CHAPTER 8

CONCLUSION

Although a systematic study of crystal structure and magnetic behaviour of Laves phase compounds has been performed in the past, no such detailed study has been made with regard to superconductivity. Here we report the first systematic study of electronic structure and their physical properties of as many as fourteen Laves phase systems out of which ten are superconducting. Again ten among the systems investigated belong to the more complicated hexagonal C14 type and the rest are of cubic C15 type. It was largely believed that superconductivity will be favoured in the cubic systems rather than the hexagonal systems (Vonsovsky 1982). But some of the technetium compounds which belong to the hexagonal C14 type were found to be superconducting with transition temperatures as high as 10K. Inspite of it, no band structure calculations were attempted and the reasons for this were that the number of atoms per primitive cell is as high as twelve and further the f-states have to be included in the calculations. When these factors are taken into account the order of the secular determinant became as large as 192 which really demands much greater computational time.

The structure types of the compounds studied have packing densities of nearly 70% and hence the LMTO method can be successfully used for the electronic structure study. The first electronic structure calculation performed for the C14 type compound KNa₂ is of considerable importance. It has a minimum heat of formation among all the Laves phase compounds indicating the metallic bonding in the system. Further as the electronegativity difference between the constituent atoms in KNa₂ being very small, it forms naturally the best test case to formally judge the validity of the radius ratio chosen. The charge transfer in this compound should be minimum and the bandstructure calculations demonstrate
this for the ideal radius ratio of 1.225. This is found to be true in the case of magnesium compounds also. This ratio was used for all the systems so that the band structure results could be compared.

In the strict sense one cannot talk about charge transfers in these systems with overlapping spheres, but by introducing a proper uniform interstitial charge density, the correct Madelung potentials can be obtained for a situation similar to the non-overlapping MT sphere geometry and then the concept of charge transfer would be meaningful. Though the concept of charge transfer has been exploited by many others like Pauling (1967) and Pettifor (1988) for calculating the interatomic distances of intermetallic compounds and Jarlborg (1988) for explaining the superconductivity of the high Tc oxide compound \( \text{YBa}_2\text{Cu}_3\text{O}_\text{x} \) in the present studies on the Laves phase compounds \( \text{KNa}_2\text{, CaMg}_2\text{, SrMg}_2\text{ and BaMg}_2 \), the magnitudes or the direction of charge transfers are not of much significance as they do not involve other types of bonding and one looks for only a minimum charge transfer. The band structure results show that there is no B atom dominance in these compounds unlike the case of transition metal compounds.

The rhodium compounds all crystallise in the cubic C15 type structure and they show changes in the superconducting transition temperature with regard to the substitution of the A atom. For all the alkaline earth compounds, \( \text{CaRh}_2\text{, SrRh}_2\text{ and BaRh}_2 \), the superconducting transition temperatures are around 6 K, while for \( \text{YRh}_2\text{ and LaRh}_2 \) it goes down drastically to below 1 K. Eventhough, it is often spoken of the B atom dominance, in Laves phase compounds, there are obvious examples like the rhodium compounds mentioned above where the A atom influence is quite considerable.

Our attempt to calculate the superconducting transition temperature was successful in the case of \( \text{YRh}_2\text{ and LaRh}_2 \) when we included the f-states. Inspite of the fact that the density of states differ considerably for \( \text{SrRh}_2\text{ and YRh}_2 \) (excluding f-states), the comparison of n's of the B atoms in both the compounds are found to be the same and this indicates that the inclusion of f-states for \( \text{CaRh}_2\)
and SrRh$_2$ will improve the theoretically calculated values of the superconducting transition temperatures which otherwise show poor agreement when compared with the experimental values. The included f-states are far above the Fermi energy in all the cases but for a small contribution at $E_F$ which is only due to hybridisation with the d-bands. The inclusion of the f-states has a greater influence in altering the DOS at $E_F$ only in LaRh$_2$ since the f-bands are found to be closer to the Fermi energy in this case. The electronic stiffness coefficient calculated with and without the f-states show a large variation thereby pointing to the fact that the contribution by $\eta_{\text{el}}$ to $\eta$ is of considerable significance. We conclude that for all d-band solids it is necessary to include the f-states in the bandstructure calculations so that we make a proper estimation of the electronic stiffness coefficient and hence the superconducting transition temperature.

Our band structure calculations have been highly successful in explaining the superconducting behaviour of (Sc,Y)Tc$_2$/Re$_2$ compounds. The calculated values of the density of states at the Fermi energy agrees very well with the bare density of states which were extracted from the experimental heat capacity measurements of Stewart et al. (1981). They attribute the decrement in the density of states at the Fermi energy between the technetium and rhenium compounds to be responsible for the decrement in the $T_c$ values. Our theoretical calculations show that the electronic part in the calculation of electron-phonon coupling constant is the same for the technetium and rhenium compounds inspite of the fact that the density of states show large decrement for the rhenium compounds as expected by Stewart et al. (1981). We assert that the change in $T_c$ value is not due to the change in the density of states as was claimed by Stewart et al. (1981) but it is done to the change in the phononic part $M<\omega^2>$ in $\lambda$. The appreciable mass difference between technetium and rhenium atoms as well as the changes in $<\omega^2>$ should play a role in deciding the $T_c$ value.

The value of $<\omega^2>$ or in other words, the magnitude of the Debye temperatures have been deduced using the prescription given by Joseph and Gschneidner (1968) excepting for ScTe$_2$ and ScRe$_2$ for which the experimental
Debye temperatures are available. Our calculation conclusively show that the disagreement between the theoretical and experimental values of $T_c$ for LuTc$_2$ and LuRe$_2$ should be due to the wrong selection of $\theta_D$ which we procedure obtained from the oversimplified suggested by Joseph and Gschneidner (1968) method. Attempts shoud be made to deduce more reliable $\theta_D$ values for this compounds.

Unfortunately the there are no experimental studies for instance like XPS or inverse photo emmision studies available for comparing bandstructure or the DOS curves. But a systematic comparison of the electronic structure and the DOS curves of these systems due to either the substitution of the A or the B atoms by another of the same group or the increase in the number of valence electrons of the A and B atoms follow similar trends as discussed by Yamada (1988) and Asano and Ishida (1988) for magnetic transition metal Laves phase compounds. The characteristic peaks in the DOS curves for the C14 and C15 type structures are clearly seen in all of the transition metal compounds studied in this work. The general conclusions arrived from our calculations regarding the nature of the bands and the DOS curves are summarised below.

In all the Laves phase compounds either they are of C15 or C14 structure type compounds, the bands due to the B atoms have dominant role around the Fermi energy except in KNa$_2$ and CaMg$_2$ where the broad s-bands of both the atoms equally participate near the Fermi energy. The general trends observed are

(i) For those compounds involving s-bands alone like KNa$_2$, the DOS curve is nearly parabolic. This is found to be true in the case of CaMg$_2$, SrMg$_2$ and BaMg$_2$ also and the unoccupied d-bands in these cases are all above the Fermi energy.

(ii) If B atoms are transition metal atoms then the narrow d-bands of the B atoms dominate near the Fermi energy.

(iii) For the transition metal compounds, neither the substitution of the A atom of the same group nor the B atom substitution by the same group element
bring about any change in the shape of the DOS curves and in the position of the Fermi energy.

(iv) However there are changes observed in the value of the DOS at $E_F$. The trend is that the DOS ($E_F$) gradually decreases with the increasing atomic number of the B atoms of the same group. The percentage difference introduced by the substitution of the A atom on the DOS at $E_F$ is small compared to that introduced by the B atoms.

(v) For isoelectronic and isostructural compounds, the change in the conduction band widths are mostly due to the energy shift of low lying bands of A atoms.

In the case of compounds with magnetic B atoms, from the paramagnetic bandstructure calculation and the location of the Fermi energy, the nature of magnetism present in the compound can be inferred. From our calculation on the superconducting technetium and rhenium compounds, we infer that among the technetium or the rhenium compounds, the gradual decrease in the contribution to $\eta$ from $\text{ScTc}_2(\text{Re}_2)$, $\text{LuTc}_2(\text{Re}_2)$ to $\text{YTC}_2(\text{Re}_2)$ follow the trend of the decreasing density of states at the Fermi energy and the decreasing superconducting transition temperatures.

The present calculations bring out the fact that for Laves phase systems, it is the B-B interaction which is more dominant than A-A or A-B interactions. One could anticipate this even before performing the bandstructure calculation because of the shorter B-B distance. But the bandstructure calculations give a quantitative estimate of Fermi level quantities which enables one to study the different properties.

With regard to the pressure induced superconductors which are being discussed in the Appendix, we conclude from our experience with several elementals solids that s-d electron transfer is responsible for promoting superconductivity in elemental solids Y and Te at high pressures. This is supported experimental by optical reflectivity studies.