

CHAPTER 2

GENERAL INTRODUCTION TO INTERMETALLIC COMPOUNDS

2.1 INTERMETALLICS : THE PRESENT STATUS

The increased need for new and novel materials with specified properties and particular application have attracted greater attention of materials scientists and metallurgists in the recent years. There has been a continuing interest in the processing and properties of some of the intermetallic compounds such as the aluminides of titanium and nickel which have better resistance to high temperature oxidation, lower density, better creep resistance and higher modulus than conventional titanium alloys (Engell 1991). Other recently developed materials are aluminum alloys which resist high temperature, aluminum alloys low in density and therefore low in weight, improved ceramics, high strength steels, shape memory alloys (NiTi) and heater elements like MoSi_2 (Cahn 1990, Destefani 1989). Presently lot of attention is paid to structural intermetallics as they have potential applications as aerospace materials. Considerable effort is being made in various laboratories worldwide with regard to ductilisation and diffusion in these compounds so as to achieve the desired mechanical properties.

2.2 SURVEY OF EARLIER WORKS ON INTERMETALLIC COMPOUNDS

In the beginning of the nineteenth century, when the first systematic studies of alloy systems were being made, many scientists noted that the behaviour of certain alloy compositions was strikingly like that of ordinary chemical compounds and began to speculate as to whether compounds might exist between metals. The first observation of an intermetallic was made by Karl Karsten in 1839 (Westbrook

1967), when he noticed a discontinuity in the action of acids on alloys of copper and zinc at the equi-atomic composition and suggested the formation of a compound. The compound claimed by Karsten does really exist and is now popularly called as β -brass (CuZn). During the second half of the century, similar discontinuities were observed in electrical, mechanical, magnetic as well as chemical properties in other alloy systems when the components had definite proportions and that led to the suggested formulation of more intermetallic compounds. The definition of an intermetallic compound is very elusive, but mostly it includes metal-metal compounds, both ordered and disordered, binary and multi-component. Upon occasion, when it appears useful to do so, even the metal-metal aspect of the definition is relaxed somewhat in the consideration of some metal-metalloid compounds, such as the silicides or phosphides like MoSi_2 and InP (Samsonov 1959). The intermetallics find diverse applications ranging from high strength compounds like Ni_3Al (Liu *et al* 1985) to GaAs which has a unique capability for solid-state laser action.

2.3 CONSTITUTIONAL STUDIES

The German metallurgist Tamman (Westbrook 1967) made enormous contributions in many different fields of physical metallurgy over a period of almost fifty years following the turn of the century. Much of his work was on the study of the occurrence and properties of intermetallic compounds. His works was aimed at generalising the binary constitution and studying the nature of intermetallic phases that could be feasible for a large number of systems rather than making a careful study of a few.

Thermal analysis and analysis of residues after chemical attack were the early methods used for identifying a compound and gradually they were supplemented by studies of the composition dependence of physical properties such as density, resistivity, thermal conductivity, hardness and thermoelectric power. Exploitation of this approach of "Physico-chemical analysis" is duly credited to Kurnakov (Westbrook 1967), the great Russian metallurgist. His contribution

to the understanding of intermetallics begins with the phase-diagram determination and property-composition studies. He also discussed the nature and stability of intermetallics on theoretical grounds. In 1900, a published list on intermetallic compounds contained only thirty seven confirmed systems. But within two decades the number multiplied nearly tenfold. Most of the early works naturally were concerned with binary systems, though the first ternary compounds CdHgNa and Hg₂KNa were reported as early as 1906. Scores of ternary compounds, some quaternaries, and even a few quinary compounds have been identified in the subsequent years.

2.4 CRYSTALLOGRAPHIC STUDIES

The X-ray structural studies proved to be so direct and informative that attempts were made to define intermetallics on a structural basis. With the advent of high-intensity neutron sources from nuclear reactors it was realised that a new tool was at hand for the determination of order in compounds by virtue of the very different scattering power of atoms for neutrons. A good example is Ni₃Mn. Extra reflections were found in the ordered compound Ni₃Mn, whereas nothing more could be expected from X-ray patterns due to the similar scattering power of Ni and Mn. Although many intermetallic compounds were found by X-ray diffraction to possess simple structures, identical to those of the common metals, or simple ordered variants thereof, many others were fantastically complex which required single-crystal studies for solution. Thus the crystallographic study of intermetallic phases continues to be an important and active field that provides information useful for constitutional studies, interpretation of properties and understanding of certain compounds and structures.

2.5 EARLIER THEORETICAL WORKS ON INTERMETALLICS

The British metallurgist Desch (Westbrook 1967) was the first to summarise the results of the theoretical attempts on the understanding of the constitution of intermetallic compounds. Nevitt (Westbrook 1967) attempted to understand the

theory of intermetallics from a knowledge of crystal structure, bonding and composition.

It was Hume-Rothery (Westbrook 1967) who in this regard made an outstanding contribution to the understanding of a large group of intermetallics. One of the next attempts at systematization of intermetallic compound types was that of Zintl (Westbrook 1967) who proposed a rule for differentiating intermetallics based on the nature of bonding, namely: ionic, covalent, metallic or combinations of the three.

Later Laves (1956) studied the different factors influencing the structures of the intermetallic phases based on the following geometrical principles:

1. Space-filling principle
2. Symmetry principle
3. Connection principle

2.5.1 Space-filling principle

In the case of metals the atoms tend to have higher coordination numbers (CN's) when the metal atoms are not distinguished from one another. If the atoms are assumed to be spherical and in contact then the best space filling will be that of the cubic or hexagonal close packed arrangement. When metals crystallise the tendency to have a good space filling is called the "space filling principle"

2.5.2 Symmetry principle

There are certain factors which operate against the space filling principle such as the temperature and binding factors. Other than the 12 fold coordination the next most commonly found coordination is only 8 in the case of metals. Though the other coordination numbers 9, 10 and 11 do occur with higher packing density than CN 8 the arrangements with CN 9, 10 or 11 possess lower symmetry

than the 8 fold coordination. The tendency to build configurations with higher symmetries is called the 'symmetry principle'.

2.5.3 Connection principle

The shortest link between the atoms in a solid is said to form a connection. If it connects between structurally equivalent atoms it is called homogeneous and that between inequivalent atoms is called heterogeneous. The connections can be one, two or three dimensional; accordingly they are named as islands, chains and nets or lattices. The tendency to form multi-dimensional connections is said to constitute the connection principle.

The fact that intermetallic compounds are rarely found in hcp, ccp or bcc structures only leads to the conclusion that there are additional interactions present. One of them is to study the nature of bonding between different kinds of atoms. Accordingly the intermetallic compounds are classified as follows.

1. Valence compounds.
2. Electron compounds and Interstitial compounds.
3. Laves phase (size factor) compounds.

2.5.4 Valence compounds

The main factor influencing valence compounds is sharing or transfer of electrons between atoms and thus forming the ionic or covalent bonding. The general trends observed among the valence compounds are discussed in detail by Girgis (1983). Most of the valence compounds are ionic-covalent compounds with a bonding intermediate between ionic and covalent.

2.5.5 Electron compounds and interstitial compounds

Electron compounds with particular valence electron concentrations (VEC) are found to crystallise in one group and they are referred to as Hume- Rothery phases. Table 2.1 shows some representatives of Hume- Rothery phases.

Interstitial compounds are defined as compounds of the transition metals (T) with relatively large atomic radii with non-metals (X) of small radii (H,B,C,N,O). The X atoms occupy the interstices of the T atom host structure.

2.5.6 Laves phase (size factor) compounds

Laves phase compounds denote a large group of intermetallic compounds crystallising in any one of the three closely related structures MgCu_2 (C15), MgZn_2 (C14) and MgNi_2 (C36). It is believed that one of the main factors contributing to the existence of Laves phase compounds is of the geometrical origin (size factor) i.e. filling the space in convenient way. If for maximum filling of space, the A atoms are made to contact each other and B atoms are also made to contact each other, the ratio of the atomic radii r_A/r_B that permits this is 1.225. In practice, for the known Laves phases, this ratio varies from 1.05 to 1.68. On the otherhand, there are AB_2 combinations whose radius ratio lie within the typical range which do not form Laves phases.

2.6 PROPERTIES AND SOME OF THE APPLICATIONS OF INTERMETALLICS

In general intermetallic compounds are characterised by high hardness and limited ductility-properties associated with harmful second-phase embrittlement in most alloy systems. With the need for novel materials for specific applications, the different properties have been studied experimentally and fairly well analysed theoretically. The attempted systematisation of the properties and variety of applications of intermetallics are discussed below.

Table 2.1 Some representatives of Hume-Rothery phases

VEC = 3/2		VEC = 21/13		VEC = 7/4
Bcc structure	Complex cubic "B-Mn" structure	Hcp structure	γ -brass structure	Hcp structure
CuBe	Cu ₅ Si	Cu ₃ Ga	Cu ₅ Zn ₈	CuZn ₃
AgMg	Ag ₃ Al	Ag ₃ Al	Ag ₅ Zn ₈	Ag ₅ Al ₃
CuZn		Ag ₃ Ga	Au ₅ Zn ₈	AgZn ₃

2.6.1 Mechanical properties

The hardness of many intermetallic compounds was found to be higher than that of the unalloyed component metals. The superalloys provide high strength and toughness, but are limited to low temperatures. Ceramics are useful for high temperature applications, but they are inherently brittle because of the covalent atomic bonding. The intermetallics are expected to fill the gap between the superalloys and the ceramics not only with respect to the service temperature range (Liu 1989), but also with respect to properties: higher strength than superalloys because of the strong atomic bonding and less brittleness than the ceramics because metallic bonding predominates. A phase for high temperature applications must have a sufficient strength at service temperature which means a sufficient creep resistance. The creep resistance scales with the diffusion coefficient and with the shear modulus and both parameters scale with melting temperature. Current research is focused on the aluminides of nickel, titanium and iron: Ni_3Al , NiAl , Ti_3Al , TiAl , Fe_3Al and FeAl , which serve as structural intermetallics. But the major problem of these strong intermetallics is their brittleness which, however should be less severe than that of ceramics because of the different type of bonding. Intermetallics for high -temperature applications must be oxidation-resistant and in most cases the aluminides satisfying all these conditions are the strongly favoured candidates for high-temperature applications.

2.6.2 Thermoelectric properties

The importance of intermetallic compounds for thermoelectric conversion is a result of their particularly favourable transport properties-Seebeck coefficient (thermoelectric power), electrical conductivity and thermal conductivity as compared with metals and elemental semiconductors. The principal thermoelements currently in use are PbTe and other compounds like hexaborides LaB_6 (Korsukova and Gurin 1984) which have very high melting temperatures.

2.6.3 Magnetic properties

The magnetic properties are as interesting as the mechanical properties of the intermetallics. Most frequently the intermetallic compounds were found to be non-magnetic, if one of components is ferromagnetic. The reverse case of magnetic alloys from non-magnetic constituents identified by Heusler (Kouvel 1967) were surprising. Also, other compounds like MnBi with extremely high coercivities and SmCo₅ (Brooks *et al* 1991) were found to be useful as permanent magnets. Another important milestone in the magnetic behaviour of intermetallics was the antiferromagnetic ordering suggested by Neel (Kouvel 1967). Infact, the magnetic properties ranging from para to ferrimagnetism in compounds give much better understanding of the nature of interactions and their influence on the macroscopic properties

2.6.4 Superconducting properties

The superconducting properties have been studied from several hundreds of intermetallic compounds belonging to different crystal structures. As is evident from Table 2.2, the occurrence of superconductors with $T_c > 10$ K is by no means a rare phenomenon in intermetallic compounds. The compound Nb₃Ge (Testardi 1974) with a superconducting transition temperature exceeding 23 K, is of crucial importance, since it enables one to use liquid hydrogen instead of liquid helium. There are recently found oxide superconductors, which are basically ceramics and not intermetallics still superconducting at higher transition temperatures of 90 K and 120 K after the discovery of 40 K superconductors (Bednorz and Muller 1986). More about the superconducting properties are discussed in chapter 4, as most of the compounds studied in the present thesis are superconductors.

Among the binary systems the stoichiometries AB, AB₂ and AB₃ comprise about two-thirds of the total number of binary compounds as listed by Landolt-Bornstein (1971). As the present study concentrates on the binary systems,

Table 2.2 Superconductivity in chemical compounds with their respective structures

Structure type	Bravais lattice	Max. T_c [K]	Representative systems
A1	fcc	7.19	Pb
A2	bcc	9.26	Nb
A12 (α Mn)	bcc	10.50	NbTc ₃
A13 (β Mn)	c	10.00	Mo ₃ Al ₂ C
A15 (Cr ₃ Si)	c	23.20	Nb ₃ Ge
B1	fcc	17.90	Nb(C,N)
C15 (Laves phase)	fcc	10.40	(V,Nb) ₂ Hf _{0.75}
C16 (CuAl ₂)	t	11.30	Zr ₂ Rh
C32 (AlB ₂)	h	11.20	(MoZr) ₂ B ₅
D5 _c (Pu ₂ C ₃)	bcc	17.00	Y _{0.5} Th _{0.3} C _{1.55}
E9 ₃	fcc	11.80	Zr ₃ Rh
L1 ₂	c	10.40	La ₃ In
Chalcogenides	rh	15.20	PbMo ₆ S ₈

a list of the different properties exhibited by many of these compounds with related structures are given in Table 2.3.

2.7 STUDY OF INTERMETALLICS FROM RECENT THEORIES

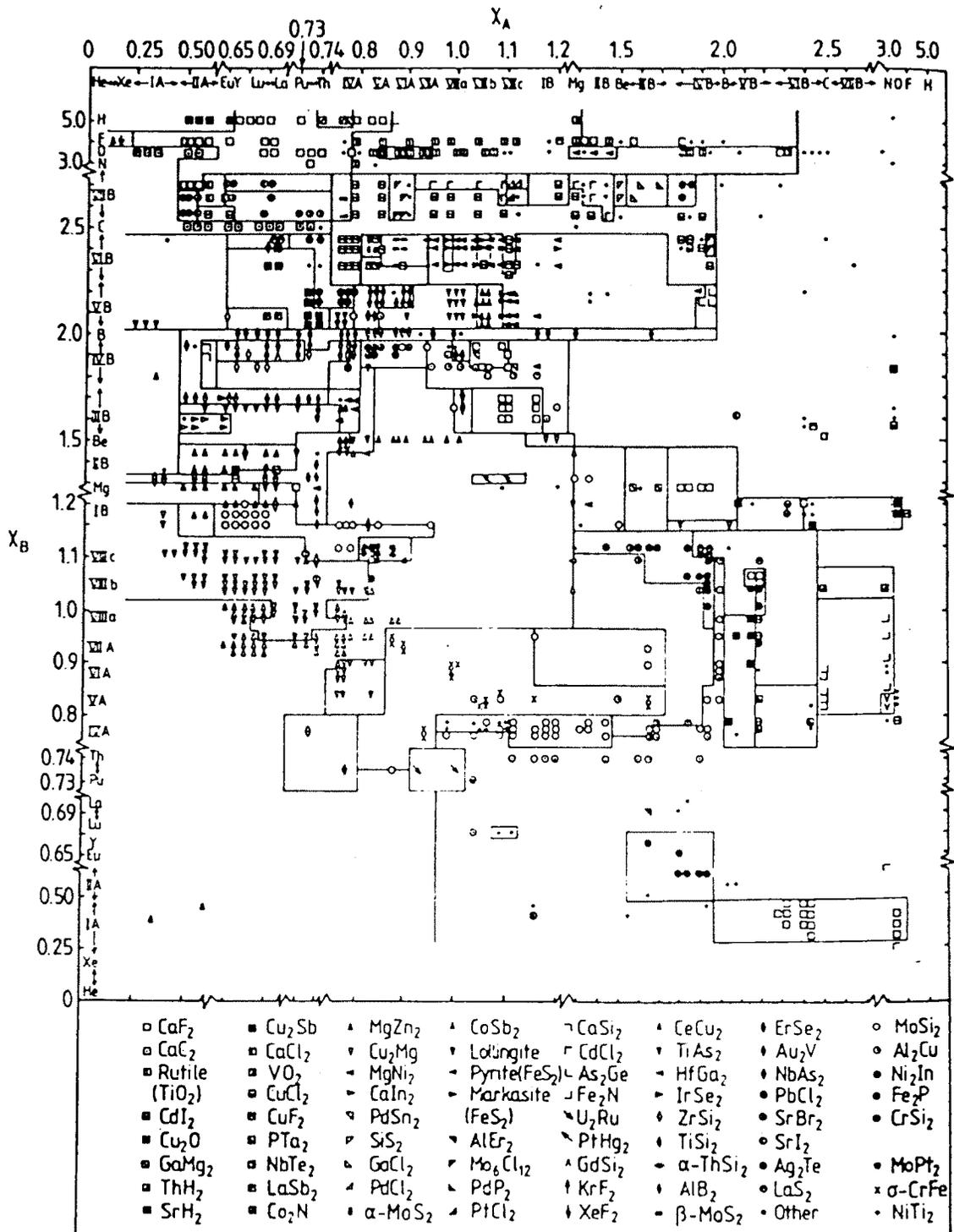
Some of the macroscopic properties for several elemental solids were successfully explained for the first time by Morruzi *et al* (1978) on the basis of quantum theory. With the success of the one-electron theory of solids in explaining the physical properties, it was later extended to compounds (Andersen 1978), clusters, surfaces and interfaces (Harris 1984). As binary compounds contain only two different types of atoms, though tedious, the computer calculations are feasible. The contributions to the understanding of even complex systems from simple theoretical calculations are due to Andersen and others (1983). On the otherhand, a semiclassical approach to the same problem was given by Pettifor (1987). His study is mostly to find the crystal structures of a lot of systems, their systematics and the nature of bonding. Phillips (1987), based on quantum theoretical ideas has constructed what are called QSD (Quantum Structural Diagrams) which are used to classify various systems. The different quantum mechanical approaches which have been made are discussed elaborately in the first chapter.

2.8 AB₂ COMPOUNDS AND THE RELATED STUDY

The AB₂ structure map where 69 different structure types as considered by Pettifor (1987) is given in Figure 2.1. The corresponding local coordination about A site is given in Figure 2.2. Pettifor assigns a value χ for every element in the periodic table. The domain marked by 12+ in Fig 2.2 has a local coordination greater than 12 which includes AlB₂ type, ThSi₂ type and Laves phases MgCu₂, MgZn₂ and MgNi₂. The first two types are commonly found between compounds of metals and metalloids, whereas the latter one provides higher coordination with different metal atoms. Most of the other structures provide lower coordination and also lower symmetries.

Table 2.3 The characteristic properties of some binary compounds with stoichiometries A_mB_n

AB	NiO NbC	Mott insulator Superconductor
AB ₂	YCo ₂ MoSi ₂	Meta-magnetic transition Oxidation resistant
AB ₃	Nb ₃ Sn Ti ₃ Al	Maximum T _c of 23 K prior to the 90 and 120 K superconductors Aerospace materials
AB ₅	SmCo ₅	High performance permanent magnets
AB ₆	LaB ₆	Good thermionic emitters and high temperature materials
AB ₁₂	TiBe ₁₂	High specific strengths
A ₂ B ₁₇	Nb ₂ Be ₁₇	High specific strengths
AB ₁₃	UBe ₁₃	Heavy Fermion systems

Figure 2.1 AB₂ structure diagram of Pettifor

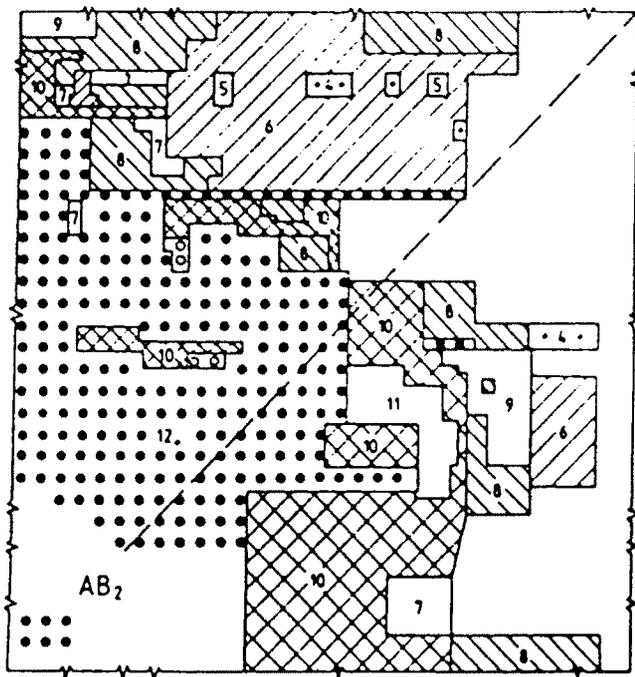


Figure 2.2 Location coordination around A site

A possible prediction of the number of compounds of a given stoichiometry and structure can be found among the 84 elements (excluding halogens, inert gases and actinides) of the periodic table based on the principles discussed earlier. Of the 6972 combinations possible with stoichiometries $A_m B_n$, the highest number of 2000 compounds are predicted to be in the $MgCu_2$ type (Laves phase). Next is the $CaCu_5$ type with 1100, β -W type 714, CsCl type 1500 and α -type with 156 (Savitskii *et al* 1980).

80 030

The fact that so many AB_2 compounds adopt Laves phases and that this structure type provides higher symmetry and higher coordination numbers with variety of properties makes the study of these Laves phase compounds more interesting. More about their structure and bonding are discussed in the next section.

53
N2

80 0130

2.9 STRUCTURAL DETAILS AND SALIENT FEATURES OF THE LAVES PHASE COMPOUNDS

The three closely related structures $MgCu_2$, $MgZn_2$ and $MgNi_2$ constitute the Laves phase. The last two are hexagonal while the first one alone is cubic. The stacking arrangement is different for the three structures. The A atoms are arranged in double layers of a hexagonal network, with each A atom of the upper layer located directly above one of the lower layers. In the case of $MgCu_2$, looking along the cube diagonal, one observes the different double layers which are labeled as X, Y and Z for convenience. The B atoms are arranged at the corners of tetrahedra. The arrangement of the double layers and the tetrahedra, in space are given in Table 2.4. and in Figure 2.3. The larger A atoms lie in the holes between the tetrahedra formed by the smaller B atoms. $MgCu_2$ (C15) contains 24 atoms per unit cell, whereas $MgZn_2$ (C14) and $MgNi_2$ (C36) have 12 and 24 atoms respectively. In the cubic $MgCu_2$ type structure, the coordination to an A atom is four other equidistant A atoms at a distance $a\sqrt{3}/4$, there are twelve B atoms at a somewhat smaller distance $a\sqrt{11}/8$. The coordination then is quite high, effectively sixteen. Each B atom is surrounded by six B atoms at a distance $a\sqrt{2}/4$

Table 2.4 The arrangements of double layers and tetrahedra in space for Laves phases

Structure type	Arrangement	
	A atom layers	B atom tetrahedra
MgCu ₂	ABC ABC (along [111])	joined point to point
MgZn ₂	ABAB (along [001])	joined point-to point and base to base alternately
MgNi ₂	ABAC ABAC (along [001])	mixture of the above two arrangement

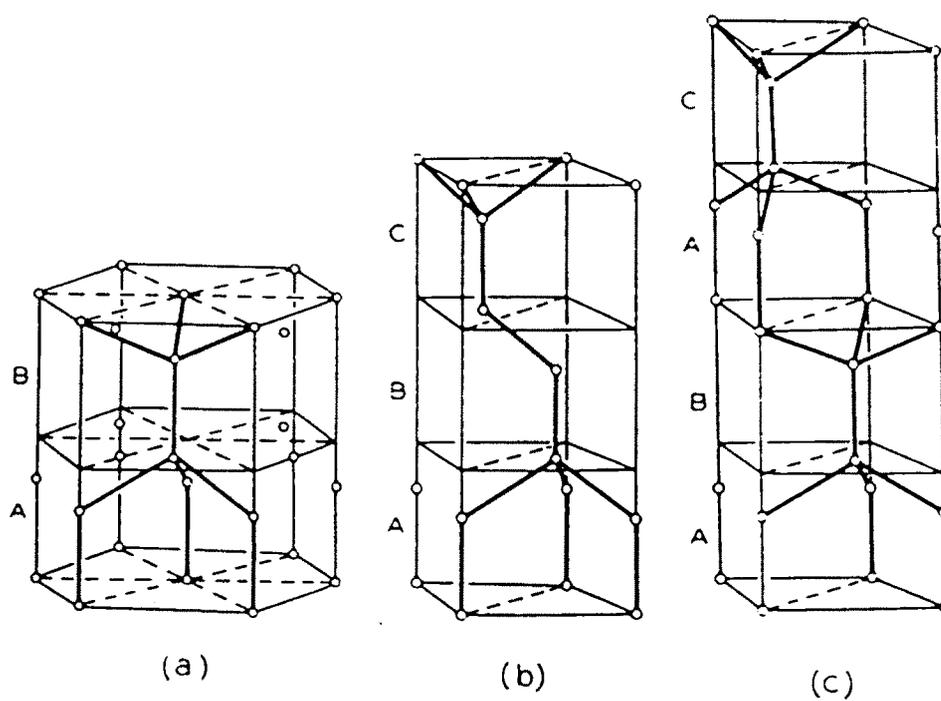


Figure 2.3 Arrangement of double layers of tetrahedra for MgCu_2 , MgZn_2 and MgNi_2

and six A atoms at a distance $a\sqrt{11}/8$. So the next nearest neighbour to a B atom is another B atom. The crystallographic data of the structure types are given in Table 2.5

The salient features of the Laves phases are given below:

- (1) Among the AB_2 type compounds, the Laves phases provide metal-metal bonding with higher coordination numbers i.e. 16, while the highest possible in the elemental case is only 12.
- (2) Size effect dominates over the rest of the factors discussed so far. The following examples will highlight the above fact.
 - (a) KNa_2 . In spite of the fact that K and Na belong to the same group, a compound like KNa_2 is formed because the atomic radii ratio has exactly the same value for the ideal packing of spheres in the Laves phase. Based on theoretical arguments the compound was first proposed by Laves himself and the experimental confirmation of the formation of the compound came later.
 - (b) $REAl_2$. The fact that all rare earths (RE) form AB_2 compounds (Purwins and Leson 1990) in the same C15 type structure and the increase of the f-electron number as one goes from $LaAl_2$ to $LuAl_2$ does not influence the formation of the compounds are indicative of the predominant size effect in these compounds. A complete systematic study of the behaviour of the f-electrons alone under the influence of the external conditions is not possible even in the elemental case as the crystal structure and bonding changes from La to Lu, whereas in the case of the Laves phase compounds like $REAl_2$ such a study is possible as the crystal structure of $(La-Lu)Al_2$ remains unchanged. The melting temperatures of all the $REAl_2$ compounds vary within a narrow range of 1300 to 1400 K and this

Table 2.5 Crystal structure and basis positions for the Laves phases

Structure	Lattice symmetry	CN	Atomic parameters
MgCu ₂	fcc Fd3m	24	origin at 1/8,1/8,1/8 Mg:8a, 0 0 0; 1/4,1/4,1/4 Cu:16d 5/8,5/8,5/8;5/8,7/8,7/8; 7/8,5/8,7/8;7/8,7/8,5/8
MgNi ₂	hexagonal P6 ₃ /mmc	24	Mg(1):4e, 0 0 z; 0 0 \bar{z} 0 0 1/2+z; 0 0 1/2-z, z=0.094 Mg(2):4f 1/3,2/3,z;2/3,1/3, \bar{z} ; 2/3,1/3,1/2+z;1/3,2/3,1/2-z, z=0.844 Ni(1):6g 1/2,0,0;0,1/2,0; 1/2,1/2,0;1/2,0,1/2; 0,1/2,1/2;1/2,1/2,1/2 Ni(2):6h x,2x,1/4;2 \bar{x} , \bar{x} ,1/4;x, \bar{x} ,1/4 \bar{x} ,2 \bar{x} ,3/4;2x,x,3/4; \bar{x} ,x,3/4 x=0.167 Ni(3):4f as for Mg(2) above, z=0.125
MgZn ₂	hexagonal P6 ₃ /mmc	12	Mg:4f 1/3,2/3,z;2/3,1/3, \bar{z} ; 2/3,1/3,1/2+z;1/3,2/3,1/2-z z=0.062 Zn(1):2a 0 0 0;0 0 1/2 Zn(2):6h as for Ni(2) above, x=0.830

indicates that the bonding does not alter very much in these compounds. Hence the f-electron behaviour can be better understood from a study of these compounds than the elements.

- (3) The size effect is again reflected in the cases of MgCu_2 and CaMg_2 , as Mg occupies the A atom position in the first case and the B atom position in the other.
- (4) The nearest neighbour of the B atom is another B atom and the B-B distance is shorter compared with the A-A distance. Hence the interaction among the B atoms will be stronger and more dominant. The influence of the A atom on the properties of the compound will only be indirect. The different A atoms, of course can be used to tune the desired properties in the compounds.

2.10 RECENT TRENDS IN THE STUDY OF LAVES PHASE COMPOUNDS

Towards the end of the 1970's began the study of the physical properties of ordered compounds and alloys from self-consistent electronic structure calculations when the efficient computational methods like LMTO and LAPW were developed (Andersen 1975 and Skriver 1984). However, there were earlier attempts to study simple systems using APW, ASW and KKR methods (Williams *et al* 1979). The transition metal Laves phase compounds are the ones which have been exhaustively studied, since they exhibit very interesting changes in the magnetic behaviour with respect to temperature and external magnetic fields (Asano *et al* 1985, Yamada 1988). The results of these calculations are in fair agreement with the experimental results. A summary of the conclusions drawn from these calculations are given below.

- (1) The crystal structure of the transition-metal Laves phase compounds AB_2 is determined by the B atom for the non-magnetic compounds: the crystal structure is of C15 type when the B atom is Cr, Co or Ni (Mo, Rh or Pd)

and of C14 type when the B atom is Mn or Fe (Tc or Ru). For compounds with magnetic B atoms if the above rule is not applicable then, the magnetism is the factor determining which crystal structure is most stable (Asano *et al* 1988).

- (2) There are in general two characteristic peaks in the density of states curve near the Fermi energy for all the Laves phase compounds. The location of the Fermi energy in the DOS curves depends on the type of the A atom and it is also partly responsible for the magnetic state of the system (Yamada 1988).
- (3) Certain systematics have been observed in these compounds with regard to the substitution of the A or the B atom. The magnetic state of the transition-metal Laves phase compound is found to be that of the B atom itself in most of the cases. The replacement of the A atom by any one of the atoms belonging to the same group does not change either the trend of the DOS curves or the physical properties. But the substitution of the A atoms of different groups, leads to changes in the physical properties and especially the magnetic property drastically gets changed. For instance ACo_2 compounds show anomalous variation of the susceptibility with temperature and magnetic fields if A is one of the group IIIA elements like Sc, Y or Lu. On the otherhand for A atoms of group IVA, the susceptibility decreases monotonically with increasing temperature and applied field (Yamada 1988).
- (4) The electronic structure calculation of most of the transition metal compounds which have been performed so far, were to study their magnetic behaviour. Here the d-d interactions among the B-B atoms are very important. In the case of rare earth compounds, which again exhibit a variety of magnetic properties, the interactions are more complicated. Magnetism in most of the rare earth compounds are due to the f-electrons which do not take part in bonding. As the rare-earths mostly occupy the A

atom position it has been found that the A-B interactions should also be taken into account for rare-earth compounds. The interactions include f-f among the A atoms, d-d among the B atoms if B is a transition metal (T), otherwise s-p interaction and f-d interaction between the A and the B atoms (T) (Levitin 1990).

2.11 THE PRESENT STUDY

From what has been said so far, one observes that considerable amount of work has been done to understand the crystal structure and magnetic behaviour of the Laves phase systems. The present thesis aims at making a systematic study of the superconducting behaviour of the Laves phase compounds apart from calculating other electronic properties. The compounds considered for the present study involve different interactions as the constituent atoms A and B in AB_2 have different valence configurations.

- (i) (A) s- element - (B) s- element [$KNa_2, CaMg_2, SrMg_2, BaMg_2$]
- (ii) (A) s- element - (B) sd- element [$CaRh_2, SrRh_2$]
- (iii) (A) sd- element - (B) sd- element [$YRh_2, LaRh_2, (Sc, Y, Lu)Tc_2$
and
 $(Sc, Y, Lu)Re_2$]

The third chapter deals with the electronic structure study of the compounds KNa_2 , $CaMg_2$, $SrMg_2$ and $BaMg_2$. KNa_2 shows predominantly the size effect. The interactions in all these compounds are mostly s-p type.

In the fourth chapter, we consider those cases, where A is a non-transition element (divalent atoms Ca, Sr) and B is a transition element (Rh). They have the same crystal structure and nearly the same superconducting transition temperatures (T_c). The interactions involved are d-d among the B atoms and s-d between A and B atoms. Their superconducting transition temperatures are calculated theoretically and are compared with the experimental values.

Though the transition metal compounds have been exhaustively studied, the non-magnetic systems have been rarely studied. In the fifth chapter, the electronic structure calculations of YRh_2 and $LaRh_2$ are reported. The role of the substitution of B atom on their electronic structures and other physical properties are discussed. At this stage mention should be made that a compound like $ScRh_2$ is not formed inspite of the fact that the radius ratio lies in the range of the rest of the rhodium compounds. On the otherhand, $ScRh$ is formed in the NaCl type structure and till now there are no detailed theoretical study on the phase diagram of this system.

All the technetium compounds $ScTc_2$, YTc_2 and $LuTc_2$ have fairly high superconducting transition temperatures which are around 10K. Among them $ScTc_2$ has the highest T_c value of 10.9K. The sixth chapter deals with the electronic structure study of these compounds and the results of which are used in the calculation of their superconducting transition temperatures (T_c).

Rhenium which belongs to the technetium group also forms Laves phase compounds with Sc, Y and Lu in the same crystallographic structure. But their superconducting transition temperatures are very low. The electronic structure study of these compounds gives valuable information about the changes in the electronic structures between technetium and rhenium compounds which in turn will be used to understand the change in the transition temperatures when compared to the technetium compounds.

The last chapter summarises the results of the electronic structure calculations of the Laves phase compounds. The practical difficulties involved in the present calculations on AB_2 systems are also discussed. The systematics observed in the DOS curves and the other calculated electronic properties are also brought out in this chapter.