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The Crystal Structures of Semiconductors and a General Valence Rule

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Compound semiconductors are valence compounds, the great majority of which contain anions lying to the right of the Zintl border (atoms of Groups IV–VII excluding transition metals). These therefore satisfy a general valence rule and this provides a systematic means of discussing their crystal chemistry based on anion substructural arrays. The discussion embraces *polyanionic*, *polycationic* and *normal* valence compounds. Essential features of structures of polyanionic compounds were first pointed out by Busmann.

1. Introduction: crystal chemistry

Crystal chemistry is a study of the interactions between atoms in the solid state. If the atoms in a compound or element were entirely without character, other than resembling incompressible billiard balls of uniform size, then the crystal structures that they might form would be in accordance with Laves's (1956) principles of the densest packing and the highest possible coordination and symmetry. That many actual crystal structures are not in accordance with these principles results from the character of the component atoms and their interactions one with the other. In considering crystal structures, the most important aspects of atomic character are: (i) the valence properties (valency, bond-orbital symmetry and perhaps electron concentration), (ii) atomic size (although this cannot be rigorously defined, there are two empirical scales — ionic and covalent-metallic — either one or the other of which may be applicable to a particular compound), and (iii) effective atomic charge, resulting from the balance of the ionization potentials and electron affinities of the component atoms. From the point of view of semiconductors, valency is undoubtedly the most important of these properties, since a necessary condition for semiconductivity is that the anions* attain (by electron sharing) filled valence subshells. It is the presence of the anions with filled valence subshells that prevents arrays of chemical bonds between any atoms with vacant 'metallic' orbitals in their valence shell from running continuously throughout the structure, and thus differentiates semiconductors from metals (see also the Appendix). The second most important property is the directional character of the chemical bonds formed by the component atoms of a semiconductor, since the arrangement of the atoms in the crystal structure must satisfy these requirements. Here semiconductors differ from characteristically ionic and metallic compounds since the chemical bonds in these are essentially non-directional. Nevertheless because regular coordination polyhedra such as tetrahedra and octahedra also satisfy the symmetry of the common directed-bond-orbitals, semiconductors, metals, ionic and semipolar compounds frequently adopt the same structural types as for example in the rocksalt, fluorite and cadmium iodide structures.

The crystal structures of semiconductors can be discussed on the basis of a general valence rule (§ 2, below) and in this way both atomic valency and coordination can be related to structural arrangement. They can also be considered in relation to parameters describing the directional character of the chemical bonds. These group together simple metallic phases and ionic compounds, because in each the bonding is predominantly non-directional, and the structures that they adopt are in accord with Laves's principles discussed above. Between these two groups lie substances with directed covalent bonds, and changes of structure can be examined as the directional property of the bonds becomes more important on passing either from metallic or from ionic to covalent compounds (Mooser & Pearson, 1959). Although the bonding in both metallic and ionic phases is predominantly non-directional, there is nevertheless one important difference which leads to very much larger coordination numbers in many metallic phases. The coordination in ionic structures because of ionic repulsions is restricted by the limiting condition that the anions must not come into contact so that the cations 'rattle', wherefore coordination numbers do not generally exceed 8 in binary ionic phases. Since the bonding in metallic structures is of the resonating-covalent type (Pauling, 1960) and atomic charges are small, this restriction no longer applies, and fractional bond strengths between an atom and its ligands allow coordination numbers as large as 20 or 22, and 12, 14, 15 and 16

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* For lack of any other terms, 'anion' and 'cation' are used to designate respectively the most electronegative atoms and the remaining atoms in compound semiconductors.

are very common. Many metallic structures are based on the principle of sphere packing in which layers of atoms suitably stacked give large coordination polyhedra (Frank & Kasper, 1958; 1959). The common 12, 14, 15 and 16-atom polyhedra so obtained have the atoms distributed over their surfaces in equilateral triangles or slightly distorted forms thereof.

Finding the reasons for structural distortions is an important aspect of crystal chemistry, since if these can be understood, information is gained on the character of atomic interactions in the solid state. Nevertheless the recognition of structural distortion presupposes that some regular structure should have occurred, and so such discussions are generally limited to normal valence compounds or elements, where the nature of the structural distortion can be clearly prescribed. Dunitz & Orgel (1960), adopting an ionic model, have accounted for many structural distortions in compounds of the transition metals and of *B* group metals by the splitting of the degeneracy of the *d* or valence electrons of the cations by the anion ligand fields. In other cases, as for example in the structure β-Sn or compounds such as GeS, structural distortion undoubtedly results from an admixture of bond orbitals with different symmetries (Pauling, 1960; Coulson, 1952). Such distortions may be expected in the structures of elements and compounds of intermediate (average) atomic number where the predominant symmetry of bond orbitals is changing from tetrahedral to octahedral.

In the following pages we examine broadly the crystal chemistry of semiconductors in relation to a general valence rule, showing how a structure-building principle can be developed which involves the anion sub-arrays. We shall not be concerned with details of structural distortions, or particular effects due to the underlying *d* shells in compounds containing transition metal atoms, and the distinctions between semiconductors and ionic conductors are not important to the arguments. Although there are such a very large number of semiconductors having structures in accordance with this building principle as to justify its discussion, it must be remembered that some semiconducting compounds have structures bearing no relation to it.

2. A general valence rule

A general valence rule which valence compounds obey if they contain anions lying to the right of the Zintl border* (Group IV–VII atoms excluding the transition metals), can be expressed as follows:

$$(n_e+b_a-b_c)/n_a=8$$

where n_e is the total number of valence electrons; n_a is the number of anions; b_a is the number of electrons involved in forming anion–anion bonds; b_c is the number of electrons involved in forming cation–cation bonds, and including any 'unshared' valence electrons on the cations, *all of these values being calculated per formula unit of the compound.* Thus for example for the tetragonal form of the semiconductor ZnP_2 (Fig. 8): $n_e=12$, $n_a=2$, $b_a=4$ and $b_c=0$; for PbSe: $n_e=10$, $n_a=1$, $b_a=0$, $b_c=2$ (unshared electron-pair on Pb); for GaSe (Fig. 21): $n_e=9$, $n_a=1$, $b_a=0$, $b_c=1$ (cation–cation bond). The valence rule expresses the bonding requirements for the anions to attain a filled valence subshell of eight (atomic) *s* and *p* electrons. If N is the Group number of the anion, then it has N valence electrons and $(8-N)$ more have to be supplied through the formation of bonds with neighbouring cations and/or anions. The original $(8-N)$ rule which applied to elements lying to the right of the Zintl border states that they crystallize in structures with nearest-neighbour coordination numbers equal to the value of $(8-N)$ (see *e.g.* Hume-Rothery, 1945). The new valence rule is in a sense an extension of the old $(8-N)$ rule to include also compounds, but in order to make it more exact, it deals essentially with the number of electrons employed in forming anion–cation, anion–anion and cation–cation bonds, rather than nearest-neighbour coordination numbers.

Semiconductors, insulators and ionic compounds whose anions lie to the right of the Zintl border satisfy the general valence rule.† Specifically-metallic compounds do not obey the rule, but some compounds which at first sight appear to satisfy it may exhibit metallic conductivity. However, knowledge of the crystal structure of a compound generally leaves little doubt whether the rule will be obeyed, unless perhaps the compound contains a transition metal atom and there is an overlap of *d* orbitals. Thus, for example, in BiIn which is metallic: $n_e/n_a=8$, but the close approach of the Bi atoms in the structure indicates some Bi–Bi bonding so that $b_a>0$, and the rule is not obeyed.

Since *polyanionic* valence compounds ($n_e/n_a<8$), *polycationic* valence compounds ($n_e/n_a>8$), and *normal* valence compounds ($n_e/n_a=8$) satisfy the rule, it provides a basis for discussing the crystal chemistry of compounds whose anions occupy only one set of crystallographically equivalent sites in the structure (see below, § 3). Busmann (1961) first pointed out that recognizable arrays of anions bonded together in polyanionic compounds resemble the arrays of atoms in the structures of elements having the same number of nearest-neighbours. In terms of the valence rule we would say that the anions in polyanionic compounds and the Group IV–VII elements having respectively the same b_a/n_a and $(8-N)$ values generally have similar structural arrangements (Table 1), provided that the anions occupy only one set of equivalent sites in the

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* For the general valence rule stated in an earlier incomplete form see *e.g.* Mooser & Pearson (1960).

† There are only a few semiconductors or ionic compounds such as CsAu and the alkali hydrides where the anions attain a filled valence subshell of two valence electrons.

Table 1. *Correlation of anion arrays in polyanionic compounds with the* $(8-N)$ *structures of the elements*

b_a/n_a for compound	$8-N$ for element	Elements	C.N. of element	Structural arrays
4	4	C, Si, Ge, α-Sn	4	Three-dimensional: tetrahedral coordination
		Graphite	3	Hexagonal-net layers: multiple bonds
3	3	White P	3	Tetrahedra
		Black P, As, Sb	3	Double layers
		N_2	1	Pairs: multiple bonds
2	2	O_2	1	Pairs: multiple bonds
		S, Se, Te	2	Rings, spirals, chains
1	1	Br, I	1	Pairs

structure of the polycompound or, if they occupy more than one equivalent site, provided that the anions on the different sites have the same number of anion nearest-neighbours. If the anions occupy more than one set of equivalent sites, and especially if the anions on the different sites have different numbers of anion nearest-neighbours and form bonds with each other, then this building principle for the structures of polycompounds is likely to become confused. Nevertheless, it provides a convenient means for considering the many observed structures of polyanionic compounds, and furthermore, Hulliger & Mooser (1963) have developed Busmann's ideas in discussing the electrical properties of polyanionic and polycationic compounds. It may also provide assistance in the solution of crystal structures, in the interpretation of Patterson projections by specifying what atomic arrangements and nearest-neighbour contacts are probable, but it is not a means of predicting with certainty what structural arrangements must occur. This is because it is impossible to specify *a priori* whether the anions occupy one or more sets of equivalent sites, and whether the

Table 2. *Partition of valencies of anions and cations for possible polyanionic compounds with anions occupying only one crystallographic site*

Partition of valencies	Example of compound	Symmetry or structure type*	n_e/n_a	b_a/n_a	Anion X sub-arrays
$M_2{}^{\mathrm{I}}X^{\mathrm{II}}$	Cu_2Mg	Cubic, *C*15*	4	4	Diamond type
$M^{\mathrm{I}}X^{\mathrm{III}}$	NaTl	Cubic, *B*32*	4	4	Diamond type
$M^{\mathrm{II}}X_2{}^{\mathrm{III}}$	$CaGa_2$	Hexagonal, *C*32*	4	4	Graphite type
$M_2{}^{\mathrm{I}}X^{\mathrm{III}}$	—	—	5	—	—
$M^{\mathrm{II}}X^{\mathrm{III}}$	—	—	5	—	—
$M^{\mathrm{I}}X^{\mathrm{IV}}$	KGe (Busmann, 1961)	Cubic†	5	3	Ge_4 tetrahedra as in white P
—	NaPb	Tetragonal	5	3	Pb_4 tetrahedra as in white P
$M^{\mathrm{II}}X_2{}^{\mathrm{IV}}$	$CaSi_2$	Rhombohedral,† *C*12*	5	3	Double-layer As type
—	CaC_2	Tetragonal, *C*11*a**	5	3	C_2 pairs as in N_2 structure
$M^{\mathrm{III}}X_3{}^{\mathrm{IV}}$	—		5	—	—
$M_3{}^{\mathrm{I}}X^{\mathrm{III}}$	—	—	6	—	—
$M_3{}^{\mathrm{II}}X_2{}^{\mathrm{III}}$	—	—	6	—	—
$M_2{}^{\mathrm{I}}X^{\mathrm{IV}}$	Li_2Si Li_2Sn	—	6	—	—
$M^{\mathrm{II}}X^{\mathrm{IV}}$	CaSi	Orthorhombic	6	2	Planar zigzag chains
$M_2{}^{\mathrm{III}}X_3{}^{\mathrm{IV}}$	—	—	6	—	—
$M^{\mathrm{I}}X^{\mathrm{V}}$	LiAs (Cromer, 1959)	Monoclinic†	6	2	Spiral chains
$M^{\mathrm{II}}X_2{}^{\mathrm{V}}$	ZnP_2 (Hegyi *et al.*, 1962)	Tetragonal†	6	—	Spiral chains
$M^{\mathrm{III}}X_3{}^{\mathrm{V}}$	$CoAs_3$	Cubic	6	2	Squares: 4-fold rings possibly as in γ-O_2 (ignoring rotations)
$M^{\mathrm{IV}}X_4{}^{\mathrm{V}}$	—	—	6	—	—
$M_3{}^{\mathrm{I}}X^{\mathrm{IV}}$	—	—	7	—	—
$M^{\mathrm{III}}X^{\mathrm{IV}}$	—	—	7	—	—
$M_3{}^{\mathrm{II}}X_2{}^{\mathrm{IV}}$	—	—	7	—	—
$M_2{}^{\mathrm{I}}X^{\mathrm{V}}$	Na_2As ?	—	7	—	—
$M^{\mathrm{II}}X^{\mathrm{V}}$	ZnSb	Orthorhombic	7	1	Pairs
$M^{\mathrm{IV}}X_2{}^{\mathrm{V}}$	$SiAs_2$?	—	7	—	—
$M_2{}^{\mathrm{III}}X_3{}^{\mathrm{V}}$	—	—	7	—	—
$M^{\mathrm{I}}X^{\mathrm{VI}}$	NaS ?	—	7	—	—
$M^{\mathrm{II}}X_2{}^{\mathrm{VI}}$	FeS_2	Cubic, *C*2*; orthorhombic, *C*18*	7	1	Pairs
$M^{\mathrm{III}}X_3{}^{\mathrm{VI}}$	$GaTe_3$? $InTe_3$	—	7	—	—
$M^{\mathrm{IV}}X_4{}^{\mathrm{VI}}$	—	—	7	—	—
$M^{\mathrm{V}}X_5{}^{\mathrm{VI}}$	—	—	7	—	—

* *Strukturbericht* types.

† In these structures the anions actually lie on more than one crystallographic site, but b_a/n_a has the same value for each.

anion–anion coordination numbers are the same for anions on different sites. If valence considerations indicate a fractional value for the ratio b_a/n_a, then it seems certain that the anions must occupy more than one set of sites.

Organic compounds can be regarded as polyanionic or polycationic compounds depending on whether they are paraffins, or aldehydes, amides, *etc.*, but the numerous carbon atoms generally occupy many different crystallographic sites and molecular compounds are formed rather than structures of the type which we discuss in § 3 below.

In the structures of *normal* valence compounds where $n_e/n_a = 8$, there are no chemical bonds between the anions and the anion arrays would therefore be expected to correspond to the structures of the inert gases, where there are only central forces between the atoms. This is indeed the case, and many *normal* valence compounds are known in which the anions lie on close-packed cubic or hexagonal arrays. Similarly in *polycationic* semiconducting compounds where $n_e/n_a > 8$, there are no chemical bonds between the anions, so that close-packed anion arrays might be expected, but this is probably incompatible with the condition for semiconductors that the cation–cation bonds must be isolated by arrays of bonds between the anions.

3. Polyanionic compounds with anions on one crystallographically distinct site

The formulae of all possible polyanionic compounds obeying the general valence rule, and having anions on one set of equivalent sites only in the structure, can be determined by partitioning the valencies of the anions and cations as shown in Table 2. We now discuss some of the observed structures of these compounds, showing that the anions do indeed occupy sub-arrays corresponding to the structures of elements with the same $(8-N)$ values as the b_a/n_a values of the anions in the compounds.

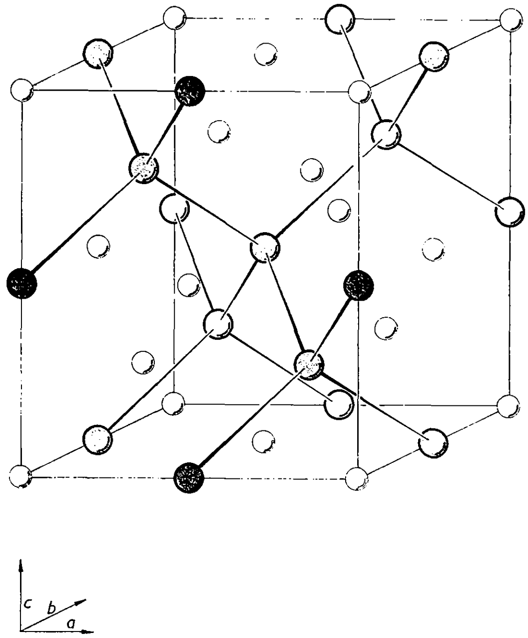

Fig. 1. The unit cell of the NaTl structure (cubic, $B32$ type) with the array of Tl atoms emphasized.

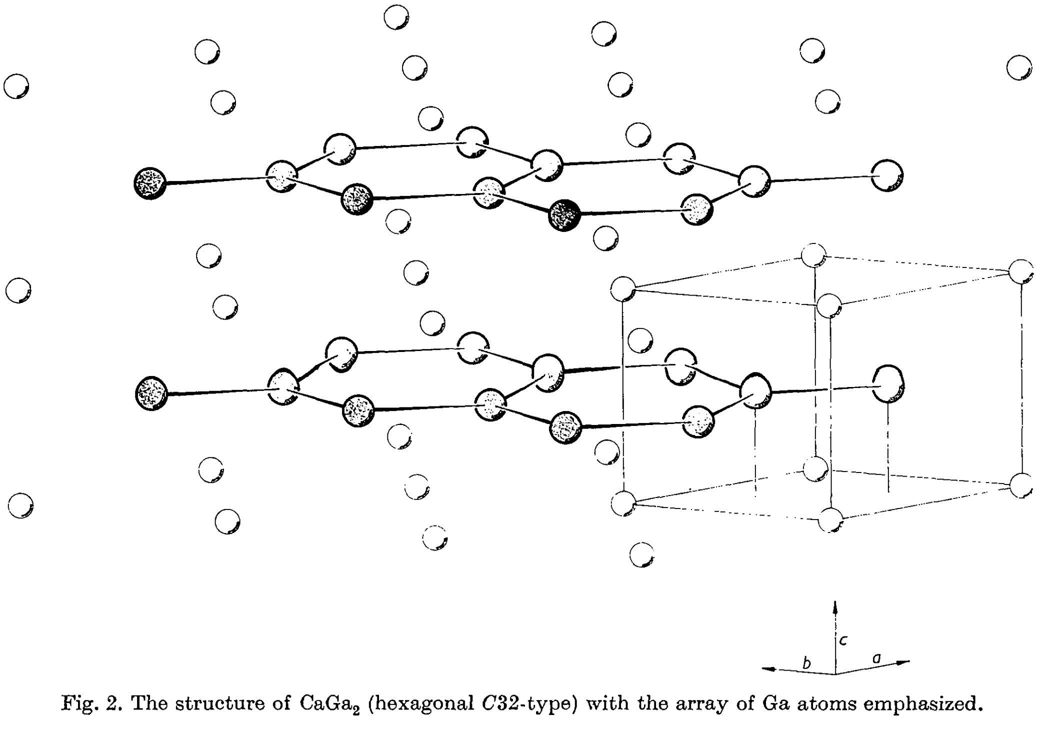

Fig. 2. The structure of $CaGa_2$ (hexagonal $C32$-type) with the array of Ga atoms emphasized.

(i) *Structures with 'anions' in Groups II and III*

The building principle is even found to extend to the structures of some metallic compounds if the element of highest valency is considered as an 'anion'. Examples are the Cu_2Mg and NaTl-type structures (cubic) in which Mg and Tl lie on the diamond-like array of elements with $(8-N)=4$ (Fig. 1) and the AlB_2-type structure (hexagonal) of $CaGa_2$ in which the Ga atoms lie on a graphite-like array (Fig. 2). If it is imagined that the Cu, Na or Ca valence electrons are transferred respectively to the Mg, Tl or Ga atoms, then appropriately $b_a/n_a=4$.

(ii) *Compounds with* $b_a/n_a=3$ *and anion* (8-*N*) *structures corresponding to Group V elements.*

In compounds with the KGe structure (cubic, Fig. 3) and in NaPb with $b_a/n_a=3$, the anions form tetrahedra similar to the P_4 tetrahedra in the structure of white phosphorus $(8-N=3)$. The Si atoms in the structure of $CaSi_2$ (rhombohedral) lie on two crystallographically distinct sites. There are no bonds between Si(1) and (Si(2) and each has three anion near-neighbours. The resultant double layers of Si atoms (Fig. 4) are similar to the double layers in the arsenic structure for which $(8-N)=3$.* In the tetragonal structure of the acetylide CaC_2, triple bonds occur between the C atoms and $b_a/n_a=3$. The structure thus contains C_2

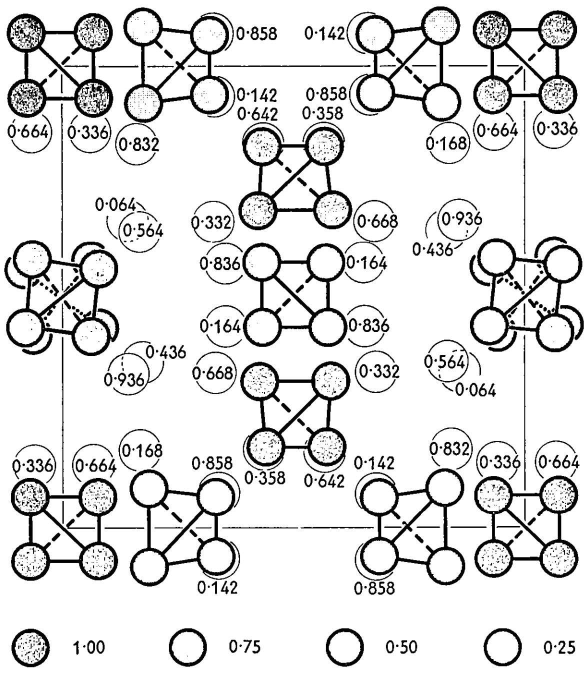

Fig. 3. Projection of the KGe structure (cubic) on (001) emphasizing the array of Ge atoms (after Busmann, 1961). Numbers indicate fractional heights of K atoms along the c direction. The centres of Ge_4 tetrahedra are at heights indicated by the different shadings.

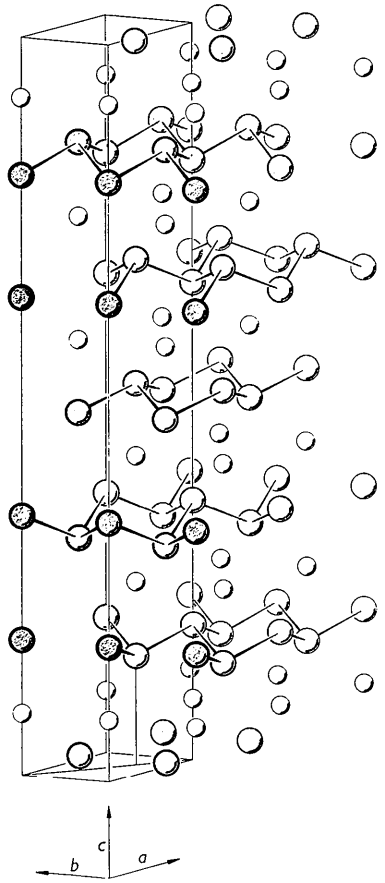

Fig. 4. $CaSi_2$ structure (rhombohedral), drawn on hexagonal axes, showing four hexagonal unit cells with the arrays of Si atoms emphasized.

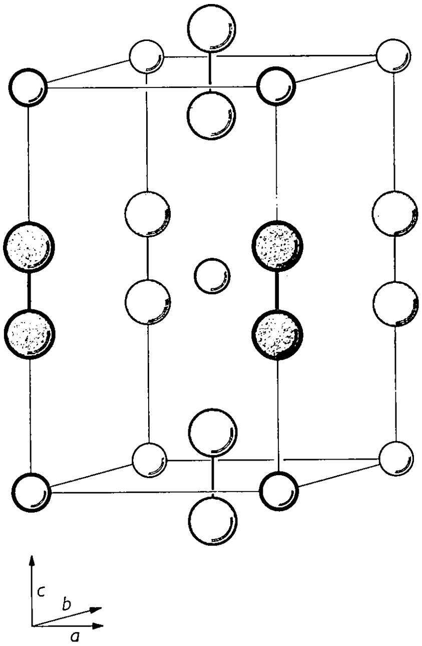

Fig. 5. The CaC_2 structure (tetragonal), showing C_2 pairs.

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* Dr Mooser informs me that this compound appears to be a metallic conductor.

pairs (Fig. 5) as in the nitrogen structure where multiple bonds also occur between the pairs of N atoms.

(iii) *Compounds with* $b_a/n_a = 2$ *and anion* (8-N) *structures corresponding to Group VI elements*

In the structures of the polyanionic compounds CaSi (orthorhombic, Fig. 6), LiAs (monoclinic, Fig. 7) and ZnP_2 (tetragonal, Fig. 8) the general valence rule is satisfied with $b_a/n_a = 2$, and planar zigzag chains or spiral chains of anions are formed, similar in principle to the chains in the structures of the elements Se or Te for which $(8-N)=2$. The As atoms in LiAs and the P atoms in ZnP_2 occupy two different crystallographic sites, but the anions on each site have two anion

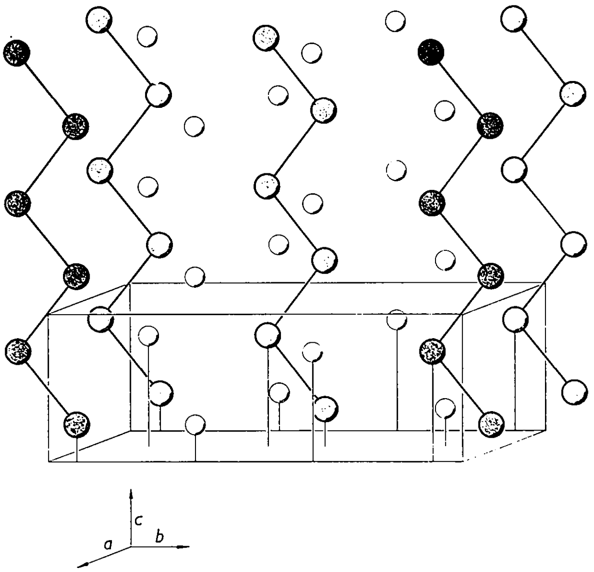

Fig. 6. Three unit cells of the CaSi structure, emphasizing the arrays of Si atoms in zigzag chains.

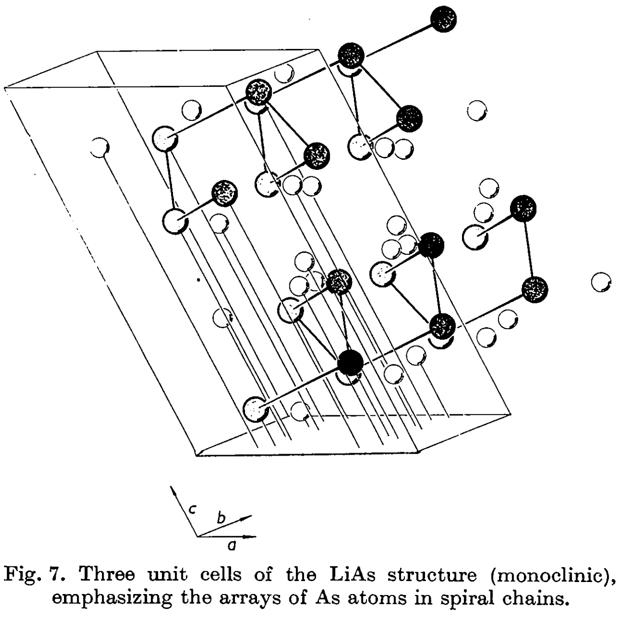

Fig. 7. Three unit cells of the LiAs structure (monoclinic), emphasizing the arrays of As atoms in spiral chains.

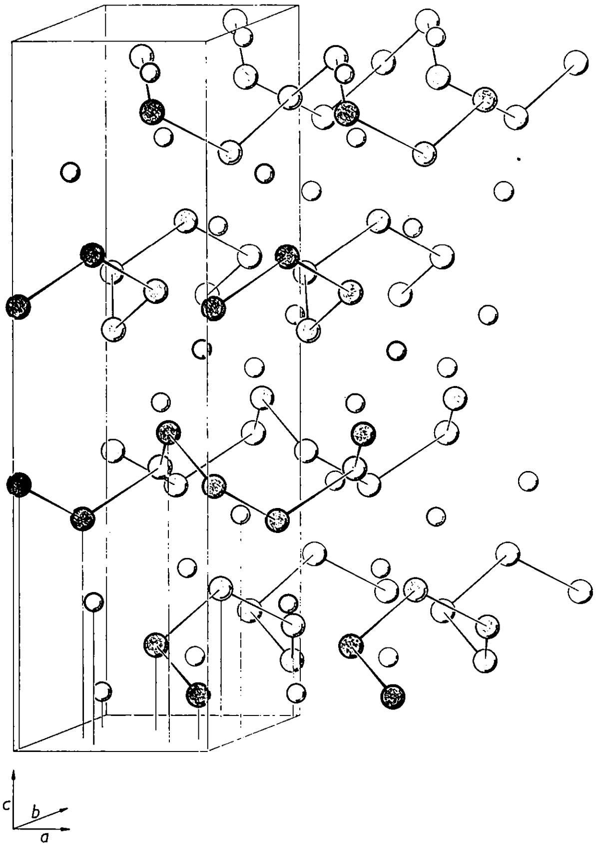

Fig. 8. Four unit cells of the tetragonal modification on ZnP_2, emphasizing the arrays of P atoms in spiral chains.

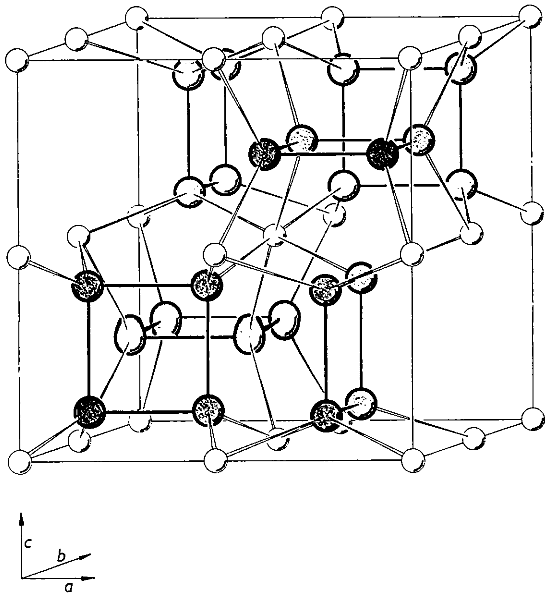

Fig. 9. Unit cell of the $CoAs_3$ structure (cubic), emphasizing the square arrays of As atoms.

nearest-neighbours and bonds occur between the two types forming the spiral chains of anions. $CoAs_3$ is a polyanionic compound satisfying the general valence rule with $b_a/n_a=2$ when Co is assumed to provide three valence electrons. The As atoms form squares (Fig. 9), such as may possibly occur in the structure of γ-oxygen, ignoring rotation of the molecules.

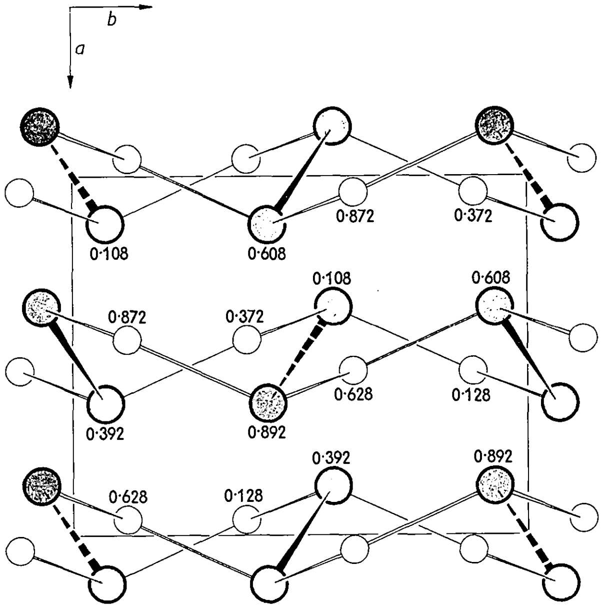

Fig. 10. Plan of the ZnSb structure (orthorhombic) on (001) emphasizing the pairs of Sb atoms. Numbers give the fractional heights of atoms in the c direction. Heavy, broken Sb–Sb bonds indicate that one of the Sb atoms forming the pair lies in a unit cell either above or below the cell indicated.

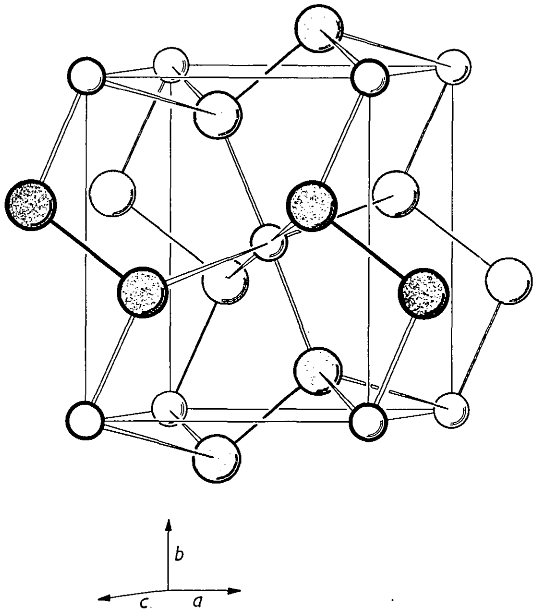

Fig. 11. Diagram of the orthorhombic, marcasite structure of FeS_2 showing S–S pairs.

(iv) *Compounds with* $b_a/n_a=1$ *and anion* $(8-N)$ *structures corresponding to Group VII elements*

Structures of very few of the possible compounds are known at present, but the structures of ZnSb (Fig. 10) and FeS_2 (pyrite or marcasite types, Fig. 11) with $b_a/n_a=1$ contain anion pairs, whose arrays are thus similar to the atomic arrays in the structures of bromine or iodine with $(8-N)=1$.

4. Polyanionic compounds with anions on more than one crystallographic site

When the anions in a polyanionic compound occupy more than one crystallographic site it is not possible to specify *a priori* whether they are expected to lie on structural arrays, similar to those of the corresponding $(8-N)$ elements, although this seems probable if the different anions have the same anion coordination numbers. In the structure of CdP_4 (Krebs, Müller & Zürn, 1956), for instance, there are two crystallographically distinct sites for the P atoms, the anion–anion coordination being 2 for P(1) and 3 for P(2). The P(1) and P(2) atoms are bonded together to form spiral chains which are linked together in a three-dimensional array by P(2)–P(2) bonds (Fig. 12). The P(2)–P(2) bonds lie in layers extending throughout ba planes in the structure and the general arrangement of the anion sub-array bears a strong resemblance to that of monoclinic ZnP_2 discussed in § 6 below.

Quite different behaviour is fond in $CaSi_2$, which we have discussed above; here Si(1) and Si(2) remain independent of each other, each forming arsenic-like double layers of atoms bonded together. In the structure of $GeAs_2$ (orthorhombic; Bryden, 1962) there are four crystallographically distinct As sites. Arsenic atoms on two of these sites (As(1) and As(4)) have no As neighbours but the As(2) and As(3) atoms each have two As neighbours and accordingly form zigzag chains running throughout the structure, corresponding to the structure of the Group VI elements Se and Te (Fig. 13). If the As atoms were assumed to be all crystallographically similar, then application of the general valence rule, which takes an average for the structure as a whole, would have predicted pairs of As atoms in the structure, since with $n_e=14$, $n_a=2$, the requirement that $(n_e+b_a-b_c)/n_a=8$, gives $b_a/n_a=1$. A number of polysulphides, polyselenides and polytellurides of the transition metals are known. In $ZrSe_3$, for example, n_e/n_a has a value of $7\frac{1}{3}$ on the assumption that Zr contributes four valence electrons. Thus $b_a/n_a=\frac{2}{3}$ and the Se atoms are expected to occupy two different sets of equivalent sites in the structure, two-thirds of them forming one anion–anion bond and the other third no anion–anion bonds. Such expectations appear to agree with a preliminary report of the structure of the compound (Krönert & Plieth, 1958).

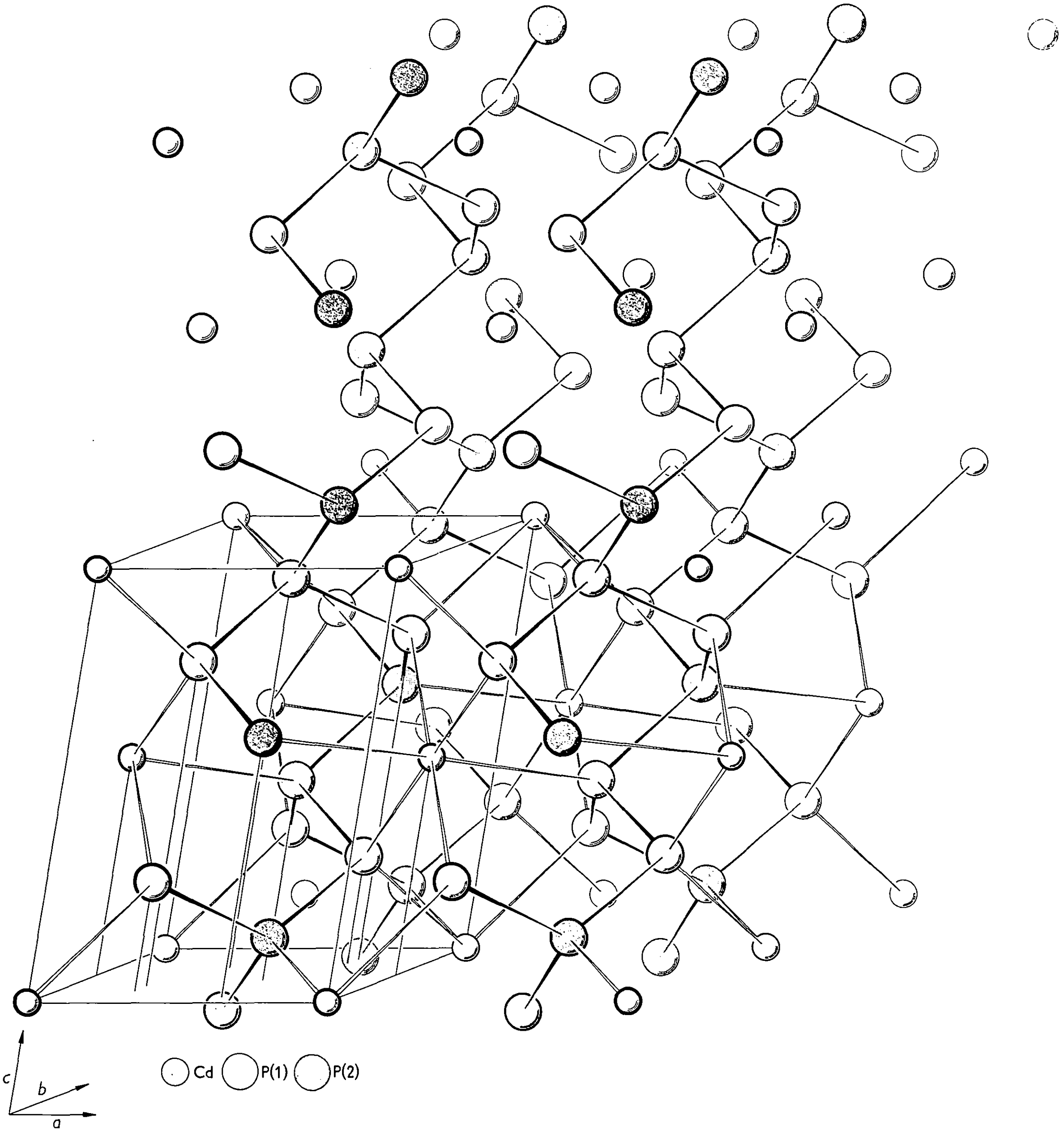

Fig. 12. The structure of CdP_4 (monoclinic). Bonds between all atoms are shown in the lower part, and the anion sub-arrays are emphasized in the upper part of the diagram.

5. *Normal* valence compounds with $n_e/n_a = 8$

Since there are no anion–anion bonds in *normal* valence compounds, the substructures of the anion arrays may be expected to have close-packed cubic or hexagonal arrangements corresponding to the structures of the inert gases, and very many semi-conducting and ionic compounds are known to have structures in accord with this principle. Ionic compounds have such structures because the octahedral interstices in the close-packed anion arrays provide sites of suitably high symmetrical coordination for the cations. In semiconducting compounds there is no doubt that the symmetry of the possible bond orbitals plays the dominant role in the choice of structures with close-packed anion arrays. Thus the most common bond-orbital symmetries of anions having a filled valence subshell composed of electrons from atomic s and p states are tetrahedral and octahedral. Since any close-packed array of anions contains two tetrahedrally and

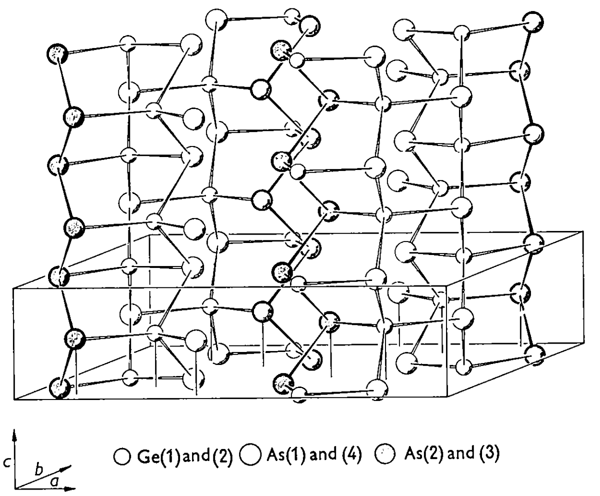

Fig. 13. Three unit cells of the $GeAs_2$ structure (orthorhombic), emphasizing the zigzag arrays of As(2) and As(3) atoms which are bonded together.

one octahedrally-coordinated interstice per close-packed atom site, the required bond-orbital symmetries are satisfied in structures where the anions occupy the close-packed sites and the cations occupy the tetrahedral and/or octahedral holes. Indeed, when the bond arrays in such structures run continuously throughout the structure, the conditions for semiconductor bonds are satisfied, provided that the cation

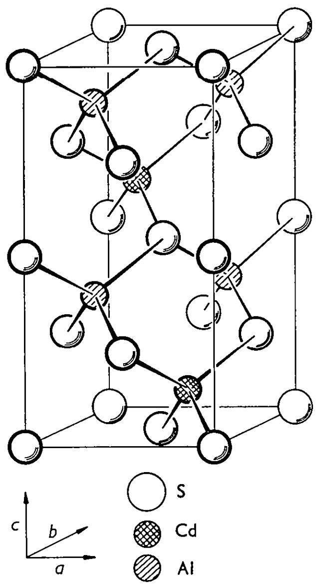

Fig. 15. Unit cell of the $CdAl_2S_4$ structure (tetragonal), showing the close-packed cubic array of anions, and ordering of the cations in the tetrahedral interstices of this array. The origins of the unit cells in Figs. 15 to 20 are chosen so as to demonstrate the close-packing of the anions.

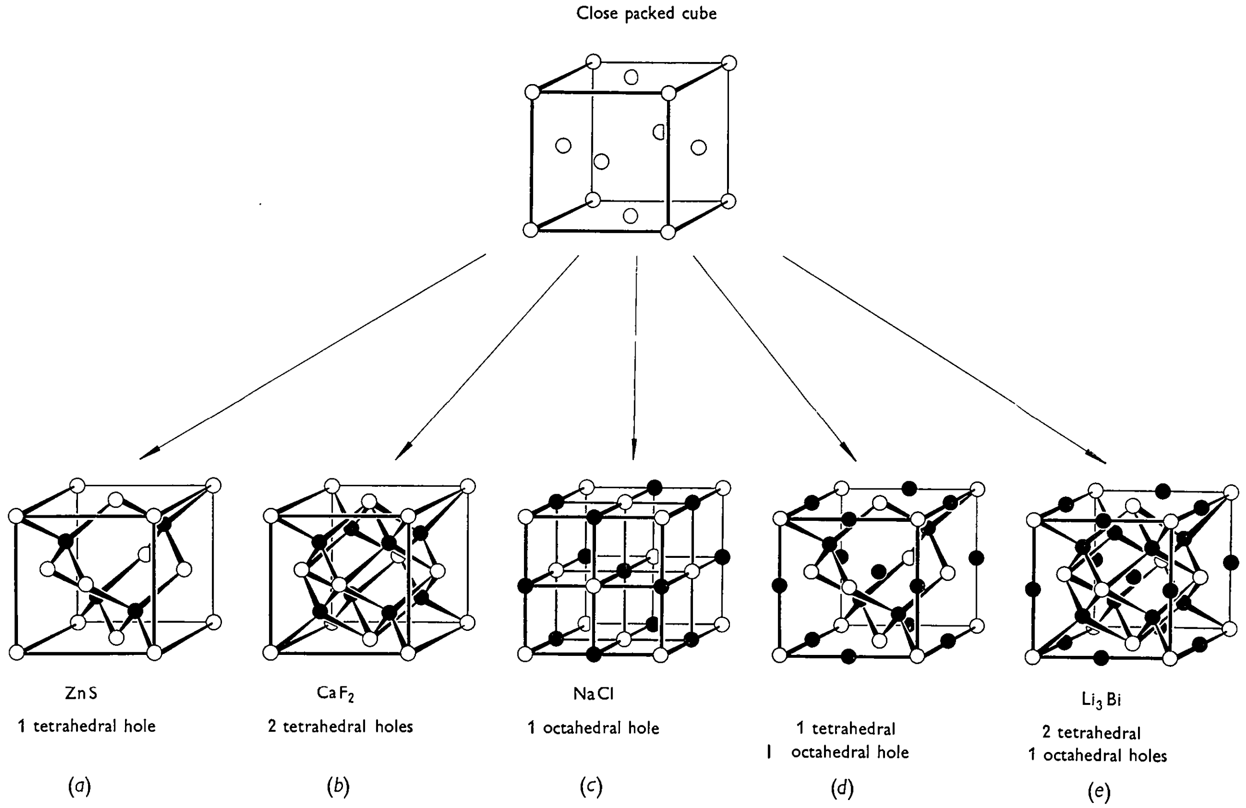

Fig. 14. Five possible binary structural types formed from a close-packed, face-centred cubic array of atoms in which each of the two sets of tetrahedral or single set of octahedral holes are either completely occupied or left vacant.

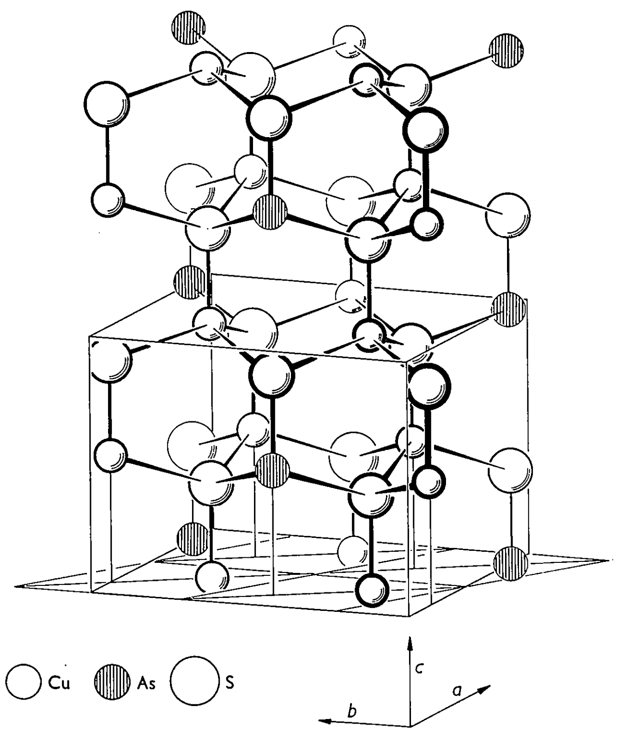

Fig. 16. Structure of enargite Cu_3AsS_4 (orthorhombic) showing the close-packed hexagonal array of anions and the ordering of the cations in the tetrahedral interstices of this array.

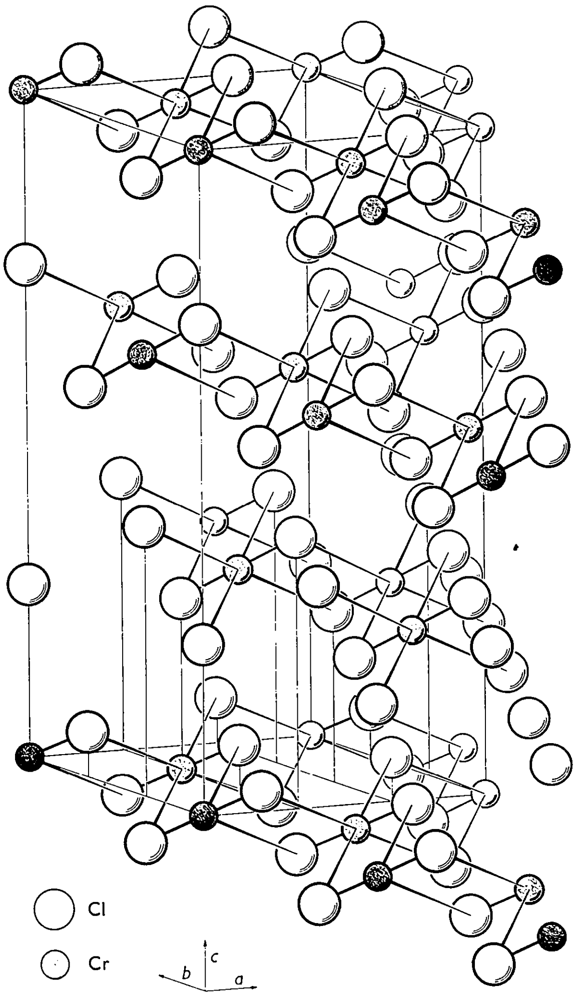

Fig. 17. The $CrCl_3$ ($D0_4$) structure (hexagonal), showing the close-packed cubic array of anions and the ordering of cations in the octahedral interstices of this array.

valencies exactly equal the anion valencies, so that the anions attain a filled valence subshell (Mooser & Pearson, 1960). In compounds with structures formed according to this principle there is only one anionic component, and the anion sites are fully occupied. The number of cations (one or more components) in the tetrahedral and/or octahedral interstices is such that the anion valencies are satisfied; it is only on the cation sites that disorder or vacancies occur. Cation valencies for molecular proportions with 1, 2, 3, ... anions can therefore be partitioned to specify all possible formulae of compounds of this type that may be obtained, since through structural limitations the maximum number of cations per anion is three. Thus, there are five different binary structures which can be formed from an undistorted close-packed cubic array of anions by either completely filling, or leaving empty, each of the three sets of interstices (Fig. 14); five structures can similarly be formed from a hexagonally close-packed array. Four of the possible cubic types are definitely known and two of the hexagonal types. From these by structural distortion, or by increasing the number of cations and/or vacancies, many other structures can be obtained. Several of these are shown in Figs. 15–20 and more are listed in Table 3, together with the fractional filling of the tetrahedral and octahedral interstices in the anion array. In many of the structures listed, structural distortion occurs to some extent, but the building principle is nevertheless clearly recognizable. It should, however, be noted that the building principle for these structures is different from that of the true interstitial carbides, nitrides, borides and hydrides of the transition metals, which are metallic. They form for geometrical reasons when the non-metal atom has a covalent size ($r_{\text{anion}}/r_{\text{cation}} < 0{\cdot}60$) sufficient for it to lie in the interstices of an array of metal atoms. The semiconducting compounds are not interstitial compounds in this sense, and the cations are only to be regarded as located at the centres of the interstitial sites which satisfy the required bond symmetries (see also Mooser & Pearson, 1957, 1959, 1960).

6. Polycationic and polycationic-polyanionic compounds which are semiconductors

Polycationic compounds can be semiconductors provided that the bonds between the metal atoms do not run continuously throughout the structure. Thus the

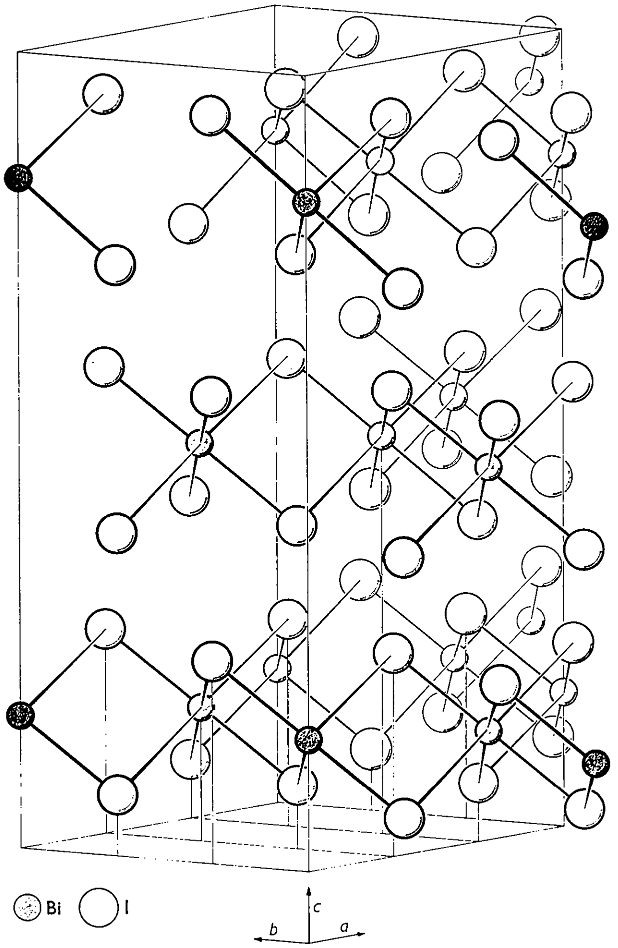

Fig. 18. The BiI_3 structure (hexagonal), showing the close-packed hexagonal array of anions and the ordering of the cations in the octahedral interstices of this array.

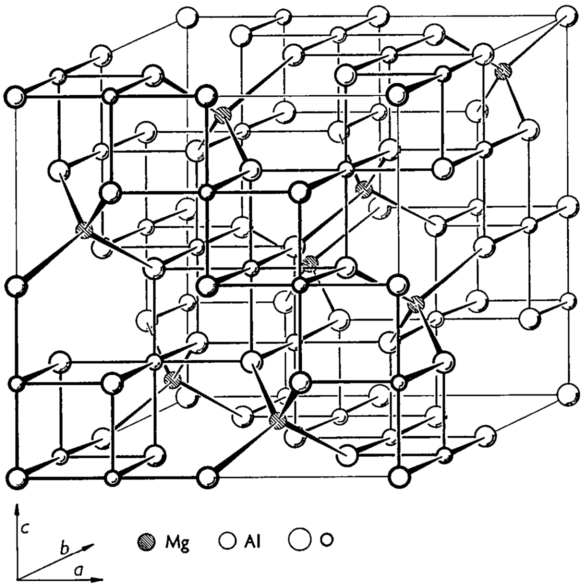

Fig. 19. The spinel structure ($MgAl_2O_4$, cubic), showing the close-packed cubic array of anions, and the ordering of the cations in the tetrahedral and octahedral interstices of this array.

Table 3. *Structures of some normal valence compounds with anions occupying close-packed cubic or hexagonal arrays (or distorted forms thereof) and cations located at the centres of tetrahedral and/or octahedral interstices in the arrays*

Fraction of holes occupied by cations		Compounds with anions on close-packed cubic arrays	Compounds with anions on single or double close-packed hexagonal arrays
Tetrahedral	Octahedral		
$\frac{1}{8}$	0	SnI_4 ($D1_1$)*	
$\frac{1}{6}$	0		Al_2Br_6
$\frac{1}{4}$	0	HgI_2 ($C13$) SiS_2 ($C42$)	
$\frac{1}{3}$	0	β-Ga_2S_3 ($B3$)	
$\frac{3}{8}$	0	α-Ag_2HgI_4 ($B3$) $CdAl_2S_4$ ($E3$) $CdIn_2Se_4$	$ZnAl_2S_4$ (H.T.) ($B4$)
$\frac{1}{2}$	0	ZnS ($B3$) (zinc blende) CuTe $AgInSe_2$ ($E1_1$) Cu_2FeSnS_4 ($H2_6$)	ZnS ($B4$) (wurtzite) SiC III ($B5$) Cu_3AsS_4 ($H2_5$)
$\frac{3}{4}$	0	Mg_3As_2 ($D5_3$) Zn_3P_2 ($D5_9$)	
1	0	Mg_2Sn ($C1$) LiMgSb ($C1_b$) Li_3AlN_2 ($E9_d$) Li_5GeP_3 ($C1$)	
0	$\frac{1}{6}$		α-WCl_6
0	$\frac{1}{3}$	$CrCl_3$ ($D0_4$)	BiI_3 ($D0_5$)
0	$\frac{1}{2}$	$CdCl_2$ ($C19$) TiO_2 ($C5$) (anatase)	CdI_2 ($C6$, $2H$) $HgBr_2$ ($C24$) $HgCl_2$ ($C25$) CdI_2 ($C27$, $4H$)
0	$\frac{2}{3}$		α-Al_2O_3 ($D5_1$) $LiSbO_3$ $FeTiO_3$ (ilmenite)
0	1	NaCl ($B1$) HgS ($B9$) GeS ($B16$) $AgBiSe_2$ ($B1$) $AgBiSe_2$ ($NaCrS_2$)	NiAs ($B8$) MnP ($B31$)
$\frac{1}{8}$	$\frac{1}{2}$	$MgAl_2O_4$ ($H1_1$) (spinel)	Mg_2SiO_4 ($H1_2$) (olivine)
$\frac{1}{2}$	$\frac{1}{8}$	Co_9S_8 ($D8_9$)	
$\frac{1}{2}$	$\frac{1}{3}$	Cu_4Te_3	
$\frac{1}{2}$	$\frac{1}{2}$		Mg_3Bi_2 ($D5_2$)
$\frac{1}{2}$	1	Cu_2Sb ($C38$)	
1	1	Li_3Bi ($D0_3$) Li_2MgSn ($D0_{3b}$)	

* *Strukturbericht* types. The compounds listed to indicate structure type are not necessarily themselves semiconductors.

compounds α-GaSe (rhombohedral), GaS (hexagonal) and β-GaSe (hexagonal) (Fig. 21), which are semiconductors, have layer structures, built up of units of four planes of atoms in the sequence Se–Ga–Ga–Se. The general valence rule is satisfied with $b_c/n_a = 1$ for the structures. Succeeding layers in these three compounds are packed as shown in Fig. 22. The structure of GaTe and GaAs (monoclinic; Bryden, private communication) is interesting since here portions of the structural units consisting of four planes of atoms extending indefinitely in the direction of the crystal *b* axis, are joined together by other Te–Ga–Ga–Te

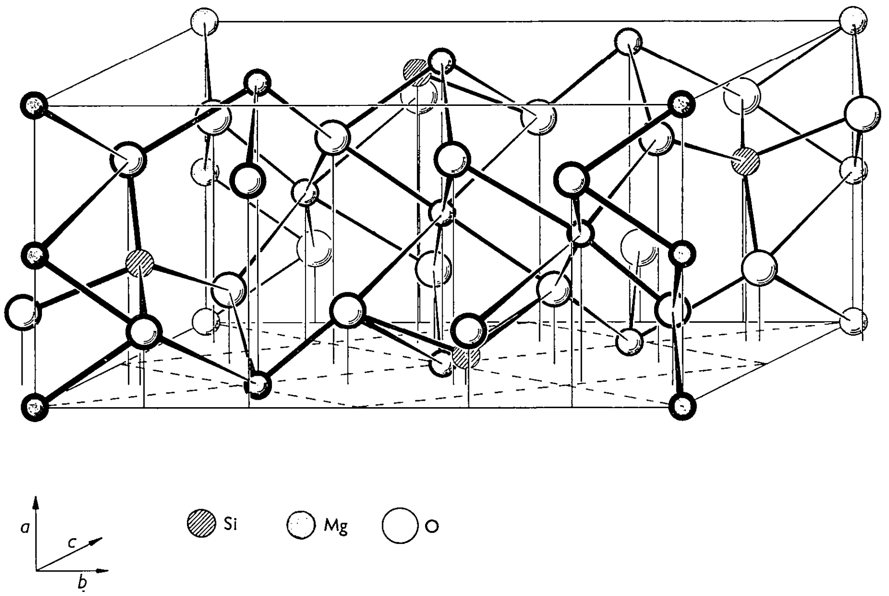

Fig. 20. The olivine structure (Mg_2SiO_4, orthorhombic), showing the close-packed hexagonal array of anions, and the ordering of the cations in the tetrahedral and octahedral interstices of this array.

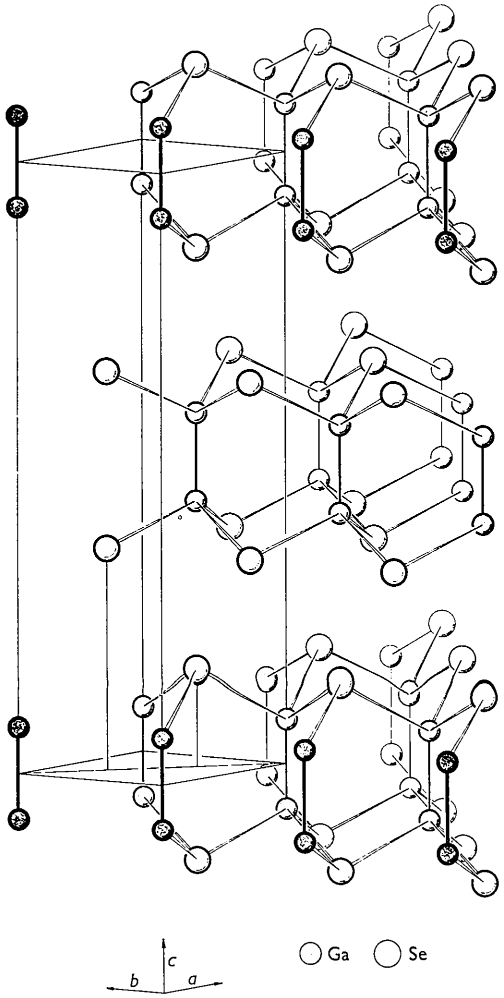

Fig. 21. The structure of β-GaSe (hexagonal), showing the Ga–Ga pairs.

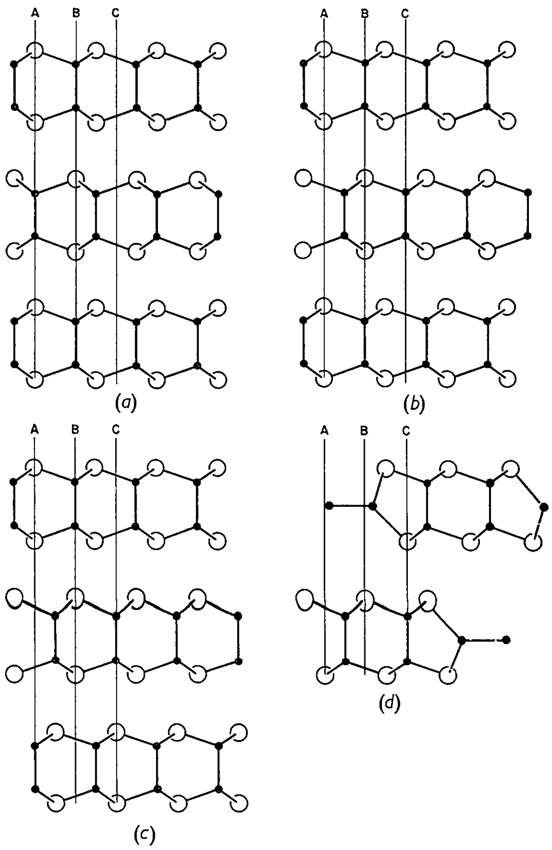

Fig. 22. Comparison of the arrangement of layers in the structures of (*a*) GaS, (*b*) α-GaSe, (*c*) β-GaSe and (*d*) GaTe. In part after Basinski, Dove & Mooser (1961).

● Ga, ○ S, Se or Te.

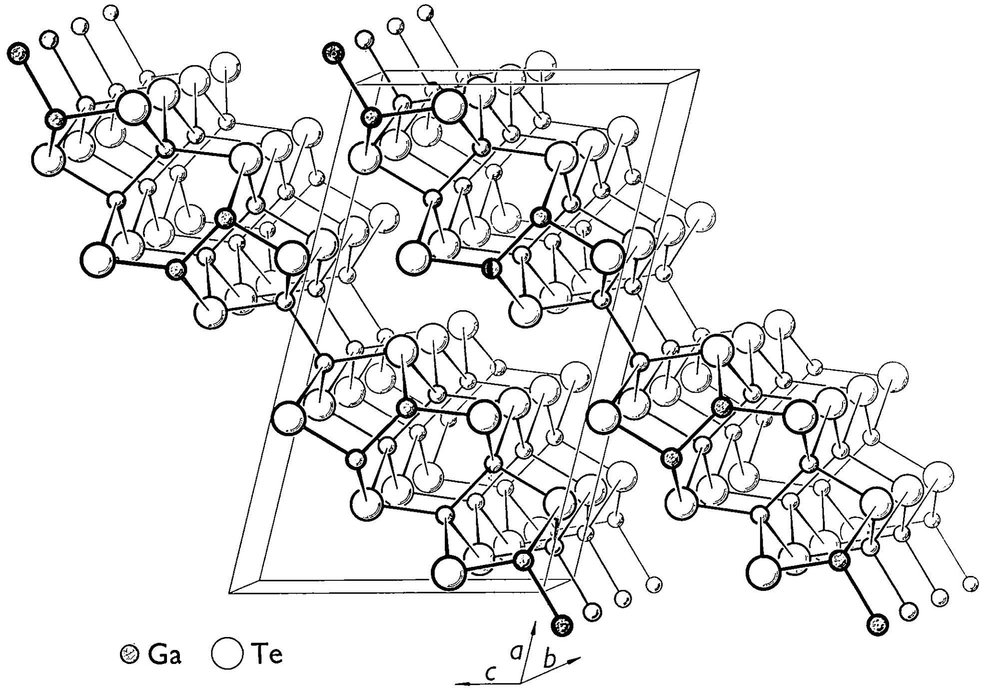

Fig. 23. The GaTe structure (monoclinic), showing the two kinds of Ga–Ga pairs.

strips in which the Ga–Ga bonds lie approximately at right angles to the other Ga–Ga bonds (Fig. 23). Since, however, the bonds between Ga atoms do not run continuously throughout the structure GeAs and GaTe are semiconductors.

Three-dimensional bond arrays occur in the structure of β-InS in which each In atom forms one In–In and two In–S bonds so that $b_c/n_a = 1$ (Fig. 24).

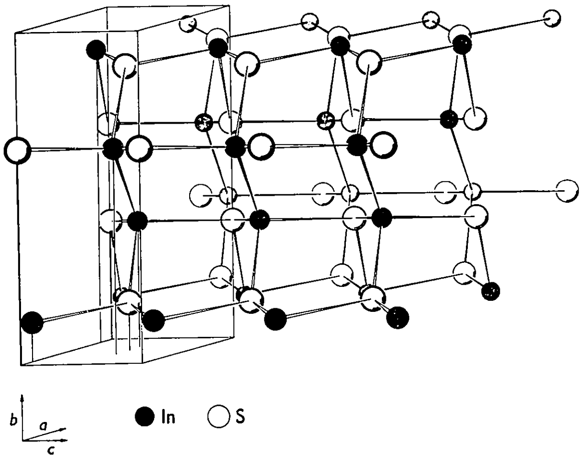

Fig. 24. Six unit cells of the β-InS structure (orthorhombic), showing In–In pairs.

The most interesting structure of all is the monoclinic form of ZnP_2 (Hegyi, Loebner, Poor & White, 1962) in which both anion–anion and cation–cation bonds occur. The general valence rule is satisfied with

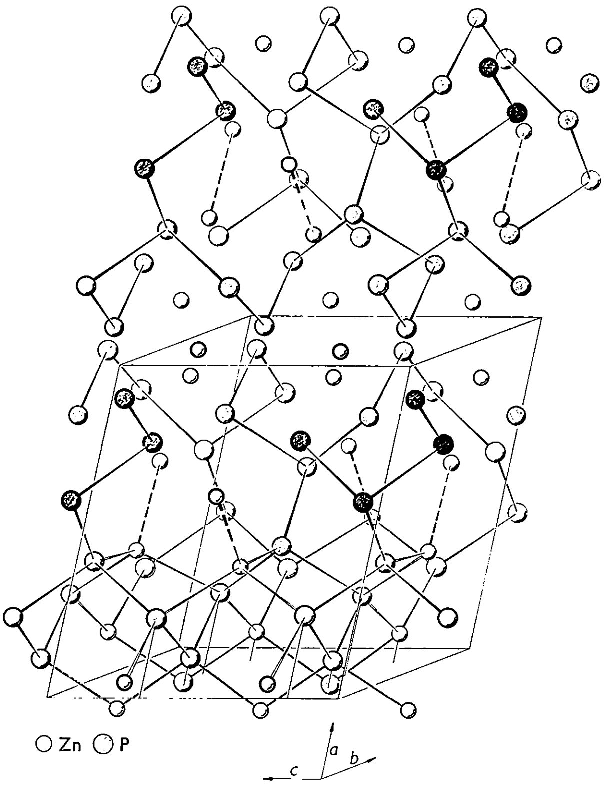

Fig. 25. The structure of the monoclinic modification of ZnP_2. General bond arrays are indicated in the lower part. In the upper part cation–anion bonds are omitted; full bonds indicate the anion–anion bonds and broken bonds indicate the cation–cation bonds.

the values $(n_e+b_a-b_c)/n_a=(12+4\frac{1}{2}-\frac{1}{2})/2=8$. There are two different zinc and four different phosphorus sites in the structure. Half of the Zn atoms form bonds with 3 P and 1 Zn atom; the other half form bonds with 4 P atoms. Of the P atoms, one quarter (P(1)) form bonds with 3 P atoms and 1 Zn atom and three quarters (P(2), P(3) and P(4)) form bonds with 2 P atoms and 2 Zn atoms. The structural arrangement of this semiconductor is shown in Fig. 25. The phosphorus atoms form chains which are joined together in a three-dimensional array by interchain bonds between the P(1) atoms. These bonds and the Zn(2)–Zn(2) bonds lie together in layers extending throughout *bc* planes of the crystal structure. The building principle of this structure therefore has marked similarities to that of CdP_4 shown in Fig. 12.

7. Summary

The discussion emphasizes the importance of the anions in determining the structures of semiconducting compounds, an importance already recognized from the correlation of the valence band with the anions in semiconductors, and from the difference between the metallic bond and the semiconductor bond (see Appendix). It also provides a certain amount of systematization of the structures of polycompounds by fitting them, through use of a general valence rule, into an overall picture embracing the structures of semiconductors which are *normal* valence compounds with bonds between anions and cations only. By itself, however, the valence rule which we have used is not a certain means of predicting semiconductivity if the atomic coordination in the structure of a compound is unknown, nor can it be used to predict structural arrangements with certainty, although it may be useful in solving certain crystal structures.

APPENDIX

We can consider that there are three fundamental types of chemical bond, ionic, covalent and van der Waals, in which electron configuration is specified. 'Metallic' and 'semiconductor' bonds can then be described as secondary bond types in which the *relative filling of the atomic valence orbitals is specified.* Both may be regarded as shared-pair covalent types. When the metallic bond occurs, there are arrays of bonds between atoms with vacant orbitals in their valence shells (permitting uninhibited resonance of the bonds) running continuously throughout the structure, and the electrons are free to move under the influence of an applied electric field. When the semiconductor bond occurs, atoms attaining filled valence subshells by electron-sharing prevent any such bond paths (between atoms with vacant orbitals) from running continuously throughout the structure, and electronic conduction requires an energy of activation. This principle is illustrated very schematically in Fig. 26.

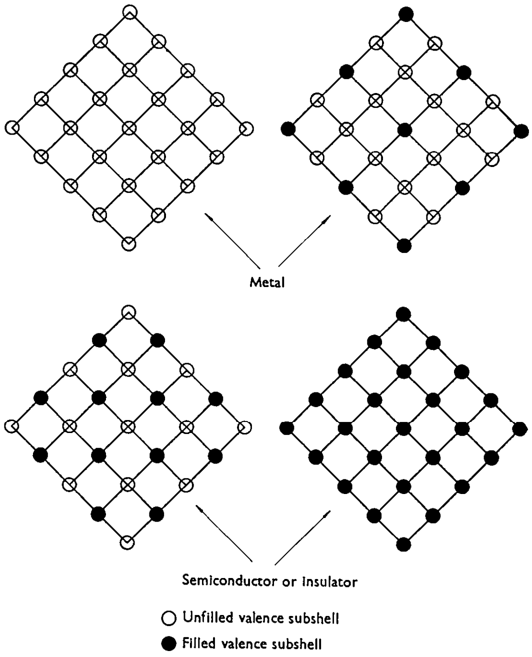

Fig. 26. Schematic diagram of two-dimensional atomic arrays illustrating the difference between metallic and semiconductor bonds. Metallic bonds occur when there are bond paths running throughout the structure between atoms having vacant orbitals in their valence subshells. Semiconductor bonds occur when atoms having filled valence subshells interrupt these bond paths, or when all atoms attain filled valence subshells by electron sharing.

I am very grateful to Drs F. Hulliger and E. Mooser for showing me their paper on semiconductor polycompounds prior to publication, to Dr J. G. White and his co-authors (Hegyi *et al.*, 1962) for the atomic parameters of both ZnP_2 structures and permission to use them prior to publication, similarly to Dr J. H. Bryden for information on the structures of GaTe and GeAs prior to publication, to Dr N. R. Stemple for information on the structure of $CdAs_2$, and finally to Dr E. Mooser and Dr A. Kjekshus for discussion and collaboration. Information on structures not given a specific reference here, can be found in Pearson (1958).

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On the Construction of Matter Tensors in Crystals

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Matter tensors, complying with the symmetry of a crystal, may be found by application of Wigner's theorem. For higher-order tensors a modification of Fumi's method is useful for all classes. The trigonal and hexagonal classes present no special difficulty. The two methods are illustrated on a sixth-order tensor.

1. Introduction

The derivation of tensors in the several crystal classes has been considered by many authors. The simplest method is the direct inspection method, which is used in the textbook of Nye (1957; *cf.* Fumi, 1952*a*, *b*). The application to trigonal and hexagonal classes, however, leads to rather intricate calculations. Fumi (1952*a*; *cf.* Fieschi & Fumi, 1953) has also devised a group-theoretical method for these two crystal systems. Only the latter method will be referred to here as the Fumi method, the term 'direct inspection method' being reserved for the former.

It is possible to modify the direct inspection method in such a way that trigonal and hexagonal crystals can be treated in the same way as others, at least for second-, third- and fourth-order tensors. Fumi's method is more powerful for higher-order tensors. But here it is not necessary to study each crystal class in detail, as he has done. It will be shown that quite simple calculations define the tensors for all classes at the same time.

This paper will not deal with detailed group-theoretical studies; thus the papers by Jahn (1937, 1949) and Bhagavantam (1952) will not be used. For the sake of completeness, attention is drawn to the work of Sirotin (1960), who builds the tensors from a collection of so-called basic tensors.

I. THE MODIFIED DIRECT METHOD

2. Basic concepts

It is well known that tensor components transform as products of coordinates. Let us denote temporarily the coordinates x, y, z by x_i, $i=1, 2, 3$; then a transformation of space (*e.g.* a rotation) is given by

$$x'_i = u_{ik}(s)x_k$$

where s is the symbol for the transformation we consider. Now the transformation of a tensor component t_{ijk} is the same as the transformation of the product $x_i x_{1,j} x_{2,k}$ of the coordinates of three vectors $\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2$.

$$t'_{ijk} = u_{ip}(s)u_{jq}(s)u_{kr}(s)t_{pqr} .$$

We may denote this transformed component by $t_{ijk}(s)$.

A matter tensor in a crystal must be invariant with respect to all symmetry operations s of the class we consider. Let $\mathbf{T}$ be an invariant tensor. The direct method puts

$$T_{ijk}(s) = T_{ijk}$$

for all operations. This method is in general very simple, but it is rather unwieldy for trigonal and hexagonal classes. Let us take as an example the rotation of 180° around the Z axis:

$$x'_1 = -x_1,\ x'_2 = -x_2,\ x'_3 = x_3 .$$