Acta Crystallographica Section A
Foundations of Crystallography
ISSN 0108-7673

On the density of homogeneous sphere packings

E. Koch,* H. Sowa and W. Fischer

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

Received 15 April 2005
Accepted 9 May 2005

For some types of sphere packing with typical one- and two-dimensional parameter regions, the sphere-packing density as a function of the free parameters is discussed. In addition, some sphere-packing types with extraordinary density properties are presented. Until now, it was generally assumed that sphere packings with minimal density are also those of highest inherent symmetry. An example to prove the opposite is given.

1. Introduction

Sphere packings may be used for the description and classification of crystal structures and they can help to recognize interrelationships between structures belonging to different types. Especially in physical and mineralogical papers, the term 'sphere packing' is frequently applied in a restricted sense, namely only for densest sphere packings or for sphere packings with high coordination numbers, *e.g.* for a sphere packing with coordination number 8 that corresponds to a cubic body-centred lattice. In the present paper, the term 'sphere packing' will be used in the wider sense as introduced first by Heesch & Laves (1933). A set of non-intersecting spheres that are symmetrically equivalent with respect to a space group is called a (*homogeneous*) *sphere packing* if a chain of spheres with mutual contacts connects any two spheres (*cf. e.g.* Fischer, 1991*a*).

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 vertices of the graph are connected by an edge if and only if the corresponding spheres are in contact (*cf.* Fischer, 1971; *Mittelpunktsfigur*, Heesch & Laves, 1933).

Two sphere packings belong to the same *sphere-packing type* if the spheres of one sphere packing can be mapped onto the spheres of the other one and *vice versa* under preservation of all contact relationships between the spheres, *i.e.* if the corresponding two sphere-packing graphs are isomorphic (*cf. e.g.* Fischer, 1991*a*). This conventional, purely graph-theoretical, approach is sufficient for most purposes and also for the present investigation. Very recently, however, some examples have been described where graph theory does not differentiate between sphere packings that are different from the crystallographic point of view. Then, additional arguments from knot or braid theory have to be taken into account (Koch & Sowa, 2004; Fischer, 2004).

Sphere packings belonging to the same type may be generated within different Wyckoff positions of the same space group or of different space groups of the same type or even of different types. Such Wyckoff positions are either assigned to the same lattice complex or they are related by some limiting-complex relationships (*cf.* Fischer & Koch, 2002*b*). As a consequence and in analogy to point configurations, the inherent symmetry of a sphere packing may be higher than the space group used for its generation. Moreover, sphere packings of the same type may show different inherent symmetries.

In most cases, a sphere packing with space-group symmetry G may be deformed without losing symmetry or sphere contacts. Then, the corresponding sphere-packing type occurs in G with $1 \leq n \leq 5$ 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. The highest possible number of degrees of freedom may be calculated as $n_{\max} = j - g$ and depends on the regarded crystal system. j is the number of metrical and coordinate parameters that may be varied in the regarded crystal system and g is the minimal number of symmetry operations forming a set of generators of a corresponding space group: $j = 4$, $g = 2$ and $n_{\max} = 2$ for the cubic system, $j = 5$, $g = 2$ and $n_{\max} = 3$ for the hexagonal, trigonal and tetragonal systems, $j = 6$, $g = 2$ and $n_{\max} = 4$ for the orthorhombic system, $j = 7$, $g = 3$ and $n_{\max} = 4$ for the monoclinic system, and $j = 9$, $g = 4$ and $n_{\max} = 5$ for the triclinic system.

The *density* ρ *of a sphere packing* is defined as the volume of all spheres within one unit cell divided by the unit-cell volume.

For some years, a group of Hungarian mathematicians (*cf. e.g.* Molnár *et al.*, 2002) has tried to derive the densest sphere packings that are compatible with the symmetry of selected space groups. They use the term 'optimal ball packings'. For crystal-chemical applications, however, sphere packings with low and high density may be equally useful (*cf. e.g.* O'Keeffe & Hyde, 1996). In the case of a sphere-packing type with an n-dimensional parameter region ($n > 0$), the respective sphere packings with minimal density are of special interest because the corresponding 'maximal expanded' anion arrangements offer particularly large voids as cation locations. Such sphere packings often show a higher inherent symmetry than the other ones belonging to the same type. In that case, the position of their sphere centres belongs to a limiting complex of the lattice complex under consideration.

To our knowledge, systematic studies of the change of the density within the parameter region of a sphere-packing type have not been performed yet. Information is available only on the sphere packings belonging to lattice complex $R\bar{3}m\,6c$ (Zobetz, 1983).

The present study aims to investigate the sphere-packing density as a function of the free parameters for some typical one- and two-dimensional parameter regions. In addition, some sphere-packing types with extraordinary density properties will be presented.

Table 1
The boundary of the parameter region of sphere-packing type 4/6/*h*1 in $P3_221\,3a\,x0\frac{2}{3}$; the parameters refer to the corresponding sphere packings with minimal densities ρ.

Type	x	c/a	ρ
4/6/*h*1	0.5	1.06066	0.39270
8/4/*c*1	0.33333	0.61237	0.68017
6/4/*c*1	0.33333	1.22474	0.52360
12/3/*c*1	0.33333	2.44949	0.74048
10/3/*h*3	0.5	2.59808	0.69813
12/3/*c*1	0.66667	2.44949	0.74048
6/4/*c*1	0.66667	1.22474	0.52360
8/4/*c*1	0.66667	0.61237	0.68017
6/4/*h*3	0.5	0.53033	0.51013

2. Typical behaviour of sphere-packing types

Some types of sphere packing refer exclusively to zero-dimensional parameter regions. The corresponding sphere packings cannot be deformed without losing sphere contacts – apart from pure changes of the scale. In these cases only, the sphere-packing density cannot vary. Frequently, such sphere packings have high contact numbers, *e.g.* the cubic or the hexagonal closest packing or the cubic sphere packing with eight contacts per sphere that refers to the oxygen packing in pyrochlore (*cf. e.g.* O'Keeffe & Hyde, 1996); but there are also some cubic sphere-packing types with coordination number four and some tetragonal and hexagonal types with coordination number five showing this property. For all other sphere-packing types with n-dimensional parameter regions ($1 \le n \le 5$), the density depends on the choice of the free coordinate and metrical parameters.

2.1. Sphere-packing types with a minimum of density

For most types, a sphere packing with lowest density is uniquely defined – apart from pure changes of the scale. It refers to a certain point inside the respective parameter region, which may be either symmetric or asymmetric with respect to that point.

2.1.1. Symmetric parameter regions. A typical example is the one-dimensional parameter range $\frac{1}{3} < x < \frac{2}{3}$ in $P3_221$ $3a\,x0\frac{2}{3}$ of the trigonal sphere-packing type 6/4/*h*3 (*cf.* Sowa *et al.*, 2003). Fig. 1 displays the dependence of the sphere-packing density ρ on the coordinate parameter x. Both ends of the parameter region correspond to sphere packings of type 8/4/*c*1, *i.e.* to cubic body-centred lattices with $\rho = 0.68017$. The midpoint at $x = \frac{1}{2}$ is located on the twofold rotation axis at $\frac{1}{2}0z$ belonging to the Euclidean normalizer $P6_422$ ($\mathbf{a}+\mathbf{b}, -\mathbf{a}, \frac{1}{2}\mathbf{c}$) of $P3_221$ (*cf.* Koch *et al.*, 2002). Accordingly, the point $\frac{1}{2}0\frac{2}{3}$ belongs to a limiting complex of lattice complex $P3_221\,3a\,x0\frac{2}{3}$, namely to $P6_222\,3c$, where type 6/4/*h*3 occurs with highest symmetry and no degree of freedom. The twofold rotation around $\frac{1}{2}0z$ maps the two halves of the parameter region of 6/4/*h*3 onto each other. As a consequence, any two sphere packings with parameters x and $\frac{1}{2}-x$ are congruent, and the sphere-packing density $\rho = 0.51013$ at $x = \frac{1}{2}$ is necessarily an extreme value. It is a minimum, as it is in the normal case.

Sphere-packing type 4/6/*h*1 occurs also in $P3_221\,3a\,x0\frac{2}{3}$ (*cf.* Sowa *et al.*, 2003), but with a two-dimensional parameter range (*cf.* Fig. 2) that is bounded by four one-dimensional (red lines) and four zero-dimensional parameter regions (red circles) belonging to types of sphere packing with higher

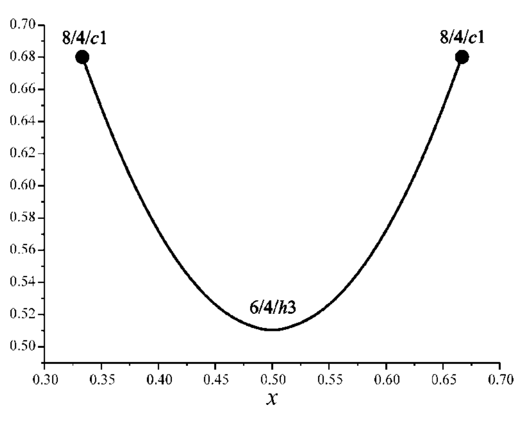

Figure 1
Sphere-packing density ρ as a function of the coordinate parameter x for sphere-packing type 6/4/*h*3 in $P3_221\,3a\,x0\frac{2}{3}$.

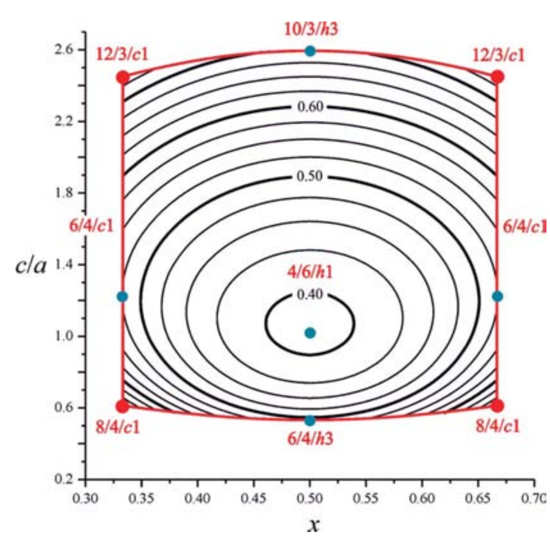

Figure 2
Symmetric parameter region of sphere-packing type 4/6/*h*1 in $P3_221\,3a\,x0\frac{2}{3}$. Full black lines are equidistant isopycnics. Blue circles mark the positions of the sphere packings with minimal densities.

contact numbers (*cf.* Table 1). The twofold rotation around $\frac{1}{2}0z$ maps the right half of the parameter range of 4/6/*h*1 onto its left half and *vice versa*. As a consequence, the sphere-packing types 12/3/*c*1, 8/4/*c*1 and 6/4/*c*1 occur twice, namely at the left and at the right side of the boundary, whereas the parameter ranges of 4/6/*h*1 itself and of 10/3/*h*3 and 6/4/*h*3 are symmetrical. The black contour lines in Fig. 2 are *isopycnics*, *i.e.* lines of constant sphere-packing density. They also show the twofold symmetry. The blue circles inside the parameter field of 4/6/*h*1 and at its boundary mark the positions of the sphere packings with minimal densities. All sphere packings with $x = \frac{1}{2}$ belong again to the limiting complex $P6_222$ 3*c*. Only one half of the parameter range of type 4/6/*h*1 may belong to any asymmetric unit of the Euclidean normalizer of $P3_221$. The Si atoms in α-quartz form a sphere packing of type 4/6/*h*1. The parameters [*cf. e.g.* Glinnemann *et al.* (1992), $x_{\rm Si} = 0.4698$, $c/a = 1.1006$] deviate only slightly from those for the minimum of density in Fig. 2.

2.1.2. Asymmetric parameter regions. The one-dimensional parameter regions of the hexagonal sphere-packing type 4/4/*h*5 in $P6_3/mmc$ 12*j* $xy\frac{1}{4}$ (Sowa & Koch, 2004) and in $P6_322$ 12*i* *xyz* (Sowa & Koch, 2005*a*) do not show any symmetry. The ends of the parameter region at $y = 0$ and at $y = \frac{1}{9}$ correspond to sphere packings of types 5/4/*h*5 with $\rho = 0.40307$ and 6/3/*h*28 with $\rho = 0.35828$, respectively. The minimal density $\rho = 0.27768$ for type 4/4/*h*5 is obtained at $y = \frac{1}{12}$. As the parameter region (Fig. 3) is asymmetric, all sphere packings corresponding to the various values of *y* are geometrically different. The special sphere packing with $y = \frac{1}{12}$ stands out only by its density but not by its geometric or symmetry properties. The sphere-packing type corresponding to the Si arrangement in the α-$ThSi_2$ structure is a well known example demonstrating that minimal density and special geometric properties do not necessarily coincide (*cf. e.g.* Koch, 1985). The Si configuration corresponds almost exactly to a sphere packing of the tetragonal type 3/10/*t*4 with an one-dimensional parameter region in $I4_1/amd$ 8*e* 00*z*. The minimal density $\rho = \frac{9}{128}\pi = 0.22089$ occurs at $z = \frac{13}{32} = 0.40625$ and $c/a = 2\surd 2 = 2.82843$. The geometrically most favourable Si configuration, however, with three Si neighbours at the vertices of an equilateral triangle requires the parameters $z = \frac{5}{12} = 0.41667$ and $c/a = 2\surd 3 = 3.46410$. It gives rise to the slightly higher density $\rho = \frac{2}{27}\pi = 0.23271$.

The parameter region of sphere-packing type 3/6/*h*3 in $P6_322$ 12*i* *xyz* (*cf.* Sowa & Koch, 2005*a*) represents an analogous two-dimensional example (Fig. 4). It is bounded by five one-dimensional (red lines) and five zero-dimensional parameter ranges (red circles) (*cf.* Table 2). Again, the blue circles indicate the parameters of the sphere packings with minimal densities. The contour lines in Fig. 4 do not show any symmetry and no congruent sphere packings referring to different pairs (*y*, *c*/*a*) exist.

If the parameter region of a sphere-packing type is asymmetric, it is always possible to define for the Euclidean normalizer of the space group under consideration an asymmetric unit that comprises the entire region.

Sphere-packing type 10/3/*h*2 exhibits an unusual one-dimensional parameter field in the general position of $P6_122$ (*cf.* Sowa & Koch, 2005*a*). The respective curve lies in the $x, x{-}\frac{1}{3}, z$ plane. For each parameter quadruplet $(x, x{-}\frac{1}{3}, z, c/a)$ that refers to a sphere packing of type 10/3/*h*2, there exists a

Table 2
The boundary of the parameter region of sphere-packing type 3/6/*h*3 in $P6_322$ 12*i* *xyz*; the parameters refer to the corresponding sphere packings with minimal densities ρ.

Type	*x*	*y*	*z*	*c*/*a*	ρ
3/6/*h*3	0.44096	0.10763	0.14714	0.60475	0.20537
5/4/*h*5	0.33333	0	0.25	0.66666	0.40307
4/4/*h*5	0.41667	0.08333	0.25	0.40825	0.27768
6/3/*h*28	0.44444	0.11111	0.25	0.22222	0.35828
5/4/*h*36	0.45274	0.11941	0.15653	0.21777	0.34405
7/3/*h*18	0.46667	0.13333	0	0.23094	0.38694
5/4/*h*21	0.48100	0.14767	0	0.35182	0.34503
7/3/*h*19	0.5	0.16667	0	0.47140	0.37024
5/3/*h*17	0.48468	0.15135	0.10120	0.86476	0.26274
10/3/*h*2	0.33333	0	0.13763	2.09751	0.66568
4/6/*h*2	0.33333	0	0.1875	0.94281	0.34009

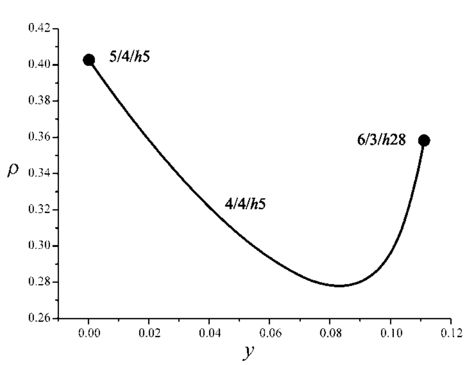

Figure 3
Sphere-packing density ρ as a function of the coordinate parameter *y* for sphere-packing type 4/4/*h*5 in $P6_3/mmc$ 12*j* $xy\frac{1}{4}$ or $P6_322$ 12*i* *xyz*.

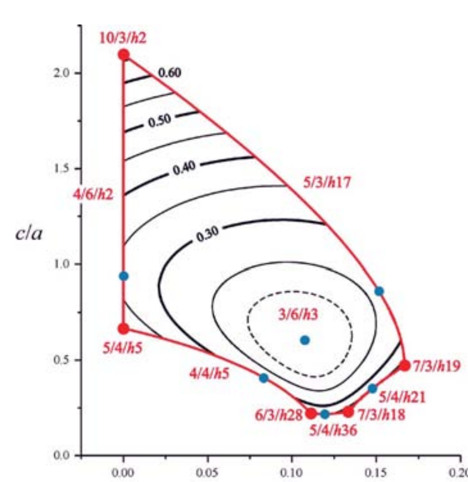

Figure 4
Asymmetric parameter region of sphere-packing type 3/6/*h*3 in $P6_322$ 12*i* *xyz*. Full black lines are equidistant isopycnics. The dashed line refers to $\rho = 0.225$. Blue circles mark the positions of the sphere packings with minimal densities.

Table 3
The boundary of the parameter region of sphere-packing type 4/6/t4 in $P4_2/mbc$ 8h xy0; the parameters refer to the corresponding sphere packings with minimal densities ρ.

Type	x	y	c/a	ρ
7/3/t8	0.18301	0.18301	0.96343	0.60304
6/4/c1	0.25	0.25	1	0.52360
7/3/t5	0.31699	0.18301	1.03528	0.56119
5/4/t15	0.29289	0.14645	1	0.54689
12/3/c1	0.25	0	0.70711	0.74048
5/5/t2	0.21062	0.14031	0.92035	0.59021

second one ($\frac{4}{3}-x$, $1-x$, z, c/a) that belongs to a packing of the same type. The two packings have the same density ρ and the same sequence of distances from a central sphere to all the other spheres in the various coordination shells. The coordinate relationships may be explained either by a twofold rotation around an axis at $\frac{2}{3}\frac{1}{3}z$ or by a mirror reflection with mirror plane at $x+1, -x, z$. Fig. 5 illustrates the sphere-packing density ρ as a function of the coordinate parameter x. Both ends of the parameter region correspond to sphere packings of type 11/3/h1, the minimal density is obtained at the midpoint at $x = \frac{2}{3}$. Although Fig. 5 looks very similar to Fig. 1, neither space group $P6_122$ nor its Euclidean normalizer $N_E(P6_122) = P6_222(\mathbf{a}, \mathbf{b}, \frac{1}{2}\mathbf{c})$ contains a twofold rotation axis at $\frac{2}{3}\frac{1}{3}z$ or a mirror plane at $x+1, -x, z$. As a consequence, the entire parameter region of type 10/3/h2 belongs to one asymmetric unit of $N_E(P6_122)$ and there is no symmetry reason that requires the congruence of two sphere packings with parameters x, $x-\frac{1}{3}$, z, c/a and $\frac{4}{3}-x$, $1-x$, z, c/a. A thorough geometrical discussion shows that the sphere packings of such a pair are indeed not congruent: for instance, they are not homometric because the calculated reflection intensities for two corresponding hypothetical crystal structures do not agree. As lattice complex $P6_122$ 12c contains $P6_3/mmc$ 4f as a limiting complex at $\frac{2}{3}\frac{1}{3}z$ (*cf.* Engel *et al.*, 1984), the sphere packing with $x = \frac{2}{3}$ shows an enhancement of its symmetry.

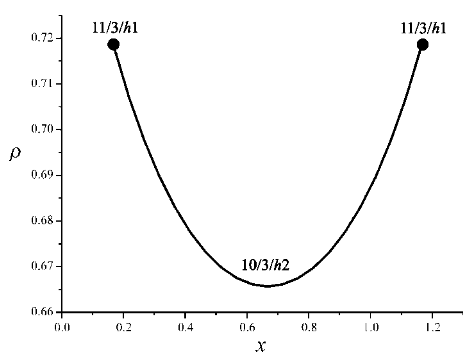

Figure 5
Sphere-packing density ρ as a function of the coordinate parameter x for sphere-packing type 10/3/h2 in $P6_122$ 12c xyz.

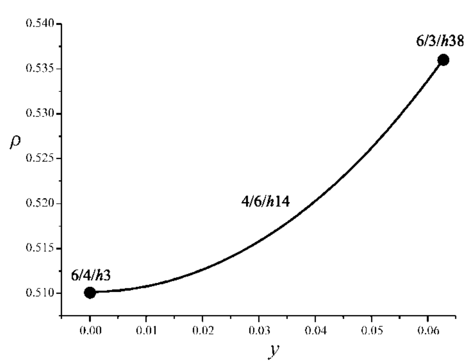

Figure 6
Sphere-packing density ρ as a function of the coordinate parameter y for sphere-packing type 4/6/h14 in $P6_122$ 12c xyz.

2.2. Sphere-packing types without a minimum of density

The smaller quantity of sphere-packing types does not comprise packings with a minimal density.

The one-dimensional parameter region $0 < y < 0.06274$ in $P6_122$ 12c xyz of the hexagonal sphere-packing type 4/6/h14 (*cf.* Sowa & Koch, 2005*a*) is a typical example (Fig. 6). The sphere-packing density ρ increases continuously from $\rho = 0.51013$ at $y = 0$ (type 6/4/h3) to $\rho = 0.53605$ at $y = 0.06274$ (type 6/3/h38). As the curve $\rho(y)$ has a horizontal tangent at $y = 0$, the minimal value $\rho = 0.51013$ may only be approximated by a sphere packing of type 4/6/h14, but it cannot be reached except if additional contacts between spheres give rise to a sphere packing of type 6/4/h3.

A two-dimensional parameter range with analogous properties belongs to the tetragonal sphere-packing type 4/6/t4 in $P4_2/mbc$ 8h xy0 (*cf.* Fischer, 1991*b*, 2005). It is surrounded by three one-dimensional (red lines) and three zero-dimensional

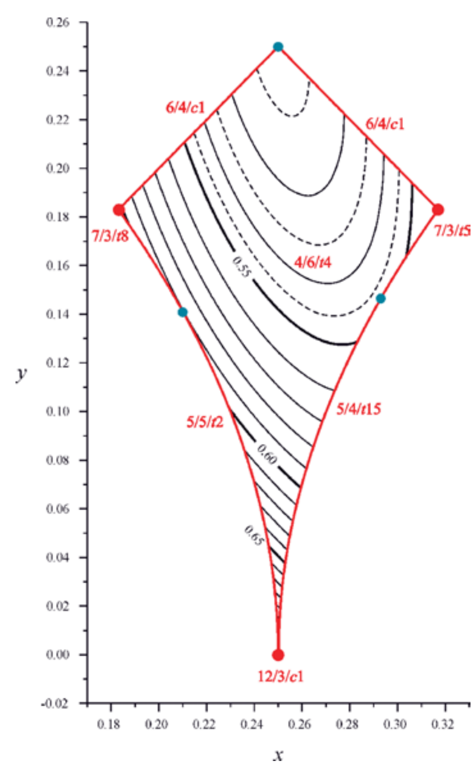

Figure 7
Asymmetric parameter region of sphere-packing type 4/6/t4 in $P4_2/mbc$ 8h xy0. Full black lines are isopycnics with distance 0.01. Blue circles mark the positions of the sphere packings with minimal densities.

parameter regions (red circles), where the one-dimensional region of 6/4/*c*1 is composed of two segments of straight lines (*cf.* Fig. 7 and Table 3). The blue circles in Fig. 7 indicate the sphere packings with minimal density. As Fig. 7 shows, the central point of the set of isopycnal lines is located at the boundary and refers to a sphere packing of type 6/4/*c*1. Again, the minimal density $\rho = 0.52360$ can only be approximated for a sphere packing of type 4/6/*t*4.

The one-dimensional parameter range of the cubic sphere-packing type 5/3/*c*12 in *I*23 24*f* *xyz* (*cf.* Fischer, 1974, 2004) shows a somewhat different but also typical behaviour (*cf.* Fig. 8). The density ρ increases continuously from $\rho = 0.58006$ at $y = 0.17678$ (type 6/3/*c*16) to $\rho = 0.64691$ at $y = 0.18600$ (type 9/3/*c*3), but in contrast to type 4/6/*h*14 the curve $\rho(y)$ has no horizontal tangent.

An analogous two-dimensional parameter region with the same symmetry belongs to the type of cubic sphere packing 3/12/*c*1 (*cf.* Fischer, 1974, 2004). Three one-dimensional (red lines) and three zero-dimensional (red circles) parameter ranges form its boundary (*cf.* Fig. 9 and Table 4). The common central point of the isopycnal lines lies far beyond the parameter range of 3/12/*c*1 and its boundary.

3. Atypical behaviour of sphere-packing types

In the following, some types of sphere packing with very unusual density properties are discussed.

3.1. Double minimum

(*A*) Sphere packings of type 6/3/*h*19 may be generated in only three trigonal lattice complexes. They occur with highest symmetry and no degree of freedom in $R\bar{3}c$ 18*e* $x0\frac{1}{4}$ (*cf.* Sowa *et al.*, 2003). The corresponding density is $\rho = 0.59542$. Type 6/3/*h*19 has one degree of freedom in *R*3*c* 18*b* *xyz* (*cf.* Sowa & Koch, 2004) and in $R\bar{3}$ 18*f* *xyz* (*cf.* Sowa & Koch, 2005*b*).

Fig. 10 illustrates the density ρ as a function of the coordinate parameter *y* in *R*3*c* 18*b*. The parameter region is symmetric with respect to a twofold rotation around *x*00, a symmetry operation of the Euclidean normalizer of *R*3*c*. Accordingly, the sphere packing with $y = 0$ ($x = 0.19098$, $c/a = 0.66158$) corresponds to the limiting complex $R\bar{3}c$ 18*e* of *R*3*c* 18*b* and to the minimum of density $\rho = 0.59542$. Owing to other limiting-complex relationships [$I\bar{4}3d$ 12*a* is a limiting complex of *R*3*c* 18*b*, *cf.* Koch & Sowa (2005)], both ends of the parameter region ($x = \frac{5}{24}$, $y = \frac{1}{24}$ and $x = \frac{3}{24}$, $y = -\frac{1}{24}$; $c/a = \frac{1}{4}\surd 6$) refer to sphere packings of the cubic type 8/3/*c*1 with density $\rho = 0.64284$. This behaviour is in full agreement with that described in §2.1.1 for sphere packings with symmetrical parameter regions.

In contrast to this, the sphere packings of type 6/3/*h*19 show an anomalous behaviour in $R\bar{3}$ 18*f* with respect to their densities. Fig. 11 illustrates the change of the density as a function of the *y* coordinate for $-0.04762 < y < 0.04762$. This parameter region is symmetric as the Euclidian normalizer of

Table 4
The boundary of the parameter region of sphere-packing type 3/12/*c*1 in *I*23 24*f* *xyz*.

Type	*x*	*y*	*z*	ρ
6/3/*c*16 4/4/*c*9	0.32322	0.17678	0.03033	0.58006
6/3/*c*10 5/4/*c*2	0.31699	0.18301	0	0.61623
9/3/*c*3 5/3/*c*12	0.30096	0.18600	0	0.64691

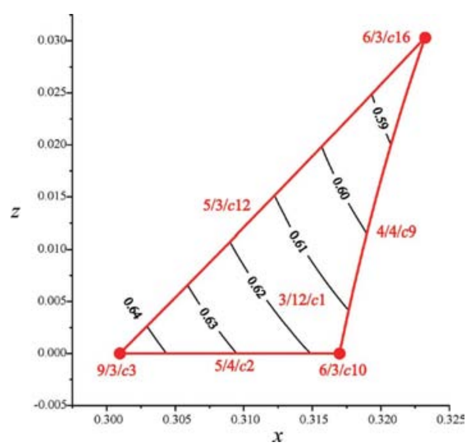

Figure 9
Asymmetric parameter region of sphere-packing type 3/12/*c*1 in *I*23 24*f* *xyz*. Full black lines are isopycnics.

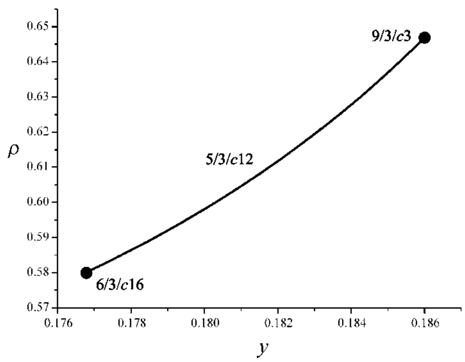

Figure 8
Sphere-packing density ρ as a function of the coordinate parameter *y* for sphere-packing type 5/3/*c*12 in *I*23 24*f* *xyz*.

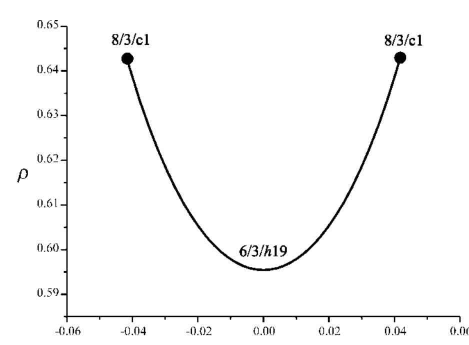

Figure 10
Sphere-packing density ρ as a function of the coordinate parameter *y* for sphere-packing type 6/3/*h*19 in *R*3*c* 18*b* *xyz*.

Table 5
The boundary of the parameter region of sphere-packing type 4/3/*h*2 in $R\bar{3}$ 18*f* *xyz*; the parameters refer to the corresponding sphere packings with minimal densities.

Type	*x*	*y*	*z*	*c*/*a*	*ρ*
4/3/*h*2	0.21922	0	0.25	1.43317	0.41571
10/3/*h*1	0.19048	−0.04762	0.16667	0.92582	0.63470
6/3/*h*44	0.21328	−0.04340	0.22543	1.62773	0.46814
12/3/*h*1	0.33333	0	0.25	2.82843	0.74048
6/3/*h*44	0.25668	0.04340	0.27457	1.62773	0.46814
10/3/*h*1	0.23810	0.04762	0.33333	0.92582	0.63470
6/3/*h*19	0.20389	0.01672	0.29829	0.72071	0.59132
	0.18716	−0.01672	0.20171	0.72071	0.59132

$R\bar{3}$ contains a twofold rotation around $x0\frac{1}{4}$, and again the sphere packing with $y = 0$ ($x = 0.19098$, $z = \frac{1}{4}$, $c/a = 0.66158$) corresponds to the limiting complex $R\bar{3}c$ 18*e* of $R\bar{3}$ 18*f* and has the density $\rho = 0.59542$. Here, however, the parameter $y = 0$ gives rise to a local maximum of sphere-packing density and not to a minimum, as in the normal case. As a consequence, the minimal density for sphere-packing type 6/3/*h*19 is not accompanied by an enhancement of the inherent symmetry resulting from a limiting-complex relationship. Owing to the twofold axis of the normalizer, the parameter region shows two minima of density with $\rho = 0.59132$. The corresponding parameters are $x = 0.20389$, $y = 0.01672$, $z = 0.29829$ and $x = 0.18716$, $y = -0.01672$, $z = 0.20171$; $c/a = 0.72071$. Both ends of the parameter region ($x = 0.23810$, $y = 0.04762$, $z = \frac{1}{3}$ and $x = 0.19048$, $y = -0.04762$, $z = \frac{1}{6}$; $c/a = 0.92582$) refer to sphere packings of type 10/3/*h*1 with $\rho = 0.63470$.

Until now, it was generally assumed – though it could never be proved – that those sphere packings of a certain type that show minimal density are also those of highest inherent symmetry (*cf. e.g.* O'Keeffe, 1991; Fischer & Koch, 2002*a*). Type 6/3/*h*19 is the first, and may be the only, example to prove the opposite. Within the cubic, hexagonal, trigonal, tetragonal and triclinic crystal systems, no other such examples have been found but, as a consequence, such a behaviour must be taken into account for future assignments of sphere packings to types.

(*B*) The double minimum for type 6/3/*h*19 in $R\bar{3}$ 18*f* has consequences for some other types of sphere packing: 4/3/*h*2, 4/5/*h*2 and 5/3/*h*21 share the one-dimensional parameter region of 6/3/*h*19 as a common boundary of their two-dimensional parameter ranges in $R\bar{3}$ 18*f*; this applies also to

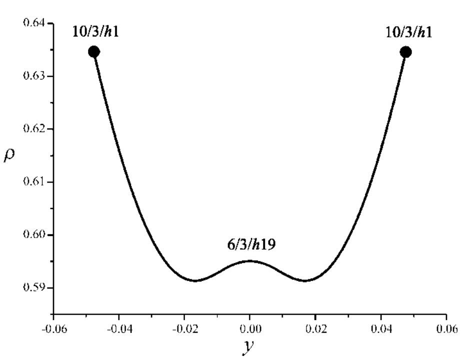

Figure 11
Sphere-packing density *ρ* as a function of the coordinate parameter *y* for sphere-packing type 6/3/*h*19 in $R\bar{3}$ 18*f* *xyz*.

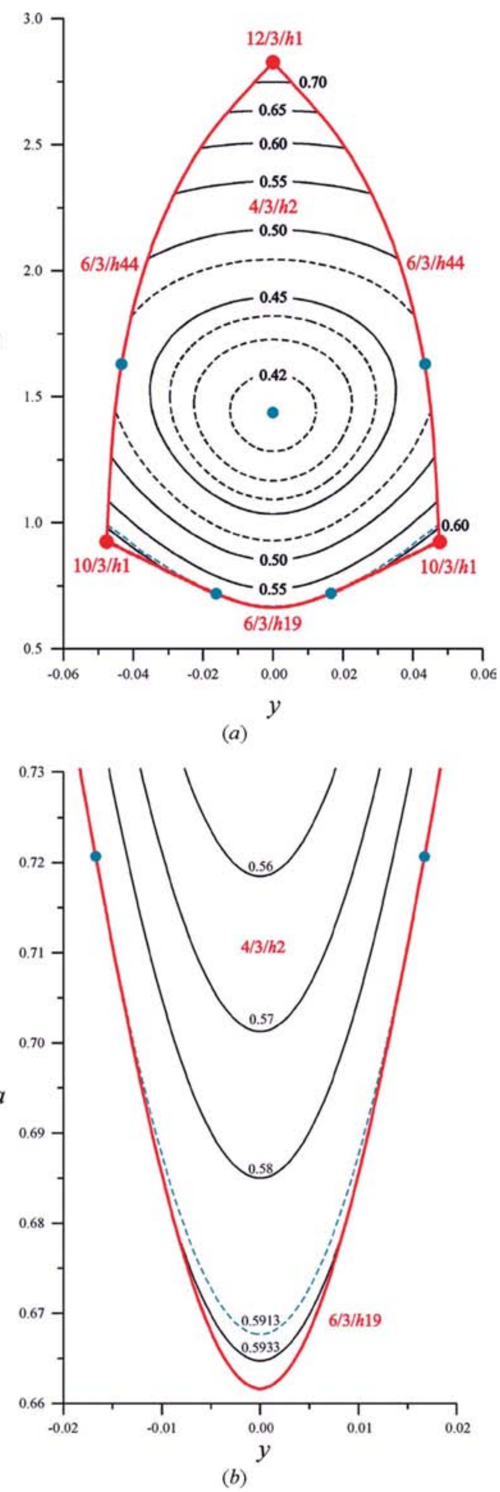

Figure 12
(*a*) Symmetric parameter region of sphere-packing type 4/3/*h*2 in $R\bar{3}$ 18*f* *xyz*. Black lines are isopycnics. Blue circles mark the positions of the sphere packings with minimal densities. The dashed blue line is the isopycnic with $\rho = 0.59132$. It touches the red line corresponding to 6/3/*h*19 at two points, referring to the two density minima of 6/3/*h*19. (*b*) Detail of (*a*).

Table 6
The boundary of the parameter region of sphere-packing type 5/3/*h*21 in $R\bar{3}$ 18*f* *xyz*; the parameters refer to the corresponding sphere packings with minimal densities.

Type	*x*	*y*	*z*	*c*/*a*	ρ
10/3/*h*1	0.23810	0.04762	0.33333	0.92582	0.63470
7/3/*h*24	0.20816	0.02319	0.30955	0.73360	0.59463
9/3/*h*2	0.18681	0.01099	0.25	0.51355	0.65911
7/3/*h*23	0.20519	0.01855	0.30844	0.72560	0.59198
10/3/*h*1	0.19048	−0.04762	0.16667	0.92582	0.63470
6/3/*h*19	0.20389	0.01672	0.29829	0.72071	0.59132
	0.18716	−0.01672	0.20171	0.72071	0.59132

Table 7
The boundary of the parameter region of sphere-packing type 5/3/*t*24 in $I4_1/a$ 16*f* *xyz*; the parameters refer to the corresponding sphere packings with minimal densities ρ.

Type	*x*	*y*	*z*	*c*/*a*	ρ
12/3/*c*1	0.25	0.25	0.0625	4	0.74048
6/3/*t*44	0.25	0.10522	0.08072	2.37608	0.56286
12/3/*c*1	0.25	0	0.125	1.41421	0.74048
7/3/*t*31					
8/3/*t*17	0.22059	0.13235	0.09375	1.94029	0.58803
6/3/*t*46	0.22786	0.14714	0.08072	2.37608	0.56286

the three-dimensional parameter ranges of types 3/8/*h*1 and $h[4/3/h1]^2$ (*cf.* Sowa & Koch, 2005*b*).

As types 4/3/*h*2 and 4/5/*h*2 show a similar behaviour, only 4/3/*h*2 is discussed in the following: Fig. 12(*a*) represents the parameter region of 4/3/*h*2 in $R\bar{3}$ 18*f*. It is symmetrical with respect to the twofold rotation around $x0\frac{1}{4}$ belonging to the Euclidean normalizer of $R\bar{3}$ (see above). The boundary is formed by three zero-dimensional (red circles) and three one-dimensional (red lines) parameter ranges, one of which belongs to type 6/3/*h*19. The isopycnics in Fig. 12(*a*) indicate a point on the twofold axis as belonging to the unique minimum of density (*cf.* Table 5). The dashed blue contour line with $\rho = 0.59132$ has a remarkable property: it touches the parameter region of 6/3/*h*19 not just at one point, as usual, but at two symmetrical points according to the two minima of density of type 6/3/*h*19. Fig. 12(*b*) shows this behaviour on a larger scale.

This property may be transferred to the three-dimensional parameter region of type 3/8/*h*1 with its minimum of density $\rho = 0.17248$ inside its parameter range at $x = \frac{1}{3}$, $y = 0.07360$, $z = \frac{1}{6}$, $c/a = 0.40693$.

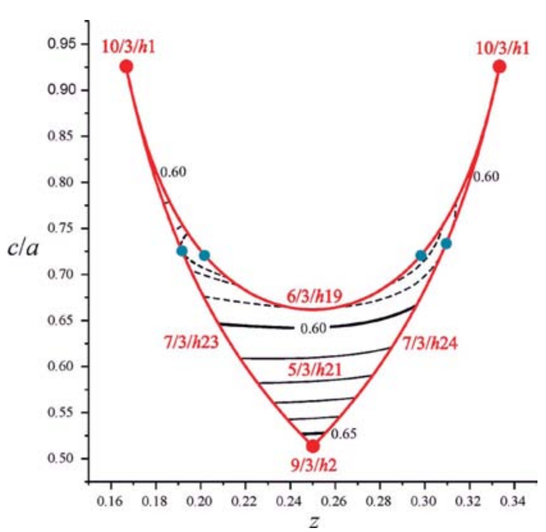

Figure 13
Asymmetric parameter region of sphere-packing type 5/3/*h*21 in $R\bar{3}$ 18*f* *xyz*. The full black lines are isopycnics with a distance of 0.01, the dashed black lines refer to $\rho = 0.595$, 0.5924 and 0.5920. Blue circles mark the positions of the sphere packings with minimal densities.

Sphere packings of type 5/3/*h*21 can be generated only in the general position of $R\bar{3}$. Fig. 13 shows its asymmetric parameter region that is bounded by three one-dimensional ranges (red lines) and three zero-dimensional ranges (red circles). The blue circles indicate the minimal densities for types 7/3/*h*23, 7/3/*h*24 and 6/3/*h*19 (*cf.* Table 6). The central point of the set of isopycnal lines clearly lies outside the parameter range of 5/3/*h*21. In contrast to the parameter field of 3/12/*c*1 (§2.2, Fig. 9), there exist two points with equal lowest densities at the boundary line corresponding to 6/3/*h*19. The sphere packings of type 5/3/*h*21 with similar parameters, however, are geometrically different.

The three-dimensional parameter region of the type of interpenetrating sphere packings $h[4/3/h1]^2$ shows an analogous behaviour. It also has two points with equal lowest densities at its boundary line referring to 6/3/*h*19, but it is symmetric with respect to the twofold rotation around $x0\frac{1}{4}$.

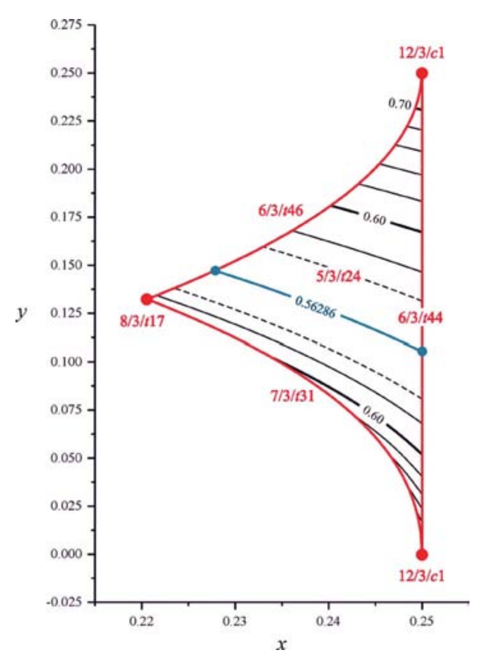

Figure 14
Asymmetric parameter region of sphere-packing type 5/3/*t*24 in $I4_1/a$ 16*f* *xyz*. Full black lines are isopycnics with distance 0.02. The dashed black lines refer to $\rho = 0.57$. The blue line and the blue circles mark the positions of the sphere packings with minimal densities.

3.2. Density valleys

The tetragonal sphere-packing type 5/3/*t*24 (*cf.* Fischer, 1993, 2005) occurs exclusively with symmetry $I4_1/a$ 16*f xyz*. Its minimal density $\rho = 0.56286$ refers not only to a certain point in the inner of its two-dimensional parameter region but to an entire line, namely to a segment of the circle $(x^2+y^2)a^2 = 2z^2c^2$ in the *x*, *y* plane with $a^2 = (16z^2 + 4z - \frac{1}{4})c^2$ and constant values $z = 0.08072$, $c = 4.38006$ and $a = 1.84340$ (referred to a sphere diameter of 1). All other isopycnics are also such circular segments but with different values of *z*, *a* and *c*. Fig. 14 displays the parameter range of type 5/3/*t*24. It is bounded by three one-dimensional (red lines) and three zero-dimensional (red circles) parameter regions (*cf.* also Table 7). The blue line represents the bottom of the density valley with $\rho = 0.56286$.

Each sphere packing of type 5/3/*t*24 is built up from ideal tetrahedra, the centres of which form a tetragonally distorted diamond configuration. The tetrahedra are connected by zigzag chains of spheres that run parallel to the *a* or *b* direction (straight lines in a projection along **c**). Figs. 15(*a*), (*b*) show two sphere packings with minimal density and with a relatively small and large *x* parameter, respectively. In each sphere packing, the tetrahedra occur in two orientations. The tetrahedra in the two sphere packings are rotated by slightly different angles around their axes parallel to **c**. The angle between the *a* or *b* direction and those edges of the tetrahedra that are perpendicular to **c** changes with increasing *x* parameter, whereas the size of the unit cell, the size of the tetrahedra or the form of the zigzag chains do not change. The tetrahedra can be rotated over a range of 10.03° maintaining the minimal density.

Starting from a point at the density valley (*cf.* Fig. 14), the sphere-packing density increases with increasing as well as with decreasing *y* parameter whereas the tetrahedra rotate in different directions. Fig. 16 shows two sphere packings of type 5/3/*t*24 with $\rho = 0.66$. At $x = y = \frac{1}{4}$ and $c/a = 4$, a cubic closest sphere packing (type 12/3/*c*1) is formed. Some edges of the tetrahedra (and of the octahedra) are running in the *x*, *x* direction. At $x = \frac{1}{4}$, $y = 0$ and $c/a = \surd 2$, a second closest cubic packing in a different orientation occurs. Here, some edges of the tetrahedra (and octahedra) are parallel to **a** and to **b**.

Until now, only one similar case is known, namely the tetragonal sphere-packing type 3/8/*t*6. It has a three-dimensional parameter range in $I\bar{4}2d$ 16*e xyz* and is discussed in some detail by Koch & Fischer (1995).

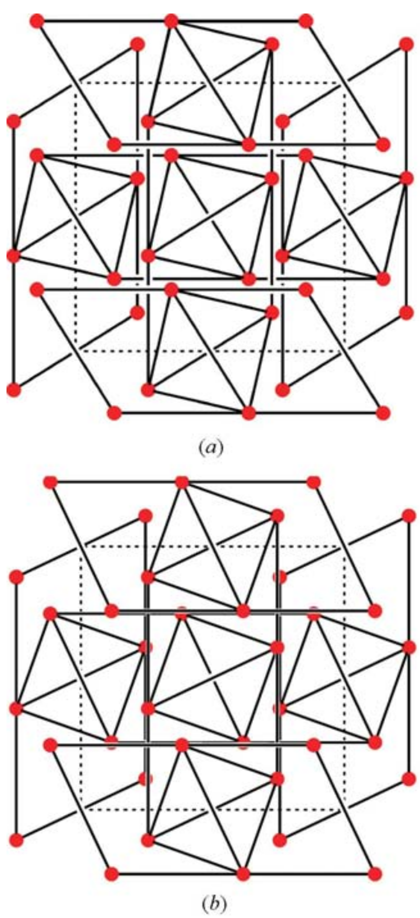

Figure 15
Two sphere packings of type 5/3/*t*24 with minimal density and different parameters: (*a*) $x = 0.23$, $y = 0.14377$, $z = 0.08072$, $c/a = 2.37608$; (*b*) $x = 0.245$, $y = 0.11638$, $z = 0.08072$, $c/a = 2.37608$. The dashed lines indicate the unit cell. The range $0 \le z \le 1$ is shown.

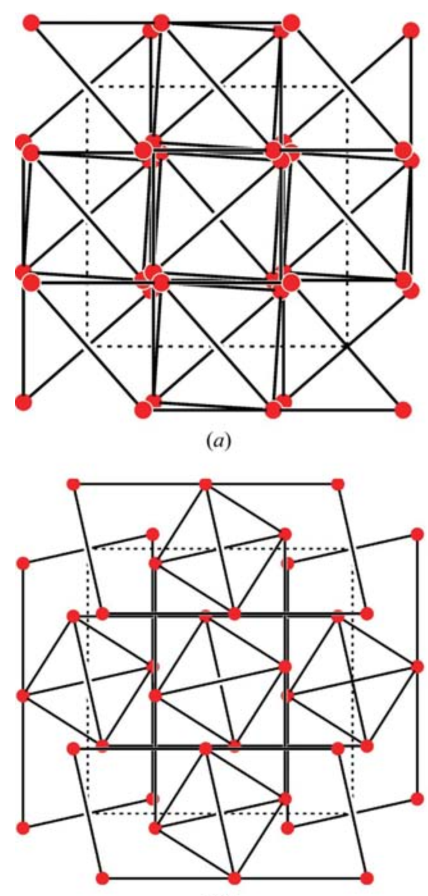

Figure 16
Two sphere packings of type 5/3/*t*24 with equal density $\rho = 0.66$ and with high or low *y* parameter: (*a*) $x = 0.245$, $y = 0.21037$, $z = 0.06553$, $c/a = 3.51766$; (*b*) $x = 0.245$, $y = 0.05498$, $z = 0.11045$, $c/a = 1.60755$. The dashed lines indicate the unit cell. The range $0 \le z \le 1$ is shown.

4. Conclusions

Considering the sphere-packing types known so far, about 85% contain a packing with minimal density (*cf.* §2.1). Presumably, this number will decrease when the sphere packings with orthorhombic or monoclinic symmetry are included.

As type 6/3/*h*19 shows, the minimal density is not necessarily tied to the highest inherent symmetry accessible within the parameter region of a sphere-packing type. This must be taken into account when the minimum of density is used to assign sphere packings to types.

We would like to thank the Deutsche Forschungsgemeinschaft for the support of this work under KO 1139/1-1.

References

Engel, P., Matsumoto, T., Steinmann, G. & Wondratschek, H. (1984). *Z. Kristallogr. Suppl.* **1**.

Fischer, W. (1971). *Z. Kristallogr.* **133**, 18–42.

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. (2005). *Acta Cryst.* A**61**, 435–444.

Fischer, W & Koch, E. (2002*a*). *Acta Cryst.* A**58**, 509–513.

Fischer, W & Koch, E. (2002*b*). *International Tables for Crystallography*, Vol. A, 5th ed., edited by Th. Hahn, Section 14. Dordrecht/Boston/London: Kluwer Academic Publishers.

Glinnemann, J., King, H. E., Schulz, H., Hahn, Th., La Placa, S. J. & Dacol, M. (1992). *Z. Kristallogr.* **198**, 177–212.

Heesch, H. & Laves, F. (1933). *Z. Kristallogr.* **85**, 443–453.

Koch, E. (1985). *Z. Kristallogr.* **173**, 205–224.

Koch, E. & Fischer, W. (1995). *Z. Kristallogr.* **210**, 407–414.

Koch, E., Fischer, W & Müller, U. (2002). *International Tables for Crystallography*, Vol. A, 5th ed., edited by Th. Hahn, Section 15. Dordrecht/Boston/London: Kluwer Academic Publishers.

Koch, E. & Sowa, H. (2004). *Acta Cryst.* A**60**, 239–245.

Koch, E. & Sowa, H. (2005). *Z. Kristallogr.* Accepted.

Molnár, E., Prok, I. & Szirmai, J. (2002). *Studia Sci. Math. Hungar.* **29**, 9–23.

O'Keeffe, M. (1991). *Z. Kristallogr.* **196**, 21–37.

O'Keeffe, M. & Hyde, B. G. (1996). *Crystal Structures.* Washington, DC: Mineralogical Society of America.

Sowa, H. & Koch, E. (2004). *Acta Cryst.* A**60**, 158–166.

Sowa, H. & Koch, E. (2005*a*). *Acta Cryst.* A**61**, 331–342.

Sowa, H. & Koch, E. (2005*b*). *Acta Cryst.* A**61**. In preparation.

Sowa, H., Koch, E. & Fischer, W. (2003). *Acta Cryst.* A**59**, 317–326.

Zobetz, E. (1983). *Z. Kristallogr.* **163**, 167–180.