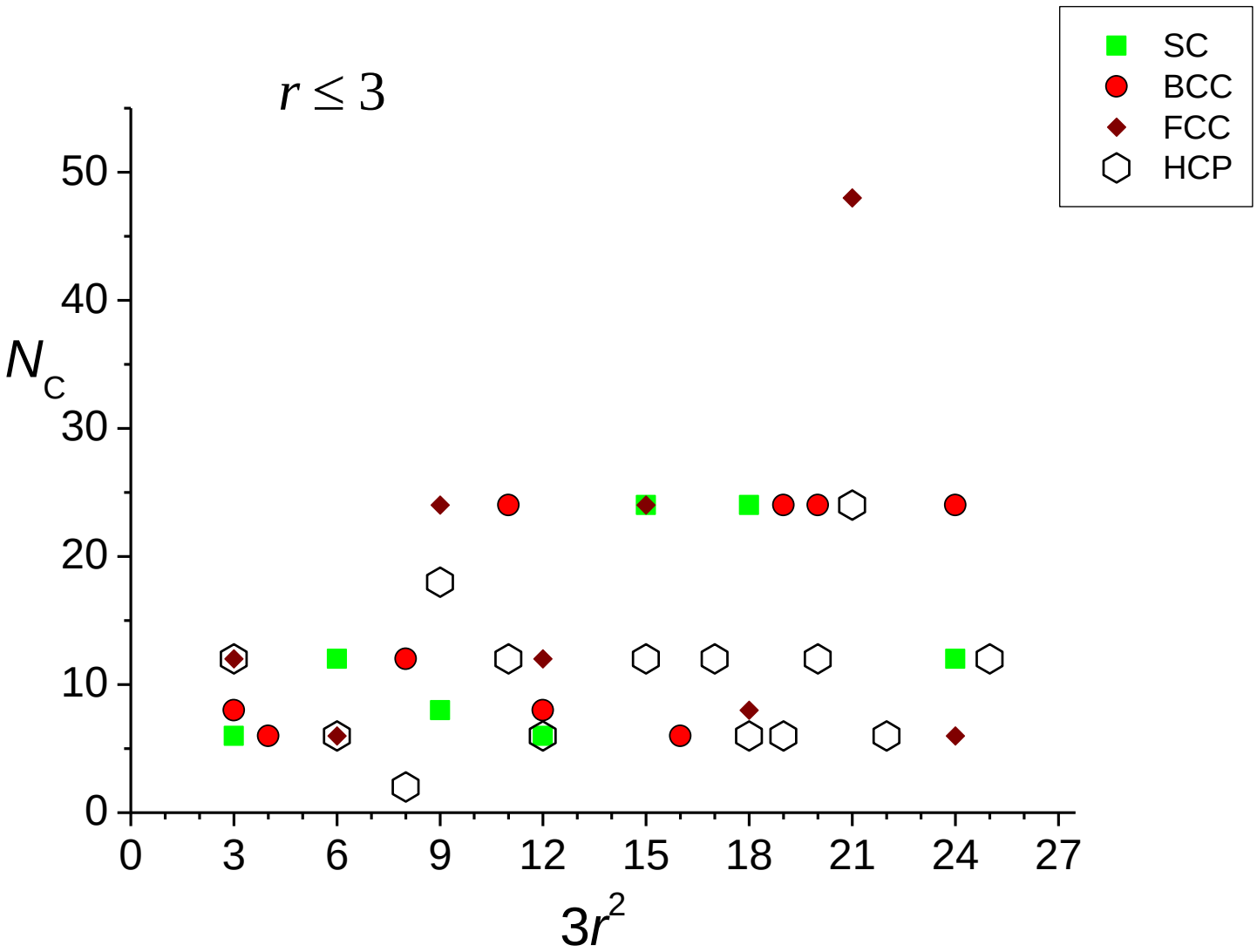
(68%, jednak energetycznie porównywalna z FCC)

(74% - struktura gęstego upakowania)

O stabilności struktury decyduje liczba kolejnych sąsiadów

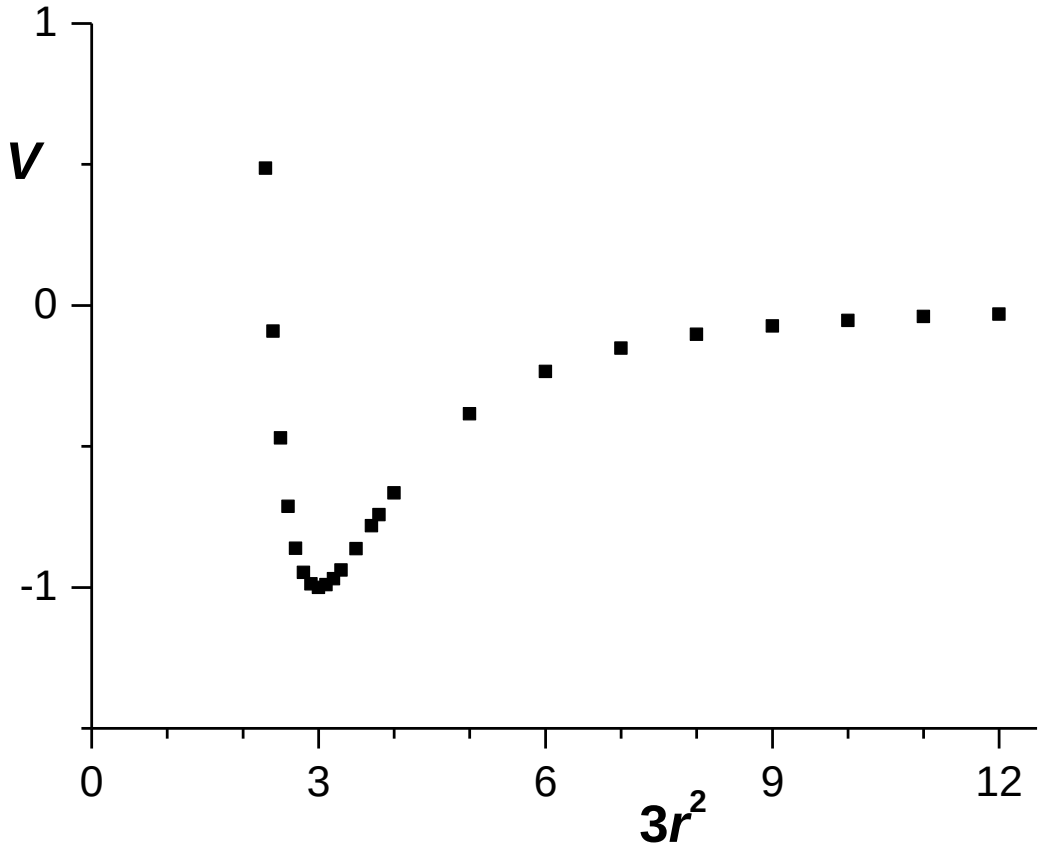


Liczba kolejnych sąsiadów

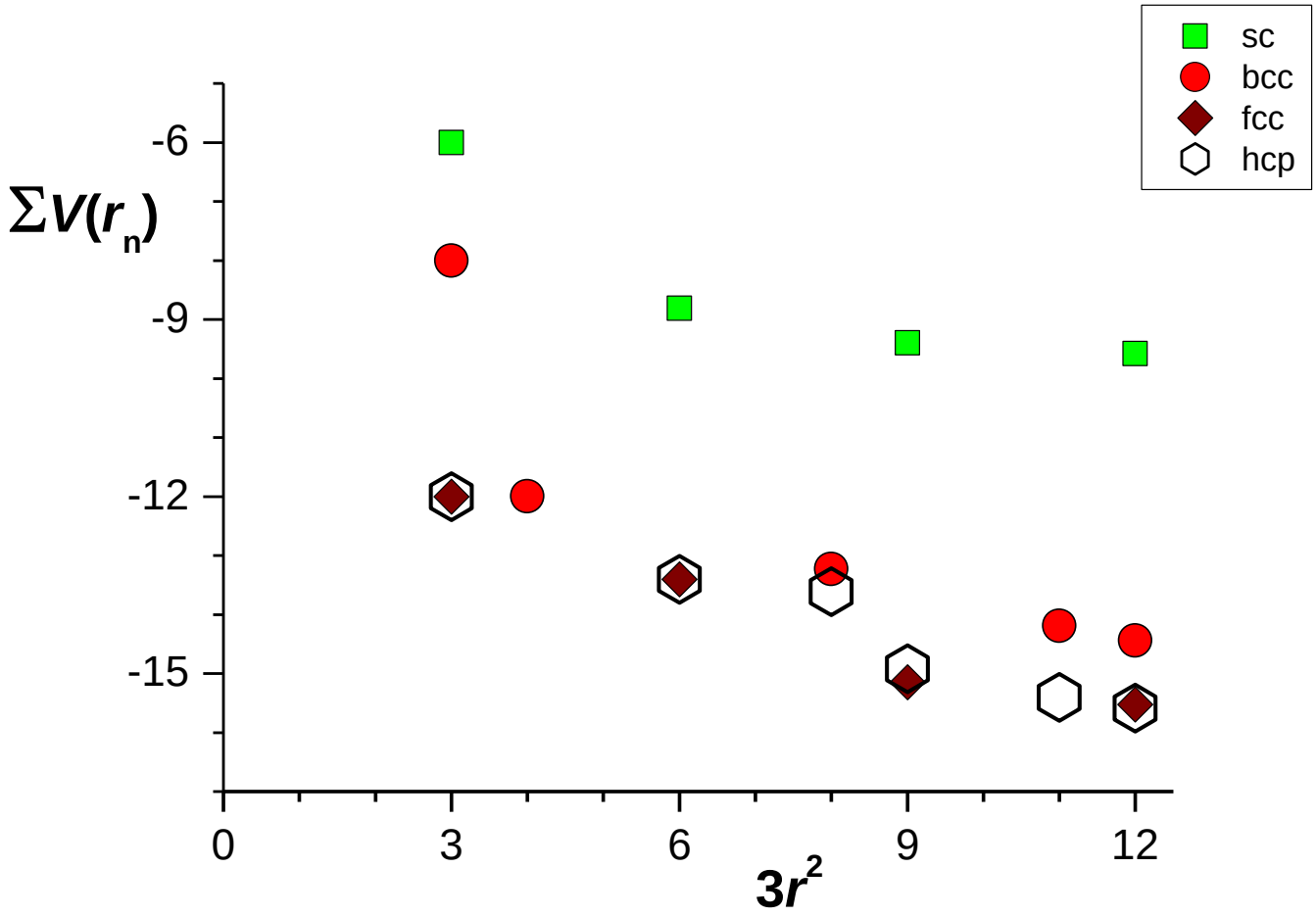


Znormalizowany potencjał Lennarda-Jonesa:

$$V = 1/r^{12} - 2/r^{6}$$



Sumaryczna energia układu modelowego



Dla upakowania sztywnych kul najbardziej stabilne są fazy FCC, HCP, DHCP itp.

Dla potencjału typu Lennarda-Jonesa stabilność faz FCC, HCP i BCC jest porównywalna.

W ekstremalnych warunkach (wysokie ciśnienie) stabilna może być faza SC (np. Polon). Taką możliwość stwarza mała liczba najbliższych sąsiadów (6) i dwa razy większa liczba kolejnych sąsiadów (12) dla n=6.

W układach gęsto upakowanych, stosunek odległości między warstwami heksagonalnymi do stałej sieci heksagonalnej wynosi $d_h/a_h = (2/3)^{1/2} \approx 0.816$.

Sekwencja warstw **dla wszystkich sieci regularnych jest ABC**. Stosunek d_h/a_h wynosi odpowiednio:

0.816 dla FCC
0.408 dla SC
0.204 dla BCC;

Inna wartość stosunku prowadzi do sieci heksagonalnej (dowolna sekwencja warstw) lub romboedrycznej (sekwencja AB).

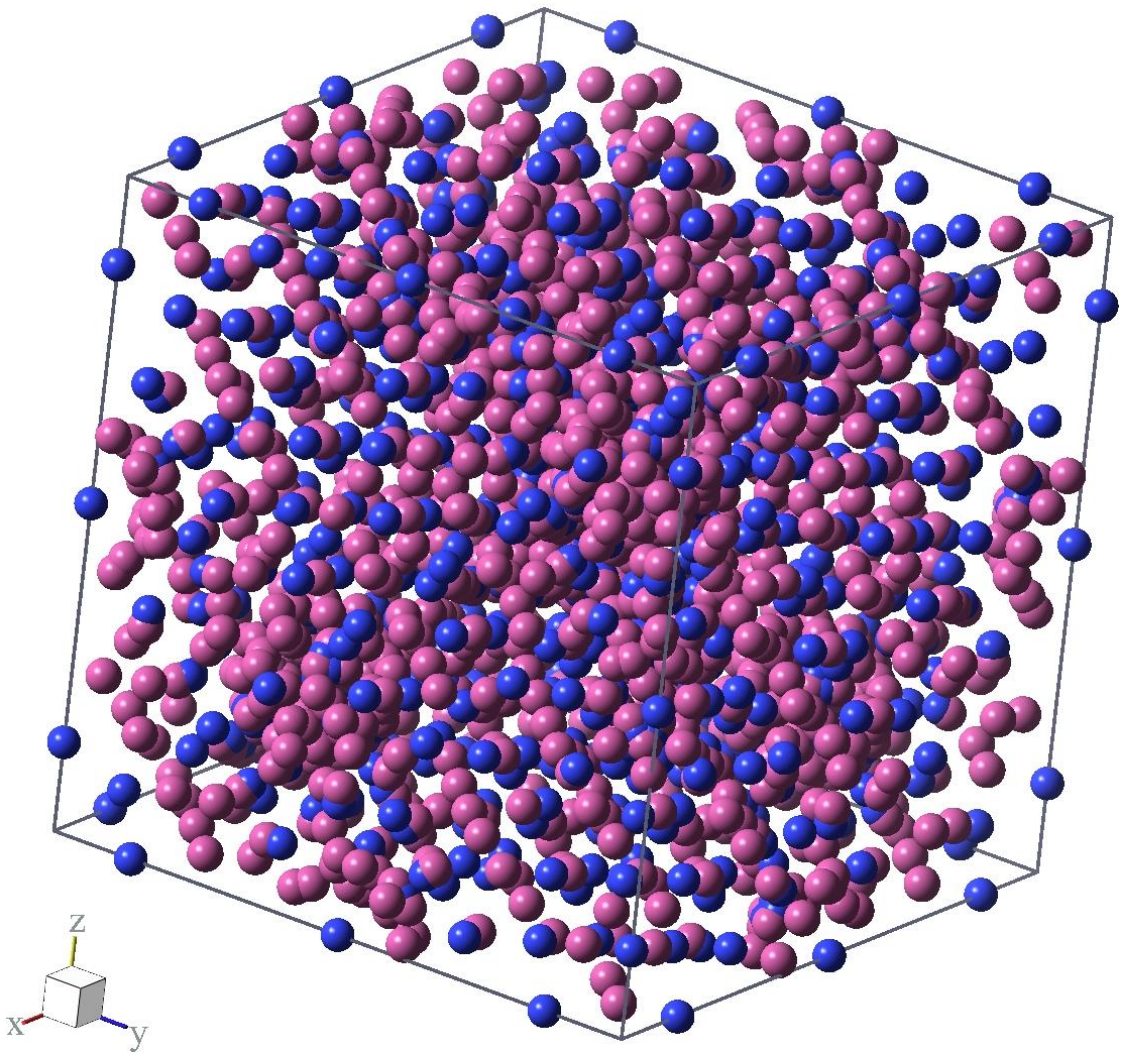
β - Mg_2Al_3

The Samson phase is one of the most complex intermetallic structures. The first description of the β-Mg_2Al_3 structure was provided by S. Samson in 1965. Its cubic elementary cell (Fd-3m, no. 227 space group) contains **1168 atoms** which are distributed over 1832 atomic positions. About 75% of atoms (879 to be exact) form the firm framework of the structure - 528 of them are Al and 351 are Mg. By “the framework” or “skeleton atoms” we understand a set of Samson’s positions which are occupied by atoms with the probability of 100%. The remaining 289 (25%) atoms partially occupy 953 positions with the average occupation probability of 30%. They form clusters arranged in an elementary cell in a tetrahedral lattice.

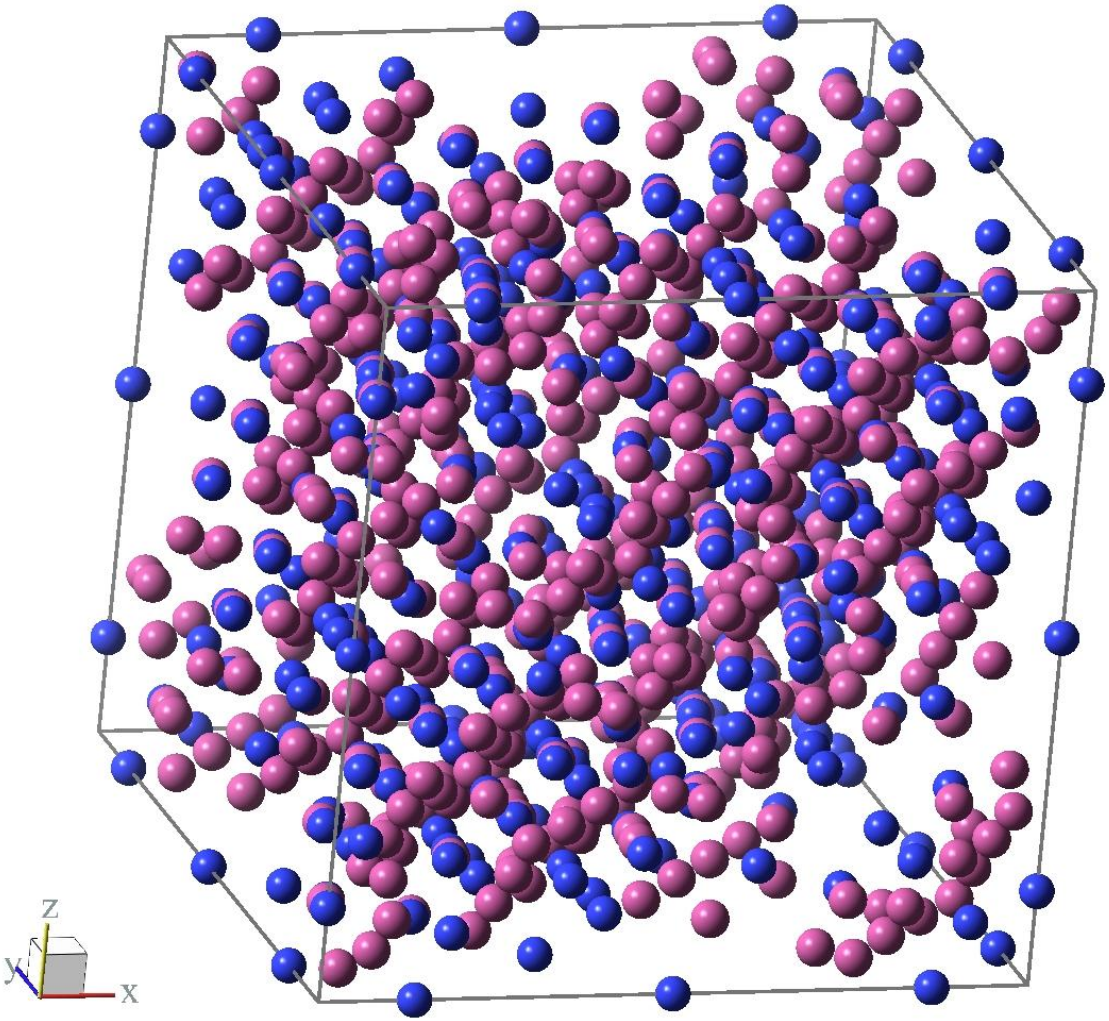
The lattice constant of the Samson structure is gigantic: a_c=2.8242(1) nm.

β-Mg_2Al_3; 1168 atoms; a_c=2.8242 nm

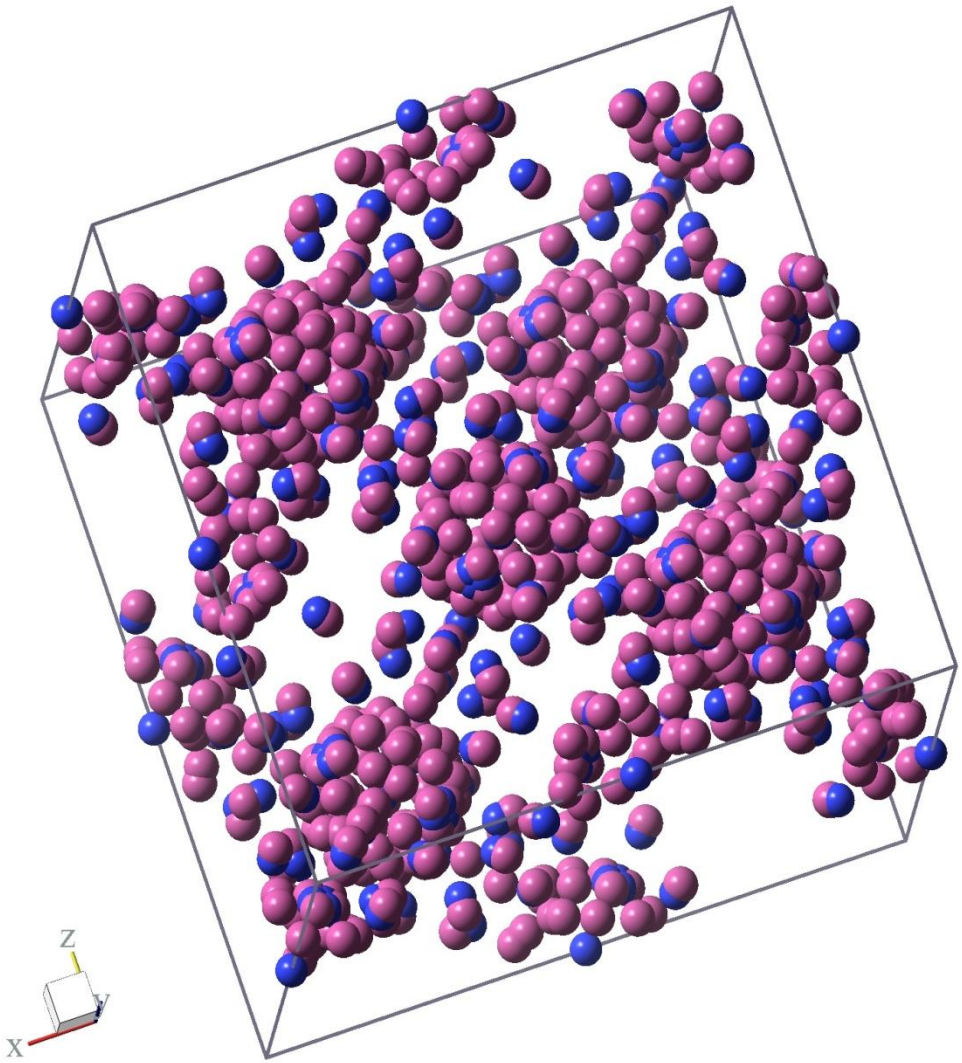
all the data used in this presentation come from Feuerbacher M. *et al.*, Z. Krist. 222 (2007) 259



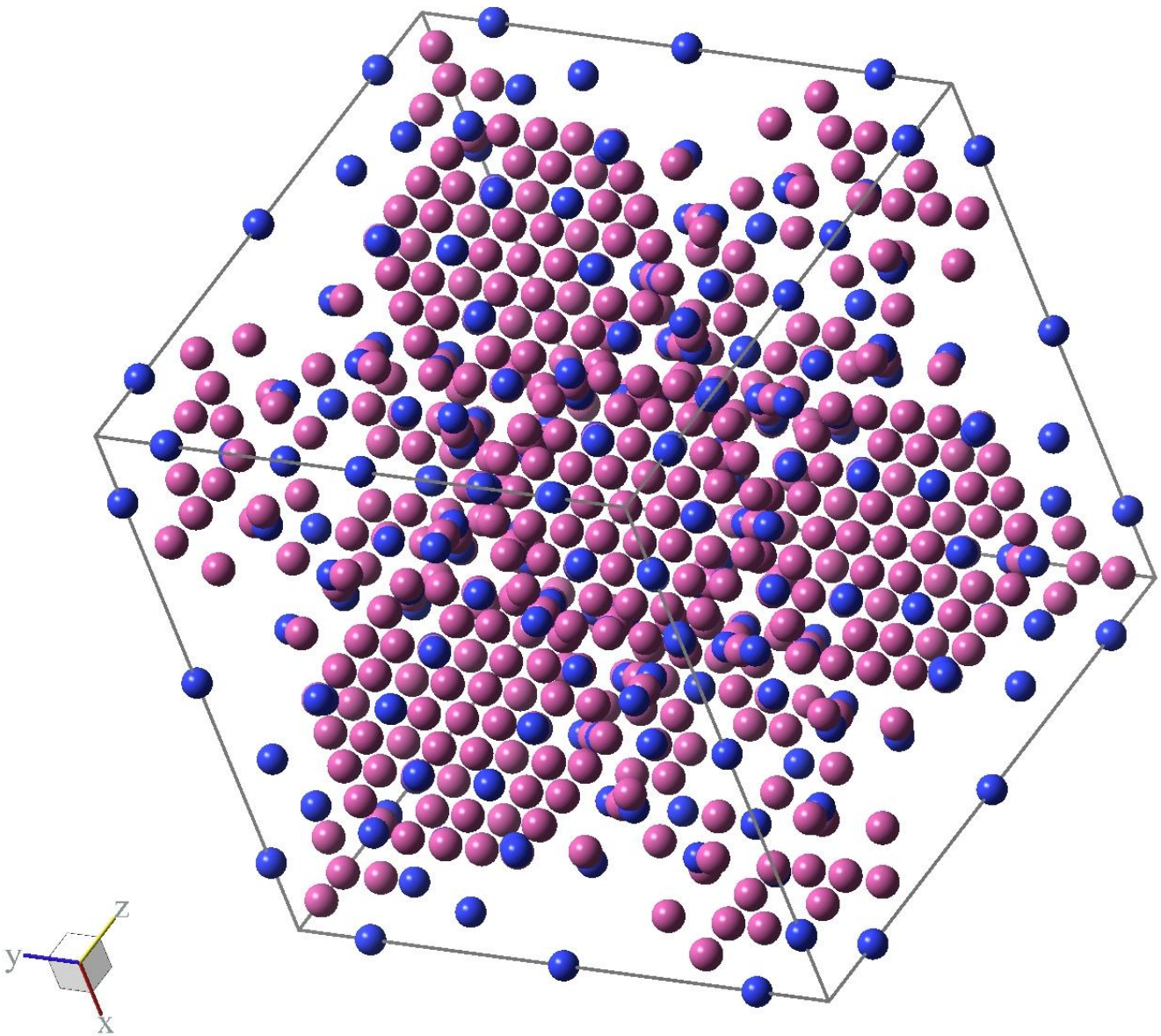
β - Mg_2Al_3; SOF=1; 879 skeleton atoms (they form 75% of atoms)



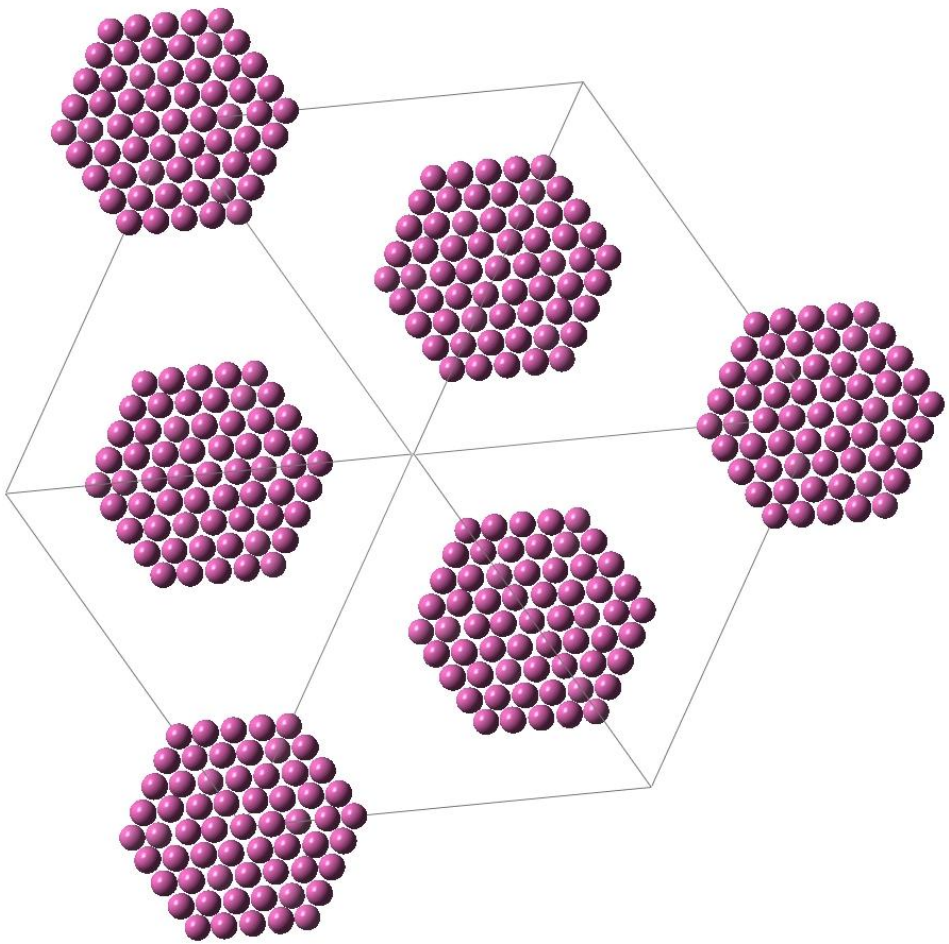
β - Mg_2Al_3 ; SOF < 1 ; 289 atoms (25%)



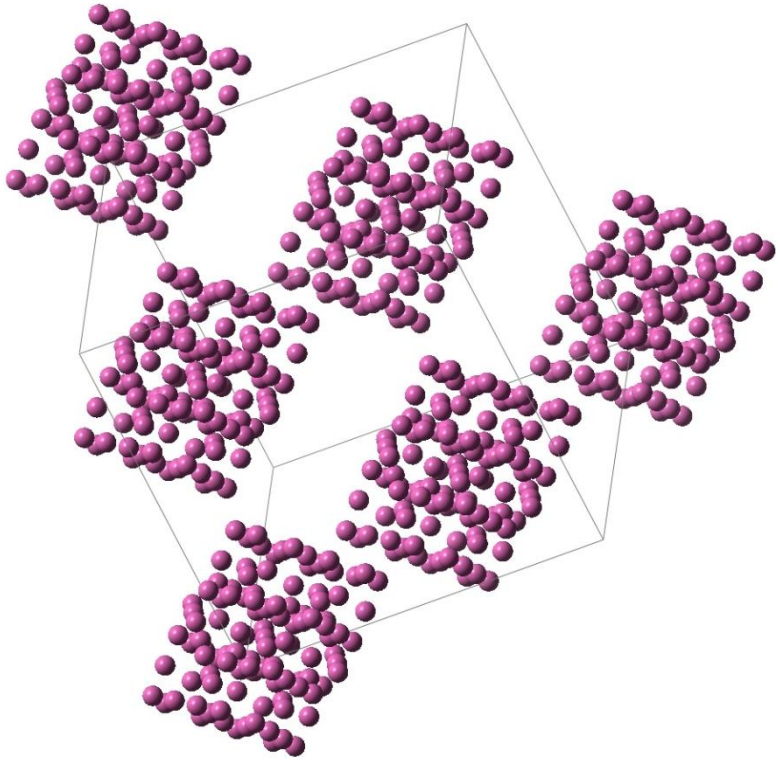
β-Mg_2Al_3; skeleton atoms along [111]

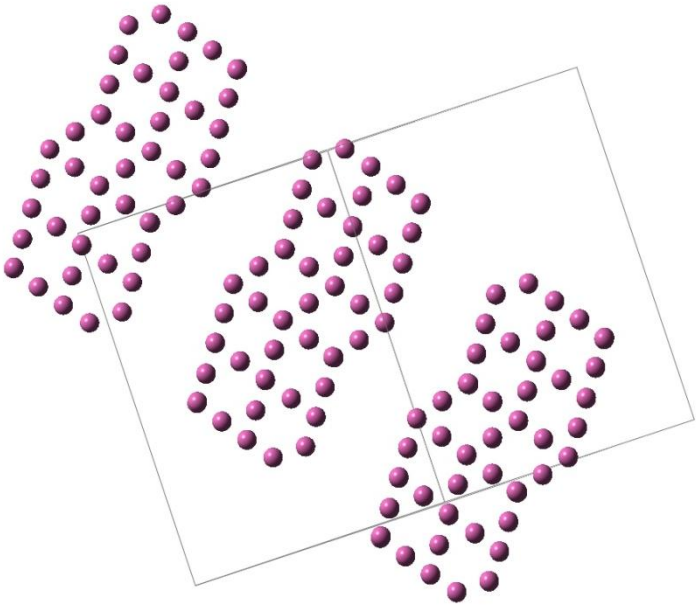


β - Mg_2Al_3; along [111] – hexagonal lattice of domains

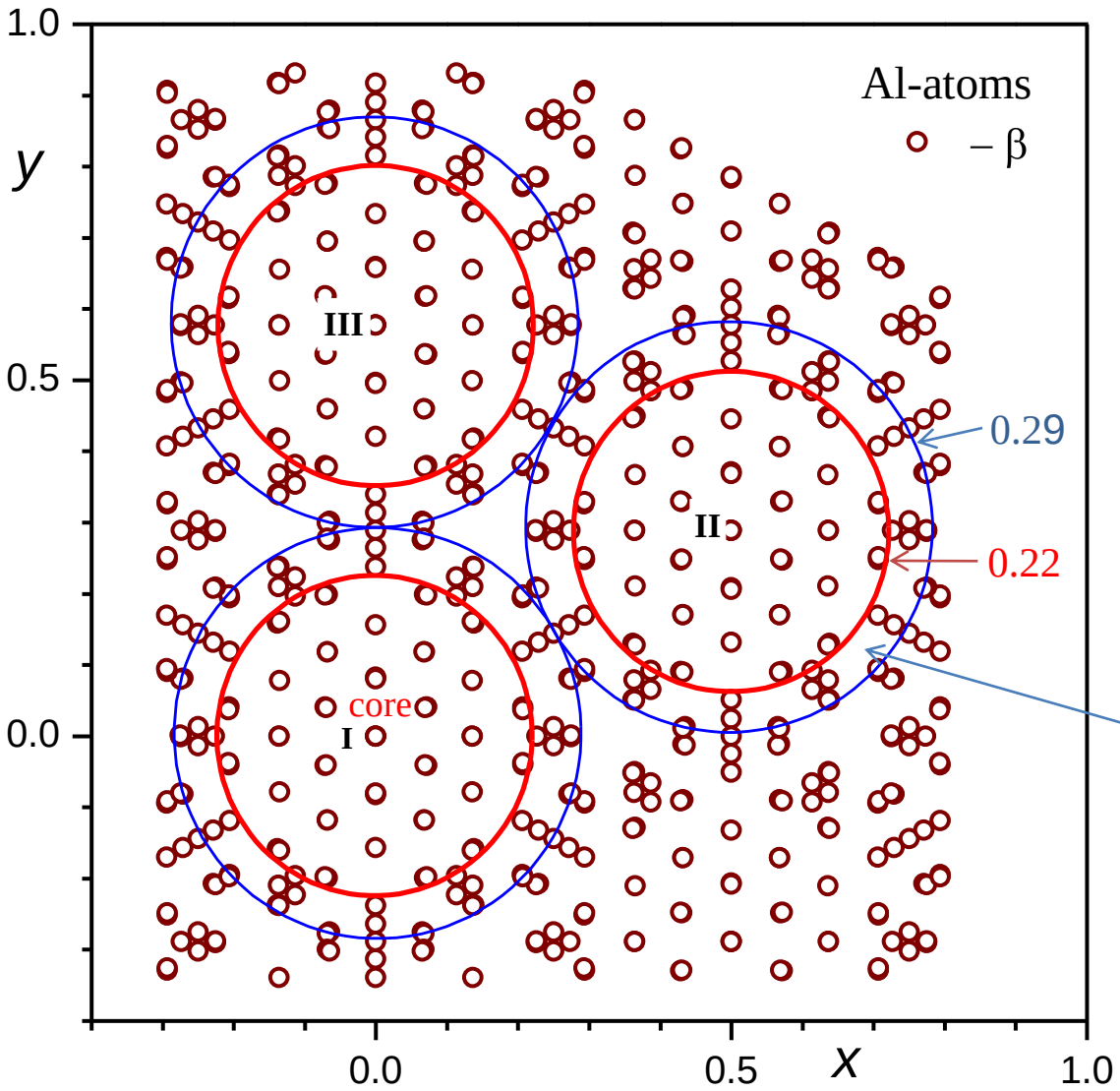


β - Mg_2Al_3; 6 domains-III (Al - skeleton atoms)





Projection of Al-skeleton atoms into base hexagonal plane

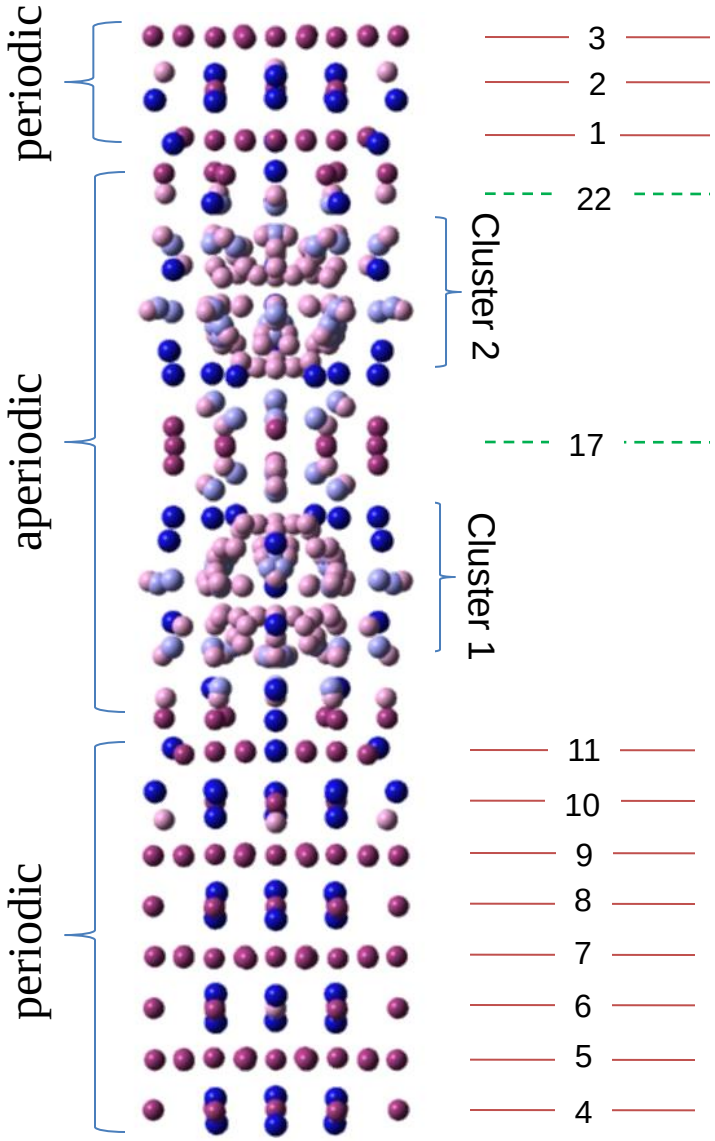


Relative units:

x / a_r
y / a_r
z / c_r

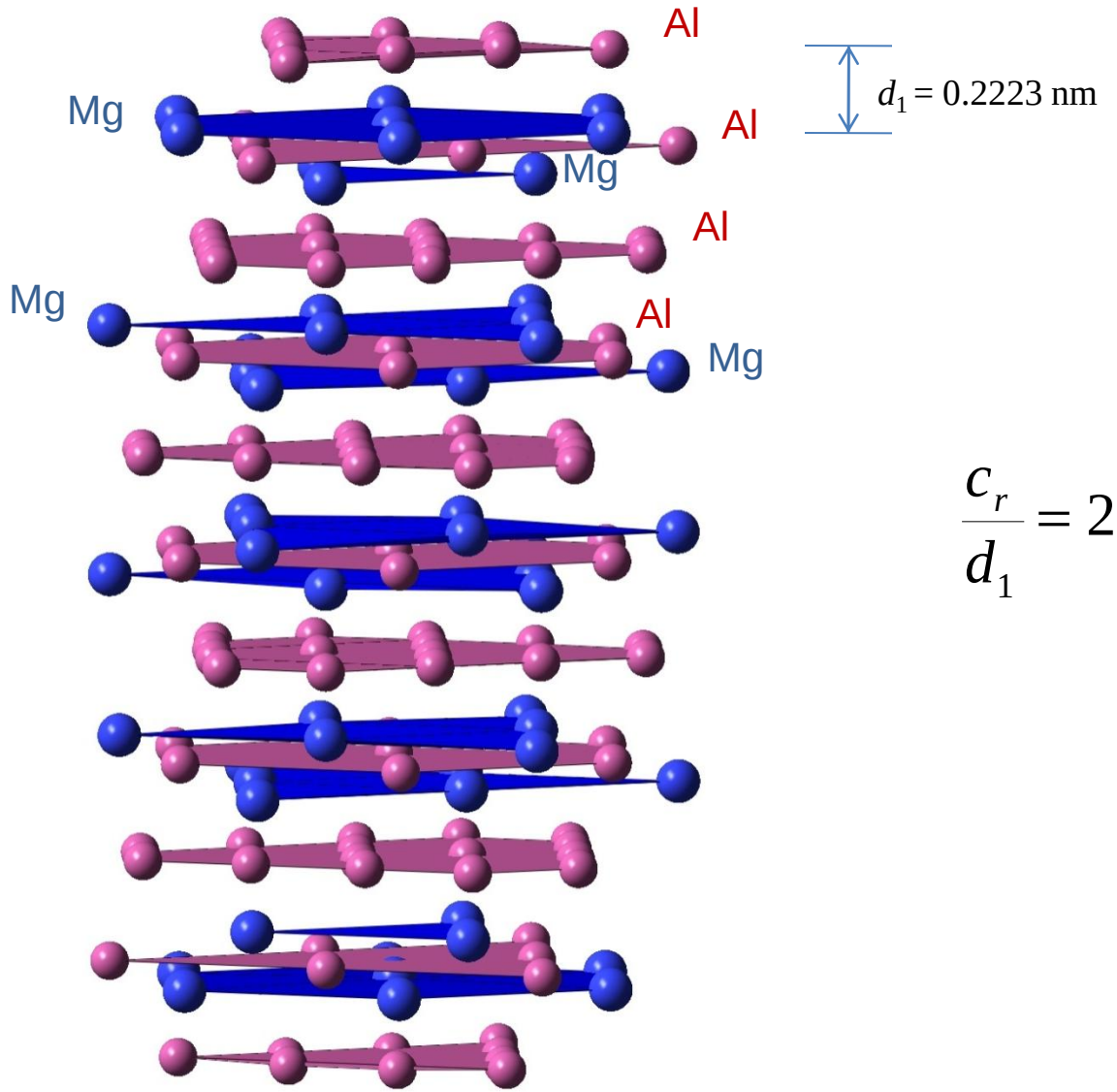
$a_r = 1.9968$ nm
$c_r = 4.8911$ nm

β-Mg_2Al_3; single domain (Al + Mg along [111])



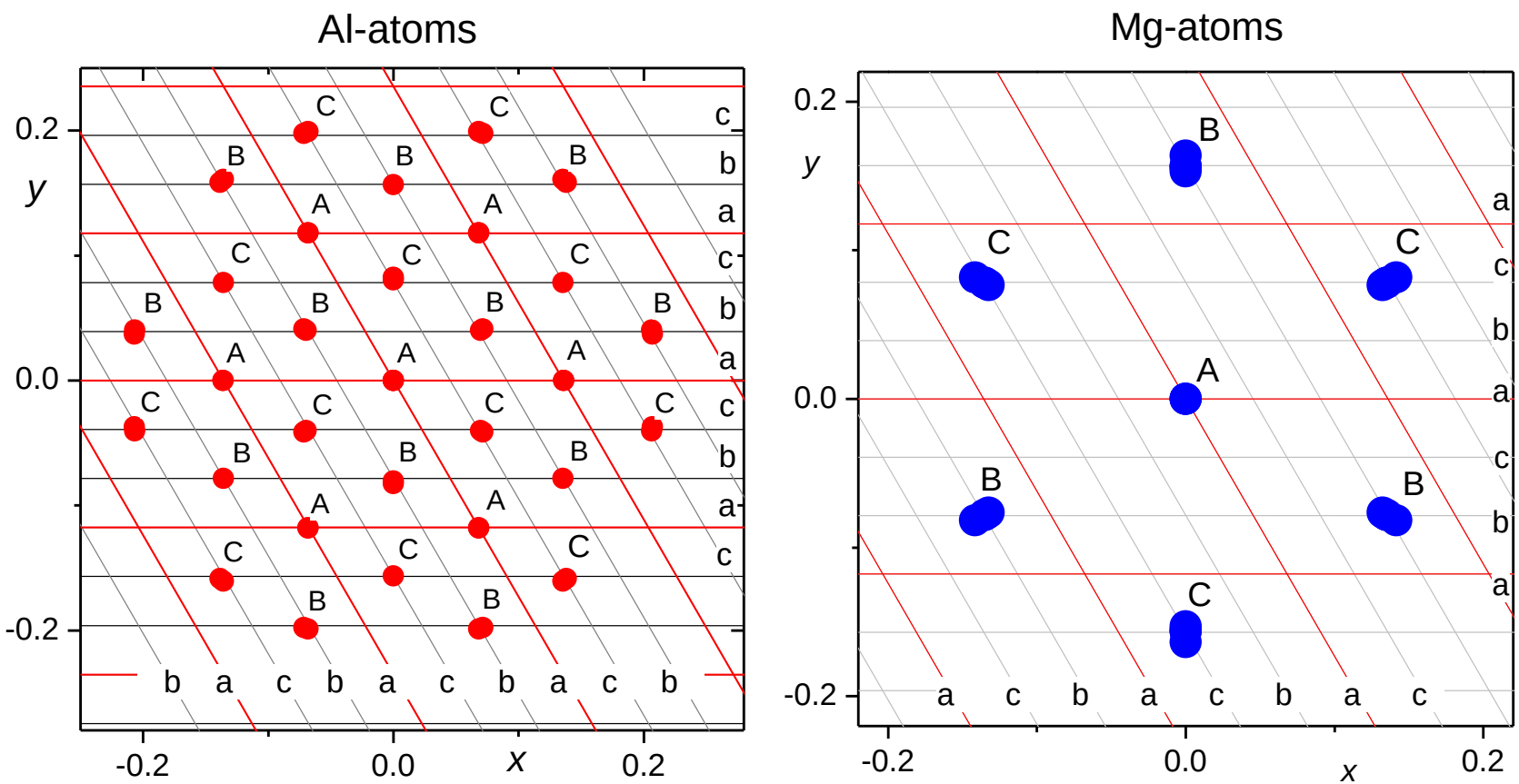
- eleven parallel and evenly distant hexagonal Al layers occupied by skeleton atoms
- two aperiodic clusters occupied by atoms with SOF<1

β - Mg_2Al_3; skeleton atoms of single domain (11 Al +10 Mg layers)



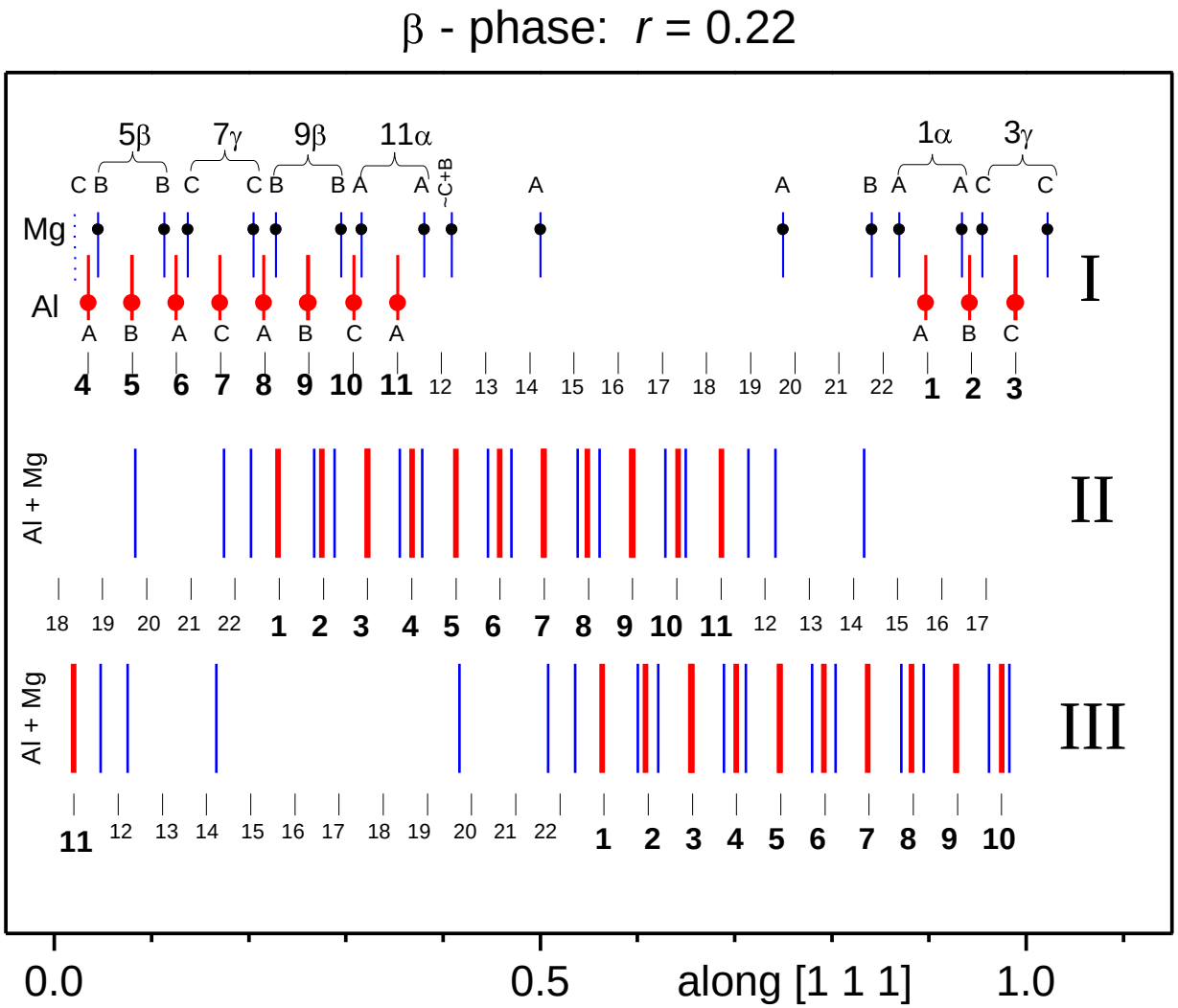
$$\frac{c_r}{d_1} = 22$$

Projection of skeleton core atoms of domain-I for β-Mg_2Al_3 into xy plane

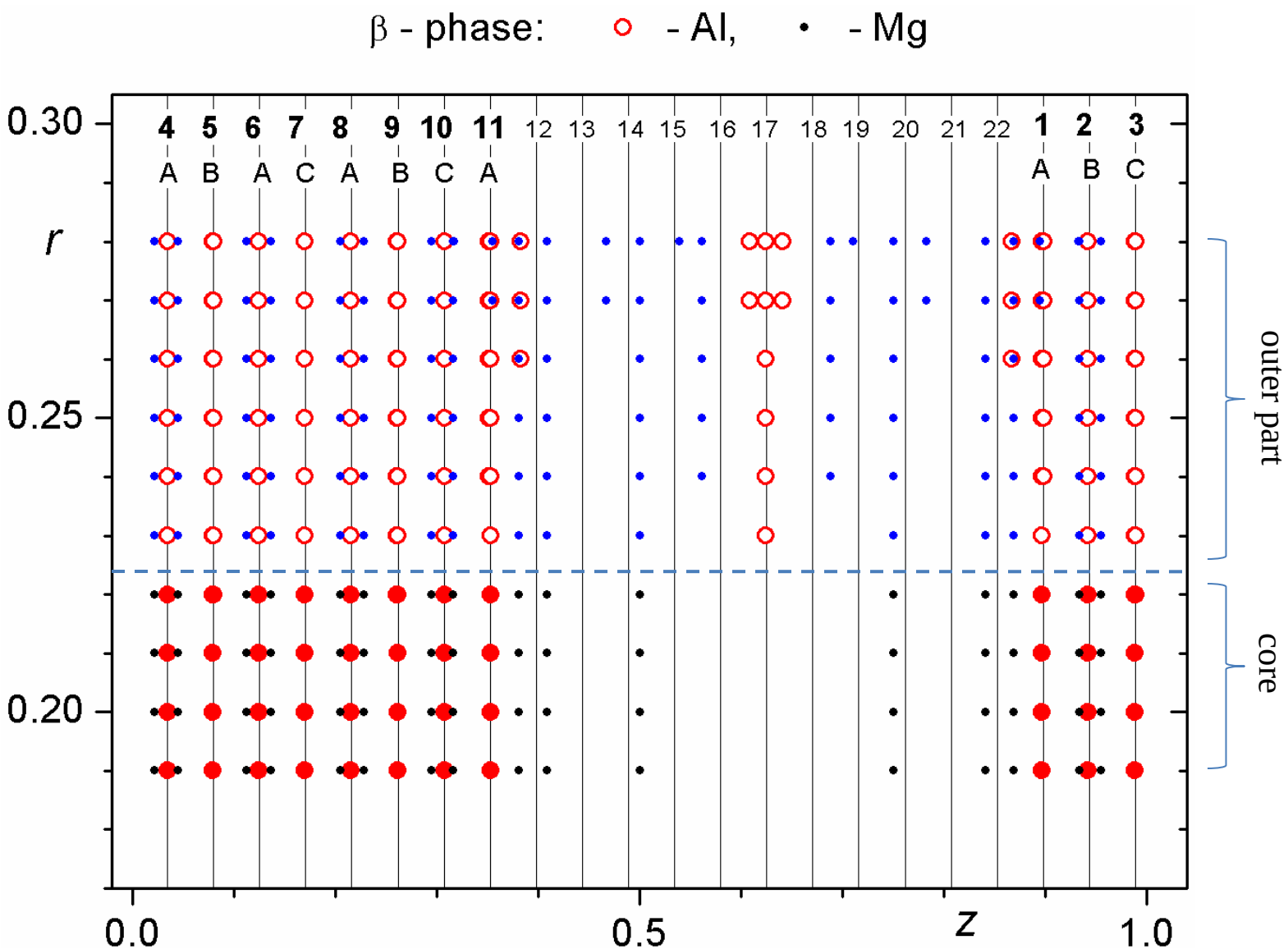


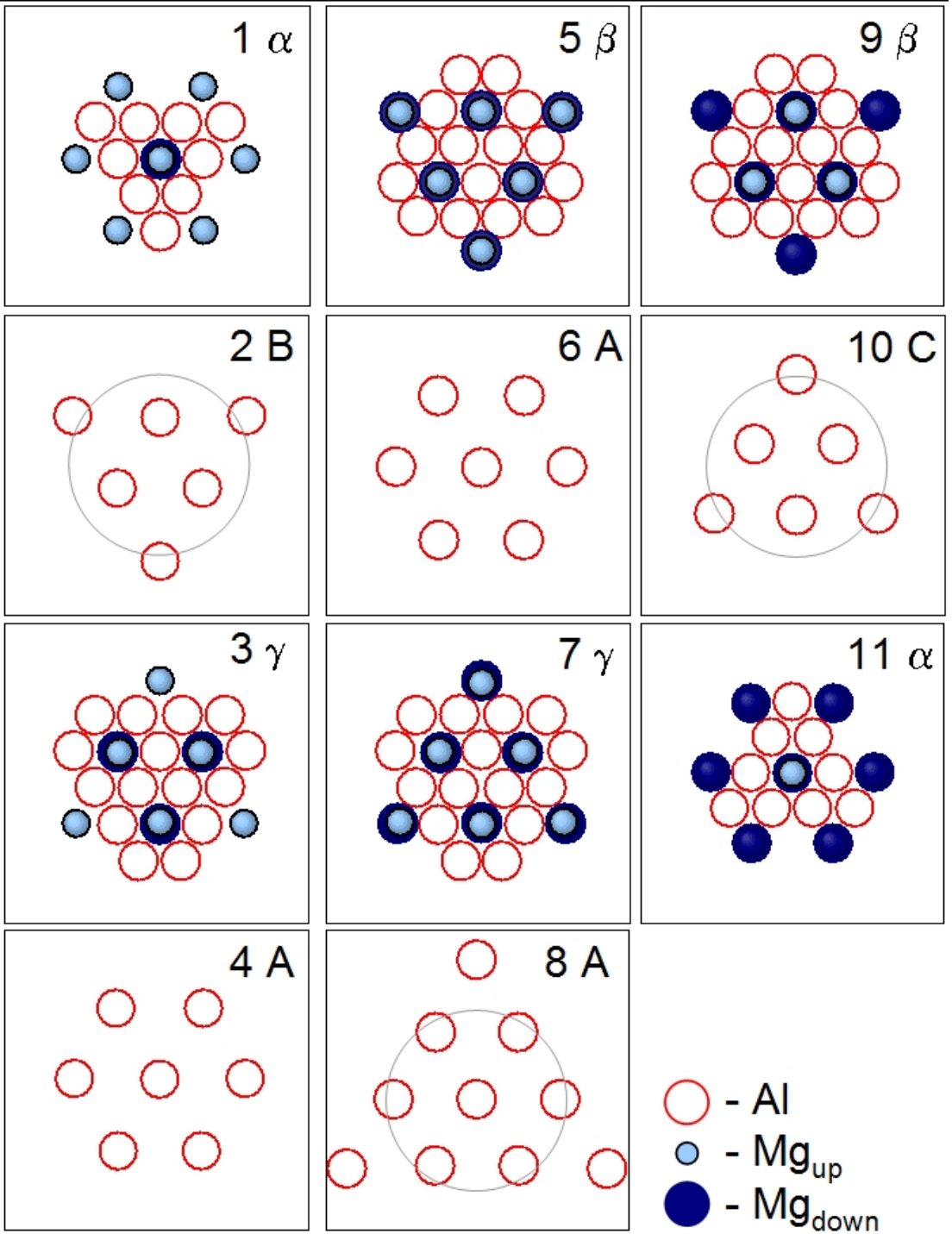
Only A, B or C positions of hexagonal lattice are occupied

Three domains of skeleton atoms of β-Mg_2Al_3 along the main diagonal



Z-component of β-Mg_2Al_3 skeleton-atoms decorating domain-I





Core: 11 Al + 10 Mg layers

The nominal composition is

$$Mg_2Al_3$$

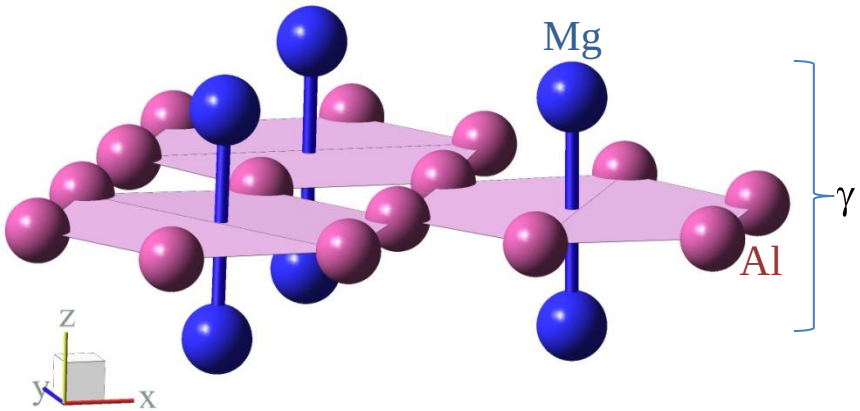
The real composition for layers is

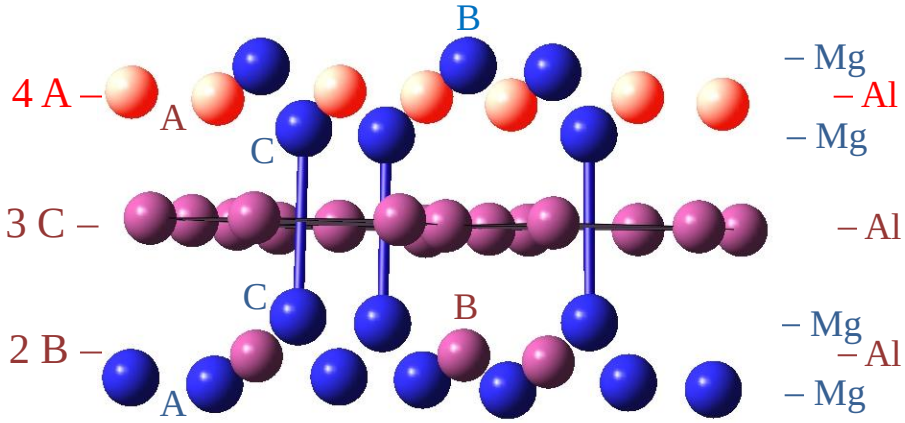
$$Mg_1Al_2$$

– the magnesium atoms are in deficiency,

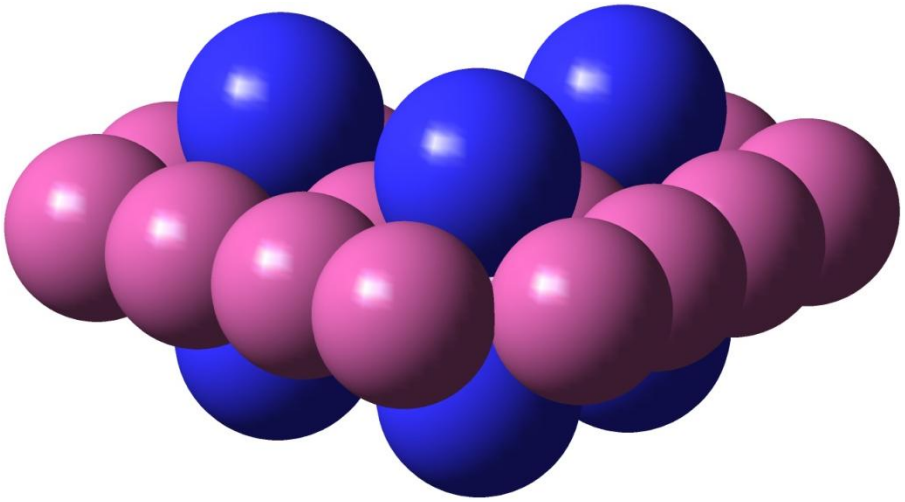
– the chemical balance is restored by Mg atoms scattered within outer parts of the structural domains

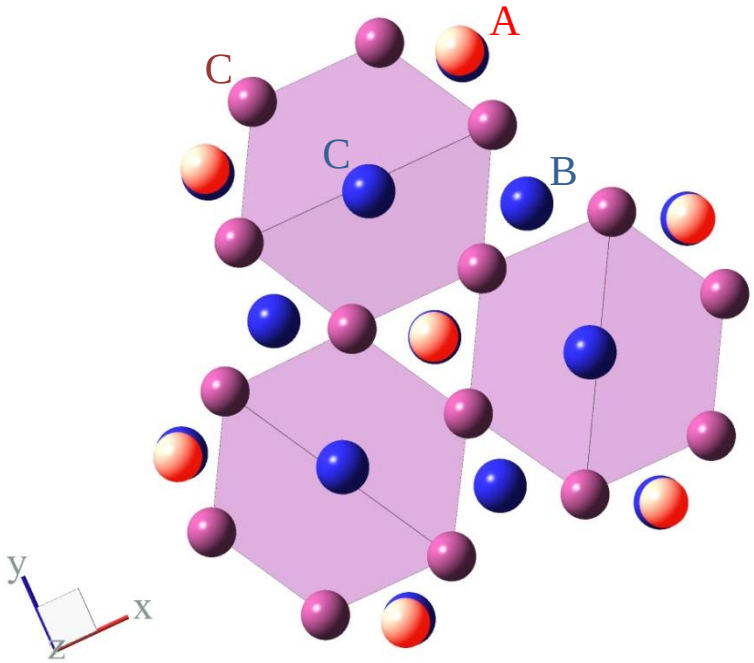
Position of Mg atoms in respect to 11 hexagonal Al-layers



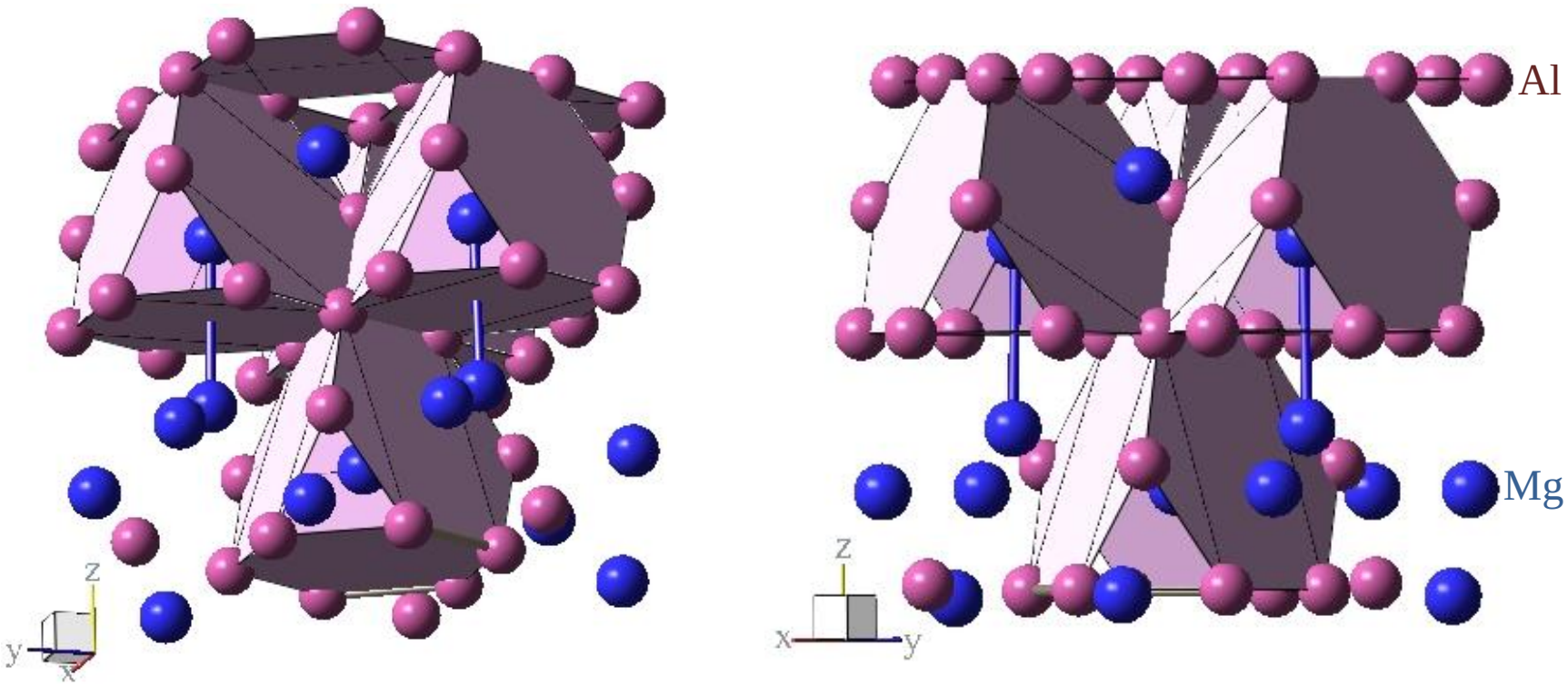


„real scale”

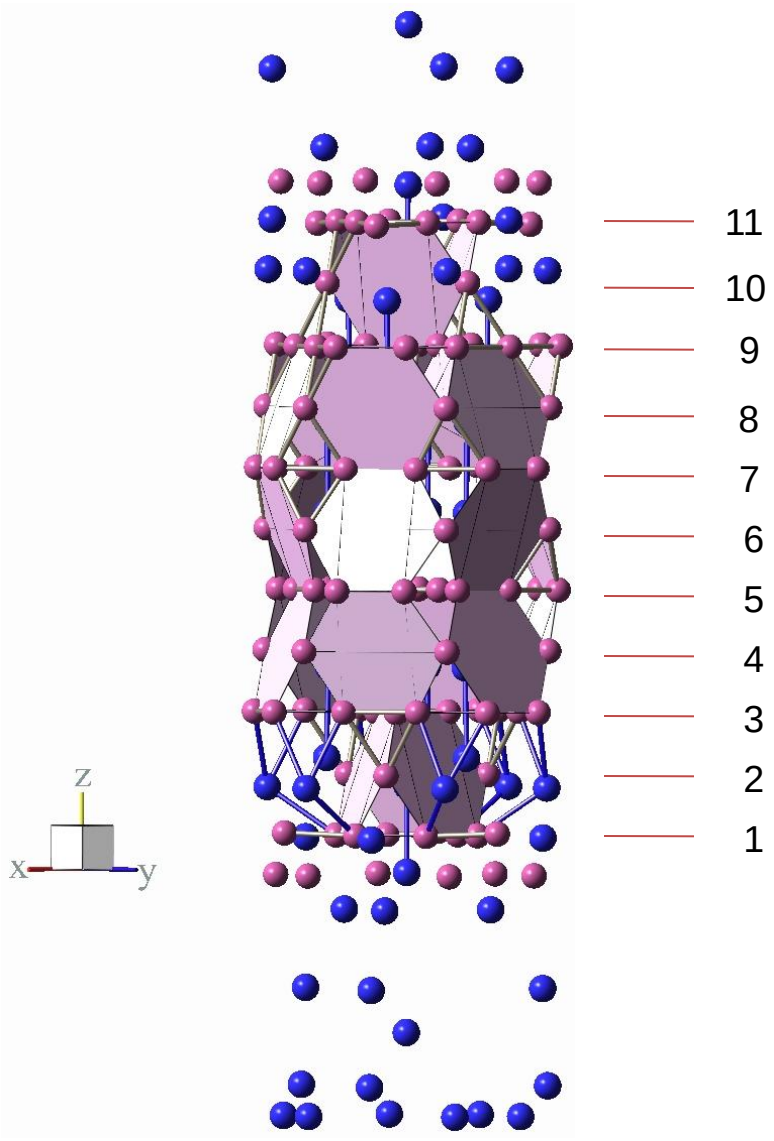




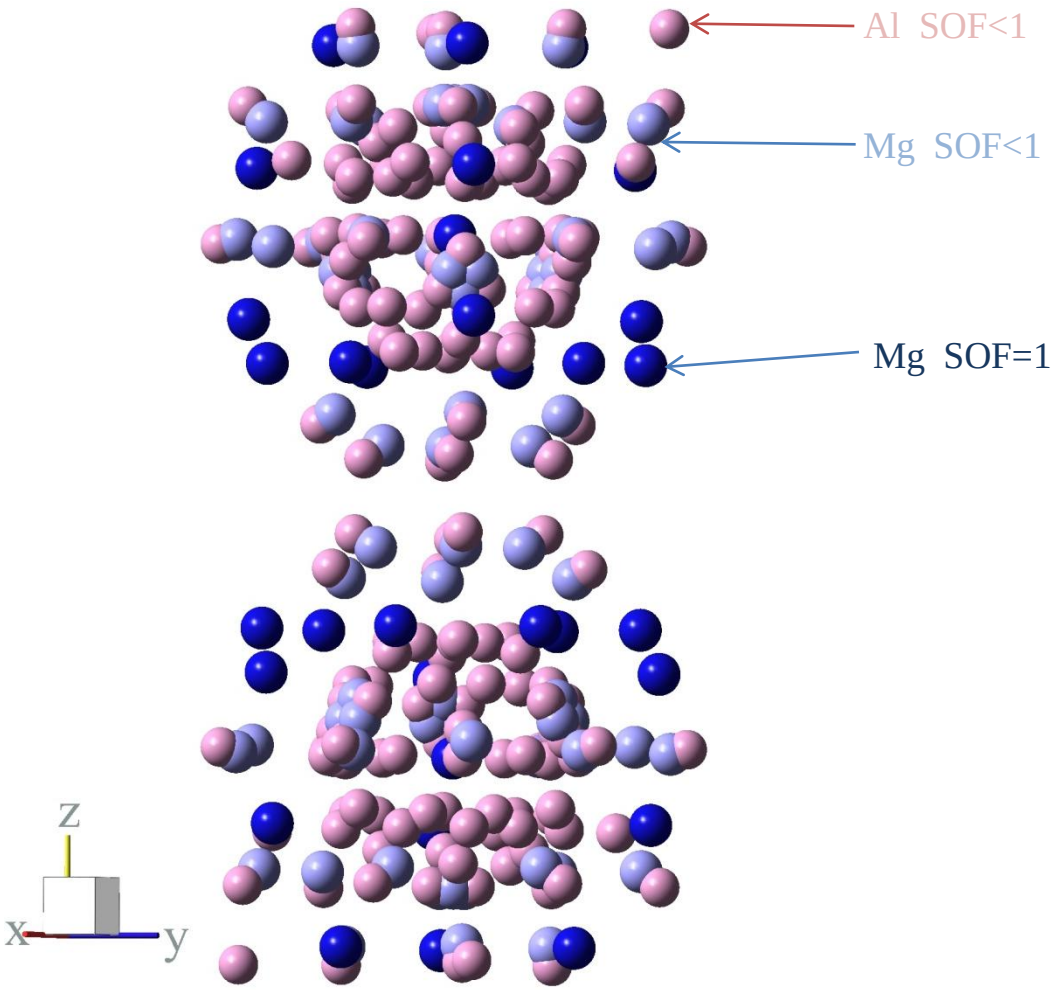
Skeleton atoms of β-Mg_2Al_3: hexagonal layers and Friauf polihedra



Single domain of skeleton atoms of β-Mg_2Al_3: 11 hexagonal layers and Friauf polihedra

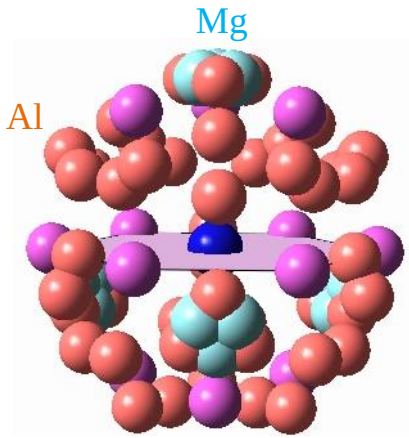


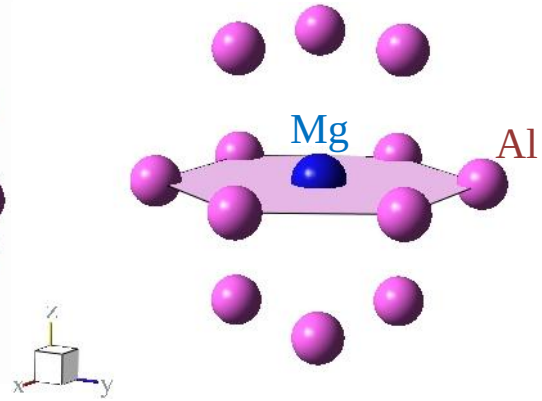
Clusters in β-Mg_2Al_3



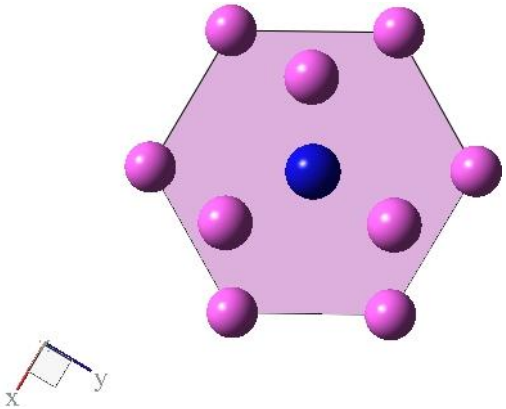
Cluster 2 of β-Mg_2Al_3

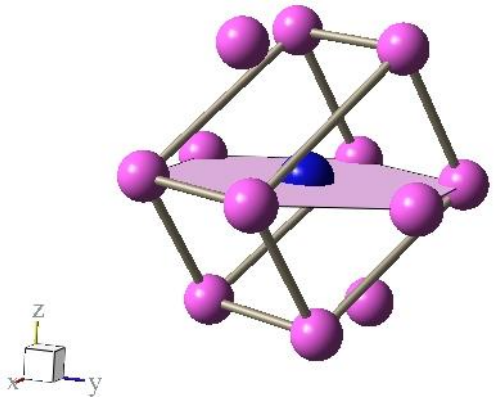
SOF<1





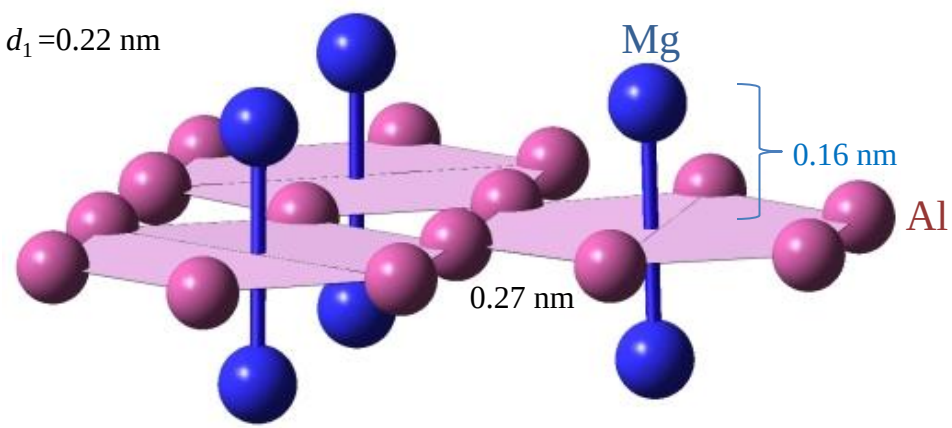
Deformed hexagonal ring





Position of Mg atoms in respect to hexagonal Al-layers

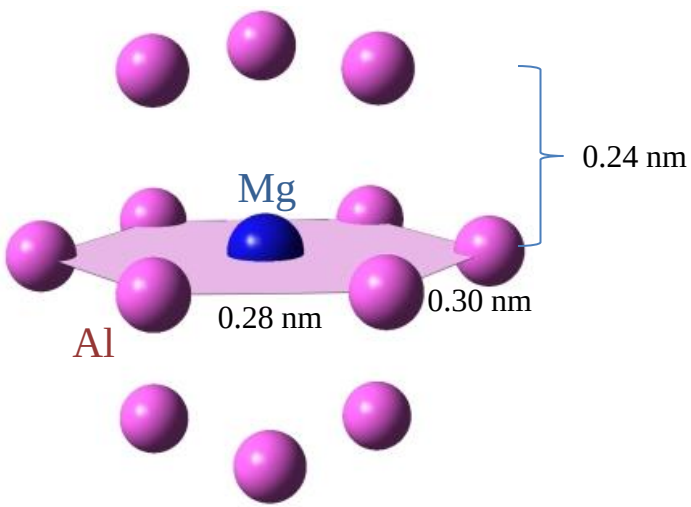
- for periodic set of 11 hexagonal layers



Very stable and unique configuration (Friauf polyhedron)

Corresponding composition: Mg_1Al_2

- for aperiodic clusters



Plenty of room in a ring (size effect). Energetically less stable; at higher temperature stabilized by entropy

Mg_1Al_1

β’- Mg_2Al_3

At a temperature of 214°C (for cooling rate of 5 C/min), the structure undergoes a phase transformation to the rhombohedral β’-Mg_2Al_3 (space group *R3m*, no. 160, which is a subgroup of the *Fd*-3*m* group - index 4) with a_r=1.9968(1) nm, c_r=4.89114(8) nm.

Important relations between cubic and rhombohedral lattice constants

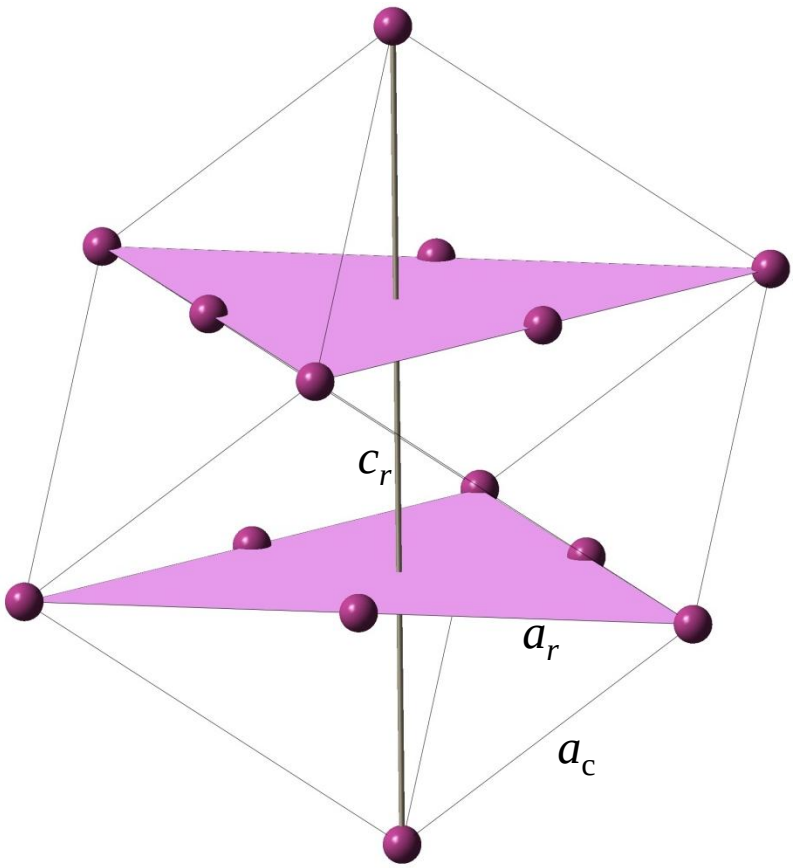
$$\frac{c_r}{a_c} = \sqrt{3} \quad \text{and} \quad \frac{a_c}{a_r} = \sqrt{2}$$

The size of unit cell of β and β' structures is exactly the same, the symmetry – not.

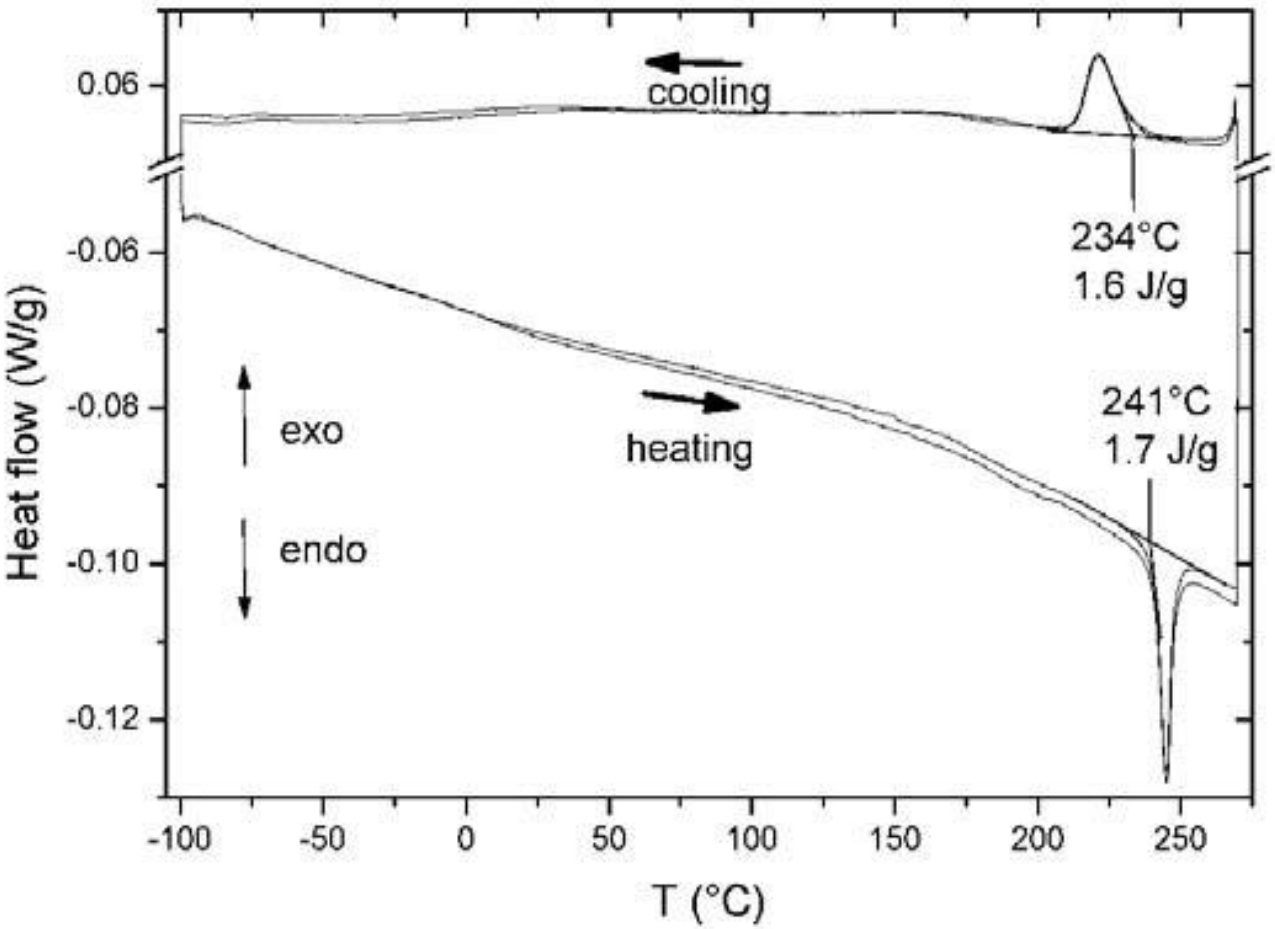
$$V_r = 75\% \cdot V_c$$

from the experiment:

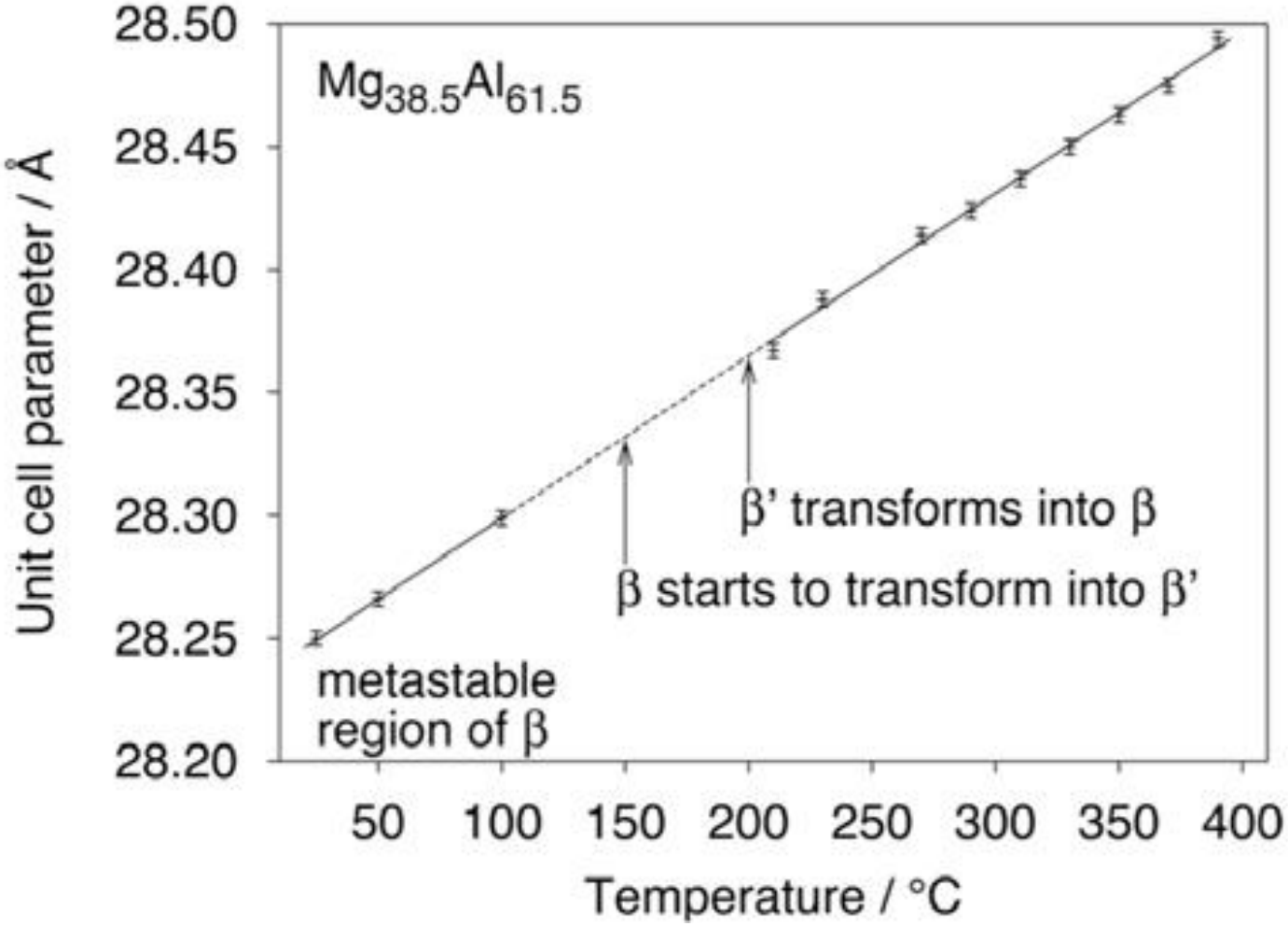
16889/22519 = 0.74999



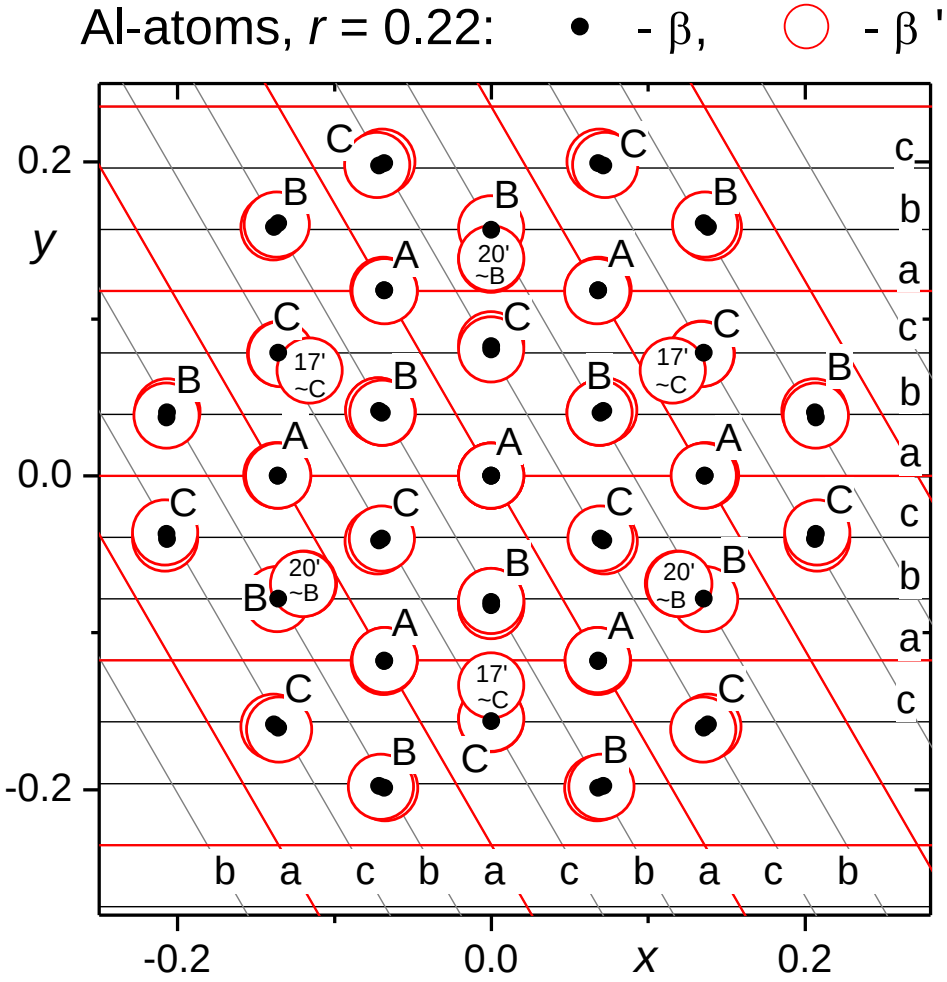
β - $Mg_{35}Al_{65}$ DSC scans [Z. Krist. 222 (2007) 259]



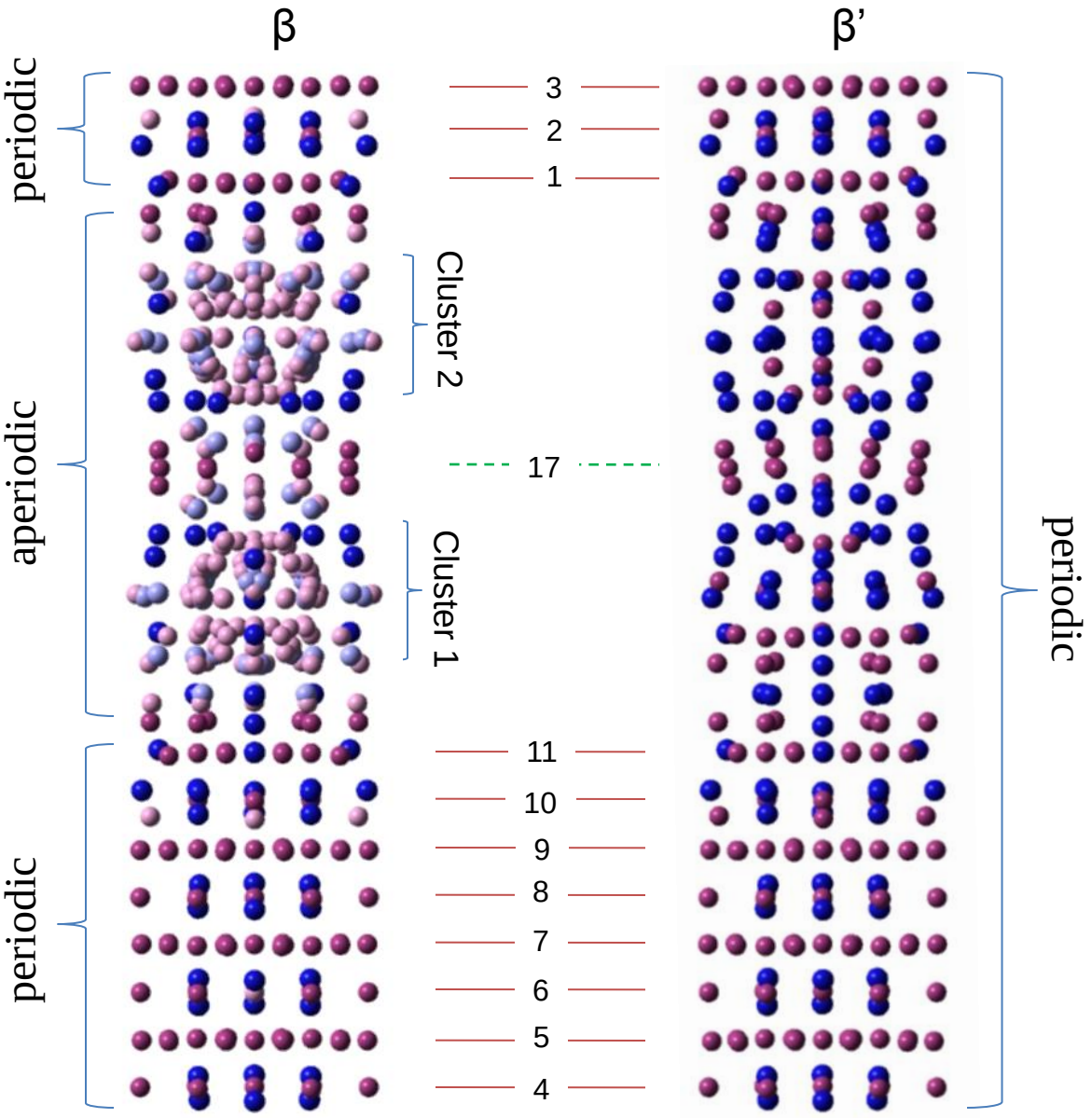
β - $Mg_{38.5}Al_{61.5}$ annealed at 400 C [Z. Krist. 222 (2007) 259]



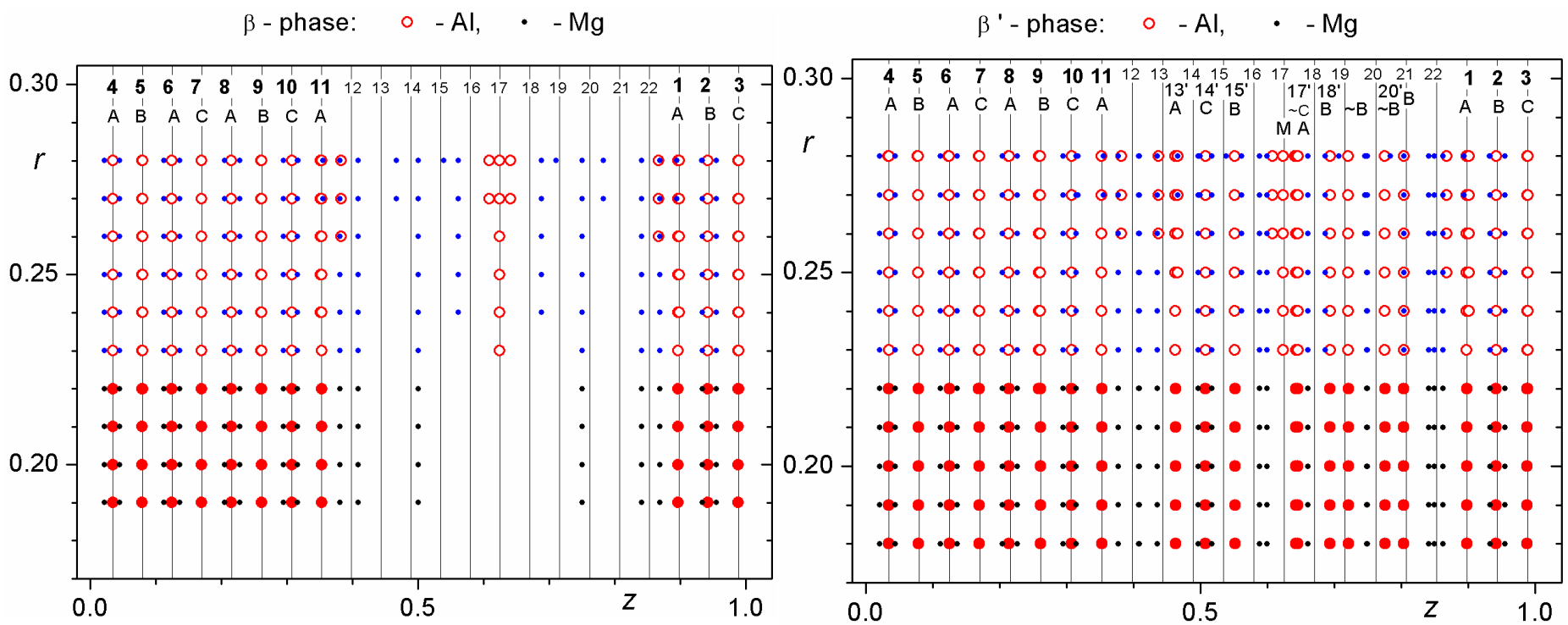
Projection of skeleton atoms of domain-I into xy plane for Mg_2Al_3



Mg_2Al_3; domain-I (Al + Mg)

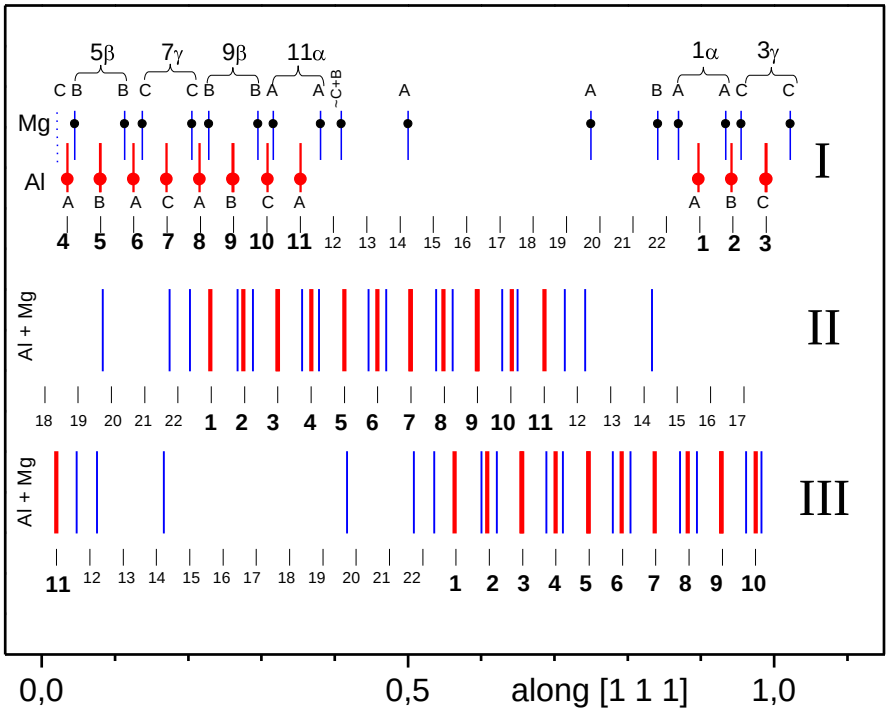


Position of atoms decorating domain-I in perpendicular direction to the hexagonal plane

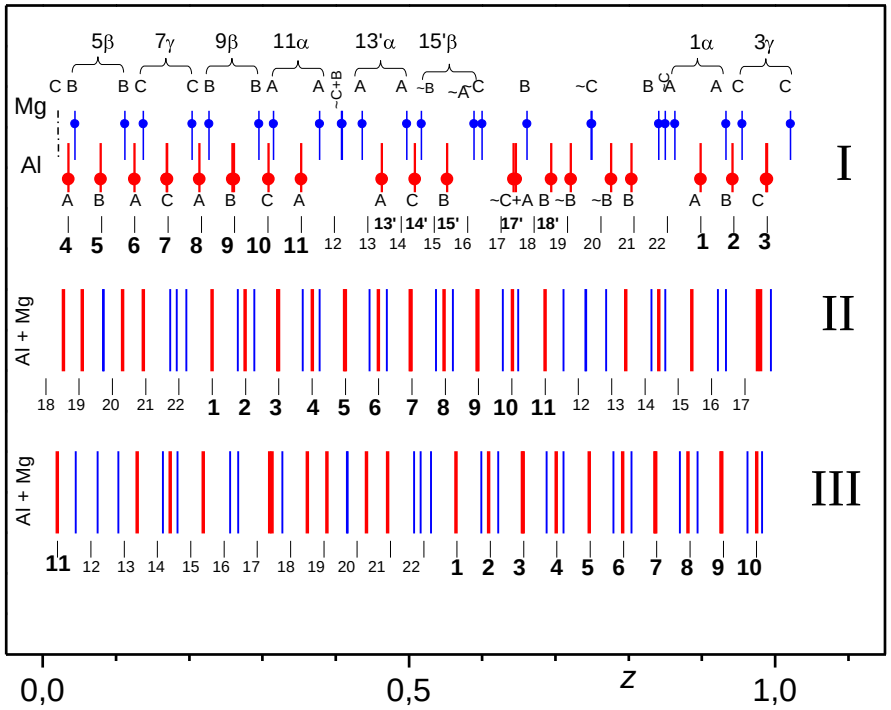


Three domains of skeleton atoms of Mg_2Al_3 along the main diagonal

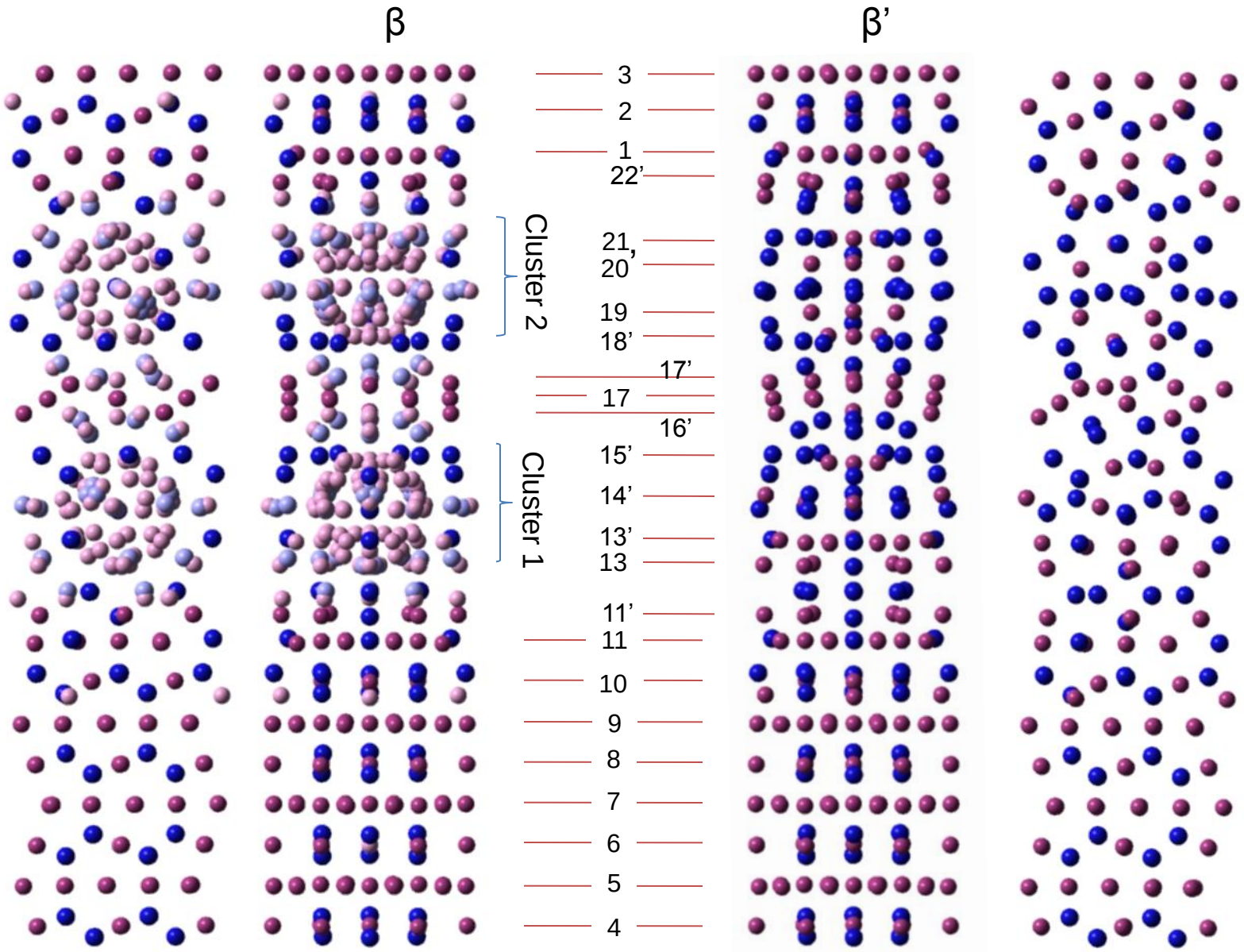
β - phase: *r* = 0.22



β ' - phase: *r* = 0.22



Mg_2Al_3; domain-I (Al + Mg)



Superstructure of domains in *xy* plane

c_r=4.891 nm

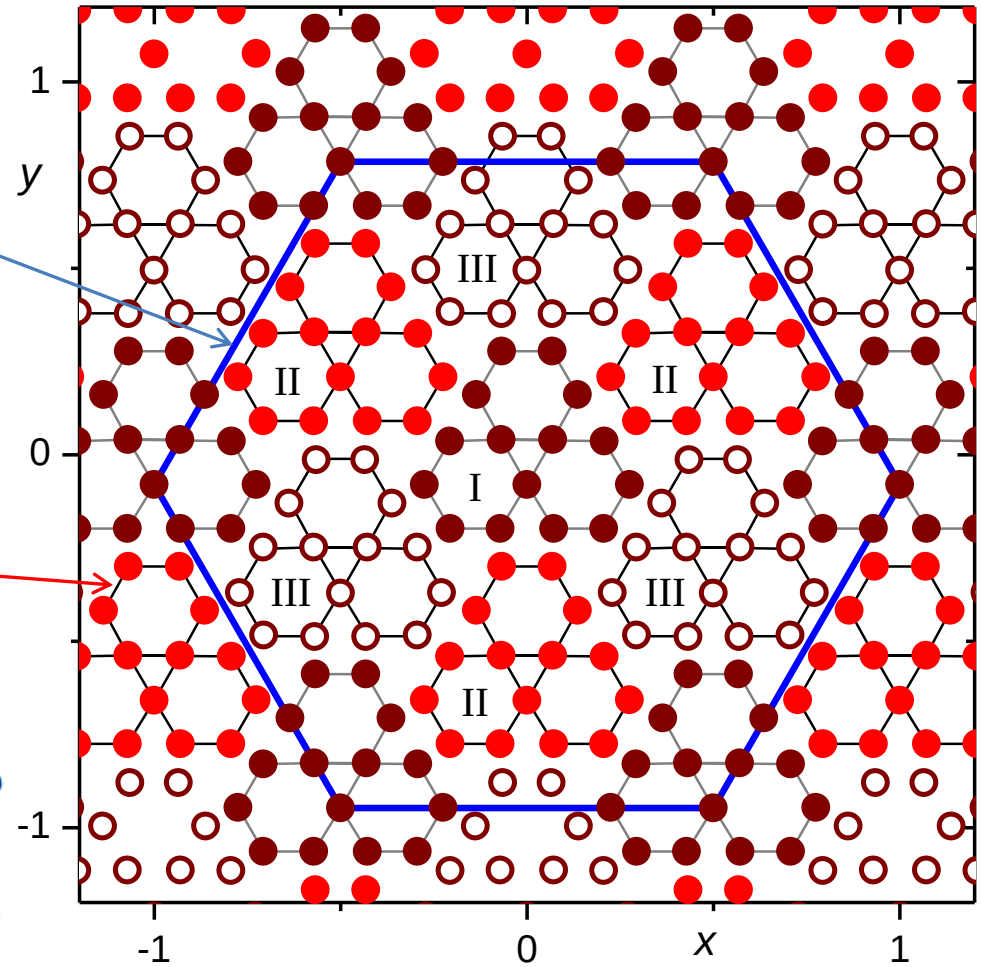
a_r=1.997 nm

a_0=0.273 nm

d_1=0.222 nm

$$\frac{d_1}{a_0} = \sqrt{2/3} \approx 0.816$$

close packed structure

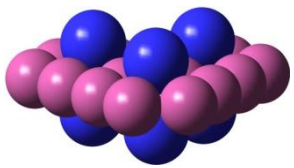


$$\frac{a_r}{a_0} = \frac{22}{3} \approx 7.3$$

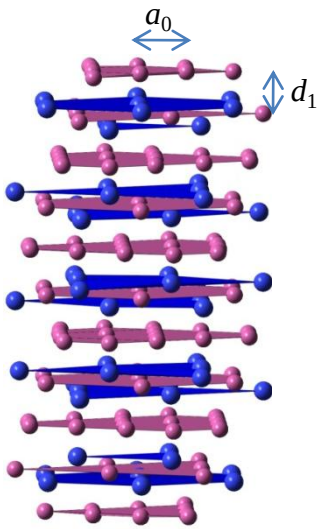
$$\frac{c_r}{d_1} = 22$$

Layer 9B

Conclusions

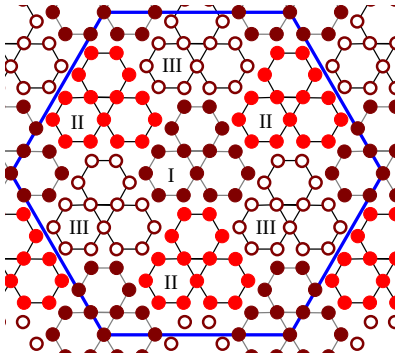


1. The most stable building element of Mg-Al compounds is a hexagonal ring of Al atoms (**a_0 = 0.273 nm**) filled with a couple of Mg atoms which are pushed out from the base plane (equivalent to the Friauf polyhedron) of a real local composition Mg_1Al_2.



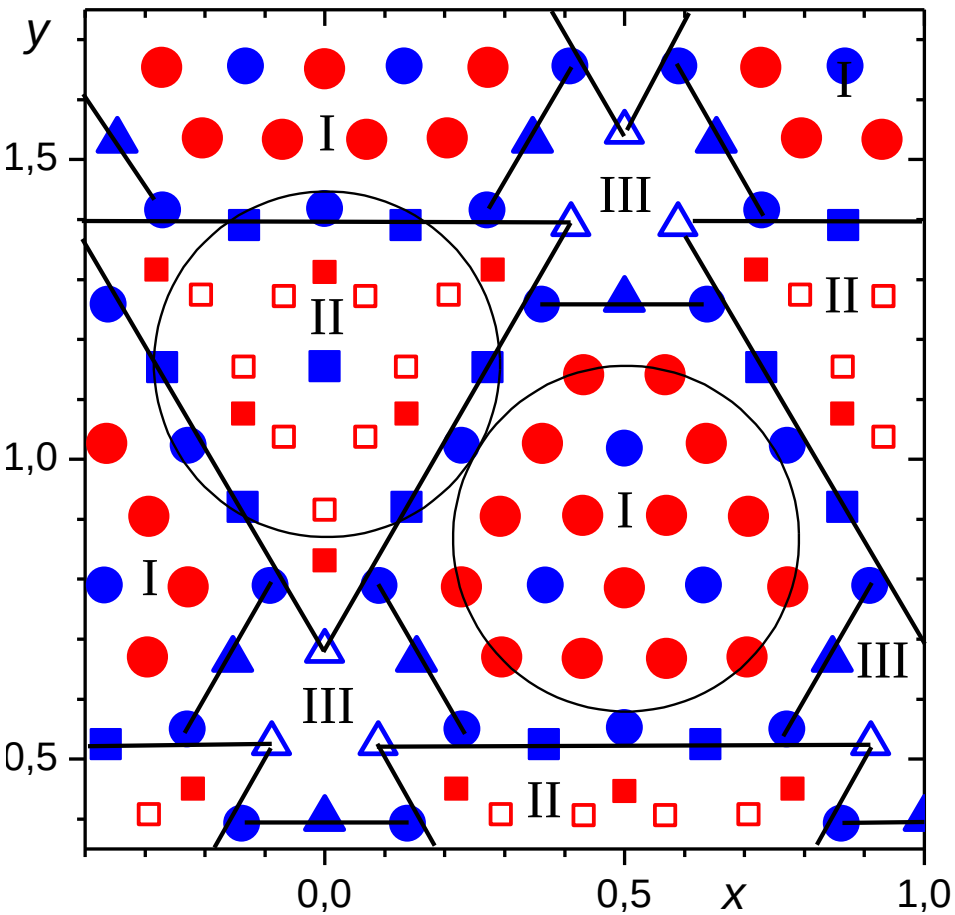
2. Close packing of Al atoms brings to distance between hexagonal layers equal to **d_1= 0.222 nm** = $(2/3)^{1/2}a_0$. Additional: $22 \cdot d_1 = c_r$.

3. The core of each domain consists of a main chain of 11 hexagonal layers. It doesn't change during the β-β' transition.



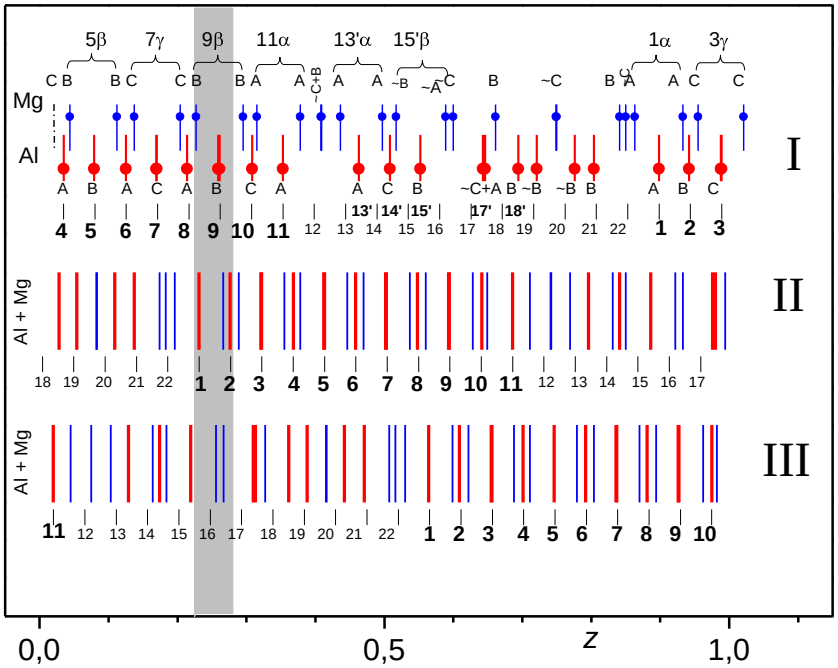
4. The unit cells of β and β' phases of Mg_2Al_3 can be also regarded as the superstructures with the modulation vector equal to (3/22) (as the multi-*q* modulated structures).

Crossection through the β'-Mg_2Al_3 in xy plane: domain-III almost disappeared

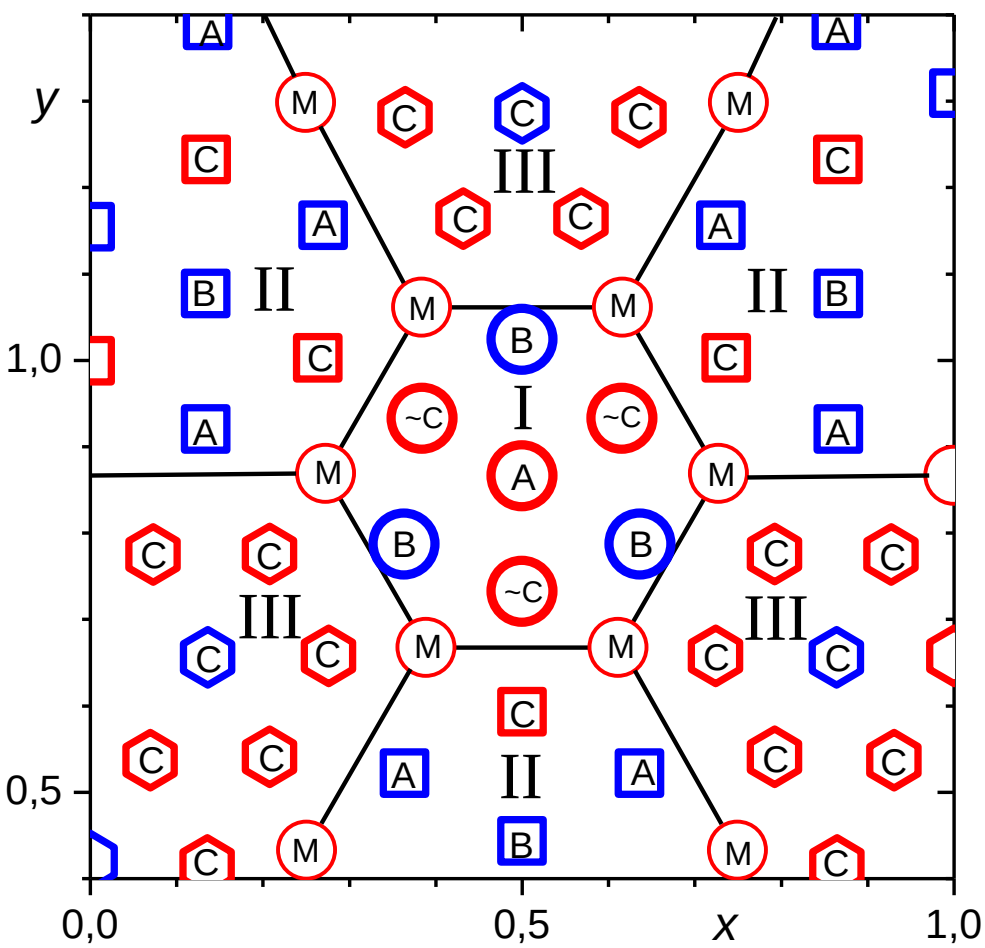


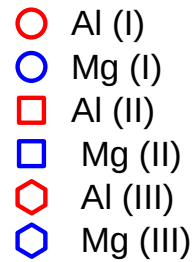
Al I-9B
Mg I-9B
Al II-1A
Al II-2B
Mg II-1A

β ' - phase: r = 0.22

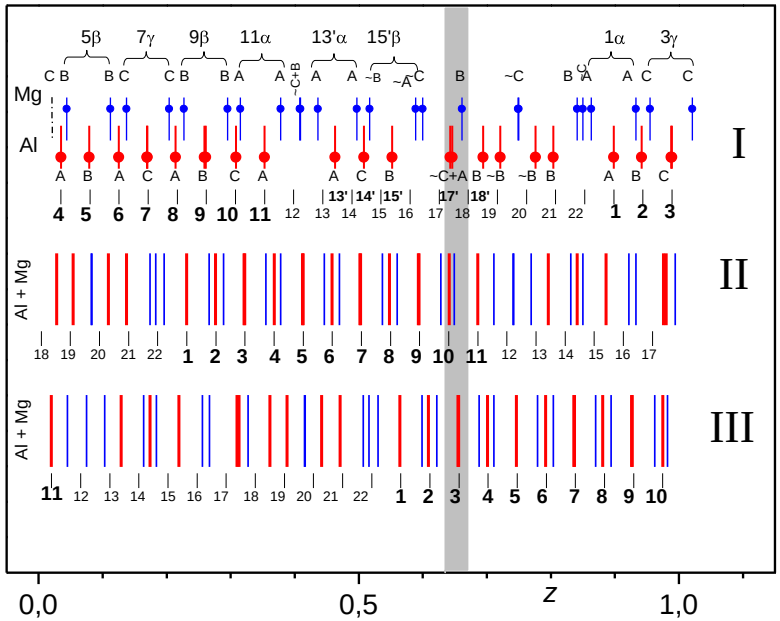


Crossection through the β'-Mg_2Al_3 in xy plane: near I-17'





β ' - phase: r = 0.22



Crossection through the β'-Mg_2Al_3 in xy plane: intergrowth of domains I and III