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Coordination Formulation of Tetrahedrally Close Packed Structures: An Addendum to the Observations of Yarmolyuk and Kripyakevich*

E. HELLNER

Institute for Mineralogy, Philipps-University, Marburg, Federal Republic of Germany

AND W. B. PEARSON

Departments of Physics and Chemistry, University of Waterloo, Waterloo, Ontario, Canada

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Ya. P. Yarmolyuk and P. I. Kripyakevich (*Kristallographiya* **19**, 539 (1974)) showed that all tetrahedrally close packed (t.c.p.) structures have coordination formulae $P_pQ_qR_rX_x \rightarrow (PX_2)_i(Q_2R_2X_3)_j(R_3X)_k$, where P, Q, R, and X represent coordination numbers (CN) 16, 15, 14, and 12 polyhedra respectively: p, q, r, and x indicate the numbers of such polyhedra in the unit cells of t.c.p. structures and i, j, and k are positive integers. We propose and demonstrate a limitation to the above formulation: if $i \geq 1$ and $k \geq 1$, then $j \geq 1$ (or if both $p > 0$ and $r > 0$, then $q > 0$). We give reasons for this and discuss the *Aufbauprinzip* of t.c.p. structures and the results of C. B. Shoemaker and D. P. Shoemaker (*Acta Crystallogr. B* **42**, 3 (1986)).

Introduction

Introductions describing the characteristics and geometrical properties of tetrahedrally close packed (t.c.p.) structures, the atoms in which are surrounded by coordination number (CN) 16, 15, 14, or 12 (icosahedron) polyhedra with triangulated surfaces (*1*, *2*), are now so numerous that we should not here indulge the situation further; particularly recommended is that of Shoemaker and Shoemaker (*3*) (hereinafter referred to as S&S) which also gives reference to any crystal structure types referred to here. This S&S paper deals with the finding by Yarmolyuk and Kripyakevich (*4*) (hereinafter referred to as Y&K) that the coordination formula of all known t.c.p. structure types can be written as

$$P_pQ_qR_rX_x \rightarrow (PX_2)_i(Q_2R_2X_3)_j(R_3X)_k, \quad (1)$$

where P, Q, R, and X indicate CN 16, 15, 14, and 12 polyhedra respectively, p, q, r, and x indicate the number of such polyhedra in the unit cells of known t.c.p. structures, and i, j, and k are positive integers (or simple rational fractions). This formulation was found by Y&K to apply to all 16 t.c.p. structures known in 1974 and S&S show that also it applies to the structures of four t.c.p. phases subsequently discovered, and thus it has predictive value. In particular if

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the numbers p, q, and r of atoms surrounded by CN 16, 15, and 14 polyhedra in a t.c.p. structure are known, the number of icosahedrally surrounded atoms in the structure is determined (relationship (1) and S&S eq. (3)).

The rearrangement on the right-hand side of (1) is interesting since the three formulae composing it are those for which i, j, and k are severally one and the remaining subscripts, respectively, j and k, i and k, and i and j are zero. PX_2 is the $MgCu_2$ or $MgZn_2$ structure ($i = 1, j = k = 0$). In $MgCu_2$, the point symmetry of the P atoms on 8(a) of $Fd\bar{3}m$ is $\bar{4}3m$ and they form a D lattice complex and framework (5). Each P atom is at the center of a CN 16 polyhedron composed of 12 X atoms and 4 P atoms. The P–P connections thus form the D framework of major bonds in the structure. Major bonds are the connections between atoms of CN 16, 15, and 14 polyhedra that have a surface coordination number (SCN) of 6. Since the coordination polyhedra of t.c.p. structures are interpenetrating, the central atoms of these polyhedra are part of major-bond arrays. R_3X is the Cr_3Si type of structure ($k = 1, i = j = 0$). The point symmetry of the R atoms on 6(c) of $Pm\bar{3}n$ is $\bar{4}m2$ and they form a W lattice complex. Each R atom is located at the center of a CN 14 polyhedron composed of 4X, 8R, and two close R atoms that are collinear with the central atom and form the major bonds of the polyhedron. $Q_2R_2X_3$ is the Zr_4Al_3 type of structure ($j = 1, i = k = 0$). The array of major bonds about the atom at the centers of the CN 15 polyhedra is a 6^3 graphite-type (G) framework in (001) planes which has interpenetrating rods (L) of major bonds running normal to the G framework through the centers of the hexagons and joining together atoms that center the CN 14 polyhedra.

Thus the arrays of major bonds in the structures of t.c.p. phases have D, W, or [$G + L$] frameworks or are made up of portions of these frameworks about the atoms that center the CN 16, 15, and/or 14 polyhedra. Thus, for example, in the P phase structure ($i = j = k = 1$), four of the atoms comprising the CN 16 polyhedron, together with the atom that centers it, form a portion of the D framework. Three of the atoms comprising the CN 15 polyhedron together with the atom that centers it comprise a portion of the G framework. Ten atoms in the vicinity of the atom that centers each of the CN 14 polyhedra form a portion of the W framework. The appropriate bonds between these 11 atoms are all major bonds for the CN 14 polyhedra arising from $k = 1$, but they are not all major bonds for the CN 14 polyhedra arising from $j = 1$.

The object of this paper is to show that both Y&K and S&S have missed what appears to be a further condition to the formulation (1)—that t.c.p. structures cannot be made up of arrays of major bonds that contain elements of D and W frameworks alone; that is to say, if both i and $k > 1$, j cannot be zero.

S&S observed that Y&K gave no fundamental explanation of the existence of formulation (1), and applied their considerations thereto. We quote the following paragraph from the S&S paper since it succinctly expresses the problem that they have so elegantly solved wherein a requirement on the average dihedral angles (*vide infra*) permits, with suitable adjustments, the precise calculation of the number of icosahedrally surrounded atoms in the unit cells of t.c.p. structures—or indeed accounts for the information in the Y&K coordination formulation.

> We have looked for a long time without success for some explanation of the Y&K principle in geometrical properties such as those of the major networks of the t.c.p. structures. However, while the major networks by themselves define the numbers of

P, Q, and/or R atoms present, they present no clear indication of the relative numbers of X atoms needed to complete the structure, unless each structure is drawn out in detail. In other words, they do not contain the information given in Eq. (3) [$x = 2p + 7q/6 + r/3$, $q \leq r$]. In this paper we will show that this additional information, and thus an explanation of the Y&K principle, is provided by a requirement on the average dihedral angles between faces of the interstitial tetrahedra meeting at an edge, or atom–atom "bond"; we call this requirement the "dihedral angle principle."

Discussion

We maintain that there is a further condition—not yet stated—to the Y&K formulation, $(PX_2)_i(Q_2R_2X_3)_j(R_3X)_k$ ((1) above), that if both i and $k \geq 1$ then also $j \geq 1$ (i.e., then j cannot be zero). This also indicates that if both $p > 0$ and $r > 0$, then $q > 0$ because of relationship (1) above, as S&S point out in private communication. Thus this limitation involves only the CN 16, 15, and 14 polyhedra, or the arrays of major bonds, since the CN 12 icosahedron does not give rise to any major bonds. The specifications of this postulate are consistent with the data presented by S&S for the 20 known t.c.p. structures in their Table 4.

Any t.c.p. crystal structure made up of CN 16, 14, and 12 (P, R, and X) polyhedra only (i.e., with $i \geq 1$, $k \geq 1$, and $j = 0$) must contain, no matter what the structural arrangement, CN 16 polyhedra fused to other CN 16 polyhedra via lines of 1, 2, 3, 4, . . . , CN 14 polyhedra unless possibly a t.c.p. structure can be created with interpenetrating *D* and *W* frameworks. Thus there are three distinct methods by which t.c.p. structures might be generated that contain only CN 16, 14, and 12 polyhedra: (i) They might be generated by interpenetrating *D* and *W* frameworks. (ii) They might be generated by separating centered CN 16 polyhedra (as in the $MgCu_2$ structure) by a single line of fused centered CN 14 polyhedra, P–R–P, P–R–R–P, P–R–R–R–P, etc., lying in a plane and running parallel to each other as in the μ phase structure (Fig. 1), or not all parallel to each other as in the M phase structure. (iii) They might be generated by fusing 2, 3, or 4 hexagonal anti-prisms to each centered CN 16 polyhedra. In such a structure the CN 16 polyhedra fused to the other side of the CN 14 polyhedra (or lines thereof) can

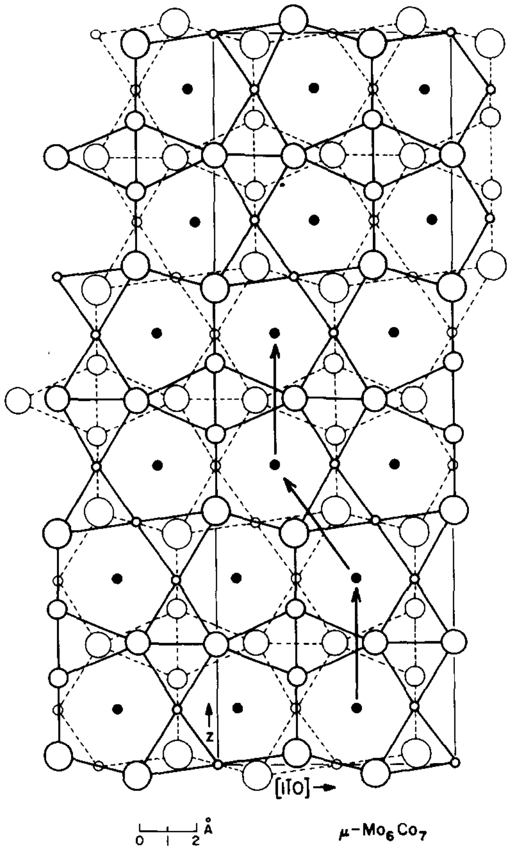

FIG. 1. Diagram of the μ phase structure of Mo_6Co_7 projected onto (110) of the hexagonal cell (after (7)). The circles indicate, in decreasing order of size, atoms with CN 16, 15, 14, and 12.

have several different orientations 60° apart as permitted by the hexagons to which they are fused.

Space group–subgroup relations between $Pm\bar{3}n$ and $Fd\bar{3}m$ (*6*) show that a structure containing both D and W lattice complexes can only be described in $P2_13$ (or $F23$ with greater multiplicity) or subgroups in the lower classes derived therefrom. Such a structure (Table I) is of eighth order in W; indeed it is a defect superstructure of Cr_3Si with half of the eighth-order I_{222} atoms omitted to give a D lattice complex. However, it is not a t.c.p. structure since the CN of the atoms of the W framework is no longer 14 owing to absence of half of the I_{222} atoms and since, the D–D distances are so large that the D array is not a framework but only a lattice complex. Therefore an atom on a D site is surrounded by an icosahedron, not a CN 16 polyhedron.

Similar arguments apply when other cubic space groups $P\bar{4}3n$ and $P4_232$, in which W lattice complexes occur, and $F4_132$ and $Fd\bar{3}$, in which D lattice complexes occur are considered, since they lie in the chain of space group–subgroup relationships between $Pm\bar{3}n$ and $Fd\bar{3}m$ that lead to $P2_13$ and/or $F23$. Thus it appears that it is not possible to create a t.c.p. structure containing only CN 16, 14, and 12 polyhedra on the basis of interpenetrating D and W lattice complexes or frameworks.

Next we consider the essential component of any t.c.p. structure that could contain CN 16, 14, and 12 polyhedra only ($i \geq 1$, $k \geq 1$, $j = 0$), no matter what the arrangement—the joining together of CN 16 polyhedra via CN 14 polyhedra.

TABLE I

IDEAL COORDINATES AND LATTICE COMPLEXES OF A STRUCTURE DESCRIBED IN POSITIONS $4(a)$ x,x,x AND $12(b)$ x,y,z OF $P2_13$

$$\begin{tikzcd}
D & = & & F & & + & & F'' & \\
& & & 4(a)\,000 & & & & 4(a)\,\tfrac{1}{4}\tfrac{1}{4}\tfrac{1}{4} & \\
W_{222} & = & & S^{*}_{(\bar{4})} \arrow[dl] \arrow[dr] & & + & & V^{*}_{222} \arrow[dl] \arrow[dr] & \\
& & S & & {}'S & & {}^{+}V & & {}^{-}V \\
& & 12(b)\,\tfrac{3}{8}0\tfrac{1}{4} & & 12(b)\,\tfrac{7}{8}0\tfrac{1}{4} & & 12(b)\,\tfrac{1}{8}0\tfrac{1}{4} & & 12(b)\,\tfrac{5}{8}0\tfrac{1}{4}
\end{tikzcd}$$

It can be shown in structures which contain a single line of CN 14 polyhedra fused to each CN 16 polyhedron either that the atoms centering the CN 14 polyhedra are not surrounded by 10 atoms that form a portion of the W framework in which the bonds are *all major bonds* or that some but not all of them are. Also it is found that polyhedra other than CN 16, 14, and 12 occur in these structures. Thus in a structure so constructed with P–R–P links, CN 11 polyhedra occur. In a structure such as that of the μ phase (Fig. 1) although the central atoms of the CN 14 polyhedra are surrounded by 10 atoms on the sites of a portion of the W framework, the bonds running between the pairs in the [110] direction of the hexagonal cell of the μ phase structure are not major-bond arrays (Fig. 1). Concomitantly it is seen that the structural arrangement has introduced atoms with CN 15. Therefore the CN 14 polyhedra arise from $(Q_2R_2X_3)_j$ and not from $(R_3X)_k$, i.e., $j \neq$; 0 indeed for the μ phase structure $i = 1, j = 1, k = 0$. Similarly in the P–R–R–P arrangement of the M phase, atoms with CN 15 are introduced. The CN 14 atoms are surrounded by 10 atoms in the arrangement of a portion of the W framework but the appropriate bond arrays between them are not all major bonds. Such observations are consistent with $i = 2, j = 1, k = 0$ of the M phase structure.

Also it is seen that structures containing longer strings of CN 14 polyhedra running parallel, e.g., P–R–R–R–P and P–R–R–R–R–P, do not satisfy the conditions of $i \geq 1$, $k \geq 1$, $j = 0$ for a t.c.p. structure or indeed give t.c.p. structures. Structures created on these two bases contain respectively also CN 13, and CN 11 and 13 polyhedra.

Thus it is well demonstrated that t.c.p. structures with $i \geq 1$, $k \geq 1$, and $j = 0$

cannot be generated on the basis of centered CN 16 polyhedra linked to other centered CN 16 polyhedra by single strings of centered CN 14 polyhedra, whether or not such strings lie in directions parallel to each other.

The remaining case to consider is a structure composed only of CN 16, 14, and 12 polyhedra in which a centered CN 16 polyhedron is fused to two, three, or four centered hexagonal anti-prisms, which separate it from other CN 16 polyhedra. For example, surround a centered CN 16 polyhedron with four fused centered hexagonal anti-prisms that are fused to further centered CN 16 polyhedra on their opposite hexagonal faces. Orient this assembly so that two of the arrays of P–R–P major bonds from the centered CN 16 polyhedron lie in the plane considered as in Fig. 2. Now consider the CN 14 polyhedron that lies below this plane. The 16 coordination of the central polyhedron (Fig. 2) predicates that the central atom of this CN 14 polyhedron has 10 neighbors, but their distribution, even if the final structural arrangement results in CN 14, cannot be consistent with a portion of the *W* framework. For example, the pairs of atoms vertical to the plane of Fig. 2 are not orthogonal to the major-bond array of P–R–P; second, the bonds joining the pairs of atoms are not major bonds. This fact is independent of the orientation of the CN 16 polyhedron on the other side of the CN 14 polyhedron considered, and indeed of the structural arrangement generally. This argument also applies to a centered CN 16 polyhedron with only two, or only three centered CN 14 polyhedra fused to it.

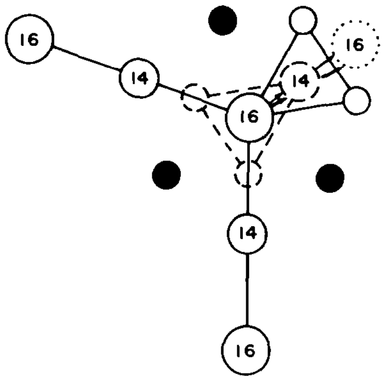

FIG. 2. Diagram of an atom with CN 16 surrounded by four atoms that may have CN 14 (fusion of four centered hexagonal anti-prisms to a centered truncated tetrahedron). Circles in decreasing size represent atoms with CN 16, 14, and 12, respectively. Solid lines represent bonds and atoms lying in the plane of the paper; broken lines represent atoms and bonds lying in planes a distance *d* above and below; and dotted lines represent atoms lying a distance 2*d* above and below. Filled-in circles represent atoms lying $\frac{1}{2}d$ above and below the plane of the paper.

Thus, in summary, it appears that any crystal structure that contains interpenetrating *D* and *W* lattice complexes or frameworks cannot be a t.c.p. structure. Second, since the conditions $i \geq 1$, $k \geq 1$, and $j = 0$ predicate a t.c.p. structure that contains only CN 16, 14, and 12 polyhedra and in any such structure fusions of CN 16 and 14 polyhedra must occur, we have now shown by considering examples of all possible cases of such fusion that these conditions cannot be met in a t.c.p. structure. In such structures as might be formed, polyhedra with coordination numbers other than 16, 14, and 12 are introduced and/or all atoms centering the CN 16 and 14 polyhedra are not surrounded by portions of *D* and *W* frameworks, respectively, that are major-bond arrays.

We can give some explanation of the necessity for CN 15 polyhedra in a t.c.p. structure that otherwise contains CN 16 and 14 polyhedra (i.e., why the conditions $i \geq 1$, $k \geq 1$, and $j = 0$ are impossible in a t.c.p. structure). The Cr_3Si structure (R_3X) involves $3^26^2 + 3636$ (2 : 1) main layers (i.e., with hexagons) with 4^4 secondary layers of atoms, whereas the $MgCu_2$ structure (PX_2) involves $3535 + 35^3$ (2 : 3) main layers (i.e., with pentagons) with 3^6 secondary layers. There is no crystallographic means of joining portions of these without involving portions of Zr_4Al_3 arrangement ($Q_2R_2X_3$). The reason portions of Zr_4Al_3 structure can effect this union appears to lie in the duality of description of this structure. It can be described either in terms of pentagon–triangle main layers of atoms lying in (110) planes, $53^253 + 5^23^2 + 5353$ (2 : 2 : 1), which are separated by 4^4 secondary nets of atoms (Fig. 3), or in terms of hexagon–triangle, 3636, and hexagon, 6^3 (G), main layers of atoms lying in (001) planes, which are separated by 3^6 secondary nets of atoms (Fig. 4).

Zr_4Al_3 ($Q_2R_2X_3$) units make use of this dual-orientation facility of being able to present either pentagon or hexagon layers in uniting pentagon-layer units of PX_2 with a hexagon-layer units of R_3X. For example, in the P phase structure $((PX_2)_1(Q_2R_2X_3)_1(R_3X)_1$ projected onto (001), one sees CN 15 polyhedra both in the orientation of Zr_4Al_3 projected onto (110) (pentagon layers, Fig. 3) and in the orientation projected onto (001) (hexagon layers, Fig. 4). On the other hand the M phase structure $((PX_2)_2(Q_2R_2X_3)_1)$, the main layers of which lie in (001) planes and contain only pentagons, has CN 15 polyhedra in relation to M (001) only in the orientation of Zr_4Al_3 projected onto (110) (pentagon layers). The σ phase structure $((Q_2R_2X_3)_1(R_3X)_2)$, the main layers of which lie in (001) planes and contain only hexagons, has CN 15 polyhedra in relation to σ (001) only in the orientation of Zr_4Al_3 projected onto (001) (hexagon layers).

Conclusions

The fundamental geometrical property of t.c.p. structures is the interpenetration of the centered CN 16, 15, 14, and 12 polyhedra which have respectively four, three, two, and zero atoms with SCN 6. This

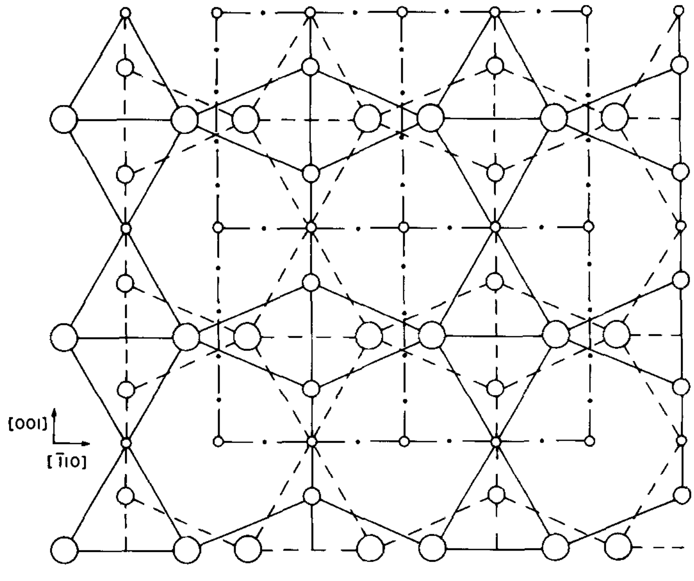

FIG. 3. Diagram of the structure of Zr_4Al_3 projected onto (110). Solid lines represent $53^253 + 5^23^2 + 5353$ (2 : 2 : 1) nets at $x = y = 1.0$; dash-dot represent 4^4 nets at $x = \frac{1}{2}$, $y = \frac{1}{2}$; and broken lines represent $53^253 + 5^23^2 + 5353$ (2 : 2 : 1) nets at $x = 0$, $y = 0$. Circles indicate, in decreasing order of size, CN 15, 14, and 12.

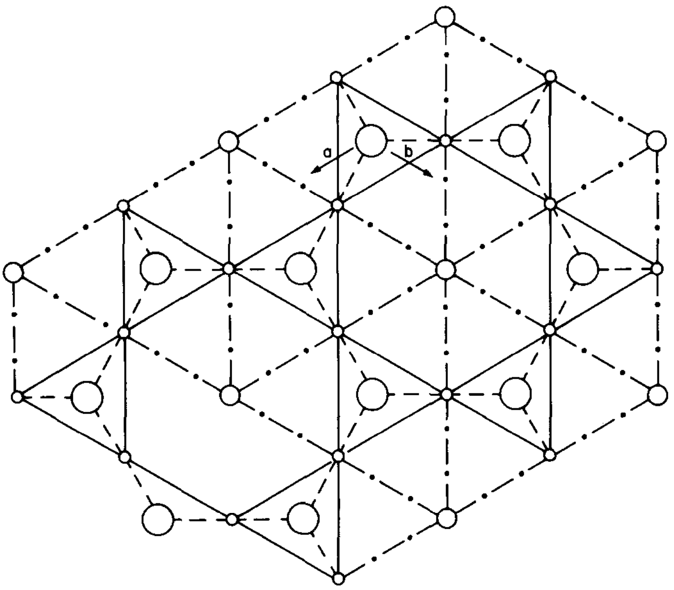

FIG. 4. Diagram of the structure of Zr_4Al_3 projected on to (001). Solid lines represent 3636 nets at $z = 0$; dash-dot lines represent 3^6 nets at $z = \frac{1}{4}, \frac{3}{4}$; and broken lines represent 6^3 nets at $z = \frac{1}{2}$. Circles indicate, in decreasing order of size, CN 15, 14, and 12.

requires fusion of the hexagons of the truncated tetrahedra, truncated trigonal prisms, and hexagonal anti-prisms of the CN 16, 15, and 14 polyhedra, respectively. The way in which this occurs in any particular t.c.p. structure is defined by the array of major bonds that run between polyhedra atoms with SCN 6. As the icosahedron does not have any atoms with SCN 6, it can fuse to any CN 16, 15, and 14 polyhedra on the pentagonal face surrounding any atom with SCN 5—and without other orientation restrictions. Thus the relative arrangement of the CN 16, 15, and 14 polyhedra in the structures must control the structural arrangement and the role of the CN 12 polyhedra is that of a filler. Therefore the arrays of major bonds must be the controlling feature in the *Aufbauprinzip* of these structures and responsible for the Y&K formulation. Since the CN 12 icosahedra do not contain major bonds, they are not essential to the *Aufbauprinzip* and hence the missing information concerning them, referred to in the S&S quotation above. Nevertheless there must still be some feature that controls the number of icosahedra that might be part of a crystallographic arrangement of CN 16, 15, and/or 14 polyhedra, and this is the dihedral angle principle as demonstrated by S&S. Thus it is our opinion that the arrays of major bonds in t.c.p. structures provide their *Aufbauprinzip* and the dihedral angle principle of S&S in a consequence thereof that specifies the number of CN 12 icosahedra required to complete the crystal structure.

The restriction on the Y&K formulation that we have proposed and demonstrated in terms of the portions of major-bond arrays that surround the central atom of CN 16 and 14 polyhedra of PX_2 and R_3X structures is an example of the operation of the major-bond *Aufbauprinzip* that prevents the condition $i \geq 1$, $k \geq 1$, and $j = 0$ in t.c.p. structures. It does not appear necessary to apply to the dihedral angle principle to account for it, whereas consideration of major-bond arrays is essential to it. This view of the significance of major-bond connections appears to be compatible with a broader picture of the significance of major-bond arrays in crystal structures that is developing in relation to physical properties such as magnetism and superconductivity and crystal geometry generally (cf., e.g., Bennett *et al.* (*8*); Bennett and Watson (*9*)).

Acknowledgments

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