1. It is tempting to attribute the lowering of the symmetry of O polyhedra in olivenite to the Jahn–Teller effect associated with the Cu^{2+} ion. The difference in the shape of the ZnO_5 and CuO_5 trigonal bipyramids is probably related to the same cause. In connection with the structure of olivenite, a revision of the symmetry of libethenite, $Cu_2PO_4(OH)$ (Walitzi, 1963), seems to be desirable. According to Walitzi, the symmetry of libethenite is *Pnnm*, the same as the symmetry of adamite.

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On the Binding in Phases of T^{10}–B^6 Mixtures

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The two-correlations model for electrons in crystal structures allows the binding of a phase to be described by two correlation types and two commensurabilities. Since empirical rules are valid for the occupancy of the correlations, predicting whether or not a compound will appear at a certain composition may be possible. Therefore, the two-correlations model is a valence model giving new insights and explaining more facts than older valence models. The model is crystallographic in character, as it assumes the existence of lattice-like spatial correlations of electrons in crystal structures. Applied to T^{10}–B^6 mixtures the model yields three main types of binding: CuZn, In and PtS binding. These main types undergo certain modifications in order to stabilize a phase at a simple composition. Certain rules are valid for transformations in a compound or for morphotropics of it, *i.e.* structural changes when the homologous representative is changed.

Introduction

A T^{10} element is defined as an element in the same homologous class as Ni, a B^6 element is either S, Se or Te, and T^{10}–B^6 represents alloys between a T^{10} element and a B^6 element, in other words, a set of homologous mixtures. [The term 'mixture', common in thermodynamic literature (*e.g.* Guggenheim, 1950), replaces the 'system' which has in its original sense, and in its major present day use, a different meaning.] It is of interest to have a chemical valence model for T^{10}–B^6 mixtures, which indicates whether or not a compound is formed at a given composition. (The term 'compound' is used in the sense of 'intermediary phase'.) Such a valence model does not yet exist; however, since the two-correlations model (Schubert, 1976) helped to better understand brass-like mixtures, it seems possible that it could also help to better understand T^{10}–B^6 mixtures.

Reviews of T^{10}–B^6 mixtures have been given by Hulliger (1968) and Jellinek (1968); these should be consulted for original references and structure drawings, and also for some physical properties [for further structural information see Schubert (1964) and Pearson (1972)]. In the reviews cited the binding is discussed from the standpoint of negative and positive valencies, occupied atomic orbitals, pair bonds, band structures in the tight-binding approximation, *etc.* In contrast to these concepts which we now know to be unsatisfactory with respect to the spatial correlations in the binding, the two-correlations model [which has the advantage of being transparently connected (Schubert, 1976) with the decisive binding concept, the density matrix] is used here.

The two-correlations model assumes that the specification of two spatial correlations of electrons is necessary and sufficient for the description of the binding in a large class of chemical compounds. The two correlations together might be named a 'bonding system'; the simpler term 'binding' is preferred since the two correlations in a crystal have some similarity to the binding of a book and the term 'bonding' is too reminiscent of the bonding between two atoms. The two-correlations model does not try to divide the binding into a multitude of bonds, an idea which has in the past hampered the understanding of what is happening in a metallic crystal.

One of the correlations of a binding is populated by the valence electrons (V correlation), and the other by the outer-core electrons (C correlation). Both correlations are lattice-like in order to give low energies for the populations. This does not mean that the electrons form a lattice, since the periodicity radius of the correlations is finite [from experience $\simeq$ 100 Å, Schubert (1964)]. Each correlation is commensurate with the crystal structure in order to give a low interaction energy of the population with other populations.

A commensurability may be described by a matrix equation $a_{iB} = \Sigma_A a'_{iA} K_{AB}$, where $a_{iB} = (a_{i1},a_{i2},a_{i3})$ represent the elementary translations relative to a coordinate system i of the crystal B, $a'_{iA} = (a'_{i1},a'_{i2},a'_{i3})$ are the elementary translations of the correlation 'lattice' A, and $K_{AB} = (K_{11},K_{12},K_{13};K_{21},K_{22},K_{23};K_{31},K_{32},K_{33})$ is the commensurability matrix. We write $(K_{11},0,0;0,K_{22},0;0,0,K_{33}) =: (K_{11};K_{22};K_{33})$ and $(K;K;K) =: (K)$. The above matrix equation may be written simply as $\mathbf{a}_B = \mathbf{a}'_A K$, and it may be used to describe commensurabilities between two atomic correlations (AA), between atomic and electronic correlations (AV or AC), and between V and C correlations (VC).

A spatial correlation is not necessarily fully occupied, but an empirical rule asserts that the V correlation is mostly fully occupied, while the C correlation is occupied to 80 ± 15%. The C correlation is very often of the $A2$ type or of its deformed variant the $C11$ type; the V correlation is more variable: it may be of the $A1$, $A2$, $A0$ (cubic primitive correlation) or AH (hexagonal primitive correlation) types. The type symbol may serve incidentally as an index of the correlation matrix (even though it consists of two characters). The V or C correlations are distinguished from the A correlation by one or two primes.

It has transpired that certain main bindings are especially frequent: a binding $\mathbf{a}'_{A2} = \mathbf{a}''_{A2}(2)$ may be called CuZn binding since it is found at the valence-electron concentration $N_V/A = 1{\cdot}5$, which was detected by Hume-Rothery as a stability rule for CuZn and its homologue isotypes; a binding $\mathbf{a}'_{A1} = \mathbf{a}''_{A2}(2)$ may be called In binding since the crystal structure of In [and of all the so-called 'tetrahedral structures' (Parthé, 1964)] is easily understood with this binding. From these main bindings may be derived similar bindings with more or less V electrons; they may be named post- or pre-main bindings.

The method of finding a correlation is that of inductive logic: assumptions are compared with extended empirical material; from the probable assumptions certain rules are inferred (here: electron numbers, correlation types, commensurability rules, the dependence of electron distances on composition, occupation rules, structural phenomena caused by the correlation, *etc.*), and these rules make it easier to find the binding in further phases. A check of the correlations of a mixture with the help of graphs of electron distances *versus* composition will demonstrate that the proposals are not a matter of chance but a result of the analysis of the empirical data.

This analysis will also give access to an improved binding theory of metallic phases. As an example, the correlative interaction between valence and core electrons, which is characteristic for the two-correlations model, has not been considered in present-day metal theory; however, one electron moves not only in the field of an atomic correlation but also in the field of the core-electron correlation. Furthermore, the importance of the spatial correlation gives more attention to the two-electron density matrix; this may be built up from two-electron wave functions which satisfy an eigenvalue equation containing a potential related to the correlation lattice. These examples show that the present analysis leads to an improved possibility of understanding binding in crystals.

It is a frequent misunderstanding of the model to expect that it should immediately 'predict' structures. When a binding is to be expected at some composition, the numbers of the places per atom in the valence-electron correlation, $N_{p'}/A$, and in the core-electron correlation, $N_{p''}/A$, have yet to be chosen, and on these depends the array of electrostatic dipole vectors, the low energy of which determines the structure. Only when we have attained a better understanding of these effects do predictions become feasible.

It may be added that a charge-density wave is a consequence of spatial correlation, but the correlation is not a consequence of a charge-density wave. Therefore, the aim of an analysis of the empirical data must be the spatial correlation in the electron gas, not a charge-density wave. It is easy to understand that quite distinct spatial correlations may exist without any charge-density waves; therefore spatial correlation is relevant for all structures. We now consider the different mixtures of the indicated homologous set of mixtures.

The mixture Ni—S

The phase $Ni_3S_2.h$ is of the Fe_3Si type with vacancies (Liné & Huber, 1963). The binding may be found by comparing the electron distances of other phases and also by considering the symmetry of the crystal as $\mathbf{a}_{Ni_3S_2.h} = \mathbf{a}'_{A1}(2) = \mathbf{a}''_{A2}(4)$; these binding descriptions are collected in Table 1, together with the metric data for the structures (in order to facilitate checking the metric coherence of the assumed bindings). The binding is of the In type, and gives the number of places per cell in the V correlation as $N_{p'}/C = 32$, while the number of V electrons per cell is only $N_V/C = 24$. It must be assumed, therefore, that the Ni atoms contribute electrons to the V correlation. This may also be understood in terms of the electron affinity of the S atoms. The number of C places per atom, $N_{p''}/A$, is calculated from the number of C places per cell ($N_{p''}/C$

Table 1. *Crystal phases in T^{10}–B^6 mixtures*

Symbols: r = room-temperature phase, h = high-temperature phase, p = high-pressure phase, V = containing vacancies, S = superstructure, H = hexagonal basal vectors, $A0$ = cubic primitive, $A1$ = cubic face centred, $A2$ = cubic body centred, $C11$ = tetragonally compressed W type.

Phase	Structure	Reference	Elementary cell a/Å=Binding/Å
Ni	(Cu)	1.15	(3.524)=a'A2=a"A2(2,$\bar{2}$,0;2,2,0;0,0,2.8)
Ni3S2.h	(Fe3Si.V)	1963LH	(5.23)=a'A1(2)=a"A2(4)
Ni3S2.r	(Ni3S2.r)	11.299	(H5.741;7.139)=a'A1.H(3;3;4.4/3)=a"A2.H(3;3;18/3)
Ni6S5.h	(Ni6S5.h)	38.129	(3.274;11.359;16.157)
Ni6S5.r	( )	1972F	(9.343;11.250)
NiS.h	(NiAs)	1.86	(H3.428;5.340)=a'A0.H(3/2;3/2;5.7/3)=a"C11.H(3;3;5.4/2)
NiS.r	(NiS.r)	2.6 26.209	(H9.616;3.152)=a'A1.H(5;5;2/3)=a"A2.H(5;5;8/3)
Ni3S4	(Co3S4)	11.288 27.294	(9.480)=a'A1(3.5)=a"A2(7)
NiS2	(FeS2.h)	1.150 26.209	(5.689)=a'A0(4)=a"A2(4)
Pd	(Cu)	1.15	(3.890)=cf.Ni
Pd4S	(Pd4Se)	27.315	(5.115;5.590)=a'A2(3/2,1,0;$\bar{1}$,3/2,0;0,0,2)=a"A2(3,2,0;$\bar{2}$,3,0;0,0,4)
Pd3S.h	(Pd3S.h)	33.121	(6.088;5.374;7.453)=a'A0(2,0,-2.5;2,0,2.5;0,2.5,0)=a"C11(4,0,0;0,0,5;0,4.3,0)
Pd16S7	(Pd16S7)	1976MS	(8.930)=a'A1(2,$\bar{2}$,0;2,2,0;0,0,2.8)=a"C11(4,$\bar{4}$,0;4,4,0;0,0,7)
PdS	(PdS)	5.3 20.166	(6.429;6.608)=a'A2(2,$\bar{2}$,0;2,2,0;0,0,2.9 3)=a"C11(4;4;5)
PdS2	(PdSe2)	21.15 21.162	(5.460;5.541;7.531)=a'A2(5/2,1/2,0;-1/2,5/2,0;0,0,3.75)=a"A2(3,$\bar{2}$,0;2,3,0;0,0,5)
Pt	(Cu)	1.15	(3.924)=cf.Ni
PtS	(PtS)	24.211	(3.470;6.110)=a'A2(3/2,-1/2,0; 1/2,3/2,0;0,0,2.7)=a"A2(2,1,0;$\bar{1}$,2,0;0,0,4)
PtS2	(CdJ2)	24.211	(H3.54;5.039)=a'A1.H(1,1,0;$\bar{1}$,2,0;0,0,1)=a"A0.H(1,1,0;$\bar{1}$,2,0;0,0,2)
Ni3Se2.h2	(Fe3Si.V)	1966GMR	(5.42)=cf.Ni3S2.h
Ni3Se2.h1	( )	1966GMR	(7.289;11.568)
Ni3Se2.r	(Ni3S2.r)	21.157	(H6.03;7.26)=cf.Ni3S2.r
Ni6Se5.h	(Ni6Se5.h)	1971RH	(3.437;11.86;17.06)=a'A1.H(0,0,10;0,6,5;2.1/3,0,0)=a"A2.H(0,0,10;0,6,5;8.5/3,0,0)
NiSe.h	(NiAs)	26.210	(H3.66;5.35)=cf.NiS.h
NiSe.r	(NiS.r)	3.257	(H10.01;3.33)=cf.NiS.r
Ni1-Se	(NiAs.S)	26.210	( )
Ni46Se54	(NiAs.S)	20.158	(6.293;10.901;15.957)
Ni44Se56	(NiAs.S)	20.158 26.116	(6.22;3.64;10.52;90.52^{0})
Ni3Se4	(Co3S4)	29.127	(9.94)=cf.Ni3S4
NiSe2	(FeS2.r)	29.127	(3.67;4.89;5.96)
NiSe2+	(FeS2.h)	26.210	(5.962)=cf.NiS2
Pd4Se	(Pd4Se)	27.315	(5.232;5.647)=cf.Pd4S
Pd17Se15	(Rh17Se15)	27.315	(10.606)=a'A1(3.5)=a"A2(7)
PdSe	(PdS)	21.14	(6.73;6.91)=cf.PdS
PdSe2	(PdSe2)	21.14	(5.741;5.866;7.692)=cf.PdS2
Pt55Se45	( )	24.210	(6.581;4.625;11.145;78.4^{0})
PtSe2	(CdJ2)	1.781	(H3.728;5.081)=cf.PtS2
Ni3Te2.h2	(Fe3Si.V)	1966BGRV	(5.760)=cf.Ni3S2.h
Ni3±xTe2.h1	(Cu2Sb.V)	30.75	(3.782;6.062)=a'A1(5,$\bar{1}$,0;1,5,0;0,0,2)/2=a"A2(5,$\bar{1}$,0;1,5,0;0,0,4)
Ni3-xTe2.h	(Cu2Cb.VS)	1965KWJ	( )
Ni3.3Te2.r	(Cu2Sb.VS)	30.160	(7.540;3.799;6.089;91.2^{0})
Ni2.8Te2.r	(Cu2Sb.VS)	30.160	(7.564;6.062)
Ni10.3Te8	( )	30.160	(3.912;6.872;12.376)
Ni0.9Te	(NiAs)	24.197	(H3.96;5.35)=cf.NiS.h
NiTe2	(CdJ2)	24.197	(H3.84;5.26)=cf.PtS2
NiTe2.p	(FeS2.h)	1971EK	(6.37)=cf.NiS2
Pd4Te	(W.VS)	20.167	(12.674)
Pd20Te7	(Pd20Sb7)	1977WS	(H11.797;11.172)=a'A2.H(3;3;14/3)=a"A2.H(6;6;28/3)
Pd3Te2	(Rh3Te2)	1976MS	(7.900;12.687;3.858)=a'A1.H(4,0,0;2,6,0;0,0,2.1/3)=a"A2.H(4,0,0;2,6,0;0,0,8.5/3)
PdTe	(NiAs)	1.781	(H4.152;5.672)=a'A0.H(3/2;3/2;5)=a"C11.H(3;3;4.75 5)
PdTe2	(CdJ2)	1.781	(H4.037;5.126)=cf.PtS2
PtTe	(PtTe)	34.120	(6.86;3.96;7.04;108.98^{0})=a'A1.H(3,$\bar{1}$,$\bar{1}$;3,1,$\bar{1}$;0,0,3.5/3)=a"A2.H(3,$\bar{1}$,$\bar{1}$;3,1,$\bar{1}$;0,0,14/3 5)
Pt3Te4	Pt3Te4)	34.137	(6.91;3.99;12.02;101.03^{0})=a'A1.H(3,$\bar{1}$,$\bar{1}$;3,1,$\bar{1}$;0,0,6.25/3≈7/3)=a"A2.H(3,$\bar{1}$,$\bar{1}$;3,1,$\bar{1}$;0,0,25/3 28/3)
Pt2Te3	Pt2Te3)	34.138	(6.93;4.00;17.12;97.75^{0})=a'A1.H(3,$\bar{1}$,$\bar{1}$;3,1,$\bar{1}$;0,0,9/3 10/3)=a"A2.H(3,$\bar{1}$,$\bar{1}$;3,1,$\bar{1}$;0,0,36/3 40/3)
PtTe2	(CdJ2)	1.781	(H4.026;5.221)=cf.PtS2

References: 1963LH: Liné & Huber (1963), 1976MS: Matković, El-Boragy & Schubert (1976), 1966GMR: Grönvold, Möllerud & Röst (1966), 1971RH: Röst & Haugsten (1971), 1966BGRV: Barstad, Grönvold, Röst & Vestersjö (1966), 1965KWJ: Kok, Wiegers & Jellinck (1965), 1971EK: Eckerlin & Kandler (1971), 1977WS: Wopersnow & Schubert (1977). Numbers refer to *Strukturbericht* (for volumes 1–7) or *Structure Reports* (for volume 8 onwards) (*e.g.* 1,15 indicates Vol. 1, p. 15). [Note: The reference for Pd_3Te_2 is Matković & Schubert (1977) and not as defined above.]

$= 128$) as $N_{p''}/A = 128/10 = 12{\cdot}8$; this is somewhat high. Just this $N_{p''}/A$ value will be reduced by the transformation from $Ni_3S_2.h$ to $Ni_3S_2.r$.

The structure of $Ni_3S_2.r$ [$Ni_3S_2.r$ type, *Structure Reports* (SR) 11, p. 299]* belongs, as does $Ni_3S_2.h$, to an extended structure-type family which may be called the CuZn family (not to be confused with the CsCl type). This derives from the CuZn structure by certain structural variation mechanisms. The first variation mechanism is vacancy formation, which may be disordered or ordered. The second is the formation of 'small displacements' of atoms neighbouring vacancies, in the direction towards the vacancy (it was first studied in the structure of the γ-brass type). The third is a 'large displacement' of infinitely extended atom chains in the $[111]_{CuZn}$ direction, in that direction (row shear); this mechanism was first found in the NiAs type, especially in its filled variants. These three variation mechanisms lead to a structure family which is widely extended and which belongs to bindings closely related to one another. It is useful to refer members of the family to hexagonal cells (indicated by 'H') and also to refer the corresponding spatial correlations to their hexagonal cells: $\mathbf{a}_{A1.H}$, $\mathbf{a}_{A2.H}$, $\mathbf{a}_{A0.H}$, all of which are threefold primitive. A comparison of the electron distances in $Ni_3S_2.h$ and $Ni_3S_2.r$ leads to the binding $\mathbf{a}_{Ni_3S_2.rH} = \mathbf{a}'_{A1.H}(3;3;\frac{4\cdot4}{3}) = \mathbf{a}''_{A2.H}(3;3;\frac{18}{3})$, which is once again of the In type; but now $N_{p''}/A = 162/15 = 10{\cdot}8$ and $N_{p'}/C = 40{\cdot}5$, while $N_V/C = 36$. $N_{p''}/A = 10{\cdot}8$ should be compared with the value for $Ni_3S_2.h$ (12·8). This decrease of $N_{p''}/A$ during the transformation may be understood as follows: in the h modification more V electrons are transferred from Ni atoms to the V correlation, therefore the pressure of the V electrons on the crystal at high temperatures is greater than at low temperatures; thus a structure with a larger $N_{p''}/A$ value is stabilized at high temperatures. We shall see below that $NiS.r$ also shows some variant of the In binding. Different structures with the same binding may crystallize as a result of different atomic compositions; this leads to different commensurabilities. At this point the question arises as to why no phase with CuZn binding is stabilized in the Ni–S mixture. On the assumption that the V contribution of Ni is somewhat above zero, and that of S is 6, the CuZn binding is to be expected at an S content below the composition 'Ni_3S'; at this low S content the distance of the valence electrons from their donors becomes fairly large, so that such a compound may no longer be stabilized.

The structure of $NiS.r$ is of the $NiS.r$ type (SR 2, p. 6) and belongs to the CuZn structure family. One might assume its binding to be $\mathbf{a}_{NiS.rH} = \mathbf{a}'_{A1.H}(3,3,0;-3,6,0;0,0,\frac{2}{3}) = \mathbf{a}''_{A2.H}(3,3,0;-3,6,0;0,0,\frac{8\cdot3}{3})$ which is of the In type, with $N_{p''}/A = 216/18 = 12$ and $N_{p'}/C = 54 = N_V/C$; however, a consideration of the $Ni_6Se_5.h$ structure and a comparison of electron distances suggest that the binding is more probably $\mathbf{a}_{NiS.rH} = \mathbf{a}'_{A1.H}(5;5;\frac{2}{3}) = \mathbf{a}''_{A2.H}(5;5;\frac{8}{3})$, with $N_{p'}/C = 50$ and $N_{p''}/A = 11{\cdot}1$; four V electrons are to be assumed inserted in the $A1$ correlation in the primitive cubic $A0$ mode. Such an insertion becomes more probable at low temperatures, and must be understood as a phenomenon of post In binding. The simple atomic ratio 1:1 which must be considered as energetically favourable is achieved at the expense of a more complicated electron correlation. The simple In binding is to be expected in Ni_6S_5.

The phase $NiS.h$ (NiAs type, SR 1, p. 86) has a lattice constant $|\mathbf{a}_1|$ which is not in a simple relation to the $|\mathbf{a}_1|$ of $NiS.r$. We are led, therefore, to conclude that in $NiS.h$ there is no $A2$ C correlation. The $C11$ correlation, on the other hand, which is closely related to the $A2$ correlation, gives the binding $\mathbf{a}_{NiS.h} = \mathbf{a}'_{A0.h}(\frac{3}{2};\frac{3}{2};\frac{5\cdot7}{3}) = \mathbf{a}''_{C11.H}(3;3;\frac{5\cdot4}{2})$. The commensurability elements K'_{33} and K''_{33} are written in a form which makes evident the number of electron layers per a_3 distance; the close similarity of the K_{33} values makes it probable that they are equal. This proposal for the binding gives $N_{p''}/A = 12{\cdot}2$ and $N_{p'}/C = 12{\cdot}8$; the NiAs structure gives more V and C places per atom than does the $NiS.r$ structure, in agreement with the rule that V electrons may be transferred from Ni atoms and to then favour a higher $N_{p''}/A$ value. A closer packing of the correlation corresponds to a closer packing of the S atoms. The transformation $NiS.h \rightarrow r$ is an example of a shearing transformation in the CuZn family. The phase Ni_3S_4 (Co_3S_4 type, SR 11, p. 288, SR 27, p. 294) has a Cu-type closest-packed partial structure for the S atoms; such a partial structure is quite generally favoured by the existence of a valence-electron correlation which, by its lattice-like character, is uniformly spread in the structure. Comparing the distances of the C electrons gives $\mathbf{a}_{Ni_3S_4} = \mathbf{a}''_{A2}(7)$, with $N_{p''}/A = 686/56 = 12{\cdot}2$; the interference of this odd commensurability with the atomic correlation furnishes a new argument for the spinel-like ordering of the Ni atoms, which all have the same atomic radius, so that the argument for $MgAl_2O_4$ is no longer valid, namely that different atomic radii seek different interstices in the oxygen partial structure. If In binding is assumed, we have $\mathbf{a}_{Ni_3S_4} = \mathbf{a}'_{A1}(3{\cdot}5)$ and, therefore, $N_{p'}/C = 171{\cdot}5$, while $N_V/C = 192$. The low stability temperature of this phase leads to the assumption that $N_V/C - N_{p'}/C = 20$ electrons are inserted into the $A1$ correlation in an $A0$ manner, giving a further argument for the spinel-like ordering of the Ni atoms. When the $A0$ V correlation is adhered to in the resulting compound we have to expect an increase of the C distance with increasing S content, since fewer C places are needed (because fewer Ni atoms per S atom are in the formula unit).

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* *Structure Reports* are cited throughout by the letters SR followed by the volume number and page number. Full references are contained in *Strukturbericht*, Leipzig: Akademische Vrlgsgs (for volumes 1-7) and *Structure Reports*, Utrecht: Oosthoek (for volume 8 onwards).

In the phase NiS_2 ($FeS_2.h$ type, SR 1, p. 150) we can therefore assume a partially 'filled' In-type binding: $\mathbf{a}_{NiS_2} = \mathbf{a}'_{A0}(4) = \mathbf{a}''_{A2}(4)$, which gives $N_{p''}/A = 10{\cdot}7$. The filling process in the V correlation proceeds from $NiS.r$ to Ni_3S_4 to NiS_2 with increasing V concentration. However, a binding with statistically distributed $A2$ V correlation might also be considered (*cf.* PdS_2).

The mixture Pd–S

The phase Pd_4S (Pd_4Se type, SR 27, p. 315) has the valence-electron concentration $N_V/A = 1{\cdot}2$; therefore it is probable that CuZn binding is realized here. In fact, the following binding is probable: $\mathbf{a}_{Pd_4S} = \mathbf{a}'_{A2}(\frac{3}{2},1,0;-1,\frac{3}{2},0;0,0,2) = \mathbf{a}''_{A2}(3,2,0;-2,3,0;0,0,4)$; this gives $N_{p'}/C = 13$, $N_{p''}/C = 104$, which should be compared with $N_V/C = 12$, $N_C/C = 96$; it follows that $N_{p''}/A = 10{\cdot}4$. Here also a small V contribution from the Pd atoms may be assumed. Evidently the hemihedral distribution of the atoms is caused by the hemihedral commensurability of the C correlation in that structure. The hemihedral commensurability seems to be necessitated by the special $N_{p''}/A$ value. The possibility of CuZn binding represents the first valence argument for this phase, which is sometimes described as 'subvalent'.

In the phase $Pd_3S.h$ ($Pd_3S.h$ type, SR 33, p. 121) we find the C correlation $\mathbf{a}_{Pd_3S.h} = \mathbf{a}''_{C11}(4,0,0;0,0,5;0,4{\cdot}3,0)$, which gives $N_{p''}/A = 10{\cdot}7$. The following V correlation is possible: $\mathbf{a}_{Pd_3S.h} = \mathbf{a}'_{A0}(2,0,-2{\cdot}5;2,0,2{\cdot}5;0,2{\cdot}5,0)$, giving $N_{p'}/C = 25$ while $N_V/C = 24$. The commensurability between the V and C correlations has been changed in the $\mathbf{a}_1 \times \mathbf{a}_3$ plane of the structure because the valence-electron concentration has increased. Since in an $A2$ V correlation this would give too many places, the V correlation is transformed into the $A0$ type, and the C correlation gives a greater distance in the $\mathbf{a}_1 \times \mathbf{a}_3$ plane by becoming the $C11$ type. With further increasing V concentration, the VC commensurability in the $\mathbf{a}_1 \times \mathbf{a}_3$ plane will be conserved but the type of V correlation will become the closer packed $A1$ type, thus giving In binding. The binding in $Pd_3S.h$ is, therefore, some kind of pre-In binding.

In the phase $Pd_{16}S_7$ [$Pd_{16}S_7$ type, Matković, El-Boragy & Schubert (1976)] we might assume the In binding to be $\mathbf{a}_{Pd_{16}S_7} = \mathbf{a}'_{A1}(3) = \mathbf{a}''_{A2}(6)$. This yields $N_{p'}/C = 108$, while $N_V/C = 84$; the occupation of the V correlation is surprisingly low. On the other hand, we find $N_{p''}/C = 432$, while $N_C/C = 432$, which would be a rare event. It might be an indication that many core electrons take part in the V correlation. The shortcomings of the assumption of In binding are so striking that further proposals should be considered. With the $C11$ C correlation of Pd_3S we get $\mathbf{a}_{Pd_{16}S_7} = \mathbf{a}''_{C11}(4,-4,0;4,4,0;0,0,7)$ with $N_{p''}/C = 448$ for the C electrons and $\mathbf{a}_{Pd_{16}S_7} = \mathbf{a}'_{A1}(2,-2,0;2,2,0;0,0,2{\cdot}8)$ with $N_{p'}/C = 89$ for the V electrons. This proposal must be assumed in statistical relation to the structure, so that cubic symmetry becomes possible. The binding is very similar to In binding but the relation $\mathbf{a}'_{A1} = \mathbf{a}''_{A2}(2)$ is valid in only two directions. In the third direction the C correlation is heavily compressed. This is why $Pd_{16}S_7$ is so much poorer in S than Ni_3S_2. Since an increase of N_V/A might lead to In binding, the binding in $Pd_{16}S_7$ should be classified as pre-In binding. It is curious that a phase with In binding does not exist in the mixture Pd–S; it transpires that PdS has post-In binding. The reason for this strange observation lies in some incompatibility of the V and the C correlations.

The phase PdS (PdS type, SR 5, p. 3) has, like Pd_4S, a tetragonal structure. If we accept the C correlation $\mathbf{a}_{PdS} = \mathbf{a}''_{C11}(4,0,0;0,4,0;0,0,5)$, we find $N_{p''}/A = 10$. In the phase PdSe this correlation was once more completely occupied. Since $Pd_{16}S_7$ had pre-In binding, we have to expect post-In binding: $\mathbf{a}_{PdS} = \mathbf{a}'_{A2}(2,-2,0;2,2,0;0,0,2{\cdot}9 \simeq 3)$ giving $N_{p'}/C = 48 = N_V/C$. The commensurability in the $\mathbf{a}_1 \times \mathbf{a}_2$ plane is that of the In binding, but, as compared with In binding, the V correlation has been compressed in the $\mathbf{a}_3$ direction. There is a related proposal for the binding which seems to fit even better: $\mathbf{a}_{PdS} = \mathbf{a}''_{C11}(4,-1,0;1,4,0;0,0,5) = \mathbf{a}'_{A2}(1{\cdot}5,-2{\cdot}5,0;2{\cdot}5,1{\cdot}5,0;0,0,3)$, with $N_{p'}/C = 51$ and $N_{p''}/A = 10{\cdot}6$; this binding has a very good relation to the atomic sites of PdS. The middle part of the cell has a strong similarity to PtS, but PtS has fewer C places than PdS in the comparable cell, in agreement with the rule (Schubert, 1974) that $N_{p''}/A$ decreases with increasing average atomic number.

The phase PdS_2 ($PdSe_2$ type, SR 21, pp. 15, 162) is not isotypic with NiS_2 but has a tetragonally strained pyrite structure. The simplest assumption is that the V correlation remains as in PdS, but the C correlation is relaxed as less Pd atoms per S atom are contained: $\mathbf{a}_{PdS_2} = \mathbf{a}'_{A2}(\frac{5}{2},\frac{1}{2},0;-\frac{1}{2},\frac{5}{2},0;0,0,3{\cdot}75) = \mathbf{a}''_{A2}(3,-2,0;2,3,0;0,0,5)$, so that $N_{p'}/C = 48 = N_V/C$ and $N_{p''}/A = 10{\cdot}8$. The change, as compared with NiS_2, lies in the fact that the V correlation has remained in the $A2$ type found in PdS, and this gives a smaller $N_{p'}/A$ value; in the quasi-tetragonal basal plane the VC commensurability is factorial. It should be noted that the cubic space-group symmetry of NiS_2 is so low that a tetragonal strain gives orthorhombic symmetry. The binding in PdS_2 is of a similar type to that in PdS (the commensurability of the binding to the crystal structure has, of course, changed). In the next paragraph we shall call this binding 'PtS binding'.

In order to confirm the binding for PdS_2 a discussion of a phase of another homologous set of mixtures seems desirable. The phase PdP_2 (PdP_2 type, SR 28, p. 35) has a cell $\mathbf{a}_{PdP_2} = (5{\cdot}763,0,0;0,5{\cdot}857,0;-2{\cdot}305,0,5{\cdot}874)$ Å in which the $\mathbf{a}_2 \times \mathbf{a}_3$ plane is quasi-tetragonal. This leads to the commensurability $\mathbf{a}_{PdP_2} = \mathbf{a}'_{A2}(2{\cdot}75,2,2;-0{\cdot}75,-2,2;-0{\cdot}75,0,0)$, giving $N_{p'}/C = 8 \times 5{\cdot}5 = 44$, while $N_V/C = 40$ if the V contribution of

Pd disappears; because of the commensurability element of 2·75 we have to double the $\mathbf{a}_1$ axis and obtain the coordinates $2\mathbf{a}_1 = (11{\cdot}526,0,-4{\cdot}610)^T$, where T indicates the transposed matrix. From these we find the difference of the x_3 coordinates $5{\cdot}874 - 4{\cdot}610 = 1{\cdot}264 \simeq \frac{5\cdot8}{4} = 1{\cdot}4$ giving a commensurability gain for the V correlation in the eleventh layer parallel to the $\mathbf{a}_2 \times \mathbf{a}_3$ plane. The C correlation must be $\mathbf{a}_{\mathrm{PdP}_2} = \mathbf{a}''_{A2}(4,0,0;0,4,0;-1{\cdot}5,0,4)$ and it is seen that the correlation is in good relation to the atomic sites. The binding is once more of the PtS type. In the structure of PdPS (Jeitschko, 1974) the commensurability of PtS binding is not whole numbered in the quasitetragonal basal mesh, so that at lower temperatures transitions of the compound are to be expected.

The mixture Pt–S

Here only two intermediary phases, PtS and $\mathrm{PtS_2}$, have been observed and both have crystal structures which do not occur in the mixtures Ni–S or Pd–S. Neither CuZn nor In binding occurs in Pt–S; this may be explained by the fact that the Pt atoms, rich in outer-core electrons, do not support the building up of a uniformly distributed V correlation when they are in the majority.

The phase PtS (PtS type, SR 2, pp. 9, 234) has a tetragonally strained Pt partial structure of the Cu type, where the S are inserted in tetrahedral interstices. Following the rule that heavy elements have low $N_{p''}/A$ values the following binding seems acceptable $\mathbf{a}_{\mathrm{PtS}} = \mathbf{a}'_{A2}(\frac{3}{2},-\frac{1}{2},0;\frac{1}{2},\frac{3}{2},0;0,0,2{\cdot}7) = \mathbf{a}''_{A2}(2,1,0;-1,2,0;0,0,4)$ with $N_{p'}/C = 13{\cdot}5$ and $N_{p''}/A = 10$. This kind of binding results from the In binding by strongly compressing the V correlation in the $\mathbf{a}_3$ direction and may be called PtS binding. It is clear that the low $N_{p''}/A$ value results from the fact that the outer electrons of the Pt atoms are forced outwards because of the large number of electrons in the atom. As compared with PdS, the value of $N_{p'}/A = 3{\cdot}5$ for PtS is essentially greater; it might be that the electron-rich Pt atom does not accept the $C11$ C correlation as easily as Pd, or that the Pt atom contributes several V electrons.

For $\mathrm{PtS_2}$ ($\mathrm{CdI_2}$ type, SR 24, p. 211) we might assume the V correlation $\mathbf{a}_{\mathrm{PtS}_2} = \mathbf{a}'_{A1.H}(2,0,0;0,2,0;0,0,\frac{3\cdot5}{3})$ with $N_{p'}/C = 14$; it seems that Pt contributes some V electrons to the V correlation. For the C correlation it might be assumed that $\mathbf{a}_{\mathrm{PtS}_2} = \mathbf{a}''_{A0.H}(2,0,0;0,2,0;0,0,\frac{7}{3})$, with $N_{p''}/C = 28$. In this case the C correlation would be drastically different from that in PtS because of the high S content. However, the other proposal that $\mathbf{a}_{\mathrm{PtS}_2} = \mathbf{a}''_{A0.H}(1,1,0;-1,2,0;0,0,2)$, with $N_{p''}/C = 18$, gives a C distance $d'' = 1{\cdot}45$ Å, which is admittedly somewhat large compared with the other values in the mixture. It could, however, be locally filled to give an $A2$ V correlation in the neighbourhood of the Pt atoms; also, the V electrons could build up a commensurability $\mathbf{a}_{\mathrm{PtS}_2} = \mathbf{a}'_{A1.H}(1,1,0;-1,2,0;0,0,1)$ which could be locally filled to give an $A0$ correlation. This correlation will in fact be supported by structures in the mixture Pt–Te; once again it represents a filled In binding, but $N_{p''}/A = \frac{36}{3} = 12$, while $N_{p''}/A = 10{\cdot}7$ for $\mathrm{NiS_2}$. The $\mathrm{CdI_2}$ type will therefore be preferred at higher V concentrations, as has already been empirically found (Schubert, 1964, p. 329).

The mixture Ni–Se

This mixture is closely related to the mixture Ni–S. The following phases may be interpreted completely analogously to the corresponding compounds in the mixture Ni–S: $\mathrm{Ni_3Se_2}.h$ ($\mathrm{Fe_3Si}.V$ type, In binding), $\mathrm{Ni_3Se_2}.r$ ($\mathrm{Ni_3S_2}.r$ type, In binding), NiSe.r (NiS.r type, weakly filled, In binding), NiSe.h (NiAs type, NiAs binding), $\mathrm{Ni_3Se_4}$ ($\mathrm{Co_3S_4}$ type, filled In binding) and $\mathrm{NiSe_2}$, ($\mathrm{FeS_2}.h$ type, filled In binding).

The phase $\mathrm{Ni_6Se_5}.h$ ($\mathrm{Ni_6Se_5}.h$ type) has an orthorhombic structure (Röst & Haugsten, 1971). From the atomic positions it is to be concluded that the structure is related to the NiS.r and not to the NiS.h structure. Since the projection of the Se onto the $\mathbf{a}_2 \times \mathbf{a}_3$ plane is the same as in NiSe.r, the projection onto the basal plane, the structure of $\mathrm{Ni_6Se_5}.h$ is to be considered as a filled millerite variant containing row shear analogous to NiAs and filled NiAs variants. The filling process indicates that the V correlation is essentially the same as in NiSe.r. For the C correlation it may be assumed that $\mathbf{a}_{\mathrm{Ni_6Se_5}.h} = (3{\cdot}438,0,0;0,11{\cdot}856,0;0,0,17{\cdot}065)$ Å $= \mathbf{a}''_{A2.H}(0,0,10;0,6,5;\frac{8\cdot5}{3},0,0)$, with $N_{p''}/C \simeq 510/44 = 11{\cdot}6$; it follows that for In binding $N_{p'}/C = 127$ while $N_{I'}/C = 120$. From this it may be concluded that in $\mathrm{Ni_6Se_5}.h$ unfilled In binding exists while in NiSe.r slightly filled In binding is to be assumed. Therefore the phase with the rare composition $\mathrm{Ni_6Se_5}$ becomes stable, since no more filling in the V correlation is necessary; this is a valency argument for the surprising composition $\mathrm{Ni_6Se_5}.h$. The commensurability element $K''_{31} = \frac{8\cdot5}{3}$ makes a doubling of the a_1 axis possible; it has in fact been found by Åkesson & Röst (1975).

The mixture Pd–Se

The phase $\mathrm{Pd_4Se}$ ($\mathrm{Pd_4Se}$ type, SR 27, p. 315) fits the CuZn binding, as we found in $\mathrm{Pd_4S}$.

Therefore, $\mathrm{Pd_{17}Se_{15}}$ ($\mathrm{Rh_{17}S_{15}}$ type, SR 27, p. 315) should have In binding. In fact, we find $\mathbf{a}_{\mathrm{Pd_{17}Se_{15}}} = \mathbf{a}''_{I1}(3{\cdot}5) = \mathbf{a}''_{I2}(7)$. While the In binding was found in $\mathrm{Ni_3S_2}.r$ and NiS.r, it was somewhat modified in Pd–S at the composition $\mathrm{Pd_{16}S_7} \simeq \mathrm{Pd_{70}S_{30}}$, and gave $N_{p''}/A = 9{\cdot}4$; therefore, the $\mathrm{Pd_{16}S_7}$ structure cannot be expected in the mixture Pd–Se. In $\mathrm{Pd_{17}Se_{15}}$ we find $N_{p''}/C =$

686 and $N_{p''}/A = 10{\cdot}7$; this value compares well with the high occupation of the C correlation in homologous phases. The number of V places, $N_{p'}/C = 172$, does not fit very well with $N_V/C = 180$, but in this case a local filling of the $A1$ correlation to give an $A0$ correlation seems possible.

The phases PdSe (PdS type, SR 21, p. 14) and $PdSe_2$ ($PdSe_2$ type, SR 21, p. 14) correspond to the binding in the isotypic homologues PdS and PdS_2.

The mixture Pt–Se

Here only the structure of $PtSe_2$ (CdI_2 type, SR 1, p. 781) has been solved so far; the assumption of the second proposal of PtS_2 for $PtSe_2$ gives a good comparison with the mixture Pt–Te.

The mixture Ni–Te

The crystal structure of $Ni_3Te_2.h_2$ [$Fe_3Si.V$ type, Barstad, Grönvold, Röst & Vestersjö (1966)] is isotypic with $Ni_3S_2.h$ and, because of an identical electron count, also has the same binding. The phase $Ni_3Te_2.h_1$ is of a Cu_2Sb type with vacancies which are statistically distributed in those Ni positions which are six-coordinated by Te (Kok, Wiegers & Jellinek, 1965; SR 30, p. 75). Since at lower temperatures an ordering of the atoms occurs which doubles the a_1 and a_3 axes, it is tempting to try to find the binding in the bigger cell: $\mathbf{a}_{Ni_3Te_2.h_1} = (7{\cdot}55;7{\cdot}55;6{\cdot}06)$ Å $= \mathbf{a}'_{A1}(5,-1,0;1,5,0;0,0,2)/2 = \mathbf{a}''_{A2}(5,-1,0;1,5,0;0,0,4)$; this binding gives $N_{p'}/\mathrm{Te} = \frac{52}{8} = 6{\cdot}5$ while $Ni_3Te_2.h_2$ gave $N_{p'}/\mathrm{Te} = 8$, so we may assume that in the high-temperature phase more V electrons require a place than in the low-temperature phase.

The phases $Ni_{3\cdot3}Te_2.r$ and $Ni_{2\cdot8}Te_2.r$ are superstructures of $Ni_3Te_2.h_1$ and have, therefore, a similar binding.

The phase $Ni_{0\cdot9}Te$ (NiAs type, SR 24, p. 197) is isomeric with $NiS.h$ (*i.e.* has the same binding).

The phase $NiTe_2$ is isomeric with PtS_2. It is according to the rules that $NiTe_2.p$ (high-pressure modification) is of the $FeS_2.h$ type (Eckerlin & Kandler, 1971), since $N_{p''}/\mathrm{Ni} = 32$ for the $FeS_2.h$ type and $N_{p''}/\mathrm{Ni} = 36$ for the CdI_2 type, and also since the application of pressure reduces $N_{p''}/\mathrm{Ni}$ (Schubert, 1974).

The mixture Pd–Te

The phase $Pd_{20}Te_7$ [$Pd_{20}Sb_7$ type, Wopersnow & Schubert (1977)] has a rhombohedral structure (with 81 atoms in the hexagonal cell) belonging to the CuZn family of structures, which mostly belong to the CuZn binding or to a variant of it. The comparison with the binding in Pd_8Sb_3 (Wopersnow & Schubert, 1976) leads to $\mathbf{a}_{Pt_{20}Te_7} = (11{\cdot}797,0,0;0,11{\cdot}797,0;0,0,11{\cdot}172)$Å $= \mathbf{a}'_{12.H}(3,0,0;0,3,0;0,0,\frac{14}{3}) = \mathbf{a}''_{A2.H}(6,0,0;0,6,0;0,0,\frac{28}{3})$, which evidently is the CuZn binding. It turns out that $N_{p'}/C = 126 = N_V/C$ and $N_{p''}/C = 1008$, $N_C/C = 810$, which gives a reasonable occupancy of the C correlation.

Two further Te-poor phases, the structures of which are as yet unknown, must correspond to some pre-In binding.

The phase Pd_3Te_2 [Rh_3Te_2 type, Matković & Schubert (1977)] shows In binding. The structure is orthorhombic with 20 atoms in the cell. A comparison of the electron distances gives the C correlation $\mathbf{a}_{Pd_3Te_2} = (7{\cdot}900,0,0;0,12{\cdot}687,0;0,0,3{\cdot}858)$Å $= \mathbf{a}''_{A2.H}(4,0,0;2,6,0;0,0,\frac{8\cdot5}{3})$. From this correlation it follows that $N_{p''}/A = 10{\cdot}2$, a value below that of $Ni_3S_2.r$ (10·8), conforming to the rule. For the V correlation we may assume $\mathbf{a}_{Pd_3Te_2} = \mathbf{a}'_{A1.H}(4,0,0;2,6,0;0,0,\frac{2\cdot1}{3})$, giving $N_{p'}/C = 48 = N_V/C$.

For PdTe (NiAs type, SR 1, p. 781) we find the C correlation $\mathbf{a}_{PdTe} = \mathbf{a}''_{C11.H}(3;3;4{\cdot}75/2)$, with $N_{p''}/A = 10{\cdot}7$. For the valence electrons we may assume $\mathbf{a}_{PdTe} = \mathbf{a}'_{10.H}(\frac{3}{2};\frac{3}{2};5)$, but this only gives $N_{p'}/C = 11{\cdot}3$. Whether or not the composition of the phase PdTe gives support to this assumption needs to be investigated. Another possibility is $\mathbf{a}_{PdTe} = \mathbf{a}'_{A0.H}(1,1,0;-1,2,0;0,0,5{\cdot}7/3 \simeq 1{\cdot}6)$, but it is highly strained, which seems improbable.

In the phase $PdTe_2$ (CdI_2 type, SR 1, p. 781) the a_1 axis decreases as compared with PdTe. Since the C distance should increase we must conclude that the C correlation has changed: $\mathbf{a}_{PdTe_2} = \mathbf{a}''_{A2.H}(1,1,0;-1,2,0;0,0,\frac{11}{3})$. This commensurability corresponds to the $C11$ correlation in PdTe; it might be associated with the V correlation $\mathbf{a}_{PdTe_2} = \mathbf{a}'_{A0.H}(1,1,0;-1,2,0;0,0,5{\cdot}5/3)$, giving $N_{p'}/C = 16{\cdot}5$. However, the distance becomes too small (since the correlation is only partly occupied, the distance is on the average greater).

The mixture Pt–Te

The phase PtTe (PtTe type, SR 34, p. 120) has a monoclinic C centred cell with a quasihexagonal $\mathbf{a}_1 \times \mathbf{a}_2$ plane and four atoms in the primitive cell $\mathbf{a}_{PtTe} = (6{\cdot}865,0,-2{\cdot}291;0,3{\cdot}962,0;0,0,6{\cdot}661)$ Å. The structure may be described to a first approximation as an $A0$ packing of atoms of average species. The binding $\mathbf{a}_{PtTe} = \mathbf{a}'_{A1.H}(3,-1,-1;3,1,-1;0,0,\frac{3\cdot5}{3}) = \mathbf{a}''_{A2.H}(3,-1,-1;3,1,-1;0,0,\frac{14}{3})$ gives $N_{p'}/A = \frac{84}{8} = 10{\cdot}5$ and $N_{p'}/C = 21$, while $N_V/C = 24$. We must assume three valence electrons filling the $A1$ correlation in $A0$ manner; this insertion favours the non-uniform distribution of the Pt atoms. Evidently the electron-rich Pt atoms do not favour the $C11$ correlation (and with it the NiAs structure).

The phase Pt_3Te_4 (Pt_3Te_4 type, SR 34, p. 137) has the cell $\mathbf{a} = (6\cdot906,0,-2\cdot300;0,3\cdot991,0;0,0,11\cdot797)$ Å. The binding is $\mathbf{a}_{Pt_3Te_4} = \mathbf{a}'_{11.II}(3,-1,-1;3,1,-1;0,0,\frac{6\cdot25}{3}) = \mathbf{a}''_{12.II}(3,-1,-1;3,1,-1;0,0,\frac{25}{3})$, with $N_{P'}/C = 37\cdot5$, while $N_V/C = 48$, so that five V electrons for every two Te layers must be inserted.

For Pt_2Te_3 (Pt_2Te_3 type, SR 34, p. 138) we find $\mathbf{a} = (6\cdot933,0,-2\cdot309;0,4\cdot002,0;0,0,16\cdot963)$ Å $= \mathbf{a}'_{11.II} \times (3,-1,-1;3,1,-1;0,0,\frac{9}{3}) = \mathbf{a}''_{12.II}(3,-1,-1;3,1,-1;0,0,\frac{36}{3})$, with $N_{P'}/C = 54$ and $N_V/C = 72$, so that six V electrons for every two Te layers must be inserted.

For $PtTe_2$ (CdI_2 type, SR 1, p. 781) we have $\mathbf{a} = (6\cdot973;4\cdot026;5\cdot221)$Å $= \mathbf{a}'_{11.II}(3,-1,0;3,1,0;0,0,\frac{2\cdot75}{3}) = \mathbf{a}''_{12.II}(3,-1,0;3,1,0;0,0,\frac{11}{3})$, with $N_{P'}/C = 16\cdot5$ and $N_V/C = 24$. Perhaps the C correlation is (for reasons at present unknown) somewhat compressed so that $K'' = (3,-1,0;3,1,0;0,0,4)$ and $N_{P'}/C = 18$, and just one layer of inserted electrons is present. Also, K'_{33} could have the values three for $PtTe_2$, ten for Pt_2Te_3 and seven for Pt_3Te_4, so that the number of V layers parallel to the basal plane would be equal to the number of atom layers. An alternative to the compression would be a somewhat different commensurability in the basal plane.

Conclusion

The analysis of the electron spatial correlations gives a surprisingly consistent picture of the T^{10}–B^6 mixtures. Where formerly a pure empiricism gave the intermediary phases, we now have a small number of main bindings and derived bindings which give an indication as to whether or not in some concentration range a phase should be stabilized. The main types of binding may be modified by certain mechanisms in order to give stabilization at simple compositions and cells containing few atoms (Schubert, 1964, p. 71). In many cases energetic arguments are possible, where in the former models of chemical binding no such arguments have been found (for instance the high electron density in the neighbourhood of Pt atoms preventing the formation of intermediary phases at low B^6 contents; or the stabilization of phases at unusual compositions, such as $Pd_{16}S_7$, Ni_6Se_5 and $Pd_{17}Se_{15}$, in order to realize simple In binding). Formerly the appearance of a phase (say Ni_3S_2) had to be accounted for by assuming that Ni was partly univalent and partly divalent in that compound, an assertion which is energetically meaningless. We can now state that there is a tendency to form In binding and in the phases $Ni_3S_2.h$ and $Ni_3S_2.r$ this binding is realized (in the h phase with a higher $N_{P''}/A$ value, and in the r phase with a lower $N_{P''}/A$ value), and this difference has an energetic meaning connected with the pressure of the V electrons on the structure. Also, the two-correlations model gives a general solution to the vacancy-formation mechanism which occurred here, for example, in the phases of Ni_3Te_2, and which is present in many other alloy series.

Which influences favour the realization of a binding type at a certain composition in a certain mixture? To answer this question the energetics of the correlations must certainly be analysed more quantitatively. However, before dealing with this problem the question must be answered as to whether in other homologous sets of mixtures a certain limited number of bindings causes the stabilization of phases. This sort of analysis of empirical data is a first step to an atomistic interpretation of alloys; it gives an extension of Hume-Rothery's empirical N_V/A rules (being valid only for brass-like phases) to many other compounds. While Hume-Rothery's rules were maintained only as rules for the N_V/A numbers and stimulated a search for similar relations, which evidently remained without much success, in the present analysis the valence electrons and the core electrons are considered together, and use is made of the crystal structure, especially of the lattice dimensions and cell content.

In addition to the fact that helpful new energetic arguments are given by the two-correlations model, it cannot be overlooked that several older concepts are not to be reconciled with the statements of the model. For instance, in NiS, which is often formulated as $Ni^{2+}S^{2-}$, the present binding gives no indication of a valence-electron contribution as high as two electrons per Ni atom; in fact, if there were such a V contribution the structure of NiS.*r* and NiS.*h* could no longer exist following the two-correlations model.

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Coordination de Constituants des Acides Nucléiques avec des Métaux de Transition. III. Structure Moléculaire et Cristalline du Diaquabis(6-azauracilato)cuivre(II)

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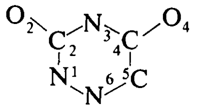
Diaquabis(6-azauracilato)copper(II) crystallizes in space group $P\bar{1}$ with a = 6·774 (2), b = 8·348 (2), c = 4·878 (2) Å, α = 92·75 (2), β = 102·16 (3), γ = 74·94 (2)°. The crystal structure has been determined from four-circle diffractometer data recorded at 21 °C and refined by full-matrix least-squares calculations to R = 0·031. It consists of $Cu(C_3N_3O_2H_2)_2(H_2O)_2$ molecules, where the Cu atom, in a square-planar environment, is a centre of symmetry for one molecule; the Cu is bonded to two monodentate azauracil ligands through the N(3) atoms and two water molecules in a *trans* arrangement. Each molecule is hydrogen bonded to four neighbouring ones in such a way that the structure can be described as a stacking of parallel layers.

Introduction

De nombreux analogues de constituants des acides nucléiques (6-mercaptopurine, 5-fluorouracile, aza analogues, *etc.*) sont connus depuis quelques années pour leur activité anticancéreuse et antivirale (Sorm & Keilova, 1958; Sorm & Vesely, 1964; Frei, 1967; Regelson, 1967; Roy-Burman, 1970). Le 6-azauracile, connu par son activité bactériostatique (Sorm, Jakubovic & Slechta, 1956) et comme inhibiteur de la croissance de certaines tumeurs (Bieber, Elion, Nathan & Hitchings, 1957), conduit en milieu bactérien au 6-azauridine (Skoda, Hess & Sorm, 1957), plus actif et moins toxique (Handschumacher, Calabresi, Welch, Bond, Fallon & Frei, 1962). Par ailleurs, certains de ces composés voient leur activité anticancéreuse augmenter s'ils sont administrés sous forme de complexes métalliques (Williams, 1972).

C'est dans ce contexte que nous avons été amenés à l'étude des complexes de constituants d'acides nucléiques avec des métaux de transition (Bonnet, Jeannin & Mosset, 1975; Mosset, Bonnet & Galy, 1976). Le présent article décrit la structure cristalline et moléculaire du complexe 1:2 cuivre(II)–6-azauracile.

La numérotation des atomes dans le ligand recommandée par l'IUPAC pour les cycles pyrimidine a été adoptée.



Synthèse – analyse

Le composé est obtenu par chauffage à 60°C, pendant une heure, d'un mélange résultant de l'addition de solutions aqueuses (0,01*M*) de nitrate de cuivre(II) et de 6-azauracile, dans le rapport stoechiométrique 1:2. Par lente évaporation à température ambiante, la solution laisse déposer des cristaux violets.

L'analyse pondérale du complexe ainsi préparé montre qu'il est du type 1:2 et qu'il répond à la formule globale $CuL_2(H_2O)_2$, où L représente le ligand azauracile $C_3N_3O_2H_2$. Malgré le grand soin apporté au tri des cristaux l'accord entre le dosage et la formule

Tableau 1. *Composition chimique des cristaux étudiés*

	C	H	N	O	Cu
Mesuré (%)*	23,40	3,17	28,27	27,61	17,55
Calculé (%)	22,10	2,45	25,79	29,47	19,51

* Dosage effectué par le Service Central de Microanalyse du CNRS, Thiais.