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Pauling's second crystal rule for nitrogen-substituted crystal structures

PETER E. D. MORGAN
Rockwell International Science Center, Thousand Oaks, California 91320, USA

The use of Pauling's second crystal rule possibly for predicting anion aliovalent substitutions, particularly those of nitrogen replacing oxygen, in crystallographic isotypes is examined. Bond length/bond strength sums are also reviewed for some structures where nitrogen-substitution is known.

1. Introduction

Pauling's second crystal rule (PSCR), states that the bond strength sums from cations arriving at an anion approximately equal the valence of the anion. The bond strength arriving from each cation (V_{cation}) is approximately the valence (not, as in the older form, charge) of the cation divided by its coordination (C_{cation}). This assumes that all bonds on a cation are of equal strength. Thus for n cations around the anion:

$$V_{\text{anion}} \simeq \sum_{1}^{n} \frac{V_{\text{cation}}}{C_{\text{cation}}}$$

This rule was found to work well with many of the early crystal structures that were examined by X-ray diffraction (XRD); these were mostly oxide mineral types, and it greatly simplified the guessing of trial structures. It does not work well for sulphides. The obverse for cations also does not work in this simple form. The rule is exemplified by garnet; in garnet, prototypically grossular $Ca_3Al_2Si_3O_{12}$, we have Ca^{VIII}, Al^{VI}, Si^{IV} and O^{IV} (roman numerals denote coordination, arabic numbers, valence). Each oxygen is coordinated to 2Ca + 1Al + 1Si so that the bond sum at oxygen is

$$\frac{2 \times 2}{8} + \frac{1 \times 3}{6} + \frac{1 \times 4}{4} = 2.$$

The rule is exactly obeyed (as it must be if there is only one type of oxygen). In more complicated cases with different oxygen sites, or with oxygen and, for example, fluorine sites together in one structure, some deviations can occur; although, again, in minerals these are quite small, not usually more than ~15%. The theory still remains important as a guideline to the crystallographic site locations of, say O, OH and F in a mineral, e.g. apatite, topaz or grunerite [1].

For synthetic materials, the deviations from PSCR are sometimes greater, e.g. ±25%, and, as will be noted later, the deviations are often in structures with important physical properties, i.e. ferroelectrics, fast ion conductors, etc. A molecular orbital theory approach has recently given new theoretical underpinning to PSCR [2].

By incorporating bond length/bond strength considerations (that is, not considering all bonds at a cation to be of equal strength) and using a term of the Born repulsion type, Brown, Shannon and Wu (BSW) [3–5] derive a bond sum of the type:

$$V \simeq S = \sum_{1}^{n} K \left(\frac{R}{R_0}\right)^{m}$$

where V is the formal valence, S the bond sum, n the number of coordinated atoms, K, R_0 and m are empirical constants for each cation around oxygen and are derived by computer refinement so that, in known common structures, the value of S is as near to V as possible. R corresponds to the particular measured bond length and R_0, a "normalized standard or average bond". In this case, the bond sums at both cations and anions are best fitted to nearly equal the valencies. It transpires that the degree of covalence or ionicity is unimportant, and that values of m roughly concord with Born expectations (the Born concept is itself empirical). Furthermore, the concept introduced is that of resultant force being the most important bond consideration, rather than the electronic distribution itself. This is a viewpoint that is gaining currency and appears to be applicable to many types, including sulphides, nitrides and others whenever bonds can be discerned as being between an "anion" and a "cation". The materials scientist is referred to an excellent two volume series [6] that gives a good overview of these recent developments in crystal chemical bonding.

2. Methods

We use roman numeral superscripts to indicate the coordination of each atom. For relatively simple nitrides, say, $Li_2^{IV}Zr^{VI}N_2^{VII}$ [7] with one type of nitrogen, $S = 4 \times \frac{1}{4} + 3 \times \frac{4}{6} = 3$, or $Th^{VIII}Be^{IV}N_2^{VI}$ [7], one type of nitrogen, $S = 4 \times \frac{4}{8} + (2 \times 2)/4 = 3$; these are trivial cases where S must equal 3. This is true of $MnSiN_2$, Th_2SiN_4, Ca_3N_2, Be_3N_2, Li_3AlN_2 and so on. With more than one type of nitrogen site, e.g. $La^{VI}Si_3^{IV}N_2^{III}N_3^{IV}$ [8], we find $S_{N(1)} = 3 \times \frac{4}{4} = 3$ and $S_{N(2)} = 2 \times \frac{3}{6} + 2 \times \frac{4}{4} = 3$; again, exact agreement occurs, although, with different nitrogens this need not be so.

For oxynitrides, more complexity is found; in the simple case of $Si_2^{IV}N_2^{III}O^{II}$, $S_N = 3 \times \frac{4}{4} = 3$ and $S_O = 2 \times \frac{4}{4} = 2$, as expected for the nitrogen and

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TABLE I The Brown–Shannon–Wu (BSW) bond sums for cations and anions and the Pauling bond sums at anions in cuspidine

	BSW	PSCR
Si(1)	4.06	–
Si(2)	4.03	–
Ca(1)	2.09	–
Ca(2)	2.13	–
Ca(3)	1.90	–
Ca(4)	1.90	–
O(1)	2.22	2.54
O(2)	1.81	1.87
O(3)	1.77	1.90
O(4)	1.94	1.87
O(5)	1.90	1.91
O(6)	1.95	1.87
O(7)	1.91	1.82
F(1)	1.28	1.16
F(2)	1.32	1.07

TABLE II Bonds sums (type indicated) for other cuspidine structure types

Anion position	BSW		Pauling	
	$Eu_4Al_2O_9$	$Ca_4Si_2O_7F_2$	$Y_4Al_2O_9$	$Y_4Si_2O_7N_2$
1	2.04	1.91	2.11	2.36‡
2	2.04	1.90	2.11	2.36‡
3	1.73	1.82	1.68	1.93
4	1.88	1.87	2.11	2.36‡
5	2.15	2.54	2.36	2.86‡
6	1.92	1.87	2.04	2.29
7	1.73	1.87	2.11	2.36‡
8	1.92	1.16*	1.79	1.79
9	2.16	1.07*	1.71	1.71

*In cuspidine, fluorine goes to 8 and 9, each four coordinate to calcium only.

‡In $Y_4Si_2O_7N_2$, nitrogen goes to 5, four coordinate to 2Si and 2Y, and 1, 2, 4, or 7, four coordinate to 1Si and 3Y.

oxygen sites. For the wurtzite-like $Li^{IV}Si^{IV}O^{IV}N^{IV}$, neutron diffraction indicates that nitrogen and oxygen are ordered [9, 10], nitrogen is linked to 3Si and 1Li, $S_N = 3 \times \frac{4}{4} + \frac{1}{4} = 3\frac{1}{4}$, O is linked to 1Si + 3Li, $S_O = \frac{4}{4} + 3 \times \frac{1}{4} = 1\frac{3}{4}$. This arrangement therefore leads to values near 2 (for oxygen) and near 3 (for nitrogen) and might have been predicted. A range of at least $\pm\frac{1}{4}$ around the whole number value is immediately suggested as possible. However, this encouraging case is offset by cases such as rocksalt, Mg_2NF, all anion bond sums 2, and wurtzite Al_2OC, all anion bond sums 3.

It is particularly instructive to look at a case where oxides, oxyfluorides and oxynitrides are already known in one crystal family, e.g. as in the cuspidines. The numbering schemes and conventions are as in the cited references and the reader is referred to these for the structural details.

The Brown, Shannon and Wu (BSW) [3–5] bond sums for all ions and the PSCR sums for anions for cuspidine, $Ca_4Si_2O_7F_2$, [11], a fairly rare mineral, are given in Table I. This structure is monoclinic and all anion sites are nonequivalent. The mineral does not closely obey PSCR. In sites assumed occupied by oxygen for the refinement, O(1)–O(7), wide variations occur with a greatly overbonded site O(1) at 2.54 where the coordination is to 2Si and 2Ca. At the low bonded O(7) site, the sum is 1.82. For the BSW bond sums, the situation is slightly better in that the O(1) site is now 2.22, but the lowest oxygen site is 1.81 for O(2). Unfortunately, bond lengths, only obtainable from crystal refinements, are necessary *in advance* for these calculations. We will need calculated bond length/bond strength values for M–N and M–F bonds to proceed further (a few, tabulated in [6], generally very similar to M–O bonds). Assuming the same values for M–F as for M–O, produce the F(1) and F(2) values in the table. The simple PSCR values are better at 1.16 and 1.07, approximating 1 as expected, obeying a rule, not perhaps sufficiently well-known, that fluorine is never bonded to silicon in silicate minerals.

By varying the valencies of the cations, as for a substitution of Al^{3+} for Si^{4+} or Y^{3+} for Ca^{2+}, using the normal ionic radii and crystallochemical guidelines for likely substitutions, we may calculate the PSCR bond sums shown in Table II. BSW sums for anions are calculated here for the isotypic $Eu_4Al_2O_9$ [12] (the numbering of sites in the refinements of the latter and for $Ca_4Si_2O_7F_2$ [11] is different in the literature); comparing BSW and PSCR we see a better fit for the former. In terms of predictability of structures, starting with cuspidine and attempting to predict the existence of $Y_4Al_2O_9$, we would have noted the low values at the 3 and 9 sites, but a better fit at the 5 site than for cuspidine itself. For predicting $Y_4Si_2O_7N_2$, a known cuspidine [13, 14], we would observe a low value at site 9, a high value at site 5 (2.86), very suitable for nitrogen and other sites at 2.36 where other nitrogens might go.

We conclude immediately that poor Pauling sums do not rule out the existence of the isotypic species. The question then remains as to whether good bond sums actually imply the existence of a substituted isotope.

As an example, we may consider melilites (Table III). Simply, these are continuous tetrahedral sheet structures (i.e. sheets of tetrahedral silicon, aluminium, magnesium, beryllium, etc.) with oxygen bridges within the sheets and terminal oxygens at the faces of sheets bonding across to large cations between the sheets [15, 16]. In normal oxygen mellilites, Pauling bond sums are very variable (the very ability for a structure to have wide values probably accounts for the wide variety of substitutants that it may contain). The yttrium nitrogen variety [17] in fact, more closely approximates good fit values with the inference that nitrogen is in the sheet bridging sites (with one left

TABLE III Pauling anion bond sums for melilites

	Anion	Bond sum
$NaCaAlSi_2O_7$		
$Ca_2Al_2SiO_7$	O(ter.)	1.5–2.125
$Ca_2MgSi_2O_7$	O(br.)	1.75–2.25
$Y_2Be_2SiO_7$		
$Y_2Si_3O_3N_4$	(ter.)	2.25 2 sites
	(br.)	2.75 5 sites
$Ca_2Si_3O_5N_2$	(ter.)	1.75
	(br.)	2.75

TABLE IV Pauling and BSW bond sums in α-wollastonites

	PSCR bond sums			BSW bond sums	
	α-$CaSiO_3$	$YSiO_2N$	$YbBO_3$	$YbBO_3$	$YbBO_3$
Large cation	Ca^{VIII}	Y^{VIII}	Yb^{VIII}	Yb^{VIII}	$Yb^{VI} + Yb^{XII}$ [20]
Coordination	8O	6O + 2N	8O	8O	6O 12O
				3.26	2.82 2.03
Small cation	Si^{IV}	Si^{IV}	B^{IV}	B^{IV}	B^{IV}
Coordination	4O	2O + 2N	4O	4O	4O
				2.99	2.91
Anion(s)	O^{IV}(ter.)	O^{IV}(ter.)	O^{IV}(ter.)	O^{IV}(ter.)	O^{IV}(ter.)
Coordination	3Ca + Si	3Y + Si	3Yb + B	3Yb + B	$2Yb^{VI} + Yb^{XII}$ + B
	1.75	2.13	1.88	1.95	1.81
	I^{IV}(br.)	N^{IV}(br.)	O^{IV}(br.)	O^{IV}(br.)	O^{IV}(br.)
Coordination	2Ca + 2Si	2Y + 2Si	2Y + 2B	2Y + 2B	$2Yb^{XII}$ + 2B
	2.50	2.75	2.50	2.35	1.85

over) and the oxygen primarily in the terminal sites. Values for recently synthesized $Ca_2Si_3O_5N_2$ [18] are also given. A complete range of solid solution from $Ca_2Al_2SiO_7$ to $Ca_2Si_3O_5N_2$ has been identified. The last two cases suggest a guideline (rule?) that nitrogen most usually prefers bonding to silicon in nitrogen silicates (as opposed to fluorine). Given the stability of the oxygen melilites in spite of the poor Pauling bond sums, we might have predicted the possibility of the nitrogen-containing isotypes.

The α-wollastonites (Table IV) are an important group. In order to explain the "busy" table, in the first column for α-$CaSiO_3$ we have: Ca^{VIII} coordinated by eight oxygens, Si^{IV} coordinated by four oxygens. Oxygens and silicons are in six membered rings of alternating silicon and oxygen. Terminal oxygens coming off silicon in the ring are coordinated to 3Ca and Si for a bond sum of 1.75. Bridging oxygens in the rings are coordinated to 2Ca and 2Si for a bond sum of 2.50, which is overbonded, accounting perhaps for the fact that α-$CaSiO_3$ is not the most stable form of wollastonite. For $YSiO_2N$, [19] O(term.) is 2.13 and N(br.) is 2.75 (assuming that the terminal site contains oxygen and the bridging site nitrogen because of these values), fitting the formula requirements exactly as there are twice the number of terminal positions as bridging ones. The close approach of these bond sums to the "ideal" values may explain where here the α-wollastonite structure appears to be the most stable, if not the only, form of $YSiO_2N$. BSW calculations allow us to decide that $YbBO_3$ is probably also an α-wollastonite, for, as in column 4, this type gives much better BSW bond sums than the former suggested type [20] in column 5. $CeSiO_2N$ and $LaSiO_2N$ behave similarly to $YSiO_2N$ [21].

The apatites form a flexible group of structures; we begin to note that it is the structures with more unusual higher coordinations and the possibility of long bonds which can lead to this. In hydroxyapatite [22], there are two distinct calcium sites, each of which has "long bonds" which various authors have treated differently in bonding relationships. Here, we treat the structures in two ways, and the BSW sums allow some interesting discriminations. Table V summarizes the case where we include the long Ca_I–O_{III} bonds in the coordination scheme. This leads to Ca_I^{IX} and Ca_{II}^{VII}. For this scheme, the BSW sums come close to the valency values; the "long bonds" are, indeed, contributing in $Ca_5(PO_4)_3OH$, and illustrate the value of the BSW calculations. Pauling sums are also satisfactory for this assumption.

On this basis, for $Y_5(SiO_4)_3N$, the formula originally proposed [17], we find no good site for nitrogen, although for a defect case, assuming a vacancy as a zero valent atom [23], we improve the bond sum at the O_{III} site. As yttrium is a little smaller than calcium, and with higher formal charge, it could be expected that the coordination at yttrium might decrease so that it is effectively six coordinated, as minor shifts of atoms cause the "long bonds" to become noncontributing. This possibility is illustrated in Table VI; here the BSW values for $Ca_5(PO_4)_3OH$ become unsatisfactory, especially at Ca_I; the Pauling sums also agree less well. But, we see a much better suggested site for nitrogen

TABLE V Bond sums in hydroxyapatite, including long Ca(1)–O(3) and Ca(2)–O(1) bonds

Position	No. atoms in unit cell	Coordination	BSW $Ca_5(PO_4)_3OH$	PSCR bond strength sums at equivalent anion sites		
				$Ca_5(PO_4)_3F$	"$Y_5(SiO_4)_3N$"	$Y_5(SiO_3N)_3$□
$Ca(1)^{IX}$	4	3O(1) + 3O(2) + 3O(3)	2.001			
$Ca(2)^{VII}$	6	OH + O(1) + O(2) + 4O(3)	2.057			
P^{IV}	6	O(1) + O(2) + 2O(3)	5.197			
$O(1)^{IV}$	6	P + 2Ca(1) + Ca(2)	1.985	1.98	2.10	2.16
$O(2)^{IV}$	6	P + 2Ca(1) + Ca(2)	2.077	1.98	2.10	2.16
$O(3)^{IV}$	12	P + Ca(1) + 2Ca(2)	2.096	2.04	2.19	2.33†
OH^{III}	2	Ca(2)	1.000*	0.86	1.29	0 for □

*Assumed – confirmed by bond sum at Ca_{II} nearly equal to 2.0.
†O_{III} sites half filled with nitrogen.

TABLE VI Bond sums in hydroxyapatite, not including long bonds

Position	No. atoms in unit cell	Coordination	BSW $Ca_5(PO_4)_3OH$	PSCR bond strength sums at equivalent anion sites		
				$Ca_5(PO_4)_3F$	"$Y_5(SiO_4)_3N$"	$Y_5(SiO_3N)_3$□
$Ca(1)^{VI}$	4	3O(1) + 3O(2)	1.622			
$Ca(2)^{VI}$	6	OH + O(2) + 4O(3)	1.907			
P^{IV}	6	O(1) + O(2) + 2O(3)	5.197			
$O(1)^{III}$	6	P + 2Ca(1)	1.834	1.92	2.00	2.06
$O(2)^{IV}$	6	P + 2Ca(1) + Ca(2)	2.077	2.25	2.50	2.60†
$O(2)^{III}$	12	P + 2Ca(2)	1.970	1.92	2.00	2.20
OH^{III}	2	Ca(2)	1.000*	1.00	1.50	0 for □

*Assumed – confirmed by bond sum at Ca_{II} nearly equal to 2.0.
†O_{III} sites half filled with nitrogen.

in "$Y_5(SiO_4)_3N$"; and for the defect case, the O_{II} position appears to be where nitrogen would reside. Moreover, there are three O_{II} sites per formula unit, and if nitrogen goes here, then nitrogen richer compositions are possible than if nitrogen were restricted to the trigonal OH type sites. This idea supports the notion that nitrogen is bonded to silicon in nitrogen-apatites, and that the formula is more closely represented by $Y_5(SiO_3N)_3$ □ than by "$Y_5(SiO_4)_3N$"; nitrogen-rich apatites have indeed been observed [24]. It is further suggested that Y^{3+} is probably 6-coordinate in this compound.

$CaAl_4O_7$ [25] is an interesting crystal structure, with all Al^{IV}, where a nitrogen containing isotype is definitely predicted with coupled substitution of silicon. Table VII shows the coordination arrangement in this structure, with four independent anion sites, and with the aliovalent cation substitutions. The first column for $CaAl_4O_7$ shows the bond range for the variable structural type. A computer program, written for the task, by trying all possible substitutions of aliovalent ions in the Ca, Al(1) and Al(2) sites and then calculating bond sums of the O(1)–O(4) sites, found 16 cases where each bond sum was $n \pm 0.30$ for $n = 1$(F), 2(O), or 3(N) and with the necessary restriction that the total bond sum at anions also equals the total valency of the cations.

The fourth column illustrates such a case for substitution of Al(2) by Si(2); the O(4) site, with a bond sum of 2.75, becomes a potential site for nitrogen; the other sites remain oxygen sites. The synthesis of "$CaAl_2Si_2O_5N_2$" was, therefore, attempted, but proved to be difficult. Several techniques were tried including firing chemically prepared hydroxide mixtures in ammonia to ~1200° C, heating to higher temperatures to form glasses and then cooling, firing mixed Si_3N_4, $CaCO_3$ and $Al(OH)_3$, in N_2/6% H_2 etc. About ten attempts were made in all, always with the result that mixtures were achieved which seemed to contain lines for "$CaAl_2Si_2O_5N_2$", but which also contained glasses and, in some cases, a nitrogen-gehlenite.

TABLE VII Pauling bond sums in the monoclinic $CaAl_4O_7$ type

Position	Coordination	Pauling bond sums	
		$CaAl_4O_7$	"$CaAl_2Si_2O_5N_2$"
Ca^{VIII}	O(1) + 4O(2) + 2O(3)		
$Al(1)^{IV}$	2O(2) + O(3) + O(4)		
$Al(2)^{IV}$	O(1) + O(3) + 2O(4)		
$O(1)^{III}$	Ca + 2Al(2)	1.786	2.286
$O(2)^{IV}$	2Ca + 2Al(1)	2.071	2.071
$O(3)^{III}$	Ca + Al(1) + Al(2)	1.786	2.036
$O(4)^{III}$	Al(1) + 2Al(2)	2.250	2.750(N)

Table VIII illustrates a similar analysis for the K_2NiF_4 group of structures [26] where nitrogen-containing species have been found [27]. For the oxyfluorides, which are well-known, it appears that fluorine goes to the O(1) or apical site in octahedral sheets of small cations [28]. However, for the nitrides, nitrogen should occupy preferentially the bridging sites between the octahedra. The structures with nitrogen in them do not obey PSCR well and could not have been predicted to exist by this approach.

Table IX covers the β-K_2SO_4 types [29], where nitrogen members have been observed [30]. Using the parent K_2SO_4 data with the aliovalent substitutions, the $KBaPO_4$ and Ba_2SiO_4 types are predicted (they are known), but K_2PO_3F, which is known, would not be predicted. For $LnEuSiO_3N$, values calculated would not have predicted that the type might be stable (it is [30]).

3. Conclusions

1. When the PSCR rule is well obeyed in an oxide, as in most minerals, then we can expect that for stable nitrogen-substituted isotypes the rule will still apply. This is the case for most simple nitrides, e.g. Mg_3N_2 (antibixbyite), Th_2SiN_4 (Ca_2SiO_4 type), AlN or $MgSiN_2$ (wurtzite), etc. If calculations indicate that poor agreement would be achieved in nitrogen-substitution, i.e. sums not within ±0.25 of whole numbers, then it appears unlikely that the compound would form, a compound of type 2 below being preferred or a new type or none at all.

2. When PSCR rule applies poorly in an oxide, as for apatite, cuspidine, melilites and generally rarer mineral types, and also for many synthetic materials with unusual properties such as β-aluminas [32] or ferroelectrics, then nitrogen substituted cases may follow the rule even more poorly. But it is just in these cases where nitrogen-substitution is sometimes encountered (other factors, radii, electropositivity, etc., permitting). So when there is poor agreement, when the likelihood cannot be strictly predicted, these are cases which should, in fact, be investigated.

3. In spite of the proviso in 2 above, in many cases

TABLE VIII Pauling bond sums in tetragonal K_2NiF_4, (A site)$_2$ (B site) (anion)$_4$

Position	Coordination	K_2NiF_4	K_2TiO_2F	Sr_2FeO_3F	Sr_2TiO_4	La_2NiO_4	$LaSrAlO_4$	La_2AlO_3N	$La_2TiO_2N_2$
A^{IX}	5O(1) + 4O(2)								
B^{VI}	2O(1) + 4O(2)								
$O(1)^{VI}$ apical	5A + B	0.89	1.22	1.61	1.78	2.00	1.89	2.17	2.42
$O(2)^{VI}$ bridge	4A + 2B	1.11	1.78	1.89	2.22	2.00	2.11	2.33	2.67

*$NaLaTiO_4$ is a different, most unusual, type [31].

TABLE IX Pauling bonds sums for the β-K_2SO_4 structure type

Position	Coordination	K_2SO_4	K_2PO_3F	$KBaPO_4$	Ba_2SiO_4	$LnEuSiO_3N$ [28]
$K(1)^{XI}$	2O(1) + 3O(2) + 6O(3)					
$K(2)^{IX}$	3O(1) + 2O(2) + 4O(3)					
S^{IV}	O(1) + O(2) + 2O(3)					
$O(1)^{VI}$	2K(1) + 3K(2) + S	2.015	1.65	1.947	2.030	2.364
$O(2)^{VI}$	3K(1) + 2K(2) + S	1.995	1.94	2.018	1.990	2.030
$O(3)^{VI}$	3K(1) + 2K(2) + S	1.995	1.94	2.018	1.990	2.030

(but not always), the position of the nitrogens in the anion lattice may be predictable. In many instances, certain anion sites with clearly higher values than others, is where the nitrogens should be located. For the case studied by neutron diffraction [10], this is so. As for this case, it is expected that the nitrogen will tend to be bonded to the higher valent cations in mixed structures. In the cases studied containing silicon, the nitrogen seems to be preferentially bonded to this higher valent element. For the same reason, nitrogen will be in a different site in oxynitrides than fluorine in oxyfluorides. This is clearcut to the apatite and cuspidine cases.

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