Crystal-Chemical Formulae for Simple Inorganic Crystal Structures

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Abstract

Crystal-chemical formulae are presented which allow one to denote in condensed form the most important structural features of simple inorganic crystal structures. These formulae are not only an aid for the teaching of crystal chemistry, but are equally useful for a complementary explanation of structural drawings or a rapid description of simple crystal structures. The proposal discussed here is an extension of the constitution formulae proposed by Machatschki [*Monatsh. Chem.* (1947). **77**, 333–342]. The new formulae have been designed to allow the special structural features of polyanionic or polycationic valence compounds or tetrahedral structure compounds to be written down in a simple self-explanatory manner.

Introduction

A crystal structure is in principle sufficiently documented if lattice constants, space group and atom positions are given. However, in most cases, these crystallographic data do not permit the reader to realize without further help the spatial arrangement of the atoms. It is usually necessary to complement the crystal structure data with drawings. In fact, the exact crystallographic data are of no direct interest for crystal-chemical considerations. For the crystal chemist they serve only to derive important structural features such as the linkage type of the structure (three-dimensional, layer structure, fibre or molecule), individual atom coordinations, presence of non-bonding orbitals *etc*. For crystal-chemical studies it is advantageous to develop a simple notation for the most important geometrical properties of crystal structures. Formulae which permit one to write down the structural features in symbolized form are called crystal-chemical formulae.

Crystal-chemical formulae are burdened with the problem that simple symbols cannot reproduce all the details of a three-dimensional structure. For many crystal-chemistry problems it is, however, sufficient to indicate (admittedly with a loss of detail and precision)

only the most obvious structural features. The crystal-chemical formulae presented here have been used with success in crystal-chemistry courses. They permit the student not only to recognize readily the geometrical relationships of simple crystal structures but also help him to memorize them easily. Crystal-chemical formulae are further useful as a complementary aid to the explanation of crystal structural drawings which are not always understood at first sight. Thus it would be of some use if both structural drawings and crystal-chemical formulae are published together, which would also obviate the need for long structural descriptions.

General conditions and requirements for crystal-chemical formulae

Crystal-chemical formulae have already been proposed by various authors. Examples are the *Aufbauformeln* of Laves (1930), the notation proposed by Niggli (1945), the construction formulae of Machatschki (1947) and the inorganic structure type notation described by Lima-de-Faria & Figueiredo (1976, 1978), amongst others. The last-mentioned authors give a list of other proposals for structure classifications. Except for the crystal-chemical formulae of Machatschki, which are used occasionally by mineralogists, these notations are not applied systematically. The reasons why they are not very successful is that they are not general enough.

Crystal-chemical formulae should be devised according to the following general conditions:

(*a*) A crystal-chemical formula should retain as much as possible of the usual chemical formula. This is not the case with the formulae proposed by Laves, particularly for ternary compounds.

(*b*) A crystal-chemical formula should be simple and as far as possible self-explanatory. There should be no need to look up tables to understand the formula. This need arises, however, with the formulae proposed by Lima-de-Faria & Figueiredo (1976, 1978) which attempt to describe the finer structural details in a rather complicated fashion.

(*c*) A crystal-chemical formula should allow a flexibility in notation. Depending on the application, it

might not be necessary to indicate the structural features of all atoms in the structure. Thus, abbreviated forms of the complete crystal-chemical formula should be easily understandable.

(*d*) A crystal-chemical formula should be easy to print.

In a crystal-chemical formula one should have the possibility of denoting in symbolic form the following structural features:

(1) *The linkage type of the structure*. It should be possible to recognize if the structure is three-dimensional or if it can be described as a layer, fibrous or molecular structure. Nearly all known crystal-chemical formulae allow the linkage type to be written down. For a molecular structure we should be able not only to read the number of atoms in the molecule but also to deduce the shape of the molecule (chain, ring or cage).

(2) *The type of linkage certain atoms or atomic groups have with themselves* (partial structure features). Crystal-chemical formulae should also permit one to describe the partial structure of the individual atoms. It is to be understood here that a partial structure of one given element is completely independent of the presence or spatial arrangement of other elements in a structure. The other elements are intentionally overlooked. Thus, the observation, for example, that a partial structure molecule is present in a particular structure is not to be interpreted as meaning that there is only bonding between the atoms comprising the partial structure molecule; they may have equally strong or stronger bonds with other atoms outside the partial structure. The partial structure is, nevertheless, an important structural feature particularly for the polyanionic and polycationic valence compounds where certain partial structure features can be calculated beforehand with the extended $(8 - N)$ rule (see later). The construction formulae of Machatschki (1947) and the Niggli (1945) notation do not provide for the proper distinction between hetero- and homonuclear coordinations which are of importance for the proper description of these compounds.

(3) *The coordination polyhedra of the different atoms*. The coordination polyhedra should be characterized by the number of atoms in the first coordination sphere and also by their geometric form. Moreover, it is important to differentiate clearly between heteronuclear and homonuclear surroundings. In many simple valence compounds the coordination polyhedron is clearly defined and the formulation of a crystal-chemical formula does not create any difficulties. However, in many intermetallic compounds the coordination is not easily recognizable and one has to apply, for example, the distance-gap criterion (Brunner & Schwarzenbach, 1971) or the Voronoi polyhedron construction (Frank & Kasper, 1958) for their determination. Even then these methods may fail to give

satisfactory results, in which case no crystal-chemical formulae can be formulated for them along the lines proposed in this article. Such instances should not, however, lead to a neglect to write one in those cases where they can be easily defined.

(4) *Presence of non-bonding orbitals*. For tetrahedral structures it is possible to state where and how many non-bonding orbitals are to be found on the atoms. Non-bonding orbitals are difficult to verify experimentally. However, they can be recognized indirectly in the structure by the lack of a (possible) bond or, put another way, by the absence of a (possible) neighbouring atom.*

Description of the proposed crystal-chemical formulae

The crystal-chemical formulae we propose here are essentially based on the notation of Machatschki (1947), which has had to be extended to allow for the indication of all of the above-mentioned structural features.

1. *The linkage type of the overall structure*

One starts with the usual chemical formula and writes in front of it:

$_{\infty}^{3}$ for a three-dimensionally linked structure;

$_{\infty}^{2}$ for a layer structure;

$_{\infty}^{1}$ for a fibre structure.

For finite molecules the chemical formula is surrounded by square brackets. The number of atoms inside the square brackets corresponds to the number of atoms in the molecule. This is simply done by multiplying the composition parameters by an appropriate factor. To characterize the shape of the molecule a special symbol can be written before the square brackets:

∧[ ] an angle sign indicates a chain structure of finite length;

○[ ] a circle is used for a cyclic structure;

Ⓥ[ ] a circle with an inscribed angle is used as the symbol for a cage molecule.

It is probably difficult to find a short notation to describe the structural details of the different cage molecules. However, it was felt important to retain a simple notation even if the cage molecules are not sufficiently described. We note that the tetrahedron is the only possible regular cage molecule consisting of four atoms. Elementary structures as examples:

$_{\infty}^{3}$C   for diamond;

$_{\infty}^{2}$C   for graphite;

$_{\infty}^{1}$Se   for fibrous selenium;

∧[Cl$_2$]   for the diatomic chlorine molecule;

○[S$_8$]   for *cyclo*-octasulphur;

Ⓥ[P$_4$]   for the P tetrahedra in white phosphorus.

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* The indirect proof of the presence of non-bonding orbitals given here is important for the interpretation of crystal structures. It might, however, have to be modified in accordance with photo-electric spectroscopy results.

To simplify the crystal-chemical formula the $\frac{3}{\infty}$ symbol can often be omitted. There is also no need to write the angle sign in front of a diatomic molecule, as has been done for demonstration in the above example.

Optionally, it is possible to insert small numbers in the symbols for the molecular shapes, such as $\triangle$, ⑧ or ⑨, which then indicate the number of atoms in the finite chain, the ring or the cage molecule, respectively. This is normally not necessary because the number of atoms in the molecule can be obtained from the number of atoms inside the square brackets. However, the inscribed number should be indicated if the chain, ring or cage molecules have side chains. The inscribed numbers then correspond to the number of atoms which alone form the chain, ring or cage. An example is given in Fig. 1.

2. The linkage type of the partial structures

To indicate the linkage type which atoms have with other atoms of the same kind (or to characterize the linkage certain atomic groups have with themselves) one can apply the same symbols described above but they are now placed before each element (or atomic group). Through sufficient use of round brackets one can make certain that the interpretation is unique. We note that, as above, the number of atoms inside squar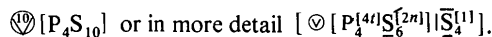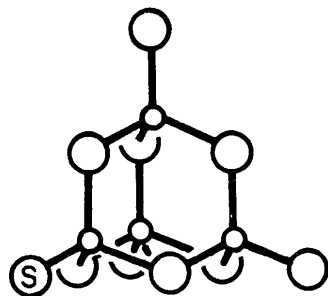e brackets must correspond to the number of atoms in the partial structure molecule. Examples are given in Figs. 2 to 6.

The same notation can also be applied to denote the linkage between certain atomic groups in the structure such as the linkage of tetrahedra. This is best demonstrated by the crystal-chemical formulae of different simple silicate structures:

Nesosilicate	Garnet	$Ca_3Al_2[SiO_4]_3$
Sorosilicate	Thortveitite	$Sc_2\triangle[Si_2O_7]$
	Kinoite	$Ca_2Cu_2\triangle[Si_3O_{10}].2H_2O$
Inosilicate Pyroxene	Enstatite	$Mg_\infty^1(SiO_3)$
Amphibole	Tremolite	$Ca_2Mg_5(OH)_2{}_\infty^1(Si_4O_{11})_2$
Cyclosilicate	Beryl	$Be_3Al_2 \circledcirc [Si_6O_{18}]$
Phyllosilicate	Petalite	$LiAl_\infty^2(Si_2O_5)_2$.

For neso-, soro- and cyclosilicates the number of tetrahedra which are linked together can be obtained from the number of central atoms, i.e. Si atoms, inside the square brackets. For additional clarity a small number can be inserted in the symbol for a finite chain or the symbol for a ring which indicates the number of tetrahedra involved in the construction of the chain or ring.

Except for the optional symbols for the finite chain or the ring molecule, these formulae are already used by mineralogists, who have developed an extensive notation, based on Machatschki's (1947) formulae, which allows one to describe the more complicated tetrahedron linkage in silicates (Liebau, 1969). The two notations are compatible, except that square brackets

⑨ $[P_4S_{10}]$ or in more detail $[\circledcirc [P_4^{[4t]}\underline{S}_6^{[2n]}]|\underline{S}_4^{[1]}]$.

Fig. 1. Structure of the P_2S_5 molecule [SR (1965) 30A, p. 353]. The cage without side chains consists of ten atoms only. For P_2S_5: $(VEC)_A = 8$, $AA = CC = 0$, $VEC = 5\frac{5}{7}$, $N_{NBO} = \frac{12}{7} \equiv 24$ non-bonding orbitals/formula P_4S_{10}.
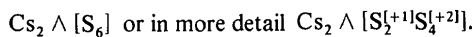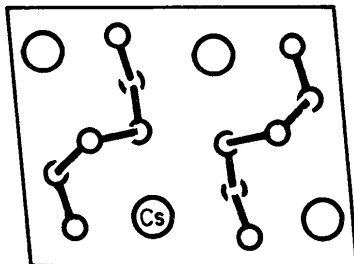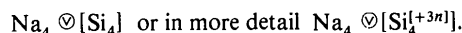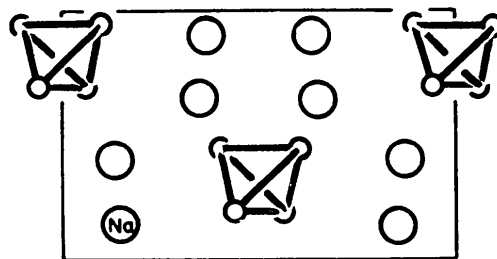

$Cs_2 \wedge [S_6]$ or in more detail $Cs_2 \wedge [S_2^{[+1]}S_4^{[+2]}]$.

Fig. 2. Structure of CsS_3 with sulphur chains consisting of six atoms [SR (1953) 17, p. 448]. For CsS_3: $(VEC)_A = 6\frac{1}{3}$, $AA = 1\frac{2}{3}$, $L = 6$.

$Na_4 \circledcirc [Si_4]$ or in more detail $Na_4 \circledcirc [Si_4^{[+3n]}]$.

Fig. 3. Structure of NaSi with Si_4 tetrahedra [SR (1964) 29, p. 57]. Only half the unit cell is shown. For NaSi: $(VEC)_A = 5$, $AA = 3$.

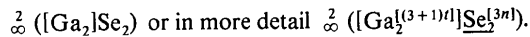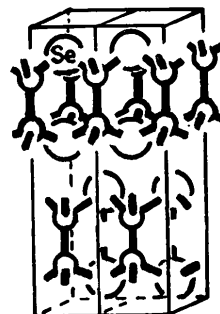$\frac{2}{\infty}([Ga_2]Se_2)$ or in more detail $\frac{2}{\infty}([Ga_2^{[3+1)t]}\underline{Se}_2^{[3n]})$.

Fig. 4. The layer structure of GaSe [SR (1966) 17, p. 166]. For GaSe: $(VEC)_A = 9$, $CC = 1$, $VEC = 4\frac{1}{2}$, $N_{NBO} = \frac{1}{2} \equiv 2$ non-bonding orbitals/formula Ga_2Se_2.

are used now exclusively for finite partial structure molecules, but round brackets for an infinite tetrahedron assembly.

3. *The individual atom coordinations*

One writes after every element an exponent, surrounded by square brackets, which corresponds to the number of atoms in the first coordination sphere. The geometrical shape of the first coordination polyhedron can be further identified by additional small self-explanatory letters as given in Table 1. A similar extension of the Machatschki (1947) formulae has been proposed by Zemann (1969). With these extended symbols it is now easy to distinguish between, for example, $Zn^{[4t]}S^{[4t]}$ and $Pt^{[4p]}S^{[4t]}$ or $Na^{[6o]}Cl^{[6o]}$ and $Ni^{[6o]}As^{[6p]}$ or $Si^{[4t]}O_2^{[2n]}$ and $Cu_2^{[2l]}O^{[4t]}$.

Furthermore, one should be able to indicate if there are atoms in the coordination polyhedron which are (chemically) identical to the atom at the centre of the polyhedron. Inside the square brackets of the coordination exponent there will then be two numbers separated by a plus sign. The first number refers to the number of atoms of different kinds (heteronuclear surrounding) and the second the number of atoms of the same kind (homonuclear surrounding). The structures shown in Figs. 2 to 6 serve as examples of this.
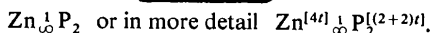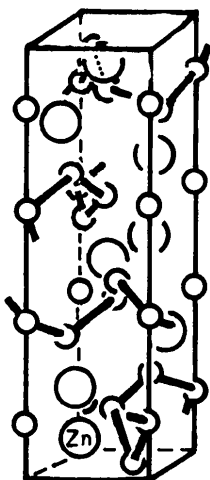

$Zn_\infty^1 P_2$ or in more detail $Zn^{[4t]} {}_\infty^1 P_2^{[(2+2)t]}$.

Fig. 5. The structure of red ZnP_2 with infinite phosphorus chains [SR (1963) 28, p. 37]. For ZnP_2: $(VEC)_A = 6, AA = 2, VEC = 4, N_{NBO} = 0$.
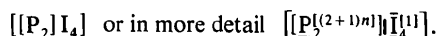

$[[P_2]I_4]$ or in more detail $[[\underline{P}_2^{[(2+1)n]}]\underline{I}_4^{[1l]}]$.

Fig. 6. The molecular structure of P_2I_4 [SR (1956) 20, p. 254]. For PI_2: $(VEC)_A = 9\frac{1}{2}, CC = 1\frac{1}{2}, VEC = 6\frac{1}{2}, N = 6, N_{NBO} = 2\frac{1}{3} \equiv 14$ non-bonding orbitals/formula P_2I_4.

Naturally it is always possible to simplify the crystal-chemical formulae. It is not necessary always to denote the coordination of all atoms. But the convention should be observed that in the coordination exponent the number of atoms of the same kind, *i.e.* the homonuclear coordination number, is always preceded by a plus sign in order to identify it as such. For example, for pyrites with its S–S dumb-bells, the formula can be written as $FeS_2^{[+1l]}$ but not $FeS_2^{[1l]}$. The + sign in the coordination exponent will in general not be misunderstood to mean a positive charge, because charges are customarily never enclosed in square brackets and are usually written as a number followed by a + or − sign, *e.g.* $Fe^{2+}[S_2]^{2-}$. However, if the need is felt to eliminate the last trace of possible doubt in the interpretation of a crystal-chemical formula both homo- *and* heteronuclear coordination can be indicated. The short formula for pyrites is then $FeS_2^{[3+1l]}$. For reasons of internal consistency one should use the + sign for the atomic coordination of elementary structures, even though all bonds are only between atoms of the same kind.

Examples: $Cu^{[+12c]}$, $Mg^{[+12h]}$, ${}_\infty^2 C^{[+3p]}$, ${}_\infty^3 C^{[+4t]}$.

In the case that the coordination is not uniquely determined by one distance, it is optionally possible also to indicate in the exponent the number of next-nearest neighbours. These numbers have to be surrounded by round brackets.

Example: $W^{[+8c(+6o)]}$.

Thus it becomes possible to distinguish between cubic diamond $C^{[+4t(+12)]}$ and hexagonal diamond (lons-

Table 1. *The simple coordination figures and the corresponding symbols for the coordination exponent of the crystal-chemical formula*

o—•—o	$2l$	*l*inear
o—•—o	$2n$	*n*on-linear
	$3p$	trigonal *p*lanar
	$3n$	trigonal *n*on-planar
	$4t$	*t*etrahedral
	$4p$	square *p*lanar
	$6o$	*o*ctahedral
	$6p$	trigonal *p*rismatic
	$8c$	*c*ubic
	$12c$	*c*ubo-octahedral as in *c*ubic close packing
	$12h$	coordination as in *h*exagonal close packing

dalite) $C^{[+4t(+12h)]}$ or between zinc blende $Zn^{[4t+(12c)]}S$ and wurtzite $Zn^{[4t+(12h)]}S$.

If different atoms participate in the formation of the coordination polyhedron it might be desirable for extra clarity to add their chemical symbols to the numbers in the coordination exponent.

Example: Perovskite $Ca^{[12cO]}Ti^{[6oO]}O_3^{[4Ca+2Ti]}$.

A first check on these formulae is given by an elementary rule which relates coordination number and composition parameters and which forms the basis for the notation proposed by Niggli (1945). For a crystal-chemical formula of the general type

$$A_m^{[aA+uB+vC]}B_n^{[wA+bB+xC]}C_o^{[yA+zB+cC]}$$

where m, n and o are composition parameters and a, b, c, u, v, w, x, y and z are coordination numbers, the following relations exist.

$$mu = nw, \quad mv = oy \quad \text{and} \quad nx = oz.$$

Expressed in words, this means that in a structure the total number of bonds which radiate from all A atoms and extend to the B atoms must be equal to the total number of bonds which radiate from all B atoms and extend to the A atoms. Corresponding relations exist for the pairs AC and BC.

One notes that the coordination numbers a, b and c which describe the homonuclear surroundings are not fixed by these relations. Only in the special cases of polycationic or polyanionic valence compounds, to be discussed later, do relations exist which determine the homonuclear coordination numbers.

There exists also the possibility optionally to indicate the linkage of atomic groups with atoms outside this group by denoting a coordination exponent for the atomic group. As an example we shall give the crystal-chemical formula of RbP_7, which is characterized by a polyphosphide anion shown in Fig. 7. The P atoms form cages of seven atoms which are connected to form an infinite chain. An appropriate crystal-chemical formula would be

$$Rb \frac{1}{\infty}(\text{\textcircled{V}} [P^{[+2]}P_6^{[+3]}]^{[+2]}).$$
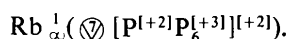
The exponent $[+2]$ after the square brackets for the cage indicates that each cage has two bonds to other P atoms, while the exponents inside the square brackets refer to homonuclear bonds of individual P atoms.
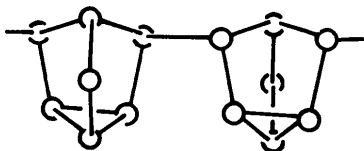

Fig. 7. The polyphosphide anion in RbP_7 (Schmettow & von Schnering, 1977) for which the crystal-chemical formula can be written as $Rb\frac{1}{\infty}$ $(\text{\textcircled{V}}[P^{[+2]}P_6^{[+3]}]^{[+2]})$. For RbP_7: $(VEC)_A = 5\frac{1}{7}$, $AA = \frac{20}{7}$ which means 20 P—P bonds for seven P atoms (six P atoms with three bonds and one P atom with two bonds).

The same method can be used to indicate in detail the linkage of the SiO_4 tetrahedra in the more complicated silicate structures, which is demonstrated further below.

The small letters introduced in Table 1 can also be used to characterize better the shape of the cage, provided it is not too complicated. They can be inserted in the cage symbol. For example, if the atom arrangement in the cage is octahedral or cubic, i.e. the atoms form a (non-centred) octahedron or cube, an a or a c can be written into the symbol. For example, for $PtCl_2$ with a cluster-type structure one can write as the crystal-chemical formula $[\text{\textcircled{V}}[Pt_6]Cl_{12}^{[2]}]$.
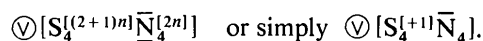
4. Notation of non-bonding orbitals

A non-bonding orbital can be indicated in the crystal-chemical formula by heavy bars surrounding the corresponding element. Examples are given in the text to Figs. 1, 4 and 6.

Non-bonding orbitals are found, in general, in the more electronegative elements. This explains an interchange of atoms in the isostructural pair AsS and NS. AsS has a cage molecule [SR (1973) **39A**, p. 15]* for which the crystal-chemical formula is

$$\text{\textcircled{V}}[\underline{As}_4^{[(2+1)n]}\overline{\underline{S}}_4^{[2n]}].$$
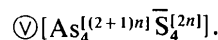
NS also crystallizes with this structure type [SR (1963) **28**, p. 54], but since N is more electronegative than S, the two elements interchange their sites and the corresponding crystal-chemical formula is

$$\text{\textcircled{V}}[\underline{S}_4^{[(2+1)n]}\overline{\underline{N}}_4^{[2n]}] \quad \text{or simply} \quad \text{\textcircled{V}}[\underline{S}_4^{[+1]}\overline{\underline{N}}_4].$$

Crystal-chemical formulae for polyanionic, polycationic valence compounds and tetrahedral structure compounds

The crystal-chemical formulae have been designed to allow the special structural features of polyanionic and polycationic valence compounds and tetrahedral structure compounds to be recognized.

It is well-known that the structural features of polyanionic and polycationic valence compounds can be obtained from the extended $(8 - N)$ rule which has been amply described (Mooser & Pearson, 1956; Pearson, 1964; Kjekshus, 1964; Hulliger & Mooser, 1965; Hulliger, 1968; Schäfer, Eisenmann & Müller, 1973; Kjekshus & Rakke, 1974). With the notation of Parthé (1973) the extended $(8 - N)$ rule can be written

$$AA - \frac{m}{n}CC = 8 - (VEC)_A \quad \text{for a compound } C_mA_n, \tag{1}$$

*SR means *Structure Reports*, IUCr. Utrecht: Oosthoek, Scheltema & Holkema.

where $(VEC)_A$ is the partial valence electron concentration of the anion, easily calculated from the known valence electron contributions of the atoms, AA is the average number of $Anion$–$Anion$ bonds per anion, CC is the average number of $Cation$–$Cation$ bonds per cation and/or the average number of electrons per cation which remain as non-bonding orbitals on the cation.

In polyanionic valence compounds with $(VEC)_A < 8$, one has essentially anion–anion bonds ($AA > 0$) and in polycationic valence compounds with $(VEC)_A > 8$ one finds cation–cation bonds and/or non-bonding orbitals on the cations ($CC > 0$). For details (and particularly for the conditions where this rule can and cannot be applied) the cited reference must be studied.

The extended $(8 - N)$ rule thus allows one to make conclusions about the homonuclear coordination of the atoms. It has already been shown how the homonuclear coordination can be incorporated in the coordination exponent of the crystal-chemical formula.

A particular case of polyanionic valence compounds with $(VEC)_A$ values between 7 and 6 and with corresponding AA values 1 and 2 is given below. These compounds have anion chains. The number of atoms forming the chain is given by

$$L = 2/(2 - AA) \quad \text{for } AA \le 2 \qquad (2)$$

and the corresponding crystal-chemical formula is

$$C_m \overset{\prime}{\frown} [A_L] \quad \text{for } 1 \le AA < 2.$$

One limiting case of the given equation is when $L = 1$, which corresponds to isolated anions. The compound is then a normal valence compound and not a polyanionic valence compound. The other limiting case occurs when $L = \infty$, which corresponds to an infinite anion chain or ring and crystal-chemical formulae of type $C_m \overset{1}{\infty} A_n$ or $C_m \bigcirc [A_n]$. Examples of different types of valence compounds and their crystal-chemical formulae are presented in Figs. 1 to 6.

The formalism which has been used to describe the anion linkage in polyanionic valence compounds can be applied in modified form to calculate the linkage of tetrahedral anion groups in silicates, phosphates, fluoroberyllates and other such compounds. The equation corresponding to (1) is now

$$TT = 8 - (VEC)_T/4, \qquad (3)$$

where $(VEC)_T$ is, in analogy to $(VEC)_A$, the total number of valence electrons of all participating atoms divided by the number of tetrahedra, and TT, also in analogy to AA, is the average number of $Tetrahedron$–$Tetrahedron$ links per tetrahedron. The information on the type of tetrahedron–tetrahedron linkage can be optionally indicated in the crystal-chemical formula by means of a (self) coordination exponent written on the anion group. For example, it is now possible to

distinguish between the two different types of chain silicates. For the pyroxene enstatite with $TT = 2$ the detailed formula is written $Mg_\infty^1 (SiO_3)^{[+2]}$ but for the amphibole tremolite with $TT = 2\frac{1}{2}$ it is $Ca_2 Mg_5 (OH)_2 \overset{1}{\infty} ((SiO_3)_2^{[+2]} (SiO_{2\frac{1}{2}})_2^{[+3]})_2$.

TT values between 1 and 2 correspond to tetrahedral chains and the equation corresponding to (2) can be written

$$L = 2/(2 - TT) \quad \text{for } TT \le 2. \qquad (4)$$

The symbolisms used above in the corresponding crystal-chemical formulae are also applicable here. Examples of neso-, soro-, cyclo- and inosilicates and their crystal-chemical formulae have already been given above.

For tetrahedral structures the number of non-bonding orbitals can be calculated by a valence electron concentration rule (Parthé, 1963, 1972) which can be written as

$$N_{NBO} = VEC - 4, \qquad (5)$$

where N_{NBO} is the average number of non-bonding orbitals per atom and VEC is the total valence electron concentration. Non-bonding orbitals occur only in defect tetrahedral structures where $VEC > 4$, while in normal tetrahedral structures with $VEC = 4$ all atoms have four tetrahedral neighbours. It was shown above that non-bonding orbitals can be indicated in the crystal-chemical formula. In such crystal-chemical formulae, the sum of the heteronuclear and homonuclear coordination plus the number of non-bonding orbitals must be four for every element. The only symbols possible in the coordination exponent are $4t$, $3n$, $2n$ and 1. A special relation exists for tetrahedral structures with $VEC > 6$. In this case we have a non-cyclic molecule, for which the number of atoms in the molecule is given by

$$N = 2/(VEC - 6) \quad \text{for } VEC > 6. \qquad (6)$$

Thus, to obtain the crystal-chemical formula, the chemical formula must be placed in square brackets and multiplied correspondingly so that the number of atoms inside the brackets corresponds to N. Examples of tetrahedral structures and their crystal-chemical formulae are presented in Figs. 1, 4, 5 and 6.

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$Sc_{11}Ir_4$, $Sc_{11}Os_4$, $Sc_{11}Ru_4$ and $Zr_{11}Os_4$ with a New Cubic Structure Type Described by Means of a Cluster Concept

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Abstract

$Sc_{11}Ir_4$ and $Sc_{11}Os_4$ crystallize with a new cubic structure type in space group $Fm3m$ with $Z = 8$. $Sc_{11}Ir_4$: $a = 13.350$ (4) Å, $D_x = 7.05$ Mg m^{-3}, μ(Mo $K\alpha$) $= 52.8$ mm^{-1}, $F(000) = 4312$. $Sc_{11}Os_4$: $a = 13.344$ (3) Å, $D_x = 7.02$ Mg m^{-3}, μ(Ag $K\alpha$) $= 27.3$ mm^{-1}, $F(000) = 4280$. The final $R = 0.055$ for $Sc_{11}Ir_4$ and 0.078 for $Sc_{11}Os_4$. $Sc_{11}Ru_4$ and $Zr_{11}Os_4$ have the same structure type. This new crystal structure is related to that of Th_6Mn_{23} or $Mg_6Cu_{16}Si_7$, but $Sc_{11}Ir_4$ has extra atoms located in the four octahedral voids. The structural relationship is shown by writing the chemical formulae in the following way: $Sc_6Sc_{16}Ir_8$, $Th_6Mn_{16}Mn_7\square$, $Mg_6Cu_{16}Si_7\square$. All these crystal structures can be described geometrically by means of clusters similar to those found in γ-brass or $Li_{22}Si_5$. Clusters here, however, are not isolated.

Introduction

Information on the Sc-rich parts of the phase diagrams containing Sc and transition elements of the Fe and Co group is scarce. Phase-diagram studies have been reported for Sc–Fe (Savitsky, Terekhova, Torchinova, Mavkova, Naumkin, Kolesnichenko & Stroganova,

1970) and Sc–Ru (Savitsky & Polyakova, 1975) which suggest that phases Sc_3Fe and Sc_3Ru should exist, but no structures have been given. Geballe, Matthias, Compton, Corenzwit, Hull & Longinotti (1965) made preliminary studies of the phases in the systems Sc–Rh and Sc–Ir and reported the phases Sc_3Rh and Sc_3Ir, but no attempt was made to solve their crystal structures. The only Sc_3T (T = transition element) structure known is Sc_3Co which may be described as a stacking variation of the Fe_3C and Re_3B structure types (Chabot & Parthé, 1978). It was of interest to find out whether the Sc_3Co type or a related structure type is also formed with the other Sc_3T compounds.

Experimental

Sc–Ru, Sc–Os, Sc–Ir and Zr–Os alloys were prepared by arc-melting techniques, under an argon atmosphere, from elements of high purity (sublimed Sc 99.95%, and Zr, Ir, Os, Ru 99.9%).

Single crystals were isolated from crushed melts with starting compositions equivalent to Sc_3Ir and $Sc_{11}Os_4$. The true composition of Sc_3Ir was revealed later to be $Sc_{11}Ir_4$. The crystal of $Sc_{11}Ir_4$ was in the form of a trigonal prism (base: $50 \times 50 \times 60$ µm, height: 110 µm); that of $Sc_{11}Os_4$ was irregular, mean diameter 50