Comment on "Filling three-dimensional space with tetrahedra: A geometric and crystallographic problem"

David P. Shoemaker and Clara B. Shoemaker
Department of Chemistry, Oregon State University, Corvallis, Oregon 97331

(Received 11 March 1988)

We discuss the filling of three-dimensional Euclidean space with tetrahedra having two possible kinds of vertex atoms and three kinds of edge lengths (interatomic distances) as described by K. Y. Szeto and J. Villain [Phys. Rev. B **36**, 4715 (1987)]. We identify certain periodic structures corresponding to the authors' third solution with members of the family of tetrahedrally close-packed (tcp) alloy structures [including Frank-Kasper (FK) phases] and discuss factors limiting the generation of additional tcp alloy structure types with the procedure described.

In a recent paper, Szeto and Villain[1] (SV) discuss the problem of filling three-dimensional space with tetrahedra having two kinds of vertices A and B, and three corresponding edge lengths d_{AA}, d_{BB}, and d_{AB}. This problem was treated as not only geometric but also crystallographic, with the vertices representing two and only two kinds of atoms, as in an inorganic compound or metal alloy. The geometric treatment was quite ingenious and we have nothing to add to it. We will be here concerned with the crystallographic aspects.

Clearly this problem is related to the more general problem of filling space solely with tetrahedra that are not excessively distorted (it being well known that filling Euclidean space with *regular* tetrahedra is impossible), a problem already well known in connection with a certain class of metallic alloys that are said to be *tetrahedrally close packed* (tcp);[2-4] those of that class that are layered are known as *Frank-Kasper* (FK) phases.[5,6] The tetrahedra concerned here are those formed by the centers of every group of four atoms all of which touch the other three. The distortions in this family are limited, the ratio of the longest edge of any tetrahedron of the shortest edge not exceeding about $\frac{4}{3}$. The number of tetrahedra that can join at a common edge is either five ("minor bonds") or six ("major bonds"), and the coordination numbers (CN's) possible for the atoms are limited to 12, 14, 15, and 16, each possessing its characteristic coordination polyhedron (that for CN12 being a somewhat distorted regular icosahedron). The distribution of coordination types in these alloys is subject to geometrical considerations somewhat related to those of SV.[2] There are at least 23 known members of the tcp family, excluding polytypes (stacking variations). This family of structures has recently attracted attention in connection with quasicrystals.[3,4,7-9]

To avoid confusion with other uses of the letters A and B in discussions of alloy crystal structures, we replace them in the treatment of SV by S (small) and L (large), respectively; with these changes the parameters of SV's treatment become

$$x = d_{SS}/d_{SL}\ , \quad y = d_{LL}/d_{SL}\ . \tag{1}$$

The SV tetrahedra may be quite irregular—much more so than in the tcp case—as the restriction placed on x and y is

$$0 \le x \le 1 \le y < \sqrt{3}\ . \tag{2}$$

Three solutions for x,y, and periodic structures corresponding to them, are presented by SV. The first ($y=\sqrt{2}$) leads to the NaCl structure. This contains regular tetrahedra *LLLL*, and very much distorted tetrahedra *LLLS* in the shape of trigonal pyramids with apex angle 90°. Eight of the latter pack to form a regular octahedron centered by an S atom. As is well known, regular octahedra pack with twice their number of regular tetrahedra to fill space. This is a feature of cubic closest packing (fcc or ccp) and also hexagonal closest packing (hcp), representing two types of stacking of close-packed plane layers of atoms. It also exists in polytypes, representing various periodic combinations of these stacking types, and in random stacking sequences. The NaCl structure is obtained by placing Na^+ ions at the centers of *all* octahedra in a ccp packing of Cl^- ions. In principle there should also exist SV structures corresponding to hcp and the polytype and random packings. However as far as we are aware none are known in nature; in ionic crystals, cation-containing anion octahedra that share faces violate one of Pauling's electrostatic valence rules.[10]

The second SV solution ($x=\sqrt{4/7}$, $y=\sqrt{12/7}$) yields a hexagonal structure which was not identified but which was stated to be "both tetragonal and hexagonal," an "accidental violation of crystallography" that would be removed by any perturbation. No violation in fact exists, as the term "tetragonal" implies existence of a fourfold crystallographic symmetry axis which is not required to be present merely because of equality of axial lengths and in fact does *not* exist even approximately in this structure, which we find to be (with some differences in actual interatomic distances) the structure type $C32$ (e.g., AlB_2). Many representatives of this structure type are found in nature with axial ratios (c_0/a_0) varying between 0.59 and 1.27.[11]

The third solution ($x=\sqrt{8/11}$, $y=\sqrt{12/11}$) leads to two periodic structures, shown in SV's Fig. 6(b) but not identified as structures existing in nature. We find that the top and bottom structures in that figure correspond to the structure type $C14$ (e.g., $MgZn_2$), and that the middle one corresponds to the structure type $C15$ (e.g., $MgCu_2$). These are the two principal types of Friauf-Laves structures.[12,13]

SV describe in connection with these structures a 44-face polyhedron with 24 surface atoms, 18 S and 6 L, composed of packed tetrahedra. Actually there is not just one but two such 44-face polyhedra, one which possesses an inversion center and another which possesses a plane of symmetry perpendicular to its trigonal axis. These polyhedra result from interpenetration of two CN16 coordination polyhedra joining at a common six-membered ring of S atoms, and the two kinds of 44-atom polyhedra are related by a twist of 60°.

If we eliminate the 4 L surface atoms of a CN16 coordination polyhedron, retaining the 12 S surface atoms, we obtain the *Friauf polyhedron,* a truncated regular tetrahedron having four equilateral triangles and four regular hexagons as faces, defined by Samson[14] and used by him in describing tcp structures as well as alloy structures with giant unit cells. Two Friauf polyhedra can be linked together in either of two ways at a common hexagonal face: at an inversion center (i) or at a mirror plane (m). The resulting polyhedra are what one gets if one removes the 6 L surface atoms from the two kinds of SV 44-face polyhedra. Samson has shown how the $C14$ and $C15$ structures can be built up by packing the Friauf polyhedra with an equal number of smaller regular tetrahedra. Both structures can be considered as modes of stacking of slabs within which the Friauf polyhedra are linked in the i manner; if the slabs are stacked to create m linkages, the $C14$ structure results; if additional i linkages are formed, the $C15$ structure results. An alternation of the two modes creates a third Friauf-Laves structure type, $C36$ (e.g., $MgNi_2$),[13] which is also certainly accessible from the SV treatment, as are alloy structures with more complicated polytypic stacking arrangements such as those found by Komura and Kitano[15] and random stacking as demonstrated in SV's Fig. 6(c).

When two Friauf polyhedra are linked in the i manner and are capped with small tetrahedra at both ends, a rhombohedron with 60° apex angle results which is the primitive unit cell of the $C15$ structure. A very similar rhombohedron, but with apex angle 63.435°, is one of the two building blocks or "tiles" often used in the discussion of quasicrystals.[2]

One may well ask why SV's procedure does not generate additional tcp structures. In the Friauf-Laves structure types there are only two coordination types present (CN12 and CN16), and every small atom present belongs to both types of coordination polyhedra; there is only one kind of S and one kind of L. This is true of only one other known tcp structure type, namely $A15$ (e.g., β-W, Cr_3Si), but this structure is not in accord with SV's hypothesis because there are two different LL distances. All other known tcp structures have at least three and often four (CN12, CN14, CN15, CN16) coordination types, and in many instances there are more than one atom of the same coordination type that are not equivalent. Thus, atoms of at least three different sizes, and often many more, are required. While more tcp structure types may remain to be discovered, it is exceedingly unlikely that any of them will have simple structures which, like the Friauf-Laves structures, have only two sizes of atoms and only three distances.

While the basic assumptions of SV are broad enough to encompass the NaCl structure (but not the equally simple CsCl structure, which requires the use of two different L-L distances differing by factor of $\sqrt{2}$), they are too restricted to be of much use with alloys. tcp structures are not even very well described by packing of spheres of two or more different sizes. We have found that good fits to interatomic distances can be obtained if, while each CN12 atom may have a single bonding radius value, for the higher coordinations each atom is allowed to have *two* different radius values: one for minor bonds and a somewhat smaller one for major bonds.[16]

The treatment of SV is ingenious and elegant as a geometrical exercise and, as far as it goes, as a contribution to crystallography. Any extension of the treatment toward description of additional crystal structures will be very much more difficult, even in the case of tcp alloys for which a treatment in terms of packing of tetrahedra is naturally best suited.

---

[1] K. Y. Szeto and J. Villain, Phys. Rev. B **36**, 4715 (1987).

[2] D. P. Shoemaker and C. B. Shoemaker, Acta Cryst. B **42**, 3 (1986).

[3] D. P. Shoemaker and C. B. Shoemaker, in *Introduction to Quasicrystals,* edited by M. V. Jaric (Academic, New York, 1988), Vol. 1.

[4] D. P. Shoemaker and C. B. Shoemaker, in *Quasicrystals,* Proceedings of the International Workshop on Quasicrystals, Beijing, Peoples Republic of China, 1987 [Mat. Sci. Forum **22-24**, 67 (1987)].

[5] F. C. Frank and J. S. Kasper, Acta Cryst. **11**, 184 (1958).

[6] F. C. Frank and J. S. Kasper, Acta Cryst. **12**, 483 (1959).

[7] C. L. Henley and V. Elser, Philos. Mag. B **53**, L59 (1986).

[8] M. Audier, P. Sainfort, and B. Dubost, Philos. Mag. B **54**, L105 (1986).

[9] K. H. Kuo, J. Phys. (Paris) Colloq. **47**, C3-425 (1986); K. H. Kuo, D. S. Zhou, and D. X. Li, Philos. Mag. Lett. **55**, 33 (1987).

[10] L. Pauling, *The Nature of the Chemical Bond,* 3rd ed. (Cornell University Press, Ithaca, New York, 1960), p. 559.

[11] W. B. Pearson, *The Crystal Chemistry and Physics of Metals and Alloys* (Wiley-Interscience, New York, 1972), p. 494.

[12] J. B. Friauf, Phys. Rev. **29**, 35 (1927); J. Am. Chem. Soc. **49**, 3107 (1927).

[13] F. Laves and H. Witte, Metallwirtsch. Metallwiss. Metalltech. **14**, 645 (1935).

[14] S. Samson, in *Structural Chemistry and Molecular Biology*, edited by A. Rich and N. Davidson (Freeman, San Francisco, 1968), pp. 687–717.

[15] Y. Komura and Y. Kitano, Acta Cryst. B **33**, 2496 (1977).

[16] C. B. Shoemaker and D. P. Shoemaker, Trans. Met. Soc. Am. Inst. Min. Metall. Pet. Eng. **230**, 486 (1964).