Cannon Balls and Pomegranates - a Quasi-Random Sphere Packing Uncovered

And:

Packings of Sphere Packings - the First Nontrivial Example

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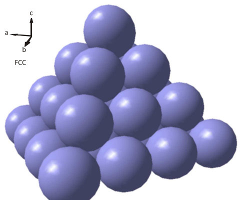
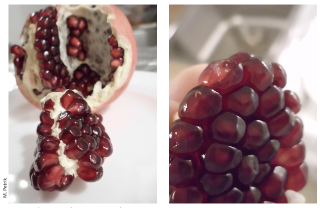
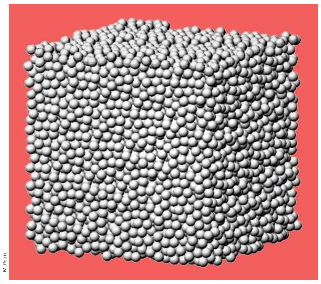


Cubic dense packing
(Johannes Keppler,
early 17th century)



Random close packing
(Johannes Keppler,
early 17th century)

Random close packing
(Stephen Hales,
early 18th century)

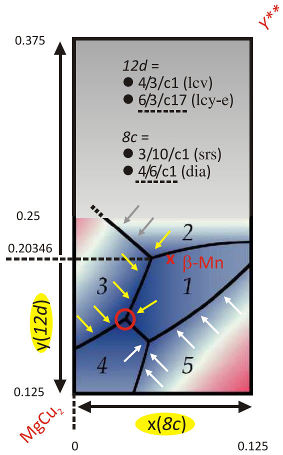


x(8c)=0.0363 *y(12d)*=0.1771

Novel quasi-random (ordered) sphere packing, isopointal with β-Mn

- Both ordered and random sphere packings have formed a subject of dedicated study for centuries.
- The most dense variants (close packings) have attracted particular attention.
- We ask: can *random* close packing be mimicked by some special kind of *ordered* packing? In analogy to the way random numbers are simulated by predetermined (pseudo- or quasi-random) number sequences?
- Nothing has been known in this regard up to now.
- In fact, such a special kind of sphere packing may be derived from the Laves net.

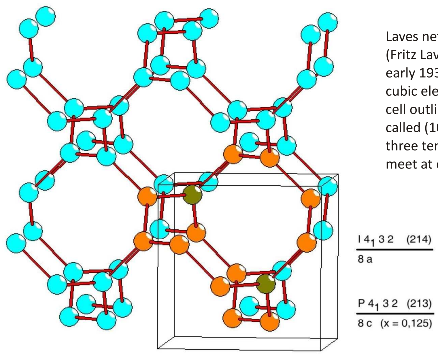
- The Laves net: arguably the simplest three-dimensional net.
- With but 3 connections to each node (3 contacts at each sphere, actually unstable by Hilbert's criterion).
- A member (*Y**) of the family of so-called lattice complexes.
- These are structures which may be generated in more than one type of space group, a property particularly important here (see next column).
- The Laves net is simple but nontrivial.
- It is chiral (comprising interconnected helices).
- It is self-interpenetrating: the left- and right-handed enantiomorphs may intertwine without mutual contact, forming the nonchiral lattice complex *Y***.



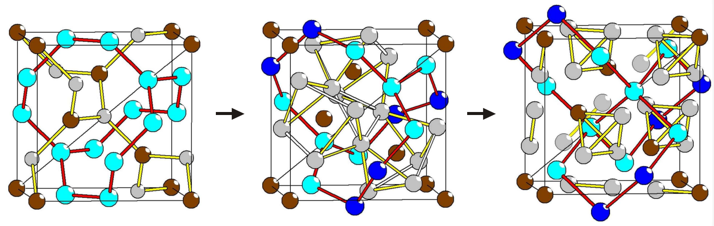
12d + 8c = New sphere packing types

Min. distance: 1 *8c-8c* 2 *12d-12d* 3 *8c-12d* 4 *12d-12d* 5 *8c-12d*

Minimum distance map of the *x/y*-parameter landscape (red=small, blue=large min. distance; adapted from W. Hornfeck, P. Kuhn, *Acta Cryst. A* **2014**, *70*, 441-447)



Laves net (Fritz Laves, early 1930ies, cubic elementary cell outlined), also called (10,3), since three ten-rings (orange) meet at each vertex (green).



Self-interpenetrating (double) Laves net: invariant lattice complex *Y***
$Ia\bar{3}d$ (*230*), *16b*

Alternative setting in $P4_132$ (*213*)

O brown *4a*
O gray *4b* (= *12d* with y=0,375)
O blue/cyan *8c* (x=0.125)

4b split in three (= *12d*):

β-manganese type
(two degrees of freedom)

O brown *4a* (VOID)
O gray *12d* (y=0.2035)
O blue/cyan *8c* (x=0.0678)

Yellow and white bonds ideally of equal length

4a filled
(two degrees of freedom fixed):

$MgCu_2$ type

O brown *4a*
O gray *12d* (y=0.125)
O blue/cyan *8c* (x=0)

- By transforming the invariant lattice complex *Y*** from $Ia\bar{3}d$ (*230*) to the enatiomorphic $P4_132$ (*213*), two degrees of freedom *x* and *y* (at Wyckoff positions *8c* and *12d*, respectively) are attained.
- Then, a systematic exploration of the *x/y*-parameter landscape reveals that both the β-Mn type (with *4a* unoccupied) and the $MgCu_2$ type are located within it or at its border.
- A generic relationship between β-Mn and $MgCu_2$ was in fact already established in the first half of the 20th century (only recently rediscovered, see *Z. Anorg. Allg. Chem.* **2014**, *640*, 2328).

- Beyond β-Mn, $MgCu_2$ and the Laves net:
- *x* and *y* are adjusted so that the *8c-8c*, *12d-12d* and *8c-12d* distances all become equal and attain a maximum value.
- A heterogeneous, novel sphere packing results, isopointal with β-Mn, for the first time bearing marked traits of quasi-randomness (density, number of contacts, shape of radial distribution function).
- In fact, two previously known interpenetrating homogeneous sphere packings (3/10/c1, or *srs*, and 4/3/c1, or *lcv*) are brought into contact, thereby forming the quasi-random packing.
- This new structure, besides being quasi-random, is also the first nontrivial example of a packing of sphere packings (two in this case).
- It is best described on the basis of the two partial structures, employing the unequivocal nomenclature available for the latter.
- Even today, with thousands of sphere packings known, this obvious way of describing new structures is rarely practiced in crystallography.