A PHENOMENOLOGICAL VALENCE MODEL FOR METALLIC PHASES [*]

K. Schubert
Max-Planck-Institut für Metallforschung, Institut für Werkstoffwissenschaften,
Seestraße 75, 7000 Stuttgart 1, F.R.Germany

Summary

The valence problem of a mixture is the assessment of the compositions of its
intermediate phases. The known valence models may be judged by means of the
reduced density functions of electrons. The electron pair density (spatial
correlation) is decisive for valence assessment and it suggests a synthesis
of the known phenomenological valence models. The system of all electrons
of a crystal contains two or three chemically relevant subsystems b,e,c
which display strong internal and weaker external interaction. The internal
interaction causes a lattice-like spatial correlation of the electrons in the
subsystem . Although only a small fraction of all probable configurations
belongs to the lattice, this fraction is essential for the bonding as it con-
stitutes the main portion of the rearrangement of electron pair density. The
lattice-like property is described by the averaged spatial correlation exhi-
biting unessential maxima near the atom cores not rearranging during bond
formation, and essential maxima strongly influenced by rearrangement of elec-
tron pair density. The external interaction causes commensurability between
the crystal cell a and the electron correlation cells b,e,c. An energetically
favourable commensurability between the cells a,b,e,c (a harmony between the
subsystems) determines the composition of a stable phase. The correlation types
and commensurabilities define bonding types (bindings) which allow to classi-
fy all phases with respect to bonding. Numerous crystal chemical rules are
interpreted by the model, and the method of determination of the binding is
simple and straightforward.

The valence problem

A closed chemical system of two components may be described macroscopically by the internal energy $\underline{U}$ as a function of the external variables volume $\underline{V}$, entropy $\underline{S}$, mole numbers $\underline{N}_1, \underline{N}_2$ of the components, and of internal variables $\underline{M}_i$ which take a value to minimize $\underline{U}$. The molar internal energy $\underline{U}/\underline{\Sigma N} = U'$ as a function of the mole fraction $\underline{N}_2/\underline{\Sigma N} = N_2'$ often has $\underline{N}_2'$-intervals in which $U'(N_2')$ is a linear function, as the system is composed there of two phases approximately not interacting. The question for the $\underline{N}_2'$ with non-linear $U'(\underline{N}_2')$ (one phase mole fractions) is the valence problem (or stability problem) of the chemical system (see appendix 1).

This problem might be solved deductively by calculation of $\underline{U}$ from the microscopic description of the system by its Hamiltonian operator $\underline{H}_{X,X'}$ which is symmetrical and depends two times on the (positional and spin) coordinates $\underline{X}$ of the members of the system of all electrons, (configuration), while the coordinates of the nuclei are contained in $\underline{H}$ as internal variables which may be determined by energy minimization. $\underline{H}$ defines an energy eigenvalue problem permitting to calculate the eigen vectors ψ_{uX} and eigen values $\underline{u}$, and from the vectors the hermitian pure states $\psi_{uX}^{*}\,\psi_{uX'} = D_{XX'}^{(u)}$ are formed which are combined to the mixed state (or density matrix or bonding) $\underline{D}_{XX'}^{(VSN)}$ by the Boltzmann factor $\underline{W}_u = \underline{Z}\exp{-u/k_B}(\partial\underline{U}/\partial\underline{S})$ where $\underline{Z}^{-1}$ is a normalizing factor and k_B the Boltzmann constant. The internal energy is then $\underline{U}_{VSN} = \int_{XX'} \cdot \underline{H}_{X,X'} \cdot \underline{D}_{XX'}^{(VSN)}$.

This calculation has been carried out so far for very simple molecules only, therefore numerous models have been devised for an inductive valence problem solution, which accepts the decisive role of the bonding and infers from the knowledge of the empirical data special features of the bonding and uses them for a classification of bondings into bonding types (bindings).

The following influences on the phase stability have been investigated:

(1) Volumina and radii of atoms (34Biltz,56Laves)
(2) Electrical charge of atoms (18Madelung,54Born,75Urusov,81O'Keeffe)
(3) Electron density redistribution (76Miedema,81Johnson)
(4) Pair potential of atoms (74Machlin)
(5) Energy bands (34Mott & Jones, 67Rudman)
(6) Valence electron concentration (62Hume-Rothery & Raynor)
(7) Shell occupation in atoms (64,69Engel,67Brewer,73Samsonov)
(8) Covalent bonds (27Heitler & London,39Pauling)
(9) Spatial correlation of electrons (11Haber,26Hume-Rothery)
(10) Plural-correlations model (64,80Schubert).

Besides these models also surveys of phases have been written which ad-

vance various explanations of valence phenomena:

34 Goldschmid: Crystal chemistry,

34 Hassel: Crystal chemistry,

35 Dehlinger: Structures of metallic phases,

41 Niggli: Crystal chemistry of inorg. phases,

54 Bokii: Introduction to crystal chemistry,

55 Amer.Soc.Met.: Theory of alloy phases,

58 Massalski: Lattice spacing relationships in alloys,

63 Beck: Valence problem of transition metal alloys,

63 Laves: Factors governing the structure of metallic phases,

64 Schubert: Crystal structures of two component phases,

65 Hulliger,Moser: Bond description of semiconductors,

65 Massalski: Alloying behaviour and effects in concentrated solid solutions,

67 Westbrook: Intermetallic compounds,

69 Gießen ed.: Developments in the structural chemistry of alloy phases,

69 IstNáray-Szabó: Inorganic crystal chemistry,

71 Gladyshevkii: Crystal chemistry of silicides and germanides,

72 Pearson: Crystal chemistry of ally phases,

72 Povarennikh: Crystal chemical classification of minerals,

75 Wells: Structural inorganic chemistry,

76 Hulliger: Crystal chemistry of layer type phases,

77 Kripyakevich: Structural types of metallic compounds,

80 Bennett: Theory of alloy phase formation,

80 Harrison: Electronic structure of solids,

81 Simon: Condensed metal clusters,

82 Gladyshevskii, Bodak: Crystal chemistry of rare earth alloy phases,

83 Bennett, Massalski, Gießen: Alloy phase diagrams

83 Weiß, Witte: Crystal structure and chemical bond.

Assessing valence models by simplified statistics

To get an overview of the multitude of valence models it should be apprecia-
ted that an inductive model aims only at assessing the one-phase compositions.
Therefore the exact microscopic energy calculation may be essentially sim-
plified.

(a) from the virial theorem, $-\underline{U}^{pot}=2\underline{U}^{kin}$, it is seen that $\underline{U}=\underline{U}^{pot}+\underline{U}^{kin}$ and
$\underline{U}^{pot}$, the expected potential energy, are both low or not low, so that for an
assessment of stability it is sufficient to consider only $\underline{U}^{pot}$. This allows
that only the diagonal of the density matrix needs be examined which is the

probability density function of the electron configurations $\underline{D}_X$. A minimum theorem is not valid for $\underline{U}^{pot}$. The electrostatic lattice theory first made use of this simplification.

(b) From the invariance of $\underline{D}_X$ under exchange of coordiante vectors $\underline{x}_n$ and from the fact that $\underline{H}^{pot}$ is a sum of contributions $\underline{h}(\underline{x}_n)$ and $\underline{h}'(\underline{x}_n,\underline{x}_{n'})$ where $\underline{h}$ and $\underline{h}'$ do not depend on n it may be concluded (56Löw) $\underline{U}^{pot}=\int_{\underline{x}_1,\underline{x}_2}\frac{N_E}{E}[\underline{h}(\underline{x}_1)+ (N_E-1)\underline{h}'(\underline{x}_1,\underline{x}_2)]\int\int_{\underline{x}_3,\dots}\underline{D}_X^{(USN)}$ where $\underline{N}_E$= number of electrons of the system and $\int_{\underline{x}_3,\dots}\underline{D}_X^{(\overline{VSN})}=\underline{D}_{\underline{x}_1,\underline{x}_2}^{sc}$ is named the two-electron reduced density function of the electrons or briefly the spatial correlation of the electrons (see appendix 2). When $\underline{H}^{pot}$ does not depend on **sp**in it is simplifying to reduce also over the spin coordinates.

(c) The fact that in chemistry the concept of valence electrons is very useful, shows that the system of all electrons is composed of subsystems exhibiting strong interaction within the system and weak interaction between different systems . The spatial correlation will therefore be a (symmetricized) product of subcorrelations. Only the actual binding analysis can suggest how many subsystems are essential for valence in a given mixture.

The reduced density functions form a sequence of concepts to judge the valence models; for instance the one-electron density $\int_{\underline{x}_2}\underline{D}_{\underline{x}_1,\underline{x}_2}^{sc}=\underline{D}_{\underline{x}_1}^{ed}$ follows from $\underline{D}^{sc}$ but $\underline{D}^{sc}$ does not follow from $\underline{D}^{ed}$. Since atomic radii and atomic charges are properties of the $\underline{D}^{ed}$ fuctions it may be said that the valence models (1) and (2) belong to the $\underline{D}^{ed}$ function and are therefore not sufficient to form a satisfactory valence model for metallic phases. The same is valid for the redistribution and pair-potential models (3), (4). The bandmodel (5) has a set of basal wave functions but the consideration of the density matrix is quite unsatisfactory. The valence electron concentration model (6) foreshadows the extension of a valence electron correlation over the whole crystal. The shell occupation model (7) foreshadows the existence of several electron subsystems (valence electrons $\underline{b}$, **d-e**lectrons $\underline{e}$, peripheral core electrons $\underline{c}$)and therefore the coexistence of several correlations $\underline{b},\underline{e},\underline{c}$, in a crystal; and the covalent bonding model (8) is related to the spatial correlation of electrons, but this relation is very unhappy as it dismembers the crystalline spatial correlations into numerous molecular spatial correlations which are independent from one another, i.e. which do not interact, contrary to reality. The model (9) shows that the idea of a spatial correlation is nearly as old as our century and the model (10) tries to expound a synthesis of the earlier models. These earlier models describe parts of the valence phenomenon, their essential results therefore will be conserved. For instance the system

of atomic radii serves satisfactorily since more than half a century for
examination of acceptability of structure proposals, and this important use
will not be changed.

The plural-correlations model (64,74,77,80,81,82,83Sch)

The concept of a spatial correlation may be studied in a quite simplified
system. A one dimensional space in form of a circle with radius 1 contains
two electrons. The configuration-space, being incidentally the pair-space
here, is a square with edge 2π. The spatial correlation $\underline{D}^{sc}$ for the case of
strong repulsion of the electrons consists of two stripes parallel to the
diagonal of coordinate-equality (Fig.1). A section of $\underline{D}^{sc}$ for $\underline{x}_1$=const may
be considered as a momentary configuration. The electron density of this
system is constant and completely conceals the strong correlation. It becomes
apparent here, that a redistribution of pair density may perfectly conserve
the electron density. However, another density, the averaged spatial corre-
lation $\underline{D}_{\underline{x}}^{av} = \int_{\underline{x}_1} \underline{D}_{\underline{x}_1,\underline{x}_1+\underline{x}}^{sc}$ clearly exhibits a peak for $\underline{x}=\pi$. If now in the circle
at $\underline{x}=\pi$ a nucleus with positive charge is fixed, the pair density, the elec-
tron density, and the averaged density change distinctly, but the spatial
correlation peak remains (Fig.1). Even if the attractive center is quite
strong the electrons "feel" the allotted space and form their spatial corre-
lation. The peak hight decreases, as much density flows into the unessential
peaks which are caused by the nucleus and do not have any susceptibility to
rearrangement and therefore do not influence the energy of formation. It is
striking how small a fraction of all configurations make chemistry. The con-
tinuity consideration of Fig.1 suggests clearly that a lattice-like spatial
correlation exists and is decisive for the bonding. The bond formation con-
sists in a rearrangement of electron pair density in the peripheral ranges
of the atoms although the electron density is there quite low. The fact that
the electronic fundaments of bonding become so transparent in the plural-cor-
relations model is a gratifying advantage as compared with the band model,
which must seek the correlation in a highly complicated configuration inter-
action. The very simple influence of the allotted space on the correlation
remains hidden also in the valence bond model and its derivatives. The little
stripes at the bonding D^{sc} are in fact the little clasps which cause the
bond formation according to the early chemists.

The results of the simplified system may be extended to crystals. In the case
of strong dilution a valence electron system   can be in the state of a
Wigner-lattice (74Mot,75Car) found in VO_M e.g. but for higher densities spa-

tial correlation is liquid-like i.e. lattice-like only in a limited range.
The $\underline{D}_{-x}^{av}$ of the valence electrons ($\underline{b}$ electrons) is therefore lattice-like for
small $\underline{x}$, and goes over for larger $\underline{x}$ into the electron density as there is no
more interaction. The limit between small and large $\underline{x}$, the range of the spa-
tial correlation $\underline{b}$, is about 50Å (64Sch) as may be concluded from largest
lattice constants in shear structures (64Sch,69Wad,79Cow,82Gru). The comparison
of the spatial correlation with a lattice (via $\underline{D}^{av}$) requests three specifi-
cations to be advanced.

(1) The lattice say of the $\underline{b}$ correlation should have a type, say the face
centered cubic type F (see appendix 4). Possible other types are the isometric
lattices which have three linear independent smallest distance vectors. The
circumstance that all concievable isometric lattices in fact occur in nature
represents a surprising crystal chemical rule.

(2) The lattice cell $\underline{b}_F$ should have a certain volume. The number of $\underline{b}$ sites
should equal the number of $\underline{b}$ electrons in the cell $\underline{a}$ i.e. the $\underline{b}$ lattice should
be completely occupied. If the $\underline{b}$ correlation is fully occupied, then during
phase formation a rearrangement of electron density must occur. This idea has
been used by Miedema 1976 in his theory of heat of formation. The full occu-
pation may be assumed frequently also for the $\underline{e}$ correlation (see below), but
it is not possible for the $\underline{c}$ correlation. When the atomic cores do not touch,
as in Na, it should be assumed that the spatial correlation between $\underline{c}$ electrons
of different atoms is generated by the $\underline{e}$ or $\underline{b}$ correlation.

The phenomenon of shell occupation by electrons of prescribed spin (Hund's
rule) is valid also in cystals. It may be suggested to speak of "Hund inser-
tion": in a $\underline{b}_F$ correlation of spin up electrons a spin down electron may be
inserted into an octahedral interstice. It is perhaps appropriate to take the
Hund inserted electrons as a new ensemble, as in VO_M phases Wigner-crystalli-
sation of these electrons has been observed (71Goo,$\overline{8}$5Sch).

(3) The cell $\underline{b}$ should have a certain **orient a**tion to the crystal cell $\underline{a}$.
This is given by a commensurability $\underline{b}^{-1}\underline{a}=\underline{K}'$, and $\underline{K}'$ is energetically favour-
able when its elements are inte**g**ers, because in this case together with one
electron there is a large set of electrons in a favourable position. When not
all elements are integers, then as many as possible should be so (appendix 3).

As mentioned before, besides the $\underline{b}$ system additional systems may in-
fluence the bonding. A system $\underline{e}$ of d electrons forms an $\underline{e}$ correlation
which is frequently fully occupied, and the peripheral $s^2 p^6$ electrons of the
core form a $\underline{c}$ correlation which is not fully occupied but nevertheless has an
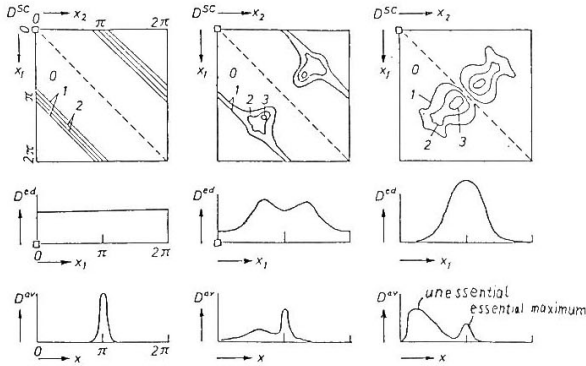influence on the bonding. The bonding type (binding) is therefore described

Fig.1: Two electrons in a circular space of radius 1.
D^{sc} = spatial correlation, $D^{ed} = \int_{x2} D^{sc}_{x1,x2}$ = el. density,
$D^{av}_x = \int_{x1} D^{sc}_{x1,x1+x}$ = averaged spatial correlation.
In $\underline{x}_1 = \underline{x}_2 = \pi$ lies a nucleus of zero, week, or strong charge.
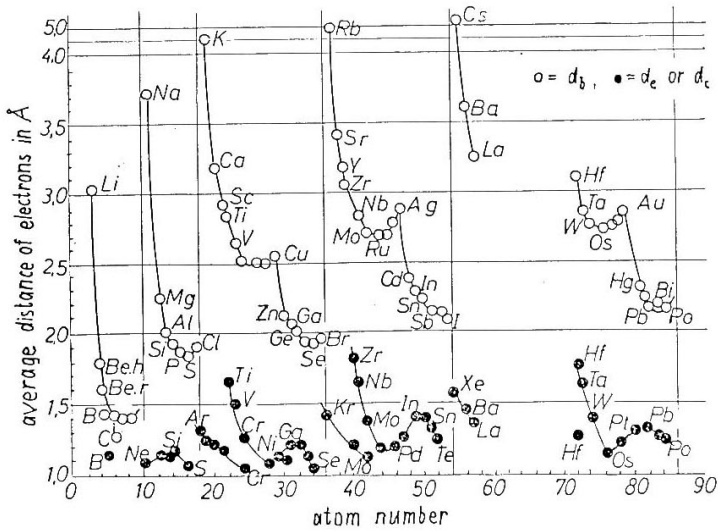
Fig.2: Electron distances

by $\underline{a} = \underline{b}K' = \underline{e}K'' = \underline{c}K'''$ and it may be said the systems $\underline{a}, \underline{b}, \underline{e}$ and $\underline{c}$ are in harmony when the commensurabilities $\underline{K}$ are favourable.

The harmony of several correlations in a phase implies a statement on the number of electrons contributed by the components to the correlations, the electron count. All valence models use an electron count, but since earlier models exclusively considered the valence electron system , one contribution only per component mattered. In the plural-correlations model there are two or three systems which influence the bonding and therefore two or three con-tributions per component must be found. The electron count is related to the spectroscopic shell occupation but it is not identical with it. For instance for Ti the shell occupation is $3s^2p^6d^2 4s^2$ while the electron count is $Ti^{1,3,8}$ where the exponents refer to $\underline{b}, \underline{e}, \underline{c}$. The electron count is a parameter of choice, from which depends whether the binding analysis will be easy and pro-bable or difficult and improbable. For Ti e.g. it is important that $V^{1,4,8}$ yields a good binding (82bSch). In a compound it must be found out how the shells of the components combine to subsystems. For the mixture TiO_M it was found for instance (85aSch) $Ti^{1,3,8}O_M^{0,6,2}$, meaning that the d electrons of Ti form a sub-system together with the valence electrons of O. The earlier valence models attempted to read the electron count from the chemical formula, for instance $Ti^{4+}O_2^{2-}$. This count did not provide an acceptable plural-correlations inter-pretation, while the above count allowed to find interpretations for most of the intermediate phases (85uSch).

It is a remarkable result of the binding analysis that commensurabilities which have in three directions integral elements are not the most frequent ones. Very often commensurabilities occur which have integral elements only in two directions. As the two-directions condition is less restrictive than the three-directions condition, it contains more binding possibilities. Further-more the two-directions condition leaves the physically important fact of interference of the $\underline{a}$ periodicity with $\underline{b}$ or $\underline{e}$ periodicity. This interference may stabilize a wave of momentary electrical dipole vectors which cause a shear structure i.e. a crystal structure containing a system of equidistant and parallel shear planes which devide the crystal into slabs each being sheared by the shear vector against the foregoing slab (see appendix 5). The frequent occurrence of shear structures is an indication for the existence of spatial correlations with commensurabilities having integral elements only in two directions.

The correlations $\underline{b}, \underline{e}, \underline{c}$ do not have all the same influence on the bonding. Therefore it is convenient to select the two most influencial correlations, say

$\underline{a}=\underline{b}_F K'=\underline{e}_B K'(2)$, and deduce from them a brief binding name FB2 where F is the type of the $\underline{b}$ correlation and B is the type of the $\underline{e}$ correlation and 2 is the first eigenvalue of $\underline{e}_B^{-1}\underline{b}_F$. The example implies $\underline{e}^{-1}\underline{b}=(2)$, a factorial commensurability; this is especially favourable as it permits a good avoidance of $\underline{e}$ and $\underline{b}$ and it is therefore named a factorial harmony. The site number ratio i.e. the ratio of number of sites per $\underline{a}$ cell in the $\underline{e}$ correlation $S(\underline{e})$, to the number of sites per $\underline{a}$ cell in the $\underline{b}$ correlation $S(\underline{b})$, written as $N_{-S(\underline{e})}^{/S(\underline{b})}$ is a helpful measure of a binding; for FB2 it has the value 4, and it is an experience of binding analysis that $N_{-S(\underline{e})}^{/S(\underline{b})}(N_{\underline{a}})$ is a smooth function. To every brief symbol of a binding there belongs a $N_{-S(\underline{e})}^{/S(\underline{b})}$ value so that the knowledge of a binding for a given phase strongly limits the possible bindings for neighbouring phases because of the smoothness of the site number ratio function (appendix 6).

Can an assessing model be of value for chemistry?

The plural-correlations model can only be used for assessing one-phase compositions, it cannot be a substitute for energy calculations as it is based on simplified energetics. However, there was always a broad demand for simplified models as they directed the attention to the essential influences. The experimental chemist wellcomes simplified models as they give him suggestions for planning experiments. The theoretical chemist is interested in wellworking simplified models as they give him an easy overview on the ample empirical data and as he perhaps may incorporate concepts of the model into his calculatory work, or as he may deduce assumptions of the model from the general theory.

The plural-correlations model is not purely qualitative as the statement that in a phase there is some bonding type realized, is more quantitative than earlier statements that the bonding is more metallic or more covalent. Even the binding statements can be further developed in future by making more quantitative use of the spatial correlations which are here only classified. Also the step from the spatial correlation to the two-electron density matrix might be performed some day, however, the first step should be done before the second.

At present the question is of interest whether the correlations are indeed realized i.e. whether the model is near to reality. It is an old difficulty that a model may contain hypotheses which are not yet fully justified. Direct experimental proofs consisting in an analysis of the feet of single crystal reflexions are missing at present, so that indirect proofs must be

considered. A phenomenological model can be confirmed by application to the empirical data; when its interpretations appear natural, easy and instructive then it confirms itself, i.e. the confidence into the usefulness of the model comes from the number of plausible interpretations. The development of the plural-correlations model is a continuation of the earlier phenomenological valence models, the method of inductive analysis remains the same. Inductive research always coexisted with deductive research and there was a permanent interaction between both methods of investigation. Understanding the multivarious possibilities of deductive calculations leads to agreeing that valence ideas assist the search for appropriate calculation methods.

Another indication of proximity to reality is presented by the fact that the model leads to new statements. This becomes visible in the comparison of different interpretations. It appears tempting to assume a correspondence between the bands of the band model and the systems of the correlations model. First it should be agreed that chemical reality may be described by different models, neither the band model can be disregarded nor the plural-correlations model can be declared as inadmissible. The only considerable point of view is, which model is more useful for a given purpose. For the calculation of the energy the pseudo potential derivative of the band model has proven quite successful, but for the assessment of the energy of formation and for the attribution of a bonding type a favourable issue was not presented. As an example, the existence of lacunae (constitutional vacancies) in VO and homologic phases had been explained (84Schw) by an idea, used earlier for Ni_2Al_3(47Sch), that the occupation of higher bands should be avoided. The plural-correlations model on the contrary found the cause for the lacunae in a good commensurability of the binding to the cell a (85aSch). While the spatial correlation interpretation presented at the same time bindings for most of the remaining VO_M phases, an analogous rationalisation had not been afforded by the band model. The concept of commensurability is missing in the band model as the configuration interaction is omitted in most calculations although it is inevitable,strictly spoken. Surprisingly the band occupation assumed does not simply correspond to the subsystem occupation. The V4s band of VO is assumed to be empty (71Goo.230) but the V4s subsystem is occupied by 1 electron per V (85aSch). The O2sp band is completely occupied and separated from the V3d band, but the O2sp shell is not completely occupied and the O2sp and V3d electrons form a common system in the correlations model; the V3sp band is not considered as essential for the bonding but the V3sp+O1s system appears to have some influence on the bonding.

The differences between bands and subsystems come from the binding analysis, so that with the noted assumptions the analysis of VO_M was successful, while with the band model assumptions the binding analysis was not successful. Sometimes a band calculation is named a first principle calculation (84And), but this distinguishing designation should not conceal the fact that different energies of electron sets remain possible as the configurational interaction of the waves and the interactions with the core electrons may change the energies.

The plural-correlations model is not yet very finished. Therefore many interpretations should perhaps be improved, however, as a first start into the application of the plural-correlations model to the crystal chemistry of metallic phases (or two-component phases) the analyses collected in appendix 8 may be helpful.

APPENDIX

(1) Thermodynamic designations and representations

U = internal energy

V = volume

S = entropy

N_K = mole number of component K

N_k' = mole fraction of component k

M_i = internal variables

M = unspecified mole number

The experimental chemists prefer as thermodynamic constitutional function the Gibbs energy G which is a Legendre transform of U and depends on the variables $T = \partial U / \partial S$, $P = \partial U / \partial V$ and N_1, N_2. Any statement in the U representation may be transformed into a statement in the G representation. The advantage of the U representation is its simple relation to the statistical theory of chemical systems.

(2) Statistical designations and names

H = energy operator

X = spin and spatial coordinates

x_n = coordinates of the electron n

h, h' = contributions to H^{pot}

N_F = number of electrons

N_E^A = number of all el. of an atom

$D_{XX'}$ = density matrix of electrons

D_y = density function of electrons

D^{sc} = spatial correlation of el. or bonding

D^{av} = averaged spatial correlation

D^{ed} = electron density

In statistical theory a probability density depending on two variables may be named a correlation (cf the concept of correlation coefficient), if the e-quality of the variables has a physical meaning. Otherwise it should be named a density in a polydimensional space. Unfortunately in chemistry the difference between real energy and Hartree-Fock energy has been named "correlation energy" irrespectively to the fact that the Hartree-Fock wave functions contain much spatial correlation because of their antisymmetry under exchange of electron coordinate vectors. It therefore appears advisable to use the name "Hartree-Fock excess energy" in chemistry.

(3) Binding analysis designations and matrix notations

$\underline{a}$= crystal cell (matrix)

$\underline{a}_1$= crystal cell edge (matr.column)

$\underline{b}$= cell of valence el.correlation

$\underline{e}$= cell of d-el.correlation

$\underline{c}$= cell of corr. of periph.core el.

$\underline{a}^{-1}\underline{a}'$= homeotypic commensurability

$\underline{b}^{-1}\underline{a}=\underline{K}'$= valence electron comm. to $\underline{a}$

$\underline{c}^{-1}\underline{b}$= internal commensurability

$\underline{a}=\underline{b}\underline{K}'=\underline{e}\underline{K}''=\underline{c}\underline{K}'''$ is a binding

d_b, d_c= distances in the $\underline{D}^{av}$ functions

$N^{/a}_A$= number of atoms per $\underline{a}$ cell

$N^{/a}_b, N^{/a}_e, N^{/a}_c$= number of el. per $\underline{a}$ cell

$N^{/a}_{S(b)}$= number of $\underline{b}$ sites per $\underline{a}$ cell

$N^{/A}_b$= number of $\underline{b}$ el.per atom, $\underline{b}$ concentration

$N^{/A}_{S(b)}$= number of $\underline{b}$ sites per atom

$N^{/S(b)}_{S(e)}$= number of $\underline{e}$ sites per $\underline{b}$ site

Phases with the same binding may be named isodesmic, and phases with closely related binding may be named homeodesmic.

The commensurabilites are expressed by (three by three) matrices, therefore an abbreviated matrix notation is used which is essentially quite old in crystallography. In the matrix $\underline{a}=\underline{a}_{i1}=(\underline{a}_{11},\underline{a}_{12},\underline{a}_{13};\underline{a}_{21},\ldots;\underline{a}_{31},\ldots)$ the index i refers to an orthonormal coordinate system and is mostly omitted; the index 1 numbers the edge vectors and may incidentally indicate the type of the Bravais lattice belonging to $\underline{a}$. An H before a numerical matrix or behind the last index of a symbolic matrix indicates that i refers to a hexanormal coordinate system. Analogously $M\beta^0$ indicates a monoclinic coordinate system and $Z\alpha,\beta,\gamma^0$ a triclinic system. For certain purposes it is preferred to refer a monoclinic cell to an orthonormal coordinate system. The following abbreviations are useful $(\underline{a}_{11},0,0;\ldots)=(\underline{a}_{11};\ldots)$, $(\ldots;0,\underline{a}_{22},0;\ldots)=(\ldots;\underline{a}_{22};\ldots)$, $(\underline{a}_{11};\underline{a}_{11};\underline{a}_{33})=(\underline{a}_{11};\underline{a}_{33})$, $(\underline{a}_{11};\underline{a}_{11})=(\underline{a}_{11})$. Furthermore it may be written $(2,1,0;-1,2,0;1)=(\sqrt{5};1)\underline{r}$ where 5=det(2,1;-1,2) and $\underline{r}$ is a rotation matrix which may be omitted for the present purpose. Similarly sometimes permutation matrices are dropped.

The hypothesis that $\underline{D}^{av}$ is lattice-like does not imply that say the $\underline{b}$ electrons "form" a lattice; the $\underline{b}$ electrons "form" the pair density $D^{sc}_{\underline{x}1,x2}$ which gives the energy; the $\underline{D}^{av}$ density serves here for classification purposes. However, a momentary configuration of $\underline{D}^{sc}$ may be compared with a deformed lattice in a certain translatoric position to $\underline{a}$.

(4) Crystal chemical designations

Homologic classes of chemical elements may be designated (71IUP) as A^1 (alkali elements), $A^2, A^3, \ldots, A^{10}, B^1, \ldots, B^8$ (noble gases). This sequence determines the sequence of elements in the formula of an intermediate phase. Sometimes a simplification in the designation of phase classes is possible by the convention $B^m = A^{10+m}$.

Phase designation. The chemical formula is composed of elements in the sequence of homologic classes, or if these are the same, in the sequence of atomic number. Separated by a point are affixes like p=high pressure phase, h=high temperature, r=room temperature, l=low temperature, i=impurity stabilized, m=metastable phase. A chemical two-component formula with the unspecified mole number $\underline{M}$ as index designates a mixture (alloy or ceramic).

Structure types are designated by the formula of the prototype added in brackets to the phase designation. If the phase itself is a prototype then the Bravais group in the designation 75AST and the numbers of atoms in the primitive cell (separated by a point) give a useful description. The Bravais group symbols are

    C,B,F = cubic primitive, body centered, face centered,
    T,U   = tetragonal primitive, body centered,
    H,R   = hexagonal primitive, rhombohedrally centered,
    O,P,Q,S= orthor.prim., body cent., one face cent., all f. centered,
    M,N,Z = monoclinic primitive, face centered; triclinic.

Sometimes the addition of these symbols to a **rare** prototype helps memory. Phases with same (cosely related) structure type are named isotypic (homeotypic). It is also of help to add to the type indication a Structure Reports (SR) reference containing numbers of volume and of page. In crystallography more recent Bravais group symbols (67Pea) are used which are not appropriate for the present purpose as they are longer.

Homeotypisms of the following kind are described by a brief symbol: R=replacement of atoms, L=lacuna formation, F=filling of interstices, D= homogeneous deformation, I=inhomogeneous deformation, S=shear of layers,

C=chain shear. These symbols may be placed affixing htp (=homeotypic to) before a prototype formula.

(5) Shear structures as indicators for non-integral commensurabilities

The well-known phase Cu_3Au with the cell $\underline{a}'$ has the valence electron concentration $N_{\underline{b}}^{/A}=1$ and the valence electron correlation $\underline{a}'=\underline{b}_F(1)$. If by statistical subtitution of Zn for Cu the valence electron concentration is increased, the favourable commensurability of $\underline{b}$ to $\underline{a}'$ in Cu_3Au is conserved for Cu_{3-N} $AuZn_N$ in $\underline{a}_1'$ and $\underline{a}_2'$ but changed in $\underline{a}_3'$. Therefore a tetragonal shear structure cell $\underline{a}=\underline{a}'(1;1;L)$ is formed (55Sch) with L=shear length obeying the empirical relation $1/L=N_{\underline{b}}^{/A}-1$ or $L+1=N_{\underline{b}}^{/A}L$. On the vector $\underline{a}_3$ there are distributed L atoms and L+1 electrons of the $\underline{b}$ correlation. The $\underline{b}$ correlation is compressed in the compliant [001]' direction (64Sch). If on the $\underline{a}_3$ vector the L atoms are plotted as equidistant little circles and the L+1 electron sites (of a momentary electron configuration) as equidistant points, it may be seen that half of the atoms have a positive dipole vector and half of them a negative vector in $\underline{a}_3$ direction. Since Au and Cu (or Zn) have a different polarizability it may be said that Au bears a difference dipole vector and Cu (or Zn) not. In the shear plane $\underline{x}_3=0$ the positive and negative vectors face each other, so that the energy is lowered when the crystal at positive values of $\underline{x}_3$ (the coordinate belonging to $\underline{a}_3$) is sheared by the shear vector $(\underline{a}_1+\underline{a}_2)/2=\underline{s}$ against the crystal at negative $\underline{x}_3$ values. This crystallographic shear should not be confused with the distributed mechanical shear. It is seen that after the shear plane $\underline{x}_3=0$ the next shear plane is $\underline{x}_3=0.5$. Besides the above interpretation of the shear phenomenon, which makes use of the spatial correlation, another explanation based on the band model has been advanced (65Sat,79Cow). As the band model omits the configurational interaction, the latter interpretation cannot be considered as acceptable. While the spatial correlation interpretation could be extended to the shear homeotypes of $MgCu_2$ (84Sch), an analogous explanation by the band model is not known.

(6) Valence rules useful for binding analysis

Rule of octet (23Lewis). In compounds of electronegative anions the valence electrons of the cations frequently complete the anion octet. (This allows an optimum spin compensation i.e. occupation of low energies).

Rule of b electron contribution (31Ekman). In a brass-like mixture an A^n element with $6<n\leq10$ does not contribute $\underline{b}$ electrons, but (58Vog) A^n with $3<n\leq6$ contribute n electrons.

Rule of electron supply (32Zintl,63Klemm). In AB_M phases with electroposi-
tive A atoms the A supply their m electrons to the B^n atoms so that the B
partial structure becomes homeotypic to a B^{n+m} element. (The influence of the
A core on the structure is small).

Rule of volume (64Sch.169). When the valence electron concentration in BB_M'
phases increases while other parameters remain constant, the atomic volume in-
creases as the structure becomes more loosely packed. (The increased energy
of the b system partially increases the energy of the e and c system)

Rule of volume of formation (02Richards,51Kubaschewski). A negative volume of
formation causes a negative energy of formation. (The b electrons enter a
lower potential energy so that by the virial theorem the energy decreases.
$V(N_2^-)$ is mostly smooth, exceptions are $A^{10}Al_M$, see 82Ell).

Rule of heavy components (83Sch.43). When components with many core electrons
are mixed to components with few core electrons an extra contribution to the
energy of formation is found. (The highly filled peripheral core shell ex-
pands in the direction to the light atoms).

Rule of lacunae (37Bradley). When in a phase with a good binding the valence
electron concentration is increased by alloying then the number of valence
electrons per cell may be conserved by lacuna formation in the partial struc-
ture of the electron poor component. (Lacuna= chemically caused vacancy. The
spatial correlation of valence electrons is conserved.)

Rule of strain (64Sch.70). When in a hexagonal or tetragonal structure the
commensurability $b^{-1}a$ is good then with valence electron concentration often
the axial ratio $|a_3|/|a_1|$ is increased (to get more sites in the b correla-
tion).

Rule of shear (64Sch.99). For appropriate commensurabilities in a structure a
system of electro dipoles at atoms may develop, the energy of which may be de-
creased by a crystallographic shear.

Rule of distribution of B^n atoms (75Wop). A B^n component in a A^{10} matrix
tends to most uniform distribution. (The B atom contributes all b electrons
so that a uniform b correlation causes a uniform B^n distribution).

Rule of correlation types (64Sch.68). A correlation type is a Bravais lattice
with three independent shortest vectors (isometric): C,R,B,F,U,H. The lattices
may be used in unconventional aspect: $C_H, R_Q, B_H, F_H, U_H, H_T, H_Q$, which also may be a
pseudo symmetry.

Rule of correlation type occupation (74Sch). The b correlation type is always
fully occupied. The e correlation type is fully occupied for an e concentra-
tion $N_e^{/A} < 6$, for higher concentrations $N_e^{/A} \approx 10$ occupations of $83\pm15\%$ have been
found. For the c correlation occupations $50\pm25\%$ have been found. (The latter
correlation is mediated by the higher correlations.)

Rule of commensurability (64Sch.68). The matrices $\underline{b}^{-1}\underline{a}$, $\underline{e}^{-1}\underline{a}$, etc. have most-
ly integral elements. If $\underline{e}^{-1}\underline{b}=\underline{n}=$integer number, the commensurability is named
a factoriality. The factoriality is especially favourable, it often leads (83Sch) to
a congruent melting point of the phase. The correlations b or e may be twinned
in a and generate a higher symmetry.

Rule of electron distances (74Sch). The smallest distances $\underline{d}_b$, $\underline{d}_e$, $\underline{d}_c$ of the
averaged correlations form in a given mixture a smooth function of the mole
fraction. For the chemical elements the distances are shown in Fig.2. It is
apparent that the d strongly depend on the electron count, therefore Fig.2
can only be a first suggestion. Furthermore d depends on the correlation type,
d decreases with decreasing coordination number in the correlation.

Rule of correlation site numbers (83Sch). The number of e sites or c sites per
atom $N_{S(e)}^{/A}$ or $N_{S(c)}^{/A}$ decreases with decreasing $N_b^{/A}$, with increasing atom num-
ber $N_E^{/A}$ and with increasing external pressure. The site number ratio $N_{S(e)}^{/S(b)}$
is a monotonous function of N_2^-.

Rule of neighbouring phases with the same site number ratio. In these phases
the higher valence electron concentration causes the closer packing of the b
correlation.

Rule of Hund insertion (64Sch.187). Hund's rule (25Hun) is not only valid for
atoms in the gas state. In the solid state the occupation of a nl shell by a
spin down electron while the shell is already fully occupied by spin up elec-
trons, takes the form of "Hund insertion" of a spin down electron into a cor-
relation of spin up electrons. The Hund insertion makes the binding analysis
of typically inorganic structures complicated, as an atomic distance with
Hund insertion is similar to a van der Waals distance.

(7) The method of binding analysis

Before the binding analysis of a two-component mixture is started the bind-
ings of the components and the electron count should be known. A binding ana-
lysis of the chemical elements (74Sch,82bSch) gives distances for the elements
(Fig.2), but in alloys the electron count depends on the other components and

Tab.1: Several plane commensurabilities $\underset{\sim}{K}$ and numbers $\underset{\sim}{N}$ of small meshes in the large mesh

1. Tetragonal

K	N	K	N	K	N
(1,0; 0,1)	1	(3,3;−3,3)	18	(6,2;−2,6)	40
(1,1;−1,1)	2	(4,2;−2,4)	20	(5,4;−4,5)	41
(2,0; 0,2)	4	(4,3;−3,4)	25	(6,3;−3,6)	45
(2,1;−1,2)	5	(5,0; 0,5)	25	(7,0; 0,7)	49
(2,2;−2,2)	8	(5,1;−1,5)	26	(5,5;−5,5)	50
(3,0; 0,3)	9	(5,2;−2,5)	29	(7,1;−1,7)	50
(3,1;−1,3)	10	(4,4;−4,4)	32	(6,4;−4,6)	52
(3,2;−2,3)	13	(5,3;−3,5)	34	(7,2;−2,7)	53
(4,0; 0,4)	16	(6,0; 0,6)	36	(7,3;−3,7)	58
(4,1;−1,4)	17	(6,1;−1,6)	37	(6,5;−5,6)	61

2. Hexagonal

K	N	K	N	K	N
(1,0; 0,1)	1	(4,1;−1,5)	21	(4,4;−4,8)	48
(1,1;−1,2)	3	(5,0; 0,5)	25	(5,3;−3,8)	49
(2,0; 0,2)	4	(3,3;−3,6)	27	(7,0; 0,7)	49
(2,1;−1,3)	7	(4,2;−2,6)	28	(6,2;−2,8)	52
(3,0;−0,3)	9	(5,1;−1,6)	31	(7,1;−1,8)	57
(2,2;−2,4)	12	(6,0; 0,6)	36	(5,4;−4,9)	61
(3,1;−1,4)	13	(4,3;−3,7)	37	(6,3;−3,9)	63
(4,0; 0,4)	16	(5,2;−2,7)	39	(8,0; 0,8)	64
(3,2;−2,5)	19	(6,1;−1,7)	43	(7,2;−2,9)	67

Tab.2: Several bindings with corresponding $\underset{\sim}{N}\dfrac{S(\underline{b})}{S(\underline{e})}$

32.0			BC4		
27.0	CC3	HH3	BB3	UU3	FF3
22.1				UB3	
16.0	CB2				FC4
14.0					FUU2
13.5			BC3		
12.5	CHFH3				
11.3	CFU2		BC$\sqrt{8}$		FUB2
9.8		HFH2			
9.8		HTFU2	BU2		
9.2		HUH2		UC$\sqrt{8}$	
8.6			BHFH$\sqrt{12}$		
8.0	CC2	HH2	BB2	UU2	FF2
7.5					FHUH2
7.0		HTC2		UHH2	
6.9	CU$\sqrt{2}$		BHFH3		
6.6					FHH2
6.5				UB2	FUHT2
6.3		HFH$\sqrt{3}$	BHUH3		
6.0		HUH$\sqrt{3}$			
6.0		HTU$\sqrt{2}$			
5.6	CB$\sqrt{2}$		BFU2		FUC2
5.5			BHH3	UHFH$\sqrt{3}$	
5.2	CHCH$\sqrt{3}$	HH$\sqrt{3}$	BHBH$\sqrt{3}$	UHUH$\sqrt{3}$	FHFH$\sqrt{3}$
5.0		HTB$\sqrt{2}$			
4.9		HBH1			FU2
4.9					FHUH$\sqrt{3}$
4.6			BHT2	UFU2	ÜHFH$\sqrt{3}$
4.5				UHH$\sqrt{3}$	
4.3				UHBH1	FHH$\sqrt{3}$
4.0	CF1		BC2		FB2
3.8			BHH$\sqrt{7}$	UHT2	
3.5		HTFU$\sqrt{2}$			
3.3	CHT$\sqrt{2}$			UC2	
2.8	CC$\sqrt{2}$	HTHT$\sqrt{2}$	BB$\sqrt{2}$	UU$\sqrt{2}$	FF$\sqrt{2}$
2.0			BF1		FC2

therefore the electron distances may differ from Fig.2. In the mixture $TiPt_M$ e.g. with the count $Ti^{4,8}Pt_M^{0,10}$ for $N'_{Pt} > 0.8$ Pt contributes valence electrons therefore at $N'_{Pt} = 0.75$ the increase of $d_e(N'_{Pt})$ with increasing N'_{Pt} stops and remains constant up to $N'_{Pt} = 1$ (85bSch). A similar effect was found in $PtSn_M$ for small N'_{Sn} (85cSch).

From the d_b and d_e (or d_c) values of the components the d values for an intermediate phase may be found by interpolation in a $d(N'_2)$ diagram (d varies from 1...3Å with $\Delta d = 0.2$Å corresponding to 1 cm, and N'_2 varies from 0...1 with $\Delta N'_2 = 0.1$ corresponding to 1 cm). Introducing such a value into an isometric cell (say b) gives the b cell edges which may be compared with the cell a. It cannot be expected that a_1 and b_1 are parallel, but it may be expected that the meshes a_1, a_2 and b_1, b_2 are commensurable. Here helps the Table 1 of plane commensurabilities. When a probable commensurability is found then from a_1 the probable b_1 may be calculated and inserted into the $d(N'_2)$ diagram. Next the stacking of b_1, b_2 is to be determined so as to satisfy the rule of correlation type occupation; this determines the type of b. A similar analysis determines the type of e and from both the site number ratio $N_{S(b)}^{/S(b)}$ may be inferred. The $N_{S(e)}^{/S(b)}(N'_2)$ curve should be monotonous and smooth. The extrapolation of this curve to the next phase yields a value which permits to determine few possible bindings from Tab.2.

(8) Examples of binding analyses

Chemical elements: Acta Cryst. B30(1974)193-204, Z.Metallkd.73(1982)594-595
Two-component Li compounds: Z.Metallkd.74(1983)111-117
Two-component Be compounds: Z.Metallkd.73(1982)403-408
Two-component borides: Comm.Math.Chem.13(1982)113-127
Two-component carbides: Monh.Chem.113(1982)651-667
Two-component nitrides: Cryst.Res.&Technol. 17(1982)553-567
Two-component oxides: to be submitted
Two-component fluorides: Comm.Math.Chem.13(1982)55-74
$A^nA_M^{1...7}$ phases: ibid. 15(1984)213-225
$A^nA_M^{8,9}$ phases: ibid. 16(1984)191-207
$A^nA_M^{10}$ phases: ibid. 16(1984)209-223
$A^nB_M^1$ phases: ibid. 15(1984)159-175
$A^nB_M^2$ phases: to be submitted
$A^nB_M^3$ phases: Comm.Math.Chem.15(1984)177-212
$A^nB_M^4$ phases: ibid.13(1982)75-111
$A^nB_M^5$ phases: ibid.17(1985)219-254

$A^n B^6_M$ phases: to be submitted

On the bindings in the crystal phases of Mn: Cryst.Res.Tech.in press 1985

On the bindings in $MoRe_M$ phases: Z.Metallk.75(1984)175-178

On the bindings in $NbRh_M^-$ phases: Z. Metallk. 76(1985)326-329

On the bindings in $TiPt_M^-$ phases: J.Materials.Sci.Letters 4(1985) in press

On the shear homeotypism in the $MgCu_2$ family: J.Sol.State Chem.53(1984)246-252

On binding and superconductivity in isotypes of Cr_3Si: Phys.Stat.Sol.(b)129 (1985)219-226

On the binding in transition metal disilicides: J.Sol.State Chem.43(1982)97-105

On the bindings in $PtSn_M$ phases: submitted

On the bindings in P.r, P.h, and homeotypes of P.r: submitted

On the bindings in RDI homeotypes of As: to be submitted

On the bindings in VP_M phases: Chem.Script.24(1984)143-146

On the bindings in TiS_M phases: submitted

On the bindings in VO_M^- phases: submitted

On the bindings in $A^{1+..2}$-silicates: Neues Jahrb.Miner.Abh.146(1983)210-220

On the phase diagram InS_M: Z. Metallk . 76(1985)358-364

A list of publications with *experimental* content and early binding interpretations, see 80bSch.

References

02Ric. T.W.Richards: Z.Phys.Chem.40(1902)597,49(1904)15

11Hab F.Haber: Verh.Dtsch.phys.Ges.13(1911)1117,1128;S.B.Preuß.Akad.(1919)506, 990

18Mad E.Madelung: Phys.Zeits.19(1918)524

23Lew G.N.Lewis: Valence and Struct. of At. a.Molec. Am.Chem.Soc. Monographs (1923)93 Chem.Cat.Co.

25Hun F.Hund: Z.Physik 33(1925)345

26Hum W.Hume-Rothery: J.Inst.Met.35(1926)295-361

27Hei W.Heitler,F.London: Z.Physik 44(1927)455-472

31Ekm W.Ekman: Z.Phys.Chem.B12(1931)57-78

32Zin E.Zintl,W.Dullenkopf: Z. Phys.Chem.B16(1932)195-205

34Bil W.Biltz: Raumchemie der festen Stoffe, Leipzig 1934, Voss Verl.

34Gol V.M.Goldschmidt:Handwörterbuch d.Naturwiss.15(1934)1128-1154

34Has D.Hassel: Kristallchemie, Dresden 1934, Steinkopff

34Mot N.F.Mott,H.Jones: Theory Prop. Metals a.Alloys,Oxford1934, Univ.Pr.

35Deh U.Dehlinger:in Handbuch der Metallphysik Leipzig 1935,Akad.Verl.Ges.

- 306 -

37Bra A.J.Bradley,A.Taylor: Proc.Roy.Soc.London A159(1937)56-72

39Pau L.Pauling: The Nature of the Chemical Bond,Ithaca 1939(see also 1945) CornellUPr.

41Nig P.Niggli: Lehrbuch d.Mineral u.Kristallchem.Vol.1,Berlin1941

47Sch K.Schubert: Z.Metallkd.38(1947)349-352

51Kub O.Kubaschewski,E.L.Evans:Metallurgical Thermo-Chem.London1951,Butterworth

54Bok G.B.Bokii:Vvedemie v Kristallokhimiyu ,Moskva1954, Izd.MGU

54Bor M.Born,K.Huang:Dynam.Theory of Cryst.Lattices,Oxford1954,Clarendon

55Sch K.Schubert,B.Kiefer,M.Wilkens,R.Haufler: Z.Metallk.46(1955)692-715

56Ame Amer.Soc.Metals: Theory of Alloy phases,Cleveland Ohio 1956

56Lav F.Laves in ASM ed.: Theory of Alloy Phases,Cleveland Ohio 1956

56Löw P.O.Löwdin: Adv.Phys.5(1956)1-172

58Mas T.B.Massalski:Metallurg.Rev.3(1958)45-96

58Vog E.Vogt: Physikal.Eig.d.Metalle,Leipzig 1958,Akad.Verl.Ges.

62Hum W.Hume-Rothery,G.V.Raynor: Structure of Met.a.Alloys,London1962The Inst. Metals

63Bec P.A.Beck: Electronic Struct.a.Alloy Chem.ofTrans.Elem.NY 1963,Wiley

63Kle W.Klemm,E.Busmann: Z.anorg.allg.Chem.319(1963)297-311

63Lav F.Laves: Adv.Xray Anal.6(1963)43-61

64Eng N.Engel:ASM Trans.Quarterly 57(1964)610-619

64Sch K.Schubert: Kistallstr.zweikomp.Phasen,Berlin1964,Springer Verl.

65Hul F.Hulliger,E.Moser:Progr.Sol.State Chem.2(1965)330-377

65Mas T.B.Massalski: Metallurg.Soc.Conf.29(1965)

65Sat H.Sato,R.S.Toth: Metallurg.Soc.Conf.29(1965)295-419

67Bre L.Brewer in Rudman et al.eds: Phase Stab.in Met.a.Alloys,NY1967,McGraw-Hill

67Pea W.B.Pearson: Handbook of Lat.Spacings a.Struct.ofMet.a.Alloys,Vol.2 Oxford 1967,Pergamon Pr.

67Rud P.S.Rudman,J.Stringer,R.I.Jaffee eds: Phase Stability in Metals and Alloys,N.Y.1967,McGraw-Hill

67Wes J.H.Westbrook: Intermetallic Compounds,N.York1967,Wiley

69Eng N.Engel in B.C.Gießen ed: Develop.Struct.Chem.Alloy Phases,N.Y.1969 Plenum Pr.

69Gie B.C.Gießen: Developments in the Struct.Chem.ofAll.Ph.,N.Y.1969,PlenumPr.

69när I.Náray-Szabó: Inorg.Cryst.Chem.Budapest,Akad.Kiadó

69Wad A.D.Wadsley,S.Anderson: Perspectives in Struct.Chem.3(1969)1-58

71Gla E.I.Gladyshevskii: Kristallokhimiya Silicidov i Germanidov,Moskva1971 Isd.Metallurgiya

71Goo J.B.Goodenough: Prgr.Solid State Chem.5(1971)145-399

71IUP IUPAC:Nomenclature of Inorg.Chemistry,London 1971,Butterworths

72Pea W.B.Pearson: Cryst.Chem.Phys.ofMet.a.All.NewYork1972,Wiley

72Pov A.S.Povarennikh: Cryst.Chem.Classification of Minerals,N.Y.1972,PlenumPr.

73Sam G.K.Samsonov,I.F.Pryadko,L.F.Pryadko: A Configurational Model of Matter NewY.1973,McGraw-Hill

74Mac E.S.Machlin: Acta Met.22(1974)95-108

74Mot N.F.Mott:Metal-Insulator Transitions,London1974,Taylor-Francis

74Sch K.Schubert: Acta Cryst.B.30(1974)193-204

75AST Amer.Soc.Test.Mat.:Book of Standards 11(1975)286

75Car C.M.Care,N.H.March: Adv.Phys.24(1975)101-116

75Uru V.S.Urusov: Energet.Kristallokhimia,Moskva 1975,Nauka

75Wel A.F.Wells: Struct.Inorg.Chem.,Oxford1975,Clarendon Press

75Wop W.Wopersnow,K.Schubert: J.Less-Com.Metals 41(1975)97-103   ReidelP.C.

76Hul F.Hulliger: Structural Chemistry of Layer-type Phases,Dordrecht1976

76Mie A.R.Miedema: Phil.Tech.Rundsch.36(1976)233-247

77Aut Autorenkollektiv: Intermetallische Phasen,Leipzig 1977 Verl.Gundstoff-ind.

77Kri P.I.Kripyakevich: Strukt.Tipy.Intermet.Soedinenii,Moskva1977,Nauka

77Sch K.Schubert Struct.Bonding 33(1977)139-177

79Cow J.M.Cowley,J.B.Cohen,M.B.Salamon,M.B.Wünsch eds: Modulated Structures
       New York 1979, Am.Inst.Phys.

80Ben L.H.Bennett,ed.:Theory of Alloy Phase Formation,The Met.Soc. ofAIME NY 1980

80Har W.A.Harrison: Electronic Struct.a.theProperties of Solids,SanFrancisco
       1980,Freeman

80Sch K.Schubert: J.Less-Comm.Metals 70(1980)167-180

80bSch K.Schubert: Russ.   Metallurgy 5(1980)157-167

81Joh O.Johnson: J.Phys.Chem.Solids 42(1981)65-76   N.Y.1981 Acad.Pr.

81O'Ke M.O'Keeffe in O'Keeffe,A.Navrotsky eds:Struct.a.Bond.in Crystals

81Sch K.Schubert: Z.Metallkd.72(1981)752-760

81Sim A.Simon: Ang.Chem.20(1981)1-22

82Gla E.I.Gladyshevskii,O.I.Bodak: Kristallokhimiya intermet.soed. redko-
       semelnikh MetalloV,Lwow (1982) Visha Shkola

82Gru R.Gruehn,W.Martin: Naturwiss.69(1982)53-62

82Ell M.Ellner,U.Kattner,B.Predel: J.Less.Com.Met.87(1982)305-325

82Sch K.Schubert: Chem.Script.19(1982)224-233

82bSch K.Schubert: Z.Metallkd.73(1982)594-595

83Ben L.H.Bennett,T.B.Massaski,B.C.Gießen eds: Alloy Phase Diagrams,Materials
       Res.Soc.Symp.Proc.19,Amsterdam1983,North-Holland

83Sch K.Schubert: Z.Krist.165(1983)23-45

83Wei Al. Weiß,H.Witte:Kristallstruktur u. chem.Bindung,Weinheim 1983 Verl.Chem.

84And O.K.Andersen,S.   Satpathy in A.Dominguez ed.: Bas.prop. bin.oxides
       Sevilla 1984,Univ.

84Sch K.Schubert: J.Solid State Chem. 53(1984)246-252

84Schw K.Schwarz in A.Dominguez ed.: Basic prop.bin. oxides, Sevilla 1984Univ.

85aSch K.Schubert: Chem.Script.,in press, TiO_M ;Cryst.Res.Tech.,in press, VO_M

85bSch K.Schubert: J.Mat.Sci.Letters 4(1985)988-993, $TiPt_M$

85cSch K.Schubert: $PtSn_M$, submitted,