On the problem of tabular reduction of crystal chemical information : metals and semiconductors

Chemical shifts of Eu have previously been studied by FADLEY et al. [9]. The levels studied were $3\,d_{3/2}$, $3\,d_{5/2}$ and $4\,p_{3/2}$. For the $4\,p_{3/2}$ level a shift in binding energy between Eu in Eu_2O_3 and $EuAl_2$ amounting to 9.2 eV was reported. The same shift within experimental errors ($\pm$ 0.5 eV) was reported for a measurement on Eu in Eu_2O_3 and EuO. In the present investigation a shift of (7.8 $\pm$ 0.2) eV is reported for this level. The discrepancy may be explained by the difficulties in measuring shifts at higher kinetic energies of the photoelectrons as was the case in the experiment by FADLEY et al.

As long as the valence electrons do not penetrate into the atomic core, one would expect the same shift in electron binding energy for all core electrons. However, if there is a penetration of valence electrons into the core, different shifts for different core electrons are expected [4]. The smallest shift would be found for the valence electrons themselves. As seen in Table 2 the $4\,f$ electrons are shifted about 1 eV less than the $4\,p$ and $4\,d$ electrons, and the observed shifts are thus in agreement with the prediction.

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On the Problem
of Tabular Reduction of Crystal Chemical Information:
Metals and Semiconductors

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Abstract. Difficulties are emphasized of bearing in mind the great amount of crystal chemical information now existing, and using it in order to select materials most likely to provide desired electrical, magnetic or other physical properties. Regarding structures as formed by the stacking of layer networks of atoms, a tabular reduction of structural information on atomic arrangement

of 220 of some 475 known structure types of metals and semiconductors is presented which covers 13 pages. Structural details can be regenerated from the rather simple coded symbols used, and comparison of structure types or determination of atomic coordination can be made directly with the coded forms without regenerating the whole structures. A further way of relating structural details is proposed by systematically considering the connections between tetrahedra, octahedra and right-trigonal prisms, the latter being taken as an example. The paper also gives a nomenclature for crystallographically identifying structure types named after a characteristic phase or compound. This combines two symbols naming the Bravais lattice with the number of atoms in the crystallographic unit cell.

1. Introduction

Much of the research which Professor Busch has inspired has been directed to finding materials with specific electrical and magnetic properties, and no doubt the compounds that have been studied were those which, by virtue of their component atoms and structural features such as coordination and interatomic distances, were expected to provide the desired properties.

In the last decade, however, the amount of information available on the crystal structures of compounds and phases has probably doubled. In the past this work has been critically evaluated and summarized in «Strukturbericht» and its successor «Structure Reports», but the latter is now having great difficulty in dealing with all the information that is produced each year. If this structural information, which is of vital importance to physicists and chemists, can not even be assessed and reported as fast as it is published, how can the physicist or metallurgist carry enough structural information in his mind to be able to select materials with structures best suited to give the properties that he seeks to study? Storing structural data on magnetic tapes does not provide a complete answer to the problem since, although interatomic distances and other information on particular substances can be recovered at will, the total print-out of all these data is just as intractable as that stored in the volumes of «Strukturbericht» and «Structure Reports», and no easier to comprehend and bear in mind. (The paper containing my print-out of data on metals structures up to 1964 has a volume of about 65 litres!) We need a method of reducing structural information so that essential data regarding coordination and atomic arrangement of whole groups of structure types can be contained in a page or two of tables, and the coding for this reduction must be such that the atomic arrangement can be regenerated simply from inspection of the coded descriptions. This requires the use of very simple crystallographically mnemonic codes, careful consideration of criteria upon which the grouping of structures is based so as to include the largest number of structure types possible, and of the information that is given in the tables and either recoverable from the code, or directly usable for comparison between structures described in the coded form.

In this paper we make a start at grouping and coding structures of metals and semiconductors in such a way that the structural information is greatly condensed without losing information about atomic coordination, etc. One of the most profitable ways to approach the problem is to consider these structures as generated by the stacking of layers of atoms. This is a principle of wide structural scope, which is readily amenable to coding, powerful for examining structural relationships, and permitting easy interpretation of atomic coordination and grouping of structures

according to coordination polyhedra. We consider three main groups of structures:
1) Those formed by the stacking together of triangular, hexagonal and/or kagomé
layers of atoms, giving tetrahedral, octahedral and right trigonal prismatic arrange-
ments of atoms. 2) Structures formed by alternating primary pentagon-triangle,
pentagon-hexagon-triangle or hexagon-triangle networks of atoms with secondary
triangular, square or square-triangle networks, giving interpenetrating triangulated
CN 12, 14, 15 or 16 polyhedra. These are tetrahedrally close packed structures in
which distorted tetrahedra of atoms pack together to fill space. 3) Structures formed
by layers of atoms containing squares.

<div align="center">

Table 1

Symbols used for the fourteen Bravais lattices

</div>

Nomenclature symbol	System	Lattice symbol
aP	triclinic (anorthic)	P
mP	monoclinic	$P^{a)}$
mC		$C^{a)}$
oP	orthorhombic	P
oC		C
oF		F
oI		I
tP	tetragonal	P
tI		I
hP	hexagonal (and trigonal, P)	P
hR	rhombohedral	R
cP	cubic	P
cF		F
cI		I

[a]) Second setting, y axis unique.

In the first place, however, we require a simple means of identifying in terms
of crystallographic information, structure types that are named after some compound
or phase characteristic of the type. This is achieved by specifying the Bravais lattice
according to the symbols given in Table 1 which make use of the crystallographic
letters to describe primitive and centred lattices, together with the number of atoms
in the crystallographic unit cell. Thus for example, the $AuCu_3$ structure is described
as $cP4$.

<div align="center">

2. Structures Formed by the Stacking of Triangular, Hexagonal
or Kagomé Nets of Atoms

</div>

Many structures are formed by the stacking together of 3^6 [1]) triangulated, 6^3
hexagonal and/or 3636 kagomé networks of atoms (Figure 1). Structures involving

[1]) Schlafli symbols, see [1].

only triangular nets of atoms located so that the nodes of one net centre the triangles of the nets above and below, are the well-known close packed cubic, hexagonal or rhombohedral types. Relative to the basal plane of a hexagonal cell, the nodes of the triangular network can be located at three different sites, 0,0; 1/3, 2/3 and 2/3, 1/3, called respectively A, B and C in the notation adopted (Figure 2), and the basal hexagonal cell contains one atom from the triangular net. Similarly the hexagonal net of atoms can be located at three corresponding positions a, b and c in the planar hexagonal cell (Figure 2), which then contains two atoms from the hexagonal net.
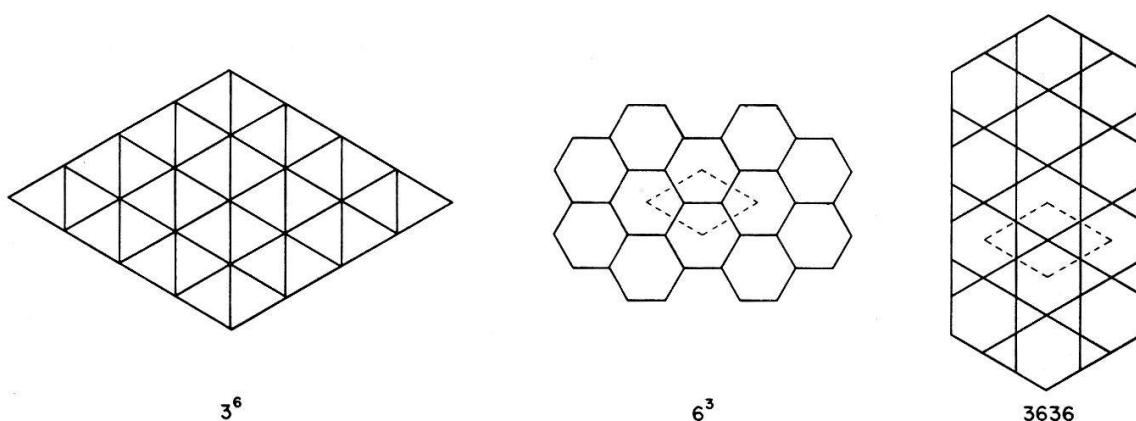

Figure 1

3^6, 6^3 and 3636 triangular, hexagonal and kagomé nets.

The kagomé net can also be located at three corresponding positions α, β and γ in the basal hexagonal cell (Figure 2) which contains three atoms from the net. The arrangement of atoms relative to the basal hexagonal cell can be described for any one of these networks by the appropriate letters. Thus for similar atoms located at 1/3, 2/3, 1/2 and 2/3, 1/3, 1/2 in a unit cell, the code letter is 'a'. When atoms in the same plane (or very nearly so) occupy two (or more) different crystallographic sites, then the symbols for these sub-networks are enclosed in square brackets to indicate that they lie in the same plane. Thus the symbol describing one component at 1/3, 2/3,0 and another at 2/3, 1/3,0 is $[BC]$. If there are several layers of atoms which are considerably

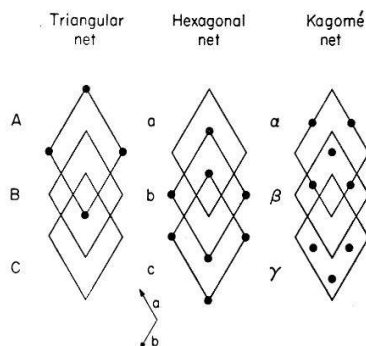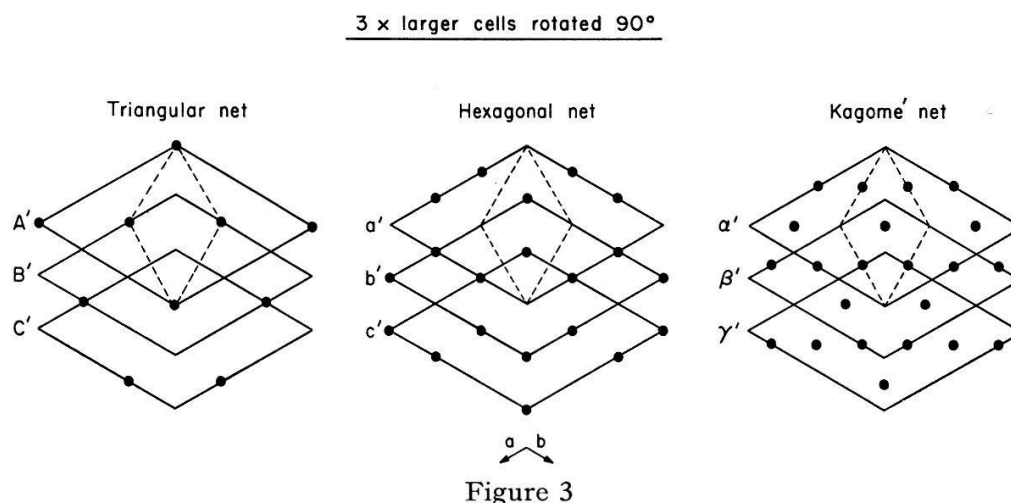Figure 2

Triangular, hexagonal and kagomé nets of atoms in three stacking positions (A, B, C; a, b, c; α, β, γ respectively) relative to a basal hexagonal cell which contains respectively 1, 2 and 3 atoms per net.

closer than the average interlayer distance in the structure, yet not close enough to be regarded as a single layer, then the symbols describing the layers are placed in round brackets, for example (ABC).

These stacking symbols for 3^6, 6^3 and 3636 networks can be used to describe structural arrangements. For example, that in the $MgZn_2$ structure is $(A\underline{B})\,\beta\,(\underline{B}A\underline{C})\,\gamma\,(\underline{C})$ where the underlined layers are those occupied by the first component in the structural formula. For a full description of the structure it is not only necessary to identify the component occupying the layer net, but also to specify the spacing between the layers. For example, structures described by arrangements of symbols A, B, C only, are close packed structures provided that the spacing between layers is approximately correct. Filling of tetrahedral and/or octahedral holes in these layers introduces new 3^6 networks of atoms (symbols A, B, C), but the relative spacing of the layers is now incorrect for overall close packing of the structure. The full symbol adopted to describe structures containing stacked 3^6, 6^3 and 3636 networks of atoms (Table 2) gives the chemical symbol for the component atom occupying the network 'on-line', the network symbol 'super' and the layer height as a fraction[2]) of the unit cell edge normal to the layers, 'sub'. Thus the $MgZn_2$ structure is fully described as $Zn_0^A Mg_{06}^B Zn_{25}^6 Mg_{44}^B Zn_5^A Mg_{56}^C Zn_{75}^\gamma Mg_{94}^C$. Description of some structures requires consideration also of a larger basal hexagonal cell rotated $90°$ relative to the other and containing respectively 3, 6 and 9 atoms per 3^6, 6^3 and 3636 net. The larger cells and stacking arrangements corresponding to those of the smaller cell are shown in Figure 3 and described by the primed symbols A', B', C'; a', b', c' and α', β', γ'.

Practically all hexagonal[3]) and rhombohedral structures and numerous cubic structures are generated by the stacking of these networks of atoms, and details of these are given in Table 2 in terms of hexagonal cells. 93% of known hexagonal and rhombohedral structures [2] (containing up to 24 or 30 atoms per cell) can be described

3 × larger cells rotated 90°

Triangular net   Hexagonal net   Kagomé net

Figure 3

Triangular, hexagonal and kagomé nets of atoms in three stacking positions (A', B', C'; a', b', c'; α', β', γ' respectively) relative to a basal hexagonal cell which contains respectively 3, 6 and 9 atoms per net.

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[2]) Expressed as a decimal with the decimal point omitted.

[3]) There are very few hexagonal structure types (such as Se or HgS) that have chains or spirals of atoms along the c axis, instead of layers of atoms normal to c.

Table 2

Structures formed by stacking triangular, hexagonal and/or kagomé nets of atoms.

See Figures 2 or 3 for code of stacking positions (letters super). Numbers sub give height of atom plane as fraction of c edge of cell (decimal points are excluded; thus 5 means 0.5). An asterisk (*) indicates a partially occupied layer. M indicates two components disordered on sites.

Hexagonal structures

Structure		Layer stacking sequence
$hP\ 2$	WC	$W_0^A C_5^B$
	Mg	$Mg_{25}^B Mg_{75}^C$
$hP\ 2.7$	ε-PtZn$_{1.7}$	$Pt_0^A Zn_{45}^{B*} Zn_{50}^{\alpha*} Zn_{55}^{C*}$
$hP\ 3$	CdI$_2$	$Cd_0^A I_{25}^B I_{75}^C$
	ω-Cr-Ti	$M_0^A M_5^a$
	Se	Chain structure
	AlB$_2$	$Al_0^A B_5^a$
	δ-UZr$_2$	$Zr_0^A M_5^a$
	NFe$_2$	$N_0^{A*} Fe_{25}^B N_5^{A*} Fe_{75}^C$
$hP\ 3.75$	Cr$_7$S$_8$	$Cr_0^A S_{25}^B Cr_5^{A*} S_{75}^C$
$hP\ 4$	NOTaZr	$Zr_0^A O_0^B Ta_5^B N_5^C$
	NLi$_3$	$N_0^A Li_0^a Li_5^A$
	NiAs	$Ni_0^A As_{25}^B Ni_5^A As_{75}^C$
	La	$La_0^A La_{25}^B La_5^A La_{75}^C$
	ZnS	$S_0^B Zn_{37}^B S_5^C Zn_{87}^C$
$hP\ 5$	Ni$_2$Al$_3$	$Al_0^A Ni_{15}^B Al_{35}^C Al_{65}^B Ni_{85}^C$
	La$_2$O$_3$	$O_0^A La_{24}^B O_{37}^C O_{63}^B La_{76}^C$
$hP\ 6$	HgS	Chain structure
	InNi$_2$	$Ni_0^A Ni_{25}^C In_{25}^B Ni_5^A Ni_{75}^B In_{75}^C$
	CaCu$_5$	$Ca_0^A Cu_0^a Cu_5^\alpha$
	CoSn	$Sn_0^A Co_0^\alpha Sn_5^a$
	TeCu$_2$	$Cu_{16}^a Te_{31}^A Te_{69}^A Cu_{84}^a$
	ReB$_2$	$B_{05}^C Re_{25}^B B_{45}^C B_{55}^B Re_{75}^C B_{95}^B$
	CaIn$_2$	$In_{05}^B Ca_{25}^A In_{45}^B In_{55}^C Ca_{75}^A In_{95}^C$
	MoS$_2$	$S_{13}^C Mo_{25}^B S_{37}^C S_{63}^B Mo_{75}^C S_{87}^B$
	NbS$_2$ (H.T.)	$S_{13}^B Nb_{25}^A S_{37}^B S_{63}^C Nb_{75}^A S_{87}^C$
$hP\ 7$	Al$_3$Zr$_4$	$Al_0^\beta Zr_{25}^B Zr_5^b Zr_{75}^B$
	Nb$_{1.4}$S$_2$	$Nb_0^{A*} S_{13}^B Nb_{25}^A S_{37}^B Nb_5^{A*} S_{63}^C Nb_{75}^A S_{87}^C$
$hP\sim7.4$	Mo$_{\sim0.84}$N	$Mo_0^{A*} N_{13}^B Mo_{25}^A N_{37}^B Mo_5^{A*} N_{63}^C Mo_{75}^A N_{87}^C$
$hP\ 8$	AsNa$_3$	$Na_{08}^C Na_{25}^A As_{25}^B Na_{42}^C Na_{58}^B Na_{75}^A As_{75}^C Na_{92}^B$
	AlCCr$_2$	$C_0^A Cr_{09}^B Al_{25}^C Cr_{41}^B C_5^A Cr_{59}^C Al_{75}^B Cr_{91}^C$
	Th$_3$Pd$_5$	$Pd_0^{C'} Pd_0^a Th^{B'}$ (distorted)
	NNi$_3$	$N_0^B Ni_{25}^{B'} N_5^C Ni_{75}^{C'}$
	AsTi	$As_0^A Ti_{13}^B As_{25}^C Ti_{37}^B As_5^A Ti_{63}^C As_{75}^B Ti_{87}^C$
	MnTa$_3$N$_4$	$M_0^A N_{13}^B Ta_{25}^C N_{37}^B M_5^A N_{63}^C Ta_{75}^B N_{87}^C$

Table 2 (Continuation)

Structure		Layer stacking sequence
$hP\,8$	ReB_3	$B_0^A B_{05}^C Re_{25}^B B_{45}^C B_5^A B_{55}^B Re_{75}^C B_{95}^B$
	$Cu_{0.65}NbS_2$	$Cu_{06}^{C*} S_{13}^B Nb_{25}^C S_{37}^B Cu_{44}^{C*} Cu_{56}^{B*} S_{63}^C Nb_{75}^B S_{87}^C Cu_{94}^{B*}$
	GaS	$S_{10}^C Ga_{17}^B Ga_{33}^B S_{40}^C S_{60}^B Ga_{67}^C Ga_{83}^C S_{90}^B$
	$\beta\text{-}Na_2S_2$	$Na_0^A S_{15}^C Na_{25}^B S_{35}^C Na_5^A S_{65}^B Na_{75}^C S_{85}^B$
	$SnNi_3$	$Sn_{25}^B Ni_{25}^\beta Sn_{75}^C Ni_{75}^\gamma$
$hP\,9$	$\delta_H^{II}\text{-}NW_2$	$W_{06}^A N_{15}^B W_{27}^B W_{39}^B N_5^A W_{61}^C W_{73}^C N_{85}^C W_{94}^A$
	Cr_2N	$N_0^c Cr_{25}^{B'} N_5^C Cr_{75}^{C'}$
	$\delta\text{-}AgZn$	$Zn_0^A M_{25}^{C'} Zn_{25}^C M_{75}^{B'} Zn_{75}^B$
	Pb_2Li_7	$Li_0^A Li_{08}^C Pb_{25}^B Li_{33}^A Li_{42}^C Li_{58}^B Li_{67}^A Pb_{75}^C Li_{92}^B$
	$CrSi_2$	$-$
	PFe_2	$P_0^{B'} Fe_0^a P_5^{C'} Fe_5^A$
	$InMg_2$	$In_0^{B'} Mg_0^a In_5^{C'} Mg_5^A$
$hP\,10$	N_2Be_3	$N_0^A Be_{08}^B Be_{25}^A N_{25}^B Be_{42}^B N_5^A Be_{58}^C Be_{75}^A N_{75}^C Be_{92}^C$
	C_2Mo_3	$C_0^{A*} C_{08}^{B*} Mo_{17}^C Mo_{25}^A Mo_{33}^C C_{42}^{B*} C_5^A C_{58}^{C*} Mo_{67}^B Mo_{75}^A Mo_{83}^B C_{92}^{C*}$
	Pt_2Sn_3	$Sn_{07}^C Pt_{14}^B Sn_{25}^A Pt_{36}^B Sn_{43}^C Sn_{57}^B Pt_{64}^C Sn_{75}^A Pt_{86}^C Sn_{93}^B$
$hP\,12$	$AgBiSe_2$	$Ag_0^A Se_{07}^C Bi_{16}^B Se_{25}^A Ag_{33}^C Se_{41}^B Bi_5^A Se_{59}^C Ag_{67}^B Se_{75}^A Bi_{84}^C Se_{93}^B$
	WAl_5	$Al_0^c W_0^C Al_{25}^{C'} Al_5^b W_5^B Al_{75}^{B'}$
	K_2S_2	$K_0^{B'} S_{18}^a S_{32}^A K_5^C S_{68}^A S_{82}^a$
	CuS	$S_{06}^A Cu_{11}^B Cu_{25}^C S_{25}^B Cu_{39}^B S_{44}^A S_{56}^A Cu_{61}^C Cu_{75}^B S_{75}^C Cu_{89}^C S_{94}^A$
	$MgZn_2$	$Zn_0^A Mg_{06}^B Zn_{25}^\beta Mg_{44}^B Zn_5^A Mg_{56}^C Zn_{75}^\gamma Mg_{94}^C$
	$NbSe_2\ (4H)$	$Nb_0^A Se_{07}^B Se_{19}^C Nb_{25}^A Se_{32}^C Se_{43}^A Nb_5^B Se_{57}^A Se_{68}^C Nb_{75}^A Se_{81}^C Se_{93}^B$
$hP\,14$	W_2B_5	$B_0^A B_{03}^C W_{14}^B B_{25}^b W_{36}^B B_{47}^C B_5^A B_{53}^B W_{64}^C B_{75}^c W_{86}^C B_{97}^B$
	$\beta\text{-}Si_3N_4$	$N_{25}^{B'} N_{25}^B Si_{25}^\gamma N_{75}^{C'} N_{75}^C Si_{75}^\beta$
	Ni_3Te_4	$-$
$hP\,16$	Si_3Mn_5	$Mn_0^a Mn_{25}^{B'} Si_{25}^{C'} Mn_5^a Mn_{75}^{C'} Si_{75}^{B'}$ (distorted)
	$TiNi_3$	$Ti_0^A Ni_0^\alpha Ti_{25}^B Ni_{25}^\beta Ti_5^A Ni_5^\alpha Ti_{75}^C Ni_{75}^\gamma$
$hP\,18$	$FeMg_3Si_6Al_8$	$Al_0^{B'} Fe_0^A Si_{22}^{C'} Al_{23}^a Mg_5^{B'} Al_5^A Al_{77}^a Si_{78}^{C'}$ (distorted)
	Ga_4Ti_5	$Ga_0^A Ti_0^a Ga_{25}^{C'} Ti_{25}^{B'} Ga_5^A Ti_5^a Ga_{75}^{B'} Ti_{75}^{C'}$
$hP\,19$	Th_7S_{12}	$-$
$hP\,20$	$\alpha\text{-}Cr_2S_3$	$Cr_0^{A'} S_{13}^{C'} Cr_{25}^B S_{38}^{B'} Cr_5^{A'} S_{63}^{C'} Cr_{75}^C S_{88}^{B'}$
	Fe_3Th_7	$-$
$hP\,22$	Sn_5Ti_6	$Ti_0^\alpha Ti_{25}^\gamma Sn_{25}^c Sn_{25}^\beta Ti_5^\alpha Ti_{75}^\beta Sn_{75}^b Sn_{75}^\gamma$
	Cr_5S_6	$Cr_0^{A'} S_{13}^{C'} Cr_{25}^b S_{38}^{B'} Cr_5^{A'} S_{63}^{C'} Cr_{75}^c S_{88}^{B'}$
$hP\,24$	HoD_3	$D_{10}^{B'} D_{17}^B Ho_{25}^{C'} D_{25}^A D_{33}^C D_{40}^{B'} D_{60}^{C'} D_{67}^B Ho_{75}^{B'} D_{75}^A D_{83}^C D_{90}^{C'}$
	$PuAl_3$	$Al_{08}^\beta Pu_{09}^B Al_{25}^\alpha Pu_{25}^A Pu_{41}^A Al_{42}^B Al_{58}^\gamma Pu_{59}^A Al_{75}^\gamma Pu_{75}^C Pu_{91}^C Al_{92}^\gamma$
	$CeNi_3$	$Ni_{04}^A Ce^B Ni_{13}^\beta Ce_{25}^B Ni_{25}^b Ni_{37}^\beta Ce_{46}^B Ni_5^A Ce_{54}^C Ni_{63}^\gamma Ce_{75}^C Ni_{75}^c Ni_{87}^\gamma Ce_{96}^C$
	VCo_3	$V_0^A Co_0^\alpha V_{17}^C Co_{17}^\gamma V_{33}^B Co_{33}^\beta V_5^A Co_5^\alpha V_{67}^B Co_{67}^\beta V_{83}^C Co_{83}^\gamma$
	PCu_3	$Cu_0^A Cu_{08}^{C'} Cu_{17}^B P_{25}^{B'} Cu_{33}^C Cu_{42}^{C'} Cu_5^A Cu_{58}^{B'} Cu_{67}^B P_{75}^C Cu_{83}^C Cu_{92}^{B'}$
	FeS	$S_0^A S_{02}^B Fe_{13}^{B'} S_{25}^{C'} Fe_{38}^{B'} S_{48}^B S_5^A S_{52}^C Fe_{63}^{B'} S_{75}^{C'} Fe_{88}^B S_{98}^C$
	$MgNi_2$	$Ni_0^\alpha Mg_{09}^A Ni_{13}^B Mg_{16}^C Ni_{25}^\gamma Mg_{34}^C Ni_{37}^B Mg_{41}^A Ni_5^\alpha Mg_{59}^A Ni_{63}^C Mg_{66}^B Ni_{75}^\beta Mg_{84}^B$ $Ni_{87}^C Mg_{91}^A$

Table 2 (Continuation)

Cubic structures

Structure		Layer stacking sequence
$cP\,2$	CsCl	$Cs_0^A Cl_{17}^B Cs_{33}^C Cl_5^A Cs_{67}^B Cl_{83}^C$
$cP\,4$	$AuCu_3$	$Au_0^A Cu_0^\alpha Au_{33}^C Cu_{33}^\gamma Au_{67}^B Cu_{67}^\beta$
	ReO_3	$Re_0^A O_{17}^\beta Re_{33}^C O_5^\alpha Re_{67}^B O_{83}^\gamma$
$cP\,5$	CFe_4	$C_0^A Fe_{25}^{A+\alpha} C_{33}^C Fe_{58}^{C+\gamma} C_{67}^B Fe_{92}^{B+\beta}$
	$CaTiO_3$	$Ca_0^A O_0^\alpha Ti_{17}^B Ca_{33}^C O_{33}^\gamma Ti_5^A Ca_{67}^B O_{67}^\beta Ti_{83}^C$
$cP\,6$	OCu_2	$O_0^A O_{17}^B Cu_{25}^{A+\alpha} O_{33}^C O_5^A Cu_{58}^{C+\gamma} O_{67}^B O_{83}^C Cu_{92}^{B+\beta}$
$cP\,8$	VCu_3S_4	$V_0^A Cu_{17}^\beta S_{24}^{A+\alpha} V_{33}^C Cu_5^\alpha S_{59}^{C+\gamma} V_{67}^B Cu_{83}^\gamma S_{92}^{B+\beta}$
$cF\,4$	Cu	$Cu_0^A Cu_{33}^B Cu_{67}^C$
$cF\,8$	C	$C_0^A C_{25}^A C_{33}^B C_{58}^B C_{67}^C C_{92}^C$
	ZnS	$Zn_0^A S_{25}^A Zn_{33}^B S_{58}^B Zn_{67}^C S_{92}^C$
	NaCl	$Na_0^A Cl_{17}^C Na_{33}^B Cl_5^A Na_{67}^C Cl_{83}^B$
$cF\,12$	CaF_2	$Ca_0^A F_{08}^B F_{25}^A Ca_{33}^B F_{42}^C F_{58}^B Ca_{67}^C F_{75}^A F_{92}^C$
	AsAgMg	$As_0^A Mg_{08}^B Ag_{25}^A As_{33}^B Mg_{42}^C Ag_{58}^B As_{67}^C Mg_{75}^A Ag_{92}^C$
$cF\,16$	BiF_3	$Bi_0^A F_{08}^B F_{17}^C F_{25}^A Bi_{33}^B F_{42}^C F_5^A F_{58}^B Bi_{67}^C F_{75}^A F_{83}^B F_{92}^C$
	NaTl	$Na_0^A Tl_{08}^B Tl_{17}^C Na_{25}^A Na_{33}^B Tl_{42}^C Tl_5^A Na_{58}^B Na_{67}^C Tl_{75}^A Tl_{83}^B Na_{92}^C$
	$AlMgCu_2$	$Al_0^A Cu_{08}^B Mn_{17}^C Cu_{25}^A Al_{33}^B Cu_{42}^C Mn_5^A Cu_{58}^B Al_{67}^C Cu_{75}^A Mn_{83}^B Cu_{92}^C$
$cF\,24$	$MgCu_2$	$Mg_0^A Cu_{13}^\alpha Mg_{25}^A Cu_{29}^C Mg_{33}^B Cu_{46}^\beta Mg_{58}^B Cu_{63}^A Mg_{67}^C Cu_{79}^\gamma Mg_{92}^C Cu_{96}^B$
	$AuBe_5$	$Au_0^A Be_{13}^\alpha Be_{25}^A Be_{29}^C Au_{33}^B Be_{46}^\beta Be_{58}^B Be_{63}^A Au_{67}^C Be_{79}^\gamma Be_{92}^C Be_{96}^B$
	$MgSnCu_4$	$Mg_0^A Cu_{13}^\alpha Sn_{25}^A Cu_{29}^C Mg_{33}^B Cu_{46}^\beta Sn_{58}^B Cu_{63}^A Mg_{67}^C Cu_{79}^\gamma Sn_{92}^C Cu_{96}^B$
$cF\,32$	$GeCa_7$	$Ge_0^A Ca_0^\alpha Ca_{17}^{C+\gamma} Ge_{33}^B Ca_{33}^\beta Ca_5^{A+\alpha} Ge_{67}^C Ca_{67}^\gamma Ca_{83}^{B+\beta}$
$cF\,56$	$MgAl_2O_4$	$O_0^{A+\alpha} Al_{08}^\beta O_{17}^{C+\gamma} Mg_{21}^B Al_{25}^A Mg_{29}^C O_{33}^{B+\beta} Al_{42}^\gamma O_5^{A+\alpha} Mg_{54}^C Al_{58}^B Mg_{63}^A O_{67}^{C+\gamma} Al_{75}^\alpha$ $O_{83}^{B+\beta} Mg_{88}^A Al_{92}^C Mg_{96}^B$
$cI\,10$	$PtHg_4$	$Pt_0^A Hg_{08}^{C+\gamma} Pt_{17}^C Hg_{25}^{A+\alpha} Pt_{33}^C Hg_{42}^{B+\beta} Pt_5^A Hg_{58}^{C+\gamma} Pt_{67}^B Hg_{75}^{A+\alpha} Pt_{83}^C Hg_{92}^{B+\beta}$
$cI\,16$	VTl_3S_4	$V_0^A Tl_0^\alpha S_{01}^C S_{11}^\gamma V_{17}^B Tl_{17}^\beta S_{18}^A S_{28}^\alpha V_{33}^C Tl_{33}^\gamma S_{34}^B S_{44}^\beta V_5^A Tl_5^\alpha S_{51}^C S_{61}^\gamma V_{67}^B Tl_{67}^\beta S_{68}^A$ $S_{78}^\alpha V_{83}^C Tl_{83}^\gamma S_{84}^B S_{94}^\beta$ (α, β, γ distorted)

Rhombohedral structures

Structure		Layer stacking sequence
$hR\,1$	Hg	$Hg_0^A Hg_{33}^C Hg_{67}^B$
$hR\,2$	As	$As_{11}^C As_{23}^A As_{44}^B As_{56}^C As_{77}^A As_{89}^B$
$hR\,3$	$\alpha\text{-}MoS_2$	$Mo_0^A S_{08}^B S_{25}^C Mo_{33}^C S_{41}^A S_{59}^C Mo_{67}^B S_{75}^C S_{92}^B$
	$CdCl_2(TaSe_2)$	$Ta_0^A Se_{08}^C Se_{25}^A Ta_{33}^C Se_{42}^B Se_{58}^C Ta_{67}^B Se_{75}^C Se_{92}^B$
	Sm	$Sm_0^A Sm_{11}^C Sm_{22}^A Sm_{33}^C Sm_{45}^B Sm_{55}^C Sm_{67}^B Sm_{78}^A Sm_{89}^B$
	$\delta_R^V\text{-}WN_2$	$W_0^A N_{15}^C N_{18}^A W_{33}^C N_{49}^B N_{51}^C W_{67}^B N_{82}^A N_{85}^B$
$hR\,4$	GaSe	$Ga_{05}^A Se_{10}^C Se_{24}^B Ga_{28}^C Ga_{38}^A Se_{44}^B Se_{57}^C Ga_{62}^B Ga_{72}^B Se_{77}^A Se_{90}^C Ga_{95}^A$
	$CrCuS_2$	$Cu_0^A S_{13}^A Cr_{19}^C S_{26}^A Cu_{33}^C S_{46}^C Cr_{53}^B S_{59}^C Cu_{67}^B S_{80}^B Cr_{86}^A S_{93}^B$
	$\beta\text{-}NiTe$	$Te_{08}^C Ni_{13}^A Ni_{20}^C Te_{26}^A Te_{41}^B Ni_{46}^C Ni_{54}^B Te_{59}^C Te_{74}^A Ni_{80}^B Ni_{87}^A Te_{92}^B$
	$CrNaS_2$	$Cr_0^A S_{07}^C Na_{17}^B S_{26}^A Cr_{33}^C S_{40}^B Na_5^A S_6^C Cr_{67}^B S_{74}^A Na_{83}^C S_{93}^B$
$hR\,4.3$	$\delta_R^{VI}\text{-}W_{1.17}N$	$W_0^A N_{06}^C W_{12}^{A*} W_{21}^{C*} N_{28}^A W_{33}^C N_{39}^B W_{45}^{C*} W_{55}^{B*} N_{61}^C W_{67}^B N_{72}^A W_{79}^{B*} W_{88}^{A*} N_{94}^B$
$hR\,5$	S_2Ni_3	$S_{08}^C Ni_{17}^{B'} S_{25}^A S_{42}^B Ni_5^{B'} S_{58}^C S_{75}^A Ni_{83}^{B'} S_{92}^B$ (distorted)

Table 2 (Continuation and End)

Structure		Layer stacking sequence
$hR\ 5$	SBi_2Te_2	$S_0^A Bi_{06}^B Te_{12}^C Te_{21}^A Bi_{28}^B S_{33}^C Bi_{39}^A Te_{46}^B Te_{54}^C Bi_{61}^A S_{67}^B Bi_{73}^C Te_{79}^A Te_{88}^B Bi_{94}^C$
$hR\ 6$	S_2Ta	$S_{04}^B Ta_{08}^A S_{13}^B S_{21}^A Ta_{25}^C S_{30}^B S_{38}^A Ta_{42}^C S_{46}^A S_{54}^C Ta_{58}^B S_{63}^A S_{71}^C Ta_{75}^B S_{79}^C S_{88}^B Ta_{92}^A S_{96}^C$
	NiS	—
	$CaSi_2$	$Si_{02}^B Ca_{08}^A Si_{15}^C Si_{19}^A Ca_{25}^C Si_{32}^B Si_{35}^A Ca_{42}^C Si_{48}^B Si_{52}^C Ca_{58}^B Si_{65}^A Si_{69}^C$ $Ca_{75}^B Si_{82}^A Si_{85}^B Ca_{92}^A Si_{98}^C$
	STi (H.T.)	$S_0^A Ti_{05}^B S_{11}^C Ti_{17}^B S_{23}^A Ti_{29}^B S_{33}^C Ti_{38}^A S_{44}^B Ti_5^A S_{56}^C Ti_{62}^A S_{67}^B Ti_{71}^C S_{77}^A Ti_{83}^C S_{89}^B Ti_{96}^C$
	$STi_{0.9}$	$Ti_0^A S_{06}^C Ti_{12}^{A*} S_{17}^B Ti_{22}^{C*} S_{28}^A Ti_{33}^C S_{39}^B Ti_{45}^{C*} S_5^A Ti_{55}^{B*} S_{61}^C Ti_{67}^B S_{72}^A Ti_{79}^{B*} S_{83}^C Ti_{88}^{A*} S_{94}^B$
$hR\ 7$	$ZnIn_2S_4$	$S_{04}^A Zn_{06}^B S_{13}^B In_{17}^A S_{21}^C In_{27}^C S_{29}^A S_{37}^C Zn_{39}^A S_{46}^B In_5^C S_{54}^B In_{60}^B S_{63}^C S_{71}^B$ $Zn_{73}^C S_{79}^C In_{83}^B S_{87}^A In_{94}^A S_{96}^B$
	Fe_3S_4	$S_{04}^C Fe_{09}^B S_{13}^A Fe_{17}^B S_{21}^C Fe_{25}^B S_{29}^A S_{38}^B Fe_{42}^A S_{46}^C Fe_5^A S_{54}^B Fe_{58}^A S_{62}^C S_{71}^A$ $Fe_{75}^C S_{79}^B Fe_{83}^C S_{87}^A Fe_{92}^C S_{96}^B$
	In_3Te_4	$In_0^A Te_{04}^C In_{09}^B Te_{13}^A Te_{21}^C In_{24}^B Te_{29}^A In_{33}^C Te_{38}^B In_{43}^A Te_{46}^C Te_{53}^B In_{57}^A$ $Te_{63}^C In_{67}^B Te_{71}^A In_{76}^C Te_{80}^B Te_{87}^A In_{91}^C Te_{96}^B$
	$SnSb_2Te_4$	$Sn_0^A Te_{05}^C Sb_{10}^B Te_{15}^A Te_{19}^C Sb_{24}^B Te_{28}^A Sn_{33}^C Te_{38}^B Sb_{43}^A Te_{48}^C Te_{52}^B Sb_{57}^A$ $Te_{62}^C Sn_{67}^B Te_{72}^A Sb_{77}^C Te_{81}^B Te_{85}^A Sb_{91}^C Te_{95}^B$
	Bi_3Se_4	$Bi_0^A Se_{05}^C Bi_{10}^B Se_{14}^A Se_{19}^C Bi_{24}^B Se_{29}^A Bi_{33}^C Se_{38}^B Bi_{43}^A Se_{47}^C Se_{53}^B Bi_{57}^A$ $Se_{62}^C Bi_{67}^B Se_{71}^A Bi_{76}^C Se_{81}^B Se_{86}^A Bi_{91}^C Se_{95}^B$
	Mo_2B_5	$B_0^a Mo_{08}^A B_{15}^C B_{17}^B B_{19}^A Mo_{26}^C B_{33}^a Mo_{41}^C B_{48}^B B_{50}^A B_{52}^C Mo_{59}^B B_{67}^b Mo_{74}^B B_{81}^A B_{83}^C B_{85}^B Mo_{93}^A$
	C_3Al_4	$C_0^A Al_{04}^C C_{12}^C Al_{13}^A Al_{21}^C C_{22}^A Al_{29}^A C_{33}^C Al_{37}^B C_{45}^B Al_{46}^A Al_{54}^B C_{55}^C Al_{63}^C C_{67}^B Al_{71}^A$ $C_{78}^A Al_{80}^B Al_{87}^A C_{88}^B Al_{96}^B$
$hR\ 8$	CNi_3	$C_0^A Ni_{08}^{C'} C_{17}^B Ni_{25}^{B'} C_{33}^C Ni_{42}^{C'} C_5^A Ni_{58}^{B'} C_{67}^B Ni_{75}^{C'} C_{83}^C Ni_{92}^{B'}$
$hR\ 10$	$\beta\text{-}Cr_2S_3$	$Cr_0^{A'} S_{08}^{C'} Cr_{17}^B S_{25}^{B'} Cr_{33}^{A'} S_{42}^{C'} Cr_5^A S_{58}^{B'} Cr_{67}^{A'} S_{75}^{C'} Cr_{83}^C S_{92}^{B'}$
	$\alpha\text{-}Al_2O_3$	$Al_{02}^B O_{08}^{C'} Al_{15}^A Al_{19}^C O_{25}^{B'} Al_{32}^B Al_{35}^A O_{42}^{C'} Al_{48}^C Al_{52}^B O_{58}^{B'} Al_{65}^A Al_{69}^C O_{75}^{C'} Al_{82}^B Al_{85}^A O_{92}^{B'} Al_{98}^C$

in terms of these layer stacking sequences and it is surprizing what a great condensation of structural information is achieved for the 118 structure types listed in Table 2. Details of the structural arrangements can be regenerated readily from the coded descriptions of the structures and the atomic coordination of the atoms can be determined by reference to Table 3. For cubic structures, particularly, this method of describing structural arrangements and recognizing coordination is inferior to the matrix distribution system of LOEB [3], but it has the over-riding advantage of being readily printed on a line. Structural relationships can be observed without regeneration of the structures, merely from comparing sequences of the layer symbols. Thus, for example, the basic structural unit of the Laves phases is seen to be of the type $\beta\,(\underline{BAC})\,\gamma$, although a minimum of two units is required to give a structure. The $CaCu_5$ structure is characterized by a unit of the type $[Aa]\,\alpha$, whence it is readily seen that the Ce_2Ni_7 and Er_2Co_7 structures, for example, are a mixture of the Laves and $CaCu_5$ types containing units of the type $(CAB)\,\beta\,[Bb]\,\beta\,[Bb]\,\beta$ in BC stacking in Ce_2Ni_7, $A\underline{B})\,\beta\,[\underline{B}b]\,\beta\,[\underline{B}b]\,\beta\,(\underline{BAC})\,\gamma\,[\underline{C}c]\,\gamma\,[\underline{C}c]\,\gamma\,(\underline{C}$ and in ABC stacking in Er_2Co_7, $\alpha\,[\underline{A}a]\,\alpha\,(\underline{ABC})\,\gamma\,[\underline{C}c]\,\gamma\,[\underline{C}c]\,\gamma\,(\underline{CA}\underline{B})\,\beta\,[\underline{B}b]\,\beta\,[\underline{B}b]\,\beta\,(\underline{BCA})\,\alpha\,[\underline{A}a]$. As another ex-

Table 3

Coordination of atoms in various layer sequences

Layer sequence	Polyhedra formed	Coordination	CN
ABC----- (cubic close packing)	Tetrahedra and octahedra	Each atom by cubo-octahedron	12
AB-- (AC) (hexagonal close packing)	Tetrahedra and octahedra	Each atom by twinned cubo-octahedron	12
	$A(B)$ form trigonal prisms		
AA	Trigonal prisms		
aa	Hexagonal prisms		
$\alpha\alpha$	Trigonal and hexagonal prisms		
Aa-----	All 'a' hexagonal prisms centred by A	A atoms by 'a' hexagonal prisms	12
	All A trigonal prisms centred by 'a'	'a' atoms by A trigonal prisms	6
$A\alpha$	All α hexagonal prisms centred by A	A atoms by α hexagonal prisms	12
	Each edge face of A prisms centred by α	α atoms by 4 planar A atoms	4
$B\alpha$-- ($C\alpha$--)	Half α trigonal prisms centred by $B(C)$	$B(C)$ by α trigonal prisms	6
	Half B trigonal prisms contain 3 α atoms, other half empty	α by $B(C)$ atoms	2
$a\alpha$---	All α trigonal prisms centred by 'a', α hexagonal prisms empty	'a' by α trigonal prisms	6
	'a' hexagons covered antisymmetrically by α hexagons	α by 4 planar 'a' atoms	4
$b\alpha$-- ($c\alpha$--)	All α hexagonal prisms and half α trigonal prisms centred by $b(c)$	Half $b(c)$ by α hexagonal prisms	12
		Half $b(c)$ by α trigonal prisms	6
	$b(c)$ hexagonal prisms have triangle of α atoms located about centre	α by $b(c)$ atoms	2

ample, the stacking unit $[A\,\alpha]$ satisfies 1:3 stoichiometry in which each plane of atoms has the composition MX_3. A variety of ordered MX_3 structures are known, from SnNi$_3$, $[\underline{B}\,\beta]\,[\underline{C}\,\gamma]$, with a c.p. hexagonal arrangement of the layers, through the BaPb$_3$, TiNi$_3$, HoAl$_3$ and PuAl$_3$ types with mixed hexagonal and cubic arrangements of the layers, to AuCu$_3$, $[\underline{A}\,\alpha]\,[\underline{B}\,\beta]\,[\underline{C}\,\gamma]$, with the close packed cubic arrangement. Structures belonging to this series are readily recognized through the occurence of $[\underline{A}\,\alpha]$ type layers (only) in their structural descriptions.

   Close packed structures are a particular group of this class in which the atoms are arranged in uncentred tetrahedra and octahedra that fill space completely. The centred polyhedra (regarding one atom of the array as centre) are CN 12 cubo-octahedra (c.p. cubic) or twinned cubo-octahedra (c.p. hexagonal arrangements). In hexagonal or rhombohedral structures alternate layers with the same stacking symbol form right trigonal prisms, and alternate prisms are centred by atoms of the inter-vening layers. Centring tetrahedra or octahedra of the original close packed sequence introduces new layers. In the case of tetrahedra these have the same stacking se-quence as one of the two layers whose atoms generate the tetrahedra, for example, $A\underline{A}B$ or $B\underline{C}C$. Octahedra are centred by layers of atoms stacked on the third site different to the two layers generating the octahedra. As pointed out above, the introduction of these 3^6 layers of atoms centring tetrahedra and/or octahedra, although placing atoms on A, B or C sites, destroys the overall close packing of the structures, because the layer spacing is no longer correct. Nevertheless, an important feature in structural considerations of semiconductors is that one of the components (the anions) forms a close packed array.

3. Classification of Structures by Connections between Tetrahedra, Octahedra or Right Trigonal Prisms

   Although consideration of 3^6, 6^3 and 3636 layer structures covers many of those containing tetrahedra, octahedra and trigonal prisms, there are also many structures not formed by this layer stacking in which these polyhedra occur, as for example the tetrahedra in GeS$_2$, pairs of octahedra in Rh$_2$S$_3$ or trigonal prisms in the FeB struc-ture. Another useful way of summarizing structural information is according to the method of connection of these polyhedra, and we choose right trigonal prisms as the example for consideration.

   When right trigonal prisms pack together to fill space they share three side faces and both basal end faces and therefore three c edges and six a edges also. Transposi-tions or rotations of neighbouring prisms or layers of prisms may reduce the number of connections between neighbouring prisms, and if we consider only connections made by (body) centred prisms with other prisms, the number of connections also depends on the distribution of the atoms centering the prisms. Structures containing trigonal prismatic arrangements of atoms can therefore be classified systematically according to the number and type of connections between the prisms, by listing the transpositions, rotations and centering arrangements responsible for these, as well as other information such as the direction of the prism axes relative to those of the unit cell and the prism axial ratios. Including the case of uncentred prisms, there are five stacking sequences (Table 4) that are useful for specifying the relative arrangements

of filled and empty neighbouring trigonal prisms that mutually share faces or edges. These are described according to the notation already given; A represents the prism-forming atom, and B, C or a are the centering atoms.

Table 4

Stacking sequence in prisms

Stacking sequence	Shared edges and faces	Structural arrangement
AA	All side and basal faces	Empty prisms filling space
$AaAa$	All side and basal faces	Filled prisms filling space
$ABAB$	Filled prisms share each c edge with two other filled prisms, basal faces with other filled prisms	Alternate columns of filled and empty prisms running in c direction
$ABAC$	Filled prism share each c edge with two other filled prisms, each basal edge 'a' with one other filled prism basal edge	Layers of alternate filled and empty prisms Filled prism sit between empty prisms of layers above and below
$ABABACAC$	Combination of two above arrangements	Filled and empty prisms alternate in each layer Filled prism has filled prism below it in layer below and empty prism above it in layer above and *vice versa*

Table 5 shows a partition of some structures containing trigonal prisms, according to the type of connections between filled prisms. The structure type is indicated in the appropriate column giving the stacking sequence describing the arrangement of filled and empty prisms in the structure. Transpositions and rotations refer to movements from a space filling arrangement of trigonal prisms. The list is by no means complete since space does not permit indefinite extension of the Table; however, it again suffices to show how essential data on many structures can be briefly condensed and compared. One point should be noted: when counting connections between filled prisms (cols. 1–4) only the basal edge connections between prisms in layers above and below the prism are counted. Thus no a edges are counted as shared if the prisms share two side faces only, even though this results in the actual sharing of 4 a edges. The reason for this is that the information is already contained in a statement of the sharing of two side faces and three c edges, so that specification of a edge connections can be reserved to give explicit information regarding connections to prisms in layers above and below the prism considered.

4. Tetrahedral Close Packed Structures: Frank-Kasper Coordination Polyhedra

There is a class of complex metallic structures formed by the alternate stacking together of pentagon-triangle, pentagon-hexagon-triangle and/or hexagon-triangle primary layers with 3^6 triangulated, 4^4 square or square-triangle secondary layers of atoms, such that all pentagons of one primary layer are covered antisymmetrically

Table 5

Some examples of structures containing right trigonal prisms arranged according to connections between neighbouring centred prisms (when none of the prisms are centred, then connections between all prisms are counted). Although sharing of a prism side face involves also the sharing of basal (a) edges, they are not so counted, as this information is already contained in the number of side faces and (c) edges shared. Counting of a edges is reserved for giving information on connections to filled prisms in layers above and below the prism concerned. a, b and c always refer to the unit cell of the structure, except in the headings of the first four, and the penultimate columns where they refer to the a (basal) and c (vertical) edges of the prism. Abbreviations: alt. alternate, o.c. off-centre

Connections				Transpositions	Rotations	Structure symbol	Stacking sequence					Prism formed by	Prism centred by	Prism axis along crystal direction	Prism axial ratio c/a	Remarks
c face	c edge	a face	a edge				A	Aa	AB	$ABAC$	$ABABACAC$					
3	3	2	6			hP 6		$CaIn_2$				Ca	in slightly o.c.	c	0.79	
						hP 6		NbS_2 (H.T.)				Nb	S o.c. alt. up and down	c	1.80	
						hP 3		ω-Cr-Ti				disordered		c	0.61	
						hP 3		AlB_2				Al	B	c	1.08	
						hP 4		NOTaZr				Zr	N + Ta alt. in columns ‖ c	c	1.06	Alt. prisms in columns ‖ c end-centred by O.
						hP 3		δ-UZr_2				Zr	(Zr + U) randomly	c	0.61	
						hP 8		β-Na_2S_2				Na(1)	Na(2) and 2S o.c. alt. in $ABAC$ arrangement	c	1.14	S also form prisms centred by Na(2).
						hP 6		$InNi_2$				Ni(1)	In + Ni(2) alt. in $ABAC$ arrangement	c	0.61	
						mC 6		$AuTe_2$				Au	Te displaced alt. up and down	c	1.20 / 1.15	
						oP 12		CMo_2				C	Mo + C alt. in columns ‖ c C o.c. at 1/4, 3/4	a		Mo also form prisms centred by half of C atoms.
				$a/2$, $b/2$ on one side, nothing on other	alt. layers 90° ⊥c about centre of ab face	tI 12		Si_2Th				Th	Si	a, b in alt. layers	1.00 / 1.00	Prism a = prism c.
						hP 8		$AsNa_3$				Na(1)	Na(2) o.c. alt., up and down	c	0.88	Alt. bases of prisms centred by As.
2	3	2	6	a, b, c		oC 4	Ga					Ga	–	a	1.08 / 0.92	
				a, b, c		oC 12		$ZrSi_2$				Zr	Si	a	1.01	Layers sep. by square net of Si.
				a, b, c		oC 8		CrB				Cr	B	a	1.09 / 1.01	
				b, c		oC 4		$\beta'Cu_3Ti$				disordered		a	0.68 / 0.60	
				b, c		oC 4		α-U				U	U	a	0.58 / 0.54	
				a, b, c		oC 12		BCU				U	B	a	1.08 / 0.99	C just outside 3rd prism face form rectangular layer between prisms.
				a, b, c		oC 19		$H_{2.7}NiZr$				Zr	Ni	a	0.96 / 0.82	Prisms base-centred by H. Double H layers (rectangular nets) between prism layers.
				a, c		oP 4		AuCd				Au	Cd	b	0.80 / 0.66	
				a, b, c		oC 16	CeAl					Ce	–	a		Distorted Ce prisms form layers in ac plane. Al(1) lie just outside centre of unshared prism faces of prisms with axial ratio (0.87 and 0.58). Al(2) lie close to centres of shared prism faces of prisms with c/a = 1.57 and 1.03.

Table 5

Connections				Transpositions	Rotations	Structure symbol	A	Aa	Stacking sequence		
c face	c edge	a face	a edge						AB	$ABAC$	$ABABACAC$
2	3	2	6	$a/2, b/2, c$ on one side c on other side	alt. layers 90° $\perp c$ about centre of ab face	tI 16		MoB			
				$b/2, c$		oP 8		β-Cu$_3$Ti			
				a		oC 12		Ga$_2$Zr			
				$a/2, b, c/2$		oC 16		BCMo$_2$			
1	3	2	6	a, b	alt. pairs prisms, rot. 90° about c direction	tP 20		Al$_2$Gd$_3$			
0	3	2	6			hP 2			LiRh		
						hP 2			WC		
						hP 2			Mg		
						oP 8			SiTi		
1	2	2	6	a, b, c		mC 12		As$_2$Nb			
				b, c		oC 8		Ga			
0	2	2	6	a, b, c		oC 12		Ag$_{0.93}$Cu$_{1.07}$S			
				a, b, c		oP 12		Co$_2$Si (anti PbCl$_2$)			
				a, b, c		mC 16		CoGe			
0	0	2	6	a, b, c		oC 16		Al$_2$CuMg			
				b, c		oC 16		CoPu$_3$			
				a, b, c		oC 16		BRe$_3$			
				$a, b/2, c$		mP 8		Se$_3$Zr			
				a, b, c		oP 8				β-Cu$_3$Ti	

(Continuation)

Prism formed by	Prism centred by	Prism axis along crystal direction	Prism axial ratio c/a	Remarks
Mo	B	a, b in alt. layers	1.12 1.00	Prism a = prism c.
Cu(2)	Cu(1) + Ti alt. in ABAC arrangements	a	1.36 1.19	
Zr	Ga(3) o.c.	c		Layers separated by square net Ga(1 and 2).
Mo(1)	B	a	1.07 1.00	Double layers Mo(2) and C in 4^4 nets between prism layers.
Gd(1 and 2)	Al slightly o.c.	c	~0.9	Distorted prisms. Gd(1) centre cubes separating prisms.
Li	Rh	c	1.64	
W	C	c	0.98	
Mg	Mg	c	1.62	Half Mg form prism about other and *vice versa*.
Ti	Si slightly o.c.	b	1.06 0.90	
As	Nb	b	1.14 0.88 0.84	
Ga	Ga	a	1.38 1.31 1.17	Off-centre Ga atoms giving Ga pairs. Centre atoms form exactly similar prisms about other Ga.
Ag + Cu	S o.c. towards Cu edge	a	1.12 1.02	Ag-Ag edges shared, Cu-Cu unshared. Cu of one prism lies just outside AgAgAgAg face of other prism.
Co	Si	b	1.49 1.46 1.40	
Co	Ge(2)	b	1.54 1.49 1.44	Ge(1) in spaces between prisms themselves form prisms with Co at basal edge centres.
Al + Mg	Cu	a	1.44 1.35	
Pu	Co	a	0.97 0.95	
Re	B	a	1.06 0.95	
Se	Zr	b	1.60 1.01 1.00	Prisms distorted.
Cu	Ti	b	1.68 1.67	

Connections				Transpositions	Rotations	Structure symbol	A	Aa	AB	$ABAC$	$ABABACAC$
c face	c edge	a face	a edge								
0	3	1	6			hP 7.4					$Mo_{0.84}N$
0	3	0	6			oP 8			$S_{0.85}V$		
						mC 8			CrS		
						mC 30			Cr_7Se_8		
						hP 3.75			Cr_7S_8		
						hP 4			NiAs		
						hP 4			La		
						hP 3			NFe_2		
						oP 8			MnP		
2	3	0	2		alt. filled prisms + or − ~25° around b about prism centre	oP 8		FeB			
3	3	0	0	a, b, c		hP 8		$AsNa_3$			
2	3	0	0	a, b, c	alt. rows prisms along a rotated slightly less than 45° alternately + and − around c axis, about prism centre	oP 16	DyAl				
1	2	0	0	a, b, c	alt. pairs of prisms rot. 90° about c direction. Prisms of one orientation filled; those of other empty and *vice versa* in layers above and below	tP 16			$CoGa_3$		
0	3	0	0	a, b, c		hP 6			MoS_2		
				a, b, c		hP 8			$AlCCr_2$		
				a, b, c		hP 8			AsTi		
				a, b, c		hP 8			$Cu_{0.65}NbS_2$		
				a, b, c		hP 8			GaS		
				a, b, c		hP 8			Na_2S_2		
				a, b, c		hP 10			C_2Mo_3		
				a, b, c		hP 10			Pt_2Sn_3		

(Continuation and End)

Prism formed by	Prism centred by	Prism axis along crystal direction	Prism axial ratio c/a	Remarks
Mo	N	c	0.98	Partially occupied Mo prisms.
V	S	a		Prisms distorted.
Cr	S	c	~0.8	Distorted.
Cr	Se	c in $F2/m$ setting	~0.8	
Cr	S	c	0.83	
Ni	As	c	0.70	
La(1)	La(2)	c	1.61	Half of La form prisms centred by rest and *vice versa*.
N	Fe	c	0.80	N prisms partially occupied.
Mn	P o.c.	a	–	Distorted.
Fe	B	in ac plane	1.12 0.99	Columns of edge-joined prisms run in b direction. Rotation of alternate lines of prisms (b direction) distorts what would have been lines of empty prisms separating filled prisms.
Na(2)	Na(1) + As, alt. in layers	c	0.59	
Dy	–	in ab plane	0.92 0.59	Columns of edge-joined prisms in c direction. Al(1) just outside centre of unshared prism faces. Al(2) in lines along c in centre of space between prisms.
Ga(2)	Co	c	1.2 0.97	Distorted prisms. Cubes between prisms centred by Ga(1).
S	Mo	c	0.94	
Cr	Al	c	1.47	Δ net of C atoms separate prism layers.
Ti	As(2)	c	0.84	Δ net of As(1) separate layers of prisms.
S	Nb	c	0.98	2 partially occupied Δ nets of Cu separate layers of prisms.
S	2 Ga o. c,	c	1.30	
S	Na	c	0.48	
Mo	Mo	c	0.81	3 partially filled Δ layers of C between prisms.
Pt	Sn	c	0.64	Prisms separated by 2 Δ layers of Sn.

by pentagons of the layers above and below, and similarly for the hexagons, and the atoms of the secondary layers centre all and only the pentagons and hexagons of the primary layers. When these conditions are satisfied the structures contain only inter-penetrating triangulated CN 12, 14, 15 or 16 coordination polyhedra of the FRANK and KASPER [4] type, and therefore the atoms are arranged in a distorted tetrahedral close packing. Such structures can conveniently be divided into two groups. 1) Those characterized by a linear (zigzag) repeat sequence of pentagons and/or hexagons along a basal row, which generates the whole of the primary net on repetition along the row and about a direction normal to it. In such structures the secondary net is generated by two sets of parallel (zigzag) lines of atoms. 2) Structures whose second-ary nets are not so characterized; in this case the basal repeat unit of the primary net may be a two-dimensional tile of pentagons and/or hexagons. Structures of this second class are rarely known, and will not be further considered here. Those of the first group can be described by a code as PEARSON and SHOEMAKER [5] have shown, which not only accounts for all known structures, but allows prediction of an un-limited number of possible structures formed according to this principle.

Four symbols are used to describe the repeat sequence of the primary net along the basal row (X direction): P for pentagons; H for hexagons; '/' for pentagons and/or hexagons joined edge to edge, and 'X' for pentagons and/or hexagons joined apex to apex with two intervening triangles (Figure 4 a). The X direction in the plane of the primary net is chosen as that along which P join other P or H at two next-but-one edges (/P/) or apexes (XPX), or at an edge and opposite apex (/PX or XP/); and hexagons join at opposite edges or apexes (/H/, XHX) or at an edge and next-but-one apex (/HX or XH/). Other connections (eg. by next-but-one apexes) are forbidden in the selection of the basal row. Connections XPX, /P/, XH/ and /HX introduce a change of direction or kink in the sequence of polygons along the X direction (Figure 4 a) (coded + when the kink is up and – when it is down towards the X axis). The basal row preeat unit contains an equal number of + and – connections and each successive

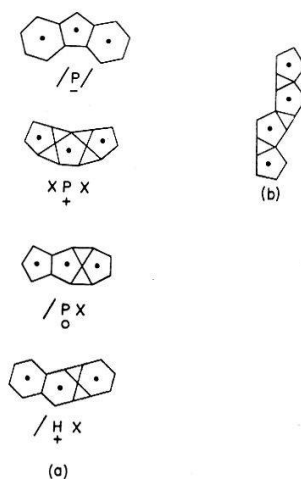

Figure 4

a) Examples of coding for various connections between pentagons and/or hexagons along the basal row of the *primary* net in Frank-Kasper structures. The +, − or ◯ refer to the X or / to the right of the symbols P or H.

b) Connection of pentagons by next-but-one apexes, with an intervening triangle, along the *Y* direction.

kink introduces a turn towards the X axis. Connections XP/, /PX, /H/ and XHX which continue the row in the same direction are coded $+$, when they follow $+$; $-$ when they follow $-$ and 0 when the row lies parallel to the X direction. $+$, $-$ and 0 symbols are actually redundant since the information is already given by the succession of P, H, /, and X symbols; however, they are included since they aid in viewing the net repeat sequences.
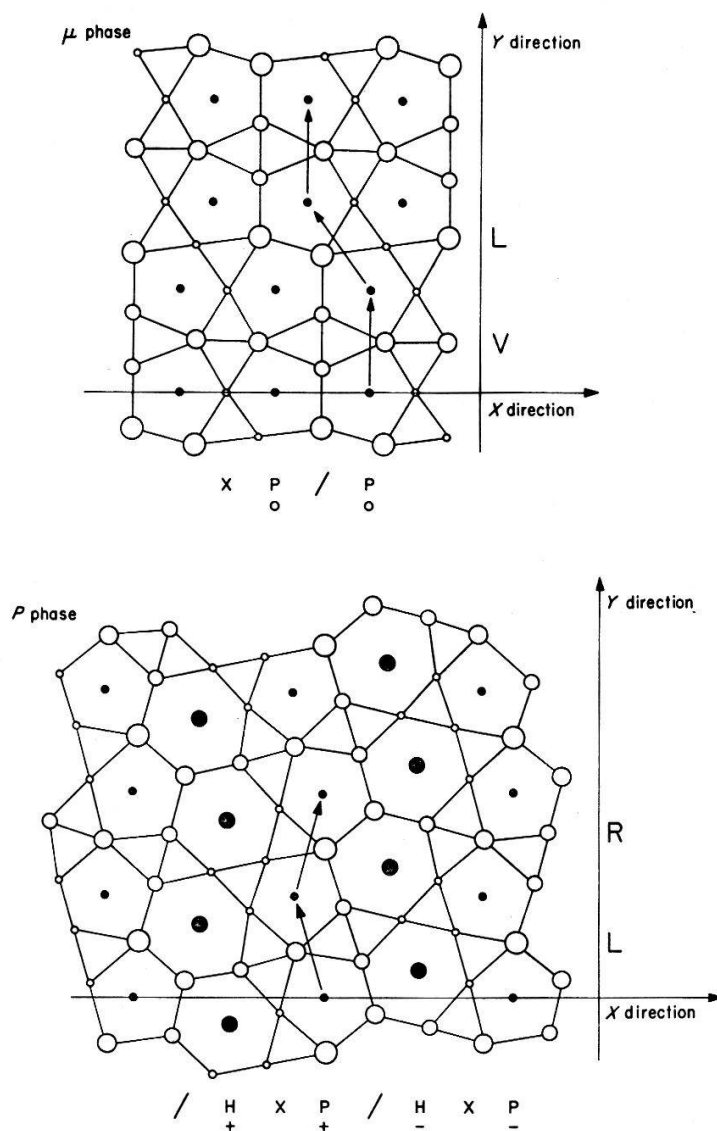
Figure 5

Examples of coding for the primary nets in the μ and P phase structures, showing the X and Y directions. The $+$, $-$ or $\bigcirc$ refer to the X or / to the right of the symbols P or H.

Along the orthogonal Y direction the basal repeat unit of the primary net repeats by movements left (symbol L), right (symbol R), or along (symbol V) so that the pentagons and/or hexagons form rows in this direction. Along these rows hexagons can join edge to edge or apex to apex, but pentagons must join by next-but-one apexes with an intervening triangle on one side (Figure 4b). This sequence establishes the direction of movement of the basal row L, R or V. With these symbols the primary

69

net of a structure such as the P or μ phase types can be described completely (Figure 5). Repetition of the repeat unit along the X and Y directions according to its repeat sequence generates the whole of the primary net. Primary nets above and below the one considered are obtained merely by interchanging the connection symbols / for X and *vice versa* (+, −, 0, L, R and V remain unchanged), because pentagons and hexagons of one primary net are covered antisymmetrically by pentagons and hexagons of the primary nets above and below. Since all of the atoms of the secondary nets centre only and all of the pentagons and/or hexagons of the primary nets, specification of the basic repeat unit of the primary net also gives the secondary net, and therefore of all of the atoms in the structure [5].

Table 6

Coding for some known Frank-Kasper structures

Structure	Coding for structure	Plane in which net lies	Schlafli symbols for secondary net
β-W	HX̰ V	[001]	4^4
Zr$_4$Al$_3$	PX̰P/̰ V	[110]	4^4
	HX̰ L or R	[001]	3^6
μ phase	PX̰P/̰ VL	[110]	$3^3 4^2$
MgZn$_2$	PX̰P/̰ RL	[110]	3^6
MgCu$_2$, MgSnCu$_4$	PX̰P/̰ L	[1$\bar{1}$0]	3^6
AuBe$_5$	PX̰P/̰ L	[1$\bar{1}$0]	3^6
MgNi$_2$	PX̰P/̰ ꝑRLL	[110]	3^6
MgAlCu (5 layer Laves phase)	PX̰P/̰ L^{4}R	[110]	3^6
MgAlCu (9 layer Laves phase)	PX̰P/̰ LLR	[110]	3^6
M phase	PXP/P/PX LR (+ + − −)	[001]	$3^2 4 3 4 + 3^3 4^2$ (1:1)
σ phase	HXH/ LR (+ −)	[001]	$3^2 4 3 4$
P phase	HXP/HXP/ LR (+ + − −)	[001]	$3^2 4 3 4 + 3^3 4^2$ (1:1)
Idealized R phase	PX̰HX̰P/̰H/̰VL	[$\bar{1}\bar{3}5$]$_{hex}$	$3^3 4^2$

Known structures of this class are coded in Table 6 and it is obvious that a great number of similar, but unknown structures could be predicted systematically using the code. Structural similarities and differences are readily apparent, and in order to determine whether an atom is surrounded by 12, 14, 15, or 16 neighbours it is only necessary to examine the polygons connected about the atom, referring to Figure 6 which shows the unique coordination numbers for the various possible connections

[5]. For convenience the secondary nets are also specified in Table 6, although this information can be readily deduced from the code describing each structure type. It may be possible to describe a given structure in more than one manner and, for example, Al_3Zr_4 can be described in terms of primary nets containing either hexagons or pentagons, depending on the plane chosen for the net. Also, in structures with 3^6 triangular secondary nets, or with hexagon-triangle primary nets, there is more than one possible choice for the X and Y axes for describing the structure. This latitude in describing the structure does not affect the usefulness of the code for reducing structural information, and the regeneration of structural details from a given repeat code is indeed unique. The rather remarkable geometrical properties of this class of structures were first recognized by KASPER [6] and FRANK and KASPER [4].

CN 12 •
CN 14 ○
CN 15 ○
CN 16 ○
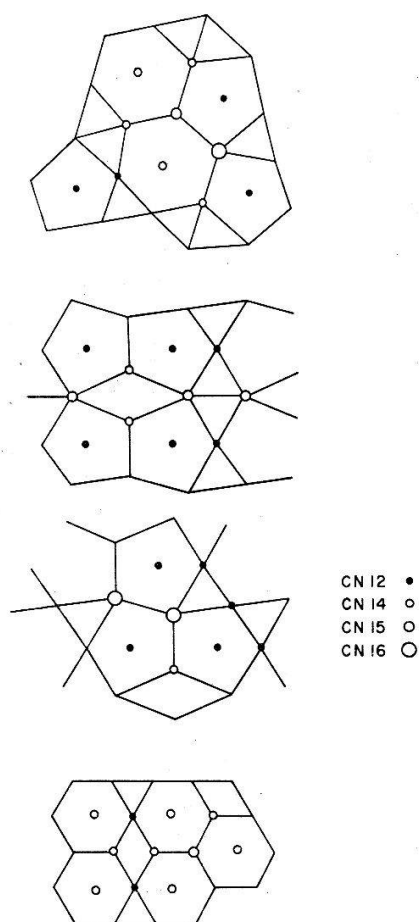
Figure 6

Coordination of atoms of primary and secondary nets for various connections between the net polygons in Frank-Kasper structures.

5. Structures Generated by Layer Networks of Atoms Containing Squares

The remaining class of layer structures is that containing squares, either in primary nets with other polygons and generally with interleaved 4^4 secondary nets, or in 4^4 networks of atoms alone. The coordination arrangements are more varied in these structures than in the Frank-Kasper structures and this makes tabular reduction of crystal chemical information more difficult. The presence of squares gives

rise to interpenetrating octahedra or centred cubes when successive 4^4 nets are displaced by half of the body diagonal, and to cubes or archimedian antiprisms when the squares overlie each other directly or antisymmetrically, although these may not be recognized as the ultimate coordination polyhedra in the structure. Thus, squares covering each other antisymmetrically and centred by an interleaving 4^4 net give CN 10 polyhedra.

We consider two main groups of these structures. The first is structures made up of 4^4 nets aligned parallel or at $45°$ to the cell edge in which the nets contain only one component without vacant sites, so that the chemical repeat unit of the net is equal to the net period. The important parameters are the separation of the nets and the net origin (node) and orientation which may be either parallel to the cell edges and

Table 7

Structures with 4^4 nets only (length of net edge a or $a/\sqrt{2}$).

Sub numbers give height of atom plane as fraction of cell edge (decimal with 0. omitted).

Super numbers locate origin and orientation of 4^4 net as follows:
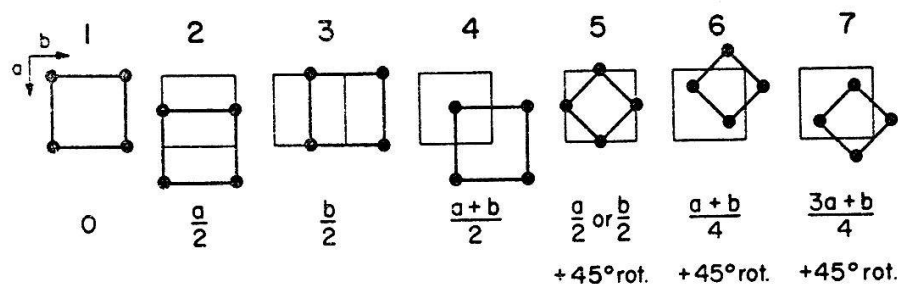
Structure	Crystal plane	Description of structure
Po ($cP\,1$)		Po_0^1
CsCl ($cP\,2$)		$Cs_0^1Cl_5^4$
AuCu$_3$ ($cP\,4$)		$Au_0^1Cu_0^4Cu_5^5$
ReO$_3$ ($cP\,4$)		$Re_0^1O_0^5O_5^1$
CFe$_4$ ($cP\,5$)		$C_0^1Fe_{27}^6Fe_{73}^7$
CaTiO$_3$ ($cP\,5$)		$Ca_0^1O_0^4Ti_5^4O_5^5$
Cu$_2$O ($cP\,6$)		$O_0^1Cu_{25}^6O_5^4Cu_{75}^7$
VCu$_3$S$_4$ ($cP\,8$)		$V_0^1Cu_0^{2+3}S_{24}^6Cu_5^1S_{74}^7$
Cu ($cF\,4$)		$Cu_0^{1+4}Cu_5^5$
ZnS ($cF\,8$)		$Zn_0^{1+4}S_{25}^6Zn_5^5S_{75}^7$
C ($cF\,8$)		$C_0^{1+4}C_{25}^6C_5^5C_{75}^7$
NaCl ($cF\,8$)		$Na_0^{1+4}Cl_0^5Cl_5^{1+4}Na_5^5$
AgAsMg ($cF\,12$)		$As_0^{1+4}Ag_{25}^6Mg_{25}^7As_5^5Mg_{75}^6Ag_{75}^7$
CaF$_2$ ($cF\,12$)		$Ca_0^{1+4}F_{25}^{6+7}Ca_5^5F_{75}^{6+7}$
AlCu$_2$Mn ($cF\,16$)		$Al_0^{1+4}Mn_0^5Cu_{25}^{6+7}Mn_5^1Al_5^{+4}Cu_{75}^{6+7}$
BiLi$_3$ ($cF\,16$)		$Bi_0^{1+4}Li_0^5Li_{25}^{6+7}Li_5^1Bi_5^{+4}Li_{75}^{6+7}$
NaTl ($cF\,16$)		$Na_0^{1+4}Tl_0^5Na_{25}^6Tl_{25}^7Tl_5^{1+4}Na_5^5Tl_{75}^6Na_{75}^7$
W ($cI\,2$)		$W_0^1W_5^4$
PtHg$_4$ ($cI\,10$)		$Pt_0^1Hg_{25}^{6+7}Pt_5^4Hg_{75}^{6+7}$

Table 7 (Continuation and End)

Structure	Crystal plane	Description of structure
FeNiN ($tP\,3$)	ab	$Fe_0^1 N_0^4 Ni_5^4$
FeSi$_2$ ($tP\,3$)	ab	$Fe_0^1 Si_{27}^4 Si_{73}^4$
AuCuI ($tP\,4$)	ab	$Au_0^{1+4} Cu_5^5$
γCuTi ($tP\,4$)	ab	$Cu_{10}^1 Ti_{35}^4 Ti_{65}^1 Cu_9^4$
CuTi$_3$ ($tP\,4$)	ab	$Cu_0^1 Ti_0^4 Ti_5^5$
βNp ($tP\,4$)	ab	$Np_0^{1+4} Np_{38}^3 Np_{63}^2$
PbO ($tP\,4$)	ab	$O_0^{1+4} Pb_{24}^3 Pb_{76}^2$
PtS ($tP\,4$)	ab	$Pt_0^3 S_{25}^1 Pt_5^2 S_{75}^1$
CCo$_2$Mn$_2$ ($tP\,5$)	ab	$Mn_0^{1+4} C_5^4 Co_5^5$
γH$_{0.5}$Zr ($tP\,6$)	ab	$Zr_0^{1+4} H_{25}^6 Zr_5^5 H_{75}^7$
Cu$_2$Sb ($tP\,6$)	ab	$Cu_0^{1+4} Sb_{28}^2 Cu_{28}^3 Cu_{72}^2 Sb_{72}^3$
SeSiZr ($tP\,6$)	ab	$Si_0^{1+4} Zr_{25}^3 Se_{38}^2 Se_{63}^3 Zr_{75}^2$
CdIn$_2$Se$_4$ ($tP\,7$)	ab	$Cd_0^1 Se_{25}^6 In_5^5 Se_{75}^7$
BBe$_{4-5}$ ($tP\,10$)	ab	$Be_0^{1+4} B_{17}^3 Be_3^{1+4} Be_5^5 Be_7^{1+4} B_{83}^2$
Pa (In) ($tI\,2$)	ab	$Pa_0^1 Pa_5^4$
Sn ($tI\,4$)	ab	$Sn_0^1 Sn_{25}^3 Sn_5^4 Sn_{75}^2$
H$_2$Th ($tI\,6$)	ab	$Th_0^1 H_{25}^5 Th_5^4 H_{75}^5$
MoSi$_2$ ($tI\,6$)	ab	$Mo_0^1 Si_{17}^4 Si_{33}^1 Mo_5^4 Si_{67}^1 Si_{83}^4$
CaC$_2$I ($tI\,6$)	ab	$Ca_0^1 C_{10}^4 C_4^1 Ca_5^4 C_6^1 C_9^4$
AsNb ($tI\,8$)	ab	$Nb_0^1 As_{17}^2 Nb_{25}^3 As_{42}^1 Nb_5^4 As_{67}^3 Nb_{75}^2 As_{92}^3$
TiAl$_3$ ($tI\,8$)	ab	$Ti_0^1 Al_0^4 Al_{25}^5 Al_5^1 Ti_5^4 Al_{75}^5$
AgTlTe$_2$ ($tI\,8$)	ab	$Tl_0^1 Te_{13}^4 Ag_{25}^3 Te_{38}^1 Tl_5^4 Te_{63}^1 Ag_{75}^2 Te_{88}^4$
ThCu$_2$Si$_2$ ($tI\,10$)	ab	$Th_0^1 Si_{13}^4 Cu_{25}^5 Si_{38}^1 Th_5^4 Si_{63}^1 Cu_{75}^5 Si_{88}^4$
αThSi$_2$ ($tI\,12$)	ab	$Th_0^1 Si_{08}^4 Si_{17}^2 Th_{25}^3 Si_{33}^2 Si_{42}^1 Th_5^4 Si_{58}^1 Si_{67}^3 Th_{75}^2 Si_{83}^3 Si_{92}^4$
BaAl$_4$ ($tI\,10$)	ab	$Ba_0^1 Al_{13}^4 Al_{25}^5 Al_{38}^1 Ba_5^4 Al_{63}^1 Al_{75}^5 Al_{88}^4$
CdAl$_2$S$_4$ ($tI\,14$)	ab	$Al_0^{1+4} S_{13}^6 Cd_{25}^3 S_{38}^7 Al_5^{1+4} S_{63}^6 Cd_{75}^3 S_{88}^7$
ZrAl$_3$ ($tI\,16$)	ab	$Al_0^5 Zr_{12}^1 Al_{14}^4 Al_{25}^5 Al_{36}^1 Zr_{38}^4 Al_5^5 Zr_{62}^4 Al_{64}^1 Al_{75}^2 Al_{86}^4 Zr_{88}^1$
HfGa$_2$ ($tI\,24$)	ab	$Ga_0^5 Hf_{07}^1 Ga_{08}^4 Ga_{16}^2 Hf_{18}^3 Ga_{25}^{1+4} Hf_{32}^3 Ga_{34}^4 Ga_{41}^1 Hf_{43}^4 Ga_5^5 Hf_{57}^2 Ga_{59}^1$ $Ga_{66}^3 Hf_{68}^2 Ga_{75}^{1+4} Hf_{82}^2 Ga_{84}^3 Ga_{91}^4 Hf_{93}^1$
CuTe ($oP\,4$)	ba	$Te_{22}^1 Cu_{45}^3 Cu_{55}^2 Te_{78}^4$
Co$_2$N ($oP\,6$)	ba	$N_0^1 Co_0^6 N_5^4 Co_5^7$ (Co atoms off-site somewhat)
Sb$_2$Tl$_2$Se$_4$ ($oP\,8$)	ba	$Sb_0^1 Tl_0^4 Se_{23}^4 Se_{27}^3 Sb_5^2 Tl_5^3 Se_{73}^3 Se_{77}^4$
Ga ($oC\,4$)	ac	$Ga_{13}^1 Ga_{38}^4 Ga_{63}^3 Ga_{88}^2$
BCr ($oC\,8$)	ac	$B_{06}^4 Cr_{15}^1 Cr_{35}^4 B_{44}^1 B_{56}^2 Cr_{65}^3 Cr_{85}^2 B_{94}^3$
ZrGa$_2$ ($oC\,12$)	bc	$Ga_0^{1+4} Zr_{15}^2 Ga_{18}^3 Ga_{32}^4 Zr_{35}^1 Ga_5^5 Zr_{65}^1 Ga_{68}^4 Ga_{82}^3 Zr_{85}^2$
VAu$_2$ ($oC\,12$)	ac	$V_0^{1+4} Au_{17}^5 Au_{33}^{1+4} V_5^5 Au_{67}^{1+4} Au_{83}^5$
ZrSi$_2$ ($oC\,12$)	ac	$Si_{06}^4 Zr_{10}^1 Si_{25}^5 Zr_{40}^4 Si_{45}^1 Si_{55}^2 Zr_{60}^3 Si_{75}^{1+4} Zr_{90}^2 Si_{95}^3$
BCU ($oC\,12$)	ac	$B_{04}^4 U_{13}^1 C_{17}^4 C_{33}^1 U_{37}^4 B_{47}^1 B_{53}^2 U_{63}^3 C_{67}^2 C_{83}^3 U_{87}^2 B_{96}^3$
TaPt$_2$ ($oC\,12$)	bc	$Ta_0^6 Pt_{17}^7 Pt_{33}^6 Ta_5^7 Pt_{67}^6 Pt_{83}^7$
BCMo$_2$ ($oC\,16$)	ac	$B_{03}^4 Mo_{07}^1 C_{19}^1 Mo_{19}^4 Mo_{31}^1 C_{31}^4 Mo_{43}^4 B_{47}^1 B_{53}^1 Mo_{57}^3 Mo_{69}^2 C_{69}^3$ $C_{81}^2 Mo_{81}^3 Mo_{93}^1 B_{97}^3$

located at the unit cell origin, or transposed by a/2, b/2, or (a + b)/2, or rotated 45° and transposed by a/2, b/2, (a + b)/4 or (3 a + b)/4 from the cell origin (see diagram at top of Table 7). By numbering these net origins, information on the components occupying the nets, and the net origins and spacings can be given in a linear set of symbols describing the structures similar to those used for structures based on triangular, hexagonal and kagomé nets. Table 7 lists a number of these structures and again a great condensation of information is achieved, although the structures themselves can be regenerated, coordinations determined, and structure types compared from the data provided. In the second group of structures primary nets containing squares together with triangles, pentagons, hexagons, heptagons or octa-gons are interleaved with secondary 4^4 nets (occasionally $3^2\,434$) of atoms. Figure 7 illustrates the primary networks involved. Table 8 presents data on such structures, giving the type, occupation and location of the primary net relative to the unit cell by listing the polygons covering the cell sites 0,0; 0,$^1/_2$ and $^1/_2$,0; $^1/_2$,$^1/_2$. It also gives the type, occupation and location of the secondary nets relative to the primary nets by listing the kind and location of primary net polygons centred by the secondary nets. The separation of the networks of atoms is also indicated. The symbols +, − describing the primary net orientation in Table 8 indicate whether successive nets are stacked over each other directly (symbols +,+ or −,−) or antisymmetrically (symbols +,−). The symbols + is generally accorded to the case where the top square edge points in the direction 45° to 90° (◁); minus when it points in the direction 90° to 135° (◇). Such tabulation, although rather more extended than those previously given, is very useful for showing relationships between these more complex structure types and for determining atomic coordination without generating the whole structure, although the complete structures can nevertheless be regenerated from the information provided.

There are also other families of structures made up of nets containing squares in which 1) 4^4 nets are oriented at an angle to the unit cell edge (eg. Al_8Mo_3), 2) the chemical repeat unit along 4^4 nets exceeds the net period (eg. Al_8Mo_3, Ni_4Mo, V_4Zn_5) and 3) the nets are made of squares and other polygons and successive nets are trans-posed so that the major polygons of one net are centred by atoms on identical nets located above and below (eg. UPt_2, UAl_4). Data on such types can also be reduced and presented in tabular form, but space does not permit a description here, and indeed the number of known structures in each class is much less than in the two cases considered above.

6. Summary

In four Tables covering only 13 pages we have given examples of coded reduction of crystal chemical data covering 220 structure types, from which crystal chemical relationships can be observed merely by inspection, atomic coordination determined either by inspection, or by brief scribbling (regeneration of the whole structure is unnecessary), and from which the essential features of any structural arrangement can be simply regenerated with reasonable accuracy from the reduced data. PEAR-SON's compilation [2] lists some 475 structures of metals and semiconductors for which atomic positions are known, and the reduction of crystal chemical information on 220 of these represents a condensation on a scale where the data can be compre-
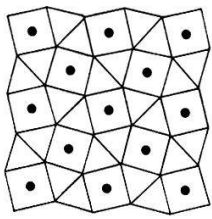
3^2 434 net
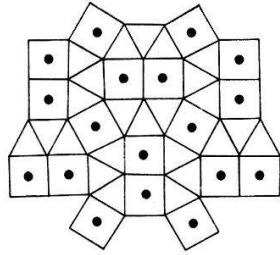
3^2 434 + $3^3 4^2$ (2:1) net
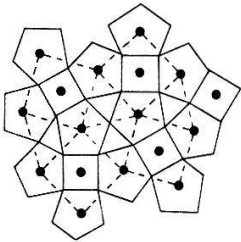
3535 + 3545 (1:4) net
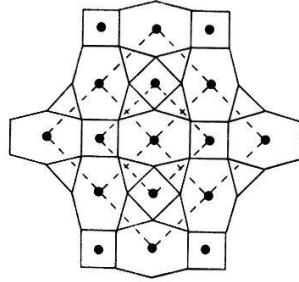
3436 + 3646 (1:1) net
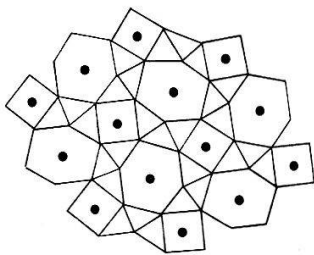
3^2 436 + 3^3 6 (2:1) net
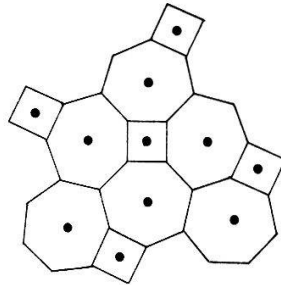
$47^2 + 7^3$ (4:3) net
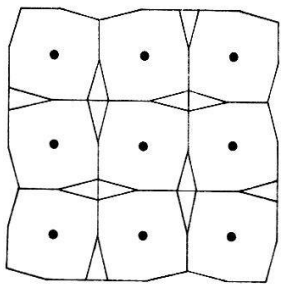
$3^2 8^2 + 38^2$ (1:1) net
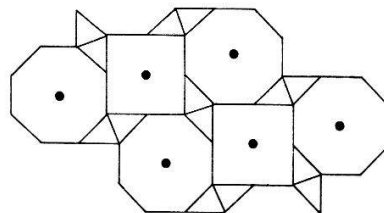
3^2 88 + 388 (1:1) net
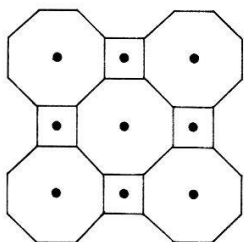
48^2 net
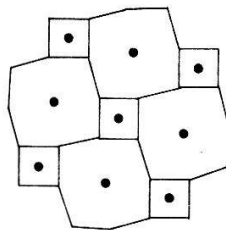
48^2 net

Figure 7

Various primary networks of atoms containing squares together with triangles, pentagons, hexagons, heptagons and/or octagons (see Table 8).

Table 8

Structures formed by primary nets containing squares together with triangles, pentagons, hexagons, heptagons or octagons

Primary net	Structure	Crystal plane	Height	Primary net: Occupation	Orientation	Polygon centering: Cell centre	Cell corner	Cell edge centre	Squares over: Cell centre	Cell corner	Edge centre	Diamonds	Triangles (1)	Triangles (2)	Secondary net
3^2434	NbTe$_4$ (tP 10) sub-cell	ab	0	Te	−	sq.	sq.	diam.							
			1/4							Nb					4^1
			1/2	Te	+	sq.	sq.	diam.							
			3/4							Nb					4^1
	PtPb$_4$ (tP 10)	ab	0						Pt	Pt					4^1
			1/4	Pb	+	sq.	sq.	diam.							
			3/4	Pb	−	sq.	sq.	diam.							
	Si$_2$U$_3$ (tP 10)	ab	0	Si	−	sq.	sq.	diam.	U(1)	U(1)					4^1
			1/2	U(2)	+	sq.	sq.	diam.							
	PdS (tP 16)	ab	0	3636 + 3²6² Pd (1 and 3)	+	diam.	hex.								
			~1/4	3²434 S	−	sq.	sq.	diam.		Pd(2)					4^1
			1/2	3636 + 3²6² Pd (1 and 3)	−	diam.	hex.								
			~3/4	3²434 S	−	sq.	sq.	diam.		Pd(2)					4^1
	CoGa$_3$ (tP 16)	ab	0	Ga(2)	−	sq.	sq.	diam.							
			1/4						Ga(1)	Ga(1)			Co (2 per diam.)		4^1; Ga(1)
			1/2	Ga(2)	−	sq.	sq.	diam.							
			3/4						Ga(1)	Ga(1)				Co	4^1; Ga(1)
	Al$_2$Gd$_3$ (tP 20)	ab	~0						Gd(3)	Gd(3)			Al[a]	Al[a]	4^1; Gd + 3²434; Al
			~1/4	Gd (1 and 2)	+	diam.	diam.	sq.							
			~1/2						Gd(3)	Gd(3)			Al[a]	Al[a]	4^1; Gd + 3²434; Al
			~3/4	Gd (1 and 2)	−	diam.	diam.	sq.							
	ThB$_4$ (tP 20)	ab	0	Th	+	sq.	sq.	diam.							
			1/2						B$_6$(1and3) (octahedra)	B$_6$(1and3)			B(2)	B(2)	3²434; B(2) {4¹; B(1) at 0.2; 0.8} {47²+7³; B(2 and 3)}
	Pb$_3$O$_4$ (tP 28)	ab	0	O	−	sq.	sq.	diam.				Pb(1)			4^1
			1/4	{O	+	sq.	sq.	diam.							
				Pb(2)	+	diam.	diam.	sq.							
			1/2	O	−	sq.	sq.	diam.				Pb(1)			4^1
			3/4	{O	+	sq.	sq.	diam.							
				Pb(2)	−	diam.	diam.	sq.							
	SeTl$_2$ (tP 30) (2 Se(1) atoms on 4 sites)	ab	0								Se(1)				4^1
			~1/12	Tl(2)	+	diam.	diam.	sq.							
			1/4	Se(2)	−	diam.	diam.	sq.		Tl(1)					4^1
			~5/12	Tl(2)	+	diam.	diam.	sq.							
			1/2								Se(1)				4^1
			~7/12	Tl(2)	−	diam.	diam.	sq.							
			3/4	Se(2)	+	diam.	diam.	sq.		Tl(1)					4^1
			~11/12	Tl(2)	−	diam.	diam.	sq.							
	CuAl$_2$ (tI 12)	ab	0	Al	+	sq.	sq.	diam.							
			1/4						Cu	Cu					4^1
			1/2	Al	−	sq.	sq.	diam.							
			3/4						Cu	Cu					4^1
	TlSe (tI 16)	ab	0	Se	+	sq.	sq.	diam.							
			1/4						Tl(1)	Tl(1)		Tl(2)			4^1; Tl(1 and 2)
			1/2	Se	−	sq.	sq.	diam.							
			3/4						Tl(1)	Tl(1)		Tl(2)			4^1; Tl(1 and 2)

[a]) displaced somewhat in height

Table 8

Primary net	Structure	Crystal plane	Height	Primary net	
				Occupation	Orientation
3^2434	PdGa$_5$ (tI 24)	ab	0		
			0.14	Ga(2)	+
			1/4		
			0.36	Ga(2)	−
			1/2		
			0.64	Ga(2)	−
			3/4		
			0.86	Ga(2)	+
	B$_3$Cr$_5$ (tI 32)	ab	0	B(2)	+
			0.15	Cr(2)	+
			0.25		
			0.35	Cr(2)	−
			0.50	B(2)	−
			0.65	Cr(2)	−
			0.75		
			0.85	Cr(2)	+
	Fe$_3$C (oP 16)	ac	∼0	Fe[b])	+
			1/4		
			∼1/2	Fe[b])	+
			3/4		
	PtSn$_4$ (oC 20)	ab	0		
			1/8	Sn	−
			3/8	Sn	−
			1/2		
			5/8	Sn	+
			7/8	Sn	+
	CoGe$_2$ (oC 23)	ab	0.01		
			1/8	Ge(1)	+
			0.24		
			3/8	4^4; Ge(2)	
			0.51		
			5/8	Ge(1)	−
			0.74		
			7/8	4^4; Ge(2)	
	PdSn$_3$ (oC 32)	bc	0	Sn(1)	−
			1/12		
			1/6	Sn(2)	+
			1/3	Sn(2)	+
			5/12		
			1/2	Sn(1)	−
			7/12		
			2/3	Sn(2)	+
			5/6	Sn(2)	+
			11/12		
	SiPt$_3$ (mC 16)	bc	0	Pt	+
			1/4		
			1/2	Pt	−
			3/4		

[b]) net rumpled   [c]) badly displaced from sq. centre   [d]) one triangle of each diamond

(Continuation)

Polygon centering			Centering by secondary nets						
			Squares over				Triangles		
Cell centre	Cell corner	Cell edge centre	Cell centre	Cell corner	Edge centre	Diamonds	(1)	(2)	Secondary net
			Ga(1)	Ga(1)					4^4
sq.	sq.	diam.							
			Pd	Pd					4^4
sq.	sq.	diam.							
			Ga(1)	Ga(1)					4^4
sq.	sq.	diam.							
			Pd	Pd					4^4
sq.	sq.	diam.							
sq.	sq.	diam.	Cr(1)	Cr(1)					4^4
sq.	sq.	diam.							
			B(1)	B(1)					4^4
sq.	sq.	diam.							
sq.	sq.	diam.	Cr(1)	Cr(1)					4^4
sq.	sq.	diam.							
			B(1)	B(1)					4^4
sq.	sq.	diam.							
sq.	sq.	diam.							
			Fe[c)	Fe[c)			C[d)		
sq.	sq.	diam.							
			Fe[c)	Fe[c)				C[d)	
			Pt	Pt					4^4
sq.	sq.	diam.							
diam.	diam.	sq.							
			Pt	Pt					4^4
diam.	diam.	sq.							
sq.	sq.	diam.							
			Co(1)	Co(1)					4^4
sq.	sq.	diam.							
			Co(2)	Co(2)					4^4
sq.	sq.	sq.							
					Co(1)				4^4
diam.	diam.	sq.							
					Co(2)				4^4
sq.	sq.	sq.							
sq.	sq.	diam.							
			Pd	Pd					4^4
sq.	sq.	diam.							
diam.	diam.	sq.							
			Pd	Pd					4^4
diam.	diam.	sq.							
			Pd	Pd					4^4
diam.	diam.	sq.							
sq.	sq.	diam.							
			Pd	Pd					4^4
diam.	diam.	diam.							
			Pt	Pt		Si			4^4, Pt; Si
diam.	diam.	diam.							
			Pt	Pt		Si			4^4, Pt; Si

Table 8

Primary net	Structure	Crystal plane	Height	Primary net Occupation	Orientation
$3^2434 + 3^34^2$ (2:1)	MnU_6 (tI 28)	ab	0	3^2434 U(2); 3^34^2 U(1)	+
			1/4		
			1/2	3^2434 U(2); 3^34^2 U(1)	−
			3/4		
$3545 + 3535$ (4:1)	Mn_2Hg_5 (tI 14)	ab	0	3545 Hg; 3535 Hg	+
			1/2		
$3436 + 3646$ (1:1)	Te_4Ti_5 (tI 18)	ab	0	3436 Te; 3646 Ti(2)	+
			1/2	3436 Te; 3646 Ti(2)	−
$3^2634 + 3^36$ (2:1)	α-S_2U (tI 30)	ab	0	3^2634 S(2); 3^36 U(2)	+
	(2 U in 4 U(1) sites)		1/4		
			1/2	3^2634 S(2); 3^36 U(2)	−
			3/4		
	Si_3W_5 (tI 32)	ab	0	3^2634 W(2); 3^36 Si(2)	+
			1/4		
			1/2	3^2634 W(2); 3^36 Si(2)	−
			3/4		
	β-$SbTi_3$ (tI 32)	ab	0	3^2634 Ti(3); 3^36 Sb	+
			1/4		
			1/2	3^2634 Ti(3); 3^36 Sb	−
			3/4		
$47^2 + 7^3$ (4:3)	ThB_4 (tP 20)	ab	0		
			0.2		
			0.5	B	+
			0.8		
$3^28^2 + 38^2$ (1:1)	β-SV_3 (tP 32)	ab	0	V	+
			1/4		
			1/2	V	−
			3/4		
$3^288 + 388^e)$ (1:1)	PNi_3 (tI 32)	ab	0		
			1/4	Ni	+
			1/2		
			3/4	Ni	−
48^2	CaB_6 (cP 7)	ab	0		
			0.2		
			0.5	B	+
			0.8		
48^2	UB_{12} (cF 52)		0	B	
			1/2	B	
	$AlTh_2H_4$ (tI 28)	ab	0	48^2 Al	+
			0.137	3^2434 H	+
			1/4		
			0.363	3^2434 H	−
			1/2	48^2 Al	−
			0.637	3^2434 H	+

e) octagon and square with atoms at mid.points of sides

(Continuation)

Polygon over			Centering			
				Squares		
Cell centre	Cell corner	Centre cell edge	Major polygon	Cell centre	Cell corner	Secondary net
single sq.	single sq.	2 sq.				
				Mn	Mn	4^4
single sq.	single sq.	2 sq.				
				Mn	Mn	4^4
sq.	sq.		pent.; Mn	•		3^2434
sq.	sq.	hex.			Ti(1)	4^4
sq.	sq.	hex.		Ti(1)		4^4
sq.	sq.	hex.	hex.; S(1)	U(1)	U(1)	4^4; S(1); U(1)
sq.	sq.	hex.	hex.; S(1)	U(1)	U(1)	4^4; S(1); U(1)
sq.	sq.	hex.	hex.; W(1)	Si(1)	Si(1)	4^4; W(1); Si(1)
sq.	sq.	hex.	hex.; W(1)	Si(1)	Si(1)	4^4; W(1); Si(1)
sq.	sq.	hex.	hex.; Ti(2)	Ti(1)	Ti(1)	4^4; Ti(2) + Ti(1)
sq.	sq.	hex.	hex.; Ti(2)	Ti(1)	Ti(1)	4^4; Ti(2) + Ti(1)
			hept.; Th			3^2434 (sq. over cell corner and centre)
				B	B	4^4
sq.	sq.			B	B	4^4
oct.	oct.	diam.				
			oct. by (V + S) diam. +			
oct.	oct.	diam.				
			oct. by (V + S) diam. −			
			oct. and sq. by (Ni + P) diam. +			
diam.	diam.	oct. and sq.				
			oct. and sq. by (Ni + P) diam. −			
diam.	diam.	oct. and sq.				
			oct. Ca			4^4
				B		4^4
sq.	oct.			B		4^4
oct.	oct.	sq.	oct. U			4^4; U[f]
sq.	sq.	oct.	oct. U			4^4; U)[g]
oct.	oct.	sq.				
sq.	sq.	diam.				
			oct. Th			4^4
sq.	sq.	diam.				
oct.	oct.	sq.				
sq.	sq.	diam.				

[f] U at centre of cubes of B at height $\pm 1/3$ [g] U atoms centre cubes of B at height $\pm 1/6$

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Table 8

Primary net	Structure	Crystal plane	Height	Primary net	
				Occupation	Orientation
			3/4		
			0.863	3^2434 H	—
	RhSn$_2$ (tI 18)	ab	0		
			1/12	48^2 Sn^{h})	
			1/6		
			1/4	4^4 Sn	
			1/3		
			5/12	48^2 Sn^{h})	
			1/2		
			7/12	48^2 Sn^{h})	
			2/3		
			3/4	4^4 Sn	
			5/6		
			11/12	48^2 Sn^{h})	
	P$_5$Ni$_{12}$ (tI 34)	ab	0	4^4 P(1 and 2)	rot. 45°
			~1/4	48^2 ^{i}) Ni(2)	+
			1/2	4^4 P(1 and 2)	rot. 45°
			~3/4	48^2 ^{i}) Ni(2)	+
Se$_{15}$Pd$_{17}$ (cP 64)			0	net with rectangles and sq. P(2 and 3) and Se(2)	
			0.16	343(12) Pd; $3(12)^2$ Se	+
			1/4		
			0.35	48^2 Pd(4)	+
			1/2	$3436 + 3646$ Se(1 and 3)	
			0.65	48^2 Pd(4)	+
			3/4		
			0.84	343(12) Pd; $3(12)^2$ Se	+

^{h}) sides 50 $^0/_0$ occupied ^{i}) oct. are really squares

hended and used with rather little mental effort. No attempt is made to provide information on unit cell dimensions or interatomic distances. The data provided in the tables are not complete; rather they should serve as examples. With the addition of two tables analysing structures from the point of view of connections between tetrahedra and between octahedra, and the addition of three minor tables completing the coverage of structures built from networks containing squares, much of the crystal chemical data on important structures of metals and semiconductors can be covered (and further possible structure types can be predicted). Since quite simple codes are used in the reduction of the data, it is possible on this basis to survey and comprehend at one time much of the crystal chemistry of metals and semiconductors, and so better to select materials for desired electrical and magnetic properties, insofar as these may be expected to depend on the structural arrangements of the component atoms.

(Continuation and End)

Polygon over			Centering			
				Squares		
Cell centre	Cell corner	Centre cell edge	Major polygon	Cell centre	Cell corner	Secondary net
			oct. Th			4^4
sq.	sq.	diam.				
			oct. Rh			4^4
oct.	sq.					
			oct. Rh			4^4
sq.	sq.					
			oct. Rh			4^4
sq.	oct.					
			oct. Rh			4^4
sq.	oct.					
			oct. Rh			4^4
sq.	sq.					
			oct. Rh			4^4
oct.	sq. P atom		oct. by Ni(1) + P(2) diam. +			
sq. P atom	sq.	oct.	oct. by Ni(1) + P(2) diam. −			
sq.	sq.					
sq.	12					
			12, Pd	Se		sq. Se(2) about cell corners
oct.	oct.	sq.				
sq.	sq.	oct.		Pd	Pd	4^4
oct.	oct.	sq.				
			12, Pd	Se		sq. Se(2) about cell corners
sq.	12					

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