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Coordination Polyhedra and Structure of Alloys: Binary Alloys of Vanadium with Group IIIB and IVB Elements

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Vanadium is found to exhibit a range of coordination numbers (CN) from 10 to 17 in its binary alloys with group IIIB and IVB elements. The polyhedra around V are characterized and a description in terms of symbols is offered. The structures of the binary alloys considered are described in terms of polyhedral packing. It is found that there are two types: a three-dimensional distribution of discrete polyhedra sharing corners, edges or faces and a layer-like distribution.

Introduction

A fruitful approach to understanding the crystal chemistry of alloy structures is to consider the coordination spheres around particular atoms. Frank & Kasper (1958) considered the coordination geometries around an atom as made up of only triangular faces and examined the topological and geometrical properties of the triangulated shells with CN 12, 14, 15 and 16. The characteristics of structural types with high CN have been studied by Kripyakevich (1960). He has also deduced the characteristics of polyhedra with CN 12 to 17, 20, 22 and 24.

A few papers (Brown, 1957, 1959; Girgis, Petter & Pupp, 1975) have dealt with the coordination polyhedra as building blocks of the structure. Such a description, even though not supported by any specific theory, arises from observations of the peculiarities of the structures and the most general inferences that can be drawn from them (Black, 1956). In this paper we characterize the polyhedra in various known binary alloys and use them to build up the structures. The aim is to present a simple explanation of the complex alloy structures and to systematize the different known structure types.

Coordination polyhedra

In order to define a coordination polyhedron it is essential to limit the coordination sphere of an atom (Brunner & Laves, 1971). The coordination sphere as defined by the maximum-gap concept (Brunner & Schwarzenbach, 1971) seems to be realistic (Brunner, 1977). Recently we have studied the coordination behaviour of V in its binary alloys with IIIB and IVB elements (Bhandary & Girgis, 1977) using the maximum-gap concept to limit the coordination sphere of V and the 'B' elements.

V exhibits a varying CN of 10 to 17 in these alloys. The various coordination geometries are listed in Table 1. The symmetry given is that found for the figure obtained from the structural parameters reported. In some cases the idealized symmetry is indicated. Each polyhedron is described in terms of symbols according to the arrangement of vertices.

$1^6{:}4^4+2^5{:}2^4+3^5{:}1^5$ means that, starting from a sixfold vertex at the top, there is a plane of four fourfold and two fivefold vertices followed by another plane of two fourfold and three fivefold vertices and a fivefold vertex at the bottom. The starting point of the description is located either on a symmetry axis or a symmetry plane. An *n*-fold vertex is taken to mean a point where *n* edges meet (for convenience we have not considered the symmetry of the vertex).

Description of alloy structures

In the following sections the structures of the different alloys are given in terms of polyhedral packing. Wherever the structure has been determined the positional parameters have been used to calculate the details of the structure; when the alloy is characterized in terms of structure type the parameters from that type have been taken. It will be seen that the structures can be explained with only a few polyhedra.

V–Al system

The data are given in Table 2. The V atoms have CN 12 in almost all cases except in V_3Al where it is 14 and in V_5Al_8 where one V atom has 13. The icosahedral geometry of CN 12 is found to occur frequently and the geometry for CN 13 and CN 14 can be derived from the icosahedron by capping appropriate edges and by rearrangement of the vertices.

$\mathbf{V_5Al_8}$ crystallizes in the cubic space group $I\bar{4}3m$ and has 52 atoms per cell. There are two crystallographically independent V atoms, V_1 and V_2, in the asymmetric unit which belongs to the Cu_5Zn_8 type. V_1 has CN 12 and V_2 13. The polyhedron around V_1 is an icosahedron having $3m$–C_{3v} symmetry (IV, Fig. 1). The 13-verticon (VII, Fig. 1) around V_2 has $mm2$–C_{2v} symmetry and is bounded by 22 triangular faces.

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The structure of V_5Al_8, and hence the Cu_5Zn_8 type, can be explained on the basis of the two polyhedra around V_1 and V_2 (Fig. 2). Two V_1 polyhedra share a triangular face with each other and another triangular face with a V_2 polyhedron to form a polyhedron chain, $V_1V_1V_2V_1V_1V_2$, along [011]. Another such chain stacks over the former by sharing the shaded atoms in Fig. 2. Such parallel columns are held together by strong contacts.

VAl_3 belongs to the $TiAl_3$ structure type and crystallizes in the tetragonal space group $I4/mmm$. The polyhedron around V is a distorted cubooctahedron with $m3m-O_h$ idealized symmetry. The structure can be explained by the packing of these polyhedra. Cubooctahedra at the same height share quadrangular faces forming a layer. Each cubooctahedron of a similar upper layer shares an edge with each of four cubooctahedra of the lower layer (Fig. 3).

V_4Al_{23} crystallizes in the hexagonal space group $P6_3/mmc$ with 54 atoms per cell. The asymmetric unit contains two independent V atoms, V_1 and V_2, each with CN 12. The polyhedra around both are almost regular icosahedra. In the structure three V_2 icosahedra interpenetrate and form a complex unit of $\bar{6}m2-D_{3h}$ symmetry (XXI, Fig. 1) with three centres. The units with centres at $z=0{\cdot}25$ share an Al_2 corner (at $z=0{\cdot}12$) with each of the three icosahedra around V_1 at 000, 100 and 110. They also share an Al_2 corner at $z=0{\cdot}38$ with

Table 1. *Description of polyhedra*

	CN	Polyhedron	Symmetry	Idealized	No. of faces*		Arrangement of vertices	Found in
					△	□		
I	10	Bicapped dodecahedron	$2-C_2$	$222-D_2$	16		$2^5:2^5:2^4:2^5:2^5$	V_2Sn_3
II	10	½ Icosahedron + ½ Cube	$3-C_3$		10	3	$1^3:3^4:3^4:3^5$	V_8Ga_{41}
III	11	Pentacapped trigonal prism	$mm2-C_{2v}$	$\bar{6}m2-D_{3h}$	18		$1^3:3^6:3^4:3^6:1^3$	V_6Ga_5
IV	12	Icosahedron	$3m-C_{3v}$		20		$3^5:3^5:3^5:3^5$	V_5Al_8, V_4Al_{23}, VAl_{10}, V_7Al_{45}, V_6Ga_7, V_6Ga_5
V	12	Cubooctahedron	$m3m-O_h$	Idealized	8	6	$4^4:4^4:4^4$	VAl_3, V_8Ga_{41}
VI	12	Bicapped pentagonal prism	$mm2-C_{2v}$	$\overline{10}m2-D_{5h}$	10	5	$1^5:5^4:5^4:1^5$	V_2Ga_5
VII	13	13-verticon of Cu_5Zn_8 type	$mm2-C_{2v}$		22		$1^4:2^5:2^6:4^5:2^5:2^5$	V_5Al_8, V_6Ga_7
VIII	13	13-verticon of $V_{11}Ge_8$ type	$m-C_s$		16	3	$1^6:4^4+2^5:2^4+3^5:1^5$	$V_{11}Ge_8$
IX	14	14-verticon of $CrSi_2$ type	$2-C_2$	$6/mmm-D_{6h}$	4	10	$1^4:2^4:2^4:2^3:2^3:2^4:2^4:1^4$	VSi_2
X	14	Kasper (distorted)	$mm2-C_{2v}$	$\bar{6}m-D_{6d}$	24		$1^6:6^5:6^5:1^6$	*A*15, V_5Si_3
XI	14	Kasper-like 14-verticon	$3-C_3$		18	3	$1^6:3^5+3^4:3^5+3^4:1^6$	V_5Ge_3, V_6Si_5, $V_{11}Ge_8$
XII	14	Rhombic dodecahedron	$m3m-O_h$			12	$1^4:4^3:4^4:4^3:1^4$	V(Ga)
XIII	14	14-verticon of $Cr_{11}Ge_8$ type	$m-C_s$		14	5	$1^5:5^5:5^4:3^4$	$V_{11}Ge_8$
XIV	15	15-verticon of Mn_5Si_3 type	$mm2-C_{2v}$		18	4	$1^4:4^5:2^4:2^5:4^5:2^4$	V_5Ge_3
XV	15	15-verticon of W_5Si_3 type	$m-C_s$		20	3	$1^5:2^6+1^5+2^4:5^5+2^4:1^4+1^5$	V_5Si_3, V_6Si_5, $V_{11}Ge_8$
XVI	16	16-verticon of $Cr_{11}Ge_8$ type	$m-C_s$		24	2	$1^6:4^5:2^5+3^4:2^6+3^5:1^5$	$V_{11}Ge_8$
XVII	17	17-verticon of V_6Si_5 type	$m-C_s$	$mm2-C_{2v}$	20	5	$1^5:2^6+3^5:5^4:2^5:3^5:1^3$	V_6Si_5
XVIII	17	17-verticon of $Cr_{11}Ge_8$ type	$mm2-C_{2v}$		24	3	$1^4:4^5:2^4:4^6+2^5:2^4+2^5$	$V_{11}Ge_8$
XIX	10	Bicapped square antiprism	$\bar{8}2m-D_{4d}$		16		$1^4:4^5:4^5:1^4$	For Si in V_6Si_5, V_5Si_3
XX	11	11-verticon	$1-C_1$	$m-C_s$	16	1	$1^5:5^5:3^4:2^5$	For Ge_1 in $V_{11}Ge_8$

* △ Triangular; □ Quadrangular.

Table 2. *Crystal data of the* V–Al *system*

Alloy	Pearson symbol	Structure type Space group	Unit-cell dimensions (Å, °)	Atom	Polyhedra used	Packing in	Crystal data from
V_3Al	$cP8$	Cr_3Si $Pm3n$	$a=$ 4·699	V	Kasper (14) (*D*)	Present work	Holleck, Benesovsky & Nowotny (1963) Structure type given
V_5Al_8	$cI52$	$Cu_5Zn_8(D8_2)$ $I\bar{4}3m$	$a=$ 9·207	V_1 V_2	Icosahedron (*D*) 13-verticon of Cu_5Zn_8	Present work	Carlsson, Kenny & Wilhelm (1955) Structure type given
VAl_3	$tI8$	$TiAl_3$ (DO_{22}) $I4/mmm$	$a=$ 5·343 $c=$ 8·324	V	Cuboctahedron (*D*)	Present work	Brauer (1943) Structure type given
V_4Al_{23}	$hP54$	V_4Al_{23} $P6_3/mmc$	$a=$ 7·692 $c=$17·04	V_1 V_2	Icosahedron (*D*) Complex unit of icosahedra	Present work	Smith & Ray (1957, 1960) Structure complete
V_7Al_{45}	$mC104$	V_7Al_{45} $C2/m$	$a=$25·604 $b=$ 7·6213 $c=$11·081 $\beta=$128·9	V_1 V_2	Icosahedron (*R*) Complex unit	Original paper	Brown (1959) Structure complete
$VAl_{(10)}$ (*a*)	$cF176$	$VAl_{(10)}$ $Fd3m$	$a=$14·516	V	Icosahedron (*D*)	Original paper	Brown (1957) Structure complete
$VAl_{(10)}$ (*b*)	$cF180$	$Fd3m$	$a=$14·492	V	Icosahedron (*D*)	Brown (1957)	Ray & Smith (1957) Structure complete

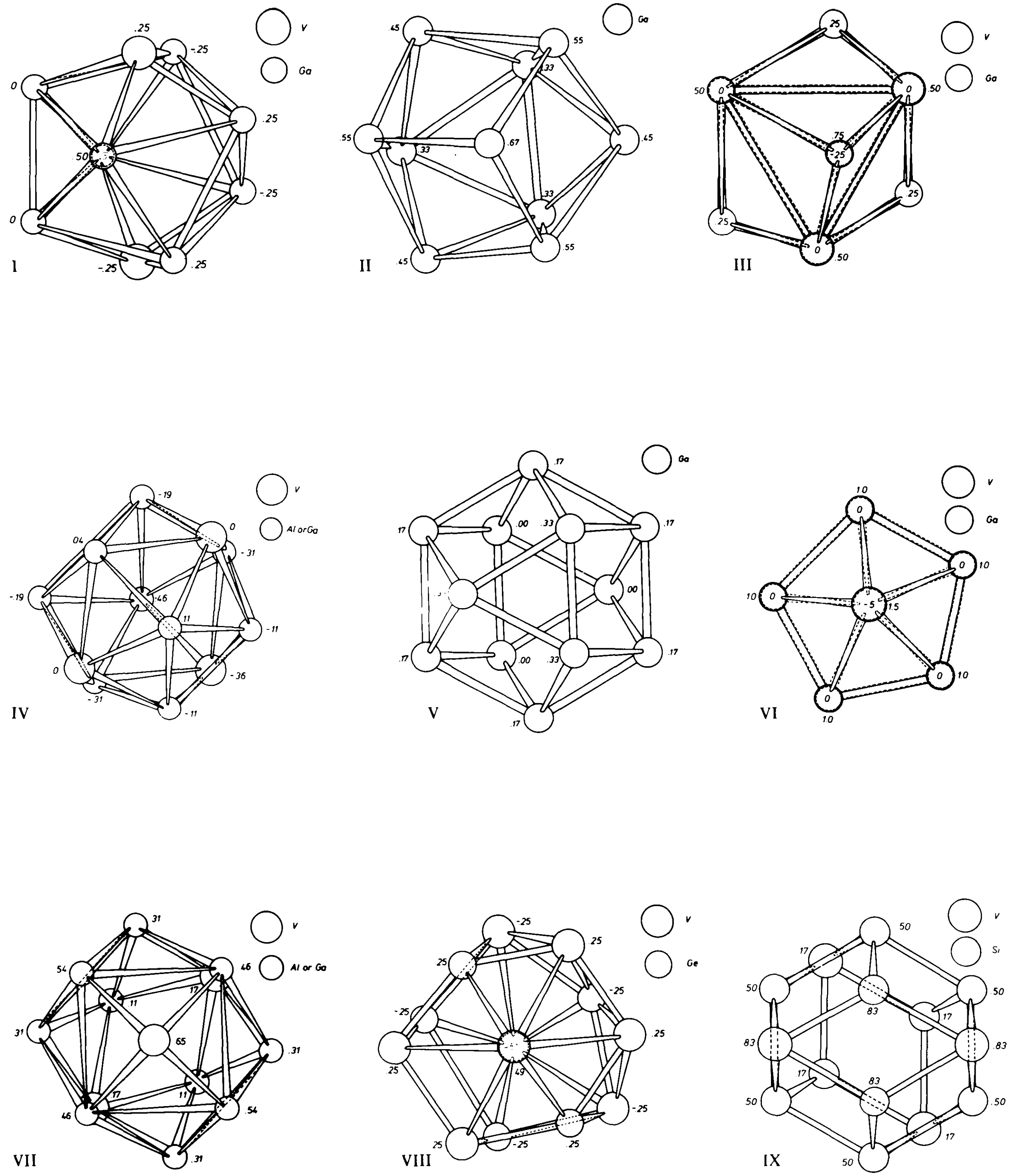

Fig. 1. Polyhedra arranged according to the number of vertices. I V Polyhedron in V_2Sn_3 (bicapped dodecahedron); II V_1 Polyhedron in V_8Ga_{41} ($\frac{1}{2}$ icosahedron + $\frac{1}{2}$ cube); III V_1 Polyhedron in V_6Ga_5 (pentacapped trigonal prism); IV V_1 Polyhedron in V_5Al_8 (icosahedron of C_{3v} symmetry); V Ga_1 Polyhedron in V_8Ga_{41} (cubooctahedron); VI V Polyhedron in V_2Ga_5 (based on pentagonal pyramid); VII V_2 Polyhedron in V_5Al_8 (13-verticon of C_{2v} symmetry); VIII V_1 Polyhedron in $V_{11}Ge_8$ (13-verticon of C_s symmetry); IX V Polyhedron in VSi_2 (14-verticon of C_2 symmetry).

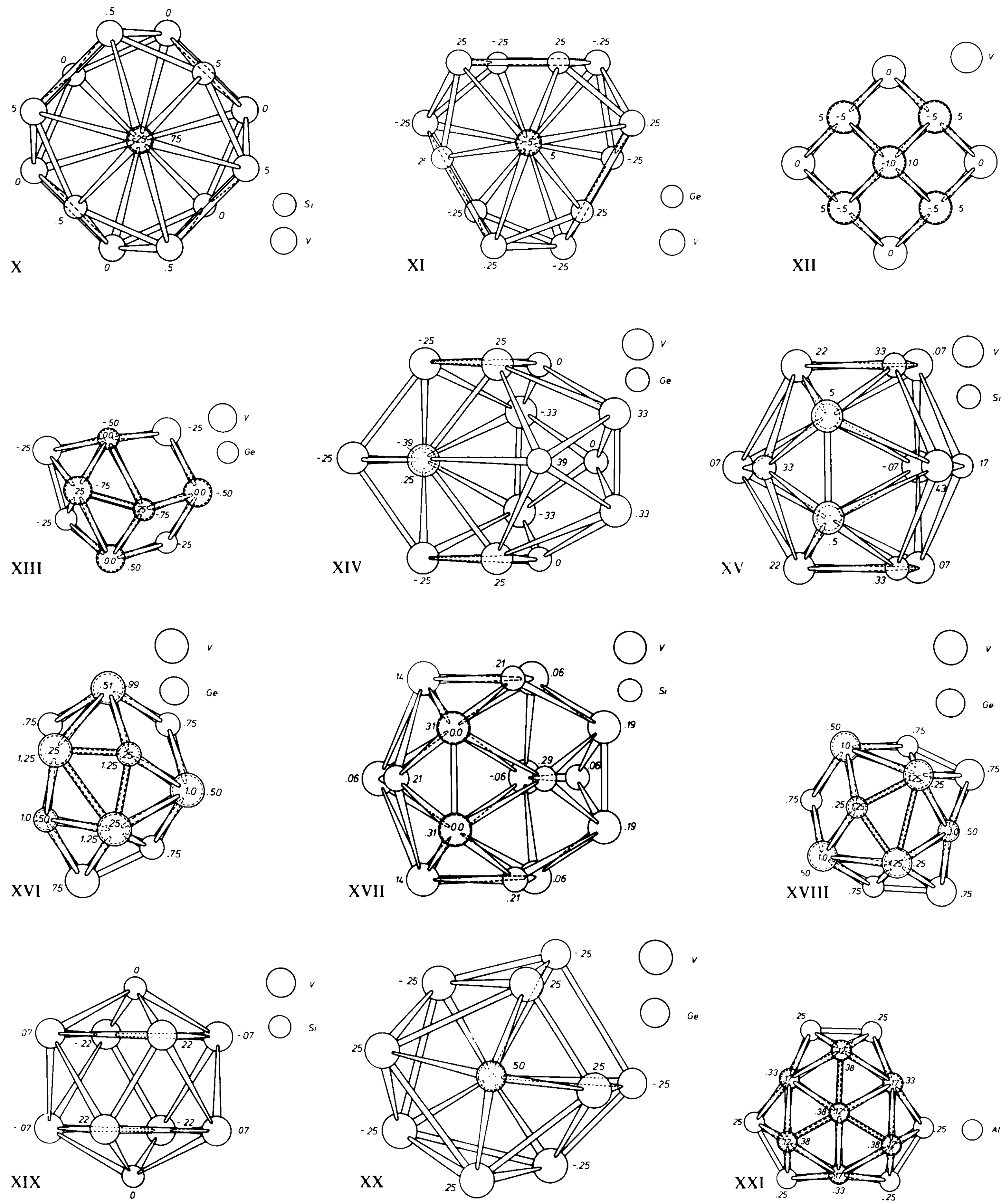

Fig. 1. (*cont.*) X V_1 Polyhedron in V_5Si_3 (Kasper polyhedron of C_{2v} symmetry); XI V_1 Polyhedron in V_5Ge_3 (Kasper-like polyhedron of C_3 symmetry); XII V Polyhedron in V(Ga) (14-verticon of O_h symmetry); XIII V_5 Polyhedron in $V_{11}Ge_8$ (14-verticon of C_s symmetry); XIV V_2 Polyhedron in V_5Ge_3 (15-verticon of C_{2v} symmetry); XV V_2 Polyhedron in V_5Si_3 (15-verticon of C_s symmetry); XVI V_3 Polyhedron in $V_{11}Ge_8$ (16-verticon of C_s symmetry); XVII V_1 Polyhedron in V_6Si_5 (17-verticon of C_s symmetry); XVIII V_6 Polyhedron in $V_{11}Ge_8$ (17-verticon of C_{2v} symmetry); XIX Si Polyhedron in V_5Si_3 (bicapped square antiprism); XX Ge_1 Polyhedron in $V_{11}Ge_8$ (11-verticon); XXI Complex unit of three V_2 polyhedra in V_4Al_{23} (tricentered complex of D_{3h} symmetry).

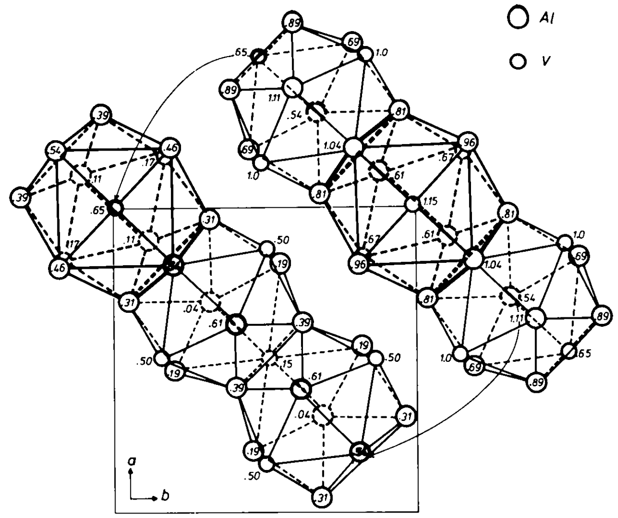

Fig. 2. Structure of V_5Al_8 (*cI*52, Cu_5Zn_8 type).

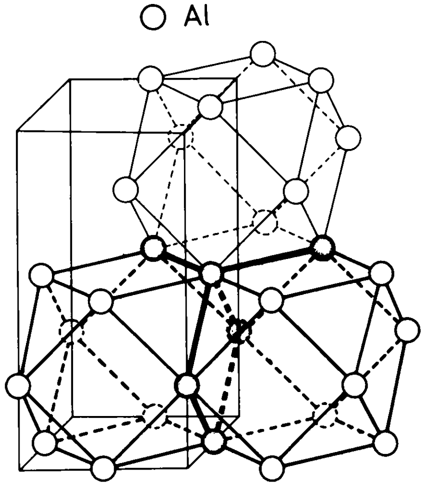

Fig. 3. Structure of VAl_3 (*tI*8, $TiAl_3$ type).

each of the three icosahedra around V_1 at $00\frac{1}{2}$, $10\frac{1}{2}$ and $11\frac{1}{2}$. Another tricentred complex related to the former by a *c* glide shares in a similar way an Al_2 atom $z=0{\cdot}62$ with each of the three icosahedra around V_1 at $00\frac{1}{2}$, $01\frac{1}{2}$, $11\frac{1}{2}$ and an Al_2 at $z=0{\cdot}88$ with each of three V_1 polyhedra around V at 001, 011 and 111 (Fig. 4).

V_7Al_{45}: see original paper (Brown, 1959).

$VAl_{(10)}$ (*a*) and (*b*): see original papers (Brown, 1957; Ray & Smith, 1957).

V–Ga system

Table 3 gives the data. V exhibits CN 10 to 14 and has a variety of polyhedral geometries.

V_3Ga is a representative of the Cr_3Si type with only 8 atoms per unit cell. The V atom has CN 14 and its polyhedron is a distorted Kasper (X, Fig. 1) with $mm2$–C_{2v} symmetry. The structure of V_3Ga, and hence Cr_3Si-type structures, is built up of face-sharing V polyhedra (Fig. 5). In the perpendicular direction the polyhedra share apices occupied by V atoms forming the V–V chain.

V_6Ga_5 crystallizes in the hexagonal space group $P6_3/mmc$ and belongs to the α-Ti_6Sn_5 type with 22 atoms per cell. The asymmetric unit contains two independent V atoms, V_1 and V_2, which have CN 11 and 12 respectively. The polyhedron around V_1 is a distorted pentacapped trigonal prism (III, Fig. 1). In addition to the capping of the prism faces, the two triangular faces are also capped, giving 11 vertices. The polyhedron is bounded by 18 triangular faces and has $mm2$–C_{2v} symmetry. The polyhedron around V_2 is a very distorted icosahedron.

The structure of V_6Ga_5 can be built up by packing the V_2 polyhedra alone. Of the independent Ga atoms, Ga_2 occupies the corners of the cell. Surrounding this atom there are six V_2 polyhedra sharing triangular faces with each other and forming a layer of polyhedra

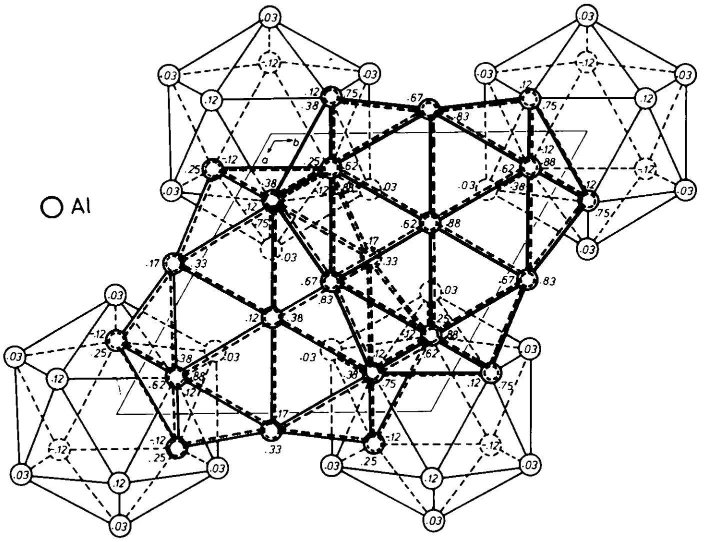

Fig. 4. Structure of V_4Al_{23} (*hP*54, V_4Al_{23} type).

Table 3. *Crystal data of the* V–Ga *system*

Alloy	Pearson symbol	Structure type Space group	Unit-cell dimensions (Å)	Atom	Polyhedra used	Packing in	Crystal data from
V_3Ga	*cP*8	Cr_3Si *Pm*3*n*	$a = 4{\cdot}82$	V	Kasper (14) (*D*)	Present work	Meissner & Schubert (1965) Structure type given
V(Ga)	*cI*2	W *Im*3*m*	$a = 3{\cdot}07$	V	14-verticon of W type	Not treated	Meissner & Schubert (1965) Structure type given
V_6Ga_5	*hP*22	α-Ti_6Sn_5 $P6_3/mmc$	$a = 8.496$ $c = 5{\cdot}176$	V_2	Icosahedron(*D*)	Present work	van Vucht, Donkersloot & Gomes de Mesquita (1964) Structure type given Meissner & Schubert (1965)
V_6Ga_7	*cI*52	Cu_5Zn_8 $I\bar{4}3m$	$a = 9{\cdot}14$	V_1 V_2	Icosahedron (*D*) 13-verticon of Cu_5Zn_8 type	Present work	van Vucht *et al.* (1964) Structure type given
V_2Ga_5	*tP*14	Mn_2Hg_5 *P*4/*mbm*	$a = 8{\cdot}968$ $c = 2{\cdot}693$	V	Bicapped pentagonal prism	Present work	Reddy, Storm & Knox (1965) Structure complete
V_8Ga_{41}	*hR*49	V_8Ga_{41} $R\bar{3}$	$a = 13{\cdot}9382$ $c = 14{\cdot}8924$	$V_1 + V_2$ Ga	½ Icosahedron + ½ cube Cuboctahedron	Original paper	Girgis *et al.* (1975) Structure complete

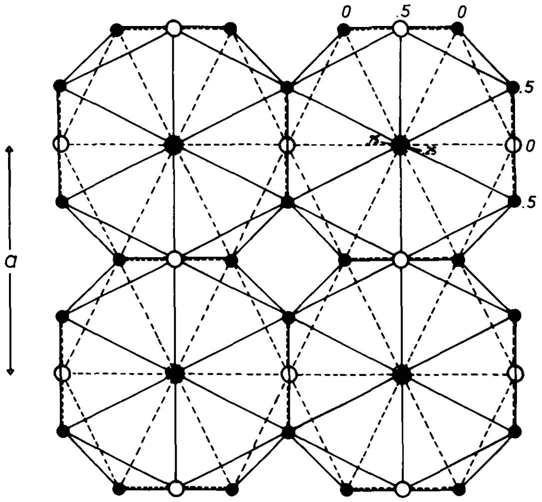

Fig. 5. Structure of V_3Ga (*A*15 type).

(Fig. 6). Another layer of V_2 polyhedra stacks over the former by sharing the apices occupied by the V_2 atoms, thus forming chains of V_2 atoms parallel to **c**. In the centre of the V_2 polyhedra the Ga atoms form similar chains running through the channel formed by the six V_2 polyhedra, which is also parallel to **c**. Thus two chains, V–V and Ga–Ga, are evident. The V–V and Ga–Ga contact distances along the chain are both 2·59 Å. There are some shorter V–Ga contacts, but no V–V or Ga–Ga contacts less than 2·59 Å.

V_6Ga_7 belongs to the Cu_5Zn_8 type and hence is similar to V_5Al_8.

V_2Ga_5 belongs to the Mn_2Hg_5 type and crystallizes in the tetragonal space group *P*4/*mbm* with 14 atoms per cell and one V atom per asymmetric unit with CN 12. The polyhedron can be described as a bicapped pentagonal prisms (VI, Fig. 1) having $mm2$–C_{2v} symmetry. The figure has 10 triangular and 5 quadrangular

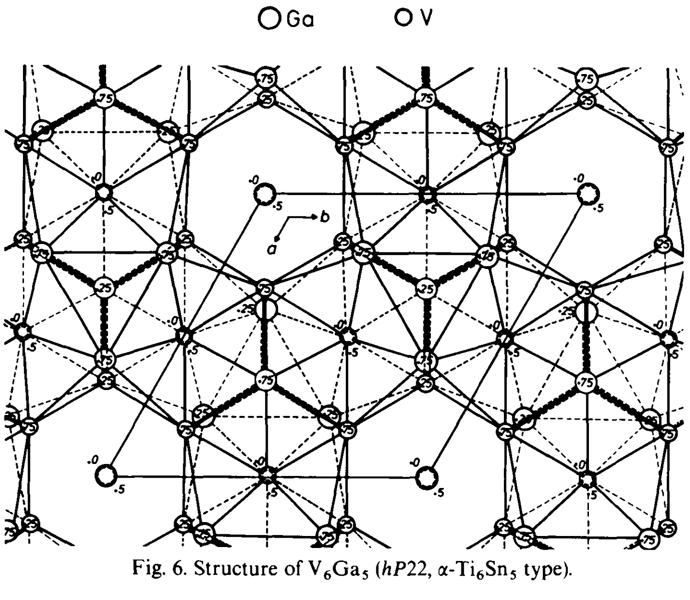

Fig. 6. Structure of V_6Ga_5 (*hP*22, α-Ti_6Sn_5 type).

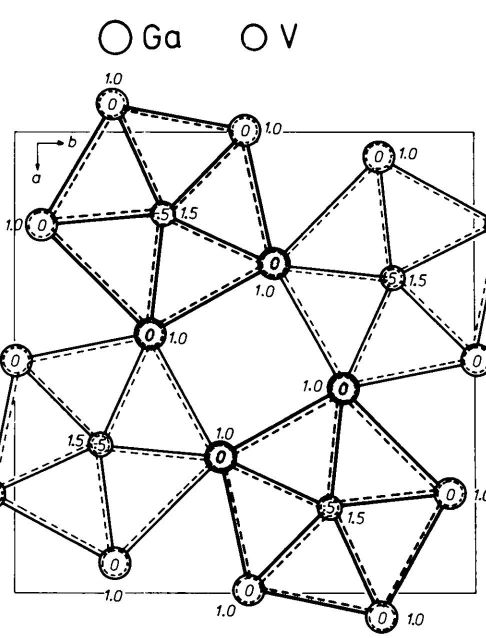

Fig. 7. Structure of V_2Ga_5 (*tP*14, Mn_2Hg_5 type).

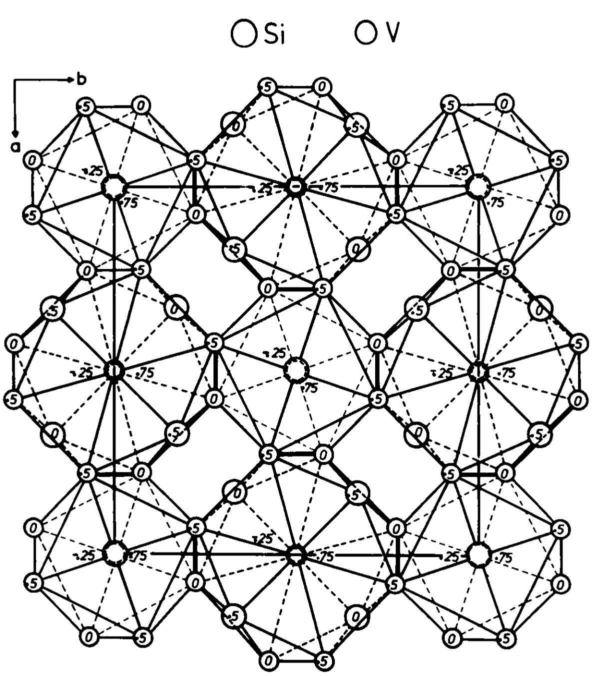

Fig. 8. Structure of V_5Si_3 (*tI*32, W_5Si_3 type).

faces. The structure can be built up by edge-sharing of the V polyhedra along **c** as well as V corners forming V–V chains parallel to this direction (Fig. 7), the atoms being 2·59 Å apart. As with V_6Ga_5 there are some V–Ga contacts which are shorter than the V–V distances.

V_8Ga_{41}: see original paper (Girgis *et al.*, 1975).

V–Si system

Table 4 gives the data. The V atoms show CN 14, 15 and 17.

V_3Si belongs to the Cr_3Si type (see V_3Ga).

V_5Si_3 exists in two structural types W_5Si_3 and Mn_5Si_3. The former is tetragonal, the latter hexagonal. Here we describe the structure of the tetragonal form which crystallizes in the space group *I*4/*mcm* with 32 atoms per cell. The asymmetric unit contains two V atoms, V_1 and V_2, having CN 14 and 15 respectively. The 14-verticon around V_1 (X, Fig. 1) is a slightly distorted Kasper polyhedron. The 15-verticon around V_2 (XV, Fig. 1) is bounded by 20 triangular and 3 quadrangular faces and has only mirror symmetry. Of the two Si atoms in the asymmetric unit Si_1 has CN 10. The geometry of the latter (XIX, Fig. 1) is a bicapped square antiprism of $\bar{8}2m$–D_{4d} symmetry. The figure is bounded by 16 triangular faces.

The packing in the binary alloy can be explained in terms of the V_1 and Si_1 polyhedra. These share edges with each other alternately and extend along **a** and **b** forming a layer. These layers stack one above the other by sharing V and Si apices, forming chains of V_1 and Si_1 atoms along **c** (Fig. 8). The V_1–V_1 and Si_1–Si_1 contacts are 2·39 Å which is the shortest distance in the structure.

Table 4. *Crystal data of the* V–Si *system*

Alloy	Pearson symbol	Structure type Space group	Unit-cell dimensions (Å)	Atom	Polyhedra used	Packing in	Crystal data from
V_3Si	*cP*8	Cr_3Si *Pm*3*n*	*a* = 4·725	V	Kasper (14) (*D*)	Present work	Nowotny, Machenschalk, Kieffer & Benesovsky (1954) Structure type given
V_5Si_3	*tI*32	$W_5Si_3(D8_m)$ *I*4/*mcm*	*a* = 9·44 *c* = 4·77	V_1 Si_1	Kasper (14) (*D*) Bicapped square antiprism	Present work	Parthé, Nowotny & Schmid (1955) Structure type given
	*hP*16	Mn_5Si_3 $(D8_8)$ $P6_3/mcm$	*a* = 7·135 *c* = 4·842		Kasper-like (14) see V_5Ge_3	Present work	Pearson (1967)
V_6Si_5	*oI*44	V_6Si_5 *Ibam*	*a* = 15·966 *b* = 7·501 *c* = 4·858	V_3 Si	Kasper-like (14) Bicapped square antiprism (*D*)	Present work	Spinat, Fruchart & Herpin (1970) Structure complete
VSi_2	*hP*9	$CrSi_2$ (*C*40) $P6_222$	*a* = 4·571 *c* = 6·372	V	14-verticon of $CrSi_2$ type	Present work	Wallbaum (1941) Structure qualitative

V_6Si_5 crystallizes in the orthorhombic space group *Ibam* with 44 atoms per cell. The asymmetric unit contains three independent V atoms, V_1, V_2 and V_3, with CN 17, 15 and 14 respectively. The 17-verticon (XVII, Fig. 1) around V_1 has m–C_s symmetry and is bounded by 20 triangular and 5 quadrangular faces. The polyhedron around V_2 is the same as that of the 15-verticon (XV, Fig. 1) around V_2 in V_5Si_3 (tetragonal form). The 14-verticon (XI, Fig. 1) around V_3 is a Kasper-like polyhedron having 3–C_3 symmetry. The polyhedron is bounded by 18 triangular and 3 quadrangular faces, as opposed to the 24 triangular faces in the Kasper polyhedron. The idealized polyhedron approximates to the Kasper polyhedron of the 14-verticon found in V_5Si_3 (tetragonal). Of the three independent Si atoms Si_3 has CN 10 and bicapped square antiprism geometry (XIX, Fig. 1) as in V_5Si_3 (tetragonal).

The structure of V_6Si_5 can be explained, as for V_5Si_3, on the basis of packing of the 14-verticon around V_3 and 10-verticon around Si_3. The Kasper-like 14-verticons around V_3 share quadrangular faces with each other, forming zigzag chains parallel to **b**. Two such chains are bridged by the bicapped square antiprism sharing edges. Each bicapped square antiprism thus shares one edge with six V_3 polyhedra, forming a layer of polyhedra. These layers stack over each other by sharing the V_3 and Si_3 apices, forming V–V and Si–Si chains parallel to **c** (Fig. 9), the contacts being 2·429 Å. There are some shorter V–Si distances in this structure.

VSi_2 crystallizes in the hexagonal space group $P6_222$ with the $CrSi_2$ type. The V atom has CN 14; the polyhedron (IX, Fig. 1) is bounded by 4 triangular and 10 quadrangular faces, having 2–C_2 symmetry. The structure can be described in terms of the packing of these V polyhedra, each being surrounded by six others, four of which share triangular faces and two of which are edge-sharing, thus building up a layer of V polyhedra. These layers are held together by strong contacts between the layers along **c** (Fig. 10).

V–Ge system

The data are given in Table 5. The V atoms have CN 13 to 17.

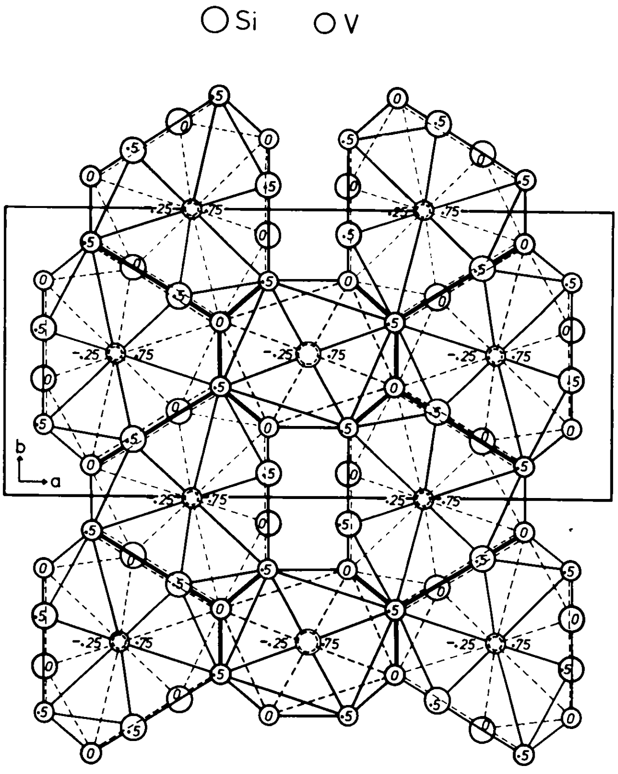

Fig. 9. Structure of V_6Si_5 ($oI44$, V_6Si_5 type).

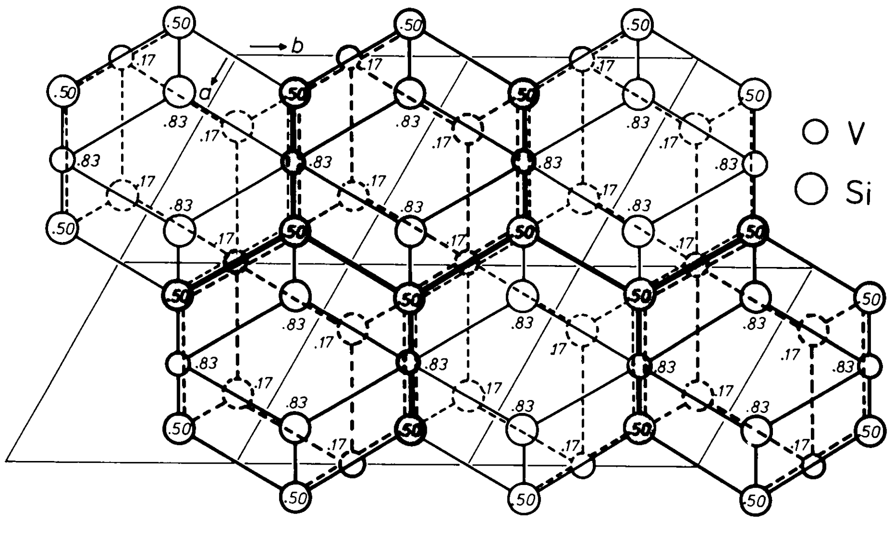

Fig. 10. Structure of VSi_2 ($hP9$, $CrSi_2$ type).

Table 5. *Crystal data of the* V–Ge *system*

Alloy	Pearson symbol	Structure type Space group	Unit-cell dimensions (Å)	Atom	Polyhedra used	Packing in	Crystal data from
V_3Ge	*cP*8	Cr_3Si *Pm*3*n*	$a = 4{\cdot}769$	V	Kasper (14) (*D*)	Present work	Holleck, Nowotny & Benesovsky (1963*b*) Structure type given
V_5Ge_3	*hP*16	Mn_5Si_3 $P6_3/mcm$	$a = 7{\cdot}294$ $c = 4{\cdot}97$	V_1	Kasper-like (14)	Present work	Holleck *et al.* (1963*b*) Structure type given
$V_{11}Ge_8$	*oP*76	$Cr_{11}Ge_8$ *Pnma*	$a = 13{\cdot}398$ $b = 5{\cdot}017$ $c = 16{\cdot}135$	V_1 V_2	13-verticon of $Cr_{11}Ge_8$ type Kasper-like (14)	Present work	Israiloff, Voellenkle & Wittmann (1974) Structure complete
$V_{17}Ge_{31}$	*tP*184	$V_{17}Ge_{31}$ $P\bar{4}n2$	$a = 5{\cdot}91$ $c = 83{\cdot}65$			Not treated	Völlenkle, Preisinger, Nowotny & Wittmann (1967) Structure complete

Table 6. *Crystal data of the* V–Sn *system*

Alloy	Pearson symbol	Structure type Space group	Unit-cell dimensions (Å)	Atom	Polyhedra used	Packing in	Crystal data from
V_3Sn	*cP*8	Cr_3Si *Pm*3*n*	$a = 4{\cdot}96$	V	Kasper (14) (*D*)	Present work	Geller, Matthias & Goldstein (1955) Structure type given
V_2Sn_3	*oF*48	$CuMg_2$ *Fddd*	$a = 9{\cdot}498$ $b = 5{\cdot}484$ $c = 18{\cdot}675$	V	Bicapped dodecahedron	Present work	Jonault & Pecocq (1965) Structure qualitative

V_3Ge belongs to the Cr_3Si type (see V_3Ga).

V_5Ge_3 crystallizes in the hexagonal space group $P6_3/mcm$ and is isotypic with the hexagonal form of V_5Si_3. Belonging to the Mn_5Si_3 type, it contains 16 atoms per cell and two independent V atoms, V_1 and V_2, in the asymmetric unit. V_1 has CN 14 and V_2 15. The polyhedron around V_1 is a Kasper-like 14-verticon similar to the one found around V_3 in V_6Si_5. The 15-verticon has $mm2$–C_{2v} symmetry and is bounded by 18 triangular and 4 quadrangular faces.

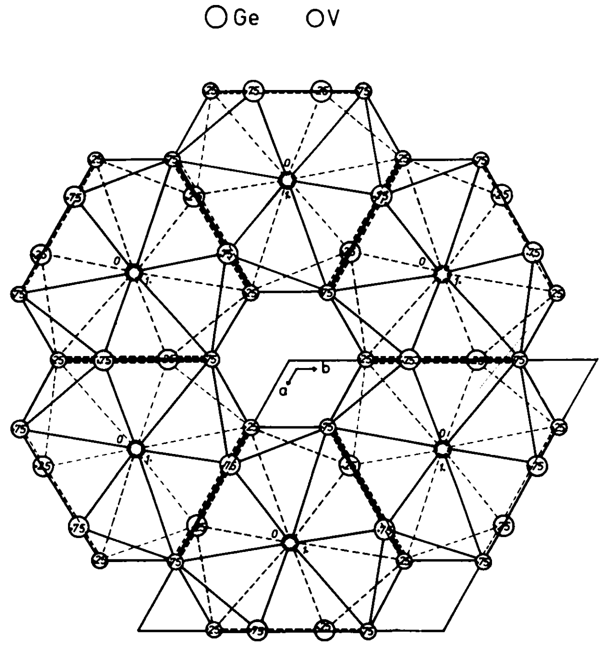

Fig. 11. Structure of V_5Ge_3 (*hP*16, Mn_5Si_3 type).

The structure can be explained in terms of the packing of the Kasper-like 14-verticons around V_1. There are only two such polyhedra in the cell; they share a quadrangular face. Along **c** these polyhedra share apices forming V–V chains with the V atoms 2·49 Å apart. Six V_1 polyhedra share quadrangular faces with each other and form a hexagonal channel (Fig. 11).

$V_{11}Ge_8$ crystallizes in the orthorhombic space group *Pnma*, and belongs to the $Cr_{11}Ge_8$ type with 76 atoms per cell. There are nine independent V atoms in the cell, one of which has CN 13, three 14, two 15, two 16 and one 17. The 13-verticon around V_1 has m–C_s symmetry and is bounded by 16 triangular and 3 quadrangular faces (VIII, Fig. 1). The 14-verticons around V_2, V_5 and V_9 are Kasper-like polyhedra found in V_5Ge_3 and V_6Si_5. The 16-verticon around V_3 and V_4 (XVI, Fig. 1) has m–C_s symmetry and is bounded by 24 triangular and 2 quadrangular faces. The polyhedra around V_7 and V_8 are 15-verticons like those around V_2 in V_5Si_3 and V_6Si_5. The 17-verticon around V_6 has $mm2$–C_{2v} symmetry and is bounded by 24 triangular and 3 quadrangular faces (XVIII, Fig. 1).

The structure can be described in terms of the packing of V_1 and V_2 polyhedra. Each V_1 polyhedron shares a quadrangular face with two V_2 polyhedra which in turn share a quadrangular face with another V_2 polyhedron thus forming a closed chain of 10 polyhedra which include two channels (Fig. 12). There are four such channels in the cell in which the Ge_1 atoms form chains parallel to *b*. The polyhedra stack one

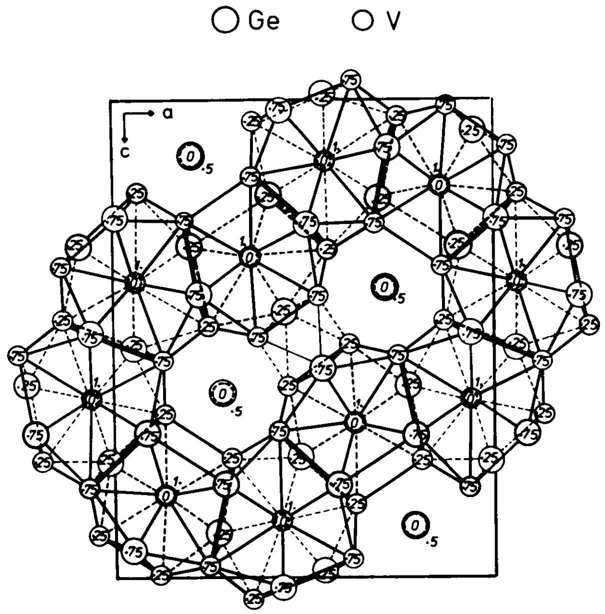

Fig. 12. Structure of $V_{11}Ge_8$ (*oP*76, $Cr_{11}Ge_8$ type).

above the other by sharing the apices occupied by V_1 and V_2, forming chains of V_1 and V_2 atoms along **b** in addition to the Ge_1 atoms. In the V chains the V atoms are 2·45 and 2·44 Å apart while the Ge atoms are 2·503 Å apart. There are some V–Ge contacts of the same magnitude as the contacts in the V–V and Ge–Ge chains.

V–Sn system

The data are given in Table 6. V has CN 10 and 14.

V_3Sn belongs to the Cr_3Si type (see V_3Ga).

V_2Sn_3 belongs to the $CuMg_2$ type. It crystallizes in the orthorhombic space group *Fddd* with 48 atoms per cell and one V atom per asymmetric unit. The V has CN 10 and the geometry is a bicapped dodecahedron, one of the three ground-state geometries for decacoordination. The polyhedron has 2–C_2 symmetry (222–D_2 in the ideal case) and is bounded by 16 triangular faces (I, Fig. 1).

The structure can be explained on the basis of the packing of the V polyhedra. The polyhedra around V at 0 share with the V polyhedra around V at 0·5 corners at $y = 0{\cdot}25$ (atoms shaded fully). Every two V polyhedra

Table 7. *Crystal data of the* V–In, V–Tl, V–Pb *systems*

Alloy	Pearson symbol	Structure type Space group	Unit-cell dimensions (Å)	Atom	Polyhedra used	Packing in	Crystal data from
V_3In	*cP*8	Cr_3Si *Pm*3*n*	$a = 5{\cdot}42$	V	Kasper (14) (*D*)	Present work	Savitskii, Baron & Efimov (1966) Structure type given
V_3Tl	*cP*8	Cr_3Si *Pm*3*n*	$a = 5{\cdot}23$	V	Kasper (14) (*D*)	Present work	Savitskii *et al.* (1966) Structure type given
V_3Pb	*cP*8	Cr_3Si *Pm*3*n*	$a = 4{\cdot}937$	V	Kasper (14) (*D*)	Present work	Holleck, Nowotny & Benesovsky (1963*a*) Structure type given

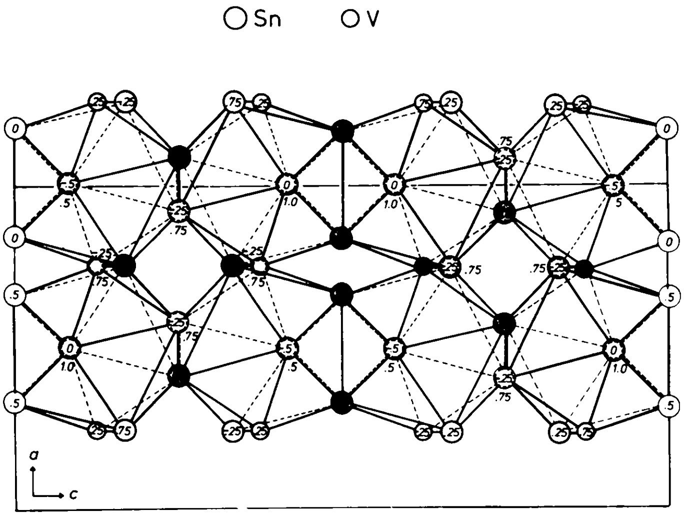

Fig. 13. Structure of V_2Sn_3 (*oF*48, $CuMg_2$ type).

at the same height share one edge with each other. Along **b** the polyhedra share the Sn atoms at the top (Fig. 13).

V/Pb, V/In and V/Tl systems

Only the A15 phase has been reported in these systems. The data are given in Table 7. For the description of the Cr_3Si (*A*15) type see V_3Ga.

Conclusions

V has CN 10 to 17 and a wide variety of coordination polyhedra around it.

In almost all cases the structure can be explained on the basis of the packing of V polyhedra alone. In a few cases (V_5Si_3, V_6Si_5), however, a polyhedron around the 'B' element has to be involved. Hence it seems that one can explain the alloy structures, irrespective of the number of atoms, in terms of packing of one or two polyhedra.

The binary alloy structures considered here can be considered as being of two types: a three-dimensional distribution of discrete polyhedra sharing corners, edges or faces, or a layer-like distribution of polyhedra. In the latter there are chains of V and/or 'B' atoms in the direction perpendicular to the layers.

Icosahedra, Kasper and Kasper-like 14-verticons play a big role in the explanation of these structures, although they belong to different structure types.

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