

A General Sharing Coefficient for the Classification of Structures with Defined Polyhedron Complexes*

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Abstract

30 years ago, T. Zoltai [*Am. Mineral.* (1960), **45**, 960–973] defined a 'sharing coefficient' in order to classify structures with tetrahedral coordination. The parameter and its variants have been used extensively and in particular have been applied by mineralogists to the study of silicate structures. In this paper, the sharing coefficients, which are based on topological criteria alone, are shown to be still of great use for classification purposes. They are generalized further to cover any polyhedra of fixed coordination found in any kind of structure, covalent, metallic or ionic. A general formula is proposed and discussed which is not restrictive in terms of apex coordination. Furthermore, a modification of this general parameter is proposed for the case of miscellaneous coordination polyhedra in semi-metallic structures. Theoretical and practical examples illustrate the validity of these formulae.

Introduction

Structural classifications are mainly based on topological features; such as the well-known silicate and phosphate classifications based on O tetrahedron complexes. At the same time, it has always been a challenge for authors to define appropriate numbers or letters in order to classify and compare structures, e.g. Pearson symbols. The sharing coefficient (c_z), introduced by Zoltai (1960), was a new kind of parameter, which described the physical aspects of a structure (linking between tetrahedra) and could therefore be used for either classification purposes (particularly for silicates) or for the evaluation of structures from chemical formulae. Consequently, much interest has been shown in this parameter (see its variants in Table 1). Coda (1969) proposed a modified sharing coefficient (c_c), which he applied to silicate structures. Similar parameters have been defined by Liebau (1985), also for silicates. Parthé & Engel (1986) extended the sharing coefficients to any

kind of linked anionic tetrahedron complexes for normal-valence compounds and derived a parameter (the so-called *TT* parameter) from anion and cation valences. Recently, Parthé & Chabot (1990) classified anionic tetrahedron complexes considering not only normal-valence compounds but also polyanionic and polycationic compounds (among them, the semi-metallic 'Zintl phases') with a modified sharing coefficient called $C'AC'$.

The advent of databases has meant that parameters which express the topological features of structures are now of great interest, 30 years after the publication of Zoltai's paper. These parameters may be considered as shorthand descriptions of structures, being easier to handle than a list of atomic or bond-length data. Furthermore, developments in the field of computers mean that more and more complex mathematical expressions may be of direct use.

In this paper, the derivation of a general sharing coefficient is presented, which is valid for any kind of coordination polyhedra having any chemical composition and any coordination of the polyhedron apices. Like Zoltai's coefficient, this general parameter is derived from topological criteria only, so that it may be used for any structures, metallic or iono-covalent. Its definition is based on the clear relationships within structures, which are often used by authors; for the sake of clarity, these relationships have been redefined in the section below. We discuss some further aspects of coordination polyhedra and linking, and a modification of this general sharing coefficient is proposed, which expresses miscellaneous polyhedra links in semi-metallic compounds and takes account of valences for the ionic part of these structures. Finally, suggestions for future definitions of parameters are presented.

Basic structural algebra

Let us consider a structure of chemical composition: $K_k \dots Z_z (C'_m A_n)$ + other molecules or complexes. C' are atoms which centre the considered polyhedra built of A atoms. In this definition more than one kind of atom (indifferently anions or cations) can be

* Dedicated to Tibor Zoltai on the 30th anniversary of the publication of his paper defining the sharing coefficient.

Table 1. Existing sharing coefficients and other parameters describing structures with tetrahedral complexes

Authors	Parameter	Formula or examples	Authors' definition
Zoltaï (1960)*	Sharing coefficient	$c_z = 2a + 1 - a(a+1)n/(4m')$	Average number of tetrahedra participating in the sharing of a corner in a structure
Coda (1969)	Modified sharing coefficient	$c_c = (c_z - 1)4$	Average number per tetrahedron of shared oxygens
Liebau (1985)	Linkedness	$L = 0$ (isolated tetrahedra) $L = 1$ (corner-sharing) $L = 2$ (edge-sharing)	Number of O atoms shared between two adjacent [SiO ₄] polyhedra
	Connectedness	$s = 0$ (isolated tetrahedra) $s = 1$ (2 tetrahedra linked)	Number of [SiO ₄] polyhedra that share O atoms with the [SiO ₄] polyhedron considered
Parthé & Engel (1986)	TT	$TT = 1(8 - 2n/m')$ $0 \leq TT \leq 4$ $TT = 2(8 - 3n/m')$ $4 \leq TT \leq 8$ $TT = 3(8 - 4n/m')$ $8 \leq TT \leq 12$ for $C_n(C_n, A_n)$	Average, per tetrahedron of the sum (over all four corners of a tetrahedron), of the number of tetrahedra which are connected with one corner of the tetrahedron considered
or Engel (1986)*	VEC_A	$TT = 8a - (a^2 + a)n/m'$	Partial valence electron concentration with respect to the anion (A)
Parthé & Chabot (1990)*	$C'C'$	$VEC_A = (m'e_c + m'e_{c'} + ne_A)/n$ for $C_n(C_n, A_n)$ $C'C' = (n/m')(VEC_A - 8)$ for $VEC_A > 8$	Average number of electrons per central atom for C'-C' bonds and/or lone pairs on the C' atom in polycationic compounds
	AA	$AA = 8 - VEC_A$ for $VEC_A < 8$	Average number of electrons per anion for A-A bonds in polyanionic compounds
	$C'AC'$	If $VEC_A = 8$, similar to TT ; complete definition in the Appendix	Average number of C'-A-C' links per tetrahedron

* In their descriptions, the authors consider that the apices are shared between a and $a + 1$ tetrahedra except for parameter k of Parthé & Chabot (1989) whose definition is slightly different (see Appendix).

defined as C' or A . $K_k \dots Z_z$ are other atoms K to Z needed to balance the electrical charge of the structure.

With the assumption that the coordination number of the polyhedra considered is equal to P , there are within the structure, on average (per polyhedron), N_1, N_2, \dots, N_j apices coordinated to 1, 2... j C' atoms respectively and

$$N_1 + N_2 + \dots + N_j = P. \quad (1)$$

A similar equation is applied by Parthé & Chabot (1990) to tetrahedra ($P = 4$). These N numbers are average numbers. They are defined from the chemical formula as follows. For n_1, n_2, \dots, n_j A atoms coordinated to 1, 2... j C' atoms:

$$N_x = xn_x/m' \quad (2)$$

for which $n = \sum n_x$, where x is the partial coordination number or the number of bonds (central A atom— C' atoms) with $x = 1, 2, \dots, j$. In addition to (1), a similar expression to (2) is used by Wells (1983).

Since the sharing coefficients are average values calculated over each structure, it is convenient to define an average partial-coordination number (central A atoms— C' atoms):

$$\langle x \rangle = \sum_{x=1}^j (xn_x)/n. \quad (3)$$

It is surprising to note that another similar equation can be derived [compare (1) and (2)]:

$$P = \sum_{x=1}^j (xn_x)/m'. \quad (4)$$

Consequently:

$$P = \langle x \rangle n/m' \quad (5)$$

so that the ratio of the stoichiometric compositions of C' and A atoms is strictly equal to the inverse ratio of their coordinations. This principle facilitates the calculation of $\langle x \rangle$.

Extended sharing coefficients

Let us now extend Zoltaï's sharing coefficient c_z to any kind of A -atom, partial coordination (x) and any C' coordination (P). According to the definition of Zoltaï's parameter (average number of tetrahedra participating in the sharing of a corner in a structure; Table 1), we may write the general expression for any kind of polyhedra of coordination number equal to P :

$$\{c_z\} = \sum_{x=1}^j (xN_x)/P. \quad (6)$$

The extended Zoltaï sharing coefficient ($\{c_z\}$) is related to the average partial coordination number of A atoms towards C' atoms per number of A atoms in a structure by the following equation [compare (2)]:

$$\{c_z\} = \sum_{x=1}^j (x^2n_x)/(Pm').$$

Now with $\langle x^2 \rangle = \sum_{x=1}^j (x^2n_x)/n$ and (5):

$$\{c_z\} = \langle x^2 \rangle / \langle x \rangle \quad (7)$$

which is a general equation for $\{c_z\}$.

It is in fact more convenient to work with the A -atom chemical compositions (expressed by n_x) than with the polyhedron apices (or N_x), as the n_x may be easily obtained from bond-length calculations which include the numbers of A and C' atoms

in the structure. However, in order to define a parameter relative to the C' atoms (or to the considered polyhedra), it is helpful to refer to the N parameters. Thus, each polyhedron of the structure may be bound to other polyhedra of the structure through its apices, and calculated over the structure (there are as many polyhedra as m' C' atoms), the sum of all these bonds is:

$$PPm' = \sum_{x=1}^j [(x-1)N_x]m'$$

PP , or the average number per polyhedron of polyhedron-polyhedron connections through the apices of the polyhedra considered, is similar to TT (definition given in Table 1). With (2), the equation for PP becomes:

$$PP = \sum_{x=1}^j [(x-1)xn_x]/m'$$

Comparing this with equation (3) and with $\langle x^2 \rangle = \sum_{x=1}^j (n_x x^2)/n$, one finds:

$$PP = (\langle x^2 \rangle - \langle x \rangle)n/m' \quad (8)$$

which is a general equation for PP .

Finally, using (5) and (7), one obtains:

$$\begin{aligned} PP &= (\langle x \rangle \{c_Z\} - \langle x \rangle)P/\langle x \rangle \\ PP &= P(\{c_Z\} - 1). \end{aligned} \quad (9)$$

Coda's modified sharing coefficient (see Table 1, $P = 4$) is now extended to any kind of polyhedra bound to each other with any apex coordination.

Equations (6) to (9) are valid for any A -atom coordinations and for polyhedra centered on any C' atoms. It is also possible to consider several kinds of polyhedra in the structure, *i.e.* using average values for P ($\langle P \rangle$) could be useful for some classifications [for borates with $3 \leq \langle P \rangle \leq 4$; see the classification by Christ & Clark (1977)]. One thus sees the wide range of applications for PP or $\{c_Z\}$.

In Fig. 1, values for $\{c_Z\}$ are plotted as a function of $\langle x^2 \rangle$ for different values of $\langle x \rangle$. One notices that for a given composition n/m' and a given polyhedron and therefore a given average partial apex coordination $\langle x \rangle$, the higher the value of $\{c_Z\}$, the more varied the apex coordination will be.

Equipartition or the equivalence of maximal order and minimal bonding

The difficulty in using (7) and (8) lies in choosing a value for $\langle x^2 \rangle$. Accordingly, Zoltai's expression (see Table 1) may be interpreted as a simplified formula for calculation of the sharing coefficient, which avoids calculation of $\langle x^2 \rangle$.

Considering the end terms for which all n A atoms of the formula unit are surrounded in the structure

by exactly the same number of C' atoms, we may write with $\langle x^2 \rangle = \sum_{x=1}^j (x^2 n_x)/n$:

$$\langle x^2 \rangle = x^2,$$

whence

$$c_Z = x.$$

Here x is the partial coordination number (A central atom— C' atoms).

As shown in Fig. 1, all other values for the extended Zoltai sharing coefficient $\{c_Z\}$ are linear combinations of these end terms. For structures in which the number of A atoms in the formula unit show only two different partial coordinations (n_a A atoms are coordinated to a C' atoms and n_b A atoms to b C' atoms):

$$\begin{aligned} \{c_Z\} &= (a+b) - ab[n/(n_a a + n_b b)] \\ \{c_Z\} &= (a+b) - ab[n/(m'P)] \end{aligned} \quad (10)$$

and with (9):

$$PP = (a+b-1)P - ab(n/m'). \quad (11)$$

The parameters $\{c_Z\}$ or PP are now easily calculated from the chemical composition of the structure, assuming that values for the partial coordinations (central A atom— C' atoms) (a and b) are known.

Zoltai (1960) derived his formula on the assumption that "the difference between the smallest and largest number of tetrahedra participating in the sharing of a tetrahedral corner in a structure cannot be more than 1". His equation is found when one inserts $b = a + 1$ and $P = 4$ in (10) (compare Table 1). With this assumption, Engel (1986) derived a general equation for TT [(11) with $b = a + 1$ and $P = 4$, Table 1]. Expressing the same idea with a slightly

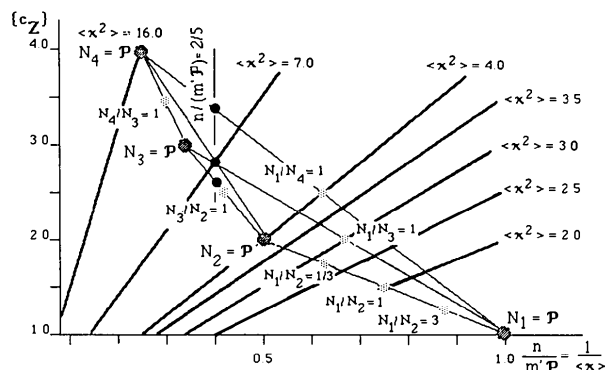


Fig. 1. The extended Zoltai sharing coefficient ($\{c_Z\} = \langle x^2 \rangle / \langle x \rangle$) calculated for apices with partial coordination up to four C' atoms ($x \leq 4$). $N_x = P$: all apices of the polyhedra considered in the whole structure are bound to x C' atoms. Linear combinations between these end terms are drawn with thin lines and illustrated with theoretical examples (the relation N_a/N_b is independent of P). Black circles: example cited in text ($n/m' = 5/8$; $P = 4$).

different formulation, Parthé & Chabot. (1990) named this observation equipartition.

In Fig. 2, values for the partial coordinations a and b are calculated with an expression derived from (3) and (5) and with $n_a + n_b = n$:

$$a = P(m'/n) - (b-a)n_b/n \quad (12)$$

$a < b$; $n_b/n < 1$; $P = 4$ (*i.e.* tetrahedra).

From Fig. 2, it may be deduced that values for the lowest partial coordination (a) may be calculated as the integer part of $[\langle x \rangle - (b-a)_{\min} + 1]$. For example: for the average chemical composition of the considered tetrahedra $m'/n = \frac{5}{8}$, $\langle x \rangle = 2.5$, $a = 2$ for half of the A atoms in the formula unit and $b = a + 1 = 3$ for the other half of the A atoms in the formula unit; this is the case of equipartition. However, if $a = 2$ for three quarters of the A atoms in the formula unit, $b = 4$ for one quarter of the A atoms, meaning non-equipartition; there are several other possibilities for non-equipartition: *i.e.* one quarter of the A atoms bond to one C' atom ($a = 1$) and three quarters of them to three C' atoms ($b = 3$); or half of the A atoms bond to 1 C' atoms ($a = 1$) and the other half to 4 C' atoms ($b = 4$). For the cases cited, the values for the extended sharing coefficient are respectively (compare Fig. 1) 2.6, 2.8 and 3.4. Thus the most economical ($\{c_z\} = 2.6$) is the case of equipartition. This may be the reason why equipartition was observed for most anionic tetrahedron complexes [*i.e.* 167 out of 172 structure types of normal-valence compounds described by Parthé & Chabot (1990)]. However, if PP is calculated on only part of a structure, non-equipartition may be observed more often than expected.

Varieties of polyhedra and linkages

The successful application of sharing coefficients to structures depends firstly on the choice of the con-

Table 2. *Regular polyhedra of A atoms centered by C' atoms with coordinations up to 8*

Polyhedron	P	Number of edges	Number of (A—A) edges (isolated polyhedron)
Triangle	3	3	2
Square	4	4	2
Tetrahedron	4	6	3
Square pyramid	5	8	3 (basis) or 4
Trigonal bipyramid	5	9	4 (basis) or 3
Trigonal prism	6	9	3
Octahedron	6	12	4
Cube	8	12	3
Square antiprism	8	16	4

sidered polyhedra. Until now, these parameters have been applied in ionic-covalent structures with tetrahedra, which are clearly defined polyhedra with minor deformations (*i.e.* oxygen tetrahedra in silicates, phosphates). In these structures, the A atoms coincide with the anions which are large atoms relative to the cations (or C' atoms). For these structures, Pauling's 1st rule (Pauling, 1960) is valid, which determines the possible polyhedra formed by A atoms around C' atoms by the ratio of their atomic radius; this corresponds to polyhedra edges being equal to at least twice the A -atom radius. Table 2 cites the most regular polyhedra observed in structures. Emphasis is placed on the numbers of ($A—A$) edges intersecting each apex (see Table 2).

It is clear, that in more compact structures, the number of $A—A$ edges should be relatively high. This is the case for tetrahedra and octahedra, which are the most commonly encountered polyhedra in structures {tetrahedra: 3 $A—A$ edges on each apex, or [number of ($A—A$)]/ $P = 0.75$, octahedra: 4 $A—A$ edges, [number of ($A—A$)]/ $P = 0.67$ }. The next highest values for isolated polyhedra are for the coordination number 5, [number of ($A—A$)]/ $P = 0.64$ (square pyramid), 0.72 (trigonal bipyramid) and the coordination number 3 {[number of ($A—A$)]/ $P = 0.67$ }. In close-packed structures the perfect fitting together of tetrahedra and octahedra enables the highest order as well as the maximum number of $A—A$ edges (12). Considering the tetrahedra occupied by the Zn atoms in the cases of wurtzite and sphalerite, one calculates a TT value of 12 (corner-shared; in these structures only half of the possible tetrahedra are centered by Zn atoms). Each A atom is thus equally bound to four C' atoms. This seems relevant for maximum coordination of A atoms to C' atoms in the case of tetrahedra in ionic-covalent compounds. In the same packed structures of composition $C'A$ (C' atoms now center A octahedra), $x = 6$ and $OO = 30$, which corresponds to eight octahedra in contact with a central octahedron (h.c.p.; six edge-shared plus two face-shared with central octahedron) or 12 octahedra (c.c.p.; apices shared between six octahedra and edges between two). As shown in Table 3, for a proper definition of a

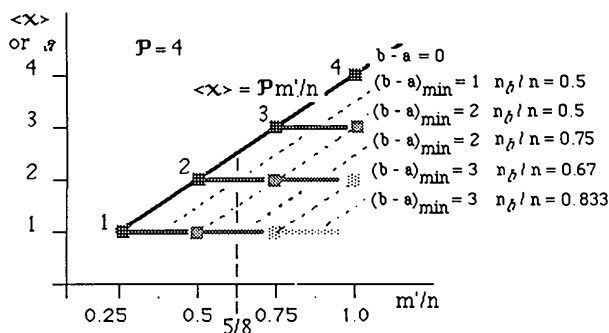


Fig. 2. Apices coordination (a and b ; integer values) calculated as a function of the apices composition (m'/n) for polyhedra with $P = 4$. The percentage of apex content (n_b/n) and the minimal possible coordination difference $(b-a)_{\min}$ are indicated for each broken line. Oblique line: average partial coordination $\langle x \rangle$ as a function of m'/n .

structure, P and PP should be indicated for each clearly defined chemical complex; a short description should be given as well, since PP is independent of the linkedness (Liebau, 1985; definition given in Table 1) and so does not indicate the real number of polyhedra linked to a considered polyhedron.

Coordination and valences

In any structure with ionic bonds, coordinations and valences are intimately related [see the bond-strength definition or electrostatic valence rule (Pauling, 1960)]. Parthé's VEC_A [see definition in Table 1 (Parthé, 1973)] may be interpreted as a measure of the metallic or highly covalent part of an otherwise ionic structure. So, if $VEC_A < 8$, the so-called polyanionic structures present valence electrons which the anions may share in anion—cation bonds; if $VEC_A > 8$, then the so-called polycationic structure may present cation—cation links or 'non-bonding orbitals' (NBO).

In the case of $VEC_A = 8$ or normal-valence compounds, by definition, there are only anion—cation bonds in the structure and the cations center polyhedra built of anions. The more the polyhedra are linked together, the less other cations (or other polyhedra bound to these cations) will be in the structure. For instance, in the SiO_2 quartz structure, all tetrahedra are linked together, all charges being compensated, whereas in $\text{Ca}_2(\text{SiO}_4)$, the charge of the tetrahedron, equal to 4, 'attracts' the Ca atoms. Furthermore, the less positive the charge of the C' atoms, the more the tetrahedra have an ability to bind together. This defines TT_{\max} as a function of the charges of anions and cations (Parthé & Engel, 1986).

This function may be simply derived from the charge equilibrium within structures. In the case of PP_{\max} , the composition of the compound will be of type $C'_m A_n$. For this normal-valence compound, the charge-balancing equation is expressed as (atoms of different kinds are now called C' or A atoms but $C' = \text{cations}$ and $A = \text{anions}$):

$$m'\langle e_{C'} \rangle = n(8 - e_A)$$

where $\langle e_{C'} \rangle$, $\langle 8 - e_A \rangle$ are respectively the average C' cationic charge per C' cation and average A anionic charge per A anion [$e_{C'}$, e_A : numbers of valence electrons of the cations (C') or anions (A)], so

$$\langle e_{C'} \rangle / \langle 8 - e_A \rangle = n/m'. \quad (13)$$

Thus, replacing $(n/m')_{\min}$ by $\langle e_{C'} \rangle / \langle 8 - e_A \rangle$ in (11), one finds for PP_{\max} :

$$PP_{\max} = (a + b - 1)P - ab \langle e_{C'} \rangle / \langle 8 - e_A \rangle \quad (14)$$

for normal-valence compounds.

PP_{\max} is a parameter dependent on the partial A -atom coordination. However, in the case of equipartition, only the minimum ($A-C'$) coordination has to be known since $b = a + 1$ and $a = \text{integral part of } \langle x \rangle$ (see above).

Miscellaneous polyhedra

For structures with anionic tetrahedron complexes, Parthé & Chabot (1990) established a classification based on the VEC_A , AA or $C'C'$ (definitions in Table 1) and a third parameter called $C'AC'$ which expresses 'the average number of $C'-A-C'$ links originating from a tetrahedron' (definition in Appendix); if $C'C' > 0$, these authors add a parameter 'x' which defines the number of $C'-C'$ bonds relative to the 'non-bonding orbitals' in the structure (also called 'lone pairs'). In these structures, the C' atoms which center the tetrahedra are cations relative to the A atoms (or anions). The tetrahedron complexes are now miscellaneous in the sense that the polyhedron geometry is altered by 'non-bonding orbitals' in the complex or that tetrahedron linking is different when anions or cations are linked together.

For these miscellaneous polyhedra we propose a modification of PP , which takes account of the chemical composition m' (cations in the polyhedra) and n_o (anions in the polyhedra), and of the AA and $C'C'$ parameters. Now, for each $C'-C'$ bond, one negative charge is added to the polyhedra, for each NBO, two charges are added to each polyhedron whereas for each $A-A$ bond, one negative charge is subtracted from the polyhedron. These particular features of the polyhedra may be needed in structures with ionic character in cases where more or less positive charges are available in the structure (*i.e.* through other cations). It is therefore worthwhile analyzing the effect of these special bonds in relation to the charge balance in the compound.

In order to calculate PP_m , one assumes that the considered polyhedron should not be altered ($P = \text{constant}$), even if polyhedra with 'non-bonding orbitals' (NBO) show a different coordination than expected (theoretical examples shown in Fig. 4). This implies that the apex composition of the polyhedra (n/m) is now equal to the anion/cation composition (n_o/m') plus $C'C'/2$ respectively minus $(AA/y)n_o/m'$ ($AA n_o/m'$: average number of $A-A$ bonds per polyhedron). The average partial coordination number for apices which, among other bonds, share $A-A$ bonds (y) is equal to 2 in most cases; the partial coordination for the C' atoms with $C'-C'$ bonds is equal to 2; the partial coordination for C' atoms with NBO's is equal to 1 and $C'C'$ is equal to twice the number of NBO's [since each NBO requires two electrons according to Parthé & Chabot

(1990)]. So the general equation for PP (8) becomes:

$$PP_m = (\langle x^2 \rangle - \langle x \rangle)[(1 - AA/y)n_o/m' + C'C'/2] \quad (15)$$

which is a general equation.

With respect to simplifying this equation, it is worthwhile redefining the concept of equipartition. With the help of Zoltai's assumption (see above), the partial coordination of all apices may be considered as the number (of polyhedra) participating in the sharing of a (polyhedral) 'corner'. So each AA or $C'C'$ link is shared between two polyhedra and each NBO is 'linked' to only one polyhedron. Now, if all apices (including $C'-C'$ bonds, $A-A$ bonds and NBO's) are shared between a and $a+1$ neighbouring polyhedra then the right part of equation (15) can be simplified and:

$$PP_m = 2Pa - a(a+1)[(1 - AA/y)n_o/m' + C'C'/2] \quad (16)$$

for equipartition among all links, where a = integral part $\{P/[1 - AA/y)n_o/m' + C'C'/2]\}$ since the average partial coordination of the apices is now: $\langle x \rangle = P/[1 - AA/y)n_o/m' + C'C'/2]$.

Function (16) is shown in Fig. 3. Theoretical examples for $P=4$ and $C'C' \geq 0$ are presented in Fig. 4 as a function of anion/cation chemical composition (n_o/m'); these examples illustrate different values for a . Among sulfide minerals, pyrite and covellite present complex structures with $AA > 0$ (Table 3). For less complex structures, as may be noted from Fig. 3, if $a=1$ and the difference between the minimum partial coordination calculated for $C'C' = AA = 0$ (a_o) and a is equal to 0, then (16) becomes simply:

$$PP_m = PP_o - C'C' + AA n_o/m' \quad (16')$$

for PP_o calculated from (11) with $n/m' = n_o/m'$, $a = 1$, $b = 2$ and $0 \leq PP_o \leq P$.

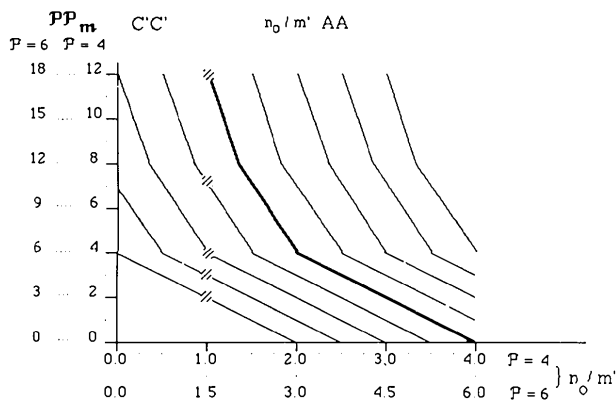


Fig. 3. Calculation of PP_m as a function of the anion/cation composition (n_o/m') for tetrahedra ($P=4$) or octahedra ($P=6$) for the case of equipartition (16). Heavy line: $n_o/m' AA = C'C' = 0$ (see Fig. 1). Other values for $n_o/m' AA$ and $C'C'$ increase by $P/4$ for each thin line. Hatched squares: examples for $n_o/m' = 1$ in Fig. 4.

Now, as for normal-valence compounds, the parameter PP_m may be related to the charge of the complex considered [(9) in Parthé & Engel (1986)]. The average charge of the complex per polyhedron (ch_{complex}/m') is deduced from the balance of charges in the compound and from the definitions of $C'C'$ and AA :

$$ch_{\text{complex}}/m' = \langle 8 - e_A \rangle n_o/m' - \langle e_{C'} \rangle + C'C' - AA n_o/m'$$

It is also worthwhile to have some idea of the maximum value of PP_m allowed for a given valence composition of anions and cations forming the considered polyhedra. In a similar way as for (14):

$$(n_o/m')_{\text{min}} = (\langle e_{C'} \rangle - C'C') / (\langle 8 - e_A \rangle - AA)$$

and using (16), calculated for the case of equipartition:

$$PP_{\text{max}} = 2Pa - a(a+1)[\langle e_{C'} \rangle + (\langle 8 - e_A \rangle / 2 - 1)C'C' - (\langle 8 - e_A \rangle / y - 1)AA n_o/m'] / \langle 8 - e_A \rangle.$$

For example: a structure with $e_{C'} = 4$, $e_A = 6$ and $C'C' = 2$, $(n_o/m')_{\text{min}} = 1$ and $PP_{\text{max}} = 4$. GeS in Parthé & Chabot (1990) is built of tetrahedra with $PP_m = 6$ and one NBO which is not an equipartition case (equipartition among all links, see above, Fig. 4 and a comment in the *Appendix*! Note further that

n_o/m'	$AA=C'C'=0$	$C'C'=1$	$C'C'=2$	$C'C'=2$	$C'C'=3$
3:2	7	4	3	3	3
4:3	8	5	4	4	4
7:6	10	6	5	5	5
1:1	12	7	6	4	3
5:6	9	8	8	5	4
3:4	10	9	9	7	7

Fig. 4. Theoretical examples for the coordination of polyhedra with $P=4$ in structures with $C'C' \geq 0$. Emphasis is given to polyhedra with $4 \geq x \geq 1$ and consequently low anion/cation compositions (n_o/m'). In bold: PP_m . The numbers in the upper-left corners of the frames are for the apices composition $n/m' = n_o/m' + C'C'/2$. Double frames indicate the cases with non-equipartition. For anion/cation compositions smaller than 1:1 (below double line), equipartition is no longer ensured.

Table 3. *PP* values and coordinations of *C'* and *A* atoms in mineral structures

<i>K</i> · <i>Z</i> (<i>C'A</i>)	Mineral	<i>P</i>	<i><x></i>	<i>PP</i>	<i>PP_m</i> ^a	Description
Sulfides						
ZnS	Sphalerite	4	4	12		C.c.p.
	Wurtzite	4	4	12		H.c.p.
MoS ₂	Molybdenite	6	3	12		Layers of edge-linked trigonal prisms
FeS ₂	Pyrite	6	4 ^b	—	18	NaCl type with S—S pairs
Cu(Cu ₂ S ₃)	Covelline	4	3·2 ^c	—	10	Framework of tetrahedra in pairs
Cu ₂ (CuS)S ₂	Covelline	3	3	6		Layers of triangles
(Cu ²⁺ Cu ₂ S ₃)	Covelline	3·67	4·4 ^d	—	12·7	Framework of triangles + tetrahedra
Oxides						
TiO ₂	Anatase	6	3	12		Edge-linked octahedra framework
ThO ₂	Thorianite	8	4	24		Fluorine type
Al ₂ O ₃	Corundum	6	4	18		Edge- and apices-linked octahedra framework
TiO ₂	Rutile	6	3	12		Edge- and apices-linked octahedra framework
Mg(OH) ₂	Bruceite	6	3	12		Edge-linked octahedra layers

Notes: (a) equation (15) or (16); (b) $AA = 1$, $y = 4$; (c) non-equipartition, $AA = 0·67$, $y = 4$, $n_o/m' = 1·5$; (d) equipartition, $AA = 0·67$, $y = 4$, $n_o/m' = 1·0$.

for polyhedra with anions with $e_A = 6$ (*i.e.* oxygen), PP_{\max} is a constant for each composition $e_{C'}/(8 - e_A)$ for any value of $C'C'$.

The parameter PP_m has been derived from topological criteria only with the help of the formulation given by Zoltai (1960). Before using this parameter, one should know which are the polyhedra to consider, their chemical composition and values for $C'C'$ and AA (formulae given in Table 1). As a result, this parameter gives the average number (per polyhedron) of polyhedron–polyhedron connections through the apices of the considered polyhedra. This is the same meaning as PP . In addition the maximum possible value is easily obtained from the charges within the complex considered. In this respect, it gives more information than the parameter $C'AC'$ given by Parthé & Chabot (1990). It may be calculated directly from the chemical formula since no precise indication of $C'—C'$ bonds or NBO's is needed. (This indication may however be used for a description of the structures or for the definition of base tetrahedra avoided here.) Finally, the general expression (15) is valid for structures with any kind of polyhedra sharing; the parameter $C'AC'$ was restricted to tetrahedra links in cases of equipartition and non-equipartition for which $b = a + 2$ [(13) to (15) in Parthé & Chabot (1990), see *Appendix*]. So, we recommend the use of PP_m for classification purposes in addition to $C'C'$ and AA , or to n_o/m' .

How to define successful parameters

Any kind of parameter may be defined with a view to classifying or comparing structures. However, the above discussion concerning sharing coefficients

offers an opportunity to draw up some recommendations. Successful parameters may be described as follows: their derivation should be based on rigid physical aspects of the structures, *i.e.* well defined coordinations, valences, or precise crystallochemical rules; they should express as many aspects of the structure as possible (coordination ratios also express valence ratios in ionic compounds; do not forget that topological criteria may offer a clue to understanding the energy distribution and order in structures); to use these parameters, the input must be kept to the minimum (*i.e.* to the input which allows an evaluation of the structure from the chemical formula); if, for any purpose, a simplification has been introduced into the formulation of the parameter, this simplification should be based on a physical aspect of the structure and as such should be clearly indicated (the problem of equipartition); although the use of computers facilitates many kinds of calculation, the results of these calculations *i.e.* the values obtained for these parameters, should express a simple concrete aspect of the structure.

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APPENDIX

The relation between the modified sharing coefficient ($C'AC'$) of Parthé & Chabot (1990) and the equations for PP_m

For the case of equipartition, the modified sharing coefficient given by Parthé & Chabot (1990) is as follows:

$$C'AC' = k[2N_{C'-A} - (k+1)(n/m')] \quad (A1)$$

where $N_{C'-A} = 4 - [(1 + 'x')C'C']/2$ for which 'x' relates the average number of $C'—C'$ bonds ($N_{C'-C'}$) to the number of non-bonding orbitals per central atom (C') ('x' = $N_{C'-C'}/C'C'$) (authors' definition) and k is the larger number of $C'—A—C'$ links on which the different anion of a tetrahedron participate and

$$k < [N_{C'-A}/(n/m')] \leq k + 1 \text{ (authors' definition)} \quad (A2)$$

For $VEC_A = 8$, $N_{C'-A} = P$, so that

$$N_{C'-A}/(n/m') = \langle x \rangle$$

and k is equivalent to the integer part of $\langle x \rangle$.

Thus with $a = k$, (A1) is identical to the equation given by Engel (1986) (Table 1). For $VEC_A < 8$,

$N_{C'-A} = P$ but $n/m' = n_o/m'$ in (A2). For $VEC_A > 8$, $N_{C'-A} = P - [1 + 'x']C'C'/2$ and $n/m' = n_o/m'$ in (A2). The definitions for equipartition given by both of us are very different and may lead to diverging results (for GeS there is non-equipartition while calculating PP_m , whereas equipartition is possible according to the calculation of $C'AC'$). A strict correlation between (16) and (A1) in the case of structures with $VEC_A \neq 8$ is therefore tedious and may lose any practical sense.

A simplified case is given by equation (16'). For this equation, k and a coincide, since no more than one $C'AC'$ or two central cations through each apex are expected in the complexes and:

$$C'AC' = PP_m - AA(n_o/m') - 'x'C'C'. \quad (A3)$$

$C'AC'$ may also be derived from the general equation of PP_m (15) with (A3) and becomes incidently a general parameter!

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A New Example of an Arrangement of Antiphase Domains: Investigation by Neutron Diffraction of Deuterated Manganese Fluosilicate

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Abstract

Manganese hexafluorosilicate–deuterium oxide (1/6), $\text{MnSiF}_6 \cdot 6\text{D}_2\text{O}$, $M_r = 317$, hexagonal, $P\bar{3}$ (No. 147), $a = 9.678$ (11), $c = 9.820$ (9) Å, $V = 797$ (3) Å³, $Z = 3$, $D_x = 1.96$ g cm⁻³, $\lambda = 0.8307$ (5) Å, $\mu = 0.50$ cm⁻¹ (evaluated), $F(000) = 32.38$, room temperature, final $R(F) = 0.118$ for 400 observed reflections. Above 244 K $\text{MnSiF}_6 \cdot 6\text{D}_2\text{O}$ is described by fitting the structural models previously proposed for $\text{MgSiF}_6 \cdot 6\text{H}_2\text{O}$ above 300 K and $\text{FeSiF}_6 \cdot 6\text{H}_2\text{O}$ above 240 K. The structure consists of an arrangement of domains of different octahedra orientations with equal volumes. The water molecule is perfectly determined: the D—O bond distances are 0.9287 (8) and 0.9351 (8) Å, and the D—O—D angle is 109.3 (1)°. The lengths of the H bonds are 1.852 (2) and 1.814 (2) Å for D(1)···F and D(2)···F, respectively. When the temperature is lowered from about 244 K, $\text{MnSiF}_6 \cdot 6\text{D}_2\text{O}$ undergoes a structural phase transition with hysteresis of ~4 K.

Introduction

In the fluosilicates $M\text{SiF}_6 \cdot 6\text{D}_2\text{O}$ (M = divalent metal), the two complex ions $M(\text{H}_2\text{O})_6^{2+}$ and SiF_6^{2-}

form octahedra, with a distribution between two orientations around the threefold axis. In the case of Co, Ni and Zn at room temperature, the disordered structure (space group $R\bar{3}$) described by Ray, Zalkin & Templeton (1973) has recently been corroborated by neutron diffraction on $\text{CoSiF}_6 \cdot 6\text{D}_2\text{O}$ at room temperature (Chevrier & Saint-James, 1990). The F sites of the disordered SiF_6 octahedra were found to have equal occupation probability (0.5/0.5), instead of 0.43/0.57 as previously determined. In the case of $\text{MgSiF}_6 \cdot 6\text{H}_2\text{O}$ ($T \geq 300$ K) and $\text{FeSiF}_6 \cdot 6\text{H}_2\text{O}$ ($T \geq 240$ K) the superstructure reflections, inconsistent with the structural models (space group $R\bar{3}m$) described by Syoyama & Osaki (1972) and Hamilton (1962), were explained in terms of an arrangement of antiphase domains. In the crystal, the juxtaposition of domains (space group $P\bar{3}$) with two different octahedra orientations related by pseudo mirrors (11.0) and with equal volumes is sufficient to explain all the experimental observations. In $\text{MgSiF}_6 \cdot 6\text{H}_2\text{O}$ these domains are extensive (Jehanno & Varret, 1975; Chevrier & Jehanno, 1979), whereas in $\text{FeSiF}_6 \cdot 6\text{H}_2\text{O}$ the domain size is a function of temperature (Chevrier, Hardy & Jehanno, 1981).

At room temperature superlattice reflections are also observed for the $\text{MnSiF}_6 \cdot 6\text{H}_2\text{O}$ fluosilicate, and