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Valence-Electron Concentration Rules and Diagrams for Diamagnetic, Non-metallic Iono-covalent Compounds with Tetrahedrally Coordinated Anions

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Considerations of the covalent and ionic limiting states of diamagnetic non-metallic iono-covalent compounds permit the derivation of mathematical equations relating the number of available valence electrons to certain features of the crystal structure of the compound (*e.g.* number of non-bonding orbitals or type of linkage between anions). It is necessary to calculate two quantities for each compound: the total valence-electron concentration and the partial valence-electron concentration of the anion. Diagrams with the total valence-electron concentration as ordinate and the cation-to-anion ratio as abscissa are introduced. It is shown that for certain types of structures (tetrahedral structures, structures with square planar and tetrahedral coordinations, and structures with octahedrally and tetrahedrally coordinated atoms) the valence-electron concentration diagrams can be used to advantage both to classify known structures or to predict structural features of unknown compounds.

Introduction

Although crystal-structure data are accumulating at an ever increasing rate, few principles are available to explain the occurrence of a particular structure type of a given compound, not to mention the prior prediction of a crystal structure. It would seem that a scheme which permits the correlation of the structural features in a simple fashion is of at least heuristic value for displaying the wealth of crystallographic knowledge.

In this paper such a scheme is proposed for diamagnetic, semiconducting iono-covalent compounds with tetrahedrally coordinated anions. To a certain degree the ideas to be presented form an extension of earlier work on tetrahedral structures (Parthé, 1972) to those containing octahedral and square planar coordinations. The iono-covalent hypothesis which forms the basis of this scheme considers distributions of the valence electrons in a compound corresponding to the limiting covalent and limiting ionic-bonding states. From a consideration of these two hypothetical electron distributions, mathematical relations can be derived which serve not only to classify a crystal structure type, but may also allow certain features of the crystal structure of the compound to be predicted. Unfortunately, even if one knows the number of valence electrons which are necessary to form the two limiting bonding states, no simple correlation between the total number of outer-shell electrons and structural features seems possible, unless the exact role of the other electrons not involved in bonding is known. To simplify the problem, we will discuss only non-metallic diamagnetic compounds, where there are no free single electrons and all lower states not used for bonding are occupied by electron pairs. These are severe restrictions which have to be kept in mind for the proper application of the valence-electron concentration rules and diagrams.

Structural features and crystal chemical formula

The structural features to be determined in this study are of two kinds which complement one another: the number of non-bonding orbitals and the type of interlinking between the anions or cations.

Let N_{NBO} be the average number of non-bonding orbitals per atom. The value of N_{NBO} may be derived from the covalent limiting formula. It is only possible to see a non-bonding orbital in a crystal structure by the lack of an expected bond, that is, by the absence of an expected atom neighbour. Non-bonding orbitals are frequently formed on tetrahedrally coordinated sp^3-hybridized atoms leading to a truncated tetrahedron as coordination figure. We shall consider only non-bonding orbitals on sp^3-hybridized atoms. For the groups of compounds to be discussed, non-bonding orbitals are found with the proper tetrahedral structures on cations and anions, while in all others only the anions are tetrahedrally coordinated.

The second kind of structural feature can be obtained from the ionic limiting formula. There are two parameters to be determined: AA and CC.

Let AA be the average number of anion–anion bonds per anion. Frequently $AA=0$, which corresponds to isolated anions in the structure. When $AA=1$, there will be either anion–anion dumb-bells or one half of the anions will be isolated and the other half will form infinite anion chains. The first case is the more common. For $AA=2$, with each anion having on the average two bonds to other anions, one expects infinite anion chains or closed rings. With $AA=3$, a two-dimensional anion net could be found in the structure. These are only the most simple solutions, but it is not difficult to deduce the anion interlinking for other values of AA.

Let CC be the average number of cation–cation bonds per cation and/or the number of electrons which remain inactively on the cation. With the exception of the first group of compounds to be discussed, the tetrahedral structures, we shall consider below only compounds where $CC=0$, *i.e.* those with no bonds between the cations and no free electron pairs on the cations.

It is of interest to have a formalism whereby structural features can be expressed in terms of the chemical formula of a compound. In this paper a crystal chemical formula similar to the one devised by Machatschki (1947) will be used, which shows in great clarity all that can be observed and predicted.

Superscripts in square brackets above the element symbol denote the number of nearest neighbours. If there are two numbers in the bracket separated by a + sign the first indicates the number of neighbours of a different kind and the second the number of neighbours of the same kind. A non-bonding orbital is indicated by a heavy bar close to the chemical symbol of the element. For the atoms with tetrahedral sp^3-hybridized orbitals the sum of the number of neighbours of different and of same kind plus the number of heavy lines around the element symbol must be equal to four. As an example, we formulate the crystal chemical formula of $IrSe_2$ in which Ir has octahedral coordination and the Se atoms have tetrahedral orbitals. Application of the valence-electron rules, to be discussed below, shows that for this compound $N_{NBO}=\frac{1}{3}$ and $AA=\frac{1}{2}$ (with $CC=0$). Thus there is one non-bonding orbital per formula unit which must be associated with one of the two Se atoms. The value $\frac{1}{2}$ for AA indicates that one Se atom is isolated whereas the other has one bond to another Se atom. These are the structural features which can be recognized in the crystal structure of $IrSe_2$ (Barricelli, 1958). The crystal chemical formula is therefore $Ir^{[6]}\underline{Se}^{[3]}Se^{[3+1]}$. A knowledge of the crystal chemical formula does not necessarily allow the prediction of the space group and the point positions of a crystal structure. It is quite often found that for a given crystal chemical formula there exist several spatial arrangements, these being different crystal structures with identical structural features.

Covalent limiting bonding state and total valence-electron concentration

To apply the model of a limiting bonding state, one has to make certain assumptions about the type of bonding in these compounds. However, it is not necessary to consider details of positions of energy levels and characteristics of absorption spectra, but only the number of electrons involved in the bonding.

For the covalent limiting formula we assume that all bonds are two-electron bonds which are formed by overlap of hybridized orbitals. The following hybridizations are assumed:

Tetrahedrally coordinated atoms have sp^3-hybridized orbitals. Each atom has to have one electron for each of the four orbitals. But each orbital not used for bonding must obtain two electrons to form a non-bonding orbital. All these electrons must come from the valence-electron pool of the compound. The electrons which remain in inner shells and which do not participate in the pool determine the configuration of atom. With few exceptions the tetrahedrally coordinated atoms have a d^0 or d^{10} configuration. The determination of the valence-electron contribution of the tetrahedrally coordinated atoms is thus simplified, giving values equal to the A or B group number of the element.* For example: $e_{Cu}=1$, $e_{Ga}=3$, $e_{Cl}=7$, *etc.*

Atoms in square planar coordination use four dsp^2-hybridized orbitals. The electron pool has to provide 1 valence electron for each orbital. These atoms have a d^8 configuration, where the 4 inner d levels are always filled with 8 electrons. To calculate the valence-electron contribution of an element one has to subtract 8 from the total number of outer-shell electrons e_T which is equal to the group number of the transition element in the periodic system. For example Pd with $e_T=10$ provides only 2 valence electrons.

Octahedrally coordinated atoms use d^2sp^3 orbitals if they are transition elements or sp^3d^2 orbitals if they are not transition elements. One valence electron is needed for each of the 6 orbitals. Transition elements with octahedral coordination occur with different configurations [see *e.g.* Hulliger (1968) or Brostigen & Kjekshus (1970)]. We restrict our considerations to those cases where the transition element has a d^6 configuration, with the inner d levels filled. To calculate the valence-electron contributions of the transition element, 6 has to be subtracted from the transition-metal group number. For example, Rh with $e_T=9$ provides only 3 valence electrons to the pool. Non-transition elements with the sp^3d^2 hybrid have a d^{10} configuration and in this case the valence-electron contribution is the same as for the tetrahedrally coordinated atoms.

Three kinds of structure families are discussed below which differ in the coordinations of the atoms which form the cations. The atoms forming the anions have always four tetrahedral sp^3-hybridized orbitals, which may be bonding or non-bonding orbitals. For simplicity, we shall use for the following list of structure families the terms cations and anions although we are concerned here with the covalent limiting formulae.

1. Both cations and anions form tetrahedral sp^3-hybridized orbitals. These are the tetrahedral structures.
2. Cations have square planar coordination, but the anions have tetrahedral orbitals.
3. Cations are octahedrally coordinated and the anions have tetrahedral orbitals.

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* Notation of the element groups after Pauling (1960).

Valence-electron rules based on the covalent-bonding state can be derived by assuming that the total number of valence electrons must be such as to provide one valence electron for every orbital and one extra valence electron for every non-bonding orbital. Assuming a compound C_mA_n or T_mA_n,* the valence-electron rules for the three structure families (denoted by self-explanatory symbols) are:

$$\triangle_m\triangle_n \qquad me_C+ne_A=4(m+n)+(m+n)N_{\rm NBO} \qquad (1.1)$$

$$\diamond_m\triangle_n \qquad m(e_T-8)+ne_A=4m+4n+(m+n)N_{\rm NBO} \qquad (1.2)$$

✡$_m\triangle_n$

$$\begin{cases} m(e_T-6)+ne_A= \\ \quad 6m+4n+(m+n)N_{\rm NBO} \text{ for } T_mA_n & (1.3a) \\ m(e_C+ne_A) \quad = \\ \quad 6m+4n+(m+n)N_{\rm NBO} \text{ for } C_mA_n\,. & (1.3b) \end{cases}$$

We introduce the total valence electron concentration, defined by

$$\triangle_m\triangle_n \qquad {\rm VEC}^{d10}=\frac{me_C+ne_A}{m+n} \qquad (2.1)$$

$$\diamond_m\triangle_n \qquad {\rm VEC}^{d8}=\frac{m(e_T-8)+ne_A}{m+n} \qquad (2.2)$$

✡$_m\triangle_n$

$$\begin{cases} {\rm VEC}^{d6}=\dfrac{m(e_T-6)+ne_A}{m+n} \text{ for } T_mA_n & (2.3a) \\ {\rm VEC}^{d10}=\dfrac{me_C+ne_A}{m+n} \text{ for } C_mA_n\,. & (2.3b) \end{cases}$$

The superscript on the VEC symbol denotes the configuration of the cation. It is unnecessary to distinguish between ${\rm VEC}^{d10}$ and ${\rm VEC}^{d0}$, as the configurations d^0 and d^{10} give rise to the same formulae.

Rearranging terms leads to

$$\triangle_m\triangle_n \qquad N_{\rm NBO}={\rm VEC}^{d10}-4 \qquad (3.1)\dagger$$

$$\diamond_m\triangle_n \qquad N_{\rm NBO}={\rm VEC}^{d8}-4 \qquad (3.2)$$

✡$_m\triangle_n$

$$\begin{cases} N_{\rm NBO}={\rm VEC}^{d6}-\left(6-\dfrac{2}{\dfrac{m}{n}+1}\right) \text{ for } T_mA_n & (3.3a) \\ N_{\rm NBO}={\rm VEC}^{d10}-\left(6-\dfrac{2}{\dfrac{m}{n}+1}\right) \text{ for } C_mA_n\,. & (3.3b) \end{cases}$$

Ionic limiting bonding state and partial valence-electron concentration of the anion

The valence electrons of the compound are distributed in such a way that every anion completes its octet shell, either by establishing isolated electron pairs or by way of bond sharing of electron pairs with other anions. Thus each anion must obtain from the valence-electron pool 8 electrons less one electron for each bond to other anions. With the tetrahedral structures there may also be bonds between cations as well as non-bonding orbitals on the cations. The valence electrons used for these cation bonds or isolated electron pairs on the cations cannot be used to complete the octet shell of the anions. The general $(8-N)$ rule for tetrahedral structures using the variables AA and CC defined above is then given by

$$\triangle_m\triangle_n \qquad me_C+ne_A-mCC=n(8-AA) \qquad (4.1)$$

This is the equation for the general valence rule which was formulated first in a rudimentary form by Busmann (1961) and was later extended and discussed by Hulliger & Mooser (1963), Pearson (1964) and Kjekshus (1964).

For the second and third structure families, we will consider only those cases where there are no cation–cation bonds or inert electron pairs on the cations. In this case the electron rules are simpler:

$$\diamond_m\triangle_n \qquad m(e_T-8)+ne_A=n(8-AA) \qquad (4.2)$$

✡$_m\triangle_n$

$$\begin{cases} m(e_T-6)+ne_A= \\ \qquad n(8-AA) \text{ for } T_mA_n & (4.3a) \\ me_C+ne_A \quad = \\ \qquad n(8-AA) \text{ for } C_mA_n\,. & (4.3b) \end{cases}$$

Introducing the partial valence-electron concentration of the anion

$$\triangle_m\triangle_n \qquad ({\rm VEC})_A^{d10}=\frac{me_C+ne_A}{n} \qquad (5.1)$$

$$\diamond_m\triangle_n \qquad ({\rm VEC})_A^{d8}=\frac{m(e_T-8)+ne_A}{n} \qquad (5.2)$$

✡$_m\triangle_n$

$$\begin{cases} ({\rm VEC})_A^{d6}=\dfrac{m(e_T-6)+ne_A}{n} \text{ for } T_mA_n & (5.3a) \\ ({\rm VEC})_A^{d10}=\dfrac{me_C+ne_A}{n} \text{ for } C_mA_n & (5.3b) \end{cases}$$

and rearranging terms one obtains:

$$\triangle_m\triangle_n \qquad AA-\frac{m}{n}\,CC=8-({\rm VEC})_A^{d10} \qquad (6.1)$$

$$\diamond_m\triangle_n \qquad AA=8-({\rm VEC})_A^{d8} \qquad (6.2)$$

✡$_m\triangle_n$

$$\begin{cases} AA=8-({\rm VEC})_A^{d6} \text{ for } T_mA_n & (6.3a) \\ AA=8-({\rm VEC})_A^{d10} \text{ for } C_mA_n\,. & (6.3b) \end{cases}$$

Valence-electron concentration diagrams

If one combines equations (2) for the total valence-electron concentration with equations (5) for the par-

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* C is a cation from the A group or B group of the periodic system, T is a cation of the transition element series, A is an anion from the B group of the periodic system.

† This is the general tetrahedral structure equation which was first derived in 1963, but at that time formulated in a less convenient way (Parthé, 1963).

tial valence-electron concentration of the anion, one finds a relation between VEC and $(\text{VEC})_A$

$$\left(\frac{m}{n}+1\right)\text{VEC}=(\text{VEC})_A \qquad (7)$$

from which VEC *versus* m/n diagrams, as shown in Fig. 1, may be drawn. The position of a compound in such a diagram is determined by its value of VEC and its ratio m/n. It is clear that all points with the same value of $(\text{VEC})_A$ lie on a hyperbola. In the diagrams various $(\text{VEC})_A$ hyperbolae have been drawn corresponding to a set of discrete $(\text{VEC})_A$ values. Since the variables N_{NBO} and AA (or CC) are related in a simple way to the values of VEC and $(\text{VEC})_A$, the position in the diagrams of a compound is related directly to the structural features of this compound.

The first diagram in Fig. 1 applies to tetrahedral structures. According to equation (3.1) tetrahedral structures can only occur if $\text{VEC}^{d10}\geq 4$.* Accordingly the region of the diagram with VEC<4 has been darkened. Further, there is a limitation on VEC^{d10} values greater than six (Parthé, 1972). For $\text{VEC}^{d10}>6$ only non-cyclic molecular structures can occur and the VEC values are given by:

$$\text{VEC}^{d10}=6+\frac{2}{N} \qquad (8)$$

where N is the number of atoms in the molecule. Possible values of VEC^{d10} are thus 8, 7, 6·66, 6·5, 6·4, 6·33, 6·25, ... The possibility of finding an acceptable VEC value thus decreases as one goes from 6 to 8. This is indicated in the diagram by the increasing shading intensity of the corresponding field.

As an example of the use of the rules and diagram, Table 1 lists more detailed information on the compounds of tetrahedral structure with $m/n=\frac{1}{2}$ which are marked in the diagram. The table contains the values of VEC^{d10}, N_{NBO}, $(\text{VEC})_A^{d10}$, CC and AA, possible crystal chemical formulae based on the above values and known structure types with examples. The examples of ZnP_2 and $GeAs_2$ show that different crystal chemical formulae can be formulated for a given $(\text{VEC})_A$ value. The two formulae for ZnP_2 have different CC and AA values, whilst those for $GeAs_2$ have the same AA value with differing anion coordinations. Several different crystal structures can exist for one crystal chemical formula. The structural feature for the first crystal chemical formula given for ZnP_2 (the infinite P–P-chains) is found both in the tetragonal structure of red ZnP_2 and in the orthorhombic structure of α-CdP_2.

Actually more than two crystal chemical formulae can be derived for ZnP_2 and $GeAs_2$. The following general chemical principles allow a selection to be made of the most probable from all the possible crystal chemical formulae.

(*a*) Non-bonding orbitals should be assigned to the more electronegative atoms.

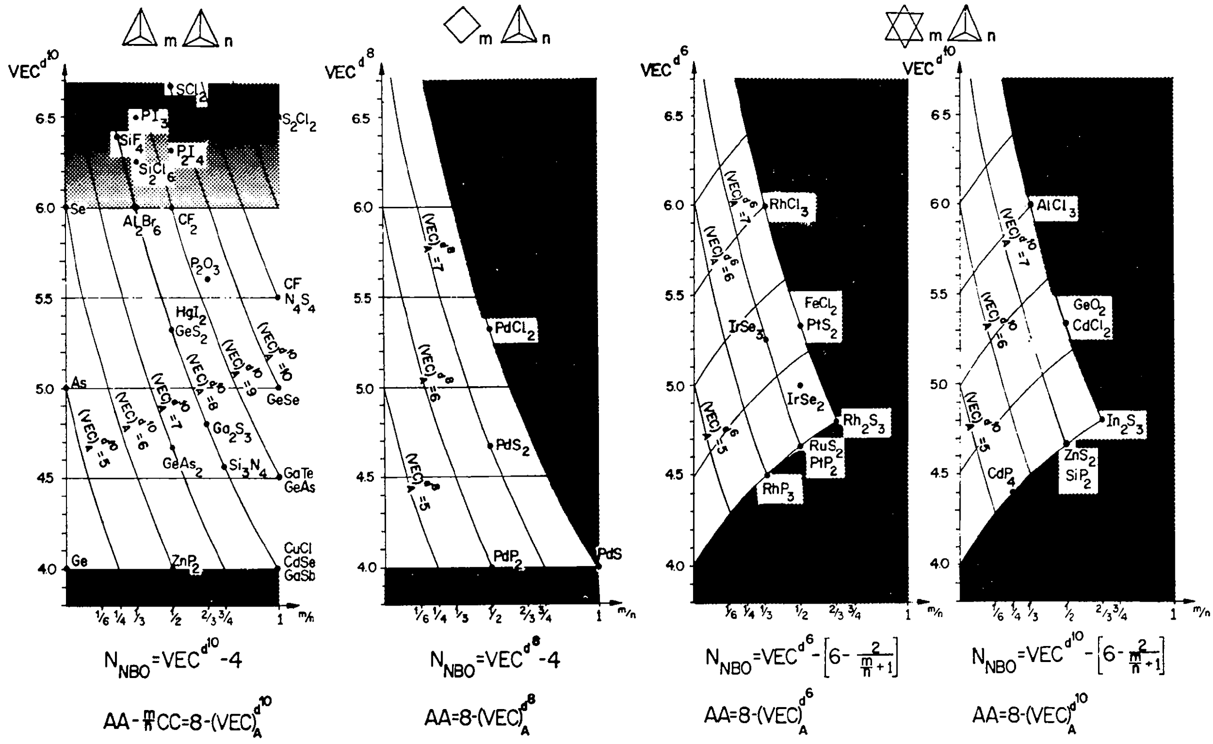

Fig. 1. Valence-electron-concentration-*vs*-m/n diagrams for three structure families with tetrahedrally coordinated anions.

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* Of the about 400 known tetrahedral structure compounds some 35 contain a transition element. These compounds will not be considered here.

Table 1. *The N_{NBO}, CC, AA values and the corresponding crystal chemical formulae for tetrahedral structures with $m/n=\frac{1}{2}$*

Compound	VEC^{d10}	N_{NBO}	Non-bonding orbitals per formula unit	$(VEC)_A{}^{d10}$	CC	AA	Possible crystal chemical formulae	Known structures (structure types are underlined)
ZnP_2	4	0	0	6	0	2	$Zn^{[4]}P_2{}^{[2+2]}$	$\underline{\text{Red } ZnP_2}$: ZnP_2, βCdP_2 $\underline{\alpha CdP_2}$: αCdP_2
					$\frac{1}{2}$	$2\frac{1}{4}$	$Zn^{[4]}Zn^{[3+1]}P_3^{[2+2]}P^{[1+3]}$	$\underline{\text{Black}}$ $\underline{ZnP_2}$: ZnP_2, $ZnAs_2$
$GeAs_2$	4·66	0·66	2	7	0	1	$Ge^{[4]}\underline{As}_2^{[2+1]}$	Unknown
							$Ge^{[4]}\underline{As}^{[3]}\underline{As}^{[1+2]}$	$\underline{GeAs_2}$: SiP_2, $SiAs_2$, $GeAs_2$
HgI_2	5·33	1·33	4	8	0	0	$Hg^{[4]}\overline{\underline{I}}_2^{[2]}$	$\underline{HgI_2}$: $ZnCl_2$, $ZnBr_2$, ZnI_2, HgI_2 $\underline{SiS_2}$: $BeCl_2$, $BeBr_2$, BeI_2, SiO_2, SiS_2, $SiSe_2$ $\underline{SiO_2}$: BeF_2, SiO_2, GeO_2 $\underline{GeS_2}$: GeS_2, $GeSe_2$
CF_2	6	2	6	9	2	0	$C^{[2+2]}\overline{\underline{F}}\vert_2^{[1]}$	$\underline{CF_2}$: CF_2 (teflon)
SCl_2	6·66	2·66	8	10	4	0	Molecular structure with 3 atoms per molecule $\overline{\underline{S}}^{[2]}\overline{\underline{Cl}}\vert_2^{[1]}$	SCl_2: SCl_2

(*b*) The number of cation–anion bonds should be as large as possible.

(*c*) The number of atoms of one kind equivalent with respect to the surroundings should be a maximum.

The most probable crystal chemical formulae for ZnP_2 and $GeAs_2$ are therefore $Zn^{[4]}P_2{}^{[2+2]}$ and $Ge^{[4]}\underline{As}_2^{[2+1]}$.

In Fig. 1 the second diagram applies to compounds with square planar cation and tetrahedral anion coordinations and the third and fourth diagrams to compounds with octahedral cations and tetrahedrally coordinated anions, the third where the cations are transition elements and the fourth where there are no transition elements. The shaded regions in these diagrams indicate that no compounds can exist with these VEC and *m*/*n* values. In comparison with the tetrahedral structures, the shaded region is more extensive as there are no compounds with $(VEC)_A > 8$. All the diagrams show iso-$(VEC)_A$ hyperbolae and lines of constant N_{NBO}. The latter are horizontal lines in the first two diagrams, but hyperbolae for the octahedral–tetrahedral compounds. Examples of binary compounds are inscribed in all four diagrams. Certain points have been labelled with more than one chemical formula. In such a case the elements all come from different groups of the periodic system and make different individual contributions to the valence-electron pool, but the compounds are isoelectronic and are liable to have either the same structure or at least the same structural features. The compounds with $m/n=\frac{1}{2}$ given in the second and third diagrams are treated in more detail in Tables 2 and 3 where the parameters needed to formulate the different crystal chemical formulae are shown explicitly.

Although the valence-electron rules do not permit the prediction of the individual atom hybridization, if this information is known, other structural features can be deduced. As an example one may consider the isoelectronic diphosphides of Pd and Pt. If the transition element has a square planar coordination, the crystal chemical formula is the one given for PdP_2 in Table 2. A crystal structure corresponding to this crystal chemical formula is characterized by infinite P–P chains. If the transition element is octahedrally coordinated, the crystal chemical formula given for PtP_2 in Table 3 applies and the corresponding crystal structure must have P–P dumb-bells. An explanation for the preference of PdP_2 for the first case and of PtP_2 for the second case is outside the scope of this paper. In the case of PtP_2 with P–P dumb-bells we have the further choice between two structure types with the same structural features: pyrite and marcasite. The reason why PtP_2 crystallizes with the pyrite structure cannot be explained at present.

As an example of the use of the rules and diagram for the prediction of unknown structural features, let us consider PdPS and PdPSe which were synthesized by Bither, Donohue & Young (1971). Both compounds are diamagnetic semiconductors of unknown structure.

Table 2. *Crystal chemical formulae and known structures for some compounds with square planar cation and tetrahedral anion coordinations*

Compound	VEC^{d8}	N_{NBO}	Number of non-bonding orbitals per formula unit	$(VEC)_A{}^{d8}$	AA if $CC=0$	Crystal chemical formulae	Known structures (structure types are underlined)
PdP_2	4	0	0	6	2	$Pd^{[4]}P_2^{[2+2]}$	$\underline{PdP_2}$: PdP_2
PdS_2	4·66	0·66	2	7	1	$Pd^{[4]}\underline{S}_2^{[2+1]}$	$\underline{PdS_2}$: PdS_2, $PdSe_2$
$PdCl_2$	5·33	1·33	4	8	0	$Pd^{[4]}\overline{\underline{C}}l_2^{[2]}$	$\underline{PdCl_2}$: $PdCl_2$, $PtCl_2$

Table 3. *Crystal chemical formulae and known structures for some transition element compounds with octahedral cation and tetrahedral anion coordinations*

Compound	VEC^{d6}	N_{NBO}	Number of non-bonding orbitals per formula unit	$(VEC)_A{}^{d6}$	AA if $CC=0$	Possible crystal chemical formulae	Known structures (structure types are underlined)
PtP_2	4·66	0	0	7	1	$Pt^{[6]}P_2^{[3+1]}$	$\underline{\text{Pyrite}}$: FeS_2, RuS_2, $RuSe_2$, $RuTe_2$, OsS_2, PtP_2, etc. $\underline{\text{Marcasite}}$: FeS_2
$IrSe_2$	5	0·33	1	7·5	$\frac{1}{2}$	$Ir^{[6]}\underline{Se}^{[3]}Se^{[3+1]}$	$\underline{IrSe_2}$: $RhSe_2$, IrS_2, $IrSe_2$
$PtSe_2$	5·33	0·66	2	8	0	$Pt^{[6]}\underline{S}_2^{[3]}$	$\underline{CdCl_2}$: PtS_2, $PtSe_2$

Table 4. *Examples of the structure change under pressure of iono-covalent compounds with $m/n=\frac{1}{2}$ where the type of anion linkage remains unchanged*

Compounds	$(VEC)_A^{d10}$	AA (if $CC=0$)	Structure of normal-pressure phase	Corresponding crystal chemical formulae	Structure of high-pressure phase	Corresponding crystal chemical formulae	Remarks	Literature
SiO_2	8	0	Quartz with a tetrahedral structure type	$\mathrm{Si}^{[4]}\overline{\underline{\mathrm{O}}_2}^{[2]}$	Stishovite with rutile structure type	$\mathrm{Si}^{[6]}\underline{\mathrm{O}}_2^{[3]}$	Isolated anions before and after transformation	(*a*)
SiP_2 $SiAs_2$	7	1	$GeAs_2$ type, a tetrahedral structure type	$\mathrm{Si}^{[4]}\underline{\mathrm{P}}^{[3]}\underline{\mathrm{P}}^{[1+2]}$	Pyrite type	$\mathrm{Si}^{[6]}\mathrm{P}_{2,}^{[3+1]}$	Isolated anions and chains before, dumb-bells of all anions after transformation	(*b*)
Red ZnP_2	6	2	Red ZnP_2 type, a tetrahedral structure type	$\mathrm{Zn}^{[4]}\mathrm{P}_2^{[2+2]}$	?	$\mathrm{Zn}^{[2x]}\mathrm{P}_2^{[x+2]}$	Transformation has not yet been investigated	
$CaSi_2$	5	3	$CaSi_2$ type	$\mathrm{Ca}^{[6]}\mathrm{Si}_2^{[3+3]}$	$ThSi_2$ type	$\mathrm{Ca}^{[12]}\mathrm{Si}_{2,}^{[6+3]}$	Three-dimensional connexions of the anions before and after transformation	(*c*)

(*a*) Stishov & Belov (1962).
(*b*) Donohue, Siemons & Gillson (1968).
(*c*) McWhan, Compton, Silverman & Soulen (1967).

Two possibilities have to be taken into consideration:

(*a*) If the Pd has square planar coordination, one can calculate the following values

$$VEC^{d8}=4{\cdot}33 \text{ and } (VEC)_A^{d8}=6{\cdot}5$$

from which follows

$$N_{\mathrm{NBO}}=\tfrac{1}{3} \text{ and } AA=\tfrac{3}{2}$$

A possible crystal chemical formula is $\mathrm{Pd}^{[4]}\mathrm{P}^{[2+2]}\underline{\mathrm{S}}^{[2+1]}$. or a formula where P and S are interchanged. This corresponds to a new structure type.

(*b*) If Pd has octahedral coordination, one obtains

$$VEC^{d6}=5 \text{ and } (VEC)_A^{d6}=7{\cdot}5$$

which leads to

$$N_{\mathrm{NBO}}=\tfrac{1}{3} \text{ and } AA=\tfrac{1}{2}\,.$$

The corresponding crystal chemical formula is $\mathrm{Pd}^{[6]}\mathrm{P}^{[3+1]}\underline{\mathrm{S}}^{[3]}$ or $\mathrm{Pd}^{[6]}\underline{\mathrm{P}}^{[3]}\mathrm{S}^{[3+1]}$ which is the same as a ternary variant of the crystal chemical formula for $IrSe_2$ discussed above.

Structural features of iono-covalent high-pressure phases

It is well known that any structure change under pressure is accompanied by a decrease in volume. This volume decrease can be achieved either by a rearrangement of atoms to give a structure with better space filling (see for example Parthé, 1961) or be a sudden decrease of the atomic diameter due to an electronic transition. Except for the latter case, a high-pressure structure will have higher atom coordinations.

For the compounds which have been discussed here an additional remark can be made which refers to the number of non-bonding orbitals and the anion linkage. Increase of pressure leads to a reduction in the number of non-bonding orbitals on the anion, but the type of anion linkage is retained (provided that the pressure is not so high that electrons are squeezed away from the atom core and the material becomes metallic). Table 4 lists examples of pressure transitions for iono-covalent compounds with $m/n=\frac{1}{2}$. Quartz after its transformation into the rutile structure has two non-bonding orbitals less. The oxygen atoms remain isolated. SiP_2 loses two non-bonding orbitals, but the AA value of both the normal and the high-pressure structure is 1. In Table 4 has been included the structure change for $CaSi_2$ where AA is 3 before and after the pressure transformation. However, the high-pressure phase of $CaSi_2$ is supposedly a superconductor and thus cannot properly be included with the iono-covalent compounds. In the case of ZnP_2 no high-pressure experiments have ever been made. If there should be a transformation under pressure, it is quite clear that the new structure will not be of the rutile or pyrite type but a new structure type where $AA=2$, which means that on the average each phosphorus atom should have two bonds to other phosphorus atoms.

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The Crystal Structure of Methyltriphenylphosphonium Bis-7,7,8,8-tetracyanoquinodimethanide at 53°C

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The crystal structure of the high-temperature modification of $(CH_3PPh_3)^+(TCNQ)_2^-$ has been determined at 53 °C. The crystals are triclinic with the space group $P\bar{1}$ and lattice constants: $a=15·780$ (5), $b=14·545$ (4), $c=8·910$ (3) Å, $\alpha=117·22$ (4), $\beta=98·05$ (7), $\gamma=97·02$ (6)° and $Z=2$. The structure was refined by the block-diagonal least-squares method with 2514 reflexions measured on a four-circle manual diffractometer to give an R value of 0·051. The structure is closely related to that of the low-temperature modification, consisting of tetrads of TCNQ molecules and methyltriphenylphosphonium ions. The tetrads are arranged to form a columnar structure along the b axis. The average interplanar distances in the tetrads increased to 3·32 and 3·26 Å, which are longer by 0·08 and 0·04 Å, respectively, than the corresponding distances in the low-temperature modification, whereas the interplanar distance between the two adjacent tetrads of 3·55 Å was shortened by about 0·02 Å. The overlapping mode of the TCNQ moieties within a tetrad is unaltered. The nearest neighbour overlap between the two adjacent tetrads changed from a modified ring–ring overlap to an overlap involving a diagonal shift of the molecular centres. The conformation of $(CH_3PPh_3)^+$ ion is different from that of the low-temperature form; two of the phenyl groups are rotated by about 56° and 45° from the positions observed in the low-temperature form. Moreover, the conformation of the phosphonium ion is disordered, two of the phenyl rings taking different orientations with a probability of about 0·1. These changes of the structure are in accord with the change in physical properties of the high-temperature phase.

Introduction

Crystals of $(CH_3PPH_3)^+(TCNQ)_2^-$ undergo a first-order phase transition at 315·7 °K (Kepler, 1963). The temperature dependence of physical properties such as electrical conductivity, magnetic susceptibility *etc.*, has been extensively studied by a number of workers (for example, Jones & Chesnut, 1963; Iida, Kinoshita, Sano & Akamatu, 1964; Iida, Kinoshita, Kawamori & Suzuki, 1964; Nordio, Soos & McConnell, 1966; Kosaki, Iida, Sorai, Suga & Seki, 1970; Shirotani, Kawamura & Iida, 1972). Models for this transition were also proposed (Chesnut, 1964; Merkl, Hughes, Berliner & McConnell, 1965). The crystal structure of this compound at room temperature has been determined by the photographic method (McPhail, Semeniuk & Chesnut, 1971). Quite independently we have determined the crystal structure by the counter method (Tsuchiya, Marumo & Saito, 1973). Positions of hydrogen atoms were also determined. The final R value was 0·060 for 3574 observed reflexions. Both results agree well, although the cell dimensions are somewhat different. The crystal structure of the high-temperature modification was determined in order to gain a better understanding of the phase transition. The result will be discussed with particular reference to the structure of the low-temperature phase.

Experimental

The crystals of $(CH_3PPh_3)^+(TCNQ)_2^-$ were kindly supplied by Dr Iida of Hokkaido University. A single-