STABILITY OF SOME INTERMEDIATE PHASES
IN
TRANSITION METAL ALLOY SYSTEMS

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C E R T I F I C A T E

Certified that the dissertation entitled "STABILITY OF SOME INTERMEDIATE PHASES IN TRANSITION METAL ALLOY SYSTEMS" is being submitted by Sri Naushad Khan in partial fulfilment for the award of the degree of Master of Engineering in Metallurgical Engineering (Physical Metallurgy) of the University of Roorkee, Roorkee, is a record of his own work carried out by him under my supervision and guidance for a total six months period during 1971-72 session.

The matter embodied in this dissertation has not been submitted for the award of any other degree.

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ABSTRACT

In the present work the electronic structure of transition metals and the formation of intermediate phases in transition metals including rare-earth elements have been reviewed. The importance of the electronic factor in the formation of intermediate phases has been emphasised. The occurrence and stability of Sigma, Chi and Laves phases formed among transition metals are discussed in terms of the formation of stable electronic configurations proposed by Samsonov. Electronic correlations presently done have suggested that the size effects are merely the consequence of the electronic states and the stability of intermediate phases can be successfully interpreted on the basis of stable electronic configurations formed by component elements in the condensed state. The comparatively large differences in SWASCd^5 of two components lead to no homogeneity ranges whereas the smaller differences in S SWASC d^5 give rise to large homogeneity ranges in Sigma phases. It is noted that the formation of stable d^5 configurations are associated with the stabilisation of $MgZn_2$-type, whereas the stable d^{10} configurations are more favourably responsible in the stabilisation of $MgCu_2$-type Laves phases.

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CHAPTER - I

INTRODUCTION

The name intermediate phase has been commonly assigned to any new phase formed in a multicomponent system. Recently this term has been used to include the ordered phases (superlattices) resulting from the atomic ordering of primary solid solutions. These phases may not exhibit the long range order at elevated temperatures but can order at lower temperatures. For the intermediate phases exhibiting long range order over the entire temperature range of stability, the more restrictive name intermetallic compound is used. These phases usually occur at a definite atomic ratio and most often exhibit a narrow homogeneity range. The homogeneity range may result by the formation of vacancies or by the small decrease in long range order (formation of a slightly random solid solution). Both these mechanisms may also result in non-stoichiometric compounds (i.e. compounds whose composition range of stability does not include the composition corresponding to the fully ordered structure.

In many cases the intermediate phases can exist over a range of composition. Therefore, for a broad classification two types of intermediate phases may be recognised-the phases stable over wide composition ranges and the phases stable over a narrow composition range.

The free energy curve for both types of phases as a function of composition will have the 'U' form at constant temperature and pressure but for a phase stable over a wide composition range the curve is 'broad shallow' indicating that the phase can exist over a wide composition range, since a change in composition of the phase does not raise the free energy appreciably; while for a phase stable over a narrow composition range the curve is 'narrow steep' where the change in the composition raises the free energy appreciably, suggesting that it is only stable at a definite composition or over a very narrow composition range (Fig.1.a). Since the partial molar free energies of two phases in equilibrium must be equal, the points of contact of a common tangent to the free energy curves of single phases gives the composition of each phase in equilibrium at that temperature. The positions of free energy curves where a nonstoichiometric phase occurs is as shown in fig.1(b).

There are three main factors controlling the stability of intermediate phases: the atomic size, related to radius ratios and space filling; the electron concentration, related to valence and composition; the electronegativity, related to charge polarization and stoichiometry.

The atomic size factor is generally discussed

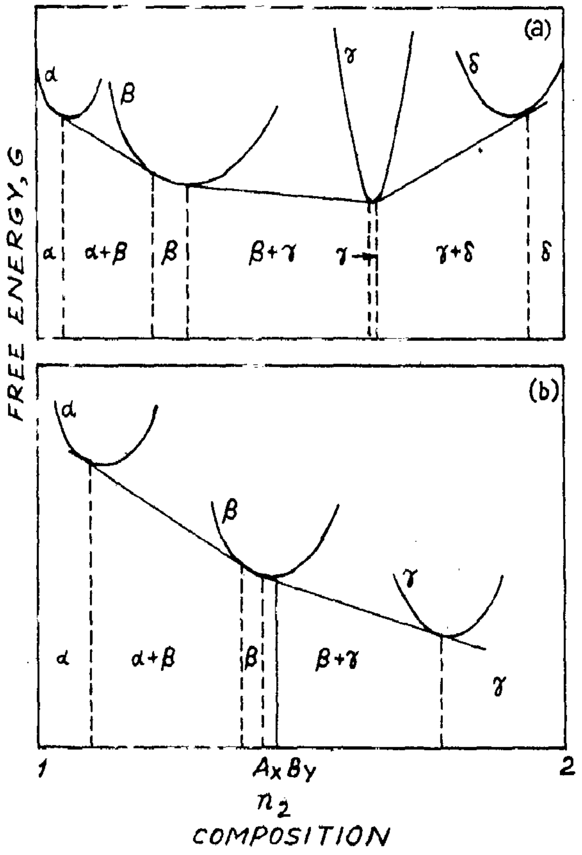


FIG. 1 THE FREE ENERGY AS A FUNCTION OF COMPOSITION AT CONSTANT TEMPERATURE FOR THE INTERMEDIATE PHASES β AND γ (a). IN FIG. b, THE RELATIVE POSITIONS OF THE FREE ENERGY CURVES α, β, AND γ ARE SUCH THAT THE COMPOSITION RANGE OF STABILITY FOR THE β-PHASE DOES NOT INCLUDE THE STOICHIOMETRIC COMPOSITION AT THE MINIMUM ($A_x B_y$).

in terms of radius ratio of the atoms and it has been found that whole families of size factor phases such as AB_2 - Laves Phases form because of the ease with which atoms of a given radius ratio can most efficiently fill the space.

The relative valency factor refers to the difference in the valencies of the component atoms, and is discussed generally in terms of the changing electron concentration (electrons/atom) within the lattice. The electron concentration is the most important consideration for the formation and stability of electron compounds. Although the formation and stability of Laves phases are mainly due to geometrical size factors, the electronic factor is apparent in a number of cases. Among the three factors, the electronic concentration factor is of primary importance. Interesting correlations which emphasise the influence of e/a, are particularly evident, for example, from studies of constitution of ternary systems, where Sigma, Chi, Mu and other such phases frequently form narrow, elongated phase fields that appear to follow approximately constant contours of e/a rather than atomic radius ratio, and which show characteristic shifts from system to system. Examples of dependence upon electronic factors are also provided by the behaviour of essentially stoichiometric phases such as the family of Ti_2Ni type phases. The influence of electronic factors is of particular significance in Laves phases in determining both the type of structure and the ranges of stability. The three modifications, $Mg\,Cu_2$, $MgZn_2$ and $MgNi_2$, occur in several ternary systems, and their ranges of stability are clearly dependent on e/a. While it is true that the ratio of radii constitutes an important parameter in stabilising the Laves phases, which particular structure is chosen appears to be related to the density of states and the interactions between the Fermi surface and the Brillouin zone. Our major discussion of the intermediate phases will, therefore, be based on electronic considerations.

The electronegativity of an element or atom is a measure of its tendency to accept valence electrons and, therefore, the relative electronegativities indicate qualitatively whether or not a new phase is likely to form and thus will also indicate the nature of the bonding in the phases. When the electrochemical factor is predominant, the electrochemical or Normal valency compounds are formed.

Depending upon the above three factors, the intermediate phases in alloy systems are grouped broadly into three main classes:

a) Electrochemical or Normal valency compounds.
b) Size factor compounds/phases and
c) electron compounds/phases

The electrochemical compounds are formed when one element is strongly electropositive and the other is strongly electronegative. Their compsitions satisfy the normal valency laws and in general the range of solubility in them is small. They have usually high melting points. There are two classes corresponding to the ionic and covalent bonding. For ionic compounds the atomic arrangement is such that electron transfer enables the atoms to achieve a rare gas electron configuration. The covalent type of compounds follows the (8-N) rule. Some examples are Mg_2 (Si, Ge, Sn or Pb), Mg_3 (P, As, Sb or Bi)$_2$, Mg (S, Se or Te) and ZnS.

A large number of electrochemical compounds are formed which possess NaCl, CaF_2, Diamond, Zinc Blende, Wurtzite, Silicon carbide, or NiAs, types of structures.

Hume Rothery[20] first observed that over a wide range of alloy systems, phases of similar crystal structures are formed at the same ratios of valency electrons to atoms. These phases are termed electron compounds. The electron concentrations (e/a ratios) at which they were observed, are 3/2, 21/13 and 7/4 respectively. Some examples of electron phases are:

IA. Body -Centered Cubic (β -brass) structure, e/a= 3/2.
(Cu, Ag or Au) Zn, CuBe, Ag Mg, Cu_3 Al, Cu_5 Sn,
(Co, Ni or Fe) Al.

IB. Complex cubic (β-Mn) structure, e/a = 3/2.
(Ag or Au)$_3$ Al, Cu$_5$ Si, Co Zn$_3$.

IC. Hexagonal close packed structure, e/a = 3/2.
Ag Cd, Cu$_5$ Ge, Ag$_7$ Sb, Cu$_3$ Ga.

II Complex Cubic (γ-brass) Structure, e/a = 21/13
(Cu, Ag, or Au)$_5$ (Zn, or Cd)$_8$, Cu$_9$ Al$_4$, Cu$_{31}$ Sn$_8$,
(Fe, Co, Ni, Pd or Pt)$_5$ Zn$_{21}$

III Hexagonal closed packed (ε-brass) Structure, e/a=7/4.
(Cu, Ag or Au)(Zn or Cd)$_3$, Cu$_3$ Sn, Cu Be$_3$, Ag$_5$ Al$_3$

In determining the electron concentrations the transition metals were assigned zero valency. This is partly explainable on the basis of their electronic structures; in their alloys the incomplete outermost d band has to be filled when the electron concentration is increased, and further the outermost s band will also be completed which will reduce the contribution of these metals to the free electron cloud.

Electron phases are also found in certain ternary alloy systems at the appropriate concentrations, and in general they can exist over a small range of composition about the exact ratio. Both ordered and disordered distributions of atoms are found.

The existence of these phases is a direct consequence of the nature of the metallic bond; it is evident that the stability of such a phase depends essentially upon the electron concentrations and the pattern of atomic sites, while the actual distribution of atoms amongst these sites is of minor importance.

Size factor phases are of two main types; those where one atom is much smaller than the other, and those where the difference in atomic diameter is not of such a high order. In the first category, fall the interstitial compounds or Hägg compounds, which are hydrides, nitrides, carbides and borides of the transition metals, in which the small nonmetallic atoms H, B, C, N and Si, take up interstitial positions between the metallic atoms, the latter usually forming by themselves a complete close packed structure, or a slightly disordered form of the structure. When the radius ratio R_X/R_M is less than 0.59, the structure of intermediate phases is simple (commonly f.c.c or c.p.h. and occasionally b.c.c., simple hexagonal or slightly distorted form of one of these) and usually centered about compositions of the simple formulae MX, M_2X, M_4X and MX_2, where M and X represent metal and nonmetal atoms respectively. When the ratio of the radii exceeds 0.59 the interstices are no longer large enough to hold the non-metal atoms without distortion and more complicated structures are then formed. In this class are the carbides of Cr, Mn, Fe, Co and Ni (R_X/R_M = 0.60- 0.61) and the borides of Fe and Ni.

An important group of the second category where difference in atomic diameters of two metals, A and B, is not large and the radii ratio $r_A/r_B = 1.225$ which is the ideal radius ratio for efficient packing, are the Laves phases of the general formula AB_2, exemplified by the three prototype structures: $MgCu_2$, $MgZn_2$ and $Mg\ Ni_2$. The detailed discussion of Laves phases will form the subject of one of the later chapters.

The total number of binary systems defined by combinations of transition metals is large and a far larger number of systems result from ternary combinations and combinations of still higher orders. The intermediate phases formed by transition metals are often considered as separate groups. However, the major share of transition metal phases fall into a manageable number of structure-type families and these families of isostructural phases can be classified in two groups:

1. Phases with fixed stoichiometry -- i.e. phases which occur at simple and more or less invariant stoichiometric ratios and which represent a rather wide variety of structure types.

2. Phases with variable composition - i.e phases whose compositions shifts in a regular manner from system to system and often have wide ranges of homogeneity.

A simplified resume is shown in figure 2 for binary combinations of an element of the Sc, Ti, V or Cr group, the A component (on the left) with an element of the Mn, Fe, Co, Ni or Cu - group, the B component (on the right). The diagram includes a very large number of the phases that are known to occur though other intermediate phases may also form in some systems.

In binary systems the intermediate phases of variable stoichiometry are the σ (Sigma), μ (Mu), and χ (Chi) phases. In ternary systems two structurally related families of P and R intermediate phases appear also having variable compositions. Proceeding from the A component end, the phases occuring at fixed stoichiometric ratios have the following structures: at A_3B the Cr_3Si type; at A_2B the Ti_2Ni type or "eta-carbide" type, the $MoSi_2$ type and the $CuAl_2$ type (CN16); at AB the CsCl type, at AB_2 the $MgCu_2$ type (C15), the $MgZn_2$ type (C14), the $MgNi_2$ type (C36) ~~type~~ Laves phases and another group of $MoSi_2$ type phases; at AB_3 a group of close-packed ordered CN12 structures; and finally, at the AB_5 composition the UNi_5 type and the $CaCu_5$ type structures.

For the alloys of transition metals; in particular binary alloys of group IV, V or VIA elements with an element from group VIIA or VIII, the following

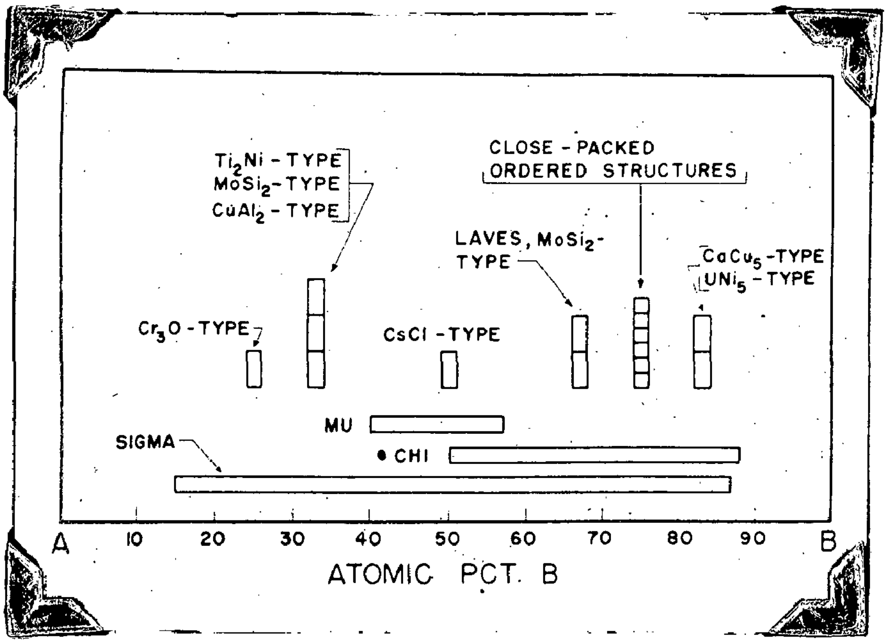


Fig.2. Occurrence and distribution of intermediate phases with fixed and variable compositions in binary systems of transition elements. The A component is an element of the Sc,Ti, V,or Cr group; the B component is an element of the Mn,Fe,Co,Ni, or Cu group.

sequence of structures is observed:

$$\begin{tikzcd}
\text{B.C.C. (Solid solution)} \arrow[r] & \text{- Cr}_3\text{Si Type} \arrow[r] & \sigma\text{- phase} \arrow[r] & \mu\text{ phase} \arrow[r] & \chi\text{ phase} \arrow[d] \\
 & & & \text{f.c.c. solid solution} & \text{C.p.h. phases} \arrow[l]
\end{tikzcd}$$

However, some structures may be missing from the sequence, but the order of appearance is always the same with increasing electronic concentration.

In the next few chapters, only the Laves phases, Sigma phases and Chiphases will be discussed in some detail. The stability of the above intermediate phases will be discussed and interpreted in terms of the latest Stable Electronic Configuration Model proposed by Samsonov[21] for transition metals. Therefore, it is necessary to have an insight into the electronic structure of the transition metals before discussing the alloy chemistry of the same. The purpose of such a discussion based on the correlations from the available % SWA^{s}C d^5 values for transition metals is to provide a new orientation in the study of the stability of intermediate phases.

C_H_A_P_T_E_R - II

ELECTRONIC STRUCTURE OF TRANSITION METALS

2.1 INTRODUCTION

The transition metals which are of importance, both industrially and from the point of view of scientific metallurgy, are defined as those which " occupy places in the periodic table of the elements where groups of 8 (s^2p^6) electrons, which acquire a provisional stability in the atoms of the inert gases, expand into groups of 18 ($s^2p^6d^{10}$) electrons by the building up of an $(nd)^{10}$ subgroup "1,2.

The transition metals occupy three horizontal rows in the Periodic Table, with the alkali metals at the beginning of each row (or period) and the noble gases at the end. If n denotes the quantum number of valence electrons, the electronic energy levels of the free atoms change from the order $ns < (n-1)\,d < np$ in the alkali metals and early transition elements to the order $(n-1)\,d < ns < np$ in the late transition elements and the noble metals, with the result that along each row the order of the s and d states is gradually reversed. On forming crystalline solids, some of the degenerate atomic energy levels broaden into bands, but the same general effect is expected, with energies of s and d states again crossing over along each row and resulting in nearly the same energy in several intermediate elements. As a consequence of this there will be a tendency for some of the elements to exist in hybrid sd states (or mixed atomic orbitals). At the same time, on moving along a transition series from left to right, the p levels are lowered nearer to the s levels, so that when the sd hybridization decreases in the late transition elements, the sp hydbridization increases. The sd and spd hybridization should give rise to the strong cohesion (bonding) and so a maximum in the strength of bonding can be expected some where in the middle of each period, depending on the electronic structure of each particular element[1,3,7].

Judging by the experimental data such as melting points, heats of sublimation, lattice spacings, compressibilities, thermal expansion etc., in the first long period, bonding increases from group IA to group VA, with manganese showing abnormally weak bonding and Fe, Co and Ni showing stronger bonding and little change on passing from Fe→Co→Ni. In the second and third long periods, the strength of bonding increases upto group VIA, remains high in groups VIIA and VIIIA and then falls on passing from Ru→Rh→Pd or Os→Ir→Pt. Also, on passing down along vertical columns between the three long periods, there is a striking increase in bonding as evidenced by the higher melting points. However, the electronic theories of the transition metals are very complicated and, as yet, incomplete without any real quantitative theory[1].

There is fairly general agreement on the electronic state of the elements K→Ti in the First Long Period and from Rb→Mo, and Cs→La (Rare earth elements) Hf→W in the Second and Third Long periods. In these elements all the outer electrons are involved in the cohesion and all are in hybrid spd states. For the latter elements, with the possible exception of divalent manganese, there is agreement that the outer-most d electrons are concerned in the cohesion, but both the general mechanisms and the exact details are in dispute[4].

There are two main schools of thoughts or alternative approaches:-

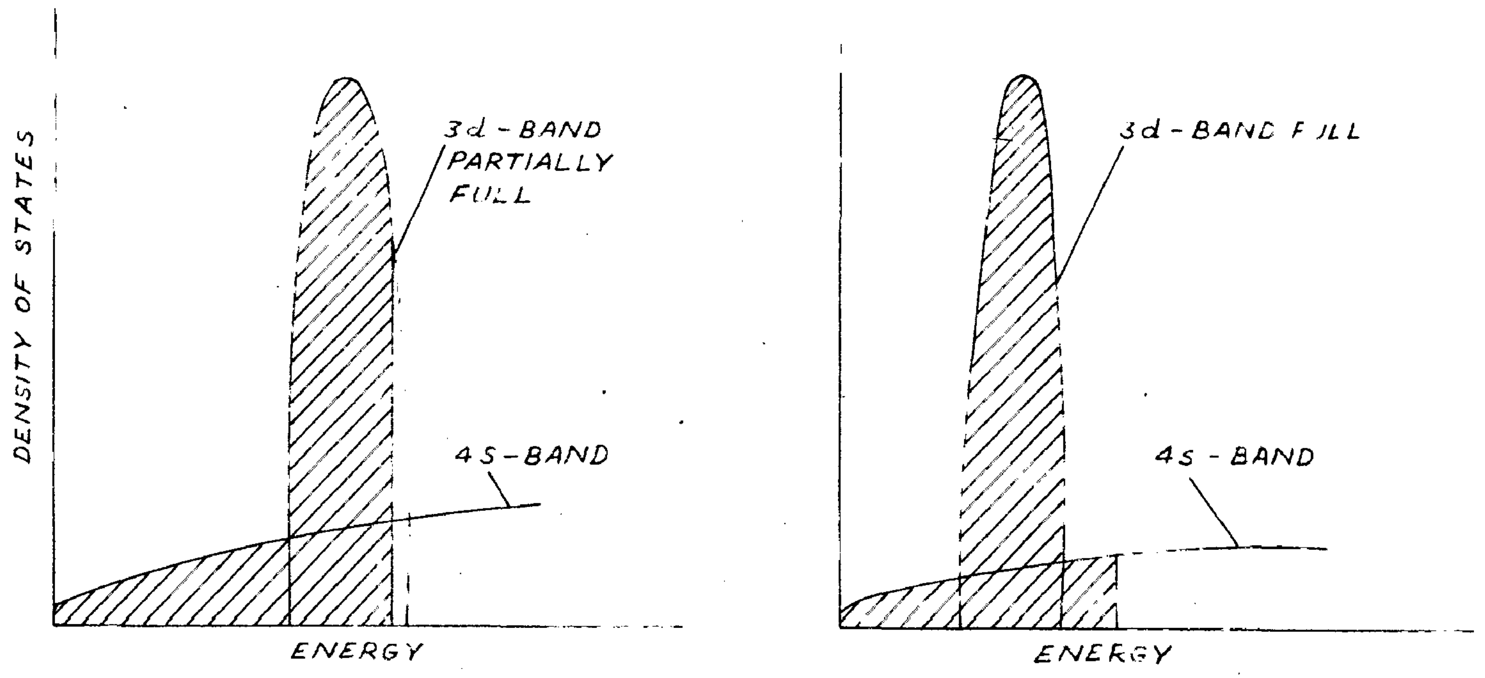
2.2 Collective Electron Theories[3,4,6]

In these theories there is no sharp division between bonding (nonlocalized) and nonbonding (localized atomic) electrons and all the electrons outside the shell of the preceding rare gas are regarded as contributing to the cohesion. The breaks in the sequence of physical properties are then regarded as due to an increase in the repulsive nature of wave-function. Subject to simplifying assumptions, the Collective-electron theories can be developed mathematically[4,27], so as to calculate physical properties without introducing numerical constants deliberately chosen to fit the facts. In this sense, the

Collective electron theories are " better" theories than the Pauling approaches, but unfortunately the assumptions made are so crude and approximate that it is not justifiable to critically compare the results with the facts. With-in the purview of Collective electron theories falls the famous classical Band Theory of Mott and Jones[23].

2.2.1 MOTT AND JONES BAND MODEL.[23,24,25]

Mott and Jones[23] discussed the structure of VIII group elements Fe, Co, and Ni. They treated the electrons collectively, with the whole assembly giving rise to a band or bands in which the number of unpaired spins per atom corresponds to the observed saturation moments (Bohr magnetons) but in which the magnetic electrons are not truly localized and could contribute to the Fermi surface. They ignored the 4p electrons and as a result they found two distinct high narrow (3d) and low broad (4s) overlapping bands derived from the (3d) and (4s) states of the free atoms (fig.3). The cohesion was regarded almost entirely due to the (4s) electrons. In order to produce ferromagnetism there must be a predominance of electrons with one spin; hence the d band is subdivided into two hypothetical subbands, with "holes" in one subband being responsible for unpaired spins. On passing from Ni to Co, the saturation moment increases from (Ni) 0.61 μ_B to (Co) 1.71 μ_B, and from the view point of the theory of Mott and Jones , the position for Co resembles that of Ni, with more holes in the d-band. A similar



(a) (b)

FIG. 3 (a) FILLING OF THE 3d-BAND, AND 4s-BAND IN NICKEL, (b) FILLING OF 3d AND 4s BANDS IN COPPER picture, but with still more holes in the d-shell, was first proposed for Iron, but this led to great difficulties because if a saturation moment of 2.22 μB for iron, indicated 2.22 holes in the d-band, the latter would contain 10-2.22 = 7.78 electrons and thus leave only 0.22s-electrons per atom to account for the cohesion[4,13].

The above model is clearly an approximate model since it made no detailed provision for hybridized states. This model has failed to explain the strong bonding in transition metals and does not work well today, but in some cases it offers a good explanation of certain physical properties.

The inadequacies of band model or collective electron theories, prompted to have a deeper view of the second school of thought[6].

2.3. LOCALIZATION MODELS

The second approach where the 3d electrons are considered to be partly bonding (nonlocalized) and partly nonbonding (atomic or localized) in nature, was pioneered by Pauling[28,30]. A number of models or hypotheses have been developed since then which fall under the Pauling's school of thought. These hypotheses or models are discussed here briefly.

2.3.1 PAULING'S HYPOTHESIS[4,13,28,30]

In the Pauling Hypothesis the trends in certain observed properties and in particular the magnetic saturation moments, were assumed to be the consequence of some of the d- electrons entering into localised atomic (or nonbonding) d-orbitals, described by localised wave functions. The remaining d-electrons were regarded as forming hybrid (spd) orbitals in association with the s and p electrons, in which electrons continuously exchange positions (resonate) and are responsible for metallic bonding. In this scheme a maximum of 2.44 electrons is considered to be in localised atomic d orbitals and at most, six electrons contribute to bond formation. Many authors consider the Pauling model unsatisfactory in that it gives no reason for the difference, between the properties of the elements in the first and later long periods (second and third); and in ascribing equal valencies to all the elements of groups VI-VIIIC in all the three periods, and in that the scheme does not agree with a number of physical properties.[4] A modification of the Pauling scheme proposed by Hume-Rothery, Irving and Williams[31] takes into account certain experimental data as well as valencies of the transition elements as observed in inorganic chemistry, but retains some idea of atomic orbitals[3]. The general approach of the Pauling Hypothesis, is often the best way of interpreting and generalising alloy structures, cohesion, magnetisation and interatomic spacing, while the band theory is better for explaining the electrical properties of metals with fewer assumptions[12].

2.3.2 MOTT AND STEVENS MODEL

Mott and Stevens[32] have presented qualitative views on the band structure of the later transition metals. According to their views, the crystal structure and symmetry of the transition elements are important determining factors of the electronic structure. For the F.c.c. metals, little is added to previous ideas. These are to be thought of as arrays of close packed ions or atoms having the configuration of full or nearly full 3d shells. The "holes" in the d-shells move from atom to atom and form a Fermi gas. The 4s or conduction band has about 0.6 electrons per atom and the cohesion is partly due to these electrons but also due to the Vander Wall type attraction between the closed d-shells. The Fermi surface extends over both the 4s and 3d bands.

2.3.3. LOMER AND MARSHALL MODEL

Lomer and Marshall[33] interpret the electronic structure from completely different assumptions. They also make use of the X-ray investigations of charge density of electrons in transition metals by Weiss and De Marco[34] and note that the remaining valence electrons, obtained after substracting Weiss and De Marco values from total number of 3d electrons in free atom, are in conduction states with a roughly uniform density distribution i.e. Cr 5.8, Fe 5.7, Co 0.6, Ni 0.6, Cu 1. The number of d-electrons is determined by the nuclear charge on the atom and crystal structure is regarded as a consequence of the electronic structure. From K to Cr, along the First Long Period as the nuclear charge is increased, electrons are added round the argon core, there are practically no 3d-like electrons, they are all conduction electrons with spatial density distribution quite unlike that of the atomic 3d-states. A sudden configurational change occurs at Co which has a high number of d-like electrons and few conduction electrons.This type of structure continues through to copper.

2.3.4 ENGEL AND BREWER HYPOTHESIS[4,6-10]

Relatively recently Engel and Brewer have proposed a fairly simple model of electronic configuration in solid state metals and have attempted to correlate it with the crystal structures. The treatment is similar to Pauling's valence-bond method but follows a modification of it as advanced by Engel[35], who suggested that the crystal structure in transition metals is determined only by the s and p electrons, the unpaired d electrons contribute strongly to the bonding but play no part in determining the type of crystal structure. A critical discussion of the theory has followed up since then in various articles[36-41] and in his critical and detailed review of the Engel-Brewer Theory, Hume-Rothery[10] assumed that the bonding electrons existed in hybrid sd or spd states, but whatever factor determined the type of crystal structure was relatively insensitive to the d-function in the hybrid, so that the structure was determined primarily by the proportions of s and p-functions. Brewer assumed that the three crystal structures - b.c.c., h.c.p. and f.c.c. result from bonding hybrids of the type d^ns, d^nsp and d^nsp^2, respectively, where n may vary within certain limits. Alternatively, it is proposed that the b.c.c., h.c.p. and f.c.c. structures correspond to the 1,2 and 3(sp) electrons per atom respectively. According to Brewer[7], this proposal of Engel was an extension of the Hume-Rothery rules in that a characteristic structure is associated with a given number of electrons per atom.

As additional electrons are added in the transition metal series, Engel would explain the gradual transition from b.c.c. to h.c.p. structure to f.c.c. structure as being due to the need to maintain as many d electrons as possible in an unpaired state and therefore, the promotion of as many electrons as possible to s and p states. Brewer attributes the maximum heat of atomization (maximum bonding energy) which occurs in the fifth group with V and Nb and then switches to the sixth group for W, to the trend in the effectiveness of d electrons in strengthening of the bonds as the atomic number is increased. He explains that the effect of the extra d electrons in the sixth group is not so important with the lighter elements so that Cr and Mo actually are low in bonding energy compared to V and Nb, whereas for U ~~and~~ the d-electrons have become so effective that the extra d electron is clearly utilized . According to Brewer[7], the structures and heat of atomization are two of the most important clues to the actual valence adopted by the element in a given structure. The average electron per atom is the key to the structure and stability.

The Engel- Brewer theory has been applied in the discussion of various binary phase diagrams and also to the problem of phase boundaries in transition metal alloys[47]. It is suggested that the permissible variation from the exact whole number values of electron concentrations with the change in composition, will be indicated by the composition limits of phases. In this way generalizations and predictions of phase boundary limits in transition - metal alloys have been made, but the applications to alloy structures are not without inconsistencies[4,11].

Hume-Rothery[10] compared the conclusions of Pauling[29] and Engel and Brewer regarding the structure of transition metals and found that conclusions based on a study of magnetic properties and interatomic distances are not very different from those based from consideration of promotion energies and heats of sublimation. In brief, the modeal proposed by Engel and Brewer made a definite advance in the field of phase stability, but it lacked in general Universality as far as correlating other properties of metals is concerned[6].

2.3.5 SAMSONOV'S STABLE ELECTRONIC CONFIGURATION MODEL

A somewhat different model was proposed by Samsonov[21] in 1965, called the Stable Electronic Configuration Model, and has been very successfully applied to remove the anomalies put forth by other hypotheses.

According to the model, during the formation of condensed solid state, valence electrons can be divided into localized and non-localized parts. This distribution has been experimentally verified by X-ray studies of some transition metals given in the following table:

TABLE -I

DISTRIBUTION OF VALENCE ELECTRONS IN SOME TRANSITION METALS[6]

Metal	No. of valence Electrons d,s	Localized Part	Non-localized Part
Zr	4	2.6	1.4
Nb	5	3.8-3.9	1.1-1.2
Cr	6	3.5	2.5
Mo	6	4.1-4.2	1.8-1.9

The localized fraction of these electrons forms a fairly broad spectrum of configurations which differ in their energetic stabilities i.e. in their stocks of free energy, so that along with the very stable configurations there appear some, which are less stable or even unstable. If we allow for the fact that the statistical weights of the most energetically stable electronic configurations are considerably greater than the weight of the unstable ones, we can assign to each atom states of a limited number of stable configurations. Between the stable configurations and the non-localized fraction of the valence electrons, there occur exchanges which are responsible for the bonds between pairs of stable configurations. The stable electronic configurations for d-metals are d^0, d^5 and d^{10} and according to the degree of descending energy stability these can be arranged in the order d^5-d^{10}-d^0. An analogous, picture is also observed for f - elements, the atoms of which can form stable f^0 ,f^7, and f^{14} configurations with f^7 having the maximum stability.

Assuming that for transition metal atoms in the free state with the number of d electrons, nd < 5, only two stable configurations d^0 and d^5, of localized electrons are formed, (using X-ray and Hall coefficient data) the statistical weights of atoms having stable d^5 - configurations (SWASC) in the metallic crystal has been determined, which are listed in the following table:

TABLE -XI

STATISTICAL WEIGHT OF STABLE ELECTRONIC CONFIGURATIONS OF TRANSITION METALS (WITHOUT CONSIDERING INTERMEDIATE SPECTRA)[6]

Metal	Valence electron configuration in isolated atoms	Statistical weight of configurations %		
		d^0	d^5	d^{10}
Sc	$3d^1\ 4s^2$	84	16	0
Ti	$3d^2\ 4s^2$	57	43	0
V	$3d^3\ 4s^2$	37	63	0
Cr	$3d^5\ 4s^1$	27	73	0
Mn	$3d^5\ 4s^2$	-	63.6°	-
Fe	$3d^6\ 4s^2$	0	54	46
Co	$3d^7\ 4s^2$	0	28	72
Ni	$3d^8\ 4s^2$	0	12	88
Cu	$3d^{10}\ 4s^1$	0	8	92
Y	$3d^1\ 5s^2$	73	27	0
Zr	$4d^2\ 5s^2$	48	52	0
Nb	$4d^4\ 4s^1$	24	76	0
Mo	$4d^5\ 5s^1$	12	88	0
Tc	$4d^6\ 5s^1$	-	84°	-
Ru	$4d^7\ 5s^1$	0	80	20
Rh	$4d^8\ 5s^1$	0	60	40
Pd	$4d^{10}\ 5s^0$	0	18	82
Ag	$4d^{10}\ 5s^1$	0	4	96

La	$5d^1\ 6s^2$	70	30	0
Hf	$5d^2\ 6s^2$	45	55	0
Ta	$5d^3\ 6s^2$	19	81	0
W	$5d^4\ 6s^2$	0	96	4
Re	$5d^5\ 6s^2$	0	94	6
Os	$5d^6\ 6s^2$	0	84	16
Ir	$5d^7\ 6s^2$	0	68	32
Pt	$5d^9\ 6s^1$	0	40	60
Au	$5d^{10} 6s^1$	0	10	90

° Taken as average - for Mn of Cr and Fe; for Tc of Mo and Ru SWASC d^5 values.

The above SWASC values, has been determined according to the formula:

$$P_5 = \frac{q}{5} \cdot 100\ \%$$

$$P_0 = \frac{5-q}{5} \cdot 100\ \%$$

where q is the number of localized electrons. Similarly for metals with $5 < nd < 10$, the SWASC of d^5 and d^{10} configurations is given by:

$$P_5 = \frac{10-q}{5} \cdot 100\%$$

$$P_{10} = \frac{q-5}{5} \cdot 100\%$$

In the case of alkali and alkaline earth metals (s-metals) the tendency is to form stable s^2- configurations.

For the third category of elements i.e. sp-elements, the following features are noticed.

1. The energetically most stable configurations are sp^3 and $s^2 p^6$.

2. The energetic stability of sp- configurations is reduced as we increase the principal quantum number of the valence sp- electrons.

3. Elements whose isolated atoms with s^2p or s^2p^2 valence electron tend to acquire the quasi-stable sp^3 configuration owing to s→p transitions.

4. Elements whose isolated atoms have $s^2 p^3$ configurations (e.g. N, P) owing to s → p transitions by the scheme $s^2 p^3 \rightarrow sp^4 \rightarrow sp^3 + p$, tend to acquire sp^3 configurations with weakly bonded electrons or three additional electrons with transition to the stable $s^2 p^6$ configuation.

5. In elements having $s^2 p^4$ or $s^2 p^5$ configuration, $s^2 p^6$ configuration is formed.

6. When possible , s→p transitions are realised only when such transitions lead to the formation of more stable sp-configurations, otherwise they may be suppressed.

It may be further noticed that while for d - and f - configurations the energetic stability increases with principal quantum number of the valence electrons, the reverse is true for s- and sp- elements. The study of configuration spectrum with variation of temperature has also concluded that the behaviour of d - and f- elements is opposite to that of s- and sp- elements; in the former case with increasein temperature the SWASC d^5 initially increases.

2.4 STABLE ELECTRONIC CONFIGURATION MODEL AND PHASE STABILITY

The occurance of solid solutions and intermediate phases in binary constitutional diagrams of transition metals can be fairly interpreted on the basis of the formation of stable electronic d^5- configurations by component atoms. When elements have similar SWASC values, then during the exchange of electrons between localized and non-localized states, as mentioned above, there is slight possibility of the formation of stable localized configurations in the system and most of the electrons are thus in the non-localized state, giving rise to solid solutions. In compound formation the position is otherwise, i.e. compound formation is favourable when there is large difference between the SWASC values of two component elements.

In accordance with the above generalization, it is found that the solid solubility of transition metals in Yttrium decreases with increasing SWASC of the solute metal atoms having a stable d^5- configuration. Further, in binary systems $Me_1^{IV} - Me_2^{IV}$, $Me_1^{V} - Me_2^{V}$, $Me_1^{VI} - Me_2^{VI}$, upto 16% difference in SWASC, continuous solid solutions are observed and with decrease in this value solid solutions approach to ideality. With a higher SWASC difference than 16% decomposition of solid solution into Sigma - phase is observed. Elements from the same group and belonging to either the 5th or 6th period form, with elements of other groups similar constitutional diagrams, while elements from the same group but belonging to the 4th period, form other types of diagrams. This is because of the fact that difference of d^5 SWASC of 5th and 6th period elements of the same group is significantly smaller than the corresponding differences between elements of the same group in the 4th and 5th periods and in the 4th and 6th periods respectively.

Among transition metal compounds typical examples may be cited from hydrides and carbides. It has been suggested to explain the maximum amount of hydrogen absorbed by the early transition metals of periodic table and its relationship with SWASC, that the donor capacity of various transition metal atoms decreases with increase in the SWASC, which gives rise to lesser probability of forming stable s^2 configurations of hydrogen atoms and consequently lesser degree of hydrogen solubility.

The stable electronic configuration model also adequately explains the nature of refractory carbide phases. Since all the transition metals are donors of valence electrons, their carbide formation can be understood in terms of the transfer of nonlocalized valence electrons so as to stabilize the sp^3- configurations of carbon atoms to different extent. The donor capacity of transition metal decreases with the increase in their valence electron localization , i.e. from III group metals to VI group metals and correspondingly the stabilization of sp^3- configuration of carbon atoms decreases. For the IV group transition metal carbides the stabilization of sp^3- configuration is maximum which makes the Me-C bond stronger incomparison to Me-Me bond. This justifies the availability of only monocarbides in case of Ti, Zr, and Hf, whereas the V group transition metals, in addition to monocarbides, forms semicarbides. Moreover, the homogeneity range in case of IV group metal monocarbides (Tic, Zrc, Hfc) is wider as compared with that of V group transition metal monocarbides (VC, Nbc, TaC).

C_H_A_P_T_E_R - III

TRANSITION - METAL INTERMEDIATE PHASES

3.1 GENERAL:

The intermediate phases in equilibrium diagrams may be formed in two ways. In the first an intermediate phase forms directly during freezing from the liquid through a maximum in the solidus and liquidus curves. The second way in which an intermediate phase may be formed during freezing is by a peritectic reaction between solid and liquid in a partly solidified alloy[12]. The formation of intermediate phases (or solid solutions) is a general process of fitting unlike atoms together on a stable arrangement in space. The equilibrium phase (or phases) is that which gives the lowest possible free energy of the system and the changes in free energy associated with the choice of alternative structures control the equilibrium phase.[4,12]

The intermediate phases are classified into three categories[3,4]: the 'Normal valency compounds' in which the atoms display their normal valencies and the formation of such compounds is governed by normal valency rules; the 'Electron Compounds' in which the appearance of a particular structure requires a particular electron: atom ratio, and no stoichiometry is associated with this type of phases; the 'Size Factor Phases' which are formed by the efficient packing together of atoms of different sizes and are usually associated with well defined stoichiomtric compositions.

It is usually found that several types of atomic interaction are simultaneously involved in a metallic phase, and of course the structure and properties actually assumed depend on the resultant effect. In extreme cases the structure can be understood in terms of one type of interaction only. The great majority of cases are intermediate in character, and although the appearance of a given structure can frequently be correlated with some one property of the atom concerned, e.g. size or valency, it is generally true that the other properties of the atom concerned must not be unfavourable to the formation of the structure. This would imply, for example that for the formation of electron phases the size factor should not be unfavourable and vice-versa .

The present chapter is intended to discuss only in brief some transition metal intermediate phases, namely, Sigma Phases, Chi phases and Laves Phases in binary systems, which will form the part of our discussion of the stability of those phases on the basis of Stable Electronic Configuration model. Sufficient literature, however, is available which deals with the various aspects of the occurrence, stability and structure of various intermediate phases[2-4,13-20].

3.2. SIGMA PHASES

The σ- phase has received much detailed attention, chiefly because of the detrimental effects which the formation of this phase has on the properties of industrial alloys. Precipitation of Sigma phase in some excellent alloys having high temperature strength results in embrittlement.

The Sigma phase has a complex tetragonal structure with $c/a \approx 0.52$ and 30 atoms per unit cell. The majority of Sigma phases is found in systems involving the transition elements of Group V or VI (referred to as the A component) with a transition metal of group VII or VIII (referred to as the B component). Evidence obtained with neutron diffraction suggests that many of the Sigma phases are ordered.[32,3] Significant features of this phase are broad homogeneity ranges and the composition and temperature range of stability are not the same in the different alloy systems. For example, in the Fe-V and Fe-Cr systems the Sigma phase forms from the primary α - solid solution and is stable to room or ordinary temperature; in Co-V system by peritectic reaction and it is stable to room temperature; and in the Nb-Re system by peritectic reaction, but it undergoes an eutectoid decomposition to the primary α-terminal solid solution and to the χ- phase (α-Mn type). In Cr-Fe system which is the best known example of the Sigma phase, it is hard and brittle, nonmagnetic at ordinary temperatures and a poor conductor of electricity. In heat resistant alloys and complex steels the σ-phase may be precipitated owing to faulty compositi control or heat treatment, in a form that confers inferior mechanical properties on the material. Consequently, considerable effort has been devoted to studying the conditions of its formation and various aspects of its mode of precipitation. There are now some forty-five known binary examples of the Sigma phase; the effect of a third element has been investigated in many important systems and in a few ternary systems the Sigma phase is formed where it is not found in the corresponding three binary systems.

This is a clear indication that electronic considerations constitute an important factor in the stabilisation of the Sigma phase. For example, in the Cr-Ni-Mo, Cr-Ni-W, Cr-Ni-Si, and Cr-Ni-P systems the Sigma phase exists in ternary alloys, while no such phase has been found in the Cr-Ni binary system. Similarly, in the binary systems V-Co, V-Ni, V-Fe, Cr-Co, Cr-Ni and Cr-Mn the Sigma phase field is expanded by the addition of Si.[49,50] On the other hand, Al has been shown to have the opposite effect reducing the composition range of Sigma formation, in Fe-Cr, Fe-V and Cr-Co alloys. It has been suggested that these tendencies can be understood in terms of electronic effects: the relatively electronegative Si (and P) increase the tolerance of the Sigma phase for electropositive elements, such as V or Cr, by accepting the additional electrons made available by these elements, while the addition of Al, a relatively electropositive element, increases the electron concentration and thus reduces the available number of V or Cr atoms in the structure. All this evidence supports the point of view that the Sigma phase is essentially an "electron compound". In the Engel-Brewer approach, the Sigma phase is regarded as controlled by the (s+p) electron concentration, which is generally in the range 1.2-1.8; the e/a ratio varies in the range 5.6 to 7.6. A change in the effective valency of a transition metal with a change in the electronic character of the surrounding atoms has been proposed by Brewer[8] and certain anomalies in the calculation of the valencies of transition metals are removed.

However, some authors[4] believe that both the atomic size factor and the electronic factor contribute to the formation and stability of Sigma phases. The importance of size factor is indicated by the observation that the temperature range of stability of some binary Sigma phases decreases as the radius ratio increases and can be increased by the addition of a third component.

The occurrence of Sigma phases in binary systems is summarised diagrammatically in Fig. 4, where each rectangle represents the phase diagram between transition metals of type A and B, and in which the ranges of Sigma phase formation are shown. It is most significant that the phase does not occur in all cases at the same approximate composition, but in general, for phases having the same A elements (from Group V or Group VI) in a number of A-B systems , the

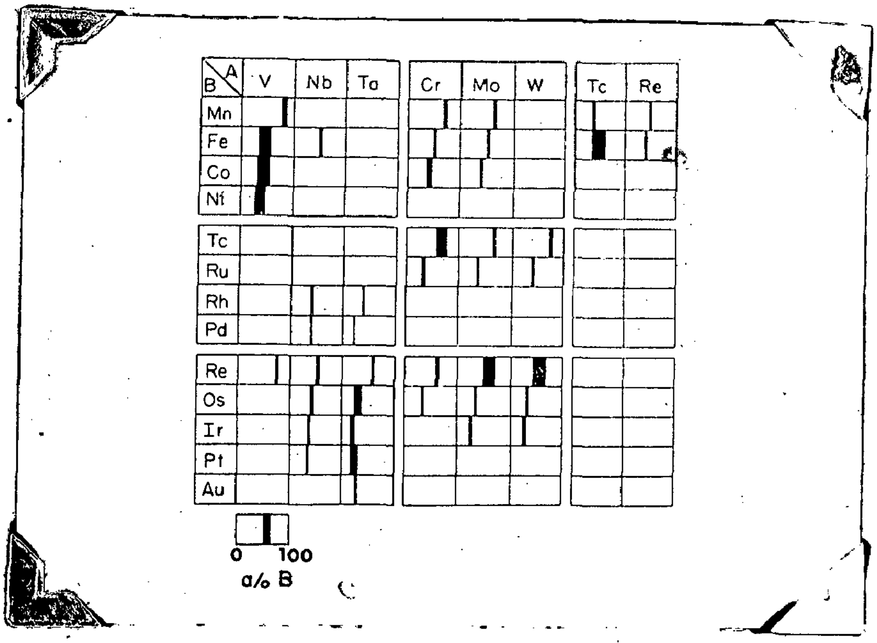


Fig.4. Occurrence and ranges of stability of Sigma phases in binary systems of transition metals.

composition shift towards A as the number of electrons outside filled shells (or Group Number) increases in the B elements (from group VII or VIII). This tendency is well illustrated in the above Figure and indicates the extent to which electronic factors control the formation of Sigma phase. The binary transition-metal systems where the Sigma phase occurs, are listed in the Appendix-I, indicating the composition ranges, R_A/R_B and electron ratios and the temperatures of their occurrence.

3.3. CHI PHASES

This intermediate phase is isomorphous with α - Mn, and is now known to occur in 17 binary systems of transition metals. All but two of the systems involve technetium or rhenium from the Mn group as the B component; in the remaining two phases Os is the B component. In every case the A component is from the IIIA to VIA transition Metal groups. These binary Chi phases are listed in Appendix-II.

The compositions of the various Chi phases also exhibit systematic shifts which depend upon the positions of the components in the periodic table. Paralleling the pattern observed for Sigma phase, the composition range of stability of phases having the same A component shifts to higher A concentration as the group number (number of electrons outside of filled shells) of the B component increases, as can be seen, for example, in the sequence

Nb-Tc, Nb-Re, Nb - Os. The effect of Si in stabilizing the χ-structure is parallel to the effect on the Sigma phase and presumably the stabilizing mechanism operates for the same reason. In ternary Chi phases the A component follows the same pattern as in binary alloys, while the other two components act together as B-type atoms.

Thus, there is strong evidence that electronic factors play a part in determining the stability of the Chi phases, the electron concentration over which the structure is table ranging from 6.3 to 7.0, as clear from the table for alloys of Tc, Re ~~and Os~~, which is much smaller than the corresponding range for σ-phase stability. This demonstrates the limited applicability of the simple criterion of average electron concentration in correlating the occurance of this and other related structure types. The radius ratio values for binary systems given in Appendix-II lie in the range of 1.017-1.207 and indeed size effects may well be an important feature of Chi-phase formation, since the A component is always from 2 to 20% larger than the B component and certain absences of Chi phases can be correlated with a failure to fulfill this condition.

Therefore, it may be concluded that both electronic structure and atomic size factor govern the occurance of Chi-phases. The former seems to be responsible for introducing a selectivity in the choice of A and B components and a systematic composition shift similar to that observed for sigma phases. The latter through its effect on space filling, may influence the extent to which the χ-phase can favourably compete for stability with other intermediate phases.

Closely related to the Sigma and Chi phases are the complex P, R, μ (Mu) and δ (delta) phases and for their study the reader may consult the work of Nevitt[2] or Hume-Rothery et.al[4].

3.4 LAVES PHASES

Many intermediate phases possess one of the following three related structures of general formula AB_2, exemplified by the three prototype structures based on magnesium[14]:

a) $MgCu_2$: the C15 structure, Cubic, with packing
ABC ABC ABC;

b) $MgZn_2$: the C14 structure, hexagonal, with packing of planes of atoms represented by the general sequence ABABAB, etc;

c) $MgNi_2$: the C36 structure, hexagonal, with packing ABACABAC.

Much of the original work on these structures is due to Laves and his associates. For this reason the whole group of these related phases are frequently called the Laves phases.

A large number of compounds are isostructural with the above Mg-compounds. Of the 223 binary Laves phases reviewed by Nevitt[2], 210 have a transition metal for atleast one of the components, 162 have the Mg Cu$_2$- type structure, 67 the hexagonal Mg Zn$_2$ type and only 4 the hexagonal MgNi$_2$-type structure[2,3]. Usually the MgNi$_2$ type is formed in ternary alloys.

The above structures involve a special partnership between larger (A) and smaller (B) atoms and they have certain geometrical features in common[3,4,16] that can be best illustrated diagrammatically. The lattices of the larger A atoms are constructed from double layers with hexagonal network, with each A atom of the upper layer directly above one in the lower layer. The Mg atoms represent the A atoms in the three prototype structures. For the Mg Cu$_2$ structure a portion of each hexagonal double layer is illustrated in fig.6(a), and the three double layers are labeled X, Y and Z. The first double layer is represented by the eight atoms in X position and the second double layer is represented by the two atoms in Y position, it is identical with the first but is shifted laterally. The third layer is again displaced laterally. The resulting sequence may be described as XYZXYZ ---.Fig.6(b) and 6(c) shows that in the same description the MgZn$_2$ and Mg Ni$_2$ structures will be represented by the XYXYXY ..... and XYXZXYXZ.....stacking of the larger Mg atoms respectively.

The smaller B atoms of the other metals are grouped

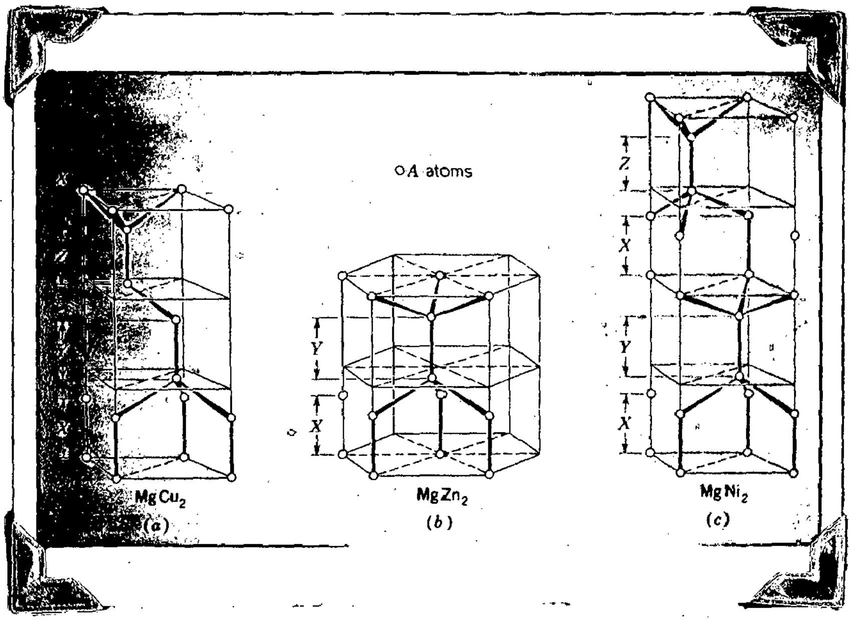


Fig.5. Distribution of A atoms and stacking of double layers in Laves phases.

around the Mg atoms in tetrahedral scheme that differ somewhat in the three types of structure. This is illustrated in Fig.6. In the $MgCu_2$ structure the Cu atoms lie at the corners of the tetrahedra which are in contact and arranged into a network as shown in fig.6(a) . The larger Mg atoms lie in the holes between the tetrahedra formed by the Cu atoms. The pattern of the tetrahedra in the $MgCu_2$ structure is such that the A atoms in this description may be shown to lie on a cubic lattice. The hexagonal arrangement of double layers is analogous to Zinc blende type of structure.

In the $MgZn_2$ type of structure the smaller B atoms (or Zn) are again arranged into tetrahedra but these are now joined alternately base-to- base and corner- to-corner as shown in fig.6(b). In this arrangement the A atoms, fitted between the tetrahedra, now occupy a wurtzite-type lattice. The arrangement of tetrahedra in the $Mg\,Ni_2$ structure represents a mixture of the other two arrangements (fig.6(c)) , and the A atoms can be described as being located on a lattice corresponding to a mixture of diamond cubic (or Zinc blende) and wurtzite type structures.

It is believed that the main reason for the existence of Laves phases is of geometrical origin - that of filling space in a convenient way[3,14] . The examination of a large number of Laves phases shows that a determining factor in the formation of these phases is the relative atomic size of the constituent atoms because they may come from any part

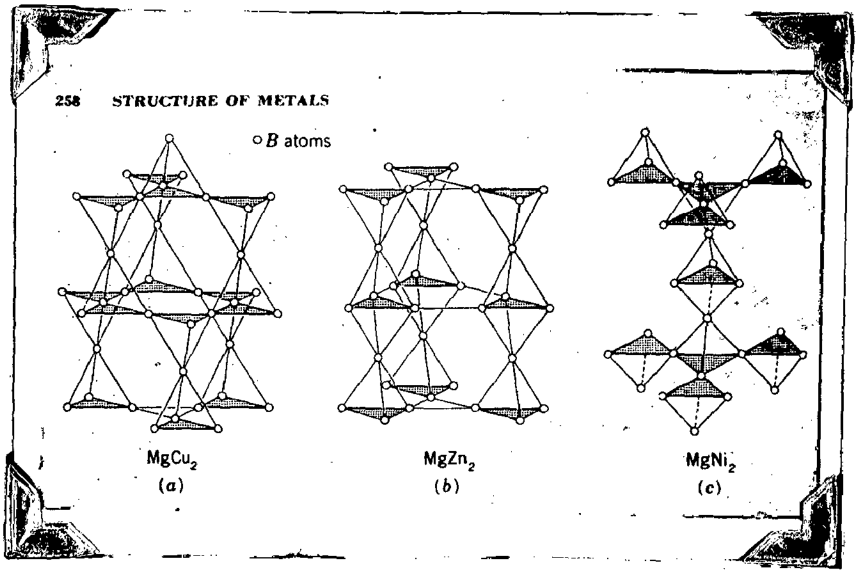


Fig.6. Distribution of B atoms and stacking of tetrahedra in Laves phases.

of the Periodic Table and the A atom in one compound may be the B atom in another. On the basis of a hard sphere packing model, the ideal ratio of the atomic diameters, d_A/d_B, for the formation of the Laves phases is $(3/2)^{1/2}$ or 1.225. Nevertheless, the ratios of the radii (or diameters) do not always seem to correspond to the most ideal packing and in many of the observed phases they deviate within a range of 1.05 to 1.68 and because of this geometrical requirement, homogeneity ranges in these compounds are generally small[2,3,4]. It is to be noted that in all cases the A component is larger in size than the B component. It has been suggested that the radii of the pure elements are not an important factor in indicating which of the three structures form, it is only necessary that the A atom be larger than the B atom and that they be able to contract or expand to achieve nearly the ideal ratio of 1.225.

Although the atomic size factor is important in the formation and stability of the Laves phases, electronic influences appear to play an important role. For example, Laves and Witte[42] have shown that the electron concentration determines which of the three structures form in the pseudo-binary systems of $Mg\,Cu_2$ and $MgZn_2$ with Al, Ag and Si. With increasing electron concentration one or more of the Laves phases are formed in the order $MgCu_2$, $Mg\,Ni_2$ and $MgZn_2$ structures[4,14].

If the size factor were the only requirement governing the existence of Laves phases, such phases would be expected for the stoichiometric compositions HfCu$_2$, Hf Ni$_2$, Mo Co$_2$, MoNi$_2$, NbNi$_2$, TaCu$_2$, TaNi$_2$, TiCu$_2$, TiNi$_2$, WCo$_2$, WCu$_2$, WNi$_2$, ZrCu$_2$ and ZnNi$_2$, all of which have a diameter ratio within the prescribed range. The non-existence of Laves phases at such compositions is further indication that something else such as electronic concentration is important[16]. The same conclusion is drawn when it is found that there are, for example, 46 combinations of Sc group elements (including the lanthanide series) with Cu group elements whose radius ratios lie between 1.11 and 1.62, but none forms a Laves phase[2]. Furthermore, the appearance of ternary Laves phases on addition of Si where no such phases formed in binary systems, again indicate a strong influence of the electronic effect on the stabilization of Laves phases[49-51].

Elliott and Rostoker[16] have based an analysis of the periodic variation of the occurrence and the crystal structure of the Laves phases in various transition metal systems on the assumption that Brillouin zone overlaps govern the structure type. In their model, Laves phases do not occur at an electron concentration below about 1.4 electrons per atom. At electron concentrations between 1.4 and 1.8 electrons per atom the MgCu$_2$ type is stable. The MgZn$_2$ occurs at electron concentration between 1.8 and 2.32 electrons per atom, while the MgCu$_2$ type again enjoys stability when electron: atom ratio exceeds 2.32. These stability ranges of binary Laves phases with Ti and Zr are

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shown in fig.7. The Laves phases formed by transition metals are listed in Appendix -III.

The Laves phases in rare earth elements are discussed by Mc Masters and Gschneidner[43]. These are listed in Appendix- It is observed that the rare earths always behave as the A element (the larger size partner). The B partner (smaller atoms) is seen to be Mn, Fe,Co,Ni and their cogeners and Mg and Al. For the B element families of Mn, Fe, Co and possibly Ni, no Laves phases are formed by the first few members of the rare earth series. For Mn the first Laves phase formed is $GdMn_2$ and for Fe the $LaFe_2$ and $PrFe_2$ and $NdFe_2$ phases do not form but $CeFe_2$ and $SmFe_2$ do form . The existance and non-existance of Laves phases for these B metals are quite interesting. If size were the only factor influencing this situation, then one would expect to find that when the radius ratio for two elements became greater than a certain critical value no Laves phase would form, and below this value they will form. A plot of radius ratios of the known and the known-non-existent rare earth manganese, Iron, - Cobalt, Nickel and the ternary rare earth-manganese, iron Laves compounds VS the B-Metal radius (i.e. r_R/r_M VS r_M Plot) is found to exhibit a curved 'critical radius ratio line' separating the two regions. It is pointed out that if only a size effect were operative one would expect a horizontal line, but the existence of a curved line indicates

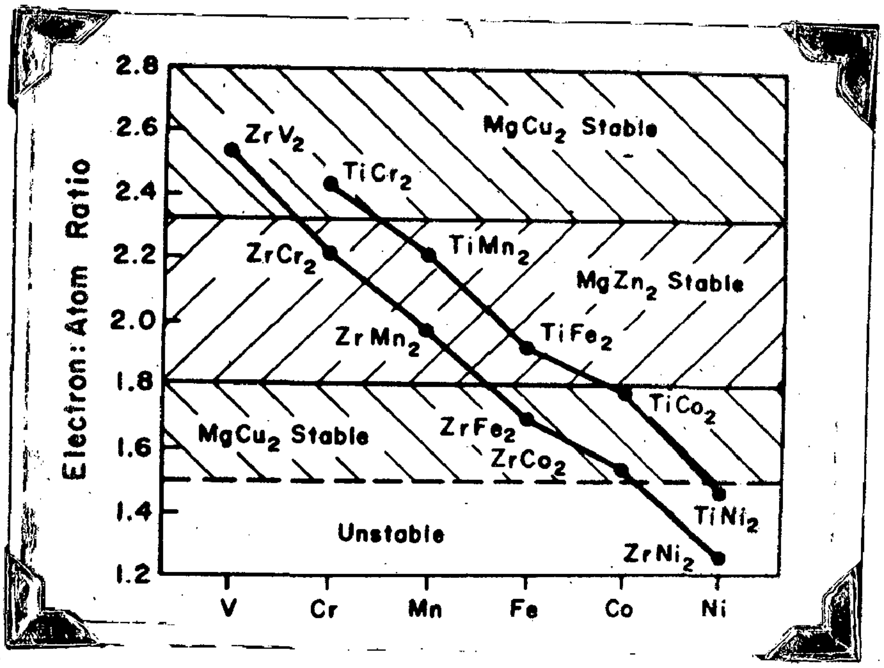


Fig.7. Stability ranges of binary titanium- and zirconium- Laves phases.

that the electron concentration effects also play an important role in determining the existence or non-existence of these phases.

Wernick and Co-workers[44] have suggested that the change in structure from $MgCu_2$-Cubic to $MgZn_2$-hexagonal for RMn_2 compounds which occurs at $ErMn_2$ is due to the filling of the Brillouin zone because of electron transfer from Mn to rare earths, which increases as we proceed along the rare earth series, giving rise to an additional decrease in the lattice constant. However, for other compounds it is not as clear as for the RMn_2 compounds.

Dwight[45] has discussed the formation of Laves phases composed of elements of I, II and III long periods as B elements. He shows that the crystal structure of the Laves phase is related to the positions of partners in periodic table and these relationships can be utilised to predict the structural relations in unknown binary, ternary and some quarternary systems.

3.6 SCOPE OF THE PRESENT WORK

During the last few years attempts have been continuously going on to arrive at some unified approach in dealing with the complex problem of alloy chemistry of metals, particularly of transition metals. Though, the theoretical Band Model satisfactorily explains some physical properties but it is unable to explain completely the stability of alloy phases in metals.

The experimental results obtained by early workers, mainly Hume-Rothery and his associates led to the proposal that the three main factors viz. electronegativity, size and electronic concentration factors, determine the structure and stability of phases. No doubt, the influence of electronegativity and size factor is well evident in certain cases, but from a detailed study of the alloy chemistry of transition metal and rare-earth elements, it is even more clearly revealed that the majority of workers in this field recognize the general importance of the electronic factor.[2,3,46,48]

The purpose of the present work is to provide a brief review of our present state of knowledge about the electronic structure of transition metals and the stability of some of their intermediate phases. Moreover, it is hoped that the present work will be able to offer a new approach for the treatment of the complex problem of the stability of intermediate phases so as to be helpful in the search of a unified approach for the alloy chemistry of metals. The treatment is based on the Electronic configuration Model proposed by Samsonov. The three phases, namely , Sigma Chi and Laves phases are selected only because more data are available in their case and also because they have been the subject of much discussion in the literature. Furthermore, the importance of electronic factor in all the three selected phases is well evident, which make them suitable for the discussion regarding their formations and stability in terms of the electronic configurations.

CHAPTER IV

DISCUSSION

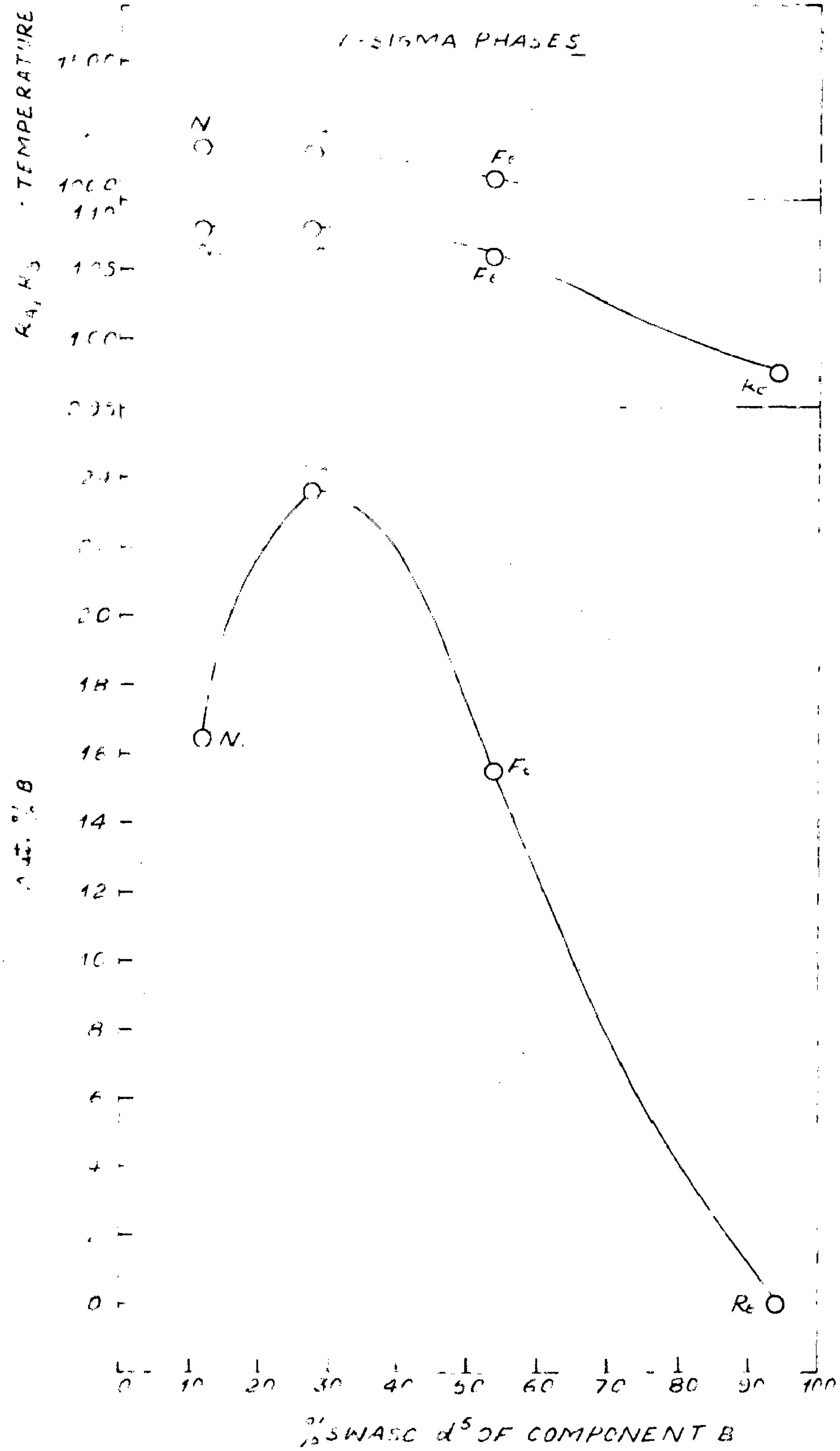
The term 'electron phase' may also be applied with some justification to intermediate phases other than those based on the noble metals. It is increasingly evident, for example, that the Sigma phase possesses features of an electron phase and so do also other variable composition phases such as Chi, Mu, P and R, based on transition elements. Since the d electrons in the transition element unquestionably contribute to e/a in the formation of these phases, the details of possible electronic interactions in the transition metal intermediate phases are bound to be complex.

The Laves phases present a particularly interesting and difficult problem. They were originally thought to be size factor compounds with radius ratio near to that of the ideal value 1.225. Further investigation have, however, shown that they may be formed with radius ratios far removed from the ideal and several authors[2,48] have suggested that it is no longer justifiable to regard them as size factor compounds. In some cases the electron cloud pattern may be sufficiently deformable for the atoms to be regarded as being expanded or compressed so as to fit a structure based on the ideal framework. In other cases changes in valency may be assumed to account for the changes in size, but it is difficult to see that is happening[48]. In some cases the Laves phases are connected with electron concentration or Average Group Number (AGN). In the case of Sigma, Chi phases, and their related structures the connection with e/a or AGN is very clear.

Although the average electronic concentration is useful as a general index of electronic factors, but so far the position is not altogether fully established. This is because of our lack of knowledge of the exact electronic state and the detailed electronic interactions during the formation of alloy phases. However, the recent theory proposed by Samsonov for the electronic structure of elements, makes it desirable to have a new look into the problem of phase stability in intermediate phases. It is in this light that the Sigma, Chi and Laves phases in transition elements including rare earths will be discussed separately.

4.1 SIGMA PHASE

In literature most of the data on Sigma phases of transition metals belonging to group VA and VIA metals are available . In appendix I the data relating the radius ratio of the components R_A/R_B (where A is group VA or VIA metal), temperature of phase transition and the homogeneity range are grouped. In figures 8 to 13, plots are made of above mentioned parameters with respect to SWASC d^5 of the component B. A comparative view reveals that the plots corresponding to elements of Ist long period with V and Cr are very much similar in nature (fig.8 and 11).


SIGMA PHASES
TEMPERATURE
N
Fe
Fe
Kc
N.
Fe
Re
20
18
16
14
12
10
8
6
0
0
10
20
30
40
50
60
70
80
90
100
% SWASC d⁵ OF COMPONENT B

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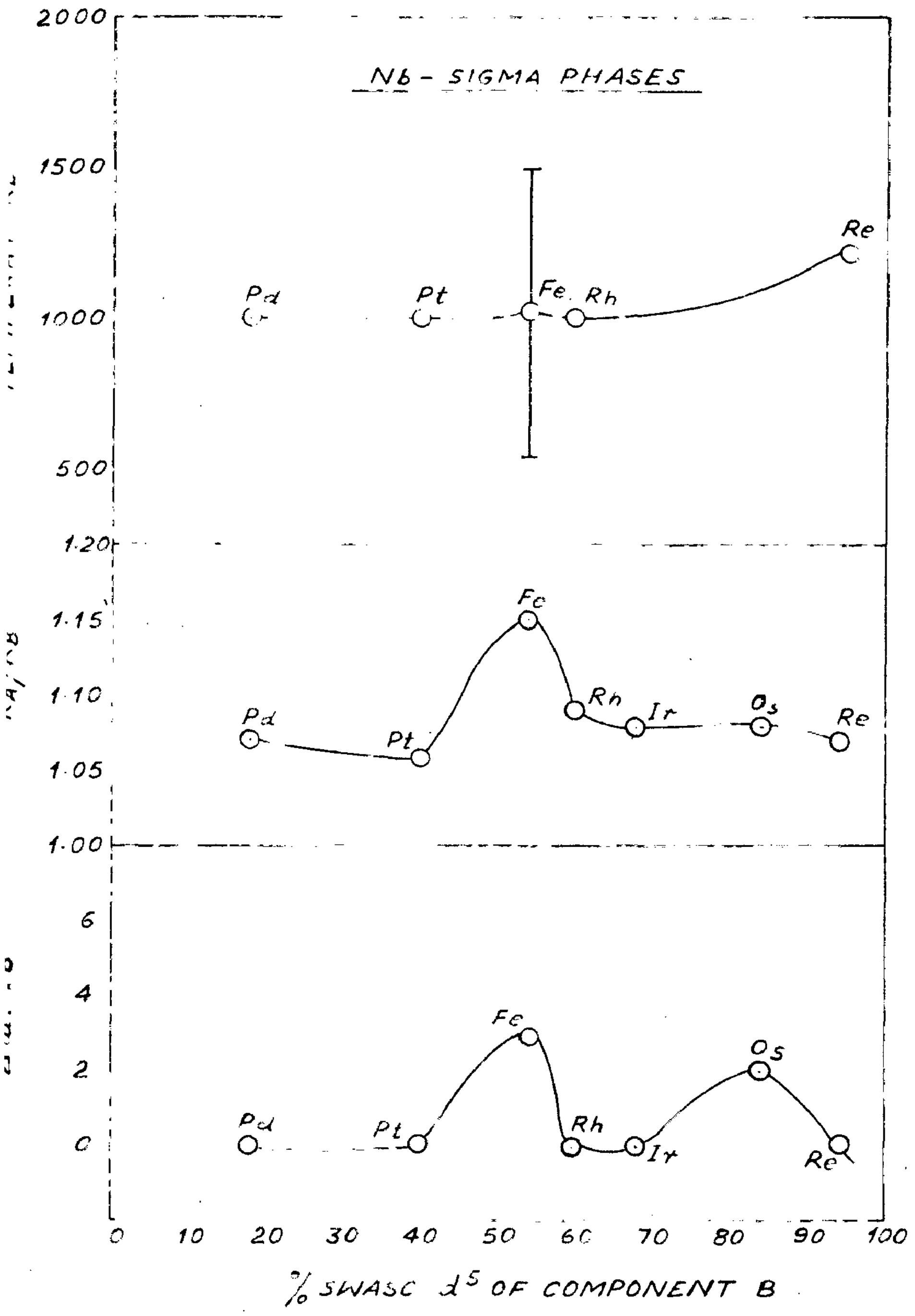
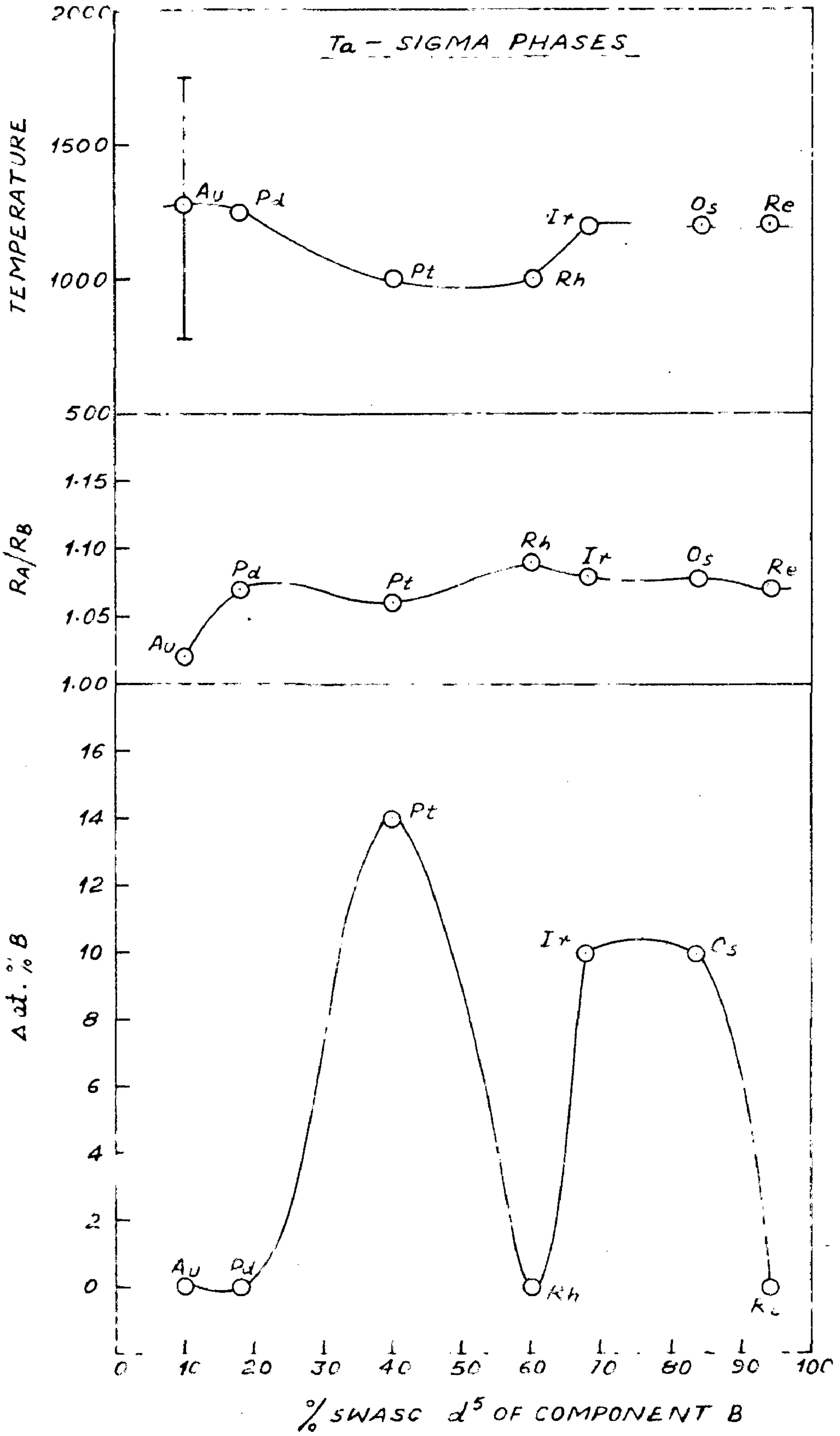


Fig. 9 Variation of phase transition temperature, radius ratio and homogeneity range of sigma phases among Nb-alloys with respect to % SWASC d^5 of component B



[illegible] Variation of [illegible] temperature, [illegible] ratio and homogeneity [illegible] sigma phases [illegible] with [illegible] of component B

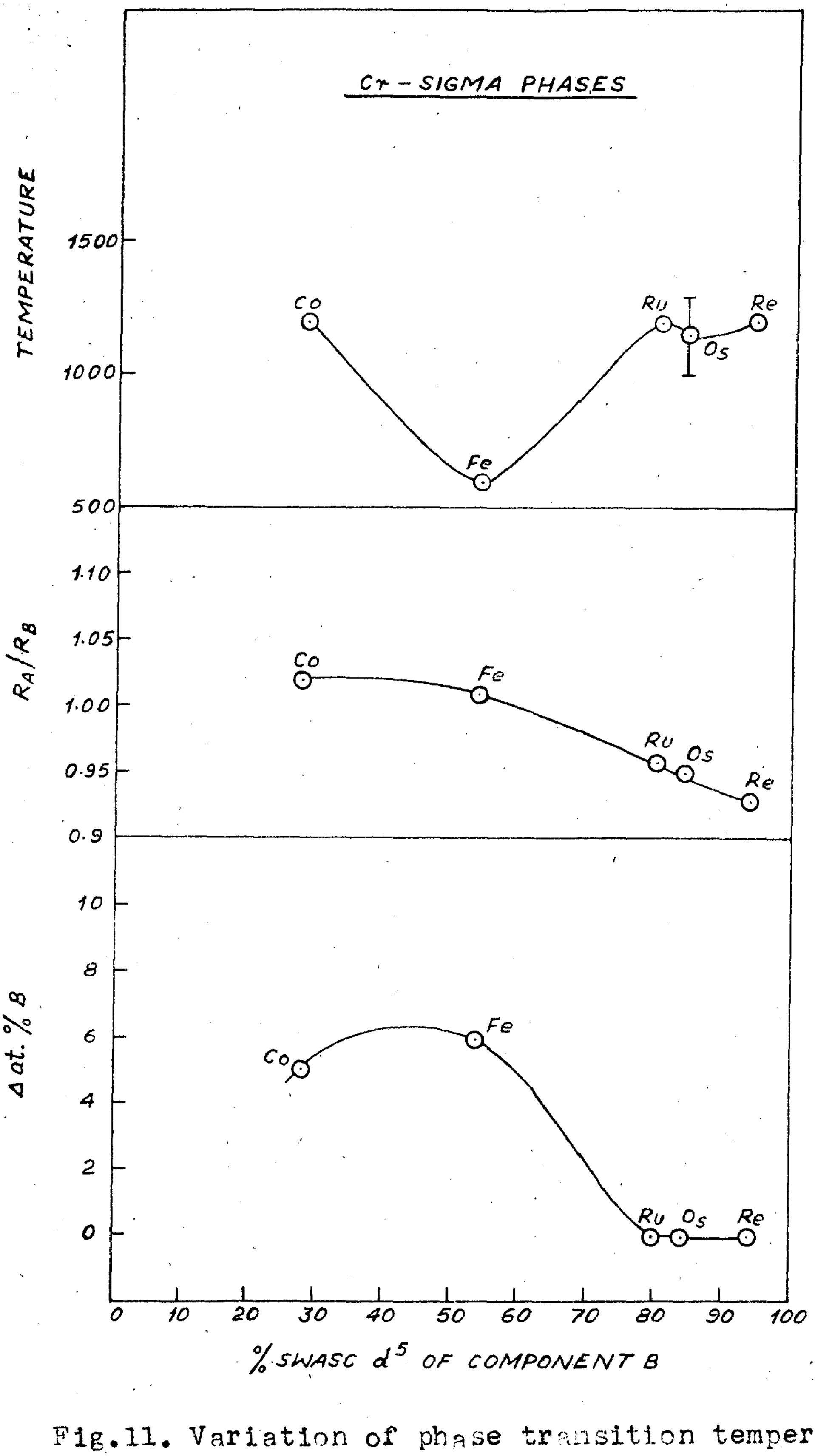


Fig.11. Variation of phase transition temperature, radius ratio and homogeneity range of Sigma phases among Cr-alloys with respect to % SWASC d^5 of component B.

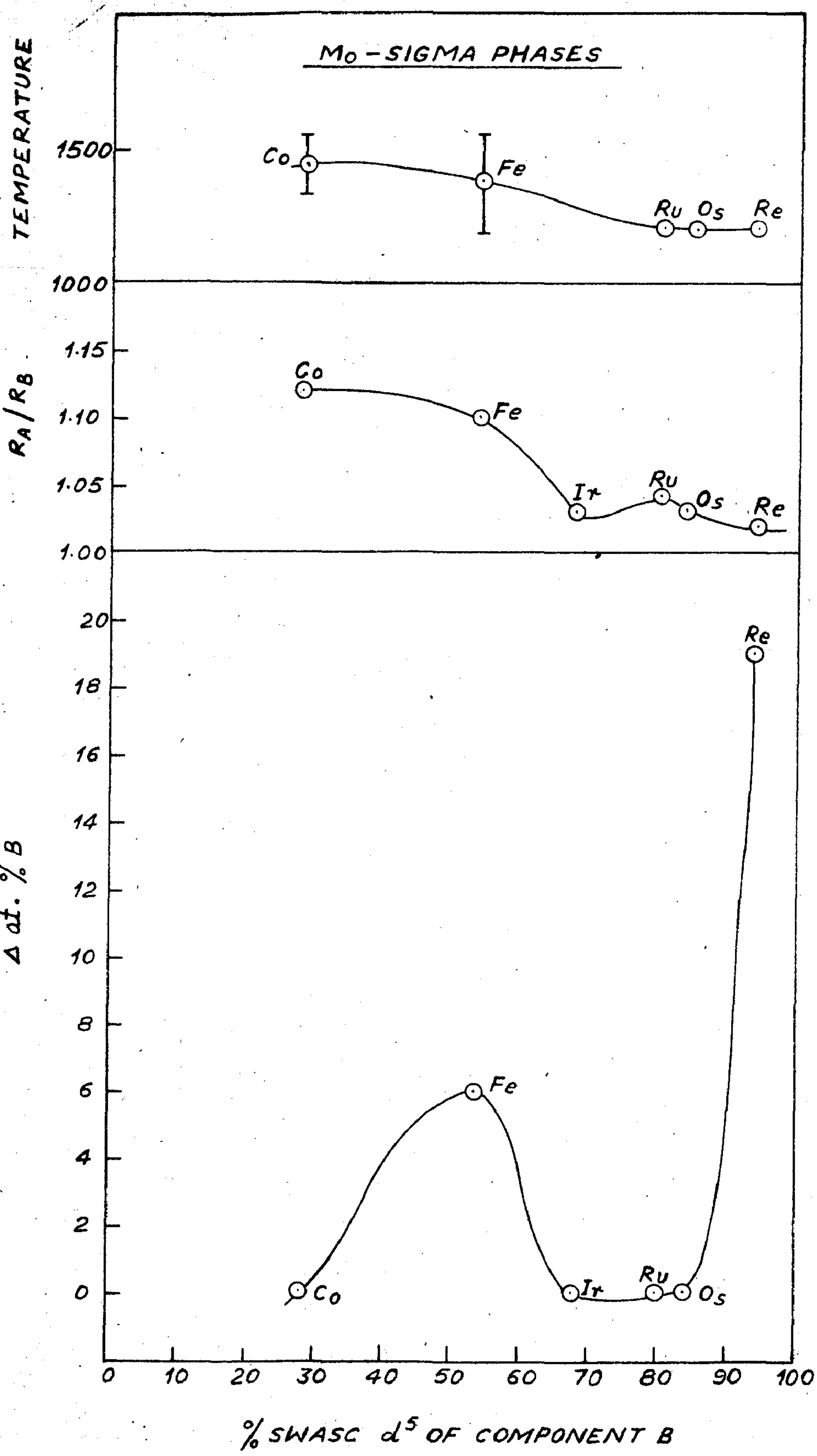


Fig.12. Variation of phase transition temperature, radius ratio and homogeneity range of Sigma phases among Mo alloys with respect to % SWASC ~~of~~ d^5 of component B.

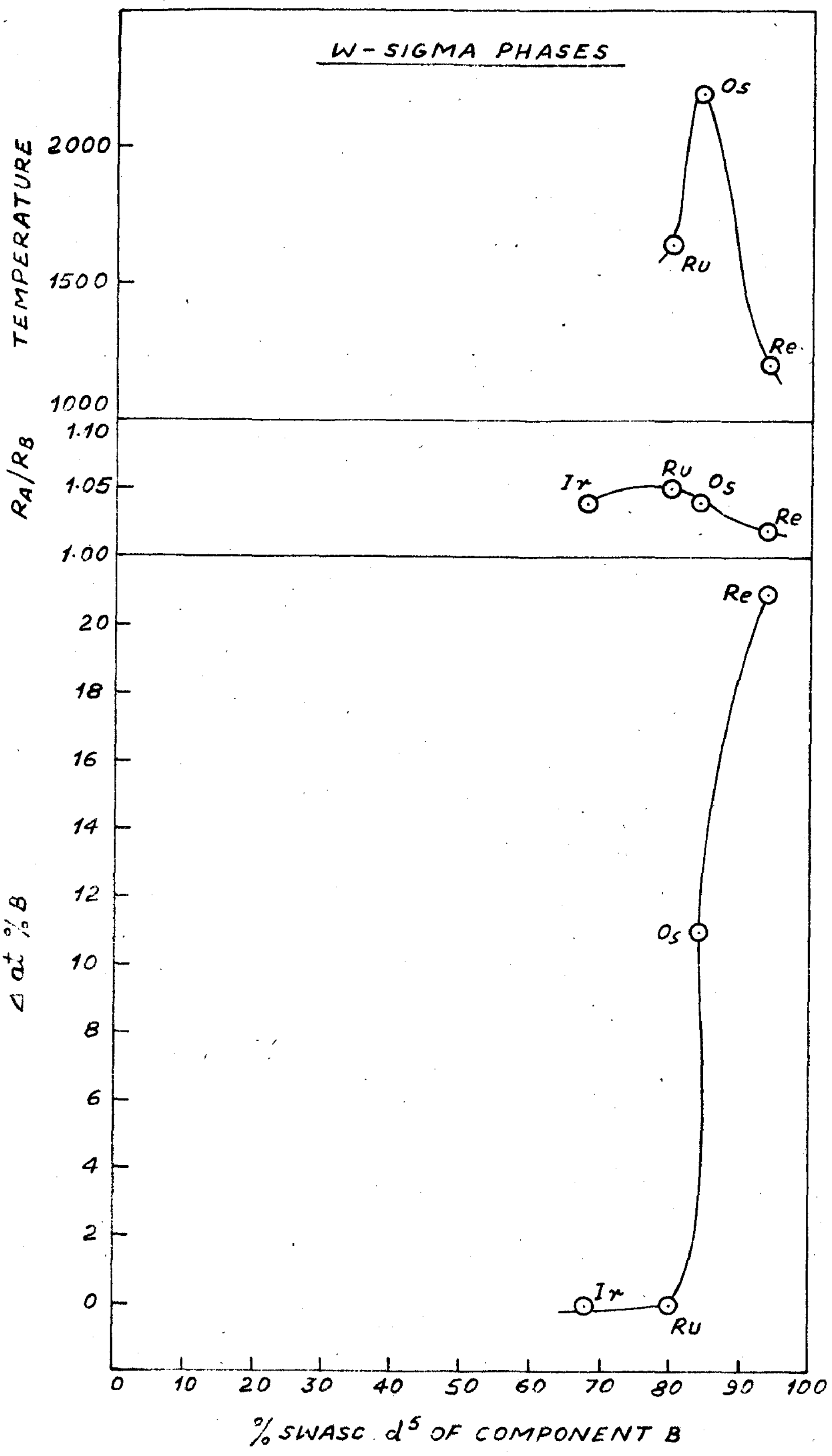


Fig.13. Variation of phase transition temperature, radius ratio and homogeneity range of Sigma phases among W-alloys with respect to % SWASC d^5 of component B.

whereas in remaining long periods the similarity is not present. This is quite evident from the fact that the difference in SWASC d^5 values between V and Cr is merely 10 whereas a similar difference between V and Nb is more (13%) while in case of V and Ta the difference still rises (18%). The similarity of plots between Nb and Ta -Sigma phases (fig.9 and 10) and Mo and W-Sigma phases (fig.12 and 13), is also very well justified on the above argument i.e. the difference of SWASC d^5 between Nb and Mo (12%) is more than that of Nb and Ta (5%). Similarly the difference in SWASC d^5 in Ta and W (16%) is more than that between Mo and W (8%). The net result emerges that lesser the difference in SWASC d^5 between two transition metals the higher is the similarity in their nature of Sigma phase formation.

If we compare in detail the plots of V and Cr-Sigma phases we find that with increase of SWASC d^5 of component B, there is a progressive decreament in R_A/R_B ratio and also in most of the cases a decreament in the transition temperature. Although, in case of V Sigma phases we still do not have complete data of various other possible phases, but the general tendency suggests presence of a maximum in the plot of homogeneity range (Δ at % B VS % SWASC d^5). In case of V this corresponds to cobalt, whereas in case of Cr this corresponds to iron. In other words in case of those A components where, for example, the SWASC d5 is less and the B component having a similar lesser SWASC d^5 value is sufficing to form a Sigma phase having large homogeneity range. In case of Cr — Fe Sigma phase it is found out that the homogeneity range is less than in case of V — Fe Sigma phase. This is quite natural since the difference in SWASC d^5 in former case is large as compared to the latter. A second similarity in the plot is the fact that after 50% SWASC d^5, there is a tendency to form intermetallic compound with no homogeneity range. A careful comparision of transition temperature plot with that of homogeneity range plot gives an indication that these are opposite in nature. This is quite logical since in such Sigma phases where homogeneity ~~range,~~ range is large the probability of cavalent or other electrochemical bonds is less and thus the transition temperature is lower than those of typical stoichiometric Sigma phases.

A comparision of Sigma phase formations in Nb and Ta alloys reveals some very interesting features. If we compare the plots of homogeneity range in each set of system, we find the presence of two maxima, i.e. two series of alloys possessing some homogeneity range whereas the remaining have none. This might indicate that in such cases an exchange between two consecutive stable d configurations are playing their roles, which might cause the scattering of non-localized or collective electrons. The reason why such features are not observed in case of V and Cr Sigma phases is not very clear. However, it should also be kept in mind that in these two series of

Sigma phases, yet data are not available for all sets of Sigma phases.

Coming to the plots corresponding to Mo and W Sigma phases, there is a departure of the relationship as observed in the previous plots. For example, Re presents a very interesting case, in both the Sigma phase series there is a large homogeneity range. However, if we compare very carefully we observe that Mo with Os does not possesses any homogeneity range whereas W with Os has some (11 at % Os). Similarly , the homogeneity range of W-Re Sigma phase is larger than Mo-Re Sigma phase. This peculiarity seems to arise from the fact that in these Sigma phases both the components possess a fairly large SWASC d^5 %, thus neither acting as donor of their non-localized electrons. In other words both are indifferent to each other, thus making it possible to have a larger homogeneity range. Since the SWASC d^5 difference between Mo and Re (6%) is more than that between W and Re (2%), it is but natural that in the former case the homogeneity range is smaller than in the latter. A similar argument can be put forth for W-OS Sigma phase. However in case of Mo-Os Sigma phase the homogeneity range should be greate than former one. But the data in literature does not suggests like wise and an intensive experimental findings may be recommended for the Mo-Os homogeneity range value.

In conclusion, one can undoubtedly say that the role of Stable Electronic configuration model is a positive one in predicting the occurrance and stability of Sigma phases among transition metals.

4.2 CHI PHASES

An exhaustive search in the literature has given information for only two sets of Chi phases, one technetium base and the other rhenium base alloys with other transition elements (Appendix -II). Figures 14,15 shows the plots of RA/RB (where B is Tc or Re and A is other transition element) and the homogeneity range of such phases with respect to % SWASC d^5 of A component. The RA/RB plot and the homogeneity range plot for either set of Chi phases show opposite character i.e. in case where RA/RB ratio is maximum, homogeneity range is minimum. As already discussed previously in the treatment of Sigma phases there is an overall decreament in RA/RB with increase of SWASC d^5 of A component. This is due to the fact that with increase of SWASC d^5 of A component the radius ratio starts evening out. Another interesting feature is that between the ranges 0 to 50 and 50-100% SWASC d^5 of A component, in both the figures there is an appearance of maximum. But A components for which these maxima appear are different. For example, in case of Tc-base Chi phases, these are at Ti and Hf whereas in case of Re base Chi phases these are at Zr and Nb. The appearance of an appreciable extent of homogeneity range at such SWASC values could be explained on the fact that an exchange might be taking place between two consecutive stable d^0 and d^5 - configurations in the environment of Tc or Re atoms which might be attributing in the scattering of nonlocalized or collective electrons. Due to this exchange process the very process of

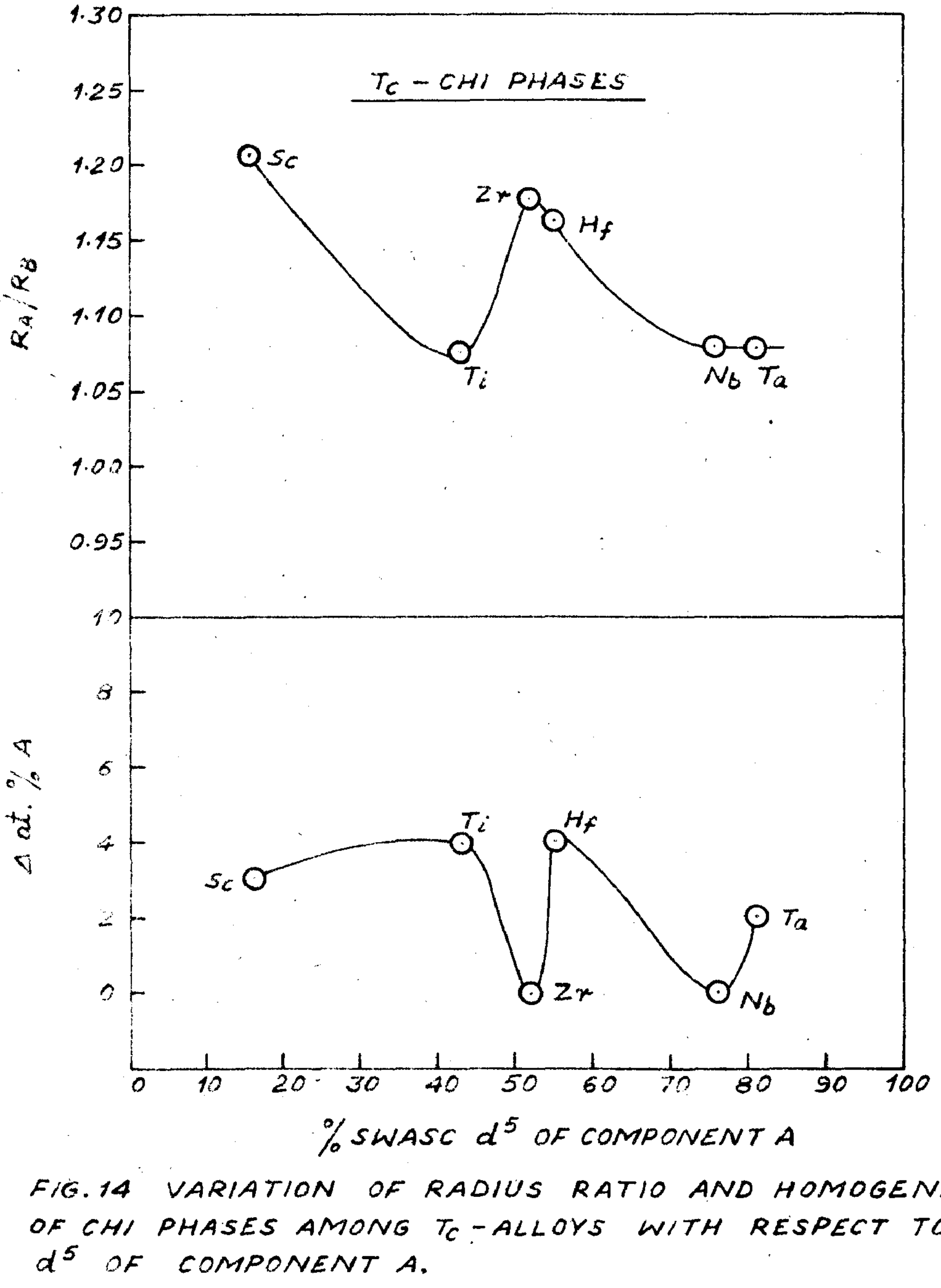


FIG. 14 VARIATION OF RADIUS RATIO AND HOMOGENEITY RANGE OF CHI PHASES AMONG Tc-ALLOYS WITH RESPECT TO % SWASC d^5 OF COMPONENT A.

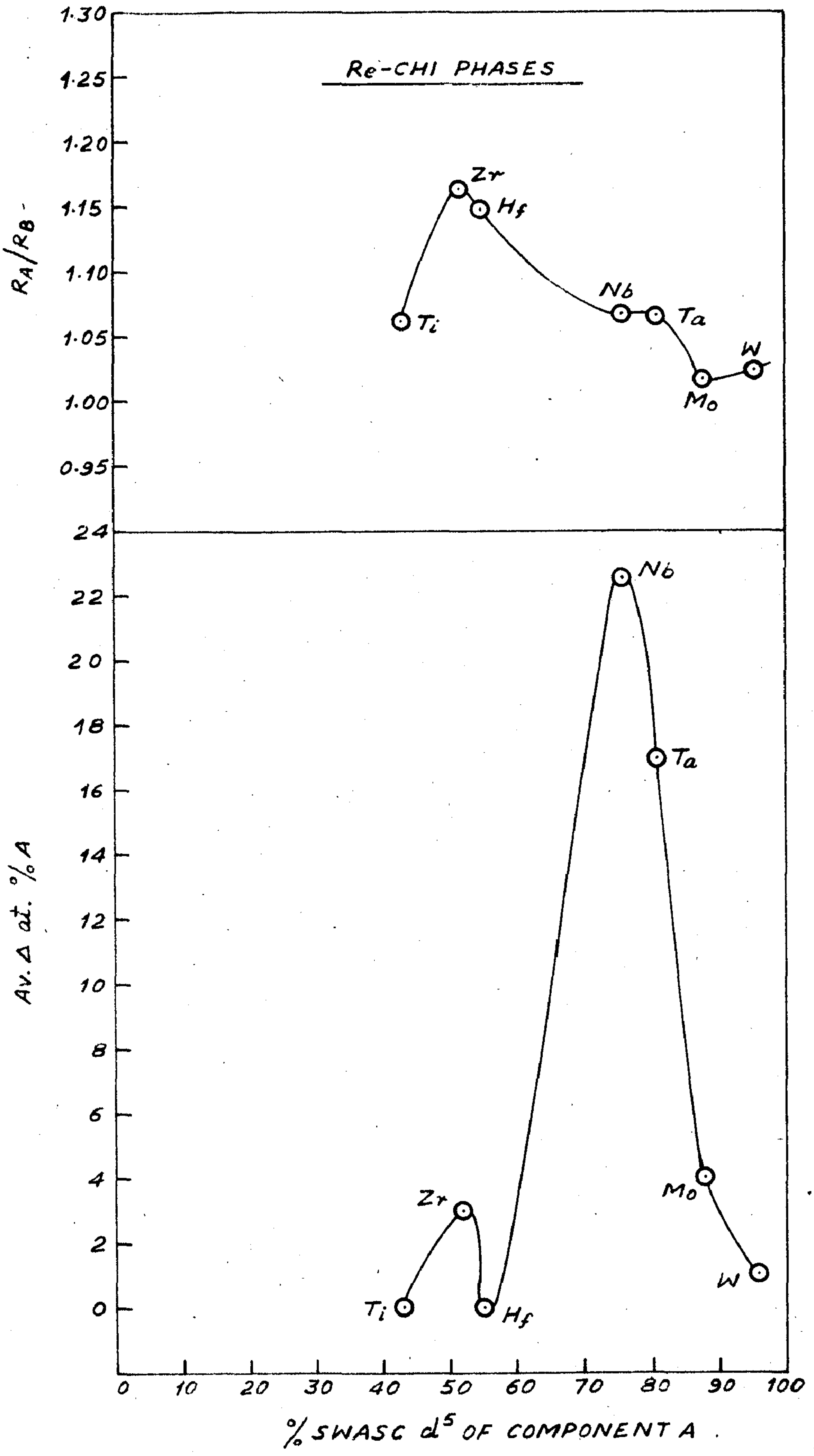


FIG. 15 VARIATION OF RADIUS RATIO AND HOMOGENEITY RANGE OF CHI-PHASES AMONG Re-ALLOYS WITH RESPECT TO % SWASC d^5 OF COMPONENT A.

donation of nonlocalized electrons to Tc or Re atoms is discouraged, thus the possibility of an in-termediate phase with larger homogeneity ranges is more. However at the same time, it should be clearly borne in mind that it is not only the total number of valency (d+s) electrons of transition metals, which matters but still important is the energetic stability of these electrons. For example in Re-base Chi phase, if the maximum is at Zr in case of Tc base alloys, this is at Ti. In conclusion we may say that electronic features of component elements in Chi phases are playing their role both in radius ratio, as well as homogeneity range. Our treatment had been a qualitative one and thus presents before us only a comparative picture between sets of Chi phases formed among transition elements.

4.3 LAVES PHASES

Recently Samsonov and Sinelnikova[52] have discussed in generalities the occurrence of Laves phases in terms of the formation of stable electronic configurations by the components. They proposed that during the formation of Laves phases with a component belonging to s-element, there is a tendency of s→p transition which tries to form stable electronic configuration of the partner element. For example, in $Mg\ Cu_2$ the scheme may be as follows:

$$\begin{tikzcd}
\text{A element: Mg -} & s^2 \arrow[r] & sp \arrow[r] & sp^3 \\
\text{B element: 2(Cu)-} & 2d^{10} \,\vdots\, 2s^1 \,\vdots \arrow[urr] \arrow[rr] & & 2d^{10}
\end{tikzcd}$$

As a result of this two stable electronic configurations sp^3 and d^{10} are formed. However, in some cases, for example, in case of $CaAl_2$ the electronic transfer may be opposite one i.e. atom A transferring their electrons to B atoms. In either case the conclusion emerges that there is a formation of stable electronic configuration.

In case of transition metal Laves phases a similar picture of stable electronic configuration may be viewed. For example, in $CeNi_2$ phase, where Ce has configuration f^2s^2 and Ni the d^8s^2; the configuration d^8 of Ni is more stable than that of Cerium with the result that Ce donates its electrons to Ni. Thus two stable configurations f^0 and d^{10} are formed in the present phase. Another example may be cited $ZrZn_2$ compound (Zn-$d^{10}s^2$, Zr-d^4s^2), where Zn atoms donate their valency electrons to the Zr atoms, thus forming two stable configurations d^5 and d^{10} in the system.

The following table shows examples of Laves phases where the radius ratios are near to that of ideal i.e. 1.23. In the same table the stable electronic configurations of isolated partners and of the system as a whole are indicated.

TABLE - III

Electronic Configuration of atoms in some Laves phases with ideal RA/RB i.e. 1.225 (Ref. 52).

Compound AB_2	RA/RB	Lattice Structure (crystal)	Electronic configurations of isolated atoms	Resultant stable configurations
KNa_2	1.23	hexagonal	$s^1 - s^1$	s^2
$ZrCr_2$	1.25	Cubic	$d^2s^2 - d^5s^1$	$d^5 - d^5s^2$
$ZrMn_2$	1.22	hexagonal	$d^2s^2 - d^5s^1$	$s^2 - d^5s^2$
$ZrRu_2$	1.21	hexagonal	$d^2s^2 - d^7s^1$	$d^0s^1 - d^{10}s^1$
UCo_2	1.22	Cubic	$f^3d^1s^2 - d^7s^2$	$f^7s^2 - d^6s^2$
UFe_2	1.21	Cubic	$f^3d^1s^2 - d^6s^2$	$f^7s^2 - d^5s^2$
UNi_2	1.24	hexagonal	$f^3d^1s^2 - d^8s^2$	$s^2 - d^{10}s^2$
$MoBe_2$	1.24	hexagonal	$d^5s^1 - s^2$	$d^6s^1 - s^2$
WBe_2	1.25	hexagonal	$d^4s^2 - s^2$	$s^2 - d^6s^2$
$PbAu_2$	1.22	Cubic	$p^2s^2 - d^{10}s^1$	$p^4s^2 - d^{10}$

From the data it is evident that in Cubic Laves phases the formation of d^5 and d^{10} is most probable, whereas in case of hexagonal Laves phases the formation of s^2 configuration is noticeable.

It is suggested that probably the atoms in case of Laves phases touch each other only when the statistical weight of stable configurations are maximum. In case of a decrease in

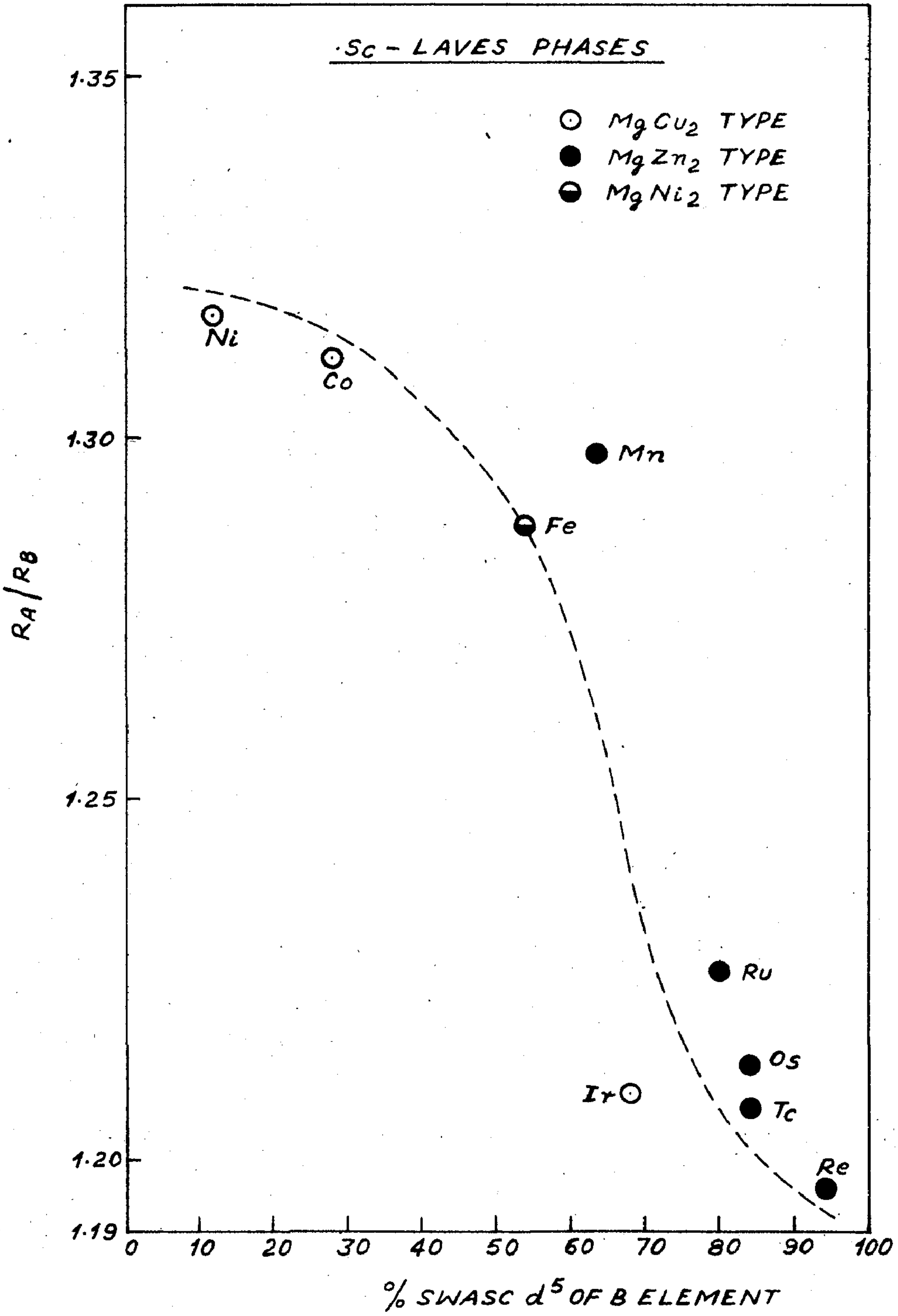


Fig.16. Variation of radius ratio of Laves phases among Sc alloys with respect to % SWASC d^5 of component B.

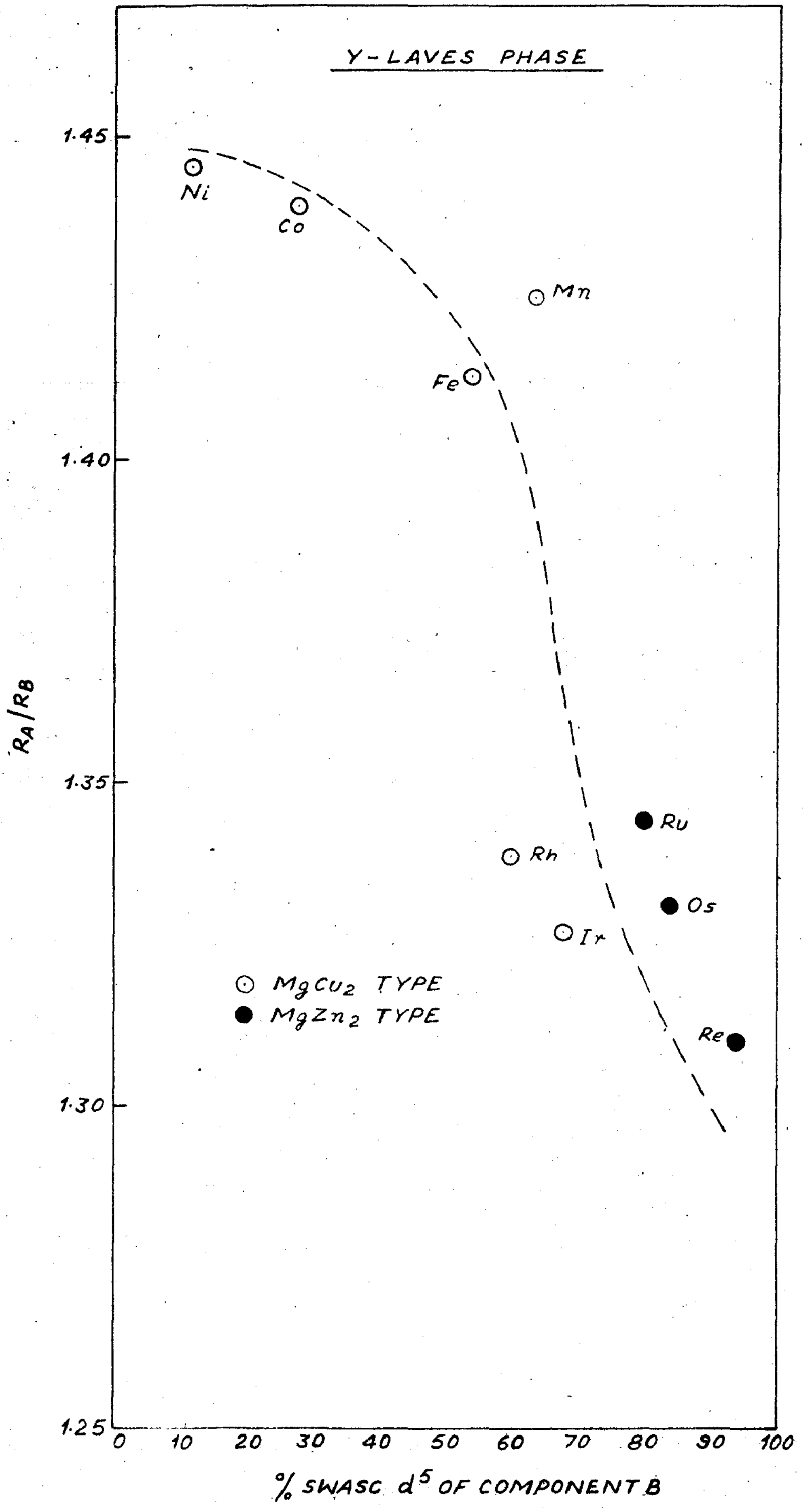


Fig.17. Variation of radius ratio of Laves phases among Y alloys with respect to % SWASC d^5 of component B.

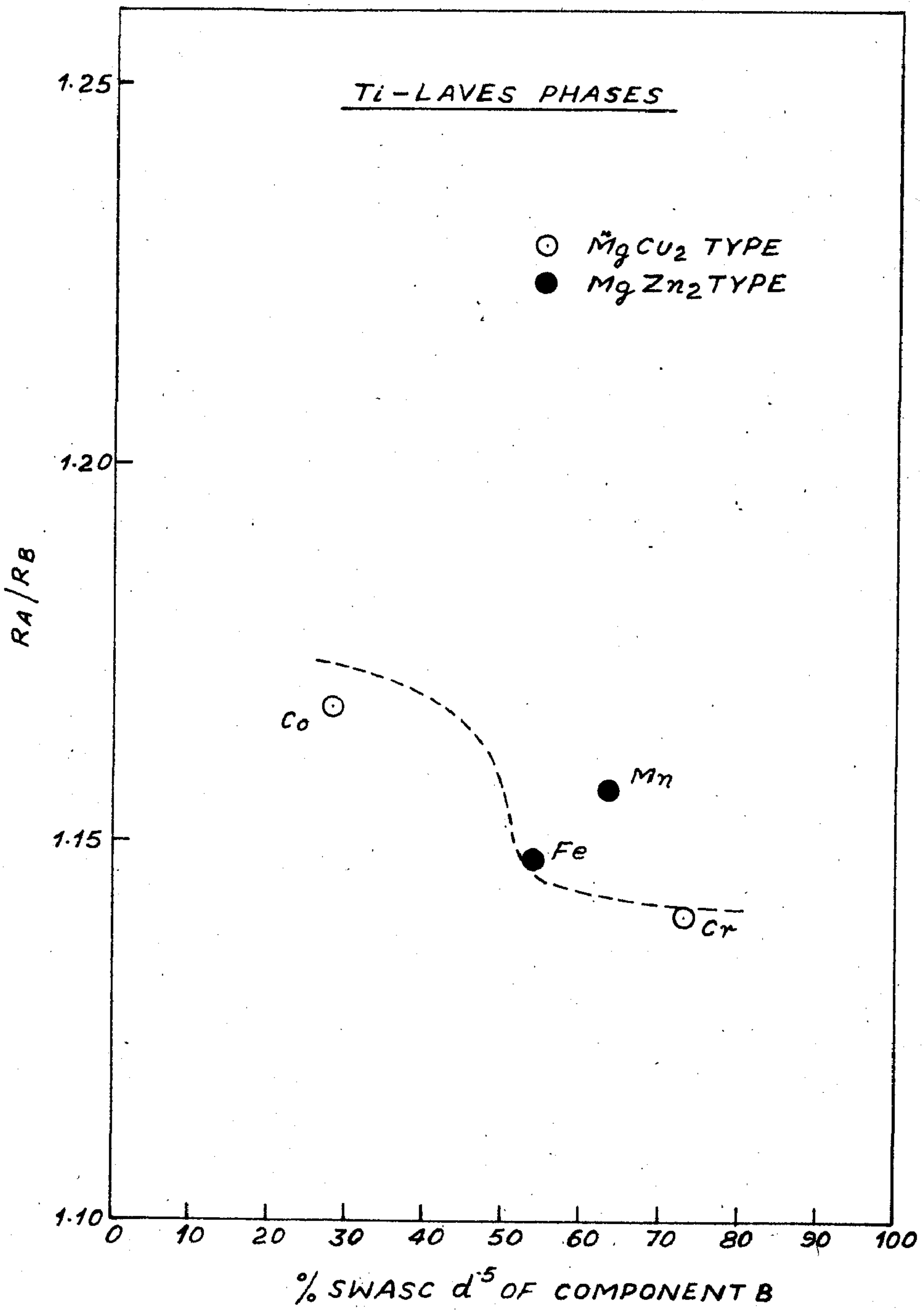


Fig.18. Variation of radius ratio of Laves phases among Ti alloys with respect to % SWASC d^5 of component B.

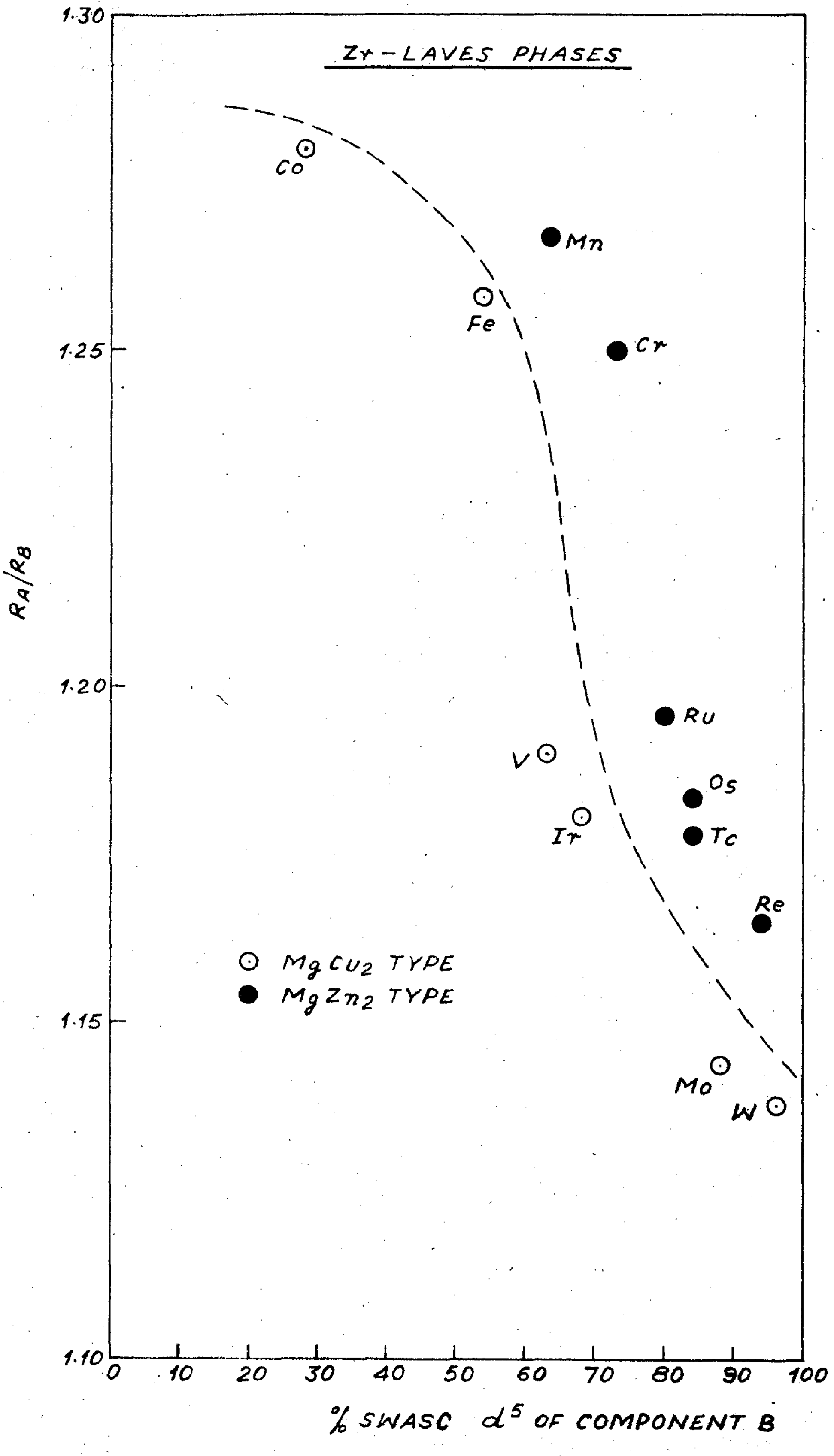


Fig.19. Variation of radius ratio of Laves phases among Zr alloys with respect to % SWASC d^5 of component B.

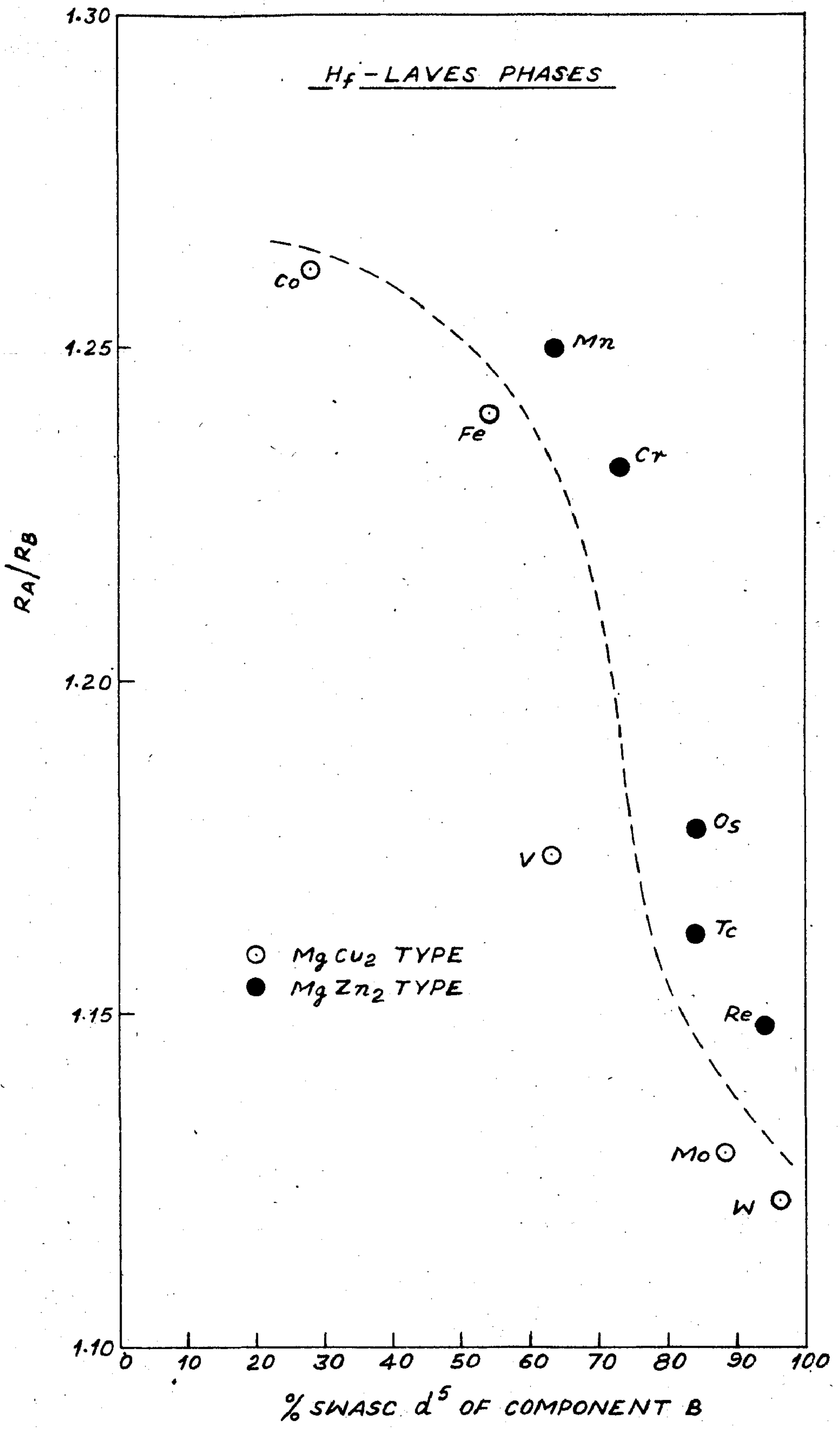


Fig.20. Variation of radius ratio of Laves phases among Hf alloys with respect to % SWASC d^5 of component B.

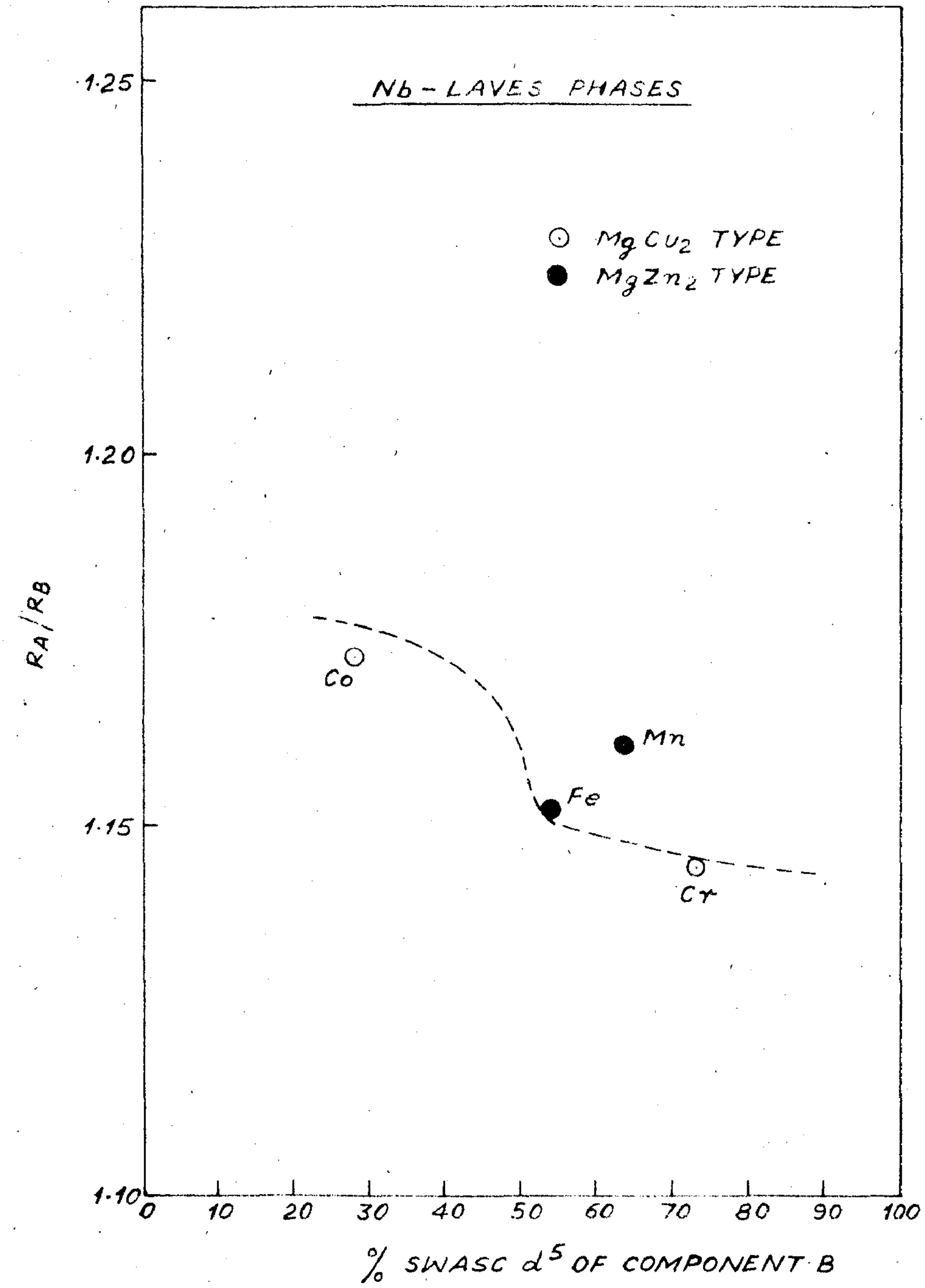


Fig. 21. Variation of radius ratio of Laves phases among Nb alloys with respect to % SWASC d^5 of component B.

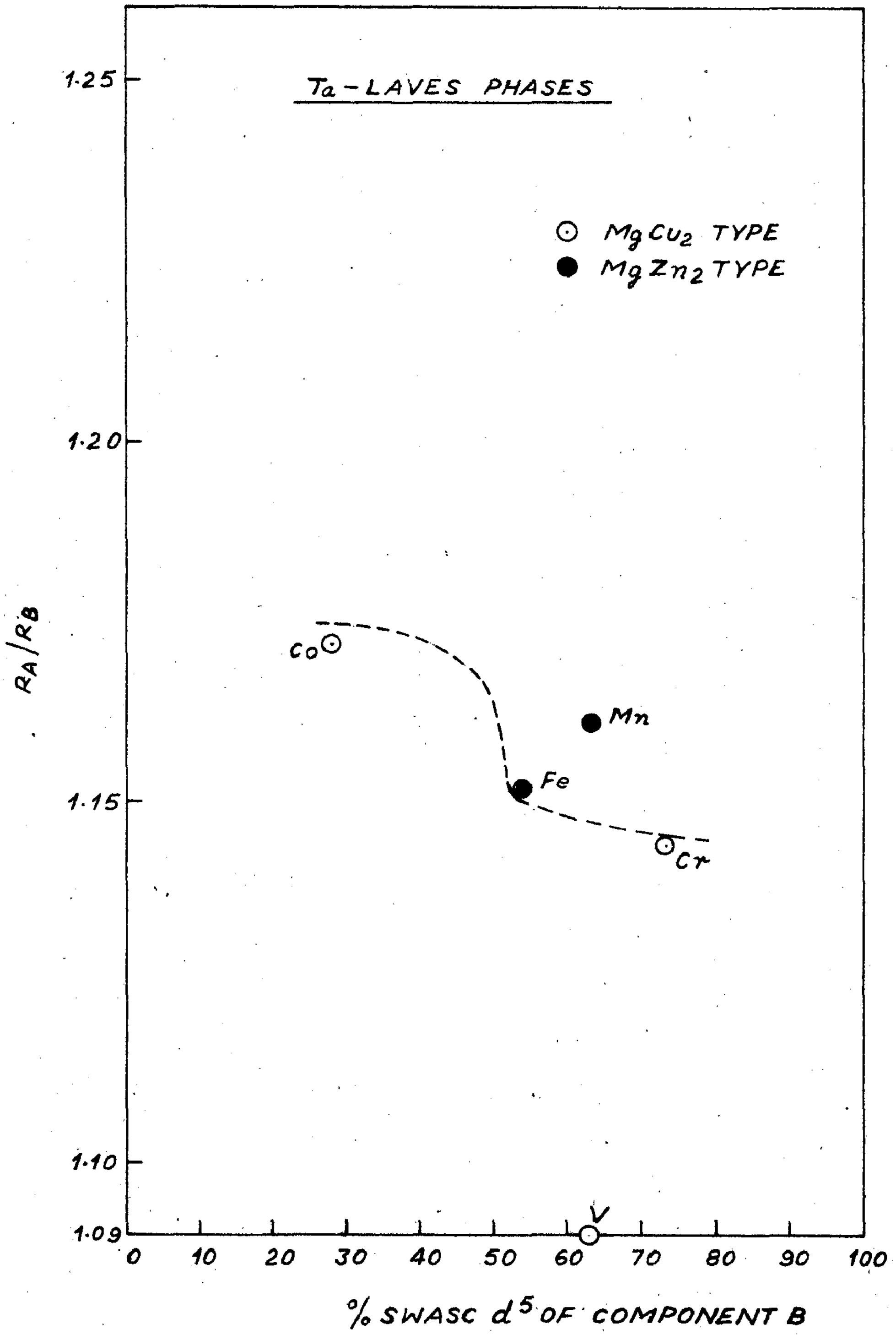


Fig. 22. Variation of radius ratio of Laves phases among Ta alloys with respect to % SWASC d^5 of component B.

the stability of electronic configurations it appears that there is a covalent type of bond in similar atoms with the result that only similar atoms touch each other.

The Laves phases which occur in transition metals, along with the RA/RB ratios, electron ratios, crystal structure type and in some cases the temperature, are listed in Appendix -III. The plots for transition metal Laves phases between RA/RB vs Σ SWASC d^5 of component B-metal are shown in figure -16 to 22. It is interesting to note that Sc, Y, Zr, and Hf resembles in their tendency to form Laves phases. Similarly, Ti, Nb and Ta behave identically in forming Laves phases with other transition metals. The approximate dotted curves in each figure are indicative of the regions of stability of $Mg Zn_2$ and $Mg Cu_2$; above these curves the $MgZn_2$- type is stable whereas below it the $MgCu_2$ - type is stable. The $Mg Ni_2$ - type Laves phase then being intermediate between $MgZn_2$ and $MgCu_2$-type, should be expected to lie at or near the dotted line. In case of $MgZn_2$-type Laves phases the RA/RB ratios are found to be greater than the RA/RB ratios for $MgCu_2$ type structure. Furthermore, the Σ SWASC d^5values corresponding to $MgZn_2$ type structure are in general greater than those corresponding to the $MgCu_2$ - type structures.

It is also observed that the RA/RB ratio decreases with an increasing Σ SWASCd^5- of component B. However, this decrease is not a linear one. In case of Sc, Y, Zr and Hf-Laves phases, the slope of RA/RB VS. SWASC d^6 plot upto about 50-60 % SWASC d^6 of solute is small, but after which the slope is rather rapid. As already described in section 2.3.6 the stability of d^6 configuration is greater than d^{10} and naturally this manifested in the nature of such plots, as Laves phases having SWASC d^6 of B component greater than 60% show a steeper variation of RA/RB. Further the RA/RB ratio decreases with the increasing % SWASC d^6 of A metal along the same period of periodic table.

For example the RA/RB plot is lowered from the Laves phases formed by Sc to the Laves phases formed by Ti in the first long period. Similarly the RA/RB plots exhibit a downward tendency starting from Y-Laves phases followed by Zr-Laves phases and then by Nb -Laves phases, in the second long period. Similarly tendency is exhibited in IIIrd long period where the RA/RB plot for Ta-Laves phases is lower than the plot corresponding to Nb-Laves phases.

The RA/RB ratio also decreases from Zr to Hf and very slightly from Nb to Ta phases but it increases from Sc to Y-phases or Ti to Zr.-phases.

It is found that Ti does not resemble in its formation of Laves phases to Sc, but instead to Hf and Ta in this respect. This anomaly however need not take too seriously, since the crystal structure of higher temperature modification Ti(B.C.C.) is identical with those of group VA metals. Thus it appears that β-Titanium is playing role in formation of Laves phases.

In conclusion the above correlation of the appearance of different types of Laves phases among transition metals can be adequately correlated with the formation of stable configuratio by the components. With increase in GUAScd^5 of B component there is invariable decrease in RA/RB that is to say that radius differences in the component atoms are getting minimised. Apart from those, the plots clearly reflect that the formation of stable d^5 configuration of B component is contributing in $MgZn_2$ structure stability, while the d^{10} configuration is promoting the formation of $MgCu_2$-type. This suggests that an isotropic structur i.e. $MgCu_2$ structure is predominant in case where all the d-electrons tend to get filled-up.

The rare-earth Laves phases are listed in Appendix-IV. Figure 23, shows the relationship between the lattice parameter (a_o) and the number of (4f+5d) electrons in rare-earth solvent for the $MgCu_2$-type Laves phases. For $MgCu_2$ type Laves-phases it is seen that, in all the cases with the filling of 4f shell, the lattice constant decreases.

The smaller size component B elements are generally from transition metals of last groups i.e. $6 < nd < 10$, in the range of 6 to 10. In the first long period i.e. Fe, Co Ni, it is observed that for any larger size rare earth element which

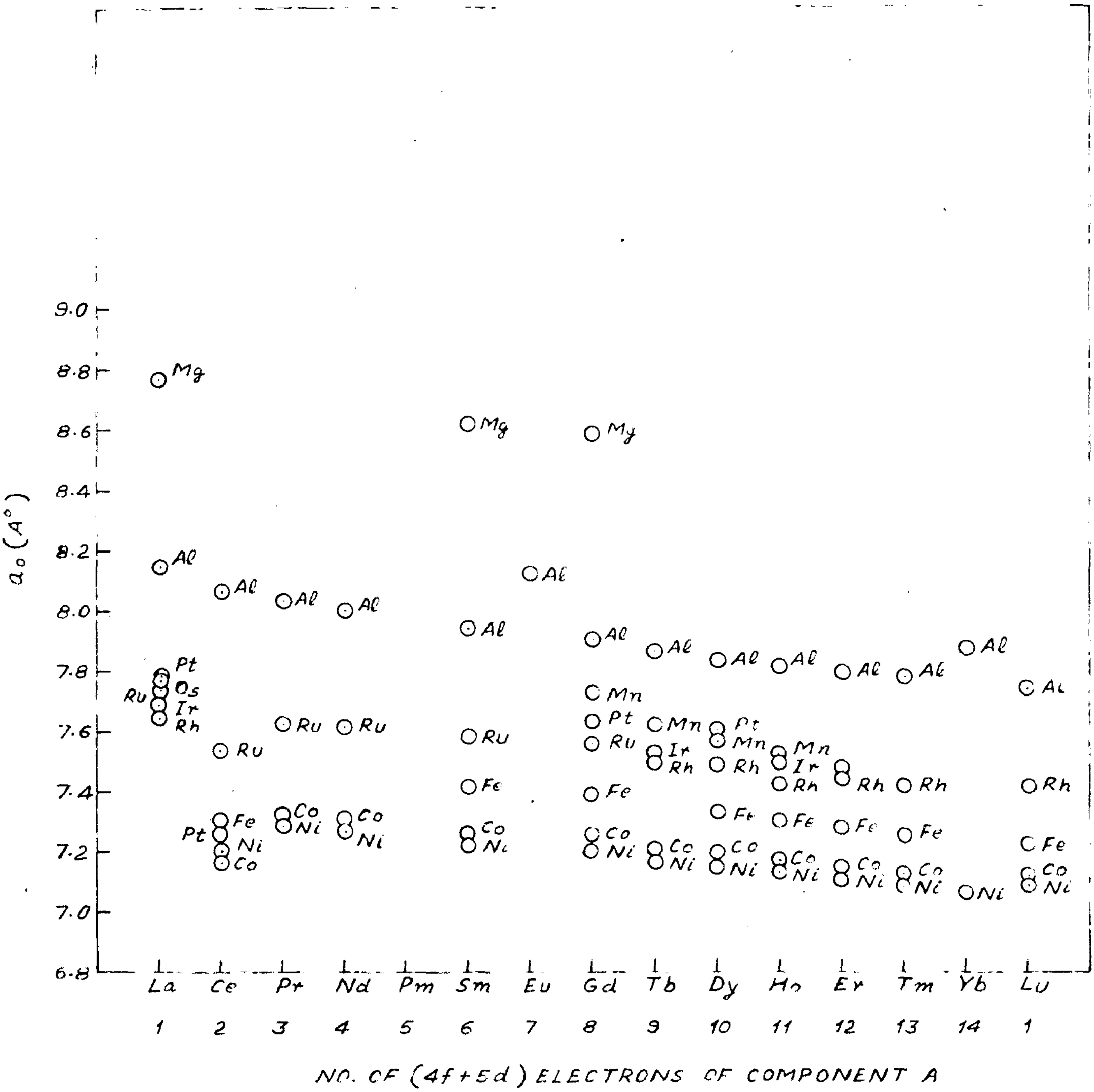


Fig. 22. Variation of Lattice Parameter of [illegible] earth Laves phases with [illegible] the number of (4f+5d) electrons of component A.

acts as A component, with increase in SWASC d^{10} (i.e. passing from Fe→Co→Ni), the lattice constant of the Laves phase decreases. A similar decrement in lattice constant is observed in case of IInd long period metals (Viz.Ru and Rh). However, the lattice constant values are more than those found in case of Laves phases with Ist long period. This is attributed to the fact that with increase in principal quantum number the SWASCd^5 increases and consequently there is a decrease in the corresponding SWASC d^{10} values. A similar picture is observed when we move on to the elements of IIIrd long period, Viz. Os, Ir, Pt, although not many examples are in literature from this group of elements.

In conclusion one can undoubtedly say that in case of $MgCu_2$-type rare-earth Laves phases with transition metals of later groups (>VIth group) it is the d^{10} and f^{14} stable configurations which are controlling the size factor.

The case of Mg-Laves phases and Al-Laves phases is also very interesting. In the former there is probability of s→p transition and eventually the formation of stable sp^3 configuration is accentuated by the donation of non-localised electrons from the rare earth elements. Since Al is already an sp-element(isolated atom configuration $3s^2$ $3p^1$), there is a still higher probability of forming stable sp^3 configurations, as compared to magnesium . This appears to be the reason why

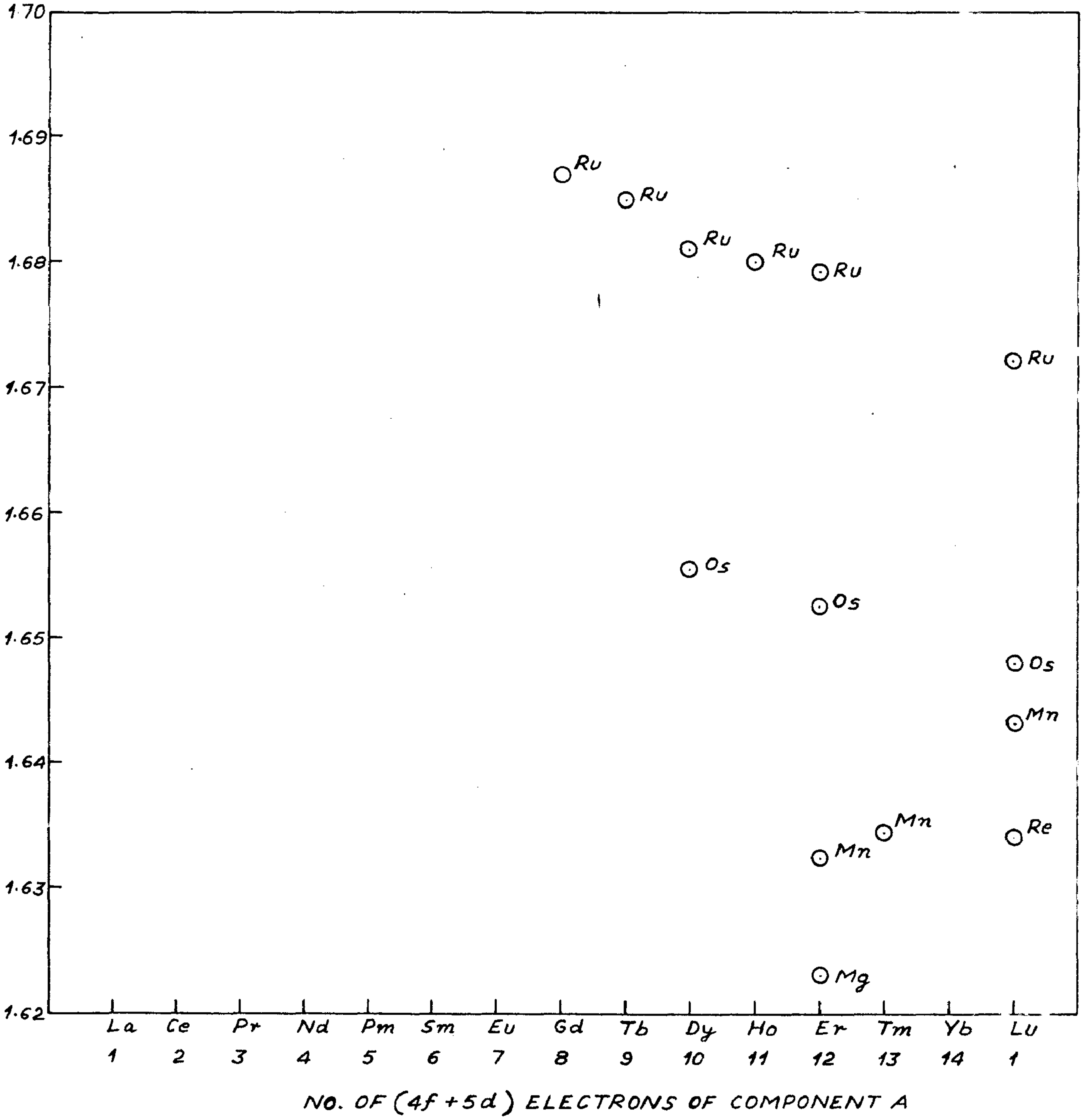


Fig.24. Variation of c/a ratio in MgZn$_2$ type rare earth Laves phases with respect to the number of (4f + 5d) electrons of component A.

the lattice constant of rare-earth Laves phases with aluminium i
less than those with magnesium.

The $MgZn_2$-type rare-earth Laves phases are shown in figure 24, as a function of (4f+5d) electrons of the rare earth elements. It is seen that with the increase of the number of f-electrons of solvent A, the c/a ratio decreases. This is in agreement what we said earlier. While passing from Ru→Os→Mn→Re the S SWASC d^5 increases and hence it is quite natural that the lattice constant of Laves phase decreases in the same order.

The above discussion suggests that the stable electronic configuration model is of great utility in explaining the stability of intermediate phases in transition metal alloy systems.

CHAPTER - V

CONCLUSIONS

From the foregoing discussions the following conclusions can be drawn about the relationship of the phase stability in Sigma, Chi and Laves phases in transition metals including the rare-earth elements :

1) The Electronic configuration model as proposed by Samsonov can be satisfactorily applied to explain various facts regarding the phase stability of the above mentioned phases.

2) On this basis, it is concluded that the electronic factor is most important factor in controlling the formation and stability of such intermediate phases and the size factor is more or less merely the consequence of the resulting electronic exchanges among the component atoms.

3) The comparatively large differences in S WASCd^5 values of component metals give rise to little or no homogeneity ranges in the formation of variable composition phases (e.g. Sigma and Chi) whereas the small differences in the S WASCd^5 of the component transition metals leads to the formation of large homogeneity ranges.

4) The formation of stable d^5 configurations results in the stabilization of $MgZn_2$-type Laves phases, whereas the stable d^{10} configuration is favourable for the formation of

$MgCu_2$ -type Laves phases in transition metal systems.

6) In case of rare-earth metal- Laves phases it is concluded that it is the d^{10} and f^{14} stable configurations which control the size factor and lead to the occurrence and stability of such phases.

R_E_F_E_R_E_N_C_E_S

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APPENDIX -X

SIGMA PHASES

A	B	B Atomic %	Temp. °C	Electrons atom ratio	rA/rB	Δ at %B
I) V-SIGMA PHASES						
V	Fe	45.5-61	1075	6.32-6.83	1.03	15.5
V	Co	32-55.6	1200	6.28-7.26	1.03	23.6
V	Ni	29-45.5	1200	6.45-7.28	1.03	16.5
V	Re	~74	-	6.48	0.93	0
II) Nb-SIGMA PHASES						
Nb	Fe	51-54	530-1500	6.53-6.62	1.16	3
Nb	Rh	~40	1000	6.60	1.09	0
Nb	Pd	40	1000	7.00	1.07	0
Nb	Re	~50	Above 1200	6.00	1.07	0
Nb	Os	39-41	Near mp.	6.17-6.23	1.08	2
Nb	Ir	35	At mp.	6.66	1.08	0
Nb	Pt	37.5	1000	6.88	1.03	0
III) Ta-SIGMA PHASES						
Ta	Rh	~40	1000	6.60	1.09	0
Ta	Pd	25	1250	6.25	1.07	0
Ta	Re	~55	1200	6.10	1.07	0
Ta	Os	25-35	1200	5.75-6.05	1.03	10
Ta	Ir	15-25	1200	5.60-6.00	1.08	10
Ta	Pt	18-32	1000	5.90-6.60	1.03	14
Ta	Au	33	800-1750	6.98	1.08	0

IV. Cr-SIGMA PHASES

A	B	B Atomic %	Temp. °C	Electron: atom ratio	RA/RB	Δat % B
Cr	Fe	50-56	600	7.02-7.14	1.01	6
Cr	Co	37-42	1200	7.11-7.20	1.02	5
Cr	Ru	34	1200	6.68	0.93	0
Cr	Rh	63.2	1200	6.63	0.93	0
Cr	Os	40	1000-1300	6.78	0.95	0

V. Mo-SIGMA PHASES

A	B	B Atomic %	Temp. °C	Electron: atom ratio	RA/RB	Δat % B
Mo	Fe	50-56	1180-1540	7.00-7.12	1.10	6
Mo	Co	40	1340-1650	7.20	1.12	0
Mo	Ru	40	1200	6.78	1.03	0
Mo	Rh	48-67	1200	6.48-6.67	1.02	19
Mo	Os	37.6	1200	6.67	1.03	0
Mo	Ir	~30	Near mp.	6.90	1.03	0

VI. W-SIGMA PHASES

A	B	B Atomic %	Temp. °C	Electron: atom ratio	RA/RB	Δat % B
W	Tc	75	700	6.75	1.04	0
W	Ru	40	1650	6.80	1.05	0
W	Rh	42-63	1200	6.42-6.63	1.02	21
W	Os	21-32	2200	6.42-6.70	1.04	11
W	Ir	30	Near mp.	6.90	1.04	0

APPENDIX XX

CHI PHASES

I. Tc-CHI PHASES

A	B	B, Atomic %	Electron: Atom ratio	RA/RB	A Atomic %	Average Atomic %
Sc	Tc	86-88	6.40-6.52	1.207	12-16	3
Ti	Tc	84-88	6.52-6.64	1.075	12-16	4
Zr	Tc	~83	6.50	1.175	~14	0
Nb	Tc	~85	6.70	1.070	~15	0
Hf	Tc	84-88	6.52-6.64	1.103	12-16	4
Ta	Tc	80-82	6.60-6.64	1.070	18-20	2

II Re-CHI PHASES

A	B	B, Atomic %	Electron: Atom ratio	RA/RB	A Atomic %	Average Atomic %
Ti	Re	83	6.49	1.032	17	0
Zr	Re	83	6.49	1.164	17	3
Nb	Re	80-86	6.40-6.68	1.104	14-20	22.6
		62-87	6.24-6.74	1.037	13-38	
		60-82	6.20-6.64	1.037	18-40	
		68-86	6.36-6.73	1.037	12-32	
		64-87	6.28-6.74	1.037	13-36	
		69-86	6.38-6.72	1.037	14-37	
Mo	Re	74-78	6.74-6.78	1.017	22-26	4.0
		75-79	6.75-6.79	1.017	21-25	
Hf	Re	83	6.49-6.55	1.148	17	0
Ta	Re	63-80	6.26-6.60	1.000	20-37	17
W	Re	75	6.75	1.033	25	1.6
		73-76	6.73-6.76	1.033	24-27	

APPENDIX XXX

TRANSITION METALS BINARY LAVES PHASES[a]

I. Sc-LAVES PHASES

AB_2	Crystal Type	Electrons atom Ratio	DA/DB	Melting Tem (Ref.16)
$ScMn_2$	$MgZn_2$	5.67	1.203	-
$ScFe_2$	$MgNi_2$	6.33	1.208	-
$ScCo_2$	$MgCu_2$	7.00	1.211	-
$ScNi_2$	$MgCu_2$	7.67	1.217	-
$ScTc_2$	$MgZn_2$	5.67	1.207	-
$ScRu_2$	$MgZn_2$	6.33	1.230	-
$ScRe_2$	$MgZn_2$	5.67	1.193	-
$ScOs_2$	$MgZn_2$	6.33	1.219	-
$ScIr_2$	$MgCu_2$	7.00	1.200	-

II. Y-LAVES PHASES

AB_2	Crystal Type	Electrons atom Ratio	DA/DB	Melting Tem (Ref.16)
YMn_2	$MgCu_2$	5.67	1.420	-
YFe_2	$MgCu_2$	6.33	1.414	-
YCo_2	$MgCu_2$	7.00	1.420	-
YNi_2	$MgCu_2$	7.67	1.446	-
YRu_2	$MgZn_2$	6.33	1.346	-
YRh_2	$MgCu_2$	7.00	1.335	-
YRe_2	$MgZn_2$	5.67	1.310	-
YOs_2	$MgZn_2$	6.33	1.331	-
YIr_2	$MgCu_2$	7.00	1.337	-

III. Ti-LAVES PHASES

AB_2	Crystal Type	e/a	RA/RB	Melting Temp
$TiCo_2$	$MgCu_2$	7.33	1.168	1250
$TiCr_2$	$MgCu_2$	5.33	1.140	1350
$TiFe_2$	$MgZn_2$	6.67	1.148	1530
$TiMn_2$	$MgZn_2$	6.00	1.167	1330

IV. Zr-LAVES PHASES

AB_2	Crystal Type	e/a	RA/RB	Melting Temp
$ZrCo_2$	$MgCu_2$	7.33	1.280	1560
$ZrCr_2$	$MgZn_2$	5.33	1.250	1700
$ZrFe_2$	$MgCu_2$	6.67	1.258	1645
$ZrMn_2$	$MgZn_2$	6.00	1.267	1340
$ZrMo_2$	$MgCu_2$	5.33	1.144	1880
ZrV_2	$MgCu_2$	4.67	1.190	1740
ZrW_2	$MgCu_2$	5.33	1.138	2178
$ZrTc_2$	$MgZn_2$	6.00	1.178	-
$ZrRe_2$	$MgZn_2$	6.00	1.165	-
$ZrOs_2$	$MgZn_2$	6.67	1.184	-
$ZrIr_2$	$MgCu_2$	7.33	1.181	-
$ZrRu_2$	$MgZn_2$	6.67	1.193	-

V. Hf-Laves Phases

AB_2	Crystal Type	Electrons atom ratio	RA/RB	Melting T
$HfCo_2$	$MgCu_2$	7.33	1.262	1570
$HfCr_2$	$MgZn_2$	5.33	1.232	1450
$HfFe_2$	$MgCu_2$	6.67	1.240	1650
$HfMn_2$	$MgZn_2$	6.00	1.260	1565
$HfMo_2$	$MgCu_2$	5.33	1.139	>2300
HfV_2	$MgCu_2$	4.67	1.174	1500
HfW_2	$MgCu_2$	5.33	1.132	>2000
$HfTc_2$	$MgZn_2$	6.00	1.162	-
$HfRe_2$	$MgZn_2$	6.00	1.149	-
$HfOs_2$	$MgZn_2$	6.67	1.168	-

VI. Nb-LAVES PHASES

AB_2	Crystal Type	Electrons atom ratio	RA/RB	Melting T
$NbCo_2$	$MgCu_2$	7.67	1.173	1570
$NbCr_2$	$MgCu_2$	5.67	1.145	1710
$NbFe_2$	$MgZn_2$	7.00	1.162	1625
$NbMn_2$	$MgZn_2$	6.33	1.161	1480

VII. Ta-LAVES PHASES

AB_2	Crystal Type	Electrons atom ratio	RA/RB	Melting T
$TaCo_2$	$MgCu_2$	7.67	1.178	1610
$TaCr_2$	$MgCu_2$	5.67	1.144	2016
$TaFe_2$	$MgZn_2$	7.00	1.162	1773
$TaMn_2$	$MgZn_2$	6.33	1.161	-
TaV_2	$MgCu_2$	5.00	1.090	-

APPENDIX IV

BINARY LAVES PHASES OF RARE EARTH ELEMENTS

I. La-LAVES PHASES

Phase	Structure Type	a_0, A°	c_0, A°
$LaAl_2$	$MgCu_2$	8.146	
$LaIr_2$	"	7.687	
$LaMg_2$	"	8.763	
$LaOs_2$	"	7.736	
$LaPt_2$	"	7.764	
$LaRh_2$	"	7.646	
$LaRu_2$	"	7.7024	

II. Ce-LAVES PHASES

Phase	Structure Type	a_0, A°	c_0, A°
$CeAl_2$	$MgCu_2$	8.057	
$CeCo_2$	"	7.162	
$CeFe_2$	"	7.302	
$CeNi_2$	"	7.159	
$CePt_2$	"	7.723	
$CeRu$	"	7.5304	

III. Pr-LAVES PHASES

Phase	Structure Type	a_0, A°	c_0, A°
$PrAl_2$	$MgCu_2$	8.030	
$PrCo_2$	"	7.312	
$PrNi_2$	"	7.285	
$PrRu_2$	"	7.6223	

IV. Nd-LAVES PHASES

Phase	Structure	a_0, A°	C_0, A°	c/a
$NdAl_2$	$MgCu_2$	8.000		
$NdCo_2$	"	7.300		
$NdNi_2$	"	7.270		
$NdRu_2$	"	7.614		
V. Sm-LAVES PHASES				
$SmAl_2$	$MgCu_2$	7.942		
$SmCo_2$	"	7.260		
$SmFe_2$	"	7.416		
$SmMg_2$	"	8.62		
$SmNi_2$	"	7.226		
$SmRu_2$	"	7.560		
VI. Eu-LAVES PHASE				
$EuAl_2$	$MgCu_2$	8.126		
VII Gd-Laves Phases				
$GdRu_2$	$MgZn_2$	5.275	8.899	1.6870
$GdTc_2$	$MgZn_2$	-	-	
$GdAl_2$	$MgCu_2$	7.901		
$GdCo_2$	"	7.256		
$GdFe_2$	"	7.389		
$GdIr_2$	"	-		
$GdMg_2$	"	8.59		
$GdMn_2$	"	7.728		
$GdNi_2$	"	7.204		
$GdPt_2$	"	7.636		
[illegible]	"	7.66		

VIII. Tb-LAVES PHASES

Phase	Structure	a_o, A°	Co A°	c/a
$TbRe_2$	$MgZn_2$	-	-	—
$TbRu_2$	"	5.263	8.869	1.6850
$TbTc_2$	"	-	-	—
$TbAl_2$	$MgCu_2$	7.867		
$TbCo_2$	"	7.206		
$TbFe_2$	"	7.524		
$TbMn_2$	"	7.620		
$TbNi_2$	"	7.160		
$TbRh_2$	"	7.492		

IX. Dy-LAVES PHASES

$DyOs_2$	$MgZn_2$	5.303	8.779	1.6555
$DyRu_2$	"	5.255	8.834	1.6810
$DyTc_2$	"	-	—	—
$DyAl_2$	$MgCu_2$	7.838		
DyCo	"	7.188		
$DyFe_2$	"	7.323		
$DyMn_2$	"	7.569		
$DyNi_2$	"	7.148		
$DyPt_2$	"	7.5966		
$DyRh_2$	"	7.483		

X. Ho-LAVES PHASES

Phase	Structure	a_0, A°	c_0 A°	c/a
$HoRe_2$	$MgZn_2$	-	-	—
$HoRu_2$	"	5.244	8.810	1.6800
$HoTc_2$	"	-	-	—
$HoAl_2$	$MgCu_2$	7.810		
$HoCo_2$	"	7.168		
$HoFe_2$	"	7.300		
$HoIr_2$	"	7.486		
$HoMn_2$	"	7.507		
$HoNi_2$	"	7.136		
$HoRh_2$	"	7.426		

XI. Er-LAVES PHASES

Phase	Structure	a_0, A°	c_0 A°	c/a
$ErMg_2$	$MgZn_2$	6.00	9.74	1.6233
$ErMn_2$	"	5.281	8.621	1.6324
$ErOs_2$	"	5.284	8.732	1.6526
$ErRu_2$	"	5.231	8.785	1.6784
$ErTc_2$	"	-	-	-
$ErAl_2$	$MgCu_2$	7.797		
$ErCo_2$	"	7.144		
$ErFe_2$	"	7.274		
$ErIr_2$	"	7.473		
$ErNi_2$	"	7.11		
$ErRh_2$	"	7.444		

XII. Tm-LAVES PHASES

Phase	Structure MgZn2 Type	a_0, A°	c_0, A°	c/a
$TmMn_2$	$MgZn_2$	5.241	8.565	1.6342
$TmRu_2$	"	-	-	—
$TmRe_2$	"	-	-	—
$TmAl_2$	$MgCu_2$	7.760		
$TmCo_2$	"	7.121		
$TmFe_2$	"	7.237		
$TmNi_2$	"	7.020		
$TmRh_2$	"	7.417		

XIII. Yb-Laves Phases

$YbAl_2$	$MgCu_2$	7.877		
$YbNi_2$	"	7.030		

XIV. Lu-LAVES PHASES

$LuMn_2$	$MgZn_2$	5.228	8.590	1.64307
$LuOs_2$	"	5.261	8.670	1.6480
$LuRe_2$	"	5.335	8.717	1.6340
$LuRu_2$	"	5.210	8.722	1.6721
$LuTc_2$	"	-	-	—
$LuAl_2$	$MgCu_2$	7.742		
$LuCo_2$	"	7.122		
$LuFe_2$	"	7.222		
$LuNi_2$	"	7.035		
$LuRh_2$		7.412		