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A Mathematical Analysis of Rod Packings

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Crystal structures in which atoms, molecules, or coordination polyhedra are repeated along infinite nonintersecting lines can easily be explained in terms of rod packings. A mathematical analysis of rod packings that are constructed from braids of slanting rods around a central, vertical rod, possessing three- or fourfold symmetry, is presented. The radius relation between the two types of rods and the density of the rod packing is determined by the elevation angle of the slanting rods and by the symmetry of repetition of the braid. The derived rod packings can be transferred into lower symmetry cases by asymmetric modulation of the rod radii, and by tilting the vertical rods. More complex packings can be created by using the same method of construction, and as an example, the sixfold braid rod packing is given. © 1995 Academic Press, Inc.

1. INTRODUCTION

Crystals represent ordered material in the solid state. They are built up by a three-dimensional unit cell of atoms that is infinitely repeated in all directions in the crystal. The chemical and physical properties of the solid are closely related to the atomic arrangement in the crystal, and hence it is important to represent this in a comprehensive way. Instead of describing a crystal structure as the packing of atoms, it is common to represent them in more understandable forms, like the packing of interconnected coordination polyhedra. In this way, the structural information is reduced to fewer elements, and is consequently easier to overview and interpret. Some structures benefit by a description one step further, in terms of infinite repetition of atoms, molecules, or polyhedra along a line, a rod. This representation is powerful in the interpretation of more complex structures, like those of garnet or β-tungsten (1). In garnet the rods represent infinite nonintersecting rows of polyhedra, and in β-tungsten infinite nonintersecting rows of atoms. This way of describing the structure makes these complex structures much easier to visualize and understand.

A mathematical analysis of some rod packings with infinite nonintersecting rods, expressing packing densities and rod radii as functions of the sloping angle of braid rods, will be presented here.

2. RULES OF CONSTRUCTION

The starting unit in the construction of a rod packing is a braid of slanting rods around a central, vertical rod (Figs. 1, 4). For the possible existence of a crystallographic packing the braid may possess two-, three-, four-, or sixfold rotational symmetry around the vertical rod. Different packings may be constructed from the same braid by modulating the symmetry of repetition of the braid in the c-direction, i.e., the direction parallel to the vertical rod. The repetition and symmetry of the braid and the elevation angle, α, of the slanting rods determine the radius relation between them and the vertical rods, and also the volume fraction of rods in the packing, i.e., the density.

The global requirements for the theoretical existence of the crystallographical packing is the nonintersecting of the rods. This can be determined by examining the projection of the packing on the plane perpendicular to the vertical rod, the ab-plane. Permissible networks are those that in projection result in Archimedean nets of unbroken lines (3^6, 3.6.3.6, 4^4-nets).

In this paper threefold and fourfold rod packings will be analyzed.

3. FOURFOLD ROD PACKING

The fourfold rod packing is based on the arrangement illustrated in Fig. 1. Here four slanting rods, with the elevation angle α, are wrapped around a central vertical rod like a braid. In order to determine the radius of the slanting (r_s) and vertical (r_v) rods, we study the two centroids $\mathbf{c}_1$ and $\mathbf{c}_2$ in Fig. 1,

$$\mathbf{c}_1 = (0\,0\,0) + s(\cos\alpha, 0, \sin\alpha) \qquad [1]$$

$$\mathbf{c}_2 = (1\,0\,0) + t(0, \cos\alpha, \sin\alpha). \qquad [2]$$

The shortest distance between $\mathbf{c}_1$ and $\mathbf{c}_2$ is perpendicular to the two centroids, and thus parallel to

$$\mathbf{c}_1 \times \mathbf{c}_2 = (\sin\alpha \sin\alpha - \cos\alpha) = \mathbf{u}. \qquad [3]$$

The projection of a vector between two arbitrary points

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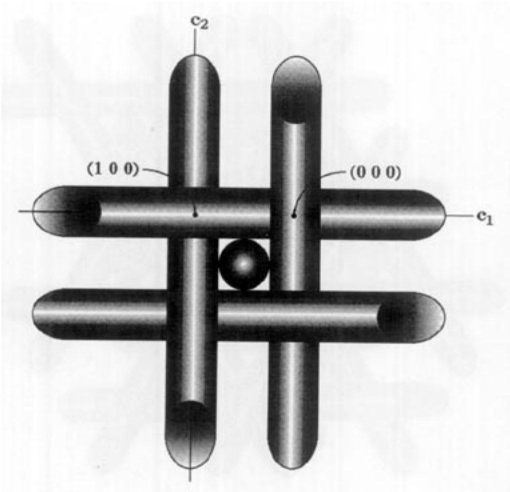

FIG. 1. Four slanting rods wrapped around a central vertical rod in form of a braid. This is the basic unit in construction of the fourfold rod packing.

on $\mathbf{c}_1$ and $\mathbf{c}_2$ onto $\mathbf{u}$ represents the distance $2r_s$. Take the vector (1 0 0),

$$2r_s = \frac{(1\,0\,0)\cdot\mathbf{u}}{|\mathbf{u}|} = \frac{\sin\alpha}{\sqrt{1+\sin^2\alpha}}. \qquad [4]$$

According to Fig. 1, this leads to

$$r_s = \frac{\sin\alpha}{2\sqrt{1+\sin^2\alpha}}, \quad 0 \le r_s \le \frac{1}{2\sqrt{2}} \qquad [5]$$

$$r_v = \frac{1}{2} - r_s, \quad \frac{\sqrt{2}-1}{2\sqrt{2}} \le r_v \le \frac{1}{2}. \qquad [6]$$

Only one crystallographic rod packing can be constructed from this fourfold braid. It is illustrated in Fig. 2, and produces a 4^4-Archimedean net in projection. This is the only Archimedean tiling of fourfold symmetry that consists entirely of unbroken lines. The space group symmetry for the tetragonal packing is $P422$, with $c/a = \tan\alpha$. Vertical rods at $(0\ 0\ z)$ are original central braid rods and generate a braid at $(1/2\ 1/2\ z + 1/2)$, cf. Fig. 2.

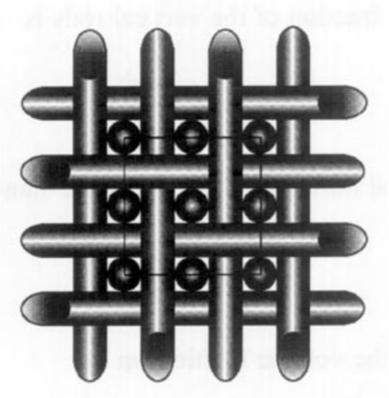

FIG. 2. The fourfold braid rod packing (viewed along c), with the unit cell outlined (space group $P422$), that produces a 4^4-net in projection. This is the only fourfold rod packing that creates a permissible Archimedean net in projection.

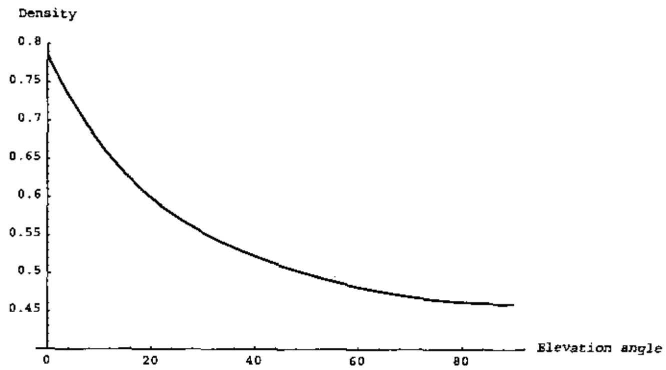

FIG. 3. The density of the fourfold rod packing as a function of the elevation angle α.

The density of the packing, i.e., the volume fraction of rods, is calculated as the sum of the density fractions in the different directions. The density fraction is equal to the area fraction, i.e., the projected volume fraction, in the respective directions. For the vertical rods the area fraction is

$$A_v = \pi r_v^2 \qquad [7]$$

and the total horizontal fraction of the slanting rods

$$A_H = \frac{\pi r_s^2}{\sin\alpha}, \qquad [8]$$

which results in the density

$$\rho = \pi\left(r_v^2 + \frac{r_s^2}{\sin\alpha}\right). \qquad [9]$$

When $\sin^2\alpha = 1/3$ all rods have equal radius, and the density is $[(\sqrt{3}+1)/16]\ \pi \approx 0.5364$. The density as a function of the elevation angle α is illustrated in Fig. 3.

The tetragonal packing constructed here can be made orthorhombic, monoclinic, or triclinic by asymmetrically modulating the radii of the braid rods, making them different in the x- and y-directions, or/and by tilting the vertical rods.

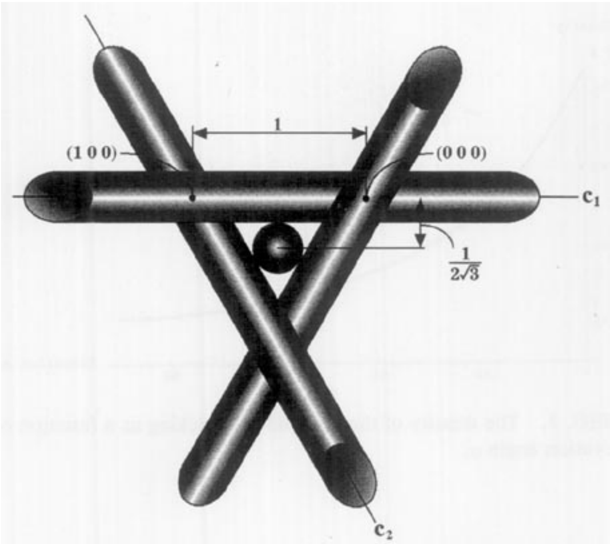

FIG. 4. A threefold braid of slanting rods around a central vertical rod. This is the basic unit in the construction of the threefold rod packings.

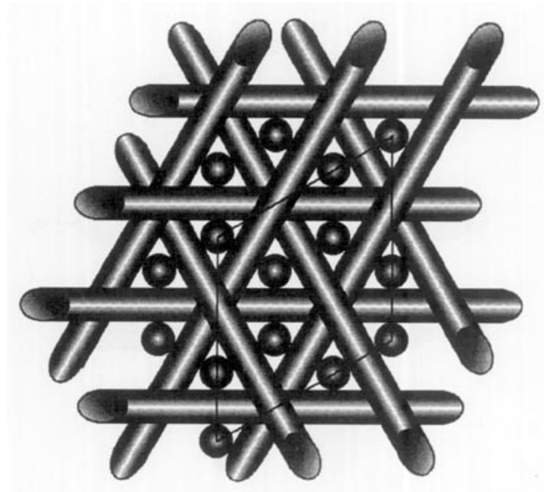

FIG. 5. The single network (plain translation of the braid in the c-direction) from the threefold braid, viewed along c, with its unit cell outlined. Its space group symmetry is $R32$ and in projection the slanting rods produce a 3^6-net.

4. THREEFOLD ROD PACKINGS

The starting unit for the threefold rod packings is shown in Fig. 4. Three slanting rods, with the elevation angle α, form a braid around a vertical rod. Here, the equations for the two centroids $\mathbf{c}_1$ and $\mathbf{c}_2$ are

$$\mathbf{c}_1 = (0\,0\,0) + s(\cos\alpha, 0, \sin\alpha) \qquad [10]$$

$$\mathbf{c}_2 = (1\,0\,0) + t\left(-\frac{1}{2}\cos\alpha, \frac{\sqrt{3}}{2}\cos\alpha, \sin\alpha\right), \qquad [11]$$

and the shortest distance between them are parallel to

$$\mathbf{c}_1 \times \mathbf{c}_2 = (\sin\alpha, \sqrt{3}\sin\alpha, \cos\alpha) = \mathbf{u}. \qquad [12]$$

Again, the distance $2r_s$ is equal to the projection of an arbitrary vector from $\mathbf{c}_1$ to $\mathbf{c}_2$ onto $\mathbf{u}$, for example the (1 0 0),

$$2r_s = \frac{(1\,0\,0)\cdot\mathbf{u}}{|\mathbf{u}|} = \frac{\sin\alpha}{\sqrt{1+3\sin^2\alpha}}. \qquad [13]$$

This results in

$$r_s = \frac{\sin\alpha}{2\sqrt{1+3\sin^2\alpha}}, \quad 0 \le r_s \le \frac{1}{4} \qquad [14]$$

$$r_v = \frac{1}{2\sqrt{3}} - r_s, \quad \frac{2\sqrt{3}-3}{12} \le r_v \le \frac{1}{2\sqrt{3}} \qquad [15]$$

$$r_q = \frac{r_s}{r_v} = \frac{\sin\alpha}{\sqrt{\frac{1}{3}+\sin^2\alpha} - \sin\alpha}, \quad 0 \le r_q \le 2\sqrt{3}+3. \qquad [16]$$

Two different rod packings can be constructed from this threefold braid, the single network, and the double network of threefold braids.

4.1. Single Network of Threefold Braids

A rod packing constructed by plain translation between two layers of threefold braids in the c-direction results in a single network. In projection on the ab-plane, this packing yields a two-dimensional 3^6-net, in which the vertical rods are represented by the nodes in the conjugate 6^3-net. The space group is $R32$, and the unit cell is hexagonal with $c/a = \sqrt{3}\tan\alpha$. Here the vertical rods at $(0\ 0\ z)$ are original central braid rods, and generate braids at $(\frac{1}{3}\ \frac{1}{3}\ z+\frac{1}{3})$ and $(\frac{2}{3}\ \frac{2}{3}\ z+\frac{2}{3})$, cf. Fig. 5.

The area fraction of the vertical rods is

$$A_v = \frac{4\pi r_v^2}{\sqrt{3}} \qquad [17]$$

and the total horizontal fraction of the slanting rods

$$A_H = \frac{2\pi r_s^2}{\sqrt{3}\sin\alpha}. \qquad [18]$$

This sums the volume fraction up to

$$\rho = \frac{\pi}{\sqrt{3}}\left(4r_v^2 + \frac{2r_s^2}{\sin\alpha}\right), \qquad [19]$$

FIG. 6. The double network (inversion of the braid in translating it in the c-direction) from the threefold braid, viewed along c, with the unit cell outlined. Its space group symmetry is $R\bar{3}c$ and in projection the slanting rods yield a 3.6.3.6-kagomé net.

which is the density of the rod packing. When $\sin\alpha = 0$ the maximal density is achieved $(\pi/(3\sqrt{3}) \approx 0.6046)$ and when $\sin\alpha = 1$ it is minimal $[17 - 8\sqrt{3})/(24\sqrt{3})]\,\pi \approx 0.2376)$.

4.2. *Double network of threefold braids*

The second rod packing from the threefold braid, the double network, is constructed by inversion of the braid in translating it between two layers in the c-direction. In projection this packing results in a 3.6.3.6-kagomé net, in which the vertical rods are represented by the nodes in a 3^6-net (Fig. 6). This packing belongs to the space group $R\bar{3}c$, and has a hexagonal unit cell with $c/a = \sqrt{3}\tan\alpha$. The braids at $(0\ 0\ z)$ generate braids at $(\frac{1}{3}\ \frac{1}{3}\ z + \frac{1}{3})$ and $(\frac{2}{3}\ \frac{2}{3}\ z + \frac{2}{3})$, cf. Fig. 6.

Its area fraction of vertical rods is

$$A_V = \frac{3\sqrt{3}\,\pi r_V^2}{2} \qquad [20]$$

and its total horizontal fraction

$$A_H = \frac{3\sqrt{3}\pi r_S^2}{2\sin\alpha}, \qquad [21]$$

which results in the density

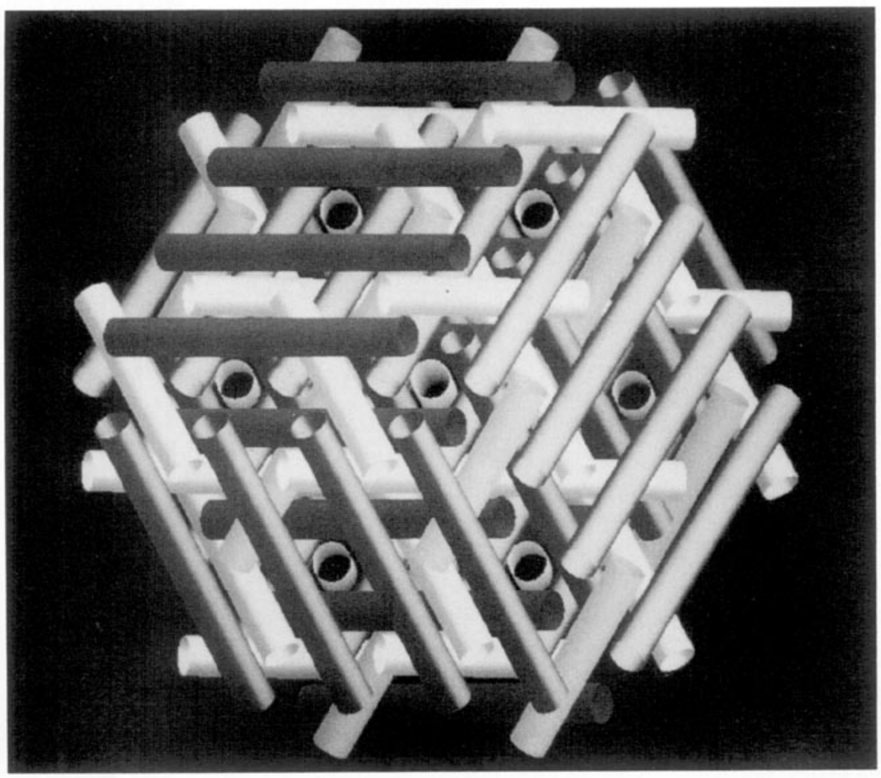

FIG. 7. A cubic packing (space group $Pm\bar{3}n$) of two interpenetrating rod packings that is constructed from the double threefold network. In order to create the cubic packing, 3/4 of the vertical rods are placed in the three other cubic space diagonal directions.

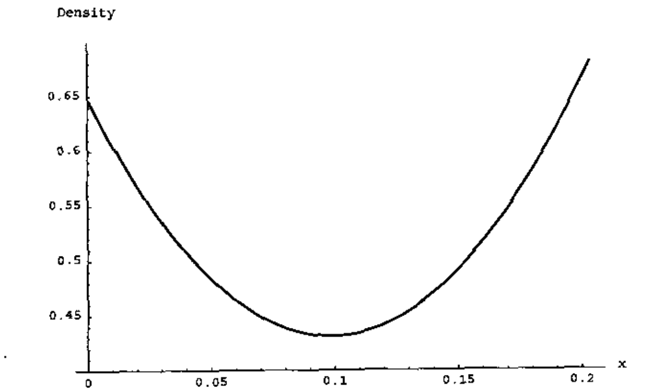

FIG. 8. The density of the cubic rod packing that is derived from the double network of threefold braids, as a function of x. The radius of garnet rods is $r_g = (\sqrt{2} - 1)/2\sqrt{6} + x$ and of the cubic primitive rods $r_p = 1/2\sqrt{6} - x$.

$$\rho = \frac{3\sqrt{3}\pi}{2}(r_v^2 + r_s^2/\sin\alpha) \qquad [22]$$

The maximal density occurs at two points, $\sin\alpha = 0$ and $\sin\alpha = 1/3$, for which the density is $(\sqrt{3}/8)\pi \approx 0.6802$, and the minimal density is $((5\sqrt{3} - 6)/16)\pi \approx 0.5223$ when $\sin\alpha = 1$.

From the radius quotient in Eq. [16] it is determined that the radius of the vertical and slanting rods are equal when $\sin\alpha = 1/3$. This corresponds to the maximal relative density $(\sqrt{3}/8)\pi \approx 0.6802$, and the packing is identical with the cubic garnet rod packing (space group $Ia\bar{3}d$) (1). The slanting rods are orthogonal when $\sin^2\alpha = 1/3$, for which the density of the slanting rods is $3/16\pi \approx 0.5890$. This corresponds to the primitive cubic rod packing (space group $Pm\bar{3}n$) (1). The density of this cubic packing including the vertical rods, resulting in a hexagonal packing is $[(3\sqrt{3} + 3 - 2\sqrt{6})/16)]\pi \approx 0.6474$, which is lower than that of garnet. The hexagonal packing can be transferred into a cubic one by placing 3/4 of the vertical rods in the three other cubic space diagonal directions (Fig. 7). This network is mentioned in (2) and consists of two interpenetrating rod packings, the primitive cubic rod packing and the garnet packing of thin rods. It has one free parameter, the radius relation between the primitive and garnet packing rods. The density is given by

$$\rho = \frac{3\pi}{2}\left\{(3 + \sqrt{3})x^2 + \frac{\sqrt{2} - 1\,\sqrt{3}}{\sqrt{2}}x + \frac{3 + \sqrt{3} - 2\sqrt{6}}{24}\right\}, \quad 0 \le x \le \frac{1}{2\sqrt{6}}, \qquad [23]$$

where the radius of the garnet rods is

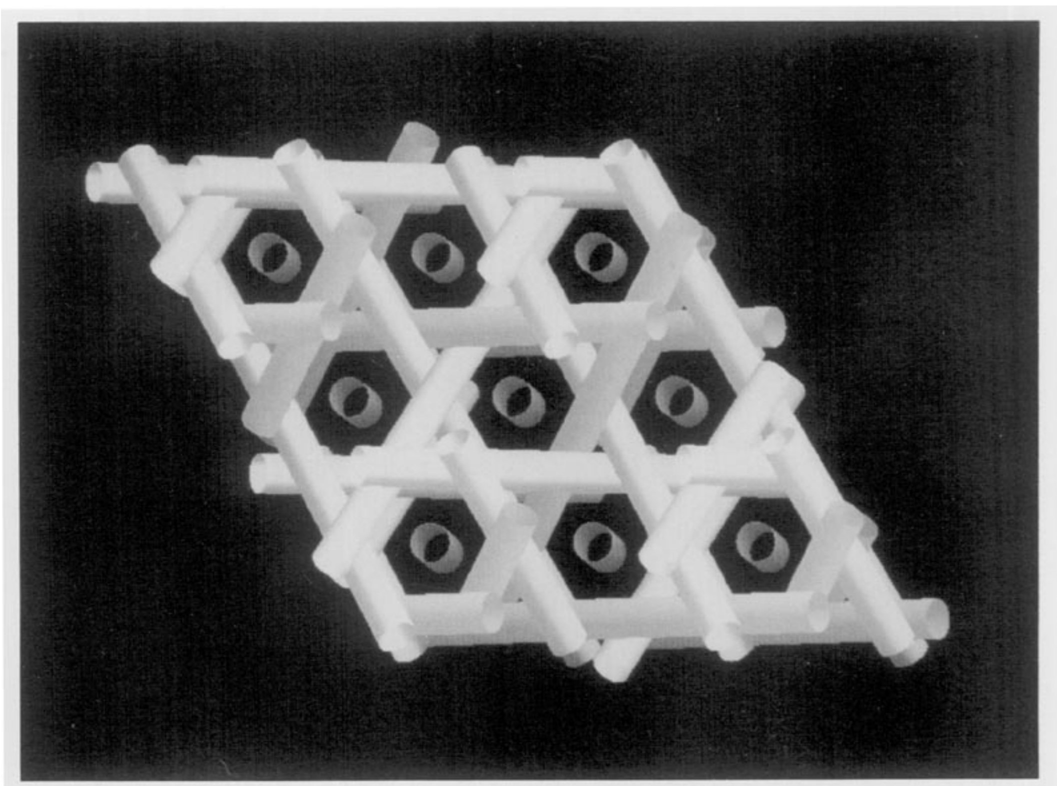

FIG. 9. The sixfold braid rod packing ($P622$) that is not analyzed here.

$$r_g = \frac{\sqrt{2} - 1}{2\sqrt{6}} + x \qquad [24]$$

and of the primitive rods

$$r_p = \frac{1}{2\sqrt{6}} - x. \qquad [25]$$

The starting point, $x = 0$, represents the primitive cubic packing interpenetrated by thin garnet rods and has a density of $(\pi-16)(3\sqrt{3} + 3 - 2\sqrt{6}) \approx 0.6474$, and the finishing point, $x = (1/2\sqrt{6})$, is the garnet packing (density $(\sqrt{3}/8)\pi \approx 0.6802$. Both these points represent maximal values of the density, cf. Fig. 8. The minimal density of the packing is $3\pi/(8(\sqrt{3} + 1)) \approx 0.4312$, and the density for rods all with equal radius is $(\sqrt{3}/16(\sqrt{3} - 1))\pi \approx 0.4646$.

5. OTHER PACKINGS

Using the same method of construction it is possible to create more complex rod packings, for example the sixfold braid rod packing (Fig. 9) with space group symmetry $P622$. Here a sixfold braid (at $(0\,0\,z)$) is wrapped around the vertical rod, and in projection this crystallographical packing results in a 3.6.3.6.-kagomé net.

This packing is, however, not analyzed here.

ACKNOWLEDGMENT

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