All Chemists Know the FCC Structure - Do They, though?

Exploring the Concept of *Packings* of Sphere Packings

- What are *packings of sphere packings* (PSPs)?
- How many PSPs do we know?
- Do they occur in real structures?

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What are PSPs?

- Sphere packings lie at the heart of structural inorganic chemistry. They provide a rationale for the classification of crystal structures. Both homogeneous [2] and heterogeneous [3] sphere packings are currently being compiled.
- Recently, we realized that a higher level of categorization is possible by considering *packings of sphere packings* (PSPs) [4].
- PSPs emerge whenever two (or more) sphere packings interpenetrate and thereby establish contact, provided the contiguity (network of contacts) in either of them is not disrupted.
- These two conditions set PSPs apart from most of the known interpenetrating structures like $MgCu_2$ or Cu_2O (and metal-organic frameworks, MOFs), in which the two substructures fail to establish contact.
- Higher-order PSPs (of more than two sphere packings) are also found, the fcc structure being a particularly notable example (Fig. 1).
- PSPs may not only serve for the classification of crystal structures, they sometimes show remarkable new characteristics in their own right as well, e.g. quasirandomness (Fig. 2) [4-6].

How many PSPs do we know?

- At the *Hemdsärmelkolloquium* at Augsburg (Germany) in March 2017, we initiated a search for PSPs by a call for contributions to an online compilation [1].
- The number of PSPs known has been growing steadily since 2017 so that now (as of September 2018) we are in a position to discuss 35 of them, for the most part previously unrecognized.

Do PSPs occur in real structures?

- The structure of a novel, quasirandom sphere packing isopointal with β-manganese consists of two interpenetrating sphere packings, or nets, forming a PSP [5].
- The two sphere packings forming this novel PSP are: on the one hand the three-connected Laves net (distorted), on the other a related net obtained by placing vertices in the centers of the bonds of the Laves net (again distorted but in a different manner).
- The Laves net may be viewed as a threedimensional variant of the *graphene* net. Then, by analogy, the second net in the foregoing structure is a kind of threedimensional *Kagome* net (vertices in place of bonds of the graphene net).
- Thus, the novel PSP - and consequently β-manganese also - is found to derive from two most simple and fundamental motifs: graphene and the Kagome net extrapolated into three dimensions!
- The novel PSP occurs in an almost ideal realization in the structure of $RbAg_4I_5$ where it forms the backbone network of iodine atoms (Fig. 2).

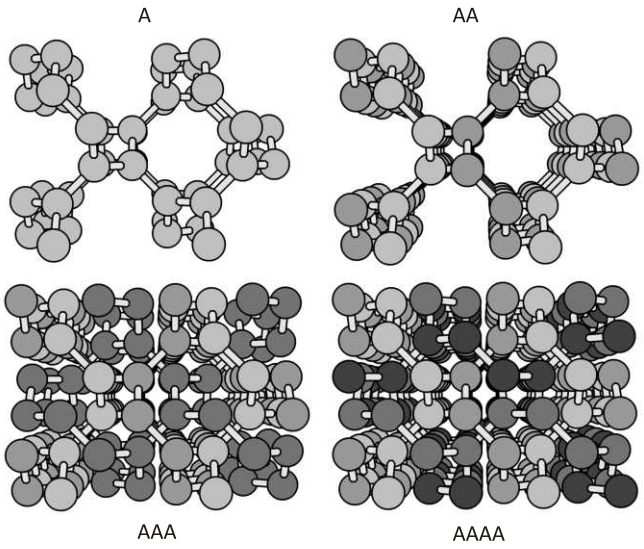

Fig. 1. The archetypal fcc structure (AAAA) - the first *quaternary* PSP!

- Four identical exemplars of the Laves net (A) interpenetrate and fit together perfectly, establishing contact without the need to readjust bond lengths or angles.
- A and AAA (the latter in itself a *ternary* PSP) are enantiomorphic.
- Either four A's of the same hand or two pairs of A's of opposite hand may be combined to form the same achiral structure AAAA (= fcc).
- This PSP epitomizes an intriguingly close relationship between the *most simple* (Laves net) and the *most efficient* (fcc) 3D-structures which exist!

[Central projection parallel to a cubic unit cell edge shown.]

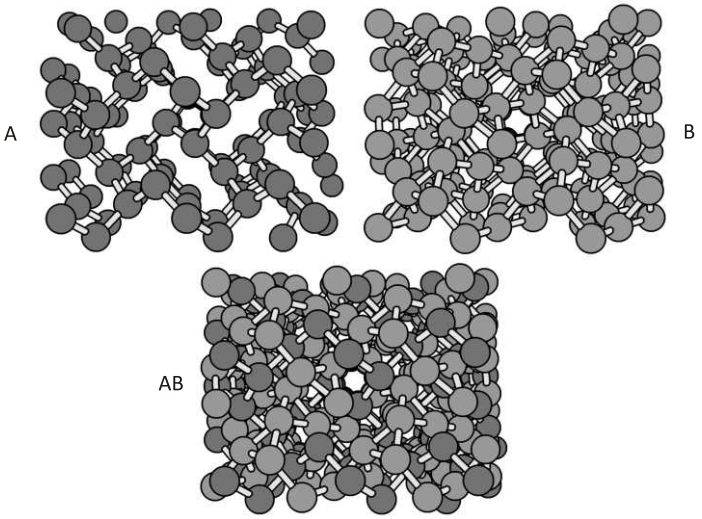

Fig. 2. The anion substructure (AB) of one of the best room-temperature ionic conductors known ($RbAg_4I_5$) - a remarkable PSP!

- An entanglement of a distorted Laves net (3D-folded distorted *graphene* net, A) with its similarly distorted *Kagome*-analog (i.e. bonds replaced by nodes, B).
- A, B and AB are all enantiomorphic.
- AB is isopointal with β-Mn, representing both the maximum in a minimal distance map [6] and a novel quasirandom sphere packing [4, 5].

[Central projection parallel to a cubic unit cell edge shown, centered on one of the empty iodine channels occupied by disordered Ag in $RbAg_4I_5$.]

References:

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