JOURNAL OF SOLID STATE CHEMISTRY 66, 26–39 (1987)

Relations between Dense Sphere Packings

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Received January 21, 1986

A survey is made of periodic three-dimensional assemblies of equal spheres in which each sphere has from 6 to 11 nearest neighbors. Space group data are derived for 34 of the more dense sphere packings formed by stacking planar layers of three kinds. The relation of the density of sphere packings to coordination number and the "symmetry-equivalence" of spheres are briefly discussed. © 1987 Academic Press, Inc.

Introduction

It has long been known that the closest packings of equal spheres are those in which each sphere is in contact with 12 equidistant neighbors. An indefinitely large number of packings may be built from planar layers in which each sphere is in contact with six others; a unit cell of the layer is shown in Fig. 1c. When such layers are packed in the closest possible way each sphere is in contact with three spheres of each adjacent layer, making a total of 12 contacts in all. The density of all these arrangements of spheres, assumed to extend indefinitely in three dimensions, is 0.7405, defined as the volume fraction of space occupied by the spheres. The two simplest packings are hexagonal closest packing (hcp) and cubic closest packing (ccp), in which the layer sequence repeats after two and three layers, respectively; these are also the only two closest packings in which each sphere has the same arrangement not only of nearest neighbors but also of all more distant neighbors. Cubic closest packing, which is the most symmetrical of these sphere packings, also results from stacking the layers formed from the repeat unit of Fig. 1a. Other sphere packings may be formed from this and other less densely packed planar layers of spheres, and it is appropriate to mention here two earlier studies in this field (*1, 2*). Unfortunately the brief communication of Clarke seems not to have been followed by the more complete account promised by the author. Both of these studies covered coordination numbers (C.N.s) ranging from 3 to 12, but Slack also enquired what meaning is to be attached to the terms "least dense" and "most dense" when applied to packings of equal spheres.

Certain packings of 8-, 9-, 10-, and 11-coordination tend to be singled out as having high densities for their particular C.N.s, notably the body-centered cubic (bcc) packing of 8-coordination, the body-centered tetragonal packing of 10-coordination, and more recently the tetragonal packings of 9-

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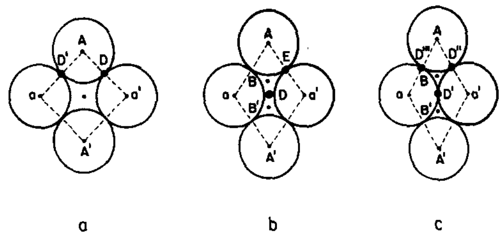

FIG. 1. Arrangement of equal spheres in (a) 4t-layer, (b) 4-layer, and (c) 6-layer. The larger black dots mark positions of spheres in adjacent layers for 2-contacts, and the small black dots in the spaces between the spheres mark positions for 4-contacts in (a) and for 3-contacts in (b) and (c).

and 11-coordination to which we refer later:

C.N.	8	9	10	11
Density	0.6801	0.6911	0.6981	0.7187

However, it has been pointed out (*2*) that although we can expect to characterize the *least dense* packing for a given C.N. this is not possible for the *most dense* packing, a point also noted by O'Keeffe (*3*) in connection with the 11-packing which represents the anion packing in the (idealized) rutile structure (*4*). We deal with this point shortly, and simply note here that Slack introduced an admittedly arbitrary limitation on the ratio d_1/d where d_1 is the distance to the next-nearest neighbors of a sphere surrounded by N spheres at the distance d. It was in fact the paper of Slack which suggested the present study, which in the main is a study in more detail of the arbitrariness of defining density for specified C.N.s. Since it is evident that the "specially dense" packings of C.N. less than 12 do *not* have the highest possible density for these particular C.N.s it is necessary to enquire as to what the special features of these "high-density" sphere packings are and what meaning (if any) is to be attached to the densities of packings of particular C.N.s (other than 12).

The packings to be described shall have the following properties:

(i) all spheres have the same radius, here taken as unity;

(ii) each sphere shall be in contact with the same number N of other spheres;

(iii) the packing shall repeat periodically in three dimensions; and

(iv) the immediate environment of each sphere shall be the same (or its mirror image).

Sphere Packings Formed by Stacking Planar Layers of Spheres

We shall consider here the sphere packings formed by stacking the three layers of Fig. 1, which are chosen because they are related to the three most symmetrical three-dimensional lattices in the following ways:

4t-layer: parallel to the 3 {100} planes of the cubic P lattice,

4-layer: parallel to the 6 {110} planes of the cubic I lattice,

6-layer: parallel to the 4 {111} planes of the cubic F lattice.

The 4t-layer, which is the 4-layer of Slack, has the special property that the P and F packings represent the least dense and most dense packings of this layer.

We now examine the ways in which the layers of Fig. 1, assumed to be horizontal and similarly oriented, may be superposed. When a second layer (of the same kind) is placed above the first there are a number of special positions for a sphere of the upper layer:

1-contact: Each sphere falls directly above a sphere of the layer below. Continuation of this process leads to the sphere packings 1-4t-1, 1-4-1, and 1-6-1, which are the packings of minimal density formed from these layers.

2-contact: Spheres fall above points D of the layer below. For the 4-layer the positions E also result in 2-contacts, but packings involving this type of contact are less dense than those resulting from D contacts and have not been studied systematically.

There is only one position of type D per sphere for the 4-layer but two for the 4t-layer and three for the 6-layer. Combinations of contacts of type D, D′, etc., between successive pairs of 4t- or 6-layers lead to infinite families of polytypes.

3-contact: Spheres fall above points B, of which there are two equivalent positions per sphere above (or below) a 4-layer or 6-layer; for the 4t-layer 3-contacts are not possible. If there are 3-contacts on both sides of each 4- or 6-layer the packings are the densest possible for these layers, and in both cases there is an infinite family of polytypes. For the 6-layer B′ is usually called C in the conventional description of closest packings.

4-contact: This is possible only for the 4t-layer, giving the unique cubic closest packing, also described as all-face-centered-cubic (fcc) packing.

Dimensional data for the layers of Fig. 1 are listed in Table I. We restrict our study to packings in which each layer has the same types of contact with adjacent layers to ensure that the C.N. of each sphere is the same. The layer sequences to be studied are listed in Table II, in which the symbol for a packing shows the type of contact on each side of every layer. Certain packings in which the type of contact is the same on *both* sides of each layer correspond to the three cubic lattices:

TABLE I

DIMENSIONAL DATA FOR THE 4t-, 4-, AND 6-LAYERS

	4t-Layer	4-Layer	6-Layer
Angle aAa	90°	70°32′	60°
Distance AA′	2.828 ($2\sqrt{2}$)	3.266 ($2\sqrt{8/3}$)	3.464 ($2\sqrt{3}$)
aa′	2.828	2.309 ($4\sqrt{3}$)	2
AB/AA′	—	3/8	1/3
Perpendicular distance between layers			
1-contact (A)	2	2	2
2-contact (D)	1.732 ($\sqrt{3}$)	1.633	1.732
3-contact (B or C)	—	1.581 ($\sqrt{5/2}$)	1.633
4-contact	1.414	—	—
Area of layer per sphere	4	3.771 ($8\sqrt{2}/3$)	3.464

TABLE II

SPHERE PACKINGS DERIVED FROM THE 4t-, 4-, AND 6-LAYERS

C.N.	4t-Layer	4-Layer	6-Layer
6	1-4t-1	1-4-1	—
7	1-4t-2	1-4-2	—
8	2-4t-2[a]	2-4-2 1-4-3	1-6-1[a]
9	1-4t-4	2-4-3	1-6-2
10	2-4t-4[b]	3-4-3	1-6-3[b] 2-6-2
11	—	—	2-6-3
12	4-4t-4[a]	—	3-6-3[a]

[a] Pairs of identical structures (see text).
[b] Different structures with the same density.

		C.N.
1-4t-1	P cubic lattice	6
2-4-2	I cubic lattice	8
4-4t-4 3-6-3	F cubic lattice	12

There are alternate symbols for cubic closest packing, but it should be noted that the packing 4-4t-4 is a unique packing of 4t-layers whereas the symbol 3-6-3 corresponds to an infinite family of packings of C.N. 12 because of the alternate positions for 3-contacts. Only one of these packings is the same as 4-4t-4. Conversely, there is only one 1-6-1 packing and this corresponds only to the simplest 2-4t-2 packing in which all contacts are of type D′ *or* D″ (Fig. 1); mixtures of D′ *and* D″ contacts give an infinite series of more complex 2-4t-2 packings. In Table II the least dense packings are at the top of each column and the most dense at the bottom.

Evidently the sphere packings corresponding to the symbols of Table II are, except for those of C.N. 12, the packings of *minimal density for a given C.N. built from the layer specified.* If the number of contacts made by any sphere with spheres of adjacent layers is less than the maximum possible, the density of the packing may be increased by sliding one layer over the other (a process we call "shearing") because the perpendicular distance between layers decreases as the number of contacts increases (Table I). If the C.N. is defined simply as the number of spheres with which each is in contact it remains constant at the lower value until actual contact with additional spheres of the adjacent layer(s). For example, the position D in Fig. 1b for a 2-contact of the 4-layer *corresponds to minimal density and is situated between two symmetry-related positions B and C for 3-contacts.* According to whether shearing takes place on one or both sides of the layer the packing 2-4-2 will tend toward 2-4-3 (C.N. 9) or 3-4-3 (C.N. 10). Obviously the most extreme case is that of the 4t-layer (Fig. 1a) where a 1-contact (A) could tend toward a 2-contact (D′) or directly toward a 4-contact, the C.N. changing from N to $N + 1$ or $N + 3$. If these changes take place on both sides of each layer, N changes to N + 2 or N + 6, that is, 1-4t-1 2-4t-2 4-4t-4. Summarizing:

(a) There is no maximal density for any C.N. except 12, for which the maximal and minimal densities are the same.

(b) If the number of contacts made by each sphere on both sides is the greatest possible number for that layer then the density of the packing is the maximum *for that layer and C.N.* These maxima are those of the packings

4-4t-4	C.N.	12	*Fm*3*m*
3-4-3	C.N.	10	*Immm*
3-6-3	C.N.	12	*Fm*3*m*

(c) We can give the minimal density for a packing of given C.N. built from a specified layer if the number of contacts on either side or on both sides is *fewer* than the maximum possible (4 for a 4t-layer, 3 for the 4- and 6-layers).

(d) All other packings can be sheared to increase the density without increasing the C.N. until the point is reached when further contacts are made by each sphere with spheres in adjacent layers. Some sheared structures are listed in Tables III–V, where S or SS after the layer symbol indicates shearing on one or both sides of each layer.

Realizing the difficulty concerning the definition of "densest" packing for a given C.N., Slack introduced an (admittedly arbitrary) lower limit to the ratio of the distance d_1 to the next-nearest neighbors to the distance d to the nearest neighbors. The structures satisfying the condition $d_1/d \geqq \sqrt{1.5}$ (or $\frac{1}{2}\sqrt{6}$) are listed on the left in Table III. Of these packings four involve shearing of structures based on 6-layers; one is a sheared version of a 1-5-1 packing based on

TABLE III

COMPARISON OF TWO SETS OF DENSE SPHERE PACKINGS

Slack	"Most dense" packing for $d_1/d \geqq \sqrt{1.5}$	Point symmetry	Density	Density	Packing	Point symmetry
11.1	2-6-3 I or II	*m*	0.7187	0.7187	2-6-3 T[a]	*mm*
11.2	2-6-3 T[a]	*mm*	0.7187			
10.1	2-6-2	1 or *mm*	0.6981	0.7025	3-4-3 I	*mmm*
10.4		4/*mmm*	0.6981			
9.4	1-6-2 S		0.6631	0.6911	2-4-3 T[a]	*mm*
8.10	1-6-1 S	2 or 2/*m*	0.6315	0.6801	2-4-2	*m*3*m*
7.9	1-5-1 S		0.5810	0.6115	1-4-2	*mm*
6.14	1-4t-1 (compressed)	$\bar{3}m$	0.5924	0.5553	1-4-1	*mmm*

[a] Highest symmetry with nonplanar layers.

TABLE IV

DISTANCES TO NEAREST AND NEXT-NEAREST NEIGHBORS IN SPHERE PACKINGS

(a)

	1-6-1-S	1-6-2	1-6-2-S	3-4*-3	2-6-2 II	2-6-2 I	2-6-3 T	2-6-3 I
2.000	8	9	9	10	10	10	11	11
2.450	4	2	4	4	4	4	2	2
2.828	4	6	2	—	—	—	3	3
3.098	—	—	—	2	—	—	—	—
3.162	4	4	6	6	8	8	4	4
3.414	—	—	—	—	—	—	4	2
3.464	8	8	9	8	10	12	10	14
Density	0.6315	0.6480	0.6631	0.6981	0.6981	0.6981	0.7187	0.7187

(b)

	1-4-1	1-4-2	2-4-2-E	1-4-3	2-4-2-D	1-6-2 SS	2-4-3-D	2-4-3-T	3-4-3-(I)	3-4-3-(II)	2-6-2-S	2-6-3 S
2.000	6	7	8	8	8	9	9	9	10	10	10	11
2.309	2	4	2	2	6	3	4	4	2	2	2	1
2.582	—	—	4	1	—	1	1	1	2	2	2	1
2.828	8	4	—	4	—	2	—	—	—	—	—	3
3.055	4	2	4	4	—	2	2	2	4	4	4	2
3.162	—	—	—	—	—	—	—	—	—	2	—	—
3.240	—	—	—	—	—	—	2	4	—	—	—	—
3.266	2	6	2	2	12	5	6	4	4	2	4	2
3.442	—	—	—	—	—	—	—	—	—	—	2	2
3.464	—	—	10	4	—	8	4	2	12	8	10	14
Density	0.5552	0.6115	0.6412	0.6203	0.6801	0.6778	0.6911	0.6911	0.7025	0.7025	0.7025	0.7209

(c)

	1-4t-1	1-4t-2	1-6-3	2-4t-4	hcp	ccp
2.000	6	7	10	10	12	12
2.828	12	12	9	8	6	6
3.266	—	—	—	—	2	—
3.301	—	—	—	4	—	—
3.464	8	6	12	10	18	24
Density	0.5236	0.5612	0.6657	0.6657	0.7405	0.7405

Note. The numerologically minded reader may notice that the more important distances to more distant neighbors in many sphere packings belong to two series of numbers, namely, $\sqrt{2m}$ in (a) and $2\sqrt{n/3}$ in (b):

(a)	$m =$	2	3	4	5	6		
		2.000	2.449	2.828	3.162	3.464, and		
(b)	$n =$	3	4	5	6	7	8	9
		2.000	2.309	2.582	2.828	3.055	3.266	3.464.

the plane net (33434) of Fig. 2, and one is a compressed version of 1-4t-1. As these packings are not included in Table V we give details here.

The packing 1-5-1 (Slack 7.9) is a sheared version of his packing 7.4, which is formed by stacking the 5-connected layers (33434) vertically above one another. This tetragonal structure is described by the position 4(g), ($xx0$), in $P4/mbm$, point symmetry mm. With $a = b = \sqrt{2}(1 + \sqrt{3})$, $c = 2$, and $x = \frac{1}{2}(1 + \sqrt{3})$, the density is the same (0.5612) as that of the two 1-4t-2 structures included in Table V. The density is in-

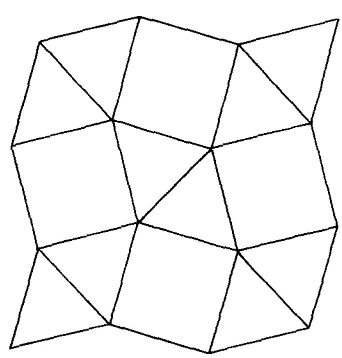

FIG. 2. The 5-connected plane net (33434).

TABLE V

Symbol	Density	Space group	Eq. posn.	a	b	c	β	Point symmetry	Notes
6-coordination									
1-4-1	0.5552	*Cmmm*	2(*a*)	2.309	3.266	2	—	*mmm*	
1-4t-1	0.5236	*Pm*3*m*	1(*a*)	2	2	2	—	*m*3*m*	
7-coordination									
1-4-2	0.6115	*Fmmm*	8(*h*)	3.266	7.266	2.309	—	*mm*	$y = 0.1376$
1-4t-2 I	0.5612	*Cmmm*	4(*i*)	2	7.464	2	—	*mm*	
1-4t-2 II	0.5612	$I4_1/amd$	8(*e*)	2	2	14.928	—	*mm*	$z = 0.0670$
8-coordination									
2-4-2	0.6801	*Im*3*m*	2(*a*)	2.309	2.309	2.309	—	*m*3*m*	
1-6-1 S	0.6552	*C*2/*m*	2(*a*)	3.464	2	2	112.63°	2/*m*	
1-6-1 S	0.6315	*C*2/*m*	2(*a*)	3.464	2	2	106.78°	2/*m*	
1-4-3	0.6203	*C*2/*m*	4(*i*)	3.266	2.309	4.122	119.41°	*m*	$x = 0.1745$ $z = 0.2792$
1-6-1 } 2-4t-2 }	0.6046	*P*6/*mmm*	1(*a*)	2	2	2	120°(γ)	6/*mmm*	
9-coordination									
2-4-3 I	0.6911	*C*2/*m*	4(*i*)	3.266	2.309	3.240	97.24°	*m*	$x = 0.2185$ $z = 0.2460$
2-4-3 II	0.6911	*Cmca*	8(*f*)	2.309	3.266	6.428	—	*m*	$y = 0.1875$ $z = 0.1230$
2-4-3 T	0.6911	$P4_2/mnm$	4(*f*)	3.239	3.239	2.309	—	*mm*	$x = 0.2818$
1-6-2 SS	0.6782	*C*2/*m*	4(*i*)	3.464	2	3.648	102.7°	*m*	$x = 0.1685$ $z = 0.2587$
1-6-2 S	0.6631	*C*2/*m*	4(*i*)	3.464	2	4.3166	122.34°	*m*	$x = 0.0917$ $z = 0.2625$
1-6-2	0.6480	*Fmmm*	8(*g*)	7.464	2	3.464	—	*mm*	$x = 0.134$
1-4t-4	0.6134	*I*4/*mmm*	4(*e*)	2	2	6.828	—	4*mm*	$z = 0.1464$
10-coordination									
3-4-3 I	0.7025	*Immm*	2(*a*)	2.582	2.309	2	—	*mmm*	
3-4-3 II	0.7025	*Cmcm*	4(*c*)	2.309	3.266	3.162	—	*mm*	$y = \frac{3}{16}$
2-6-2 S	0.7025	*Pnna*	4(*d*)	3.464	3.443	2	—	2	$x = \frac{1}{36}$
3-4*-3 I	0.6981	*I*4/*mmm*	2(*a*)	2.450	2.450	2	—	4/*mmm*	
3-4*-3 II	0.6981	*Cmcm*	4(*c*)	2.450	3.162	3.098		*mm*	$y = \frac{1}{5}$
2-6-2 II	0.6981	$P3_1$	3(*a*)	2	2	5.196	120°(γ)	1	$x = \frac{1}{3}$ $y = \frac{1}{6}$
2-4t-4	0.6657	*Cmcm*	4(*c*)	2	6.292	2	—	*mm*	$y = 0.1376$
1-6-3 I	0.6657	$P6_3/mmc$	4(*f*)	2	2	7.266	120°(γ)	3*m*	$z = 0.1124$
1-6-3 II	0.6657	*R*3*m*	6(*c*)	2	2	10.90	120°(γ)	3*m*	$z = 0.0918$
11-coordination									
2-6-3 I	0.7187	*C*2/*m*	4(*i*)	3.464	2	3.414	99.74°	*m*	$\begin{cases} x = 0.2929 \\ z = 0.7574 \end{cases}$
2-6-3 II	0.7187	*Cmca*	8(*f*)	2	3.464	6.730	—	*m*	$\begin{cases} y = \frac{1}{6} \\ z = 0.3787 \end{cases}$
2-6-3 T	0.7187	$P4_2/mnm$	4(*f*)	3.414	3.414	2	—	*mm*	$x = 0.2929$
2-6-3 S	0.7209	*C*2/*m*	4(*i*)	3.464	2	3.442	102.93°	*m*	$\begin{cases} x = 0.2791 \\ z = 0.7566 \end{cases}$

creased to 0.5810 by shearing, when the symmetry becomes monoclinic. Slack's 6.14 is formed by compressing the P cubic packing 1-4t-1 along [11$\bar{1}$] to the stage at which it is a packing of (6 + 8)-coordination. It is simply a packing intermediate between P cubic and I cubic [(8 + 6)-coordination]. The details are: rhombohedral, space group $R\bar{3}m$, point symmetry $\bar{3}m$, or for the hexagonal setting, 3(*a*), (000), $a = \sqrt{10}$, $c = \sqrt{6}$.

Slack's 6-packing is more dense than his 7-packing; moreover, his list does not include the notably dense bcc packing. These complications are avoided in the set of packings on the right of Table III, all of which (except the 11-packing) are based on the 4-layer of bcc packing, which cannot form a packing of 11-coordination. The two sets of packings are compared in Fig. 3. The first few sets of more distant neighbors (Table IV) show that in fact our packings correspond to $d_1/d \geqq 1.155$ (or $2/\sqrt{3}$) instead of Slack's 1.225 except for 2-6-3 I and II, in which there are no next-nearest neighbors closer than 1.225. If we made our condition $d_1/d \geqq 1.155$ we could include the more dense 2-6-3 S, but this (monoclinic) structure is preferably omitted for it is a sheared structure, whereas all the others are minimal density packings as defined earlier.

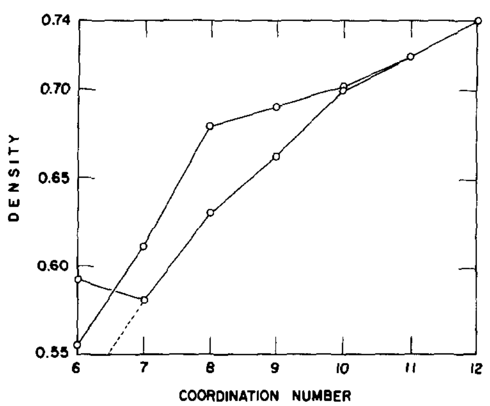

FIG. 3. Densities of sphere packings for C.N.s 6-12. The upper and lower curves correspond to the packings on the right and left, respectively, of Table III, and the broken line would continue Slack's curve to the value for 1-4t-1.

The important feature of the packings on the right of Table III, which is not a property of the packings of 6-, 7-, 8-, and 9-coordination in the left-hand column, is that each type of contact in the layer symbol of a packing other than a 3-contact for 4- and 6-layers or a 4-contact for the 4t-layer corresponds to a *minimal* density relation between a pair of layers, that is, to a position symmetrically situated between two positions corresponding to higher C.N.s.

The Symmetry of Coordination Groups

Related to this property of these packings is the high point symmetry of the coordination groups, which have either two or three planes of symmetry in the most symmetrical forms of the packings. In the case of the 9- and 11-packings the most symmetrical forms result from corrugation of the layers. The predominance of planar symmetry is to be expected in packings formed from the 6- and 4-layers if the symbol is of the symmetrical type 3-6-3, 2-4-2, or 1-4-1 owing to the symmetry of these layers, and these packings have in fact the coordination groups with the highest point symmetries. In the packings with unsymmetrical symbols high point symmetry is found only if the layers are nonplanar (2-6-3, 2-4-3) or if the structure is very simple (1-4-2). The structures on the left of Table III present a very different picture, for highly symmetrical coordination groups are found only in the packings of 11-, 10-, and 6-coordination. The sheared structures of 9-, 8-, and 7-coordination have only monoclinic symmetry and therefore at most one plane of symmetry.

The Symmetry-Equivalence of Spheres

Our condition (iv), that the immediate environment of each sphere shall be the same (or its mirror image), implies only that each layer is related in exactly the same way to the two layers in contact with it. Any packing built from planar layers that can be given a symbol of the type listed in Table II satisfies this condition. A more stringent condition is that the *complete* environment of each sphere is the same; this implies that the centers of the spheres form a set of equivalent positions in one of the 230 space groups. The spheres in such a packing are described as "symmetry-equivalent." It might have been expected that this property would be peculiar to a small number of packings. In fact it is not *in general* a very restrictive condition, for it is satisfied by all the packings of Tables III–V. Nevertheless it does exclude, and for different reasons, two categories of sphere packing, and it is therefore necessary to examine this matter of symmetry-equivalence in a little more detail.

(i) If there are alternate contacts of a given type between the layers, as for 2-contacts between 4t-layers, 2- or 3-contacts between 4-layers, or 2- or 3-contacts between 6-layers, then the symbol involving such contacts corresponds to an indefinitely large number of structures with increasingly complex layer sequences. There is an upper limit to the number of equivalent positions in a given set in space groups of each of the crystal systems, this number ranging from 2 (triclinic) through 8 (monoclinic), 32 (orthorhombic), to 192 (cubic). The spheres in a packing evidently cannot be symmetry-equivalent if the number of spheres in the unit cell exceeds the maximum appropriate to the symmetry of the packing. If sphere packings are derived by stacking layers of a particular kind it is, of course, essential to check that the most obvious unit cell is the smallest one for that packing. For example, the two 10-packings 3-4-3 and 3-4*-3 which are described later repeat after five and eight layers, respectively, suggesting Z = 10 or 16 if one axis is perpendicular to the layers. However, these two packings are referable to bc orthorhombic and bc tetragonal cells containing only two spheres.

(ii) A high value of Z resulting from a complex layer sequence is not the only reason for nonequivalence of spheres. This is evident from the fact that the only symmetry-equivalent packings 3-6-3 are hexagonal and cubic closest packings (sequences AB . . . and ABC . . .), while the next member of the family (ABAC . . .) has only four spheres in the unit cell but consists of two sets of nonequivalent spheres, the positions 2(*a*) and 2(*d*) in $P6_3/mmc$. As the highest number of equivalent positions in a hexagonal space group is 24, the reason for the nonequivalence of spheres in this packing is clearly not the high value of Z. The situation is similar in 10-packings 1-6-3, of which the only two of the infinite series of packings which have symmetry-equivalent spheres are AABB . . . and AABBCC . . . (*3*).

Finally we note that the requirement of symmetry-equivalence does *not* eliminate the indefinitely large numbers of packings which represent transitions between packings of different C.N.s, for example, packings intermediate between 2-6-3 T and hexagonal closest packing. These merely correspond to different values of the cell dimensions a and b and different values of x and y in the position 4(*g*), (x, y, 0) in the space group *Pnnm*, in which space group hcp also may be described. Similarly, sheared versions of 2-6-3 may all be described by the position 4(*i*) in *C*2/*m*.

The Sphere Packings of Table V

The following paragraphs amplify the data summarized in the Table. Some of the packings are illustrated in Figs. 4–12, of which all except Fig. 5 are projections. In these projections the layers (4t-, 4-, or 6-) run from left to right and are normal to the paper. Open and filled circles represent

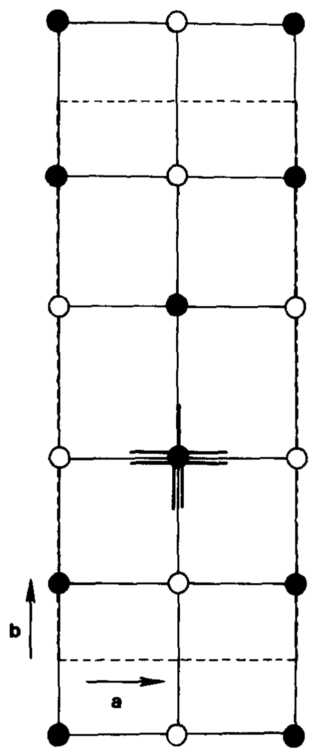

FIG. 4. The packing 1-4-2 projected on (001). There are no additional contacts in a direction normal to this projection.

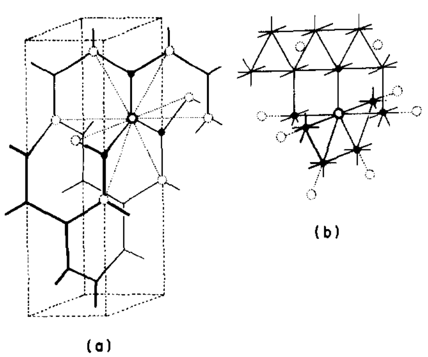

FIG. 5. (a) Unit cell of the 3-connected net $10^3 - b$ (*c* axis vertical) showing the three nearest neighbors (black circles) of one point and its two sets of four next-nearest neighbors (dotted circles). (b) Portion of the net (on the same scale) showing the relation of the four additional nearest neighbor in the packing 1-4t-2 II to four of the next-nearest neighbors in (a).

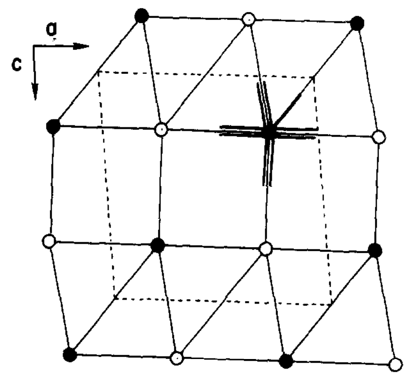

FIG. 6. Projection of the packing 2-4-3 I on (010).

spheres at height zero or one half of the repeat distance normal to the plane of projection.

Sphere Packings of C.N. 6

Both of the packings listed in Table V are lattice packings, 1-4-1 (*Cmmm*) having the higher density but lower point symmetry *mmm* as compared with *m*3*m* for 1-4t-1 (cubic P lattice).

Sphere Packings of C.N. 7

There is only one 1-4-2 packing (Fig. 4) if the *D* positions are used for 2-contacts, but there is an infinite family of the less dense 1-4t-2 packings. The simplest of these, 1-4t-2 I, has orthorhombic symmetry and four spheres in the repeat unit. It has been described previously as the packing No. 11 of

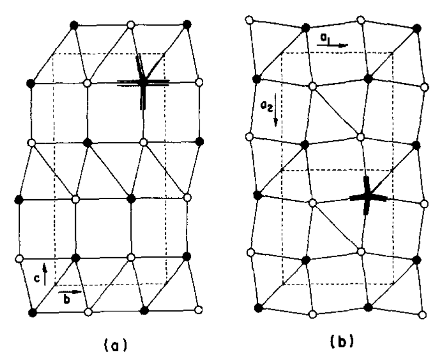

FIG. 7. (a) Projection of 2-4-3 II on (100) compared with (b) projection of 2-4-3 T on (001) (two unit cells).

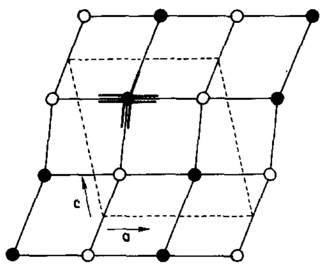

FIG. 8. Projection of 1-6-2 SS on (010). Each sphere makes two additional contacts in a direction normal to this projection.

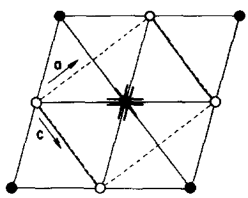

FIG. 9. Projection on (010) of bc orthorhombic cell of 3-4-3 I showing its relation to three 4-layers which are normal to the paper and run from left to right.

Clarke and the packing 7.5 of Slack. The next simplest member of this family, 1-4t-2 II, is more symmetrical though the point symmetry remains the same (*mm*). This tetragonal packing ($Z = 8$) is of interest for it has the same space group and equivalent positions as the 3-packing (Slack 3.6) in which the spheres occupy the positions of the points of the 3-connected net $10^3 - b$ (*5*). The 3-packing and 7-packing are related as follows:

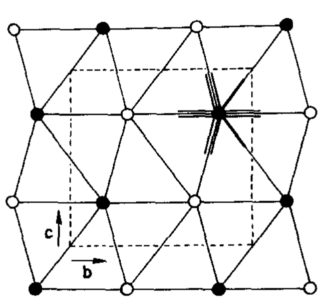

FIG. 10. Projection of 3-4-3 II on (100).

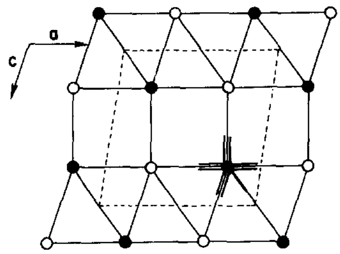

FIG. 11. Projection of 2-6-3 I on (010).

C.N. 3 $c:a = 2\sqrt{3}$, $z = \frac{1}{12}$, and
C.N. 7 $c:a = 2(2 + \sqrt{3})$, $z = \frac{1}{4}(2 + \sqrt{3})$.

The contraction of the tetragonal a axis from $2\sqrt{3}$ to 2 implies extension of the c axis from 12 to $4(2 + \sqrt{3})$, for the bond angles at a point change from three of 120° to one of 60° and two of 150°. The orthorhombic and tetragonal 1-4t-2 packings have very similar distances to more distant neighbors; the numbers in Table IVc therefore apply to both these packings. There are only minor differences after 80 neighbors beyond the first coordination sphere.

Sphere Packings of C.N. 8

The densities of 8-packings range from 0.6801 (bcc) to 0.6046. There is only one 1-6-1 packing of minimal density but an infinite number of 2-4t-2 packings (since there are alternate positions for 2-contacts be-

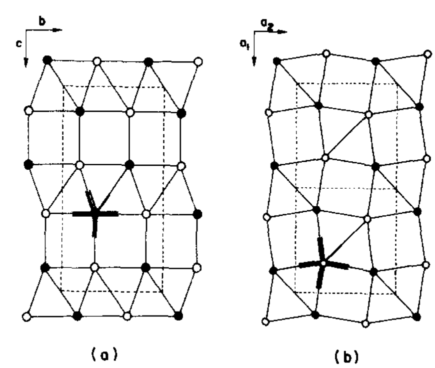

FIG. 12. (a) Projection of 2-6-3 II on (100) compared with (b) projection of 2-6-3 T on (001) (two unit cells).

tween 4t layers), one of which is the minimal density 1-6-1. This very simple packing (Clarke No. 12, Slack 8.4) consists of 6-layers stacked vertically above one another. It is a lattice packing, the hexagonal analog of primitive cubic packing. A second packing 2-4t-2 (Clarke No. 13), not included in Table V, is of interest as having the same space group and axial ratio as the 3-packing mentioned in the preceding paragraph. Sphere centers are at the positions 4(a), (000, $0\frac{1}{2}\frac{1}{4}$) of $I4_1/amd$, with $a = 2$ and $c = 4\sqrt{3}$. Packings with intermediate densities include the 1-4-3 family, of which only the simplest is included in Table V, and all sheared 1-6-1 packings, of which two examples are given.

Sphere Packings of C.N. 9

Packings of C.N. 9 can be formed from all the layers of Fig. 1, namely, 1-4t-4, 2-4-3, and 1-6-2. There is only one 1-4t-4 packing but infinite families of "least dense" 2-4-3 and 1-6-2 packings because there are alternate positions for 2- and 4-contacts between 4-layers and of 2-contacts between 6-layers. We have considered only D-type contacts between 4-layers because packings 2-4-3 E have the density 0.6703 and are not of special interest. Sheared versions of 2-4-3 packings correspond to transitions to 3-4-3 packings and are not recognized as distinct packings. In the simplest (monoclinic) 2-4-3 I (Fig. 6) the distances to all 56 next-nearest neighbors are the same as in 2-4-3 II (Fig. 7a). In addition to these two packings built of planar 4-layers there is a packing (2-4-3 T) built of nonplanar layers (*6*) which has the same density as those built from planar layers but a higher symmetry. A projection of this structure is compared with that of 2-4-3 II in Fig. 7; we comment later on the close relation of the structure of Fig. 7b to the 11-packing based on nonplanar 6-layers. The packing 1-6-2 (Clarke No. 18, Slack 9.1) can be sheared on one or both sides of each layer to give structures of higher density, and lower symmetry, which are intermediate between structures of 9 and higher C.N.s. The example shown in projection in Fig. 8, 1-6-2 *SS*, is sheared on both sides to give next-nearest neighbors at 2.309 (Table IVb). The least dense 9-packing of Table V, 1-4t-4 (Clarke No. 14, Slack 9.2), has the most symmetrical coordination group of those listed.

Sphere Packings of C.N. 10

Three groups of three 10-packings are listed in Table V with densities 0.7025 ($\pi/2\sqrt{5}$), 0.6981 ($2\pi/9$), and 0.6657 ($2\pi/3(\sqrt{2} + \sqrt{3})$). Most of those with the two lower densities were listed by Slack and some by Clarke. We consider first those of the third group.

There is an indefinitely large number of ways of stacking 4t-layers to form 2-4t-4 packings; of these only the simplest (orthogonal) packing is listed. Packings 1-6-3 also form an infinite series because there are alternate ways of achieving a 3-contact. Clarke described two (his Nos. 15 and 16) as having symmetrically equivalent spheres, but it has been pointed out (*3*) that the second of these cannot be described by a single set of equivalent positions, and that only two 1-6-3 packings have this property. Using the usual cp terminology these are the sequences AABB . . . and AABBCC . . . (1-6-3 I and II). The environments of a sphere in these two structures are, of course, very similar. In fact, the numbers of neighbors at various distances are the same for the first 72 spheres beyond the 10 nearest, after which there are minor differences.

Packings with density 0.6981 include two of the infinite family of 2-6-2 packings, each sphere of which makes 2-contacts on each side of its layer. The first ($Z = 2$) is the well-known bc tetragonal structure 2-6-2 I in which there is also closest packing in a second set of planes perpendicular to the first set. In this packing spheres of alternate layers fall above points A and D′ (Fig. 1c). In the next simplest packing, 2-6-2 II, ($Z = 3$) spheres of successive layers fall above A, D″, and D‴ related by 3_1 (or 3_2) axes. The only cp layers in this packing are the original ones perpendicular to the screw axes.

The bc tetragonal 2-6-2 packing may alternatively be built from layers which we call 4* intermediate between the 4t- and 4-layers. This layer has the angle aAa equal to 75°32′, AA′ = $\sqrt{10}$, aa′ = $\sqrt{6}$, and AB/AA′ = $\frac{2}{5}$ (nomenclature as in Fig. 1 and Table I.) If successive layers are translated by AB the packing 3-4*-3 repeats after five layers in a direction normal to the layers, but a projection along aa′ shows that the packing is referable to the bc tetragonal cell of 2-6-2 I. Because there are alternative positions for 3-contacts there is an indefinitely large number of polytypes. If 4*-layers are stacked so that successive layers fall alternately above A and B there is formed the orthorhombic packing 3-4*-3 II.

Corresponding to the two simplest structures formed from the 4* layer are the two simplest 3-4-3 packings, which have a density (0.7025) slightly greater than that of the three packings just described. In 3-4-3 I successive layers are translated by the distance AB equal to $\frac{3}{8}$ AA′ (Fig. 1b). In a direction normal to the layers the structure repeats after 8 layers, but it is referable to a bc orthorhombic cell ($Z = 2$) which is related to the layers as shown in Fig. 9. In this packing there are two sets of closest-packed layers inclined at an angle of 83°38′. In 3-4-3 II the spheres of alternate layers fall above points A and B in Fig. 1b, and like hcp the structure repeats after 2 layers (Fig. 10). The 10-packings built from the 4* and 4-layers are the analogs of the closest packings built from 6-layers (Table VI).

Also included in Table V is a third packing with the same density (0.7025) as the 3-4-3 packings; this is the simplest orthogonal sheared 2-6-2 packing. Successive layers are displaced by $a/18$ alternately to one side and the other of the normal position for a 2-contact. This is one example of the infinite number of packings intermediate between 2-6-2 and 2-6-3, and is not a "minimal density" packing symmetrically related to two packings of higher C.N.

Sphere Packings of C.N. 11

The simplest 2-6-3 packing is the monoclinic 2-6-3 I (Fig. 11), and the simplest orthogonal variant is 2-6-3 II. Like 1-6-3 packings all 2-6-3 packings have pairs of adjacent cp layers. They are therefore convertible into the various cp sequences found as the packings of the anions in, for example, the CdI_2 polytypes. The simplest relation is that between hcp, 2-6-3 I, and ccp (7). The spheres in both 2-6-3 I and II have very similar sets of more distant neighbors, the next 74 beyond the 11 nearest being at the same distances in the two packings. In a 2-6-3 packing built from planar 6-layers the positions for a 2-contact on one side of a layer and for a 3-contact on the other limit the point symmetry of the coordination group to m. There is, how-

TABLE VI

RELATION BETWEEN SPHERE PACKINGS OF 10- AND 12-COORDINATION

C.N.	AB/AA′	Symbol	Number of layers in repeat unit	Space group	Density	Symbol	Number of layers in repeat unit	Space group
10	$\frac{2}{5}$	3-4*-3 II	2	*Cmcm*	0.6981	3-4*-3 I	5	*I4/mmm*
	$\frac{3}{8}$	3-4-3 II	2	*Cmcm*	0.7025	3-4-3 I	8	*Immm*
12	$\frac{1}{3}$	hcp	2	*P6₃/mmc*	0.7401	ccp	3	*Fm3m*

ever, another packing with density 0.7187, namely 2-6-3 T, which has tetragonal symmetry and a more symmetrical coordination group (point symmetry *mm*). This packing is built from corrugated 6-layers, and it represents the arrangement of the anions in the idealized rutile structure (*4*); it is compared with 2-6-3 II in Fig. 12. The space group and equivalent positions are the same as those of 2-4-3 T, the major difference from which lies in the decrease in the c cell dimension, normal to the paper in Fig. 7b and 12b. This brings in two additional neighbors and increases the C.N. from 9 to 11.

The 2-6-3 T structure of Fig. 12b consists of columns of octahedral groups, each sharing two opposite edges, which are normal to the paper in the projection of Fig. 12b. An interesting property of this packing is that it may be converted into hcp by rotating these columns of octahedra in either direction, as indicated by the arrows in Fig. 13 (*3*).

The coordination polyhedra in 2-6-3 I and II are identical and very similar to that in 2-6-3 T. Both are irregular 4-connected polyhedra with 22 edges (18 of length 2, and 4 of 2.449) and 13 faces. Of the latter 8 are triangular (4 equilateral and 4 isosceles) and 5 are quadrilateral (3 square and 2 rectangular). The four kinds of faces are arranged differently in the two coordination polyhedra—compare the relation between the coordination polyhedra in ccp and hcp. In both of the cp structures the coordination polyhedron is a 4-connected polyhedron

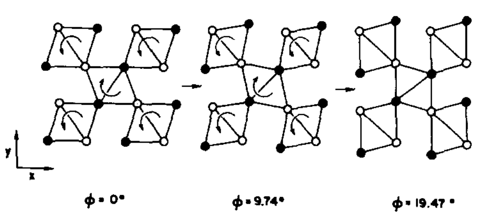

FIG. 13. Relation between hexagonal closest packing and 2-6-3 T.

TABLE VII

RELATIONS BETWEEN SPHERE PACKINGS OF 10-, 11-, AND 12-COORDINATION

(a)

C.N.			Density			Density
9	$P4_2/mnm$	4(*f*)	0.6911	*Cmca*	8(*f*)	0.6911
10	$\left\{\begin{array}{l}I4/mmm\\ Cmcm\end{array}\right.$	$\left.\begin{array}{l}2(a)\\ 4(c)\end{array}\right\}$	0.6981	$\begin{array}{l}Immm\\ Cmcm\end{array}$	$\left.\begin{array}{l}2(a)\\ 4(c)\end{array}\right\}$	0.7025
11	$P4_2/mnm$	4(*f*)	0.7187	*Cmca*	8(*f*)	0.7187

(b)

$x = \frac{1}{4}$ | $x = \frac{1}{4}$, $y = \frac{1}{8}$
Amam 4(*c*) ($\frac{1}{4}y0$) → hcp $P6_3/mmc$
Pnnm 4(*g*) (*xy*0) ↗ *Cmcm* structures of Table V | 12-Coordination
Structures intermediate between hcp and 2-6-3 T | 10-Coordination
11-Coordination ↘ $x = y$
$P4_2/mnm$ 4(*f*) (*xx*0)
11-Coordination

(c)

ϕ (Fig. 13)	a	b	c	x	y	Space group
0	3.464	3.266	2	$\frac{1}{8}$	$\frac{1}{4}$	$P6_3/mmc$
4.87°	3.451	3.352	2	0.187	0.228	*Pnnm*
9.74°	3.414	3.414	2	0.207	0.207	$P4_2/mnm$
14.61°	3.352	3.451	2	0.228	0.187	*Pnnm*
19.47°	3.266	3.464	2	$\frac{1}{4}$	$\frac{1}{8}$	$P6_3/mmc$

with 24 edges (all of equal length) and 14 faces (8 equilateral triangles and 6 squares).

A density higher than 0.7187 can be achieved by shearing a 2-6-3 structure, and the packing with d_1/d made equal to the arbitrary value 2.309 has the density of 0.7209. This is included in Table V simply as an example of a structure with C.N. tending toward 12; it does not satisfy our criterion that it is a structure of minimal density symmetrically related to two structures of higher C.N.

Certain relations between some of the packings of Table V are more easily appreciated from the simpler Table VII(a). For each of the C.N.s 9, 10, and 11 there is a tetragonal and an orthorhombic packing. The tetragonal 9- and 11-packings have the same space group ($P4_2/mnm$), and the orthorhombic 9- and 11-packings have the same space group (*Cmca*). The two 9-packings have the same density (0.6911), and the density of both the 11-packings is 0.7187. Table VII(a) also includes two 10-packings (with different densities) with the space group *Cmcm*; in fact there is an orthorhombic packing described by 4(*c*) of this space group in each of the three groups of 10-packings in Table V, namely, 3-4-3 II, 3-4*-3 II, and 2-4t-4.

The packings of 10-coordination with space group *Cmcm* are related to those of 11- and 12-coordination as indicated in Table VII(b). The set of equivalent positions 4(*g*) of *Pnnm*, $xy0$, $\bar{x}\bar{y}0$, $\frac{1}{2}+x\ \frac{1}{2}-y\ \frac{1}{2}$, and $\frac{1}{2}-x\ \frac{1}{2}+y\ \frac{1}{2}$, describes the packings intermediate between hcp and 2-4-3 T which correspond to values of ϕ between those of Fig. 13. If $x = \frac{1}{4}$ these positions become 4(*c*) of *Amam* (an alternate setting of *Cmcm*), and if $x = \frac{1}{4}$ and also $y = \frac{1}{6}$ they correspond to the orthohexagonal description of hexagonal closet packing (with $a = 3.266$, $b = 3.464$, $c = 2$). Finally, if $x = y$ (and $a = b$) the above set of equivalent positions becomes 4(*f*) of $P4_2/mnm$. Table VII(c) lists cell dimensions and values of x and y for the sphere packings of Fig. 13 and also for one intermediate value ($\phi = 4.87°$) and the complementary structure ($\phi = 14.61°$), for which the values of a and b and of x and y are interchanged. Whereas all the structures of Table VII(c) may be described by the position 4(*g*) of *Pnnm*, the special values of x and y (with the appropriate values of the cell dimensions) lead to the higher symmetries shown in the table. For these structures,

$$a = 2\sqrt{3}\cos\phi$$

$$b = 2(\sqrt{8/3}\cos\phi + \sqrt{1/3}\sin\phi)$$

$$c = 2$$

$$x = \tfrac{1}{2} - [(\sqrt{2} - \tan\phi)/3\sqrt{2}]$$

$$y = \tfrac{1}{2} - [(1 + \sqrt{2}\tan\phi)/(4 + \sqrt{2}\tan\phi)].$$

Acknowledgment

We wish to acknowledge the assistance of Dr. Terrell Hewston for carrying out some of the calculations utilizing the BONDLA computer program in the ORTEP package.

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