Since diffuse intensity distributions calculated for the models with $s = 1$, where s is the number of layer units necessary to distinguish the stacking disorder, did not resemble the broad maxima observed in Fig. 1, the various models with $s = 2$ were calculated. The results for the model of Table 1 were in agreement with the observed diffuse maxima, as shown in Fig. 4.

In the model of Table 1, the sequences such as $Q1$-$P1$-$Q1$, in which the second-neighbor layers are the same, do not occur, and $Q1$-$P1$-$Q2$ and $Q1$-$P1$-$Q3$ occur with the same probability and so on. The distance between the ordered Ti sites which belong respectively to the second-neighbor layers are shorter for $Q1$-$P1$-$Q1$ than for $Q1$-$P1$-$Q2$ or $Q1$-$P1$-$Q3$ and so on. The calculated results excluded sequences such as $Q1$-$P1$-$Q1$, $Q1$-$P2$-$Q1$, $Q1$-$P3$-$Q1$, $Q2$-$P1$-$Q2$ *etc.* This fact is reasonable with respect to the Coulomb interaction between Ti atoms and vacancies.

The diffuse streaks have not yet been detected in X-ray photographs. The calculated intensities shown in Fig. 4 are the results of kinematical scattering theory. On the assumption that the geometry of the diffuse maxima is not affected by dynamical interactions, the model of Table 1 gives an explanation for the diffuse maxima observed. The designation $\mathrm{Ti}_{1\cdot43}\mathrm{S}_2$-$4H$-$H\sqrt{3}a\sqrt{3}a$(SRO) is adopted for the structure discussed above, according to the notation system for polytypes and superstructures described previously (Onoda & Saeki, 1983).

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Concerning the Relative Numbers of Atomic Coordination Types in Tetrahedrally Close Packed Metal Structures

BY DAVID P. SHOEMAKER AND CLARA BRINK SHOEMAKER

Department of Chemistry, Oregon State University, Corvallis, Oregon 97331, *USA*

(*Received* 24 *June* 1985; *accepted* 20 *September* 1985)

Abstract

Tetrahedrally close packed (t.c.p.) metal or alloy crystal structure types are those in which the interstices are exclusively tetrahedral and the coordination types are restricted to a particular set of four, which are here called P, Q, R, and X, with fully triangulated coordination polyhedra and coordination numbers (CN) respectively 16, 15, 14, and 12. At least 20 of these are known. Yarmolyuk & Kripyakevich [*Kristallografiya* (1974), **19**, 539-545; *Sov. Phys. Crystallogr.* **19**, 334-337] have shown empirically that the coordination formula of a t.c.p. structure, which may be represented in general as $P_pQ_qR_rX_x$, can be reformulated as $(PX_2)_i(Q_2R_2X_3)_j(R_3X)_k$ (where i, j, k are integers or rational fractions) in the cases of all of the 16 t.c.p. structure types then known. This has also proved true for the four structure types discovered since. It is shown that the relationship results from the requirement that the structure average of the dihedral angles in the interstitial tetrahedra must closely match the appropriately weighted average of the up to four 'cluster' average dihedral angles, where a cluster is defined as an atom plus the 16, 15, 14, or 12 atoms of its coordination shell, and the associated 28, 26, 24, or 20 tetrahedra, respectively, coming together at the central atom. These cluster averages are themselves within about 0·1° of the dihedral angle in the regular tetrahedron, 70·529°. Given the integers p, q, and r for a t.c.p. formula, with this model x can be calculated correctly for all 20 known t.c.p. structures (although x covers a wide range, up to 49), without any assumptions from Yarmolyuk & Kripyakevich being invoked. A related problem, concerning the close packing of atoms in amorphous metallic glasses, has been treated by some workers in relation to the $\{3, 3, 5\}$ regular polytope in four-dimensional space. We conclude that while such treatments may provide useful insights for t.c.p. structures, they do not yet satisfactorily explain the Yarmolyuk & Kripyakevich observation.

0108-7681/86/010003-09$01.50

Introduction

The family of crystalline intermetallic phases characterized as tetrahedrally close packed (t.c.p.) contains at least 20 structure types having in common the following properties: (1) the interstices are exclusively tetrahedral (the tetrahedra with atomic centers as vertices being only moderately distorted, with ratios of longest to shortest edges not exceeding about 4/3); and (2) the coordination types are limited to a particular set of four, which we here call P, Q, R, and X, with triangulated coordination polyhedra and coordination numbers (CN) of 16, 15, 14, and 12 (icosahedral) respectively. These coordination types are present in various combinations in the different t.c.p. structure types; only CN12 is present in every t.c.p. structure type, although CN12 cannot exist alone; it is well known that no structure can exist in Euclidean space in which all atoms are icosahedrally coordinated. The t.c.p. structure types are exemplified by the Friauf-Laves phases, the β-tungsten or Cr_3Si structure, Zr_4Al_3, and the phases designated by the letters σ, μ, P, R, *etc.* A list of all t.c.p. structures known to us, except polytypes of known structures, is given in Table 4.

The 'empirical coordination formula' of a t.c.p. structure type may be represented in general as $P_pQ_qR_rX_x$. The values of p, q, r, and x are not all arbitrary or independent; a particular restriction on them is the subject of this paper.

The role of the four above-mentioned coordination types was first recognized independently by Kasper (1956) and by Shoemaker, Shoemaker & Wilson (1957); geometry and bonding in t.c.p. structures has been described by Frank & Kasper (1958, 1959), by Shoemaker & Shoemaker (1964, 1972), and by Pearson & Shoemaker (1969). Reviews concerning the t.c.p. family of structures have been presented by Shoemaker & Shoemaker (1968, 1969, 1971*a*). A feature of the coordination types that will figure prominently in the present discussion is the presence of two different types of interatomic contacts (which for simplicity we here call 'bonds'), pointed out by Frank & Kasper (1959): sixfold or 'major' bonds, at which six interstitial tetrahedra come together, and fivefold or 'minor' bonds, at which five interstitial tetrahedra come together; these correspond to sixfold and fivefold vertices on the corresponding coordination polyhedra. The four coordination polyhedra are shown in Fig. 1, and the relevant properties of the four coordination types are summarized in Table 1. The 'major bonds' link together to form what Frank & Kasper termed the 'major network' of a structure.

Yarmolyuk & Kripyakevich (1974), hereinafter designated as Y & K, observed that for every one of the 16 then known t.c.p. structure types the empirical coordination formula can be recast in the form

$$P_pQ_qR_rX_x \rightarrow (PX_2)_i(Q_2R_2X_3)_j(R_3X)_k. \qquad (1)$$

Table 1. *T.c.p. coordination polyhedra*

Type	Ideal point symmetry	No. of vertices 5-fold	No. of vertices 6-fold	No. of faces[c]
P CN16	T_d-$\bar{4}3m$	12	4[b]	28
Q CN15	D_{3h}-$\bar{6}m2$	12	3[b]	26
R CN14	D_{6d}-$\overline{12}.2.m$	12	2[b]	24
X CN12[a]	I_h-$\bar{5}\bar{3}2/m$	12	0	20

Notes: (*a*) Regular, or approximately regular, icosahedron. (*b*) Respectively disposed tetrahedrally, trigonally in plane, and digonally on axis, with respect to the center of the polyhedron. (*c*) Also equal to the number of interstitial tetrahedra defined by the vertices of the faces and the center of the polyhedron.

Here i, j, and k are integers or simple rational fractions for crystalline structure types, and PX_2, $Q_2R_2X_3$, and R_3X are the respective formulae of the Friauf-Laves phases [*e.g.* C15-$MgCu_2$ (Friauf, 1927*b*; Laves & Witte, 1935)], the Z phase [a designation we use here for Zr_4Al_3 (Wilson, Thomas & Spooner, 1960)], and the 'A15' structure type of so-called β-tungsten (Hägg & Schönberg, 1954) and Cr_3Si (Borén, 1933). We will refer to these henceforth as the three 'base' structure types. [The Friauf-Laves phase C14-$MgZn_2$ (Friauf, 1927*a*; Laves & Witte, 1935) behaves in our treatment in this paper exactly like C15-$MgCu_2$ when the axial ratio and positional parameters have their ideal values, and will not be mentioned specifically again except in Table 4.] Y & K gave examples of how some complex structures can be built up of fragments of the three base structure types, but recognized that 'the most complex structure types are not obliged to be combinations of the corresponding fragments'.

That the observation of Y & K has predictive power is illustrated by the fact that the four structure types known to us that have been determined since the

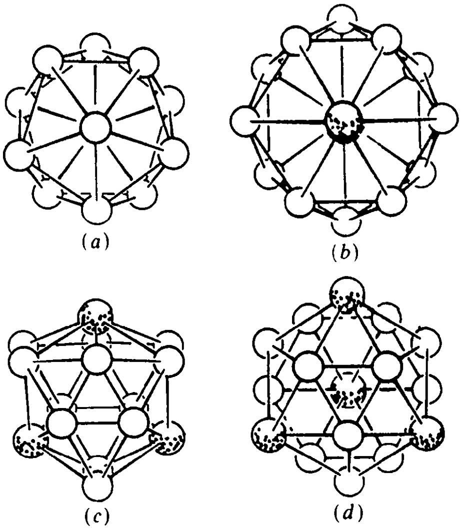

Fig. 1. Coordination polyhedra for (*a*) CN12, (*b*) CN14, (*c*) CN15, (*d*) CN16. Central atom is not shown in each case. Atoms connected to central atoms by major bonds are stippled. Adapted from Pearson (1972).

publication of the Y & K paper also fit equation (1); these are the K phase $Mn_{77}Fe_4Si_{19}$ (Shoemaker & Shoemaker, 1977), the I phase $V_{41}Ni_{36}Si_{23}$ (Shoemaker & Shoemaker, 1981), the H phase (Ye, Li & Kuo, 1984), and K_7Cs_6 (Simon, Brämer, Hillenkötter & Kullmann, 1976). The first two of these are very complicated, containing over 200 atoms per unit cell with low symmetry. The total success to date of the Y & K observation in delimiting the empirical formulae of t.c.p. structures entitles us, we belive, to refer to it henceforth in this paper as the 'Y & K principle'.

It is an evident consequence of the Y & K principle that for every t.c.p. structure type $q \le r$. Nevertheless, for convenience, we may also find useful a potentially more general formulation,

$$P_pQ_qR_rX_x \rightarrow (PX_2)_p(QX_{7/6})_q(RX_{1/3})_r, \quad (2a)$$

where

$$p=i,\ q=2j,\ r=2j+3k. \quad (2b)$$

This formulation fits all known t.c.p. structure types because

$$Q_6X_7=3(Q_2R_2X_3)-2(R_3X),$$

although there is no known structure type for Q_6X_7 itself.

It is apparent from equation ($2a$) that when the numbers of CN16, CN15, and CN14 atoms are given, the number of CN12 atoms is determined. Henceforth in this paper we will take as the algebraic expression of the Y & K principle the following:

$$x=2p+7q/6+r/3, \qquad q \le r. \quad (3a, b)$$

The three 'pseudo-base' formulae of equation ($2a$) can be denoted by the single expression M^zX_n, where for $M=P$, Q, and R, $z \equiv (\mathrm{CN}-12)=4$, 3, and 2 respectively, and $n=2$, 7/6, and 1/3 respectively. When M is any mixture of P, Q, and R, z is an average given by

$$z=(4p+3q+2r)/(p+q+r). \quad (4a)$$

Since, from equation ($3a$),

$$n=(2p+7q/6+r/3)/(p+q+r)$$

we have

$$z=(6n+8)/5, \qquad n=(5z-8)/6. \quad (4b, c)$$

The fraction of atoms that are CN12 is given by

$$f=x/(p+q+r+x)=n/(n+1). \quad (5)$$

In terms of f, from equations (4) and (5) we have

$$z=(8-2f)/(5-5f), \quad f=(5z-8)/(5z-2). \quad (6a, b)$$

For the Z phase ($Q_2R_2X_3$), for example, with $f=3/7$, equation ($6a$) correctly gives $z=2{\cdot}5$. The *average coordination number*, $\overline{\mathrm{CN}}$, is $(z+12)\ (1-f)+12f$, or

$$\overline{\mathrm{CN}}=12+12z/(10z-4)=12+(8-2f)/5$$
$$=13{\cdot}6-0{\cdot}4f \quad (7)$$

for all known t.c.p. structures. (An equivalent equation has been given by Y & K). For the $C15$ structure type PX_2, the Z-phase structure type $Q_2R_2X_3$, and the $A15$ structure type R_3X, this equation gives 13·333, 13·429, and 13·500 respectively; in consequence of the Y & K principle, all t.c.p. structures must have $\overline{\mathrm{CN}}$ values in the range 13·333 to 13·500.

Y & K did not present any explanation of their observation (beyond a demonstration that a few structure types can actually be constructed from fragments of the three base structures), nor any proof that all t.c.p. structure types yet to be discovered must conform to it. We will present here an explanation which we believe goes a long way toward constituting a proof of that part of the principle that is contained in equation ($3a$).

We shall not in this paper discuss certain metal and alloy structure types which in certain respects resemble t.c.p. structures but violate the strict definitions used by Y & K and ourselves, in having some CN's different from 16, 15, 14, and 12, and some interstices that are not tetrahedral. These include, among others, α-manganese (Bradley & Thewlis, 1927), the isostructural χ phases, the D phase Mn_5Si_2 (Shoemaker & Shoemaker, 1976), the γ-brass structure types $D8_{1-3}$ [*e.g.* Cu_5Zn_8 (Bradley & Gregory, 1931)], and several very complicated structure types determined by Samson (1968): γ-$Mg_{17}Al_2$ (related to α-Mn), ε-$Mg_{23}Al_{30}$ (a distortion of the R-phase structure type), $NaCd_2$ and the closely related β-Mg_2Al_3, and Cu_4Cd_3. The last three of these are extremely complicated and have very large cubic unit cells. The structures of Samson, like many t.c.p. structures, are described by him as being built up of many CN16-atom-centered 'Friauf polyhedra' (truncated tetrahedra, formed by the 12 minor-bond vertices around CN16) and CN12 icosahedra; generally they contain as well some CN14 and CN15 atoms, but they possess also coordinations not present in true t.c.p. structures. Other structures bearing some relation to t.c.p. structures have been described by Cenzual, Chabot & Parthé (1985). We also do not include among the t.c.p. structure types enumerated here those that are polytypes of the Friauf–Laves phases and therefore automatically conform to the Y & K principle and its consequences, for example the $C36$ structure type [$MgNi_2$ (Laves & Witte, 1935)], and several more complex polytypes based on the Friauf–Laves phases (*e.g.* Komura & Kitano, 1977).

The role of dihedral angles

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 equation (3). 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'.

Since the dihedral angles between tetrahedral faces joining at a given bond must sum to 360°, the average dihedral angle around a given bond is $360°/g$, where g is the coordination number of the bond; thus for fivefold or 'minor' bonds the average dihedral angle is 72°, and for sixfold or 'major' bonds it is 60°. The dihedral angle in a regular tetrahedron is

$$\theta_0 = \cos^{-1}(1/3) = 70{\cdot}529° \qquad (8)$$

and the corresponding effective bond coordination number is

$$g_0 = 360°/70{\cdot}529° = 5{\cdot}104. \qquad (9)$$

We here state the 'dihedral-angle principle', *in the first approximation*, as requiring that the relative numbers of P, Q, R, and X atoms must be such that the average dihedral angle $\bar{\theta}$ is close to θ_0.

The applicability of this principle in this first approximation to demonstrating the validity of the Y & K principle depends on the degreee of approximation inherent in the assumption that the distortions of the regular tetrahedron to the tetrahedra present in the t.c.p. structures produce only small changes in the average dihedral angle $\bar{\theta}$. By the calculus of infinitesimals it can be shown that any infinitesimal distortion or combination of distortions of an initially regular tetrahedron does not change the average dihedral angle. For *finite* distortions the changes in the average dihedral angle $\bar{\theta}$ are zero to first order in the displacements, and generally finite in higher orders.

We have computed average dihedral angles in tetrahedra that are distorted from regularity in various ways subject to the earlier stated restriction that the ratio of the largest to the smallest edge not exceed 4/3. We found that the change in average dihedral angle varies roughly quadratically with the distortion parameter; about a third of the distortion modes increase the average dihedral angle, and the rest decrease it, in all but two cases by no more than about three quarters of a degree. The exceptions are the prolate D_{2d} distortion, with a maximum average dihedral-angle change of $-0{\cdot}90°$ at an edge-length ratio 4/3, and the oblate D_{2d} distortion, which gives $-0{\cdot}96°$ at an edge-length ratio of 1·2 and $-3{\cdot}2°$ at a ratio of 4/3. The prolate distortion occurs in the $A15$ structure (R_3X), where the two opposite short edges of the R_4 tetrahedron are major bonds and the other four are minor bonds. (A large D_{2d} oblate distortion appears not to be possible in t.c.p. structures; it would seem to require that most or all of the four shorter edges be major bonds.) A possibly more important distortion mode for t.c.p. structure types is a C_{2v} mode obtained by shortening one of the six edges. This is found, for example, where one of the edges is a major bond. For a 25% shortening of one bond the average dihedral angle changes by $-0{\cdot}100°$. Another important type of distortion found is C_{3v}, oblate or prolate, which gives modest increases in the average dihedral angle.

If we exclude the oblate D_{2d} mode, and take into account the fact that the edge-length ratio limit of 4/3 is uncommonly approached very closely, on averaging over the wide variety of distortion modes found in a t.c.p. structure we should not be surprised that $\bar{\theta}$ differs from θ_0 by not more than about a tenth of a degree, as may be seen in Table 4.

Actual values of tetrahedron-average and global-average dihedral angles for the t.c.p. base structures are given in Table 2. It may be remarked that notwithstanding the prolate D_{2d} distortion mentioned above, which is very prominent in the $A15$ structure, the deviation of the average dihedral angle for that structure from the ideal value, $\bar{\theta} - \theta_0$, is only $-0{\cdot}094°$. The deviation is smaller for the other structures. The $A15$ (R_3X) and $C15$ (PX_2) structures are 'end members' of the t.c.p. series, if the members of that series are ordered according to z. They are simple structures, highly constrained by symmetry, and accordingly might be expected to have tetrahedral distortions about as large as any that are likely to be found in the other structures.

In Table 3 are given the local values of the average dihedral angle for the various type of 'clusters' found in the base structures. For the purposes of this paper, a cluster is defined as an atom plus the 16, 15, 14, or 12 atoms of its coordination shell, and the associated 28, 26, 24, or 20 tetrahedra, respectively, coming together at the central atom. Here again the $A15$ structure shows the largest deviation, namely $-0{\cdot}111°$ for the R atom.

Let us now attempt to employ the dihedral-angle principle to see if, given the values of p, q, and r for any of the 20 known t.c.p. structures, we can calculate a value of x that (when rounded to the nearest integer) agrees with the observed value, which is also the value calculated with equation ($3a$). For the purpose of this treatment p, q, r, and x are taken to be relatively prime integers.

For any t.c.p. structure formula, *i.e.* for any given set of values of p, q, r, and x, the global-average

Table 2. *Dihedral-angle analysis of the t.c.p. 'base' structures*

Tetrahedron	θ(°) range	θ(°) av. for tetrahedron	Maximum edge ratio	No. of tetrahedra per formula
(I) *A*15 (Cr_3Si)				
R_4	53·13–78·46	70·019	1·22	3
R_3X	58·41–77·40	70·432	1·22	12
R_3X'	67·79–73·40	70·595	1·08	8
		$\bar{\theta}$ = 70·435		Total 23
(II) *Z* (Zr_4Al_3)				
Q_2R_2	52·77–77·16	70·236	1·27	6
Q_2RX	63·62–75·99	70·521	1·13	12
QRX_2	64·17–76·42	70·647	1·13	12
R_2X_2	59·61–75·61	70·341	1·13	6
QX_3	67·49–73·78	70·631	1·15	4
		$\bar{\theta}$ = 70·500		Total 40
(III) *C*15 ($MgCu_2$)				
P_2X_2	60·00–73·22	70·569	1·22	12
PX_3	67·12–74·21	70·661	1·22	4
X_4	70·29	70·529	1·00	1
		$\bar{\theta}$ = 70·588		Total 17

Table 3. *Cluster averages of dihedral angles in the three base structure types*

CN type	CN16	CN15	CN14	CN12
Central atom	*P*	*Q*	*R*	*X*
No. of atoms in cluster	17	16	15	13
No. of tetrahedra	28	26	24	20
Average dihedral angle at central atom	68·571	69·231	70·000	72·000
	Average dihedral angles (°)			
	$\bar{\theta}_p$	$\bar{\theta}_q$	$\bar{\theta}_r$	$\bar{\theta}_x$
PX_2 (*C*15)	70·582			70·593
$Q_2R_2X_3$ (Zr_4Al_3)		70·493 70·493	70·436	70·557
R_3X (*A*15)			70·418	70·497
Cluster average over the three base structures	70·582	70·493	70·427	70·549
Cluster average, regular icosahedron				70·547

dihedral angle $\bar{\theta}$ can be calculated:

$$\begin{aligned}\bar{\theta} = {} & [(4p+3q+2r)\,.\,6\,.\,60° + 12\,.\,(p+q+r+x)\,.\,5\,.\,72°]\\ & \times[(4p+3q+2r)\,.\,6 + 12\,.\,(p+q+r+x)\,.\,5]^{-1}\\ = {} & 60°\,.\,(16p+15q+14r+12x)\\ & \times(14p+13q+12r+10x)^{-1}. \qquad (10)\end{aligned}$$

In terms of the reduced formula M^zX_n this equation becomes

$$\bar{\theta} = 60°\,.\,[z+12(n+1)]/[z+10(n+1)]. \qquad (11a)$$

[If we combine this equation with equations (4) and (6), containing the results of the Y & K principle, we obtain

$$\begin{aligned}\bar{\theta} &= 90°\,.\,(11z-4)/(14z-5)\\ &= 60°\,.\,(34-f)/(29-f). \qquad (11b)]\end{aligned}$$

As special cases of equation (10), the average dihedral angle *at a given central atom* is obtained as 60° times 16/14, 15/13, 14/12, and 12/10 for *P*, *Q*, *R*, and *X* respectively; the resulting values are given in Table 3. Alternatively, these values can also be obtained with the expression 360°/(6 – 12/CN), derived from the Euler relation $V = 12/(6-q')$ for triangulated polyhedra, where V = CN = number of vertices and $q' = g$ = (average) number of triangular faces meeting at a vertex. (The global average $\bar{\theta}$ can also be easily obtained as the appropriately weighted average of these central atom values.) From equation (10) we can easily obtain

$$\begin{aligned}\bar{\theta} - \theta_0 = {} & [p(16\,.\,60° - 14\theta_0) + q(15\,.\,60° - 13\theta_0)\\ & + r(14\,.\,60° - 12\theta_0) + x(12\,.\,60° - 10\theta_0)]\\ & \times(14p+13q+12r+10x)^{-1}.\end{aligned}$$

On setting this equal to zero as required by the dihedral-angle principle in its first approximation, we obtain

$$x = 1{\cdot}8631p + 1{\cdot}1473q + 0{\cdot}4315r, \qquad (12)$$

to be compared with equation (3*a*) with its coefficients of 2, 1·1667, and 0·3333. We have calculated x with equation (12) for all 20 t.c.p. structures, given the values of p, q, and r for those structures. The calculated x values are encouragingly close to the true ones, but fail in nearly half of the cases to round to the correct integer; the largest discrepancy is for the ν phase (Shoemaker & Shoemaker, 1971*b*), where the calculated and actual x values are 39·912 and 37 respectively. Even so, the error in x is in this case only 7·9%. Thus the dihedral-angle principle in its first approximation appears to explain equation (3*a*) in essence but is incapable of ruling out deviations from that equation in t.c.p. structures yet to be determined, especially when x is not a small integer.

Clearly the variability in dihedral-angle averages for the tetrahedra, while small, needs to be taken into account. It is evident from the data in Tables 2 and 3 that the variability in the individual 'cluster averages' $\bar{\theta}_p$, $\bar{\theta}_q$, $\bar{\theta}_r$, and $\bar{\theta}_x$ should be smaller than that in the individual tetrahedra themselves. Over the structure as a whole, the average of cluster averages, weighted with the numbers of tetrahedra in the respective clusters, is

$$\begin{aligned}\bar{\theta}_{cl} = {} & (28p\bar{\theta}_p + 26q\bar{\theta}_q + 24r\bar{\theta}_r + 20x\bar{\theta}_x)\\ & \times(28p+26q+24r+20x)^{-1}.\end{aligned}$$

If we divide numerator and denominator by 2 and combine with equation (10) we obtain

$$\begin{aligned}\bar{\theta} - \bar{\theta}_{cl} = {} & [p(16\,.\,60° - 14\bar{\theta}_p) + q(15\,.\,60° - 13\bar{\theta}_q)\\ & + r(14\,.\,60° - 12\bar{\theta}_r) + x(12\,.\,60° - 10\bar{\theta}_x)]\\ & \times(14p+13q+12r+10x)^{-1}. \qquad (13)\end{aligned}$$

When the values of the respective cluster averages from Table 3 are entered and the expression is set equal to zero, we obtain

$$x = 1{\cdot}9399p + 1{\cdot}1309q + 0{\cdot}3531r. \qquad (14)$$

This is clearly a much better approximation to equation (3*a*) than is equation (11). When it is applied to the 20 t.c.p. structures, the calculated x value fails to round to the correct integer in four cases; the largest deviation is found for the T phase, $Mg_{32}(Zn, Al)_{49}$ (Bergman, Waugh & Pauling, 1957), for which the calculated and actual values of x are 47·702 and 49 respectively, differing by only 2·6%. The predictive power of the dihedral-angle principle in this approximation for t.c.p. structures has improved but is still somewhat limited.

Any further refinement of the dihedral-angle principle must take into account the fact that the cluster averages $\bar{\theta}_r$ and $\bar{\theta}_x$, at least, are demonstrably variable among the base structure types in which the respective clusters are found. The cluster averages $\bar{\theta}_p$ and $\bar{\theta}_q$ may also be variable, but as P and Q are each present in only one base structure type there is no basis for predicting any particular sort of variability. We note that among the three base structures, $\bar{\theta}_x$ increases with increasing $\overline{\mathrm{CN}}$ in a monotonic (though nonlinear) manner; $\bar{\theta}_r$ also increases with increasing $\overline{\mathrm{CN}}$ between the two base structures that contain R. We note also that the X clusters in $C15$ contain 6 atoms of $\mathrm{CN} > 12$, those in the Z phase contain 8, and those in $A15$ contain 12; of the 20 tetrahedra in each X cluster, 12 in $C15$, 8 in Z, and 12 in $A15$ have a major bond as one edge. The major bonds are generally significantly shorter than the minor bonds between the same two given atoms; however the P–P major bonds do not differ appreciably from the P–X minor bonds which are the other edges of the P_2X_2 tetrahedron in $C15$ because, in compensation, the P atom is larger than the X atom. However, the major bond found in the corresponding tetrahedron in the Z phase is shorter than the other edges, and this is true to a much greater extent in $A15$. The effect is to distort many of these tetrahedra in such a manner (approximating the C_{2v} mode described earlier) as to decrease the average dihedral angles significantly; the effect increases in going from $C15$ to Z to $A15$. A similar situation exists for the R clusters also, in the range from Z to $A15$.

We will here assume that $\bar{\theta}_r$ and $\bar{\theta}_x$ do vary monotonically with changing content of higher coordinated atoms in the clusters for all t.c.p. structures. Rather than to use $\overline{\mathrm{CN}}$ as a parameter with which to express this variation we will use z, because, given p, q, and r, z can be calculated with equation (4*a*) altogether independently of the Y & K principle. We will make the simplest and most conservative possible choice of assumed manner of dependence of cluster averages on the parameter z: (1) the only cluster averages to be used as data are those of the three base structure types; (2) cluster averages for all other structure types will be obtained by linear interpolation between those given, where interpolation is possible; and (3) where interpolation is not possible the cluster averages will be held constant:

$$\bar{\theta}_r = \begin{cases} 70{\cdot}346 + 0{\cdot}0360z, & 2{\cdot}0 \le z \le 2{\cdot}5\ [A15 \text{ to } Z] \\ 70{\cdot}436, & 2{\cdot}5 \le z \le 4{\cdot}0\ [Z \text{ to } C15] \end{cases} \qquad (15a, b)$$

$$\bar{\theta}_x = \begin{cases} 70{\cdot}257 + 0{\cdot}1200z, & 2{\cdot}0 \le z \le 2{\cdot}5\ [A15 \text{ to } Z] \\ 70{\cdot}499 + 0{\cdot}0233z, & 2{\cdot}5 \le z \le 4{\cdot}0\ [Z \text{ to } C15]. \end{cases} \qquad (16a, b)$$

When we substitute into equation (13) the individual calculated values of $\bar{\theta}_r$ and $\bar{\theta}_x$ from the above expressions, and the fixed values of $\bar{\theta}_p$, $\bar{\theta}_q$, and (in the Z to $C15$ range) $\bar{\theta}_r$ from Table 3, and then set both sides of equation (13) equal to zero, calculated values for x are obtained which are presented in the last column of Table 4. The agreement with the actual x values is very good in all cases. In only one case does the error exceed 0·14, namely for the aforementioned T phase, for which the calculated and actual x values are respectively 48·75 and 49, differing by only 0·51%. The maximum percentage error for all 20 structures is 0·67%. If we can assume that (say) 0·70% is a reasonable upper limit of error for any t.c.p. structure yet to be discovered, then we should not fear that the calculated x will round to a wrong integer unless x itself exceeds about 70. At least within this limitation we predict that for any t.c.p. structure yet to be discovered the result of the dihedral-angle treatment described here will agree with the actual composition found for that structure and thus confirm the prediction of that part of the Y & K principle that is contained in equation (3*a*).

We have not provided any satisfactory explanation of the restriction of equation (3*b*). The best we can say about this restriction is that we have tried and failed to produce a hypothetical t.c.p. structure for Q_6X_7. We have seen in the $A15$ structure that infinite chains of R atoms can exist without Q or P atoms being present; however, a stacking of infinite sheets of major-bond-linked Q atoms generates an equal number of R atoms, giving the Z phase. We have not found a way to generalize this result to hypothetical structures in which the Q atoms are linked to different atoms and/or in different ways. Perhaps at a later time a geometrical explanation will be found that will complete the explanation of the Y & K principle in the form given by those authors.

Discussion

In the *Introduction* we mentioned that no t.c.p. structure can exist in *Euclidean* space in which all atoms are icosahedrally (CN12) coordinated. Such a structure can exist, however, in a Riemannian curved

Table 4. *Summary of data and results on t.c.p. structure types*

				Lattice constants					Equation (1) indices†							M^zX_n				
Type	Example	Reference‡	Space group	a(Å)	b(Å)	c(Å)	β(°)	N	i	j	k	p	q	r	x	z	n	$\bar{\theta}$	$\overline{\mathrm{CN}}$	x_{calc}
$A15$	Cr_3Si	*a*	$Pm\bar{3}n$	4·564				8	0	0	1	0	0	3	1	2·000	0·333	70·435	13·500	1·00
σ	$Cr_{46}Fe_{54}$	*b*	$P4_2/mnm$	8·800		4·544		30	0	1	2	0	2	8	5	2·200	0·500	70·465	13·466	4·98
H*	Complex	*c*	$Cmmm$	4·5	17·5	4·5		30	0	1	2	0	2	8	5	2·200	0·500	70·465	13·466	4·98
ν	$Mn_{81\cdot5}Si_{18\cdot5}$	*d*	$Immm$	16·992	28·634	4·656		186	6	5	10	6	10	40	37	2·393	0·661	70·489	13·441	37·11
Z	Zr_4Al_3	*e*	$P6/mmm$	5·433		5·390		7	0	1	0	0	2	2	3	2·500	0·750	70·500	13·428	3·00
P	$Mo_{42}Cr_{18}Ni_{40}$	*f*	$Pbnm$	9.070	16.983	4.752		56	1	1	1	1	2	5	6	2·500	0·750	70·500	13·428	6·04
δ	MoNi	*g*	$P2_12_12_1$	9·108	9·108	8·852		56	1	1	1	1	2	5	6	2·500	0·750	70·500	13·428	6·04
K*	$Mn_{77}Fe_4Si_{19}$	*h*	$C2$	13·362	11·645	8·734	90·5	220	7	2	5	7	4	19	25	2·600	0·833	70·510	13·418	25·14
R	$Mo_{31}Cr_{18}Co_{51}$	*i*	$R\bar{3}$	10·903		19·342		159	8	3	2	8	6	12	27	2·846	1·038	70·530	13·396	26·93
μ	Mo_6Co_7	*j*	$R\bar{3}m$	4·762		25·615		39	2	1	0	2	2	2	7	3·000	1·167	70·540	13·385	6·96
—*	K_7Cs_6	*k*	$P6_3/mmc$	9·078		32·950		26	2	1	0	2	2	2	7	3·000	1·167	70·540	13·385	6·96
$p\sigma$	$W_6(Fe, Si)_7$	*l*	$Pbam$	9·283	7·817	4·755		26	2	1	0	2	2	2	7	3·000	1·167	70·540	13·385	6·96
M	$Nb_{48}Ni_{39}Al_{13}$	*m*	$Pnam$	9·303	16·266	4·933		52	2	1	0	2	2	2	7	3·000	1·167	70·540	13·385	6·96
I*	$V_{41}Ni_{36}Si_{23}$	*n*	Cc	13·462	23·381	8·940	100·3	228	4	1	0	4	2	2	11	3·250	1·375	70·556	13·369	10·94
C	$V_2(Co, Si)_3$	*o*	$C2/m$	17·17	4·66	7·55	99·2	50	6	1	0	6	2	2	15	3·400	1·500	70·563	13·360	14·92
T	$Mg_{32}(Zn, Al)_{49}$	*p*	$Im3$	14·16				162	20	3	0	20	6	6	49	3·438	1·531	70·565	13·358	48·75
X	$Mn_{45}Co_{40}Si_{15}$	*q*	$Pnnm$	15·42	12·39	4·74		74	10	1	0	10	2	2	23	3·571	1·643	70·571	13·351	22·90
—	Mg_4Zn_7	*r*	$C2/m$	25·96	5·24	14·28	102·5	110	16	1	0	16	2	2	35	3·700	1·750	70·577	13·345	34·89
$C14$	$MgZn_2$	*s*	$P6_3/mmc$	5·16		8·50		12	1	0	0	1	0	0	2	4·000	2·000	70·588	13·333	2·00
$C15$	$MgCu_2$	*t*	$Fd\bar{3}m$	7·080				24	1	0	0	1	0	0	2	4·000	2·000	70·588	13·333	2·00

* Structures determined after publication of Y & K paper.

† Indices in each set are taken as relatively prime.

‡ (*a*) Borén (1933). (*b*) Bergman & Shoemaker (1954); a similar atomic arrangement exists in β-uranium ($a = 10{\cdot}759$, $c = 5{\cdot}656$ Å) (Donohue & Einspahr, 1971). (*c*) Ye, Li & Kuo (1984); Fe > Cr > Ni > Mo > W, and Cr > Co > Mo > Fe > Al = Ti. (*d*) Shoemaker & Shoemaker (1971*b*). (*e*) Wilson, Thomas & Spooner (1960); we have taken the liberty of naming this phase the '*Z* phase' for convenience. (*f*) Shoemaker, Shoemaker & Wilson (1957). (*g*) Shoemaker & Shoemaker (1963). (*h*) Shoemaker & Shoemaker (1977); data given are for the substructure, which differs from the superstructure only in site compositions. (*i*) Komura, Sly & Shoemaker (1960); data given are for the hexagonal cell. (*j*) Arnfelt & Westgren (1935); data given are for the hexagonal cell. (*k*) Simon, Brämer, Hillenkötter & Kullmann (1976). (*l*) Kripyakevich & Yarmolyuk (1974); the same structural arrangement is found also in Th_6Cd_7 ($a = 10{\cdot}806$, $b = 9{\cdot}954$, $c = 6{\cdot}520$ Å) (Fornasini, Palenzona & Manfrinetti, 1984); we have taken the liberty of assigning the designation '$p\sigma$', which stands for 'pentagon sigma'. (*m*) Shoemaker & Shoemaker (1967). (*n*) Shoemaker & Shoemaker (1981). (*o*) Kripyakevich & Yarmolyuk (1970); their results are reported in space group $B2/m$. (*p*) Bergman, Waugh & Pauling (1957). (*q*) Yarmolyuk, Kripyakevich & Gladyshevskii (1970); Manor, Shoemaker & Shoemaker (1972). (*r*) Yarmolyuk, Kripyakevich & Melnik (1975); their results are reported in space group $B2/m$. (*s*) Friauf (1927*a*). (*t*) Friauf (1927*b*). (*s*) and (*t*) Laves & Witte (1935).

3-space, if an atom is placed at each of the vertices of the $\{p', q', r'\} = \{3, 3, 5\}$ regular polytope in a four-dimensional (4D) manifold. This polytope, which may be regarded as a 4D analog of the regular icosahedron in ordinary space, has 120 vertices, 720 edges, 1200 faces, and 600 cells; the faces are equilateral triangles ($p' = 3$), three of which ($q' = 3$) come together at each vertex of a cell, which is a regular tetrahedron, and five cells ($r' = 5$) come together at each edge (Coxeter, 1948). A stereofigure of a 3D projection of this polytope is shown in Fig. 2. In this curved-space t.c.p. structure model all atoms are CN12, the icosahedra and tetrahedra are regular, and all bonds are minor bonds.

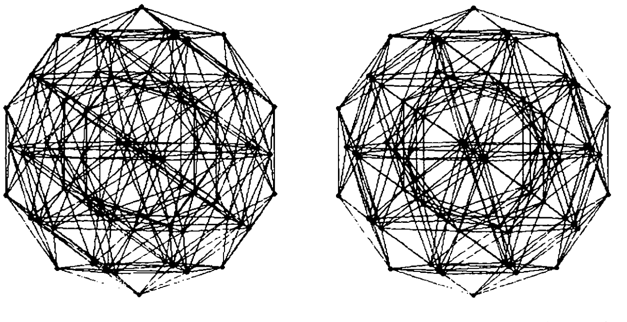

Fig. 2. Stereoscopic representation of a projection of the {3, 3, 5} regular polytope in 4-space onto a 3-hyperplane (Euclidean space). Since the projection is along a normal to a mirror plane in 4-space, the 120 vertices of the polytope project onto only 75 points in 3-space. Calculated and plotted with a Corona PC-21 microcomputer and Epson FX-80 printer using BASIC program *POLYT*335 (DPS).

This polytope, and the complementary {5, 3, 3} polytope (the cell of which is the regular pentagonal dodecahedron, the Voronoï polyhedron for an ideal icosahedrally coordinated atom) have been the focus of studies by several workers (Coxeter, 1958; Kléman & Sadoc, 1979; Sadoc, 1980, 1983; Sadoc & Mosseri, 1982; Rivier, 1982, 1983; Nelson, 1983) of coordination in amorphous metallic glasses, and in such models of those substances as froths and compressed lead shot. Most of this work dealt with means of un-curving to Euclidean space the model described above, reducing its curvature to zero by introduction of 'disclination lines' which convert some fivefold vertices to sixfold vertices (and perhaps other kinds). In the extension of this idea to crystalline metals by Sadoc (1983) it is apparent that the 'disclination lines' are the lines and/or linked line-segments that form the 'major networks' of Frank & Kasper (1959), at least where t.c.p. metals are concerned; for other crystalline metals and for metallic glasses this identification may apply approximately.

To consider the flattening of the {5, 3, 3} model of a froth, Coxeter (1958) used the Schläfli (1950) criterion for curvature of the spaces of regular polytopes and honeycombs: the quantity

$$\sin(\pi/p')\sin(\pi/r') - \cos(\pi/q')$$

is positive for a closed polytope in Riemannian (spherical) space, zero for an infinite honeycomb in Euclidean space, and negative for an infinite honeycomb in hyperbolic space. For Coxeter's $\{p', 3, 3\}$ 'statistical honeycomb' froth model in Euclidean space,

$$\begin{aligned} p'(=\bar{g}) &= \pi/\sin^{-1}(3^{-1/2}) \\ &= 2\pi/\cos^{-1}(1/3) \\ &= 2\pi/\theta_0 = g_0 = 5\cdot1043, \end{aligned}$$

where θ_0 is, as already stated, the dihedral angle of the regular tetrahedron. Thus this concept of flattening space is consistent with our dihedral-angle principle in its first approximation, although among t.c.p. structures $\bar{g}$ actually ranges from 5·1000 to 5·1111.

Sadoc & Mosseri (1982) suggested that the addition of disclination lines reduces the curvature of the ideal polytopic structure to zero owing to the introduction, along with the disclinations, of 'some regions of negative curvature' which counteract the positive curvature of the original polytope. No quantitative analytical method has been given by any of these authors for computing and combining these curvatures so as to predict, for example, the density of disclination lines needed to flatten the space occupied by the model. Our own attempts in this direction failed to yield a satisfactory prediction, for example, of the correct coefficients in equation (3a).

While the main thrust of these workers has been on amorphous structures, as already mentioned Sadoc (1983) has attempted to apply these ideas to a few metal structures: the t.c.p. structures of β-tungsten ($A15$), β-uranium (σ phase), and $MgCu_2$ ($C15$), and the non-t.c.p. structures of α-manganese and body-centered cubic metals ($A2$). He anticipated some of our work by presenting for each the values of $\overline{CN}$ and $\bar{g}$, determined empirically from the structural data (without use of curved-space arguments) and pointing out that these values of $\bar{g}$ are close to the value 5·1043 corresponding to the regular tetrahedron. We should point out here that while the values for the mentioned t.c.p. structures range from 5·1000 to 5·1111, the value for b.c.c. is 5·1414, significantly outside that range.

We conclude, for the time being, that although the curved-space description may provide valuable insights for t.c.p. crystalline structures as well as for metallic glasses, that description does not provide as satisfactory an understanding of the Y & K principle as does the dihedral-angle principle in ordinary three-dimensional space.

Presumably our dihedral-angle treatment can be extended to metallic glasses if the somewhat improbable assumptions are made that such materials have only tetrahedral interstices, g values are limited to 5 and 6, and coordination types are limited to the P, Q, R, and X types here described. It can probably be extended in an approximate way to metallic glasses not entirely conforming to these assumptions, and as well to crystalline alloy structures that are not ideally t.c.p., such as those mentioned in the *Introduction*.

The inspiration for this work came during a visit to the CNRS Laboratoire de Cristallographie in Grenoble, France, made possible by a research grant (No. 0289/82) from the North Atlantic Treaty Organization Scientific Affairs Division. We are indebted to Drs E. F. Bertaut, D. Fruchart, and R. Fruchart of that laboratory for valuable discussions. We thank also Dr N. Rivier, Imperial College, London, for penetrating comments at a colloquium in Grenoble.

Computations were made in part at the OSU Computer Center and in part on the authors' Corona PC-21 microcomputer.

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Phase Transitions in $RbLiSO_4$

BY W. STEURER, H. WITTMANN AND H. JAGODZINSKI

Institut für Kristallographie und Mineralogie der Universität, Theresienstrasse 41,
D-8000 *München* 2, *Federal Republic of Germany*

AND A. PIETRASZKO

Institute of Low Temperatures and Structure Research of the Polish Academy of Sciences,
POB 937, 50-950 *Wrocław, Poland*

(*Received* 29 *October* 1984; *accepted* 3 *September* 1985)

Abstract

The structure of the commensurate modulated phase (IV) of $RbLiSO_4$ (RLS) was determined by single-crystal X-ray diffractometry at 446 K. $M_r = 188{\cdot}5$, monoclinic, $P11n$, $a = 9{\cdot}157\,(1)$, $b = 5{\cdot}316\,(1)$, $c = 43{\cdot}654\,(3)$ Å, $\gamma = 89{\cdot}97\,(1)^\circ$, $U = 2125$ Å^3, $Z = 20$, $D_x = 2{\cdot}95$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 19{\cdot}94$ mm^{-1}, $F(000) = 1760$, $R = 0{\cdot}091$, $wR = 0{\cdot}045$ for 2191 independent reflexions (including 329 unobserved reflexions). The fivefold superstructure in the **c** direction is mainly caused by a rotation of the sulfate tetrahedra around **c**. In order to show the structural changes connected with the phase transitions difference Fourier maps and probability density functions (p.d.f.'s) of phases (I) (485 K, re-refined with anharmonic temperature factors), (III) (465 K) and (IV) were calculated and all existing orientation states of the SO_4 groups obtained. Models of the phase transitions are discussed from a structural point of view.

Introduction

In recent years the compounds MLiSO$_4$ ($M = NH_4$, Rb, Cs) have been the subject of many studies. Similar to such other A_2BX_4-type crystals as K_2SeO_4 (Iizumi, Axe, Shirane & Shimaoka, 1977) or Rb_2ZnBr_4 (Gesi & Iizumi, 1978), these substances undergo incommensurate-commensurate phase transitions and have ferroelectric and ferroelastic phases, respectively. Hahn, Lohre & Chung (1969) showed that these pseudohexagonal structures can be derived from a new type of tetrahedral framework with symmetry *Icmm*. Investigations on the system NH_4LiSO_4 (ALS) by Dollase (1969), Hildmann (1980) and Itoh, Ishikura & Nakamura (1981) exhibited the transitions:

$$\text{phase (I) } (Pcmn) \xrightarrow{460\text{ K}} \text{phase (II) (ferroelectric, } Pc2_1n) \xrightarrow{283\text{ K}} \text{phase (III) (ferroelastic, } P12_1/c1).$$