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Complex Alloy Structures Regarded as Sphere Packings. I. Definitions and Basic Principles

By F. C. Frank
H. H. Wills Physics Laboratory, University of Bristol, England
and J. S. Kasper
Research Laboratory, General Electric Company, Schenectady, N.Y., U.S.A.

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Complex alloy structures, particularly those of transition metals, are considered as determined by the geometrical requirements for sphere packing. A characteristic of the class of structures discussed is that tetrahedral groupings of atoms occur everywhere in the structure—alternatively stated, coordination polyhedra have only triangular faces. The topological and geometrical properties of such polyhedra are examined and rules and theorems regarding them are deduced. Justification is given for the prominence of four such polyhedra (for coordination numbers of 12, 14, 15 and 16) in actual structures. General principles regarding the combination of these polyhedra into full structures are deduced and necessary definitions are given for terms that facilitate the detailed discussion of this class of structures.

1. Introduction

It has been pointed out (Kasper, 1956) that a number of the relatively complex structures, particularly of transition metal alloys, may be regarded as determined by the geometrical requirements for sphere-packing in a higher degree than has generally been realized. A fruitful approach is to consider the coordination shells around particular atoms, which prove to correspond to a certain limited number of types. In accordance with a consideration due to Boerdijk (1952), who counts the number of tetrahedral groupings of four spheres as a rough test of the efficiency of a sphere-packing, it is found that the preferred coordinations are those which define a net of triangles on the surface of the sphere, and therefore tetrahedral groupings of triads of atoms in the coordination shell together with the central atom. 12-fold coordination is of course the most important case, 12 being the largest number of equal spheres which can be put in contact with one (Boerdijk, 1952). There are three distinct symmetrical 12-coordinations with rigid equal spheres. Of these, it is not the cubo-octahedral 12-coordination of the face-centred cubic structure, nor the twinned cubo-octahedral 12-coordination of hexagonal close-packing, but the icosahedral 12-coordination which is generally found in the complex structures. This arrangement has two evident advantages, both deriving from the fact that, with rigid spheres and in the most symmetrical position, the spheres of the coordination shell are not in contact with each other, as they are in the other two cases. One consequence is that, though with rigid spheres the circumscribing sphere has exactly the same radius for all three cases, with slightly compressible mutually attracting spheres the circumscribing sphere will be least for the icosahedral case: this also gives the lowest energy within the group. The second consequence, apparent by considering rigid spheres once more, is that the icosahedral grouping is in fact not one structure, but a range of structures, in all of which the twelve coordinating spheres are equidistant from the central one, allowing a freedom of deformation to comply with the simultaneous coordination requirements of other atoms than the central one.

There appears to be no space-filling structure utilizing the icosahedral coordination and providing 12-fold coordination of all atoms. For rigid equal spheres, demanding true contact coordination, this is easily proved (from the fact that not all neighbours in the icosahedral 12-shell can be in contact): when, as for real atoms, some moderate amount of variation in interatomic distances is tolerated, proof is likely to be difficult, but by trial it appears to be a fact. On the other hand, it has been shown (Kasper, 1956) that typical complex crystal structures, particularly of transition metal alloys, provide examples in which abundant icosahedral 12-coordination is combined only with 'triangulated' coordinations of larger number (14, 15 and 16) (Fig. 1) which provide appropriate sites for the larger atoms in the alloy composition. Since these coordination shells have not been frequently encountered heretofore, it would be in order to consider in some detail their nature and properties.

2. Triangulated coordination shells

As we have seen, the fact that in the closest approach of three spheres their centres form a triangle with their points of contact in each side, and in the closest approach of four spheres their centres form a tetra-

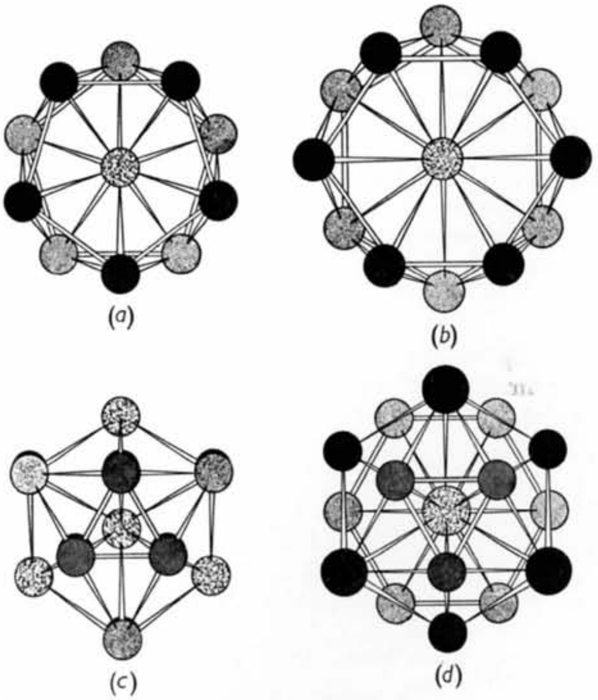

Fig. 1. The four 'normal coordination polyhedra' of complex alloy structures. For C.N. 12, two spheres above and below the central sphere, along the fivefold axis, are not shown. Similarly, two spheres above and below the central one of C.N. 14, along the sixfold axis are not shown. For C.N. 16 one sphere below the central one is not shown.

(*a*) Icosahedron, C.N. 12. (*b*) C.N. 14. (*c*) C.N. 15. (*d*) C.N. 16.

hedron with their points of contact in each edge, directs our attention to coordination shells of neighbouring atoms around any one in which the surrounding atoms are at the corners of a polyhedron with triangular faces. Such shells we shall call *triangulated coordination shells*. The identification of these coordination shells involves a judicious mixing of topology and geometry. If measure is totally omitted, there is no problem, since any number of points exceeding two can be connected together in triangles, and in various ways if the number exceeds four. If strict measure is insisted on, with the requirement that all triangles in the coordination shell are equilateral, the problem is trivial, having as solutions only the regular tetrahedron, octahedron, and icosahedron. If it is further required that the shell atoms make equilateral triangles with the centre, there is no solution at all. It is therefore necessary to tolerate some departure from equality of distances, without making this so great as to introduce ambiguity as to whether a pair of atoms are neighbours or not.

We can in fact eliminate these ambiguities by introducing new definitions of *coordination number* and of *neighbour*. The definitions that follow are precise for any exactly known structure. Border-line cases can exist, particularly at symmetry planes of the crystal structure, but turn out to be very rare in the range of structures now under discussion: none of the four special coordination shells characteristic of these structures is close to a border-line case on this definition.

2·1. *Some definitions relating to coordination*

We define the *domain* of an atom as the space in which all points are nearer to the centre of that atom than any other. It is a polyhedron, each face of which is the plane equidistant between that atom and a *neighbour*. If we describe all the planes bisecting the lines joining the central atom to all other atoms, then the innermost polyhedron bounded by these planes is the domain of that central atom, and every atom whose domain has a face in common with the domain of the central atom is, by this definition, one of its neighbours. The number of neighbours will be called the *coordination number* of the central atoms, and the set of neighbours its *coordination shell*. The polyhedron whose edges are the lines joining all the atoms of the coordination shell which are also neighbours of each other will be called its *coordination polyhedron*. The coordination polyhedron and the domain stand in dual relationship, each having a vertex corresponding to each face of the other.

It is to be noticed that the term 'coordination number' has been used in two ways in crystallography, one of which is precisely defined in principle, though seldom used with rigour, and another employed intuitively, without exact definition. According to the first, the coordination number, Z, is the number of nearest neighbours to an atom. According to this definition, in hexagonal close packing Z is 6 unless c^2/a^2 is exactly 8/3, in which case it is 12. The definition is rarely applied with rigour in this case: Z is generally regarded as 12. In the body-centred cubic lattice, however, some authors probably the majority, count Z as 8 in accordance with the nearest-neighbour definition, but others prefer to regard it as 14. The definitions we have given above provide a rigorous basis for the second view-point according to which Z is unambiguously 12 in the hexagonal close-packed metals and 14 in a body-centred cubic metal. In the more complex structures of metals and intermetallic compounds this definition yields numbers such as 14 where the nearest-neighbour definition would give 1 or 2.

Logically, since there is a one-to-one correspondence between the coordination polyhedron of an atom and its dual, the domain of that atom, there is no need to consider both. We might conduct our whole argument in terms of the space-filling packing of polyhedra, which are the atomic domains. The reason why we prefer to think primarily of the coordination polyhedron is that crystal models in which a sphere representing each atom is connected by wires to each of its neighbours are easier to construct, draw, or see through, than a model in which atoms are represented by packing polyhedra. We only need to consider the atomic domains when we are in doubt whether a pair of atoms ought to be connected by a wire in the model or not.

It is convenient to introduce the term *surface coordination number*—the number of neighbours of an atom which lie in a specified surface. We shall apply this particularly to the surface coordination of one atom of a coordination shell by other atoms of the same coordination shell. Thus in the 12-coordination shells of atoms in the face-centred cubic or hexagonal close-packed structures (which are not triangulated coordinated shells in our present sense) the surface coordination number of any atom is 4. In the icosahedral 12-coordination, the surface coordination number is 5. For brevity, we shall refer to an atom with q-fold surface coordination as an S_q atom.

2·2. *Topology of the triangulated coordination shells*

The number of equilateral triangles which can meet at a point in a non-reentrant polyhedron is 3, 4, 5 or 6 (coplanar in the case of 6). If there are contacting spheres of unit radius at each corner of the triangles, the radius of an inner sphere which touches all of these spheres is 0·225, 0·414, 0·901 and ∞ in these four cases. It is clear that the case of 5 triangles meeting at a point is admirably suited for coordination of atoms differing only slightly in their respective sizes and that surface coordinations of 3 and 4 would be more suitable for the coordination of small atoms by significantly larger ones.* Nonetheless, since all atoms cannot be S_5, the question is which of S_4 or S_6 provides least distortion from equilateral triangles when dealing with atoms of nearly the same size. A variety of geometrical considerations indicates that S_6 is to be preferred. For example, if we consider equal spheres placed at the corners of symmetrical 3-fold, 4-fold, 5-fold and 6-fold bipyramids and in each case the separation of the spheres along the axis is made equal to the edge length in the ring, then all triangles in each case are equivalent and isosceles. They are as shown in Fig. 2.

While S_6 is favoured over S_4, the latter cannot be decisively ruled out. There may be merit in considering, as a separate subject, the numerous ways of combining S_4 as well as S_6 with S_5, but our main concern here is with the class of structures which represent the closest approach to the strictly unattainable situation of having throughout the structure regular tetrahedral groupings of atoms. This class, with surface coordinations only of 5 or 6, is already quite extensive.

A theorem due to Euler states that for any polyhedron, having V vertices, E edges and F faces

$$V-E+F = 2\,. \tag{1}$$

If v_q is the number of vertices which are connected by q edges to neighbouring vertices (for short, v_q is the number of q-fold vertices), we have

$$V = \sum_q v_q \tag{2}$$

and

$$E = \tfrac{1}{2}\sum_q qv_q\,, \tag{3}$$

since each q-fold vertex has q edges each shared with one other vertex.

For polyhedra whose faces are all triangular, we have additionally

$$F = \tfrac{1}{3}\sum_q qv_q\,, \tag{4}$$

since each q-fold vertex has q faces each shared with two other vertices.

Then Euler's equation (1) becomes

$$\sum_q v_q-\tfrac{1}{2}\sum_q qv_q+\tfrac{1}{3}\sum_q qv_q = 2; \tag{5}$$

that is,

$$\sum_q (6-q)v_q = 12\,. \tag{6}$$

The cases of present interest to us are the triangulated polyhedra with 4-, 5-, and 6-fold vertices, for which

$$2v_4+v_5 = 12\,, \tag{7}$$

and more especially the case of triangulated polyhedra with only 5- and 6-fold vertices for which

$$v_5 = 12\,, \tag{8}$$

$$v_6 = Z-12\,, \tag{9}$$

where we have replaced V by Z, the conventional symbol for coordination number.

With equal spheres, if two or more contiguous ones have 6-fold surface coordination, they and all their

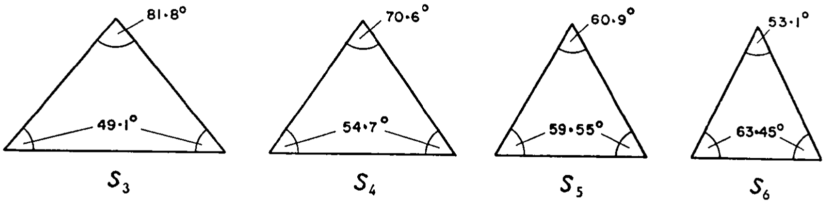

Fig. 2.

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* In order to specify more definitely the usage of small, large and nearly equal atoms, we shall consider (somewhat arbitrarily) as 'nearly equal' atoms those whose radii do not differ by more than 25%.

neighbours are co-planar. This arrangement can be wrapped around a sphere only of relatively large radius if it is not to produce large distortions of the equilateral triangles. Hence it is an appropriate arrangement only for what we may call very large coordination shells.

We may single out as an important class those triangulated coordination shells with 5-fold and 6-fold vertices in which no atoms with 6-fold surface coordination are contiguous. It turns out that there are just four of these, and that they are the four which have been recognized (Kasper, 1956) as characteristic of the complex structures of transition metal alloys.

We consider these cases in order of ascending n_6, making use of equations (7) and (8).

12-*Coordination*: $Z = 12$, $n_6 = 0$.—Around an S_5 atom A we have a ring of $5\,S_5$ atoms $B\,C\,D\,E\,F$. BC, CD etc. are also necessarily contacts to complete the triangles. Each pair $BC, CD, \ldots, FB$ must also form triangles with further atoms $G\,H\,I\,J\,K$, one for each. It is not possible that G and H are the same atom, since then C would be S_4. It is not possible that G and I are the same atom, since then H would be S_3. All other coincidences among $G, \ldots, K$ are equivalent to these two: hence $G, \ldots, K$ are distinct. GH, HI, etc. are necessarily contacts to complete the triangles. Each of these 5 requires one more neighbour to be S_5, and one more S_5 atom is required to complete the 12. Thus *one arrangement, and only one, satisfies the conditions. This is the regular icosahedral* 12-*coordination.*

13-*Coordination*: $Z = 13$, $n_6 = 1$.—Around the S_6 atom, A, we must have a contacting ring of 6 S_5 atoms $BCDEFG$, and a further ring of atoms $HIJKLM$ making triangles with each of the pairs BC, CD, $\ldots, GB$. As in the previous case, it is not possible that any two of $H, \ldots, M$ are the same atom, since that would always require that some atom or atoms was S_3 or S_4. These are therefore distinct, and, to complete the triangles, form a ring of 6 neighbours. Each of these 6 requires one more neighbour to become S_5, and we shall then have 12 S_5. The structure cannot be completed without another S_6 atom. Hence *there is no triangulated* 13-*coordination shell.*

14-*Coordination*: $Z = 14$, $n_6 = 2$.—The shell discussed in the preceding section can now be completed. We should also consider the possibility that one of the atoms in the second ring, say H, is S_6. Then this ring requires 7 more contacts, but we are allowed only one more S_5 atom to provide them. Hence *there is one and only one triangulated* 14-*coordination.*

15-*Coordination*: $Z = 15$, $n_6 = 3$.—Proceeding as before we allow two of the atoms in the ring $H, \ldots, M$ to be S_6. 8 more contacts with this ring are then required. These can be provided by the two further S_5 atoms needed, in contact with each other, in the required manner if and only if the S_6 atoms are diagonally opposite to each other. Hence *there is one and only one triangulated* 15-*coordination shell.*

16-*Coordination*: $Z = 16$, $n_6 = 4$.—The 8 contacts required by the ring $H, \ldots, M$ with $2\,S_6$ atoms cannot be provided by $2\,S_5$ and $1\,S_6$ atom, which require 10 if they form a triangle, and more otherwise.

We therefore allow 3 atoms of the ring $H, \ldots, M$ to be S_6. 9 further contacts with the atoms of this ring are required. These are provided by the required 3 additional S_5 atoms, in a triangle, when the $3\,S_6$ atoms are in alternating positions round the ring, and in no other way. Hence *there is one and only one triangulated* 16-*coordination without adjacent* 6-*fold vertices*, and *all triangulated coordination shells having* $Z > 16$ *with only* 5-*fold and* 6-*fold vertices have at least one pair of adjacent* 6-*fold vertices.*

2·3. *Detailed geometry of the four special coordination shells*

We assume that the 6-rings are plane regular hexagons, symmetrically disposed about the central atom, the length of each side of a hexagon being 2. We define a_1 as the distance from the central atom to the mid-point of a hexagon, (a_2+1) as the distance from the central atom to one of the atoms in a hexagon, and $2b$ as the distance between neighbouring atoms in different hexagons. For the regular icosahedral 12-coordination we take the distance between all neighbours in the coordination shell to be 2, and define (a_1+1) as their distance from the central atom. The departure of these a and b values from unity is a measure of the degree of incompatibility of the arrangement with contact packing of hard equal spheres. The difference between a_1 and a_2 is a measure of the incompatibility with contact packing of hard spheres, permitted to be unequal.

$$Z12\colon\ a_1 = [\tfrac{1}{2}(5+\sqrt{5})]^{\frac{1}{2}}-1 = 0{\cdot}902\,.$$

$$Z14\colon\ a_2 = (a_1^2+4)^{\frac{1}{2}}-1\,,$$

$$b = (a_1^2+2-\sqrt{3})^{\frac{1}{2}}\,.$$

Some corresponding values are:

$a_1 =$	0·8	0·856	0·9	1·0	1·1	1·2
$a_2 =$	1·15	1·18	1·19	1·24	1·28	1·33
$b =$	0·953	1	1·04	1·13	1·22	1·31

a_1 may be greater or less than 1, but is necessarily less than both a_2 and b. Thus this coordination requires the central atom to be compressed along the symmetry axis of the coordination sphere. When $b = 1$ (and $a_1 = (\sqrt{3}-1)^{\frac{1}{2}}$, $a_2 = (3+\sqrt{3})^{\frac{1}{2}}-1$) this distortion is rather severe. The required asphericity of the central atom is reduced by making b somewhat greater than 1.

$$Z15\colon\quad a_1 = 1\,,$$

$$a_2 = \sqrt{5}-1 = 1{\cdot}24\,,$$

$$b = \tfrac{1}{2}\sqrt{3} = 0{\cdot}866\,.$$

$$Z16\colon\quad a_1 = \sqrt{(\tfrac{3}{2})} = 1{\cdot}225\,,$$

$$a_2 = \sqrt{(\tfrac{11}{2})}-1 = 1{\cdot}34\,,$$

b does not exist.

3. The combination of normal coordination shells

Thus far we have discussed only the coordination of atoms around a single atom. We have identified some reasons which interpret the empirically observed preference for four particular coordination shells of 12, 14, 15, and 16 atoms. We shall call these the *normal coordinations*. We now consider the conditions imposed on complete structures when it is required that not only the atoms around one form a normal coordination, but that these atoms in turn are also surrounded by normal coordination shells. Two main principles emerge from this consideration, both of which are of considerable value in describing the main features of a complex alloy structure. One is the existence of what we call the *major skeleton*, the meaning of which will be made clear below. The other is the necessary existence in such structures of planar, or approximately planar, *layers* of atoms, containing certain necessary pattern-motifs. The latter principle introduces the possibility of systematic classification of certain families of structures in terms of the permitted stacking sequences of these layers.

3·1. *The major skeleton*

We distinguish the sites of 12-coordination as *minor* and of more than 12-coordination as *major*. If an atom A is at a minor site, it has no neighbour with which it shares 6 neighbours in common. If atom A is at a major site of coordination number Z, it has $(Z-12)$ such neighbours. If B is one of these, it follows that B has a neighbour (namely A) in its coordination shell, with which it has 6 neighbours in common. Therefore B is also a major site. We call the line joining A and B, or joining any pair of atoms which have 6 neighbours in common a *major ligand*. Every major site of coordination number Z is the meeting point of $(Z-12)$ major ligands. This is at least 2, since the case $Z = 13$ does not exist. Hence the major ligands form one or more connected networks, the totality of which we call the *major skeleton* of the structure. The nodes of the major skeleton comprise all the major sites of the structure. The geometry of the major skeleton is governed by rules which generally make it substantially simpler than the structure as a whole. Sites of $Z14$, $Z15$, or $Z16$ are the meeting points of 2, 3, or 4 major ligands, which are (accurately or approximately) in line, 120° apart in a plane, or in tetrahedral disposition, respectively. In brief, this leads to a geometry similar to that of organic chemistry in the absence of univalent elements. This absence corresponds to the absence of $Z13$. It has the consequence that each connected system of major ligands is infinite. The least ramification is provided by a continuous line of $Z14$ atoms. In topological principle, such a line could close on itself; but with the requirement that in this case the pairs of ligands at each atom are at least approximately in line with each other, this closure could only be effected in a very large circuit, requiring a structure with a very large unit cell. We believe without formal proof, that the principle of layering to be developed below excludes the possibility of this kind of closure.

In the next degree of ramification, we have infinite planar networks in the major skeleton, made up of $Z15$ atoms with or without $Z14$ atoms. In the absence of large distortions the meshes of such a network will be topologically hexagons. Atoms of the same coordination numbers could also make three-dimensional networks in the major skeleton. Three-dimensional networks naturally result when $Z16$ atoms are present, from the tetrahedral disposition of the major ligands from these sites.

A full range of examples will be given later, but by way of illustration of characteristic major skeletons we may mention at this stage three examples. In the β-tungsten structure the major skeleton consists solely of 14-coordination rows, parallel to each of the cube axes. In σ-phase it comprises 14-coordination rows parallel to the tetragonal axis threading planar networks of $Z15$ and $Z14$ atoms which lie parallel to the base plane. In the Laves phases the major skeleton is a diamond-like structure of $Z16$ atoms.

The major skeleton will as a rule define uniquely, apart from small displacements and distortions, the corresponding complete structure, if there is one at all. Around every major ligand there is a *corollary* ring of 6 atoms. Any of these may be minor or major sites. (It is important to notice that since a major ligand is defined as the line joining two sites which have 6 neighbours in common, not every line joining a neighbouring pair of major sites is a major ligand.) Along a sequence of 14-coordinated atoms the successive corollary rings are in anti-prism position with respect to each other, so that the row and its corollaries form a column three atoms thick. Fixing any one of the corollary atoms substantially fixes all atoms in its ring and in neighbour rings. If any of the corollary sites is major, it belongs to the major skeleton, and its position is already fixed, by hypothesis. There is no freedom of choice for corollary positions around $Z15$ or $Z16$ sites. Hence freedom can only exist for the corollary positions around long $Z14$ sequences, and then only when these corollary positions are all minor. If such cases exist, it is still likely that simple considerations of packing compatibility will suffice to show that there is essentially but one choice of positions, if any.

Paradoxically, the major ligands (though the name is not ill-chosen, because they connect sites of larger coordination number, mainly suited for larger atoms) may nevertheless be shorter ligands than the average. In cases of 14 and 15 coordination the atoms of the major skeleton are in relatively close contact one with another. This, together with the geometrical rules governing the major skeleton structure, can be suggestive of covalent bonding. Our argument is ambivalent with respect to the question of whether this is chemically significant. Packing considerations alone suffice to account for the system of pseudo-valences observed in the major skeleton. On the other hand a covalent bonding tendency compatible with this system could be a factor contributing to the stability of the structure adopted.

3·2. *Layering in structures with normal coordinations*

Consider a triangle of contiguous atoms $A_0B_0C_0$ belonging to a structure in which all coordinations are normal. These require the presence of a pair of atoms D_+, D_- above and below points near the centre of the triangle (Fig. 3). We use the suffixes + and − to denote positions above and below the plane $A_0B_0C_0$, and zero to denote a position which is at least approximately in this plane. Of the ligands AB, BC, CA, at most one can be major, since major ligands at one atom do not make acute angles with each other. Thus there are two possibilities:

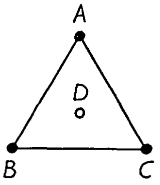


Fig. 3.

(i) All are minor. Then there exist pairs E_+, E_-; F_+, F_-; G_+, G_- above and below points outside the edges AB, BC, CA. Then, to complete the tetrahedron with $A_0E_+E_-$ there must exist an atom at H_0, and correspondingly atoms at I_0, J_0, K_0, L_0, M_0, at least approximately coplanar with ABC (Fig. 4(*a*)).

(ii) One edge, say AB, is major. Then, beyond E there is an atom H_0, placed essentially symmetrically to C with respect to AB. There are also atoms at J_0, K_0, L_0, M_0 as before, and the presence of further atoms at N_0, P_0, symmetrical to L_0, K_0 with AB, follows from the equivalence of the triangles ABC and ABH (Fig. 4(*b*)).

In either case new triangles of contiguous atoms, at least approximately coplanar with the original triangle, have been established, and continuance of the argument with reference to these triangles requires the existence in either case of an unlimited network of at least approximately coplanar contiguous atoms. The angles between ligands in this network are either approximately 60° or approximately 120°, so that the simplest continuation of either is in the form of tessellations of hexagons and triangulations. However, the mode of continuation is not uniquely defined: for one reason because of the alternative modes of connection indicated by Fig. 4(*a*) and 4(*b*); for another, because permissible distortions may allow the substitution of pentagons for hexagons in the pattern (an angle approximately 120° may also be approximately 108°).

Let us now apply similar considerations to a coplanar contiguous hexagon of atoms $A_0B_0C_0D_0E_0F_0$ around a major ligand G_+G_- (Fig. 5). If AB is a minor ligand then beyond AB there is an external atom H_0 essentially in the plane of the hexagon. There must be further coplanar atoms associated with the triangle

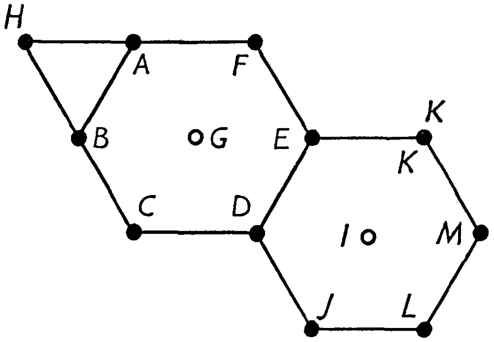
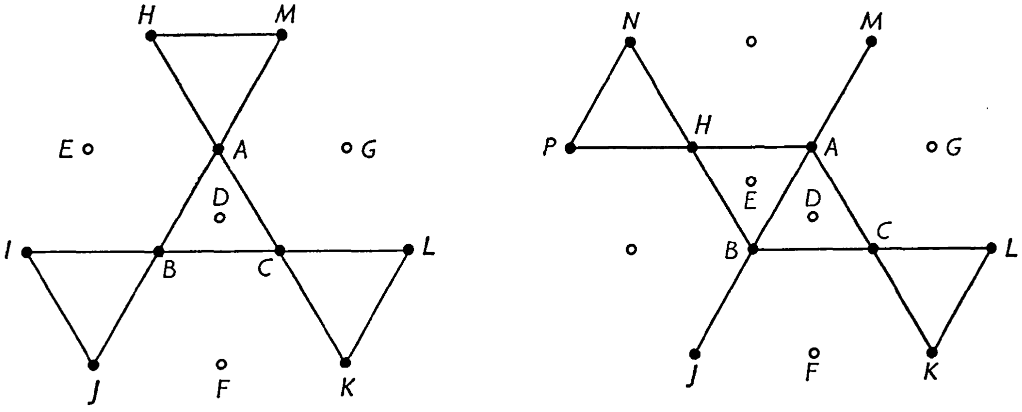


Fig. 5.



(*a*) (*b*)

Fig. 4.

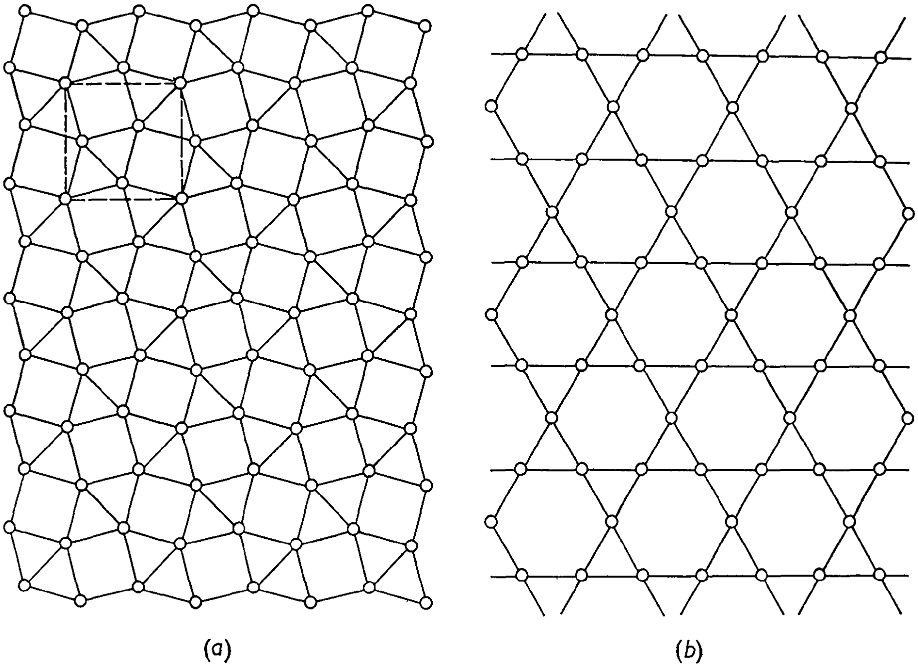


Fig. 6. The two basic nets occurring frequently in complex alloy structures: (a) $3^2, 4, 3, 4$ net; (b) Kagomé net 3, 6, 3, 6. The numerical symbols are Schlafli symbols (Cundy & Rollett, 1952), specifying the number and sequence of various polygons around each vertex.

$A_0B_0H_0$. If DE is a major ligand, then there is an external pair I_+, I_- making a tetrahedron with D and E, and completion of the second tetrahedra on DI_+I_- and EI_+I_- requires atoms J_0, K_0 essentially in the plane of the hexagon. Completion of the second tetrahedra on JI_+I_- and KI_+I_- requires further atoms L_0, M_0, but it is a possibility to be considered that these are coincident, so that $DJ(LM)KE$ is a pentagon instead of a hexagon. Continuation of the argument requires the existence of further at least approximately coplanar atoms, again without limit.

The patterns of the coplanar arrays derived from the hexagon are similar to those derived from the triangle, except that they include a tesselation consisting exclusively of hexagons.

Starting with the coplanar pentagon around a minor ligand, we may argue exactly as for the hexagon.

The *repeated* arguments employed here should be regarded as having permissive rather than compelling force: because a single application of the argument is satisfied by approximate as well as by exact coplanarity, and successive approximations may depart further from the plane. Nevertheless, they give a strong indication that structures containing exclusively 'normal coordinations' will be 'layer structures' having unlimited coplanar or approximately coplanar arrays of neighbouring atoms (each being a neighbour of at least three others in the same plane or approximate plane): and that the patterns in these arrays will correspond to tessellations of triangles, hexagons, and pentagons. Such a layer, wherein the connections correspond to interatomic distances, we shall call a *primary layer*. It is also to be noticed that the atoms above and below the planes of the layers so defined, likewise, in the examples considered, fall into layer arrangements satisfying similar rules of construction. While this point has not been investigated fully enough in the foregoing section, it may be stated as a result that this second type of layer in all known or predicted structures with normal coordination consists of tessellations of squares and triangles. This type of layer we shall designate as a *secondary layer*. In Fig. 6, there is shown an especially prominent example of each kind of layer, Fig. 6(*a*) for a secondary and Fig. 6(*b*) for a primary layer. These two examples are among the simplest of semi-regular tessellations.

The stacking compatibility of layers will be better considered in the subsequent detailed discussion of various structure types.

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