Acta Crystallographica Section A
Foundations of Crystallography
ISSN 0108-7673

Received 13 February 2004
Accepted 9 March 2004

Exceptional properties of some sphere packings in the general position of $P6_222$

E. Koch* and H. Sowa

Institut für Mineralogie, Petrologie und Kristallographie der Philipps-Universität Marburg, Hans-Meerwein-Strasse, D-35032 Marburg, Germany. Correspondence e-mail: elke.koch@staff.uni-marburg.de

Three types of sphere packing are described which show properties that have never been observed before: a certain set of generating symmetry operations corresponds to a parameter range in $P6_222$ that is not simply connected, but disintegrates into two disjoint non-congruent regions; the minimal sphere-packing density is different for these two regions; two sphere packings from different regions cannot be deformed into each other without opening sphere contacts although their sphere-packing graphs are isomorphic in the graph-theoretical sense. Two heterogeneous crystal nets with different symmetry described by Delgado-Friedrichs & O'Keeffe [*Acta Cryst.* (2003), A**59**, 351–360] show a similar behaviour. They are related to a type of tetragonal sphere packing with likewise unusual properties.

1. Introduction

Sphere packings form a useful tool to compare and to characterize crystal structures. Complete information, however, is available only on homogeneous sphere packings with cubic (Fischer, 1973, 1974), tetragonal (Fischer, 1991*a*,*b*, 1993) and triclinic (Fischer & Koch, 2002) symmetry. Within the scope of a current research project, all types of hexagonal and trigonal sphere packing (Sowa *et al.*, 2003; Sowa & Koch, 2004) will be derived in addition. In the course of these investigations, three types of sphere packing were found which show properties that have never been observed before: a certain set of generating symmetry operations corresponds to a parameter range that is not simply connected but disintegrates into two disjoint non-congruent regions; and the minimal sphere-packing density is different for these two regions.

2. Definitions

A set of non-intersecting spheres with the symmetry of a space group G is called a *sphere packing* if a chain of spheres with mutual contact connects any two spheres. It is called a *homogeneous sphere packing* if all its spheres are symmetrically equivalent (*e.g.* Fischer, 1991*a*). In the following, only homogeneous sphere packings will be considered.

Each sphere packing can uniquely be assigned to a graph, its *sphere-packing graph*, as follows: (i) each centre of a sphere is replaced by a vertex of the graph; (ii) two such vertices are connected by an edge of the graph if and only if the corresponding spheres are in contact (*cf. Mittelpunktsfigur*, Heesch & Laves, 1933; Fischer, 1971).

Two sphere packings are assigned to the same *type* if a biunique mapping exists that sends the spheres of the first sphere packing onto the spheres of the second one under preservation of all contact relationships between spheres, *i.e.* if the corresponding two sphere-packing graphs are isomorphic.

Each sphere-packing type is designated by a symbol $k/m/fn$ as was first introduced by Fischer (1971): k is the number of contacts per sphere, m is the length of the shortest mesh within the sphere packing, f indicates the highest crystal family for a sphere packing of that type (c: cubic, h: hexagonal/trigonal, t: tetragonal) and n is an arbitrary number.

A certain sphere packing is uniquely described by its generating symmetry group G together with its metrical parameters and the coordinate parameters of the centre of an arbitrarily chosen reference sphere. Distance calculations then yield the coordinates of the centres of all neighbouring spheres. If the point configuration of the sphere centres refers to a lattice complex with three degrees of freedom, *i.e.* if it belongs to a general Wyckoff position, each neighbouring sphere corresponds uniquely to that symmetry operation $g_s \in G$ that maps the reference sphere onto the neighbouring one. A complete set $\{g_s\}$ of such symmetry operations is called a *set of generators of the sphere packing* (*cf.* Fischer, 1991*a*). It is not unique because the reference sphere may arbitrarily be chosen. Each set of sphere-packing generators forms as well a set of generators of the corresponding space group.

The *density* ρ *of a sphere packing* is defined as the volume of all spheres within one unit cell divided by the volume of the unit cell. For most sphere-packing types, a *minimal density* $\rho_{\min}$ of all corresponding sphere packings may uniquely be calculated.

3. Parameter regions

In most cases, a sphere packing with symmetry G may be deformed without losing symmetry or sphere contacts. Then, the corresponding sphere-packing type occurs with $n \geq 1$ degrees of freedom, *i.e.* the metrical and coordinate parameters of an entire n-dimensional parameter region give rise to sphere packings of that type. All these sphere packings refer to analogous sets of generators.

Each symmetry operation belonging to $N_E(G)$, the Euclidean normalizer of G (*e.g. cf.* Koch & Fischer, 2002), maps a certain sphere packing either onto itself or onto a congruent one. Simultaneously, it maps by conjugation a corresponding set of sphere-packing generators onto a symmetrically equivalent or normalizer-equivalent set. Furthermore, it sends the respective parameter region onto a congruent region that is symmetrically equivalent or normalizer-equivalent to the original one.

Normally, each such parameter region corresponds uniquely to a certain set of sphere-packing generators and *vice versa*. Very few exceptional cases, however, are known where a given set of sphere-packing generators belongs to two disjoint, but congruent, regions. The sphere packings of type 5/3/*t*23 with a two-dimensional parameter region in space group $I4_1/a$ form such an example (*cf.* Fischer, 1993). Sphere-packing parameters are *e.g.* $x = y = 0.108$, $z = 0.240$ and $c/a = 0.450$. The corresponding set of generators consists of the twofold rotation around $00z$, the fourfold roto-inversions with inversion centre at 000 and the 4_3 screw rotations around $\frac{1}{4}\frac{1}{4}z$. The Euclidean normalizer $N_E(I4_1/a) = P4_2/nnm$ $[(\mathbf{a}-\mathbf{b})/2, (\mathbf{a}+\mathbf{b})/2, \mathbf{c}/2]$ contains the twofold rotation around $xx0$ (*cf.* Koch & Fischer, 2002) that maps this set of generators onto itself and, simultaneously, maps the sphere packing with the above-mentioned parameters onto a congruent one with coordinates $x = y = 0.108$ and $z = -0.240$. Both sphere packings belong to disjoint, but congruent, parameter regions. It is a necessary condition for such a behaviour that no sphere packing with minimal density exists for the type under consideration. The minimum of density for sphere-packing type 5/3/*t*23 refers to the coordinate parameters $\frac{1}{8}\frac{1}{8}\frac{1}{8}$ and the axial ratio $c/a = 1$, *i.e.* to a sphere packing of type 6/3/*t*40 with one additional contact per sphere.[1]

The properties of the recently found examples are much stranger: two disjoint non-congruent parameter regions belong to one and the same set of sphere-packing generators; the minimal sphere-packing density is different for these two regions; a sphere packing belonging to one of these regions cannot be deformed into a sphere packing of the other region without opening sphere contacts.

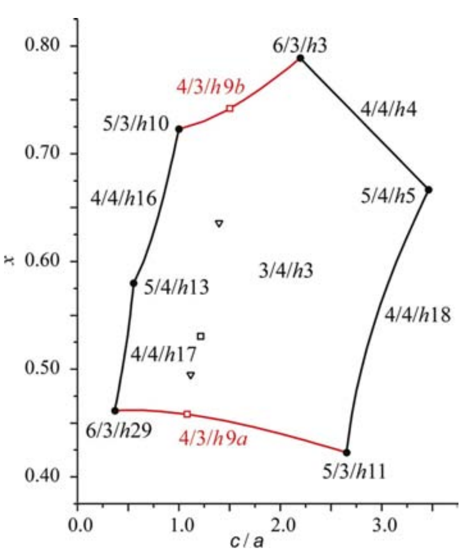


Figure 1
Projection of the parameter region of sphere-packing type 3/4/*h*3 and its boundary: sphere packings with minimal density are marked by squares (*cf.* Figs. 2*b* and 3).

4. Unusual sphere packings in $P6_222$

In the course of the examination of the general position of $P6_222$, the sphere-packing type 3/4/*h*3 attracted special attention. A corresponding set of sphere-packing generators consists of three twofold rotations with rotation axes *e.g.* at $2x, x, \frac{1}{6}$; $x+\frac{1}{2}, 2x, 0$; and $\frac{1}{2}, 0, z$. The respective parameter range in the four-dimensional $x, y, z, c/a$ space has two degrees of freedom and is bounded by six one-dimensional and six zero-dimensional parameter regions. Fig. 1 shows its projection onto the $x, c/a$ plane. The number of sphere-packing neighbours increases from three to four at all edges of the boundary; it increases to five or six at the vertices. Parameters for the sphere packing of type 3/4/*h*3 with minimal density are marked in Fig. 1 by a black square.

A closer look at the boundary reveals an unusual behaviour. One and the same symmetry operation, namely a twofold rotation around $x00$, gives rise to the additional neighbours of two different bordering parameter regions (red edges in Fig. 1). As a consequence, both parameter regions correspond to the same set of sphere-packing generators and, therefore, should be assigned to the same type of sphere packing (*cf.* §2), namely 4/3/*h*9. On the other hand, the corresponding ranges of the parameter c/a are different and, therefore, both regions cannot be mapped onto another by a symmetry operation of the Euclidean normalizer $N_E(P6_222) = P6_422$ $(\mathbf{a}, \mathbf{b}, \mathbf{c}/2)$. Moreover, the minimal sphere-packing density $\rho_{\min}$ (*cf.* Table 1) for both parameter regions is different and other sphere-packing types (*cf.* Fig. 1) bound these regions. A similar behaviour has never been observed before.

Table 1 gives information on all sphere-packing types at the boundary of the parameter range of 3/4/*h*3: the sphere-packing parameters x, y, z and c/a and the value of $\rho_{\min}$ for the respective sphere packings with minimal density. Fig. 2 displays the graphs of three sphere packings of type 3/4/*h*3. Their parameters are marked in Fig. 1 by a black square (minimal density) and by black triangles. Figs. 2(*a*) and 2(*c*) (upper and lower triangle, respectively, in Fig. 1) show different distortions compared with a sphere packing with

[1] A net corresponding to a sphere packing of type 5/3/*t*23 has the maximal combinatorial symmetry (*cf.* Delgado-Friedrichs & O'Keeffe, 2003) $I4_1/amd$ 16*g* ..2 *xx*0. With this symmetry, however, the tetrahedra of spheres contained in each such sphere packing are necessarily distorted to flat squares.

Table 1
Sphere packings at the boundary of the parameter range of type 3/4/h3: x, y, z and c/a for the sphere packings with minimal density $\rho_{\min}$.

Type	x	y	z	c/a	$\rho_{\min}$
3/4/*h*3	**0.53120**	**0.14951**	**0.10710**	**1.20898**	**0.12240**
6/3/*h*29	0.46144	0.10534	0.25	0.36491	0.34157
4/3/*h*9*a*	0.45817	0.11429	0.09211	1.07459	0.14815
5/3/*h*11	0.42265	0.21132	0.06904	2.65099	0.37959
4/4/*h*18	0.53061	0.26531	0.07959	2.88698	0.31945
5/4/*h*5	0.66667	0.33333	0.08333	3.46410	0.40307
4/4/*h*4	0.72402	0.27598	0.08333	2.86805	0.33170
6/3/*h*3	0.78868	0.21132	0.08333	2.19615	0.45821
4/3/*h*9*b*	0.74176	0.17698	0.10212	1.50095	0.39382
5/3/*h*10	0.72291	0.16318	0.14151	0.99868	0.46396
4/4/*h*16	0.60779	0.16296	0.20673	0.68268	0.25155
5/4/*h*13	0.57980	0.15959	0.25	0.55284	0.27718
4/4/*h*17	0.53657	0.14477	0.25	0.50150	0.25657

minimal density (Fig. 2*b*). The red and blue edges intersect in the projection in Fig. 2(*c*) in contrast to Fig. 2(*a*). However, all three sphere packings of type 3/4/*h*3 may be deformed into one another without losing sphere contacts.

Two sphere packings with minimal densities of type 4/3/*h*9 belonging to the two different parameter regions (red squares in Fig. 1) are shown in Fig. 3. Because of their identical sets of generators, the two graphs are clearly isomorphic. Nevertheless, they show differences that should not be neglected in crystallography. Both sphere packings are built up from screws around the 6_2 axes. Two of them are marked in red and blue. Pairs of spheres from neighbouring screws are connected by additional contacts giving rise to tetrahedra. The mutual arrangement of the screws, however, is different in the two sphere packings: the screws are separate in Fig. 3(*a*), whereas neighbouring screws are interwoven in Fig. 3(*b*). As a consequence, the two graphs cannot be distorted into each other (although they are isomorphic) and the two sphere packings cannot be deformed into each other without opening sphere contacts.[2] In order to distinguish the two variants of the sphere-packing type 4/3/*h*9, they are designated 4/3/*h*9*a* and 4/3/*h*9*b*.

The set of generators of 4/3/*h*9*a* and 4/3/*h*9*b* consists of the following four twofold rotations: $2(2x, x, \frac{1}{6})$, $2(x+\frac{1}{2}, 2x, 0)$, $2(\frac{1}{2}, 0, z)$, $2(x, 0, 0)$. It contains four subsets of three twofold rotations each:

(i) $2(2x, x, \frac{1}{6})$, $2(x+\frac{1}{2}, 2x, 0)$, $2(\frac{1}{2}, 0, z)$,
(ii) $2(2x, x, \frac{1}{6})$, $2(x+\frac{1}{2}, 2x, 0)$, $2(x, 0, 0)$,
(iii) $2(2x, x, \frac{1}{6})$, $2(\frac{1}{2}, 0, z)$, $2(x, 0, 0)$,
(iv) $2(x+\frac{1}{2}, 2x, 0)$, $2(\frac{1}{2}, 0, z)$, $2(x, 0, 0)$.

[2] Carlucci *et al.* (2003*a*) describe the polycatenated (2D → 3D) network in $[Ag(sebn)_2]X$ that is built up from 'self-penetrated layers'. Here, pairs of six-membered rings belonging to the same layer are catenated quite similar to the interwoven screws in 4/3/*h*9*b*. The same authors (Carlucci *et al.*, 2003*b*, Fig. 51) give an example of two two-periodic nets with different symmetry that are isomorphic in the graph-theoretical sense but cannot be deformed into another without cutting some of the edges. These nets, however, do not contain catenated rings. The simpler of these nets corresponds to the graphs of certain sphere packings with layer-group symmetry $P\bar{4}(b)2$ (*cf.* Koch & Fischer, 1978, type KIa), the other one cannot be related to any sphere packing of a layer group.

The first subset corresponds to sphere-packing type 3/4/*h*3 (*cf.* above), the second one to 3/4/*h*1, the third one to 3/4/*h*2, whereas the fourth one generates only a tetrahedron of spheres (the three twofold axes intersect at $\frac{1}{2}00$). The second as well as the third subset contain the rotations $2(2x, x, \frac{1}{6})$ and $2(x, 0, 0)$ that generate the screws around the 6_2 axes discussed for type 4/3/*h*9. Therefore, the properties of both corresponding sphere-packing types are very similar to those of 4/3/*h*9. For each type, there exist two disjoint non-congruent parameter regions giving rise to isomorphic sphere-packing graphs, but sphere packings from the two regions cannot be deformed into each other without losing sphere contacts. They are labelled *a* and *b* again.

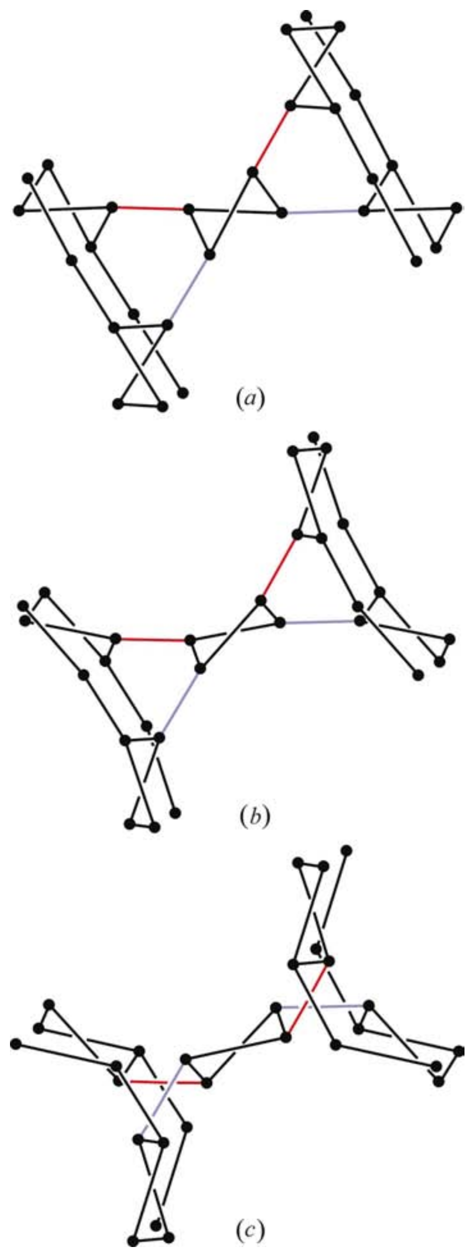


Figure 2
Three sphere packings of type 3/4/*h*3: (*b*) sphere packing with minimal density (*cf.* black square in Fig. 1); (*a*), (*c*) sphere packings referring to the black triangles in Fig. 1.

Fig. 4 shows a projection of the two-dimensional parameter regions of sphere-packing types 3/4/*h*3, 3/4/*h*1*a*, 3/4/*h*1*b*, 3/4/*h*2*a* and 3/4/*h*2*b*. The one-dimensional region of 4/3/*h*9*a* forms the common boundary of 3/4/*h*3, 3/4/*h*1*a* and 3/4/*h*2*a*, that of 4/3/*h*9*b* the common boundary of 3/4/*h*3, 3/4/*h*1*b* and 3/4/*h*2*b*.

The two variants of type 3/4/*h*1 are displayed in Fig. 5. Fig. 6 shows the respective parameter regions on a larger scale. The blue square in the range of 3/4/*h*1*a* corresponds to the respective sphere packing with minimal density (Fig. 5*a*). A sphere packing with minimal density does not exist for 3/4/*h*1*b*. The blue triangle indicates the parameters for Fig. 5(*b*).

In a similar way, the two variants of type 3/4/*h*2 and their parameter regions are displayed in Figs. 7 and 8. In analogy to Table 1, Tables 2 and 3 describe the sphere-packing types at the boundaries of the parameter ranges of 3/4/*h*1*a*, 3/4/*h*1*b*, 3/4/*h*2*a* and 3/4/*h*2*b*.

5. Other nets and sphere packings with remarkable properties

In a recent paper, Delgado-Friedrichs & O'Keeffe (2003) described a computer procedure to determine the combinatorial as well as the maximal embeddable symmetry group of a crystal net. In this connection, they consider a net as a graph with some special properties. Similar to the usual definition of sphere-packing types, only graph-theoretical properties are

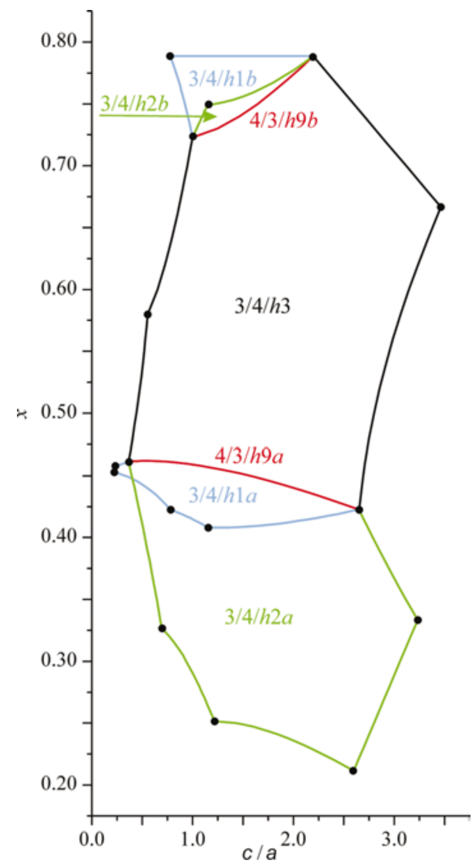


Figure 4
Projection of the parameter regions of sphere-packing types 3/4/*h*3, 3/4/*h*1*a*, 3/4/*h*1*b* and 3/4/*h*2*a* and 3/4/*h*2*b*.

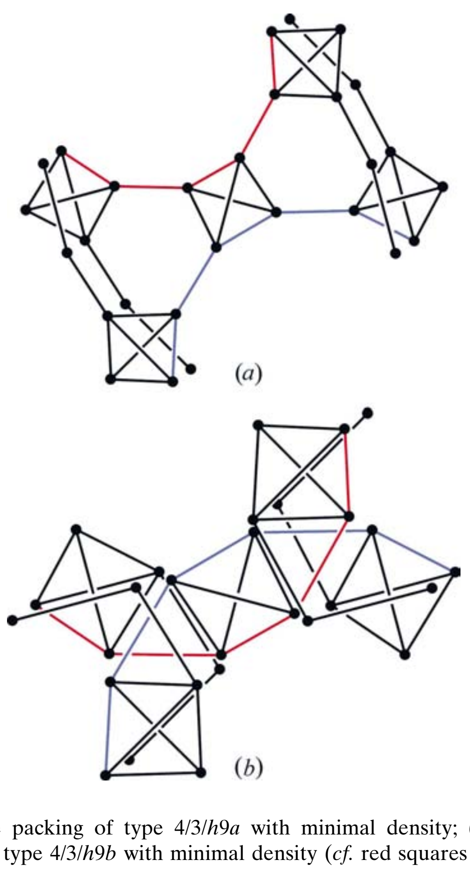


Figure 3
(*a*) Sphere packing of type 4/3/*h*9*a* with minimal density; (*b*) sphere packing of type 4/3/*h*9*b* with minimal density (*cf.* red squares in Fig. 1).

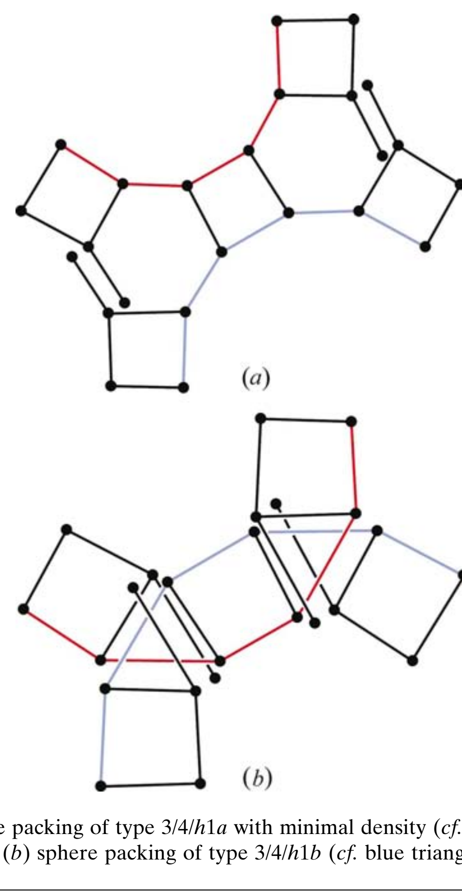


Figure 5
(*a*) Sphere packing of type 3/4/*h*1*a* with minimal density (*cf.* blue square in Fig. 6); (*b*) sphere packing of type 3/4/*h*1*b* (*cf.* blue triangle in Fig. 6).

taken into account. Additional properties concerning, for example, the interpenetration or catenations of parts of the nets are neglected during the computation. Delgado-Friedrichs & O'Keeffe (2003) describe two heterogeneous nets with two kinds of vertex each, with symmetries *Ama*2 and $P4_122$. Both nets are built up from tetrahedra that are connected by additional edges. They are isomorphic in the graph-theoretical sense 'although they cannot be interconverted without breaking bonds'.

Even if these two nets are heterogeneous and their maximal embeddable symmetry groups differ there exists a clear similarity to the two variants of the sphere-packing types 3/4/*h*1, 3/4/*h*2 and 4/3/*h*9 described above.

Delgado-Friedrichs & O'Keeffe (2003) derived their example from the so-called $CdSO_4$ net (Delgado-Friedrichs *et al.*, 2003) by replacing every vertex of the $CdSO_4$ net by a tetrahedron of vertices. The $CdSO_4$ net itself, however, is graph-theoretical isomorphic to the sphere packings of type 4/6/*t*4 (*cf.* Fischer, 1991*a*,*b*, 1993).

If sphere packings of a certain type can be generated in two Wyckoff positions that belong to different lattice complexes, normally one of the following conditions is fulfilled: (i) one of the lattice complexes forms a limiting complex of the other one, or (ii) the two lattice complexes have a common limiting complex where sphere packings of this type may also be generated.

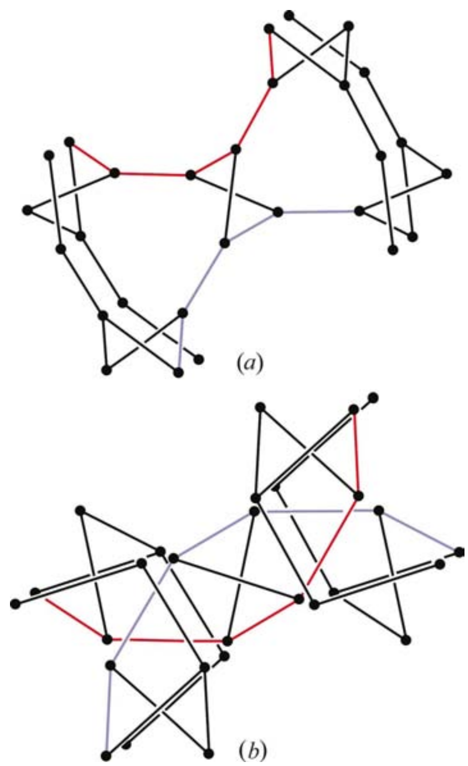


Figure 7
(*a*) Sphere packing of type 3/4/*h*2*a* with minimal density (*cf.* green square in Fig. 8); (*b*) sphere packing of type 3/4/*h*2*b* (*cf.* green triangle in Fig. 8).

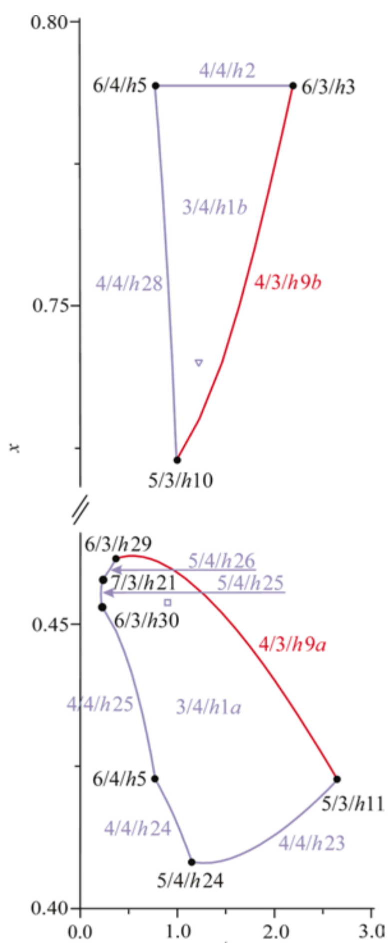


Figure 6
Projection of the parameter regions of the variants of sphere-packing type 3/4/*h*1 and their boundaries: sphere packings shown in Figs. 5(*a*) and 5(*b*) are marked by a square and a triangle, respectively.

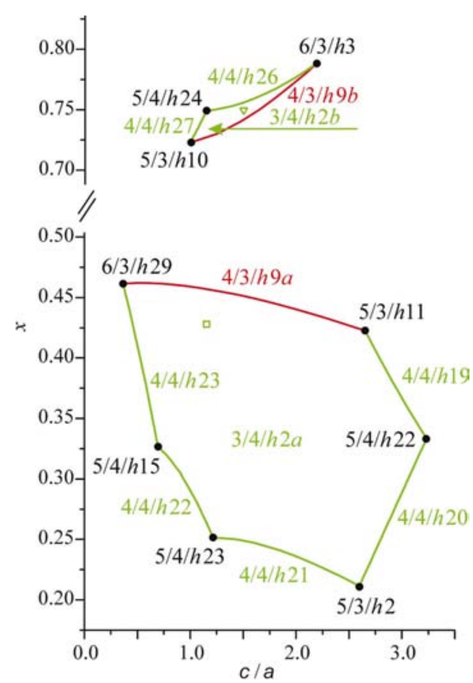


Figure 8
Projection of the parameter regions of the variants of sphere-packing type 3/4/*h*2 and their boundaries: sphere packings shown in Figs. 7(*a*) and 7(*b*) are marked by a square and a triangle, respectively.

Table 2
Sphere packings at the boundaries of 3/4/*h*1*a* and 3/4/*h*1*b*: *x*, *y*, *z* and *c*/*a* for the sphere packings with minimal density $\rho_{\min}$.

Type	*x*	*y*	*z*	*c*/*a*	$\rho_{\min}$
3/4/h1a	**0.45337**	**0.12740**	**0.07476**	**0.90013**	**0.13918**
6/3/h29	0.46144	0.10534	0.25	0.36491	0.34157
4/3/h9a	0.45817	0.11429	0.09211	1.07459	0.14815
5/3/h11	0.42265	0.21132	0.06904	2.65099	0.37959
4/4/h23	0.41446	0.23369	0.05663	2.12657	0.35647
5/4/h24	0.40819	0.25082	−0.01855	1.15110	0.52432
4/4/h24	0.41580	0.23003	−0.03993	0.97670	0.49708
6/4/h5	0.42265	0.21132	−0.08333	0.77646	0.54676
4/4/h25	0.44811	0.14176	−0.08333	0.38651	0.30704
6/3/h30	0.45292	0.12862	−0.08333	0.22594	0.37038
5/4/h25	0.45518	0.12245	0.07079	0.21425	0.33304
7/3/h21	0.45781	0.11526	0.25	0.23052	0.38553
5/4/h26	0.46116	0.10610	0.25	0.35625	0.34142
3/4/h1b†	**0.74023**	**0.17586**	**0.11362**	**1.2**	**0.41315**
6/3/h3	0.78868	0.21132	0.08333	2.19615	0.45821
4/3/h9b	0.74176	0.17698	0.10212	1.50095	0.39382
5/3/h10	0.72291	0.16318	0.14151	0.99868	0.46396
4/4/h28	0.72614	0.16555	0.13974	0.99085	0.46383
6/4/h5	0.78868	0.21132	0.08333	0.77646	0.54676
4/4/h2	0.78868	0.21132	0.08333	1.55291	0.42089

† Sphere-packing type without a minimal-density configuration. Given parameters refer to an arbitrarily chosen sphere packing of the regarded type.

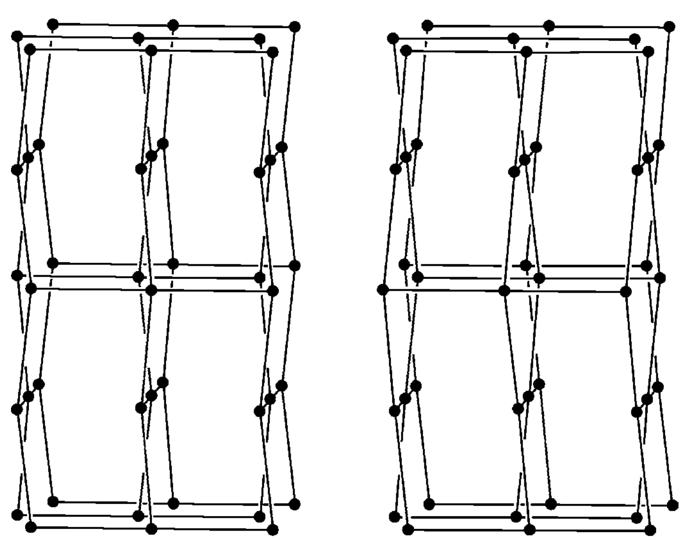
Table 3
Sphere packings at the boundaries of 3/4/*h*2*a* and 3/4/*h*2*b*: *x*, *y*, *z* and *c*/*a* for the sphere packings with minimal density $\rho_{\min}$.

Type	*x*	*y*	*z*	*c*/*a*	$\rho_{\min}$
3/4/h2a	**0.43559**	**0.09867**	**0.09899**	**1.14900**	**0.14544**
6/3/h29	0.46144	0.10534	0.25	0.36491	0.34157
4/3/h9a	0.45817	0.11429	0.09211	1.07459	0.14815
5/3/h11	0.42265	0.21132	0.06904	2.65099	0.37959
4/4/h19†	0.36701	0.18350	0.07491	3	0.40348
5/4/h22	0.33333	0.16667	0.07735	3.23205	0.43201
4/4/h20	0.26269	0.02538	0.08726	2.86499	0.32022
5/3/h2	0.21132	−0.07735	0.09623	2.59808	0.38733
4/4/h21	0.23255	−0.08512	0.10734	2.09506	0.36722
5/4/h23	0.25139	−0.09202	0.16667	1.21561	0.49270
4/4/h22	0.30668	−0.02560	0.20331	2.16449	0.39328
5/4/h15	0.32673	0	0.25	0.69309	0.43565
4/4/h23	0.42259	0.08038	0.25	0.47041	0.31490
3/4/h2b†	**0.75**	**0.17084**	**0.10972**	**1.5**	**0.41940**
6/3/h3	0.78868	0.21132	0.08333	2.19615	0.45821
4/3/h9b	0.74176	0.17698	0.10212	1.50095	0.39382
5/3/h10	0.72291	0.16318	0.14151	0.99868	0.46396
4/4/h27†	0.73704	0.16031	0.14527	1.08	0.49412
5/4/h24	0.74918	0.15737	0.14811	1.15110	0.52432
4/4/h26	0.76565	0.17988	0.09967	1.76305	0.42629

† Sphere-packing type without a minimal-density configuration. Given parameters refer to an arbitrarily chosen sphere packing of the regarded type.

In the course of the derivation of all sphere packings with tetragonal symmetry, Fischer (1970, 1971) found two sphere-packing types with outstanding properties, namely 4/6/*t*4 (*cf.* above) and 4/4/*t*29 (personal communication). Sphere packings of type 4/6/*t*4 with four contacts per sphere correspond to the following lattice complexes (*cf.* Fischer, 1991*a*,*b*, 1993): (i) $I4_1/a$ 16*f*, $I4_1cd$ 16*b* and $I\bar{4}c2$ 16*i* with the common limiting complex $I4_1/acd$ 16*e* .2., and (ii) $P4_22_12$ 8*g*, $P\bar{4}2_1c$ 8*e* and $P\bar{4}b2$ 8*i* with $P4_2/mbc$ 8*h* *m*.. as common limiting complex. There is, however, no common limiting complex of $I4_1/acd$ 16*e* and $P4_2/mbc$ 8*h* compatible with sphere packings of type 4/6/*t*4 and, therefore, type 4/6/*t*4 comprises no sphere packing with minimal density. In each of the eight lattice complexes, the limiting value of the sphere-packing density refers to a point at the boundary of the parameter region that gives rise to a sphere packing of type 6/4/*c*1 with six contacts per sphere. Sphere packings of this type occur with maximal symmetry in lattice complex *cP* built up from all primitive cubic point lattices. *cP* is also the common limiting complex of the eight lattice complexes mentioned above. As a consequence of this behaviour, two homogeneous sphere packings of type 4/6/*t*4, the first of which is generated in $P4_2/mbc$ 8*h* or in $P4_22_12$ 8*g*, $P\bar{4}2_1c$ 8*e* or $P\bar{4}b2$ 8*i* and the second one in $I4_1/acd$ 16*e* or in $I4_1/a$ 16*f*, $I4_1cd$ 16*b* or $I\bar{4}c2$ 16*i*, can only be deformed into one another if one allows additional sphere contacts during the deformation. The respective sphere-packing graphs, however, can be interconverted without breaking edges. Fig. 9 shows two sphere packings of type 4/6/*t*4 with symmetries $P4_2/mbc$ 8*h* and $I4_1/acd$ 16*e*. The maximal combinatorial symmetry of a corresponding net is higher, namely $P4_2/mmc$ 2*a* *mmm* 000 (*cf.* Delgado-Friedrichs *et al.*, 2003). This symmetry, however, does not allow a sphere packing of type 4/6/*t*4.

A similar behaviour is shown by the sphere packings of type 4/4/*t*29 that can be generated in the general positions of $P4_2/mbc$ and $P4_2/nbc$ and twice, with different generators, in the general position of $I4_1/acd$ (*cf.* Fischer, 1993). Again, the common limiting complex of these three lattice complexes is *cP* and it also refers to a point at the boundary of each of the four parameter regions.



(*a*) (*b*)

Figure 9
Sphere packing of type 4/6/*t*4 generated in (*a*) $P4_2/mbc$ 8*h* *xy*0 with $x = 1/4$, $y = 0.2$ and $c/a = 0.9899$ and in (*b*) $I4_1/acd$ 16*e* $\frac{1}{4}\,y\,\frac{1}{8}$ with $y = 0.2$ and $c/a = 1.9799$.

6. Conclusions

Up to the present, there seemed to be a common agreement in crystallography that a graph-theoretical approach is sufficient for the description and classification of three-periodic connected objects, like crystal nets, sphere packings *etc.* The examples given above, however, demonstrate the existence of probably very few exceptions where graph theory does not differentiate between cases that are different from the crystallographic point of view. In order to make a distinction between the sphere-packing variants discussed above, for example, arguments from knot or braid theory have to be taken into account in addition.

Note added in proof: In a forthcoming paper by Fischer (2004), the sphere-packing type 4/3/*c*32 is identified as a cubic analogue of 4/3/*h*9.

We thank Professor Dr Werner Fischer (Marburg) for helpful discussions, Professor Dr Michael O'Keeffe (Tempe, Arizona) for valuable remarks and the Deutsche Forschungsgemeinschaft for the support of this work under KO 1139/1-1.

References

Carlucci, L., Ciani, G. & Proserpio, D. M. (2003*a*). *Cryst. Eng. Commun.* **5**, 269–279.
Carlucci, L., Ciani, G. & Proserpio, D. M. (2003*b*). *Coord. Chem. Rev.* **246**, 247–289.
Delgado-Friedrichs, O. & O'Keeffe, M. (2003). *Acta Cryst.* A**59**, 351–360.
Delgado-Friedrichs, O., O'Keeffe, M. & Yaghi. O. M. (2003). *Solid State Sci.* **5**, 73–78.
Fischer, W. (1970). Habilitation thesis, University of Marburg, Germany.
Fischer, W. (1971). *Z. Kristallogr.* **133**, 18–42.
Fischer, W. (1973). *Z. Kristallogr.* **138**, 129–146.
Fischer, W. (1974). *Z. Kristallogr.* **140**, 50–74.
Fischer, W. (1991*a*). *Z. Kristallogr.* **194**, 67–85.
Fischer, W. (1991*b*). *Z. Kristallogr.* **194**, 87–110.
Fischer, W. (1993). *Z. Kristallogr.* **205**, 9–26.
Fischer, W. (2004). *Acta Cryst.* A**60**, 246–249.
Fischer, W. & Koch, E. (2002). *Acta Cryst.* A**58**, 509–513.
Heesch, H. & Laves, F. (1933). *Z. Kristallogr.* **85**, 443–453.
Koch, E. & Fischer, W. (1978). *Z. Kristallogr.* **148**, 107–152.
Koch, E. & Fischer, W. (2002). *International Tables for Crystallography*. Vol. A, 5th ed., edited by Th. Hahn, Section 15. Dordrecht/Boston/London: Kluwer Academic Publishers.
Sowa, H. & Koch, E. (2004). *Acta Cryst.* A**60**, 158–166.
Sowa, H., Koch, E. & Fischer, W. (2003). *Acta Cryst.* A**59**, 317–326.