

Structure and superconductivity in ternary systems of compounds

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Abstract. A survey of the known high T_c ternary systems of compounds is presented. Special emphasis has been placed on the part played by the crystal structure and bonding in the exhibition of high T_c superconductivity. The superconducting and other physical properties of the ternary borides have been discussed in relatively more detail. Finally, the available guidelines from crystal and solid state chemistry points of view, have been reiterated for a search for new high T_c materials.

Keywords. Ternary systems; superconducting compounds; metal excess systems.

1. Introduction

A ternary compound is one which contains three elements each occupying a distinct set or sets of crystallographic lattice sites and preferably one element should be a non-metal. This crystallographic definition clearly distinguishes ternary compounds from binary or pseudo-binary phases in which only two sets of lattice sites are occupied or which contain only two species of elements. Metal excess ternary system of compounds (METS) are those in which only part of the valence electrons are involved in bonding (say, with the non metal) and the excess valence electrons of the metal(s) will partially fill the conduction band formed by the overlap of the requisite metal s , p and d orbitals (Hulliger 1981; Simon 1981; Corbett 1981). Thus, METS compounds invariably exhibit high electronic conductivity and metallic behaviour. Theoretical considerations reveal that superconductivity in a metallic material can occur whenever there is a large density of electronic states at the Fermi level in a partially filled conduction band (preferably a narrow band) and a favourable electron-phonon interaction. Hence METS, in principle, satisfy the requirements for the exhibition of superconductivity.

Superconductivity, the phenomenon of vanishing electrical resistance in a material below a critical temperature ($T_c > 0$ K), is not uncommon and many elements, alloys intermetallics, binary and ternary chemical compounds exhibit the behaviour. However, of the more than 1000 superconductors known, only a very limited number possess $T_c > 10$ K and the latter are called high temperature superconductors. It is now established that certain particular crystal structure of a binary or ternary (intermetallic or chemical) compound is very conducive to give rise to high T_c superconductivity. The beta-tungsten (A_3B or A15) structure adopted by a large number of intermetallics is the well-known example. The phases Nb_3Al and Nb_3Au have a T_c of 18 and 11 K respectively when crystallized in A15 structure but when prepared in a bcc form (with the same composition) they exhibit a T_c of 4 and 1 K. The binary metallic carbides

Table 1. Structure and T_c of high temperature ternary superconductors

| Compound | Structure type | Lattice parameter (Å) | T_c (K) | Reference |
|---|--|------------------------------|-----------|---|
| LuRh ₄ B ₄ | CeCo ₄ B ₄ (tetra) | $a = 5.3; c = 7.4$ | 11.7 | Vendenberg and Matthias (1977) |
| Y(Rh _{0.85} Ru _{0.15}) ₄ B ₄ | LuRh ₄ B ₄ (tetra) | $a = 7.5; c = 14.9$ | 9.6 | Johnston (1977) |
| LuRuB ₂ | LuRuB ₂ (ortho) | $a = 5.8; b = 5.2; c = 6.3$ | 10.0 | Ku and Shelton (1980) |
| Mo ₃ Al ₂ C | Beta Mn (cubic) | $a = 6.9$ | 10.0 | Johnston <i>et al</i> (1964) |
| Mo ₂ BC | Mo ₂ BC (ortho) | $a = c = 3.1; b = 17.4$ | 7.0 | Toth (1967) |
| Sc ₅ Rh ₄ Si ₁₀ | Sc ₅ Co ₄ Si ₁₀ (tetra) | $a = 12.3; c = 4.0$ | 8.5 | Braun and Segre (1980) |
| Y ₅ Os ₄ Ge ₁₀ | Sc ₅ Co ₄ Si ₁₀ (tetra) | $a = 13.0; c = 4.3$ | 8.7 | Braun and Segre (1980) |
| YbRh _{1.4} Sn _{4.6} | Pr ₃ Rh ₄ Sn ₁₃ | $a = 9.7$ | 8.6 | Remeika <i>et al</i> (1980) |
| ZrRuP | Fe ₂ P (hexa) | $a = 6.4; c = 3.8$ | 13.0 | Barz <i>et al</i> (1980); Müller <i>et al</i> (1983) |
| NbPS | NbPS (ortho) | $a = 3.4; b = 11.9; c = 4.7$ | 12.5 | Donohue and Bierstedt (1969) |
| LaRu ₄ P ₁₂ | LaFe ₄ P ₁₂ (cubic) | $a = 8.1$ | 7.2 | Meisner (1981) |
| LiTi ₂ O ₄ | MgAl ₂ O ₄ (spinel) | $a = 8.4$ | 13.7 | Johnston (1976) |
| BaPb _{0.8} Bi _{0.2} O ₃ | CaTiO ₃ (dist. perov.) | $a \sim 5.2$ | 13.2 | Sleight <i>et al</i> (1975) |
| Zr _{0.6} Rh _{0.3} O _{0.1} | Fe ₃ W ₃ C (cubic) | $a = 12.4$ | 11.8 | Matthias <i>et al</i> (1963) |
| Pb _{0.9} Mo ₆ S _{7.5} | PbMo ₆ S ₈ (rhombo-hexa) | $a = 9.2; c = 11.48$ | 15.2 | Chevrel <i>et al</i> (1971); Matthias <i>et al</i> (1972) |
| Cu _{1.8} Mo ₆ S ₈ | PbMo ₆ S ₈ (distorted) | $a = 9.58; c = 10.25$ | 10.8 | Matthias <i>et al</i> (1972) |
| Mo ₆ S ₆ I ₂ | Mo ₆ Se ₈ | $a = 9.64; c = 10.44$ | 14.0 | Sergent <i>et al</i> (1977); Perrin <i>et al</i> (1973). |

crystallizing in NaCl or Pu₂C₃-structure types are the other examples. For the METS, the Chevrel phases (AMo₆S₈), rhodium borides (LnRh₄B₄-type), ordered Fe₂P-type phosphides constitute the relevant examples (table 1).

Since a large number of compounds are known or can be synthesized and also since chemical manipulation is more easily possible in them, the METS compounds do seem to offer a better scope for the realization of high T_c and high critical magnetic field (H_{c2}) materials. As a result of intense research activity during the past decade many ternary METS have been isolated and studied and a wealth of information and interesting physics have come out not only with respect to the superconducting behaviour but also the coexistence of magnetic order and superconductivity, reentrant behaviour, intermediate valence and mixed (electronic and ionic) conduction.

In the following we give a concise but upto date account of the known high T_c (≥ 10 K) compounds. Special emphasis will be placed on the part played by the crystal structure and bonding exhibited by them. We also give an account of some of the other known METS compounds that are yet to be tested for high T_c behaviour.

2. Ternary borides, AM_xB_y

2.1 Compounds with AM₄B₄ stoichiometry

METS borides of the formula AM₄B₄, A = rare earth (Ln), Y, Th have been synthesized by Kuz'ma *et al* (1972) with M = Co and by Vandenberg and Matthias (1977) with M = Rh. These compounds possess a primitive tetragonal (CeCo₄B₄-type) structure. Later studies have shown that AM₄B₄-type compounds with M = Os, Ir, Ru also exist

with either primitive tetragonal (NdCo_4B_4 -type), body centered tetragonal (*bct*, LuRu_4B_4 -type) or orthorhombic (LuRh_4B_4 -type) structure (Johnston 1977; Ku *et al* 1979; Kuz'ma *et al* 1979; Rogl 1979; Rogl 1980; Yvon and Johnston 1982). Compound formation with the composition AM_4B_4 has been reported with $\text{M} = \text{Fe}$ and Re but the structure has not yet been elucidated (Johnston and Braun 1982). The rhodium and iridium borides with the CeCo_4B_4 -type structure exhibit superconductivity while the isotopic cobalt borides have no transition above 1.5 K. The rhodium borides, especially those containing non-magnetic rare earth Lu and Y , exhibit high T_c (11.7 and 11.3 K respectively) (Matthias *et al* 1977; Johnston and Braun 1982). On the other hand, tetragonal compounds with the NdCo_4B_4 -type structure (LnM_4B_4 with $\text{M} = \text{Co}$, Ru , Os and Ir are only known but not with $\text{M} = \text{Rh}$) do not exhibit T_c above 1 K. The *bct* borides (LuRu_4B_4 -type) and orthorhombic phases (LuRh_4B_4 -type) do exhibit superconductivity. However, depending on the rare earth, Y or Sc occupying the lattice site, the T_c varies only from 1.4–7.2 K. Extensive studies have been carried out on the ternary borides with the CeCo_4B_4 -type structure by way of chemical substitution at the Ln and M sites and these help in establishing the systematics of superconductivity behaviour and structure-property correlations.

2.1a Structure: The four structure types exhibited by the AM_4B_4 compounds (*viz.*, primitive tetragonal CeCo_4B_4 and NdCo_4B_4 -types; *bct* LuRu_4B_4 -type and orthorhombic LuRh_4B_4 -type) can be described by an arrangement of transition metal tetrahedra, isolated A atoms (including the rare earths) and pairs of boron atoms. The CeCo_4B_4 , LuRu_4B_4 and LuRh_4B_4 structure-types are inter-related and all of them contain more or less isolated M_4 tetrahedral clusters while in the NdCo_4B_4 -type, the M_4 -clusters are fused together by sharing edges such that infinite chains are formed along the crystallographic c direction.

In the ARh_4B_4 compounds with the CeCo_4B_4 -structure, the A atoms and Rh_4 -clusters (slightly elongated with two short and four long Rh-Rh distances along the tetragonal a and c axes respectively) occupy the positions of a slightly distorted NaCl lattice (figure 1a). Two orientations of Rh_4 tetrahedra occur and the Rh network can be viewed as forming sheets in the a - b plane (quasi two-dimensional extended clusters)

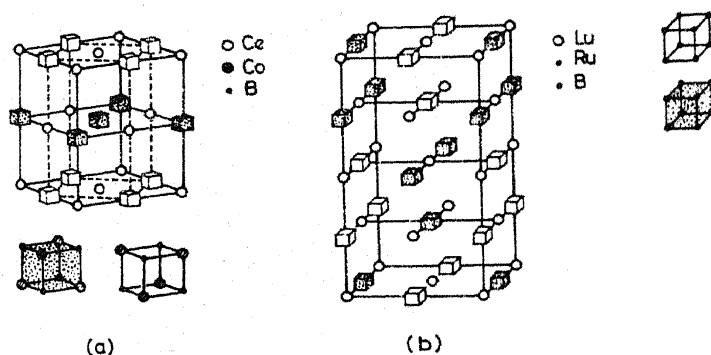


Figure 1. Idealized crystal structures of (a) primitive tetragonal CeCo_4B_4 -type and (b) body-centred tetragonal LuRu_4B_4 -type AM_4B_4 compounds. The dashed lines in (a) outline the unit cell. Two orientations of M_4 tetrahedra occur and for clarity, the M_4B_4 cubes are not drawn to scale. The lattice parameters are: CeCo_4B_4 -type: $a \sim 5.3 \text{ \AA}$; $c \sim 7.4 \text{ \AA}$; LuRu_4B_4 -type: $a \sim 7.5 \text{ \AA}$; $c \sim 14.9 \text{ \AA}$. Actual values will depend on the A and M element.

with an alternate arrangement (stacking) of tetrahedra of different orientations along the c -axis. The intra-cluster Rh-Rh distances (2.6–2.8 Å) are approximately the same as in rhodium metal (2.69 Å) but intercluster distances are larger (3.1 Å). The B-B distances are small (1.80–1.83 Å) indicating pair formation whereas the A-A distances are larger (≥ 5 Å) showing negligible interaction between them. However, significant bonding (charge transfer) exists between Rh and B atoms.

The bct (LuRu_4B_4 -type) and orthorhombic (LuRh_4B_4 -type) phases differ from the CeCo_4B_4 -type in the relative disposition of the isolated M_4 clusters in the lattice; whereas the M_4 tetrahedra of the same orientation are joined into sheets perpendicular to the c -axis in the CeCo_4B_4 -type, the M_4 tetrahedra of different orientations are distributed equally in each plane in an ordered fashion in the LuRu_4B_4 - and LuRh_4B_4 -types (figure 1b) (Johnston 1977; Yvon and Grüttner 1980; Yvon and Johnston 1982). Thus, the bct and orthorhombic structures can be viewed as containing two interpenetrating three-dimensional networks or extended clusters of M_4 tetrahedra. These extended clusters are qualitatively different from those in CeCo_4B_4 -type AM_4B_4 compounds, since in the latter phases they are quasi two-dimensional and do not interpenetrate. However, the unit cell dimensions of the three structures bear simple relationships to each other: $\sqrt{2} a \approx c(\text{CeCo}_4\text{B}_4\text{-type}) \approx a \approx (c/2)$ (LuRu_4B_4 -type) $\approx a \approx (b/3) \approx c(\text{LuRh}_4\text{B}_4\text{-type})$.

The NdCo_4B_4 -type structure differs from the CeCo_4B_4 -type in two ways, *viz.* the M_4 clusters are not isolated from each other but are fused together by sharing edges such that infinite chains are formed along the c -axis. Also, the A-A distances are small ($\sim 3.8\text{--}4$ Å $\approx c$ lattice parameter) so that they can be considered to form infinite linear chains along the tetragonal axis (figure 2). On the other hand, the A atoms in the CeCo_4B_4 structure are well-separated from each other and form nearly fcc array in the primitive tetragonal structure. The differences between the CeCo_4B_4 and NdCo_4B_4 structure types from a topological view point is also brought out by the fact that the c/a ratio is ~ 1.4 in the former while it is much smaller (~ 0.53) in the latter. As will be discussed later, these structural differences play a crucial role in the T_c behaviour of the compounds.

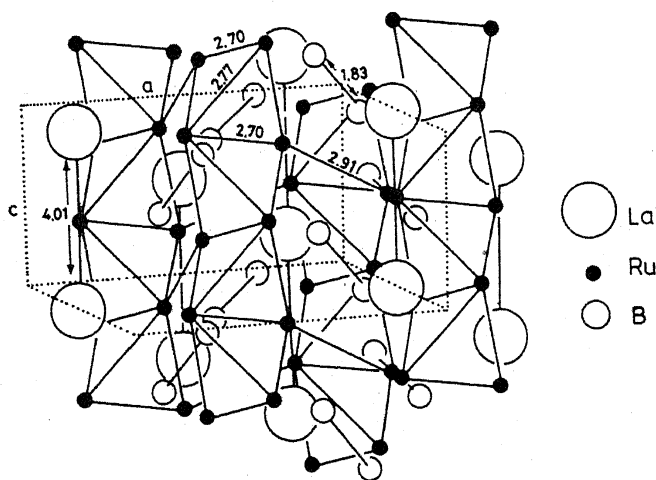


Figure 2. Structure of the tetragonal LaRu_4B_4 viewed approximately perpendicular to the tetragonal axis. The numbers indicate the Ru-Ru, La-La and B-B bond lengths. The compound is isostructural to NdCo_4B_4 . The lattice parameters are $a = 7.541$ Å, $b = 4.012$ Å (taken from Grüttner and Yvon 1979).

2.1b Formation and stability: The formation and stability of the AM_4B_4 compounds with different types of structures are dependent on the relative ionic sizes of the A and M atoms, valence electron concentration and electronic factors. Thus, the proper phase with the $CeCo_4B_4$ -type structure is formed only for the following combinations of elements: M = Co, A(Ln) = Ce, Gd \rightarrow Tm, Lu; M = Rh, A = Nd, Sm, Gd \rightarrow Tm, Lu, Y and Th; M = Ir, Ln = Ho, Er and Tm. The *bct* $LuRu_4B_4$ -structure easily forms for M = Ru and A = Sc, Y, Th, U and Ln with the only exception when Ln = La. For M = Os, only UOs_4B_4 has been isolated. We note that the proper phase with the $LuRu_4B_4$ -structure does not form for M = Co and Rh. However, the structure with M = Rh can be stabilized at the nominal AM_4B_4 stoichiometry by substitution with a few atom percent of Ru. Orthorhombic $LuRh_4B_4$ -type compounds are known only for M = Rh and Ln = Ho \rightarrow Lu. The $NdCo_4B_4$ -type structure is adopted for the following combinations: M = Co, Ln = La, Nd, Sm, Eu; M = Ru, Ln = La; M = Os, Ln = La \rightarrow Eu, Th; M = Ir, Ln = La \rightarrow Dy, Y and Th. Pseudoternary isostructural solid solutions easily form for isoelectronic M elements (M = Ru and Os or Rh and Ir) but, interestingly enough, solid solutions are also found to form for the combinations $Os_{1-x}Ir_x$ and $Rh_{1-x}Ru_x$ with a given A element.

The L vs r^{3+} plots, L being the cube root of the volume associated with one formula unit of AM_4B_4 and r^{3+} , the effective ionic radius of the trivalent rare earth atoms (Grüttner and Yvon 1979) is shown in figure 3. As can be seen the Rh- and Ru-based alloys which crystallize with the $CeCo_4B_4$ - and $LuRu_4B_4$ -structure types respectively have practically the same atomic volume (L). Since Ru and Rh atoms are very similar in size, this demonstrates the close structural relationship between these two series of compounds. Similar is the case with the Os and Ir alloys which crystallize with the

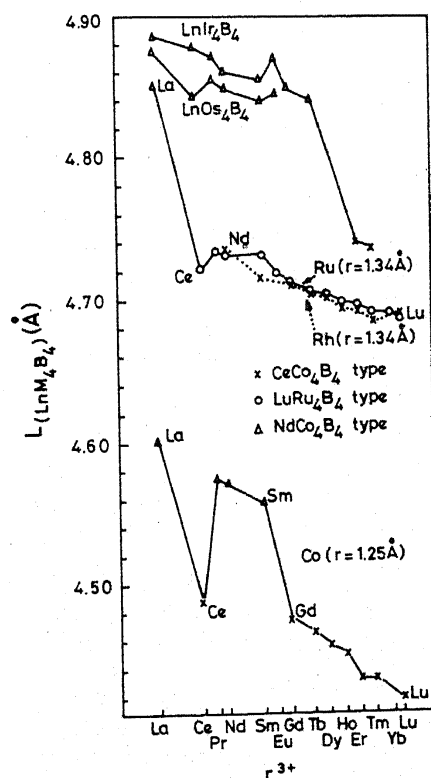


Figure 3. L versus r^{3+} diagram for the LnM_4B_4 compounds containing Co, Rh, Ru, Os and Ir. Full lines and dotted lines join compounds which contain the same transition element.

NdCo_4B_4 -type structure. The formation of the NdCo_4B_4 -structure for the Co, Ru, Os and Ir-based alloys, on the other hand, is associated with a rather strong and discontinuous volume expansion and occurs for large ionic radii (lighter) rare earths (figure 3). The switchover from the NdCo_4B_4 -structure to the CeCo_4B_4 -structure occurs in the Co- and Ir based alloys for only the smaller ionic radii (heavier) rare earths ($\text{Gd} \rightarrow \text{Lu}$) indicating that geometric factors such as the radius ratio between the Ln and M atoms plays a major role in forming the proper phase. On the other hand, the formation and stability of the CeCo_4B_4 - and LuRu_4B_4 -type compounds depends more on the electronic factors, valency of the A atom and valence electron concentration (valence electron/atom ratio). Thus, the Rh-containing phases which normally crystallize with the CeCo_4B_4 -structure adopt the LuRu_4B_4 -structure if only 15% of Rh is substituted by Ru indicating that the arrangement of M atom sublattice in these two structure types is critically dependent on the valence electrons of the M atoms (Rh: 9; Ru: 8 electrons). Perhaps, similar behaviour might be exhibited by the $\text{M}\text{Ir}_4\text{B}_4$ phases (CeCo_4B_4 -structure) doped with Os.

2.1c Superconducting properties: The LnRh_4B_4 compounds with the CeCo_4B_4 -type structure have been studied extensively with respect to superconductivity and related physical properties. As mentioned earlier, the phases containing non-magnetic rare earths Lu and Y exhibit high T_c values (table 2). For Ln = Nd, Sm, Er and Tm which can support a magnetic moment due to the 4f-electrons, superconductivity is retained but with a lower T_c (2.7–9.8 K). However, for Ln = Gd, Tb, Dy and Ho, superconductivity is destroyed and the compounds order ferromagnetically with Curie temperatures ranging from 5–12 K (figure 4). The pure compound ErRh_4B_4 exhibits a reentrant (metallic) behaviour in the sense, on cooling to 0.9 K ($T_c = 8.7$ K), the superconductivity is destroyed and the compound becomes a metal; almost simultaneously a ferromagnetic order develops and is retained up to the lowest attainable temperatures.

Solid solutions of the type $(\text{Ln}_{1-x}\text{Ln}')\text{Rh}_4\text{B}_4$ and $\text{Ln}(\text{Rh}_{1-x}\text{M}_x)_4\text{B}_4$ (M = Ir and Ru) have been examined in detail in the literature and provide a wealth of information on the interplay between superconductivity and magnetism in these materials. For the former type, an approximately linear variation of T_c is noticed with x (up to x_c , see figure 5) irrespective of the fact whether Ln and Ln' carry local magnetic moments or not, provided the end members ($x = 0$ and 1) form the proper phase with the CeCo_4B_4 -type structure. This behaviour indicates that the rare earth ion-conduction electron exchange interaction is weak in these materials.

Table 2. T_c data on some representative AM_4B_4 compounds^a

| CeCo_4B_4 -type | | bct- LuRu_4B_4 -type ^b | | Ortho LuRh_4B_4 -type | |
|---------------------------------|-----------|---|-----------|---------------------------------------|-----------|
| Phase | T_c (K) | Phase | T_c (K) | Phase | T_c (K) |
| LuRh_4B_4 | 11.7 | $\text{Lu}(\text{Rh}_{0.85}\text{Ru}_{0.15})_4\text{B}_4$ | 9.0 | LuRh_4B_4 | 6.2 |
| YRh_4B_4 | 11.3 | $\text{Y}(\text{Rh}_{0.85}\text{Ru}_{0.15})_4\text{B}_4$ | 9.4 | — | — |
| ErRh_4B_4 | 8.7 | $\text{Er}(\text{Rh}_{0.85}\text{Ru}_{0.15})_4\text{B}_4$ | 7.9 | ErRh_4B_4 | 4.3 |
| TmRh_4B_4 | 9.8 | $\text{Tm}(\text{Rh}_{0.85}\text{Ru}_{0.15})_4\text{B}_4$ | 8.3 | TmRh_4B_4 | 5.4 |

^a Taken from Johnston and Braun (1982). Phases with the NdCo_4B_4 -type structure do not exhibit superconductivity above 1 K.

^b LuRu_4B_4 and YRu_4B_4 have a T_c of 2 and 1.4 K respectively.

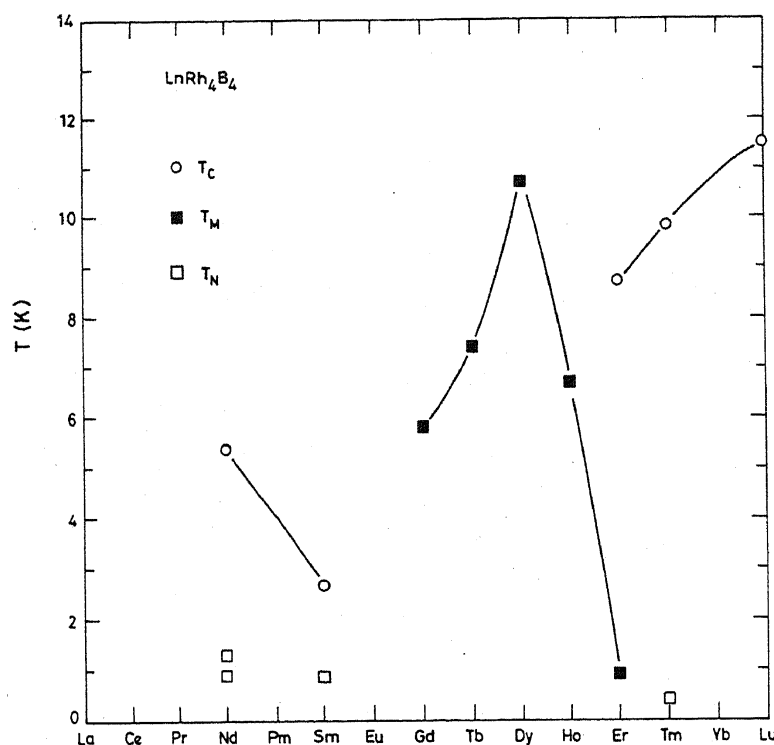


Figure 4. Superconducting (T_c), ferromagnetic (T_m) and antiferromagnetic (T_N) transition temperatures of LnRh_4B_4 compounds with the CeCo_4B_4 -structure. Phases with $\text{Ln} = \text{Nd}, \text{Sm}$ and Tm exhibit antiferromagnetic order coexisting with superconductivity below T_N while ErRh_4B_4 orders ferromagnetically below T_m with the destruction of superconductivity (re-entrant behaviour). Phases with $\text{Ln} = \text{Gd}, \text{Tb}, \text{Dy}$ and Ho exhibit ferromagnetic order below T_m and do not exhibit superconductivity. Studies on the effect of pressure on T_c and/or T_m indicate positive coefficient of $dT_c(M)/dP$ ($\sim 1 - 2 \times 10^{-5}$ K/bar) except for $\text{Ln} = \text{Nd}, \text{Sm}$ and Th where it is $\sim -0.5 \times 10^{-5}$ K/bar (Maple *et al* 1982; Shelton and Johnston 1978; Shelton *et al* 1980b).

Studies on the $\text{Ln}(\text{Rh}_{1-x}\text{Ir}_x)_4\text{B}_4$, $\text{Ln} = \text{Lu}, \text{Dy}, \text{Ho}$ and Er solid solutions with the CeCo_4B_4 -type structure have shown that: (i) superconductivity is induced for $x \geq 0.2$ for $\text{Ln} = \text{Tb}, \text{Dy}$ and Ho whereas the pure $x = 0$ phases exhibit only ferromagnetism (figure 6), (ii) the superconducting transition temperature drops precipitously with increasing x at $x = 0.5-0.6$ and goes through a minimum for $x = 0.8$ for $\text{Ln} = \text{Dy}, \text{Ho}, \text{Er}$ and also for non-magnetic Lu (see figure 6). This observation shows that electronic band structure is getting affected and the nature of rare earth ion (both magnetic and non-magnetic) has little effect on the non-linear T_c behaviour. Pseudoternary solid solutions of the non-isoelectronic type, $\text{Ln}(\text{Rh}_{1-x}\text{Ru}_x)_4\text{B}_4$ -type also exhibit interesting behaviour in the sense that superconductivity is induced for $x \geq 0.15$ for $\text{Ln} = \text{Pr}, \text{Eu}, \text{Dy}, \text{Ho}, \text{Er}$ and Tm whereas only long range magnetic ordering occurs for the isostructural *bct* LnRu_4B_4 with $\text{Ln} = \text{Nd}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}$ and Er . Also, T_c is enhanced for $x = 0.15$ with $\text{Ln} = \text{Lu}$ and Y compared to the $x = 0$ phases (see table 2). Non-linear variation of T_c with x has been found in $\text{Ln}(\text{Rh}_{1-x}\text{Ru}_x)_4\text{B}_4$, $\text{Ln} = \text{Y}, \text{Er}$ and Dy at around $x = 0.5-0.6$, a behaviour similar to that encountered in the $\text{Ln}(\text{Rh}_{1-x}\text{Ir}_x)_4\text{B}_4$ series of compounds. This indicates that non-magnetic effects like crystallographic order in the M atom array are playing a role in determining the T_c in these pseudoternaries.

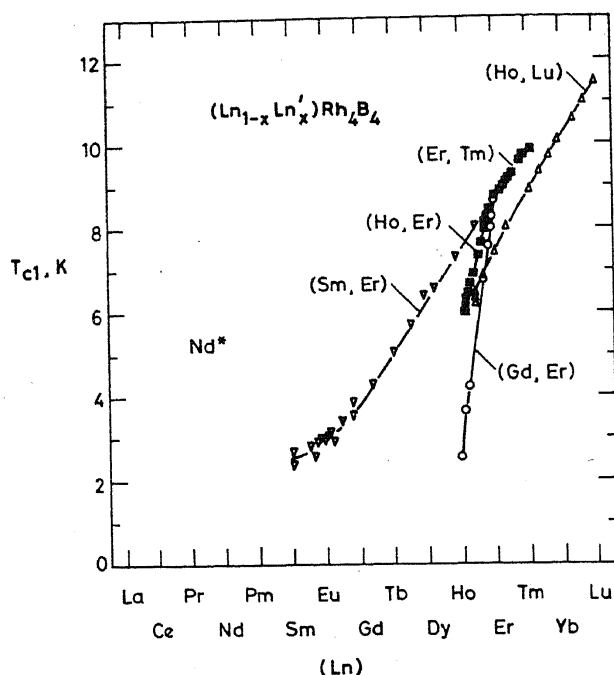


Figure 5. T_c vs atomic number (or average atomic number) curves for ternary and pseudo-ternary $(\text{Ln}_{1-x}\text{Ln}'_x)\text{Rh}_4\text{B}_4$ phases with the CeCo_4B_4 -structure (taken from Johnston and Braun 1982). The approximately linear variation of T_c with composition (for $x < x_c$) irrespective of whether Ln or Ln' carries a magnetic moment or not indicates that the conduction electron-localised spin interaction is small (x_c refers to the critical concentration at which T_{c1} , T_{c2} and T_M coincide).

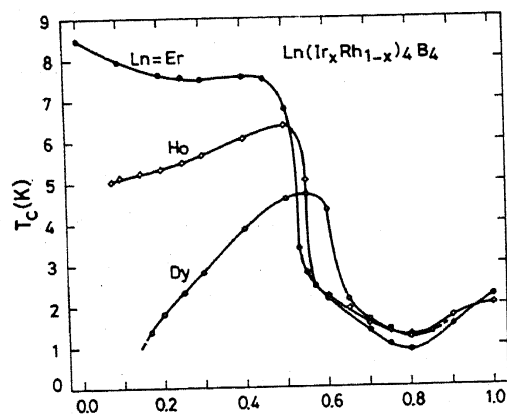


Figure 6. Variation of superconducting transition temperature (T_c) with composition in the CeCo_4B_4 -type system $\text{Ln}(\text{Rh}_{1-x}\text{Ir}_x)_4\text{B}_4$ (after Ku and Acker 1980). As can be seen T_c drops precipitously at $x \sim 0.5-0.6$ and T_c goes through a minimum at around $x = 0.8$.

The interesting and unusual properties of the LnRh_4B_4 compounds with the CeCo_4B_4 -type structure can be explained on the basis of the crystal structure: (i) the isolated Rh_4 tetrahedral clusters with strong intra and significant intercluster interactions lead to the formation of partially filled conduction bands with a large density of states at the Fermi level (E_F). Hence the Rh 4d-electrons are exclusively responsible for superconductivity and participate in the Cooper pair formation. This has been confirmed by magnetic susceptibility (χ) and other studies (Maple *et al* 1982) and band structure calculations (Freeman and Jarlborg 1982). As shown by the data in figure 5, the Ln ions have only small but non trivial effect on T_c , (ii) the rare earth ions

exist in 3+ oxidation state in the lattice and effect a charge transfer (donation of 3 electrons) to the Rh 4d-conduction band. This has been confirmed by $\chi - T$ (Maple *et al* 1982) Mössbauer (Shenoy *et al* 1980) and neutron diffraction (Moncton *et al* 1977). Because the Ln-Ln separation is large, there is negligible interaction between them and any magnetic ordering due to Ln-ions (which support a magnetic moment) occurs only at low temperatures (≤ 12 K) and (iii) the boron atoms which exist as pairs play the role of anion and stabilize the structure.

The fact that a composition-induced redistribution of the electronic density of states at the E_F may induce superconductivity and also bring drastic variation in T_c vs x is shown by the solid solutions $\text{Ln}(\text{Rh}_{1-x}\text{Ir}_x)_4\text{B}_4$ (CeCo_4B_4 -type; isoelectronic) and $\text{Ln}(\text{Rh}_{1-x}\text{Ru}_x)_4\text{B}_4$; (LuRu_4B_4 -type; non-isoelectronic) where the integrity of the rare earth sublattice is undisturbed. The nonlinear variation of T_c with composition and the precipitous decrease of it at $x \sim 0.5$ – 0.6 in both the above solid solution series have been correlated with the crystallographic c/a parameter. For example, in $\text{Ln}(\text{Rh}_{1-x}\text{Ir}_x)_4\text{B}_4$, $\text{Ln} = \text{Er}$ and Dy , Ku *et al* (1979) and Ku and Acker (1980) found that c/a ratio which is constant for $x < 0.50$, begins to decrease for $x = 0.5$ – 0.6 . Hence they suggested that for $x \leq 0.5$, at least one pure Rh_4 cluster per unit cell could exist whereas for $x > 0.5$, a random distribution of Rh and Ir atoms in the M_4 cluster may exist to give rise to an abrupt decrease in T_c . Similarly, studies on $\text{Lu}(\text{Rh}_{1-x}\text{Ru}_x)_4\text{B}_4$ system have shown that at $x = 0.5$ – 0.6 , a change in the c/a ratio (from < 2 to > 2) and anomalous changes in the interatomic B-B and M-M (intracluster) distances are observed (Yvon and Grüttner 1980; Johnston 1982).

The AM_4B_4 phases with the *bct* LuRu_4B_4 - or orthorhombic LuRh_4B_4 -type structure exhibit a lower T_c compared to those possessing the CeCo_4B_4 -type structure. This is due to the differences in the mode of arrangement of the (M_4B_4) tetrahedra of different orientations in the a - b plane as well as the stacking of them along the c -axis. This can give rise to changes in the density of states at the Fermi level and/or electron-phonon interaction leading to a lower T_c in the *bct* and orthorhombic types. However, since isolated clusters exist in all the three structure types, the phases exhibit superconductivity. On the other hand, the NdCo_4B_4 -type structure is unfavourable to the occurrence of superconductivity since it does not contain isolated (M_4B_4) clusters and also, perhaps, because of the small A-A separation.

2.1d Magnetic and non-magnetic contribution to the variation of T_c : It is important to separate the magnetic from non-magnetic contributions to the variation of T_c in analysing the data for a series of compounds containing rare earth elements. The magnetic contribution is usually analysed in terms of the Abrikosov-Gorkov (AG) theory according to which the exchange interaction between the conduction electrons with spin s and local magnetic moment with spin S ($H = -2IS \cdot s$) results in a reduction of T_c below the value $T_{c(0)}$ it would have had in the absence of exchange scattering, given by $(T_c/T_{c(0)}) = U(\alpha/\alpha_{cr})$ where U is a universal function of (α/α_{cr}) (Maple 1976). The (Cooper) pair breaking parameter α is given by $\alpha = (nN(E_F)I^2/\hbar)$ (dGF) where the deGennes factor (dGF) = $(g-1)^2 J(J+1)$, g and J being, respectively, the Lande's g factor and total angular momentum of the Ln^{3+} ion Hund's rule ground state. The n represents the concentration of magnetic ions, $N(E_F)$ is the density of states at the Fermi level (E_F) for each spin direction, I is the exchange interaction parameter. α_{cr} is the value of α at which T_c becomes zero. If n , I , $N(E_F)$ and $T_{c(0)}$ are the same for a given isostructural series of phases, then a plot of T_c vs (dGF) should scale with the universal

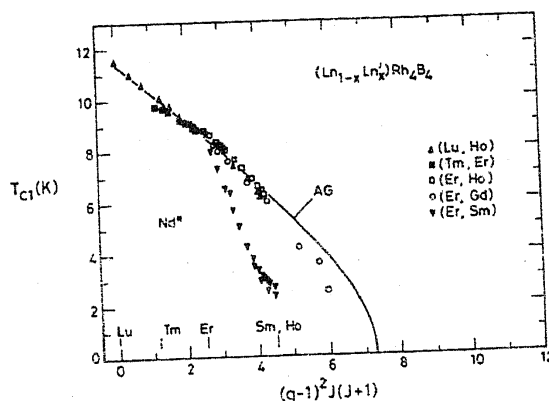


Figure 7. Superconducting transition temperature T_c vs deGennes factor for pseudo-ternary solid solutions: $(\text{Ln}_x\text{Ln}'_{1-x})\text{Rh}_4\text{B}_4$. The solid curve AG is a fit to the data using the Abrikosov-Gorkov theory with the following parameters: $T_{c(0)} = 11.4 \text{ K}$; $(dT_c/d(\text{dGF})) = -1.09 \text{ K}$; $nI^2N(E_F) = 2.04 \times 10^{-5} \text{ eV}$. The large parameters indicate an appreciably larger $N(E_F)$ and/or I^2 for heavy rare earth members of the CeCo_4B_4 structure type. Significant negative deviation from AG curve exists for $\text{Ln} = \text{Pr-Gd}$ (pure or alloys) (see text). (taken from Johnston and Braun 1982).

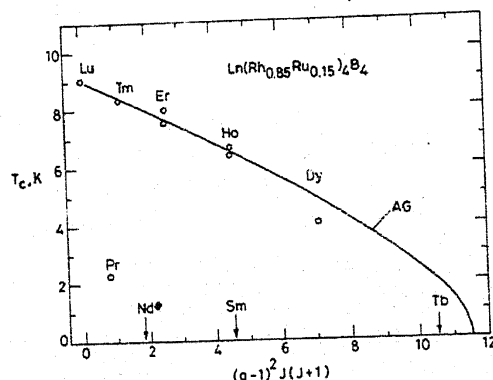


Figure 8. Superconducting transition temperature T_c vs deGennes factor for the LnRu_4B_4 -type compounds: $(\text{Rh}_{0.85}\text{Ru}_{0.15})_4\text{B}_4$. The solid curve AG is a fit to the data using the Abrikosov-Gorkov theory with the following parameters: $T_{c(0)} = 9.05 \text{ K}$; $(dT_c/d(\text{dGF})) = -0.54 \text{ K}$; $nI^2N(E_F) = 0.94 \times 10^{-5} \text{ eV}$. The parameters are only half of those of figure 7. (Johnston and Braun 1982).

curve. In figures 7 and 8 are shown the available data on $(\text{Ln}_{1-x}\text{Ln}'_x)\text{Rh}_4\text{B}_4$ phases with the CeCo_4B_4 -type structure and $\text{Ln}(\text{Rh}_{0.85}\text{Ru}_{0.15})_4\text{B}_4$ compounds with the $\text{bct-LuRu}_4\text{B}_4$ structure. As can be seen, a good fit of the AG theory to the data is obtained for $\text{Ln} = \text{Ho} \rightarrow \text{Lu}$ (for $\text{dGF} < 5$) in both the series of compounds and suggests that $T_{c(0)}$ and $I^2N(E_F)$ are independent of Ln for these compounds. However, significant negative deviations occur for the lighter rare earths ($\text{dGF} \geq 5$) and the discrepancy (between theoretical and experimental curves) increases as the average size of the Ln increases past that of Ho . The discrepancy could be due to (i) breakdown of AG theory for $\text{dGF} \geq 5$; (ii) increase of I^2 and/or $N(E_F)$ with increasing ionic radius and/or the splitting of the Ln -ion energy levels by the crystalline electric field (CEF) which is generally larger for the lighter Ln 's; (iii) non-magnetic effects, i.e. due to the inherent decrease in the value of $T_{c(0)}$. Experimental and theoretical studies on SmRh_4B_4 , $(\text{La}_x\text{Lu}_{1-x})\text{Rh}_4\text{B}_4$ ($x = 0.01-0.6$, CeCo_4B_4 -type) and $(\text{La}_{1-x}\text{Lu}_x)(\text{Rh}_{0.85}\text{Ru}_{0.15})_4\text{B}_4$ (LuRu_4B_4 -type) indicate that the negative deviations of the data from AG theory in figures 7 and 8 arise largely due to a decrease in $T_{c(0)}$ (Hamaker *et al* 1979; Mackay *et al* 1980; Kumagai *et al* 1981; Johnston 1981). However, factors mentioned in (ii) above may also be responsible to a small extent.

2.1e Coexistence of antiferromagnetism and superconductivity: Ternary rhodium borides, LnRh_4B_4 , are the ideal systems to study the interplay between magnetic order and superconductivity in materials for the following reasons: (i) The Ln ions are distributed uniformly throughout the crystal lattice (*i.e.*, form part of the network structure) but situated far off from the conduction electron system (Rh-4d conduction band) so that there is negligible exchange interaction between the localized electron spins and the electrons responsible for superconductivity. (ii) Rare earth concentration is large (~ 11 atom %) and in cases where the ions can support a large magnetic moment, magnetic ordering can be expected at low temperatures by interatomic exchange or superexchange interaction. If the rare earth spins are to order antiferromagnetically, there is no macroscopic internally-generated magnetic field to disturb the superconducting state. Hence the coexistence of antiferromagnetic order and superconductivity is expected and indeed observed in LnRh_4B_4 compounds and other related materials. Theoretical treatments have also been successfully developed (Jaric 1979, 1980; Ramakrishnan and Varma 1981; Sakai *et al* 1981; Mahanti *et al* 1981; Suzumura and Nagi 1982).

Detailed studies by way of χ - T , ρ - T , C_p , H_{c2} and neutron diffraction have shown that LnRh_4B_4 , Ln = Nd, Sm and Tm exhibit the coexistence behaviour in zero applied magnetic fields with the Néel temperature, $T_N < T_c$ (table 3 and figure 9). Pseudoternary alloys also show this behaviour but a few systems are interesting in that they have $T_N > T_c$. Theoretical models explaining the coexistence behaviour should take cognizance of this fact. The antiferromagnetism (afm) is exclusively due to the Ln-ions but the exact type of ordering has not been established in all the boride phases.

Table 3. Antiferromagnetic superconductors^a

| Compound | Superconductors T_c (K) | Antiferromagnetic Néel temperature T_N (K) |
|---|------------------------------|--|
| <i>Rhodium borides</i> | | |
| NdRh_4B_4 | 5.36 | 1.3, 0.9 ^b |
| SmRh_4B_4 | 2.72 | 0.87 |
| TmRh_4B_4 | 9.86 | 0.4 |
| $\text{Ho}(\text{Rh}_{0.3}\text{Ir}_{0.7})_4\text{B}_4$ | 1.34 | 2.7 |
| $\text{Dy}(\text{Rh}_{0.85}\text{Ru}_{0.15})_4\text{B}_4$ | 4.0 | 1.5 ^c |
| $\text{Dy}(\text{Rh}_{0.3}\text{Ir}_{0.7})_4\text{B}_4$ | 1.7 | 4.7 ^d |
| <i>Chevreil phases</i> | | |
| NdMo_6S_8 | 3.3 (3.6) ^e | 0.85 (?) |
| GdMo_6S_8 | 1.1 (1.4) | 0.85 (0.95) |
| TbMo_6S_8 | 1.45 (1.80) | 0.90 (1.05) |
| DyMo_6S_8 | 2.05 (2.15) | 0.40 (0.45) |
| ErMo_6S_8 | 1.9 (2.2) | 0.15 (0.22) |
| YbMo_6S_8 | 9.2 (9.5) | 2.6 (2.75) (?) |
| GdMo_6Se_8 | 5.6 | 0.75 |
| TbMo_6Se_8 | 5.7 | 1.03 (?) |
| ErMo_6Se_8 | 6.0 | 1.07 |

^aTaken from Subba Rao and Shenoy (1981); ^bTwo transitions are indicated; ^cHamaker and Maple (1981); ^dKu and Acker (1980); ^eValues in paranthesis are the onset temperatures. (?) indicates that the detailed nature of the antiferromagnetic order has not yet been established.

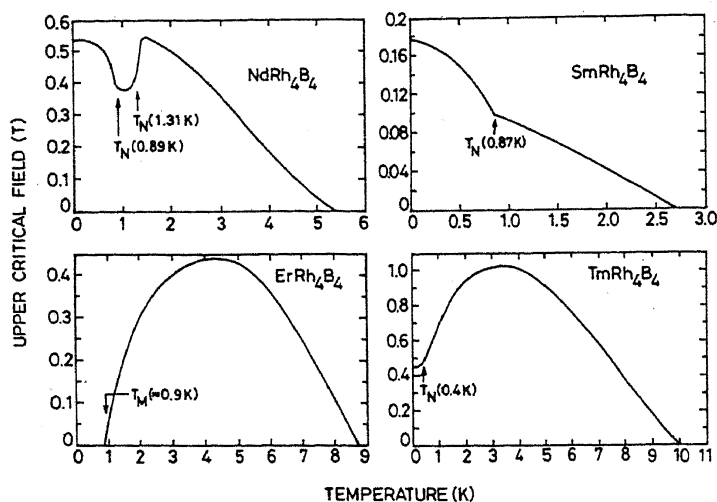


Figure 9. Upper critical magnetic field *vs* temperature for NdRh_4B_4 , SmRh_4B_4 , ErRh_4B_4 and TmRh_4B_4 . As can be seen in the compounds with $\text{Ln} = \text{Nd}, \text{Sm}, \text{Tm}$, superconductivity coexists with antiferromagnetism. ErRh_4B_4 exhibits a reentrant behaviour (taken from Maple *et al* 1982).

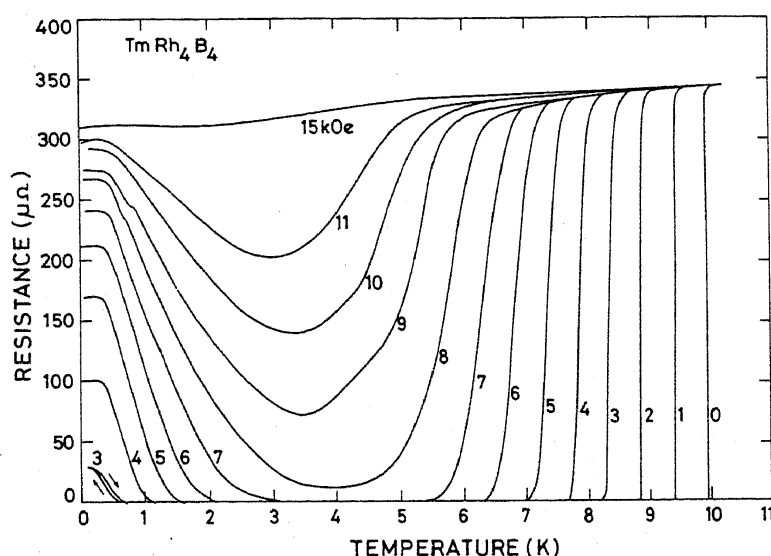


Figure 10. Resistivity *vs* temperature curves at various applied magnetic fields (kOe) for TmRh_4B_4 . Notice that antiferromagnetic order below T_c gets modified with the applied field (taken from Subba Rao and Shenoy 1981).

Ku *et al* (1980) pointed out that the complex magnetic ordering (as compared to simple afm or fm order) might be a common feature of several LnRh_4B_4 compounds where Ln is heavier than Gd. Antiferromagnetic superconducting ternary borides become normal (reentrant behaviour) at T_N and develop some sort of ferromagnetic order by the application of magnetic field ($H \leq H_{c2}$) (figure 10).

2.1f Reentrant and ferromagnetic superconductors: If the rare earth spins in a LnRh_4B_4 systems are to order ferromagnetically the macroscopic dipolar field so created will strongly become competitive with the superconductivity and destroy the

latter once the critical magnetic field value for the destruction of superconducting state is reached. Before the full realization of ferromagnetic state (reentrant behaviour), however, the ferromagnetic correlations may lead to an oscillatory magnetic state and the latter can coexist with superconductivity. This has been amply verified in ErRh_4B_4 (see below). Theoretical investigations by many workers (Suhl 1978; Ferrel *et al* 1979; Bulaevski *et al* 1979; Matsumoto *et al* 1979; Machida and Matsubara 1979; Greenside *et al* 1981) predict the possibility of several types of the oscillatory magnetic state (spiral, vortex or linearly polarized) but the experimental evidence on ErRh_4B_4 and HoMo_6S_8 are in favour of transverse linearly polarized state which is coexisting with the superconducting state.

As mentioned earlier, the compound ErRh_4B_4 exhibits reentrant superconductivity in zero applied magnetic field with the upper and lower superconducting critical temperatures $T_{c1} = 8.7$ K and $T_{c2} \approx 0.9$ K respectively, due to the onset of long range ferromagnetic order (alignment of Er^{3+} spins in the basal (a - b) plane) at a temperature $T_M \sim T_{c2}$ (see figure 9). Thermal hysteresis at T_{c2} is observed in the measured ρ , χ and C_p (Lander *et al* 1979; Moncton *et al* 1980) and thermal conductivity data (Odoni and Ott 1979) indicating that the transition is first order. Interesting precursor effects by way of the existence of a small angle peak in neutron diffraction have been observed by Moncton *et al* (1980) in ErRh_4B_4 in the superconducting state above the magnetic transition temperature. Recent careful neutron diffraction and resistivity studies at low temperatures on single crystals of ErRh_4B_4 by Sinha *et al* (1982) have shown that the transition from superconductivity to ferromagnetism proceeds through an intermediate mixed state which displays both superconductivity and long-range magnetic order. This mixed state (or pseudo phase), a mosaic of microscopic superconducting and ferromagnetic regions of size 2000 Å, sets in when the sample is cooled to below 1.2 K and exhibits a ferromagnetic moment *and* modulated moment (transverse linearly polarized, with a period of 91.8 ± 2.7 Å). On further cooling to 0.71 K, the crystal enters into a purely ferromagnetic phase, with the modulated moment *and* superconductivity disappearing simultaneously (figure 11). The latter appears suddenly on warming to 0.775 K. This first order transition is mirrored in the opposite sense by the behaviour of ferromagnetic intensity. An interesting effect of magnetic field on the intermediate mixed state has also been observed by Sinha *et al* (1982). Application of 200 Oe field to the sample at 0.74 K in the superconducting state (reached on cooling) did not produce a change in the satellite periodicity (wavelength of the modulated structure) but its intensity decreased by 45% while the ferromagnetic intensity increased by 8.8%. On switching off the external field, the intensity pattern did not restore itself to the previous zero-field value until the sample had been warmed beyond T_m (1.2 K) and re-cooled.

Reentrant superconductivity is also found in at least three pseudoternary LnM_4B_4 alloys (table 4) indicating that it is a common phenomena and is not restricted to some special systems. Ku and Shelton (1981) pointed out that a ferromagnetic order may not be necessary to destroy superconductivity in a ternary system. Thus, any type of magnetic order with an internal exchange magnetic field that is large compared to upper critical field H_{c2} when averaged over the superconducting coherence length, will be able to destroy the superconductivity and thus show the reentrant property. When searching for a pseudoternary low temperature phase diagram that may exhibit reentrant superconductivity one must consider, in addition to the ordered states of the pure ternary end members, the rate of depression with composition of both T_c and T_m which

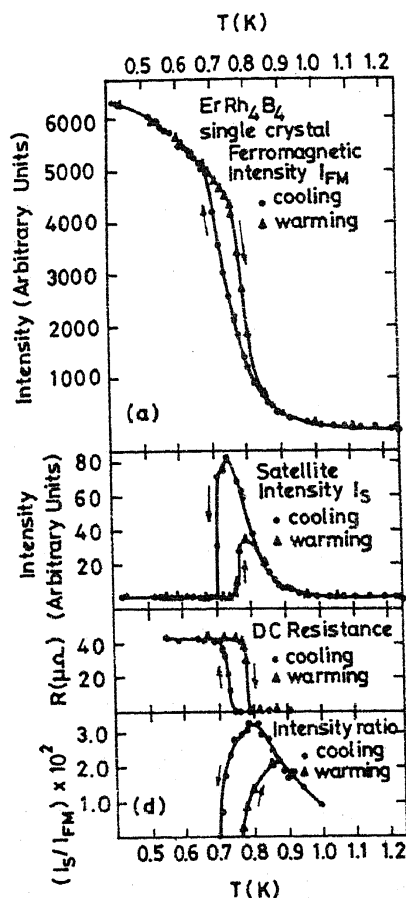


Figure 11. Neutron diffraction and resistivity study of single crystal ErRh_4B_4 in the low temperature region. Temperature dependence of (a) ferromagnetic intensity from the (101) Bragg peak (b) satellite intensity due to the modulated magnetic structure (c) bulk dc resistivity and (d) ratio of the satellite to the ferromagnetic intensity for the (101) reciprocal lattice point. Hysteresis is clearly shown in all cases (after Sinha *et al* 1982).

should be sufficiently small to allow these two types of transitions to intersect. Other pseudoternary systems similar to those shown in figure 12 and $\text{Ln}(\text{Rh}_{1-x}\text{M}_x)_4\text{B}_4$ ($\text{M} = \text{Ru}, \text{Ir}, \text{Os}$) can thus be profitably be examined.

Coexistence of ferromagnetism and superconductivity has recently been realized in the alloy system $(\text{Ho}_x\text{Er}_{1-x})\text{Rh}_4\text{B}_4$ ($0.84 \leq x \leq 0.9$) in the temperature range 4.95–5.95 K (for $x = 0.84$) and has been conclusively established by χ , ρ and neutron diffraction techniques (table 4; Lynn 1983; Lynn *et al* 1983a,b). No evidence for an oscillatory component due to the magnetization was found and in this respect the alloy system differs from the behaviour of pure ErRh_4B_4 .

2.2 Compounds with AMB_2 stoichiometry

Ku and Shelton (1980) and Shelton *et al* (1980b) discovered that LnMB_2 ($\text{Ln} = \text{rare earth, Y and Sc; M} = \text{Ru and Os}$) crystallize with the orthorhombic structure and LuRuB_2 and YRuB_2 exhibit high temperature superconductivity with T_c of 10 and 7.8 K respectively. However, the corresponding Os-containing isoelectronic compounds have T_c lowered by a factor of 4. When Ln is a magnetic ion, the phases exhibit magnetic ordering, presumably of a ferromagnetic-type. Ku and Shelton (1981) examined the pseudoternary system $(\text{Lu}_{1-x}\text{Tm}_x)\text{RuB}_2$ and found reentrant superconducting behaviour for $0.52 \leq x \leq 0.68$ (Table 4).

The structure of orthorhombic LuRuB_2 is shown in figure 13. It is a cluster compound qualitatively of a different kind from that of the AM_4B_4 -type compounds.

Table 4. Reentrant and ferromagnetic superconductors

| Compound | Superconductors $T_c (\equiv T_{c1})$ (K) | Reentrant temperature $T_{c2} (\leq T_m, \text{mag. order temperature})$ (K) | Reference |
|--|--|---|---|
| ErRh_4B_4 | 8.7 | 0.71 (cooling) ^a 0.775 (warming) ($T_m < 1.2$ K) | Sinha <i>et al</i> (1982) |
| $\text{Tm}_2\text{Fe}_3\text{Si}_5$ | 1.7 | 1.13 | Segre and Braun (1981) |
| TmOs_xSn_y | 1.1 | 0.6 | Fisk <i>et al</i> (1982) |
| $\text{ErRh}_{1.1}\text{Sn}_{3.6}$ | 1.36 | 0.46 | Remeika <i>et al</i> (1980) |
| $\text{ErOs}_{1.1}\text{Sn}_{2.7}$ | 1.3 | 0.5 | Fisk <i>et al</i> (1982) |
| HoMo_6S_8 | 1.82 | 0.612 (cooling) 0.668 (warming) | Lynn <i>et al</i> (1981, 1983a) |
| $\text{Ho}(\text{Rh}_{1-x}\text{Ir}_x)_4\text{B}_4$ ($x = 0.15$) ($0.08 \leq x \leq 0.22$) | 5.2 | 2.0 | Ku <i>et al</i> (1980) |
| $(\text{Y}_{1-x}\text{Gd}_x)\text{Rh}_4\text{B}_4$ ($x = 0.32$) | 2.82 | 1.72 | Adrian <i>et al</i> (1981) |
| $\text{Tm}_{1-x}\text{Lu}_x\text{RuB}_2$ ($x = 0.6$) ($0.52 \leq x \leq 0.68$) | 4.3 | 1.2 | Ku and Shelton (1981) |
| Ferromagnetic^b superconductors | | | |
| $(\text{Ho}_{0.84}\text{Er}_{0.16})\text{Rh}_4\text{B}_4$ | 5.95 | 4.95 (resist.) 5.30 (neutron) | Lynn 1983; Lynn <i>et al</i> (1983b) |
| $(\text{Ho}_{0.5}\text{Eu}_{0.5})\text{Mo}_6\text{S}_8$ | 2.0 | 0.6 | Ishikawa <i>et al</i> (1981; 1982) |

^a Below T_m an intermediate mixed state sets in where ferromagnetic domains and superconducting domains coexist (of size ~ 2000 Å), with the superconducting domains further divided into subdomains which contain modulated magnetic moment.

^b Coexistence of ferromagnetism and superconductivity occurs in the interval $T_{c2} < T < T_{c1}$ for the specific compositions.

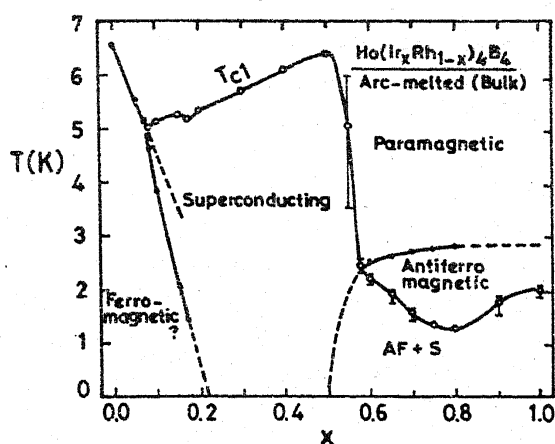


Figure 12. Low temperature phase diagram for the system $\text{Ho}(\text{Ir}_x\text{Rh}_{1-x})_4\text{B}_4$ determined from ac and static susceptibility measurements on arc melted samples. This system is interesting in that both reentrant behaviour and the coexistence of antiferromagnetism and superconductivity ($T_N > T_c$) are encountered with varying x (taken from Ku *et al* 1980).

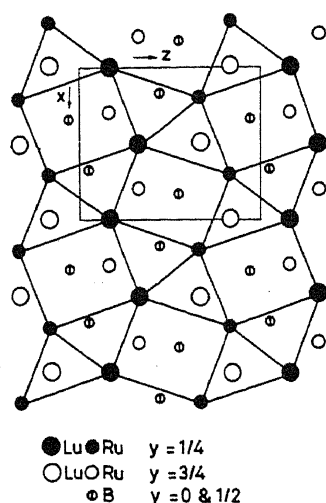


Figure 13. Projection of the orthorhombic LuRuB_2 -type structure along the (010) direction. Plane net of Lu and Ru atoms are connected by thick lines for $y = 1/4$ plane.

The Lu and Ru atoms form planar nets perpendicular to the b -axis. The Lu-Lu distance within the plane is very short (3.1 Å compared to the normal CN12 metallic distance of 3.47 Å) and interlayer distance is only slightly larger (3.34 Å). The intralayer and interlayer Ru-Ru distances are 3.03 and 4.07 Å respectively (compare Ru-Ru distance of 2.71 Å in Ru metal). The Lu atoms form zig-zag chain clusters lying in the a - c plane and running in the crystallographic a -direction. Strong Lu-Ru bonding exists as is evident by the bond length of 3.05 Å which is very close to that calculated (3.07 Å) from the CN12 metallic radii. The boron atoms are dimerized ($d(\text{B-B}) = 1.74$ Å) and are located between the Lu-Ru planes. The B_2 dimers are weakly coupled to form zig-zag chains running perpendicular to the metal planes (*i.e.*, parallel to the b -axis). This is in contrast to the AM_4B_4 compounds where the B_2 pairs are isolated from each other.

It is clear that superconductivity arises in LnRuB_2 phases from the Ru 4*d*-electrons but the Ln atoms also play a crucial role because of strong Ln-Ru bonding and Ln-Ln bonding. Superconductivity is not exhibited when Ln ion has a magnetic moment but then the magnetic ordering temperatures are also high (*e.g.*, Ln = Tb, $T_m = 45.6$; Ln = Dy, $T_m = 21.9$ K). T_m values are also high in the corresponding osmium phases, LnOsB_2 (Ln = Tb, $T_m = 39.2$ K) but the T_c values are low for non-magnetic Ln (*e.g.*, Ln = Lu, $T_c = 2.7$; Y, $T_c = 2.2$ K).

2.3 Compounds with AM_3B_2 stoichiometry

Isotypic series of compounds with ACo_3B_2 stoichiometry were first prepared and characterized by Kuz'ma *et al* (1969). Later studies revealed that a large number of compounds with the formula AM_3B_2 , A = rare earth, Zr, Hf, Th, Ba; M = Co, Ru, Rh, Os, Ir, Pt do form. The structure types adopted by them are: (i) hexagonal CeCo_3B_2 -type, (ii) monoclinic ErIr_3B_2 -type, (iii) hexagonal $\text{Ba}_{0.67}\text{Pt}_3\text{B}_2$ -type, and (iv) orthorhombic (?) YOs_3B_2 -type. In the CeCo_3B_2 -type structure the B atoms are isolated from each other and there exists an interpenetrating network of A and M atom clusters. The ErIr_3B_2 and $\text{Ba}_{0.67}\text{Pt}_3\text{B}_2$ structures are distorted derivatives of the hexagonal CeCo_3B_2 structure. The fact that the latter structure is not conducive to high temperature superconductivity can be seen from the following data: (i) for AM_3B_2 , A = rare earth; M = Ru, Os, Rh and Ir, T_c does not exceed 4.6 K (Ku *et al* 1980; Ku and Meisner 1981; Malik *et al* 1982; Dhar *et al* 1983); (ii) LnM_3B_2 (M = Rh, Ir) with the

ErIr_3B_2 structure do not have T_c above 1.2 K (Ku and Meisner 1981); (iii) for $\text{A}_{0.67}\text{Pt}_3\text{B}_2$ the T_c are 1.6, 2.8 and 5.6 K for $\text{A} = \text{Ca}, \text{Sr}$ and Ba (Shelton 1978) and (iv) AOs_3B_2 , $\text{A} = \text{Th}$, $T_c = 3$ K; $\text{A} = \text{Y}$, $T_c = 6$ K (Ku 1980).

3. Ternary carbides

Of the known ternary carbides, molybdenum borocarbide, Mo_2BC and aluminocarbide, $\text{Mo}_3\text{Al}_2\text{C}$ merit attention since they exhibit superconductivity with T_c of 7.5 and 10 K respectively. Mo_2BC has an orthorhombic symmetry (space group, cmcn) with $a = 3.086$, $b = 17.35$ and $c = 3.047$ Å and the structure can be described as a combination of boride and carbide subcells (figure 14). The carbon atoms are located at the centre of Mo_6 distorted octahedra, which share edges to form layers. The octahedron layers are separated from each other by boron layers, the boron atoms forming zig-zag chains which pass through the trigonal prisms of the Mo-atoms. Recently Lejay *et al* (1981 a,b) synthesized Mo_2BC single crystals and examined their properties. They also found that transition elements Zr, Nb, Rh, Hf, Ta and W can be substituted to a significant extent ($x = 0.15\text{--}1.1$ in $\text{Mo}_{2-x}\text{M}_x\text{BC}$) in samples prepared in polycrystalline form by arc melting techniques. While the T_c decreased with increase in x for all the alloys, the Rh-containing alloy exhibited an increase of T_c (up to 9 K) and H_{c2} (27 kOe for $x = 0$) and then a decrease (to 6.7 K) for x ranging from 0–0.3. The authors found a good correlation of T_c with the molar volume and valence electron concentration in all the alloys studied.

$\text{Mo}_3\text{Al}_2\text{C}$ has a cubic $\beta\text{-Mn}$ structure with $a = 6.867$ Å. The phase, along with the other $\text{M}_3\text{Al}_2\text{C}$ ($\text{M} = \text{Ti}, \text{V}, \text{Cr}, \text{Nb}$ and Ta), was first synthesized by Jeitschko *et al* (1963) and later Johnston *et al* (1964) discovered it to be superconducting with a T_c of 10 K. Similar to the Mo_2BC , the C atoms are located in an octahedra of Mo-atoms in $\text{Mo}_3\text{Al}_2\text{C}$ and the Mo–C distance of 2.14 Å indicates strong covalent bonding. The

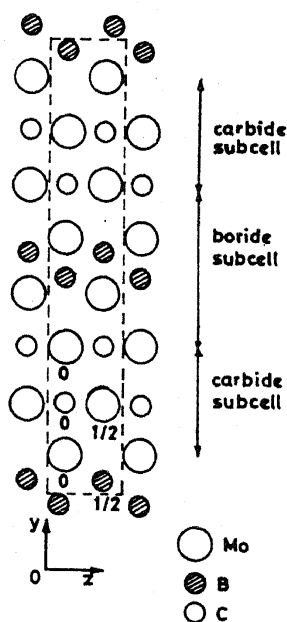


Figure 14. Crystal structure of Mo_2BC . Projection of the ZOY plane is shown.

β -Mn structure is without doubt conducive to high T_c superconductivity since other phases with $M \neq \text{Mo}$, crystallizing in a hexagonal structure do not have a T_c above 4.2 K.

4. Ternary silicides

Ternary silicides have attracted wide attention in recent years and a variety of phases with different stoichiometries have been synthesized and studied. The important systems are: (i) LnMSi , ($\text{Ln} = \text{rare earth or Y}$; $M = \text{Rh and Ir}$) with the TiNiSi structure for $\text{Ln} = \text{Gd} \rightarrow \text{Er}$ and Y and with the ZrOS (or SrSi_2 : Cubic) structure for LaRhSi and LnIrSi ($\text{Ln} = \text{La} \rightarrow \text{Nd}$) (Chevalier *et al* 1982a,b; Klepp and Parthe 1982); (ii) LnMSi_2 ($\text{Ln} = \text{La} \rightarrow \text{Gd}$; $M = \text{Rh and Ir}$) with the orthorhombic CeNiSi_2 structure (Chevalier *et al* 1982c,d; Chevalier *et al* 1983); (iii) LnRh_2Si_2 ($\text{Ln} = \text{La} \rightarrow \text{Er}$; Y) with the tetragonal ThCr_2Si_2 structure (Ballestracci 1976; Chevalier *et al* 1983; Felner and Nowik 1983); (iv) Ln_2RhSi_3 ($\text{Ln} = \text{La} \rightarrow \text{Er}$; Y) with a hexagonal structure (Chevalier *et al* 1982c,d; Chevalier *et al* 1983); (v) LnRu_3Si_2 ($\text{Ln} = \text{La} \rightarrow \text{Yb}$; Y and U) with the hexagonal LaRu_3Si_2 structure (Barz 1980; Vandenberg and Barz 1980) and LnRh_3Si_2 ($\text{Ln} = \text{La} \rightarrow \text{Er}$ and Y) with hexagonal CeCo_3B_2 -type structure (Chevalier *et al* 1981); (vi) $\text{Ln}_2\text{M}_3\text{Si}_5$ ($\text{Ln} = \text{Sm} \rightarrow \text{Lu}$; Sc and Y ; $M = \text{Fe, Ru and Os}$) with the tetragonal $\text{Sc}_2\text{Fe}_3\text{Si}_5$ -structure (Braun 1980, 1981; Braun *et al* 1981) and $\text{Ln}_2\text{Rh}_3\text{Si}_5$ ($\text{Ln} = \text{La} \rightarrow \text{Er}$ and Y) with the orthorhombic $\text{U}_2\text{Co}_3\text{Si}_5$ -type structure (Chevalier *et al* 1982e) and (vii) $\text{Sc}_5\text{M}_4\text{Si}_{10}$ ($M = \text{Co, Rh, Ir}$) and $\text{Ln}_5\text{Ir}_4\text{Si}_{10}$ ($\text{Ln} = \text{Dy} \rightarrow \text{Lu}$, Y) with the tetragonal $\text{Sc}_5\text{Co}_4\text{Si}_{10}$ -type structure (Braun *et al* 1980; Braun and Segre 1980, 1981). Of the above, many phases are superconducting for $\text{Ln} = \text{Sc, Y, La, Lu}$, but high T_c superconductivity is realized only in the phases LaRu_3Si_2 ($T_c = 7.6 \text{ K}$), $\text{Lu}_2\text{Fe}_3\text{Si}_5$ ($T_c = 6.1 \text{ K}$) and $\text{Sc}_5\text{M}_4\text{Si}_{10}$ ($M = \text{Rh and Ir}$; $T_c = 8.5\text{--}8.6 \text{ K}$). It is significant to note that LaRu_3Si_2 is a distorted version of the hexagonal CeCo_3B_2 structure and contains triangular Ru_3 clusters. On the other hand, the LnRh_3Si_2 phases crystallize with the undistorted CeCo_3B_2 -structure and the latter, as noted earlier, is not very conducive to high T_c superconductivity. Hence it is not surprising that LnRh_3Si_2 ($\text{Ln} = \text{La}$ and Y) are not superconducting above 0.05 K (Chevalier *et al* 1981).

4.1 Primitive tetragonal $\text{Sc}_2\text{Fe}_3\text{Si}_5$ and $\text{Sc}_5\text{Co}_4\text{Si}_{10}$ structures

Isostructural primitive tetragonal phases of the formula $\text{Ln}_2\text{M}_3\text{Si}_5$ exist for the following combinations: $M = \text{Fe}$, $\text{Ln} = \text{Sm} \rightarrow \text{Lu}$, Y , Sc ; $M = \text{Ru}$ and Os , $\text{Ln} = \text{Lu}$, Y and $\text{Y}_2\text{Re}_3\text{Si}_5$. The a and c values respectively are ~ 10.3 and $\sim 5.3 \text{ \AA}$. One interesting aspect is that the Fe-containing phases with $\text{Ln} = \text{Lu}$, Sc and Y exhibit T_c of 6.1, 4.5 and 2.4 K respectively, relatively high values for an iron ($3d$ metal)-based compounds. Remarkably enough, reentrant superconductivity has been discovered in $\text{Tm}_2\text{Fe}_3\text{Si}_5$ with $T_{c1} = 1.3 \text{ K}$ and $T_{c2} = 1.1 \text{ K}$ (table 4) (Segre and Braun 1981). Mössbauer studies of $\text{Ln}_2\text{Fe}_3\text{Si}_5$ (Cashion *et al* 1980, 1981) have shown that the magnetic moment on Fe atoms (iron occupies two sets of point positions in the structure) is less than $0.03 \mu_B$ and indicate that the iron $3d$ -electrons are non-magnetic and participate in strong bonding with Si atoms. When Fe is replaced by the isoelectronic Ru or Os, superconductivity disappears for $\text{Ln} = \text{Lu}$ and Y and this fact raises the important question whether the Fe- $3d$ electrons participate in superconductivity or not. When Ln is a magnetic rare earth, the Fe-containing phases exhibit antiferromagnetism with $T_N \sim 10 \text{ K}$.

Primitive tetragonal $\text{Ln}_5\text{M}_4\text{Si}_{10}$ compounds with $a \sim 12$ Å and $c \sim 3.9$ Å form for $\text{Ln} = \text{Sc}$ and $\text{M} = \text{Co}, \text{Rh}$ and Ir and for $\text{Ln} = \text{Dy} \rightarrow \text{Lu}, \text{Y}$ for $\text{M} = \text{Ir}$. In the prototype compound $\text{Sc}_5\text{Co}_4\text{Si}_{10}$, the Co and Si atoms form planar nets of hexagons and pentagons which are connected along (001) axis via Co-Si-Co zig-zag chains to form a three-dimensional network. The hexagon-pentagon layers are separated by layers of Sc atoms and the Co atoms are isolated from each other. The Sc-containing phases are superconductors with $T_c = 5, 8.5$ and 8.5 K for $\text{M} = \text{Co}, \text{Rh}$ and Ir . The Ir containing phases with $\text{Ln} = \text{Lu}$ and Y are also superconducting ($T_c = 3.8$ and 3 K) whereas those with $\text{Ln} =$ magnetic ions, are magnetic at low temperatures. It is interesting to note that the Co compound has a fairly high T_c and χ - T data reveal that the Co atoms do not carry any localized magnetic moment (Braun and Segre 1981); the quenching of the moment correlates well with the short (covalent) Co-Si and Si-Si interatomic distances in the structure.

5. Ternary germanides

Well-defined rare earth ternary germanides are few in number and have only recently been isolated and studied. They are: (i) $\text{Y}_5\text{M}_4\text{Ge}_{10}$ ($\text{M} = \text{Ir}$ and Os) with the tetragonal $\text{Sc}_5\text{Co}_4\text{Si}_{10}$ -type structure (Braun and Segre 1980, 1981; Braun *et al* 1980). For $\text{M} = \text{Os}$, $T_c = 8.7$ K whereas for $\text{M} = \text{Ir}$, T_c is only 2.6 K. (ii) $\text{Ln}_3\text{M}_4\text{Ge}_{13}$ ($\text{Ln} = \text{Ce} \rightarrow \text{Lu}, \text{Y}$; $\text{M} = \text{Ru}$ and Os) with the primitive cubic $\text{Pr}_3\text{Rh}_4\text{Sn}_{13}$ -type structure (Segre *et al* 1981). The lattice constants are ~ 9 Å and when $\text{Ln} = \text{Y}$ and Lu , the phases are superconducting with T_c less than 3.9 K. When the Ln is a magnetic ion, the compounds order magnetically with T_m as high as 16 K. (iii) LnM_2Ge_2 ($\text{Ln} = \text{La}, \text{Yb}$; $\text{M} = \text{Pd}, \text{Pt}$) with the tetragonal ThCr_2Si_2 structure (Hull *et al* 1981). T_c is around 1 K for $\text{Ln} = \text{La}, \text{Yb}$ and $\text{M} = \text{Pd}$ whereas LaPt_2Ge_2 has a T_c of 0.55 K. (iv) LnMGe ($\text{M} = \text{Co}, \text{Ni}$; $\text{Ln} = \text{Gd} \rightarrow \text{Lu}, \text{Y}$; Sc ; $\text{M} = \text{Rh}, \text{Pd}, \text{Ir}, \text{Pt}$; $\text{Ln} = \text{La} \rightarrow \text{Tm}$; Y ; Sc). The phases adopt either the orthorhombic TiNiSi - or CeCu_2 -type or hexagonal ZrNiAl (Fe_2P)-type or tetragonal LaPtSi -type structure (Hovestreydt *et al* 1982).

6. Ternary stannides

A large number of ternary stannides, AM_xSn_y , have been isolated and studied in recent years with the specific aim of examining the interplay between superconductivity and magnetic order. An advantage in these stannides is that most of them are cubic systems and large single crystals can be grown employing metallic tin as flux. The ideal stoichiometry established by single crystal x-ray data is $\text{Ln}_3\text{Rh}_4\text{Sn}_{13}$ ($\text{Ln} = \text{Pr}$ and Yb) and the phases are isotypic with the germanides, $\text{Ln}_3\text{M}_4\text{Ge}_{13}$ ($\text{M} = \text{Ru}$ and Os). However, the formula is usually written as $\text{A}_{1.00}\text{M}_x\text{Sn}_y$ with $x = 1-1.5$ and $y = 3.1-4.5$. Primitive cubic $\text{Pr}_3\text{Rh}_4\text{Sn}_{13}$ -type structure (phase I with $a \sim 9.7$ Å) is encountered for $\text{A} = \text{Ca}, \text{Sr}$ with $\text{M} = \text{Co}$; $\text{A} = \text{Ca}, \text{Sr}, \text{Ln}$ (rare earth) and Th with $\text{M} = \text{Ru}$ and Ir ; $\text{A} = \text{La}$ with $\text{M} = \text{Ru}$ and $\text{A} = \text{Ca}$ with $\text{M} = \text{Pt}$ (Espinosa 1980; Espinosa *et al* 1980; Remeika *et al* 1980; Vandenberg 1980; Hodeau *et al* 1980; Cooper 1980). Tetragonal (phase II with $a \sim 13.7$; $c \sim 9.7$ Å) stannides are found for LnRu_xSn_y , $\text{Ln} = \text{Er}, \text{Lu}$; ErCo_xSn_y ; LnRh_xSn_y , $\text{Ln} = \text{Sc}, \text{Y}, \text{Ho} \rightarrow \text{Lu}$ and LnIr_xSn_y , $\text{Ln} = \text{Sc}, \text{Er} \rightarrow \text{Lu}$ (Remeika *et al* 1980; Espinosa 1980; Cooper 1980; Andres *et al* 1981; Chenavas *et al*

1981). *Fcc* (phase III with $a \sim 13.7$ Å) stannides are found for LnM_xSn_y , $\text{Ln} = \text{Y, Er}$ and $\text{M} = \text{Ru}$ and Os ; LnRh_xSn_y , $\text{Ln} = \text{Tb} \rightarrow \text{Tm}$; LnIr_xSn_y , $\text{Ln} = \text{Y, Gd} \rightarrow \text{Yb}$ (Espinosa *et al* 1980; Remeika *et al* 1980; Espinosa 1980; Cooper 1980; Chenavas *et al* 1981; Lambert *et al* 1981). The lattice parameters of phases I, II and III are related: $\sqrt{2} a (\text{I}) \approx a (\text{III}) \approx a (\text{II}) \approx (c(\text{II})/2)$. Hence the structure of phase I, which is known in detail, might be related to the phases II and III.

The $\text{Pr}_3\text{Rh}_4\text{Sn}_{13}$ structure with 2 formula units per unit cell has a number of interesting features: (i) the tin atoms occupy two different types of positions: 2 Sn(1) atoms per unit cell form a *bcc* sublattice and appear to be cationic in character; the remaining 24 tin atoms, Sn(2), are anionic in nature and coordinate the Sn(1), Pr and Rh atoms. The formula can then be written as $\text{Sn(1)Pr}_3\text{Rh}_4\text{Sn(2)}_{12}$. Mössbauer studies have corroborated the existence of two kinds of Sn atoms in the structure (Shenoy *et al* 1980), (ii) the Pr and Sn(1) atoms together form the beta-W (A15) structure in which nonintersecting and mutually perpendicular chains of Pr atoms run across the cell faces (figure 15). However, the Pr-Pr distances are large. The Rh atoms form an interpenetrating simple cubic array and one Rh_8 cube is situated at the centre of each A15 unit cell as shown in figure 15. The $\text{Sn(1)Pr}_3\text{Rh}_4$ sublattice resembles the channel-type structure of $\text{Na}_x\text{Pt}_3\text{O}_4$. However, the Rh-Rh distances are large (much greater than the intermetallic distance in Rh metal) and there is only weak Pr-Rh bonding. Thus, there are no Sn(1)-Sn(1), Pr-Pr or Rh-Rh clusters. Hodeau *et al* (1980) have shown that Yb and Sn(1) atoms in $\text{Sn(1)Yb}_3\text{Rh}_4\text{-Sn(2)}_{12}$ show mutual substitutional disorder on the Sn(1) and Yb sites of the structure (5.7 and 8.5 atom % respectively). This disorder may have a significant effect on the superconducting and other properties of the phase I stannides, (iii) the Sn(2) atoms effectively isolate each Pr and Rh atoms from the others but they themselves form pairs with the Sn(2)-Sn(2) distance slightly less or almost equal to that encountered in tin metal. Hence the phase I stannides might, therefore, be expected to exhibit physical properties typical of sp-band metals. Also, since the A or Ln element occupies a distinct position in the crystal lattice, those ions which support a magnetic moment may exhibit magnetic ordering at low temperatures.

Phase I (primitive cubic) stannides exhibit superconductivity for $A = \text{Ca, Sr, La, Th}$ or Yb (table 5) with a high T_c of 8.7 K for the $\text{CaRh}_{1.2}\text{Sn}_{4.5}$. It is significant that the Co-containing compound also exhibits a relatively high T_c (5.9 K). The LnM_xSn_y compounds with the phase II and III structures show superconductivity when the rare earth is nonmagnetic. $\text{ErRh}_{1.1}\text{Sn}_{3.6}$ (Remeika *et al* 1980; Shenoy *et al* 1980; Ott *et al* 1981) and ErOs_xSn_y (Espinosa *et al* 1980) have been found to exhibit a reentrant behaviour at zero applied magnetic field and $\text{TmRh}_{1.3}\text{Sn}_4$ in applied fields greater than 1.2 kOe (Lambert *et al* 1981). Recent studies on phase III LnOs_xSn_y by Fisk *et al* (1982)

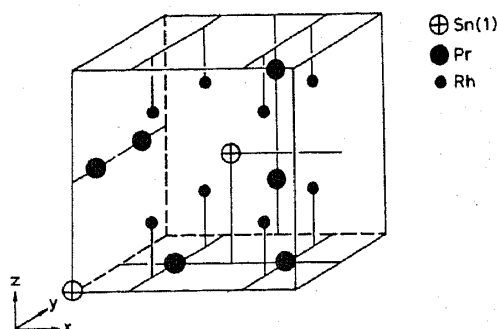


Figure 15. Structure of $\text{Sn(1)Pr}_3\text{Rh}_4\text{Sn(2)}_{12}$ showing the $\text{Sn(1)Pr}_3\text{Rh}_4$ sublattice. The disposition of the Sn(2) atoms not shown. These exist as pairs with interatomic distance similar to that in Sn metal (after Hodeau *et al* 1980). For discussion see text.

Table 5. Structure, T_c and T_m data of select AM_xSn_y stannides

| A | M | Sn | a_c (Å) | c_0 (Å) | T_c (K) | T_m (K) |
|---|-------------------|-------------------|-----------|--------------------|-----------|-------------------|
| <i>Phase I compounds (Prim. cubic; $Pr_3Rh_4Sn_{13}$-type structure)</i> | | | | | | |
| Ca | Rh _{1.2} | Sn _{4.5} | 9.702 | — | 8.7 | — |
| Sr | Rh _x | Sn _y | 9.800 | — | 4.3 | — |
| La | Rh _x | Sn _y | 9.745 | — | 3.2 | — |
| Eu | Rh _x | SS _y | 9.749 | — | — | 11 |
| Yb | Rh _x | Sn _y | 9.676 | — | 8.6 | — |
| Th | Rh _x | Sn _y | 9.692 | — | 1.9 | — |
| Ca | Ir _x | Sn _y | 9.718 | — | 7.1 | — |
| Sr | Ir _x | Sn _y | 9.807 | — | 5.1 | — |
| Ca | Co _x | Sn _y | 9.584 | — | 5.9 | — |
| La | Ru _{1.5} | Sn _{4.5} | 9.772 | — | 3.9 | — |
| <i>Phase II compounds (tetragonal structure)</i> | | | | | | |
| Sc | Rh _x | Sn _y | 13.565 | 9.558 ^a | 4.5 | — |
| Y | Rh _x | Sn _y | 13.772 | 9.707 | 3.2 | — |
| Er | Rh _{1.1} | Sn _{3.6} | 13.733 | 9.139 | 1.36 | 0.46 ^b |
| Lu | Rh _{1.2} | Sn _{4.0} | 13.693 | 9.648 | 4.0 | — |
| Lu | Ir _x | Sn _y | 13.708 | 9.661 | 3.2 | — |
| <i>Phase III compounds (fcc structure)</i> | | | | | | |
| Tb | Rh _{1.1} | Sn _{3.6} | 13.774 | — | — | 4.0 |
| Dy | Rh _{1.1} | Sn _{3.6} | 13.75 | — | — | 2.1 |
| Y | Os _x | Sn _y | 13.801 | — | 2.5 | — |
| Gd | Os _x | Sn _y | 13.773 | — | — | — |
| Tb | Os _{1.5} | Sn _{2.6} | 13.812 | — | 1.4 | — |
| Dy | Os _{1.5} | Sn _{2.5} | 13.792 | — | — | — |
| Ho | Os _{1.2} | Sn _{2.5} | 13.776 | — | 1.4 | — |
| Er | Os _{1.1} | Sn _{2.7} | 13.760 | — | 1.3 | 0.5 ^b |
| Tm | Os _x | Sn _y | 13.744 | — | 1.1 | 0.6 ^b |
| Y | Ir _x | Sn _y | 13.773 | — | 2.2 | — |

^aThe c_0 values should be multiplied by $2\sqrt{2}$ to obtain the true tetragonal c -axis values (Chenavas *et al* 1981).

^bRe-entrant superconductor.

have shown that only superconductivity is observed for Ln = Tb and Ho, those of Er and Tm are reentrant superconductors whereas those of Gd and Dy appear to exhibit some type of short-range magnetic order at low temperatures.

In contrast to the behaviour of $ErRh_4B_4$ and $HoMo_6S_8$, the stannide $ErRh_{1.1}Sn_{3.6}$ exhibits no thermal hysteresis at the reentrant transition measured either resistively or inductively. Neutron diffraction data (Remeika *et al* 1980) show that even at $T = 0.07$ K, true long-range order does not develop in the compound; presumably, the substitutional disorder at the Er site (by the Sn(1) atoms) may affect the integrity of the rare earth sublattice. This may also explain the sample dependence of the superconductivity and magnetic behaviour of stannides observed by Ott *et al* (1981). We also note from table 5 and the work of Espinosa *et al* (1982) that detailed studies are yet to be carried out on many of the stannide phases.

7. Ternary phosphides and pnictides

7.1 Niobium sulpho phosphide, NbPS

Donohue and Bierstedt (1969) discovered that niobium sulphophosphide, NbPS is superconducting with a T_c of 12.5 K. The compound, along with the other analogues TaPS and NbPSe can be synthesized only under high pressure and high temperature conditions (65 kb, 1200°C). The structure of NbPS is orthorhombic (space group Immm $Z = 4$, $a = 3.438$, $b = 11.88$, $c = 4.725$ Å). The structure shows several interesting features: The Nb atoms are 8-fold coordinated by 4 P and 4 S atoms at the corners of a bicapped trigonal prism. The prisms share faces, in pairs, through the 4 P atoms resulting in a short Nb-Nb distance of 2.93 Å (compare interatomic distance of 2.858 Å in Nb metal). This distance suggests the presence of a metal-metal bond. The pairs of bicapped trigonal prisms share triangular faces in the a axis direction, with this Nb-Nb distance being that of the a axis. The sulphur atoms are coordinated by 4 Nb atoms at the corners of a distorted tetrahedron. The P atoms are coordinated to 4 Nb atoms and one S atom. The P atoms form continuous strings in the c axis direction with alternating short and long distances (2.22 and 2.15 Å respectively). The short distances are within the normal P-P covalent bond distances found in many other compounds. This led Donohue and Bierstedt to propose an ionic formula of the type $(\text{Nb})_2^{4+}(\text{P}_2)^{4-}\text{S}^{2-}_2$ for the compound NbPS where the Nb is present in a 4+ oxidation state (d^1 system). Surprisingly enough NbPSe and TaPS, which are structurally analogous to NbPS do not exhibit superconductivity down to 1.25 K.

7.2 ZrRuP-type compounds

The fact that a particular structure for a ternary system can favour the high T_c superconductivity is nicely demonstrated by the recent work of Barz *et al* (1980), Müller *et al* (1983) and Meisner *et al* (1983) on the equiatomic (1 : 1 : 1) ternary transition metal phosphides and arsenides of the general formula, $MM'X$ ($M = \text{Ti, Zr, Hf, Nb, Ta}$; $M' = \text{Ru, Rh, Os}$; $X = \text{P, As}$). The compound ZrRuP can crystallize either in a hexagonal ZrRuSi (ordered Fe_2P or ZrNiAl, Johnson and Jeitschko 1972)-type or in the orthorhombic TiNiSi-type (ordered Co_2P or anti PbCl_2 , Shoemaker and Shoemaker 1965). Hexagonal ZrRuP and ZrRuAs show a T_c of 13 and 11.7 K (onset temperatures are 13.5 and 11.9 K) respectively whereas the orthorhombic ZrRuP exhibits a low T_c of 3.46 K (onset at 3.82 K). Detailed studies are yet to be made on many of the above phases but the available data reveal that the orthorhombic structure is adopted by the compounds with $M = \text{Nb, Ta}$ and the hexagonal arsenide phases are metastable at low temperatures. The T_c data are summarised in table 6.

An important structural feature of the hexagonal ZrRuP (space group, $\overline{\text{P6}}2\text{m}$; $Z = 3$) over that of the orthorhombic polymorph (space group, Pnam; $Z = 4$) is the layered structure of the Zr and Ru atoms (each layer, parallel to the x - y plane and separated by a distance of $c/2$, is occupied by either Zr and P atoms or Ru and P atoms only) and the existence of Ru_3 -triangular clusters (short Ru-Ru distances, 2.63 Å; figure 16). In contrast, the orthorhombic structure has layers which are filled with Zr and Ru atoms and these layers are all equivalent; also, there do not exist the Ru_3 -clusters (Müller *et al* 1983). Recent heat capacity data (Stewart *et al* 1982) on the superconducting hexagonal phosphides show that the density of states at the Fermi level is not

Table 6. T_c data on equiatomic MM'X ternary pnictides*

| Hexagonal structure (Fe_2P -type) | | | | Orthorhombic structure (Co_2P -type) | |
|--|-----------|--------|-----------|---|-----------|
| Phase | T_c (K) | Phase | T_c (K) | Phase | T_c (K) |
| TiRuP | 1.3 | — | — | ZrRuP [‡] | 3.46 |
| ZrRuP ^{**} | 13.0 | ZrRuAs | 11.7 | ZrRhP | < 1.1 |
| HfRuP | 10.9 | HfRuAs | 4.9 | NbRuP | — |
| TiOsP | 1.2 | — | — | NbRhP | 4.08 |
| ZrOsP | 7.4 | ZrOsAs | 8.0 | TaRuP | — |
| HfOsP | 6.1 | HfOsAs | 3.2 | TaRhP | 4.41 |

* The phases with $M' = \text{Fe, Co, Ni}$ exist and crystallize in the Co_2P -structure (Rundqvist and Nawapong 1966; Rundqvist and Tansuriwongs 1967) but do not exhibit superconductivity.

** $a = 6.459(6)$; $c = 3.778(4)$ Å

‡ $a = 6.4169(6)$; $b = 7.3215(8)$; $c = 3.8623(4)$ Å

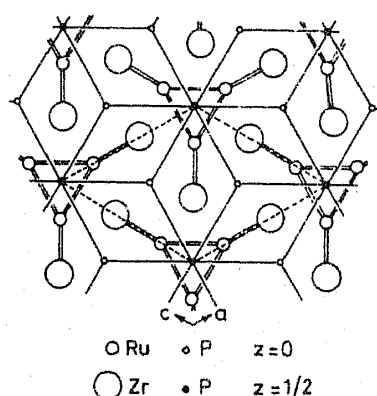


Figure 16. Projection of the ZrRuP structure along the hexagonal c axis. Double lines represent the metallic bonding of the Ru-Zr chains and Ru-Ru triangular clusters and the dashed line indicates the boundary of the hexagonal unit cell.

particularly large (0.76 ± 0.15 states/eV-atom) for ZrRuP with a T_c of 13 K and compare, 1.08 for Ru metal with a T_c of 0.5 K) and hence the high T_c must be due to increased electron-phonon interaction in the ternary system.

7.3 Pnictides of the type $\text{LnM}_4\text{X}_{12}$

Ternary pnictides of the formula, $\text{LnM}_4\text{X}_{12}$, where Ln = rare earth or Th; M = Fe, Ru and Os and X = P, As and Sb, represent a group of isostructural compounds with a bcu structure with a varying from 7.8 to 9.1 Å (space group, $Im\bar{3}$; $Z = 2$; density 5–8 g/cc). A total of 42 compounds have been synthesized by Jeitschko and coworkers (Jeitschko and Braun 1977; Braun and Jeitschko 1980a,b,c). Due to the existence of strong X-X bonding to give rise to X_4 groups, the phases can be considered to be metal excess ternary systems and interesting physical properties can be expected. Indeed, Meisner (1981) discovered superconductivity in the phosphides, $\text{LaM}_4\text{P}_{12}$ (M = Fe, $T_c = 4.1$ K; M = Ru, $T_c = 7.2$ K). Detailed studies have not yet been carried out.

In the $\text{LaFe}_4\text{P}_{12}$ structure, the Fe atom has an octahedral coordination and the La atom has a 12-fold (nearly icosahedral) coordination. Each P atom is surrounded by

two other P and two Fe atoms forming a distorted tetrahedron with an La atom outside one face of the tetrahedron. The FeP_6 octahedra share all their corners with adjacent octahedra and thus the Fe:P ratio is 1:3. The octahedra are rotated in such a way that for every 4 octahedra, one large void is formed and this is filled by the La atoms (figure 17). Also, rotation of the octahedra permits a close approach of the P (or As or Sb) atoms which thereby form rectangular, nearly quadratic, four-membered (P_4) rings (see figure 17a). The Fe or La atoms do not form clusters and the interatomic distances are large (Fe-Fe ~ 3.9 Å; La-La ~ 6.8 Å). However, significant bonding exists between the metal atoms and P and, also between the P atoms. Jeitschko and Braun (1977) suggested an ionic formula Ce^{4+} (or Th^{4+}) $(\text{FeP}_3)_4^{1-}$ or $\text{Ce}^{4+}\text{Fe}_4^{2+}(\text{P}_4)_3^{4-}$ for the Ce-containing phosphide and also proposed a one-electron energy band model for the $\text{LaFe}_4\text{P}_{12}$ -type compounds. According to the latter, the conduction band is mainly composed of Fe-metal 3d and/or 4s, 4p bands and assuming an electronic charge transfer from Ln atoms, the band is partially filled for Ln^{3+} whereas, it is completely filled for $\text{Ln} = \text{Ce}^{4+}$ or Th^{4+} . The latter compounds should be semiconductors whereas the La^{3+} compound should be metallic. This is in accord with the preliminary observed data in that $\text{CeFe}_4\text{P}_{12}$ did not show any magnetic or superconducting transition above 0.35 K. Measurements by Meisner (1981) showed that $\text{LnM}_4\text{P}_{12}$ with $\text{Ln} = \text{Pr}$ and Nd and $\text{M} = \text{Fe}$ and Ru exhibit magnetic transitions at or below 1.5 K.

Recent Mössbauer studies on $\text{LaFe}_4\text{P}_{12}$ by Shenoy *et al* (1982) show that the iron atoms in the compound carry no magnetic moment ($< 0.01 \mu_B$) and are present in a spin-paired 3d configuration. The observed centre shift and area under resonance with temperature could be fitted to a curve with $\theta_D = 450 \pm 20$ K. Assuming a value of $N(E_F) = 2$ states/(eV-spin), Shenoy *et al* (1982) estimated that the electron-phonon coupling is weak ($\lambda = 0.4\text{--}0.5$) in this material.

7.4 Pnictides of the type $\text{A}_2\text{M}_{12}\text{X}_7$

Isostructural compounds (about 55 known) of the general formula $\text{A}_2\text{M}_{12}\text{X}_7$ where A = rare earth (Ln), Y or Zr; M = Fe, Co, Ni and X = P or As are known (Jeitschko *et al* 1978). These possess the hexagonal $\text{Zr}_2\text{Fe}_{12}\text{P}_7$ -type structure with $a \sim 9$ Å and $c \sim 3.8$ Å and have high coordination for all the metal atoms, as is the case for typical intermetallic compounds. The P atoms are all isolated (and thus no P-P bond exists) and have a nine-fold coordination. The Fe

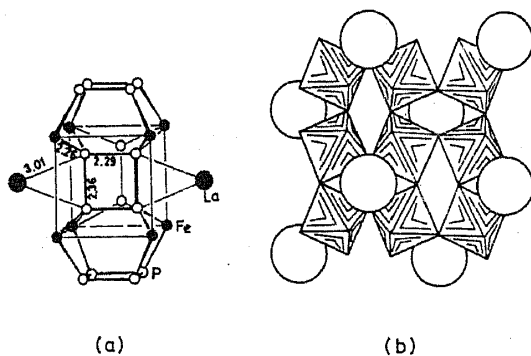


Figure 17. Crystal structure of $\text{LaFe}_4\text{P}_{12}$. (a) Near neighbours of the P_4 groups in $\text{LaFe}_4\text{P}_{12}$. Interatomic distances are in Å. (b) One layer of the corner shared FeP_6 octahedra is shown with the adjacent La atoms (spheres) above and below. The corners of the octahedra represent the P atoms. The Fe atoms inside the octahedra are not shown.

and Zr atoms have 12- and 18-fold coordination respectively. The Fe-Fe distances are small (2.495 Å compared to 2.482 Å in iron metal) indicating strong bonding and substantial Fe-P bonding also exists. Jeitschko and coworkers proposed an ionic formulation of the type $(\text{Ln}^{3+})_2 (\text{M}^{1.25+})_{12} (\text{X}_7^{3-})$ and $\text{Zr}_2^{4+} (\text{M}^{1.08+})_{12} (\text{X}^{3-})_7$ for the phases where the non-integral oxidation states written for M only means a delocalization of the electrons on the metals (Fe, Co and Ni) rather than mixed valence. Unit cell volume and crystal chemical considerations indicate that an intermediate valency may exist for Ce, Eu and Yb-containing phases.

7.5 Pnictides of the type LnM_2X_2

Rare earth ternary pnictides of the ThCr_2Si_2 -type LnM_2X_2 (Ln = rare earth or Th; M = Fe, Co, Ni and X = P, As or Sb) have been recently synthesized and characterized (Jeitschko and Jaberg 1980; Ruhl and Jeitschko 1979; Marchand and Jeitschko 1978). Isostructural phosphides CaM_2P_2 (M = Ni, Cu), BaM_2P_2 (M = Zn and Mn) and BaMn_2As_2 are also known. The compounds possess a body-centred tetragonal structure (I4/mmm; Z = 2). The M element has a tetrahedral coordination with respect to the X atom. In the Ni-containing compounds there is a tendency for square planar coordination, although a perfectly square planar P(or Si) coordination of the Ni atom cannot be achieved in the ThCr_2Si_2 -type structure. The A(Ln) atom is surrounded by 8M and 8X atoms in the Th-containing compounds, the coordination number reaches 18 instead of 16. Phosphorous atoms exist as pairs (P_2) whereas in EuCo_2P_2 , the large P-P distance indicates the existence of isolated P^{3-} ions (Marchand and Jeitschko 1978). Lanthanide contraction is apparent in the unit cell volumes of LnNi_2P_2 compounds which also indicates that Ce, Eu and Yb may be present in an intermediate valence state. Intermediate valence of Eu in EuNi_2P_2 has been verified recently by Nagarajan *et al* (1981, 1983) and Sampathkumaran *et al* (1982). Mixed valence of Eu may also be a feature in the arsenide and antimonide phases. As expected, the unit cell volume increases on going from P to As to Sb for a given LnM_2X_2 -system. Based on the interatomic distance and unit cell volumes of the Co and Ni-containing phosphides, Jeitschko proposed an ionic formulation of the type $\text{Eu}^{2+} (\text{Co}^{2+}\text{Co}^{2+}) \text{P}^{3-}\text{P}^{3-}$ and $\text{Eu}^{2+} (\text{Ni}^{1+}\text{Ni}^{1+}) (\text{P}_2)^{4-}$ where the M element is present in a low oxidation state.

Detailed physical property studies of the pnictide phases with the $\text{Zr}_2\text{Fe}_{12}\text{P}_7$ - and ThCr_2Si_2 -type structures are yet to be made. In view of the fact that metallic behaviour and superconductivity have been discovered in the related ternary phosphides $\text{LaM}_4\text{P}_{12}$ (M = Fe, Ru), it is possible that superconductivity may be exhibited by these metal excess ternary system of compounds as well.

8. Ternary oxides

Ternary oxides with the perovskite (ABO_3 -type) and spinel (AB_2O_4 -type) structure are known to be not very conducive to high T_c superconductivity (Nb-doped or reduced SrTiO_3 has a $T_c \leq 1$ K; copper containing chalcogenide spinels, CuRh_2X_4 X = S, Se, have $T_c \leq 5$ K). However, one isolated example in each of the above structure type is now known with $T_c \sim 11$ – 13.5 K: (i) $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ ($x = 0.05$ – 0.3) and (ii) $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$ ($x = 0.1$ – 0.3). The compounds are type II superconductors.

Sleight *et al* (1975) discovered that the orthorhombic BaPbO_3 and monoclinic BaBiO_3 perovskites form complete series of solid solutions and superconductivity is

induced for $x = 0.05$ – 0.30 in $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ whereas the end members ($x = 0$ and 1) are metallic and semiconducting respectively. Later studies by Khan *et al* (1977), Gilbert *et al* (1978, 1982) and Suzuki *et al* (1980) confirmed the above observations on samples in the bulk and thin-film form. Studies also showed that T_c increases from about 9 K for $x = 0.05$ to a maximum of about 13 K at $x = 0.3$. For $x \geq 0.35$, the superconductivity is destroyed and in fact the phases are semiconducting in nature. It is significant to note that T_c is maximum for that value of x which is slightly below the value where the metal-to-semiconductor transition sets in. One feature of this perovskite system is that the superconducting transitions are broad (1–2 K width) as measured by the Meisner effect. Initial experiments on alkali metal doping (at the Ba-site) indicated an improvement in the sharpness of the transition width without affecting the T_c value for a given value of x . Later experiments showed that a slight excess of Pb (over the nominal x) also produces the same effect showing thereby that the broad transition may be related to non-random distribution of Pb and Bi at site of the perovskite structure.

Since there are no d electrons in $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$, the conduction band consists overlapping Pb 6s and O 2p bands. Sleight *et al* (1975) proposed a schematic energy level diagram to explain the observed properties.

$\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$ ($0.1 < x \leq 0.3$) was first synthesized by Johnston *et al* (1973) and found to be superconducting with a high T_c ranging from 10–12 K. The homogeneity range for the spinel structure varies from $x = 0.33$ ($a = 8.36$ Å) to approximately $x = -0.2$ ($a = 8.4$ Å). The superconducting compositions are in the vicinity of the metal-to-semiconductor transition since for $x \sim 0$ – 0.1 , the samples are metallic and those with $x \approx 0.15$ – 0.33 are semiconductors. Maximum T_c is found for $x = 0$ and drops abruptly for $x \approx 0.05$ – 0.1 to a value less than 1.5 K. Magnetic susceptibility (Johnston 1976; Murphy *et al* 1982), heat capacity (McCallum *et al* 1976) and critical field measurements (Roy *et al* 1977; Foner and McNiff 1976) confirm that superconductivity is a bulk property of the LiTi_2O_4 compound and the Ti 3d electrons are responsible for the observed behaviour.

9. Ternary chalcogenides

9.1 Ternary molybdenum chalcogenides (Chevrel phases)

The ternary molybdenum chalcogenides $\text{A}_x\text{Mo}_6\text{Ch}_8$ ($A = \text{metal}$; $x = 0$ – 4 ; $\text{Ch} = \text{S, Se, Te}$) represent a family of isostructural METS compounds with remarkable chemical and physical properties. Many of them are high T_c (≤ 15 K) and high critical magnetic field ($H_{c2} \sim 600$ kOe) superconductors. Originally discovered in 1971, they have been extensively investigated in recent years. The structure and chemistry of these phases are well understood to a certain extent but a complete understanding of the physical properties including superconductivity, exciting new possibilities and phase equilibrium relationships need a lot more future research. Excellent reviews are available in the literature and hence only a brief account will be presented here (Fischer 1978; Yvon 1979; Schöllhorn 1980, 1983a, b; Umarji 1980; Shenoy *et al* 1981; Subba Rao and Shenoy 1981; Corbett 1981; Maple and Fischer 1982; Fischer and Maple 1982; Chevrel and Sergent 1982; Pobell *et al* 1982; Simon 1981; Poppe 1980).

9.1a *Structure and stoichiometry*: The compounds, $\text{A}_x\text{Mo}_6\text{Ch}_8$, possess a hexagonal-

Diagram illustrating the crystal structure of MoS₂. The structure shows Mo atoms (black spheres) at the corners of the unit cell, S atoms (white spheres) forming octahedra, and Pb atoms (hatched spheres) at the centers of the edges. The unit cell dimensions are labeled a_p and 2.

Figure 18. Structure of PbMo_6S_8 . Mo_6S_8 unit is turned by $\sim 27^\circ$ with respect to rhombohedral cell vectors. Pb occupies the channel position.

| | | | | | | | | | | | | | | | | |
|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| Li | Be | | | | | | | | | | | B | C | N | O | F |
| Na | Mg | | | | | | | | | | | Al | Si | P | S | Cl |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I |
| Cs | Ba | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At |
| Fr | Ra | Ac | | | | | | | | | | | | | | |

| | | | | | | | | | | | | | |
|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |
| Th | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No | Lw |

Figure 19. Partial periodic table showing the A elements (shaded) which form the $A_xMo_6Ch_8$ ($Ch = S, Se$) phases. *s* indicates the phases which have T_c between 8–15 K. Symbols *x* and *y* indicate that partial substitution is possible with these elements at the Mo and Ch site respectively (After Fischer 1978 with some modification).

close to 1. The A atoms effect an electronic charge transfer to the Mo_6Ch_8 unit (in essence, to the Mo-4d conduction band) (Fischer 1978; Ramasamy *et al* 1981; Yashonath *et al* 1981; Freeman and Jarlborg 1982). Chevrel phases are amenable to chemical substitution at the A, Mo and Ch sites. In addition to the $(\text{A}_{1-x}\text{A}_x)\text{Mo}_6\text{Ch}_8$ -type solid solutions, isostructural phases $(\text{Mo}_2\text{Re}_4)\text{Se}_8$, $(\text{Mo}_4\text{Ru}_2)\text{Se}_8$, $(\text{Mo}_{6-x}\text{M}_x)\text{Se}_8$, ($\text{M} = \text{Nb}, \text{Rh}$), $\text{Mo}_6\text{Ch}_6\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), $\text{Cu}_x\text{Mo}_6\text{S}_6\text{I}_2$ and $\text{Li}_2\text{Mo}_6\text{S}_6\text{Br}_2$ have been isolated and studied (Fischer 1978; Radhakrishnan *et al* 1981; Umarji *et al* 1981a, b; Sankaranarayanan *et al* 1982; Perrin *et al* 1980; Behlok and Robinson 1983; Alekseevskii *et al* 1978, 1982). Interestingly enough, and true to the nature of the channel structure, the A atoms, when small (*e.g.* Li, Cu, Co, Ni), can be leached out by a simple mineral acid treatment or electrochemical oxidation to give rise to the binary Mo_6Ch_8 compounds. Of course, the reverse process of insertion of foreign metal atoms into the channels of Mo_6Ch_8 to give ternaries is also possible and has been studied (Fischer 1978; Schöllhorn 1980; Umarji *et al* 1980).

9.1b Superconductivity and related properties: The binary Mo_6Ch_8 and many ternaries, $\text{A}_x\text{Mo}_6\text{Ch}_8$ exhibit metallic behaviour, but with fairly high resistivity ($\rho \sim 10^{-3}$ ohm cm). For A = alkali metal, post transition metal or rare earths, the ternaries exhibit superconductivity. T_c values between 8–15 K are encountered for A = Pb, Sn, Cu, Ag, La and Yb. Binary Mo_6Se_8 has a T_c of 6.3 K whereas Mo_6S_8 is superconducting below 1 K and Mo_6Te_8 does not become superconducting up to the lowest temperatures. $\text{Mo}_6\text{S}_6\text{X}_2$ ($\text{X} = \text{Br}$ and I) exhibit a T_c of 13–14 K. Magnetic susceptibility, heat capacity data and theoretical band structure calculations show that there exists a large density of states at the Fermi level in $\text{A}_x\text{Mo}_6\text{Ch}_8$ and the metallic and superconducting behaviour are exclusively due to the Mo-4d electrons (Fischer 1978; Freeman and Jarlborg 1982; Andersen *et al* 1982). The number of electrons per Mo_6 -cluster (NEC) is an important parameter in determining the properties because it determines the occupancy of the 4d-conduction bands. For Mo_6S_8 , NEC is 20 ($(6 \times 6) - (2 \times 8)$) and it becomes 21, 22 or 23 depending on the valency of A metal in AMo_6S_8 (Ag, 20 + 1; Pb, 20 + 2; La, 20 + 3 etc) but the 4d-conduction band is still partially filled in these cases. Metallic and superconducting behaviour can thus be explained. Band structure calculation and also simple chemical bonding arguments predict that the 4d-subband will be completely filled for an NEC of 24 (assuming Mo–Mo intracluster bonding, 12 edges in the Mo_6 -octa cluster require $12 \times 2 = 24$ electrons to form electron-pair bonds) and the material should exhibit semiconductor behaviour (because the upper lying Mo-4d subband is separated by an energy of 1–1.5 eV). Indeed, the compounds $\text{Mo}_2\text{Re}_4\text{S}_8$, $\text{Mo}_2\text{Re}_4\text{Se}_8$, $\text{Mo}_4\text{Ru}_2\text{Se}_8$ and $\text{Cu}_4^{1+}\text{Mo}_6\text{S}_8$ which possess an NEC of 24 are found to exhibit a semiconductor behaviour.

According to the McMillan-Allen-Dynes formalism of the original BCS theory on the origin of superconductivity in a metal, T_c is directly dependent on the density of electronic states at the Fermi level, the electron-phonon interaction and phonon density of states, the latter being proportional to the Debye temperature. Measurements till todate show that the Chevrel phases satisfy all the criteria and no exotic mechanisms other than the phonon (BCS) mechanism need be invoked to explain the superconductivity. However, in the rare earth containing Chevrel phases, LnMo_6S_8 , which order antiferromagnetically at low temperatures, the superconducting state seems to be modified to a non-BCS type due to a possible change in pairing (Ishikawa *et al* 1982). No

universal correlation between T_c and known structural, chemical or physical parameters seems to exist in the Chevrel phases examined so far. A somewhat rough correlation may exist between T_c and hexagonal lattice parameter ratio (c/a) in a related series of compounds but efforts to raise T_c beyond 15 K have not been successful. A detailed explanation for the existence of very large critical fields in Chevrel phases has been provided recently by Decroux and Fischer (1982).

9.1c. Coexistence of superconductivity and magnetic order and the reentrant behaviour: Rare earth Chevrel phases, LnMo_6Ch_8 ($\text{Ch} = \text{S, Se; Ln} = \text{rare earth or Y}$), exhibit superconductivity (except for $\text{Ln} = \text{Ce, Eu}$) despite the fact that they contain ~ 7 atom % paramagnetic ions (*e.g.*, $\text{Ln} = \text{Tb, Dy, Ho, Er}$). This indicates that the interaction of the f -electron spins with the Mo-4d conduction electrons is not much. Magnetic susceptibility and other studies have shown that the rare earth is present as Ln^{3+} ion in LnMo_6Ch_8 phases (except Eu and Yb which are present in $2+$ state) and since many of these support a large magnetic moment, there exists the possibility of long range magnetic order developing at low temperatures and still retain the superconducting behaviour. Detailed studies by a variety of techniques including neutron diffraction have indeed shown that antiferromagnetism (with Néel temp., T_N) and superconductivity (with transition temp., T_c) in many of the Ln -Chevrel phases coexist with $T_N < T_c$ (table 3). The compound HoMo_6S_8 exhibits the interesting reentrant behaviour similar to ErRh_4B_4 and other ternary systems (table 4). Neutron diffraction studies (Lynn 1983; Lynn *et al* 1981; 1983b) have shown that a sinusoidally modulated magnetized state (with a period of 250 Å) coexists with superconductivity just above T_{c2} in HoMo_6S_8 analogous to the case of ErRh_4B_4 . Coexistence of superconductivity and ferromagnetism has been realized by Ishikawa *et al* (1982) in the pseudoternary system $\text{Ho}_{1-x}\text{Eu}_x\text{Mo}_6\text{S}_8$ (see table 4). Reentrant behaviour can be induced in DyMo_6S_8 and GdMo_6S_8 to some extent by the application of magnetic field, similar to the case of LnRh_4B_4 antiferromagnetic superconductors.

9.2 Condensed molybdenum cluster phases

Ternary molybdenum compounds containing $(\text{Mo}_9\text{Ch}_{11})$, $(\text{Mo}_{12}\text{Ch}_{14})$ or $(\text{Mo}_{6/2}\text{Ch}_{6/2})$ ($\text{Ch} = \text{S, Se, Te}$) units resulting from a linear condensation of the octahedral Mo_6 clusters have been recently synthesized and studied. Representative compounds are: $\text{Ag}_x\text{Mo}_9\text{Se}_{11}$ ($x \approx 4$) (Gougeon *et al* 1983), $\text{A}_2\text{Mo}_9\text{S}_{11}$ ($\text{A} = \text{K, Tl}$), $\text{K}_2\text{Mo}_{15}\text{S}_{19}$, $\text{A}_2\text{Mo}_{15}\text{Se}_{19}$ ($\text{A} = \text{K, Ba, Tl}$), $\text{In}_x\text{Mo}_{15}\text{Se}_{19}$ ($x = 2.9\text{--}3.4$) (Chevrel *et al* 1981; Chevrel and Sergent 1982), AMo_3S_3 ($\text{A} = \text{K, Rb, Cs}$) (Huster *et al* 1983) and AMo_3Ch_3 ($\text{A} = \text{In, Tl; Ch} = \text{Se, Te}$) (Hönle *et al* 1980). The compounds crystallize with a hexagonal symmetry. The a lattice parameter is ~ 9 Å but the c parameter varies with the Mo_xCh_y content and decreases to a low value (~ 4.5 Å) for $x:y = 3:3$. The structure of the $\text{A}_x\text{Mo}_{15}\text{Se}_{19}$ phases is characterized by the presence of Mo_6Se_8 and $\text{Mo}_9\text{Se}_{11}$ units, the latter resulting from a fusion of two Mo_6 octahedra along a common face, but all the Mo atoms have the same chalcogen environment as existing in the Chevrel phases. The intracluster distance is small (~ 2.7 Å as in Chevrel phases) but intercluster distance is large ($\sim 3.4\text{--}3.5$ Å). The indium and other A atoms are situated in a three-dimensional network of channels similar to the $\text{A}_x\text{Mo}_6\text{Ch}_8$ compounds (see § 9.1). All the phases examined so far are metallic and superconducting but T_c values are

low (≤ 4.3 K). The $\text{In}_{2.9}\text{Mo}_{15}\text{Se}_{19}$ phase has been found to possess a relatively high value of H_{c2} of 210 kOe.

10. Summary and conclusions

Metal excess ternary system (METS) of compounds are usually stoichiometric, but also can be nonstoichiometric compounds (one of which is a nonmetal) occupy a distinct set or sets of crystallographic lattice sites and only a part of the valence electrons of the metals are involved in chemical bonding with nonmetallic atom. The excess electrons are delocalized and whenever there is a strong metal-metal bonding (metallic bond), the compound exhibits a metallic behaviour. This is a necessary condition for the exhibition of superconductivity by any METS compound. Only a few of the large number of known METS have been examined in detail till to-date. However, it is clear that certain specific crystal structures and a specific type of bonding between the atoms in METS are favourable for high T_c superconductivity. In fact Matthias and others have pointed out earlier that the high T_c exhibited by the LnRh_4B_4 and $\text{A}_x\text{Mo}_6\text{Ch}_8$ phases is due to the presence of Rh and Mo clusters respectively. Similarly, the carbon atoms when located inside an octahedra of metal atoms in the METS carbides give rise to high T_c superconductivity. However, from the preceding sections we note that high T_c is not obtained whenever there is an inter-penetration of different types of clusters or condensation of metal atom clusters within the structure. Hence, the presence of isolated metal atom and/or non metal atom clusters is favourable to high T_c superconductivity. Also, high crystal symmetry (cubic, rhombo or tetra) of the structure appears to favour high T_c compared to the less symmetric structures in METS compounds. The two isolated examples of the oxide systems show that electronic (and perhaps also the crystal structure) instability induced by the compositional variation is a factor which governs the high T_c behaviour. Presumably this line of approach extended to the METS may yield fruitful results in the search for new high T_c materials. Finally, we note that from the limited studies conducted on Co and Fe-containing stannides and phosphides, the 3d transition metals need not be counted out of the possible METS in the search for high temperature superconductivity.

Acknowledgements

Thanks are due to the Department of Science and Technology, Government of India, New Delhi for the award of a research grant.

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