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STRUCTURE AND SUPERCONDUCTIVITY IN TERNARY SYSTEMS OF COMPOUNDS*

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The structure and superconductivity exhibited by the metal excess ternary systems of compounds, with special references to the Chevrel phases, rare earth rhodium borides and transition metal phosphides are discussed, in addition to the other interesting physical properties. Cluster formation, 3*d*-network with simple crystal symmetry and charge transfer effects are important for the realization of high T_c superconductivity.

Key Words : Metal Excess Ternary Systems; Superconducting Compounds; Ternary Superconductors

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. Examples are : $BaTiO_3$, $Y_3Fe_5O_{12}$, $PbMo_6S_8$ etc. This crystallographic definition clearly distinguishes ternary compounds from binary or pseudo binary phases (e.g., $Li_xNi_{1-x}O$: $(V_{1-x}Cr_x)_2O_3$, $Mo_2Re_4S_8$ etc.) in which only two sets of lattice sites are occupied or which contain only two species of elements. Metal excess ternary systems (METS) of compounds 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.[1,2] Examples are $PbMo_6S_8$, $ErRh_4B_4$, $Pb_2Rh_3S_2$, ZrRuP, NbReSi etc. 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 resistivity in a substance below a certain critical temperature (T_c), is not uncommon and many metals, alloys, intermetallics, binary and ternary compounds and organic charge-transfer complexes become superconducting at low temperatures. Fig. 1 gives a survey of the known superconductors. Of the more than 1000 superconductors

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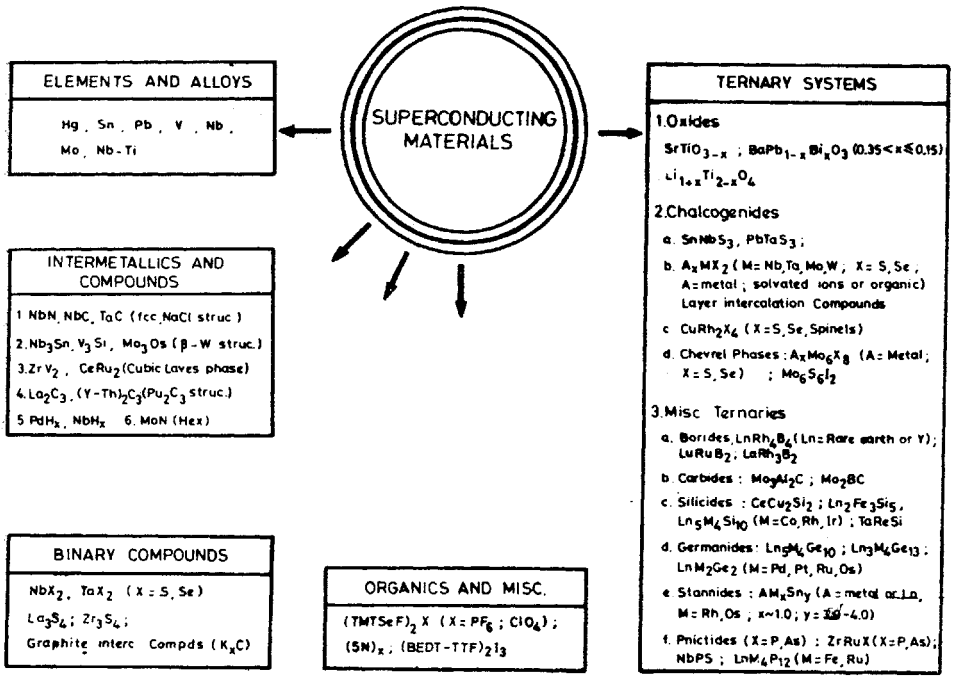

FIG 1 Survey of the known superconducting materials

known, only a handful possess T_c greater than 10 K and these are called high T_c or *high temperature* superconductors. The intermetallic binary compound Nb_3Ge has the highest T_c of 23.2 K of all the known materials whereas $PbMo_6S_8$ with T_c of 15.2 K is the highest known for a ternary METS compound. Since a large number of compounds are known or can be synthesized and also since chemical manipulation is 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 than the binary compounds and alloys. As a result of intense research activity during the past decade, many METS compounds have been isolated, their crystal structures determined and their superconducting properties investigated (Table I).[3–22] As can be seen, high T_c superconductivity is observed in several ternary borides, carbides, silicides, phosphides, oxides and chalcogenides. From the studies carried out on these METS compounds a wealth of information and interesting physics and chemistry have come about not only with respect to the superconducting behaviour but also the coexistence of magnetic order and superconductivity, reentrant behaviour, intermediate valence, heavy Fermion behaviour and mixed (electronic and ionic) conduction. The unique superconducting and magnetic behaviour of the ternary compounds must necessarily arise due to their detailed crystal structures and stoichiometries in a fundamental way.

In the following Sections we shall reiterate the available guidelines and crystal structure-property correlations established for the METS superconductors and

TABLE I

Structure and T_c of known high temperature ternary superconductors

Compound	Structure Type	Latt. Param. (Å)	T_c,K	Reference
$LuRh_4B_4$	$CeCo_4B_4$ (tetra)	a = 5.3; c = 7.4	11.7	Matthias *et al.*[6]
$Y(Rh_{0.85}Ru_{0.15})_4B_4$	$LuRu_4B_4$ (tetra)	a = 7.5; c = 14.9	9.6	Johnston[7]
$LuRuB_2$	$LuRuB_2$ (ortho)	a = 5.8; b = 5.2; c = 6.3	10.0	Ku and Shelton[8]
Mo_3Al_2C	β-Mn (cubic)	a = 6.9	10.0	Johnston *et al.*[9]
Mo_2BC	Mo_2BC (ortho)	a = c = 3.1; b = 17.4	7.0	Toth[10]
$Sc_5Rh_4Si_{10}$	$Sc_5Co_4Si_{10}$ (tetra)	a = 12.3; c = 4.0	8.5	Braun and Segre[11]
$Y_5Os_4Ge_{10}$	$Sc_5Co_4Si_{10}$ (tetra)	a = 13.0; c = 4.3	8.7	Braun and Segre[11]
$YbRh_{1.4}Sn_{4.6}$	$Pr_3Rh_4Sn_{13}$ (cubic)	a = 9.7	8.6	Remeika *et al.*[11a]
ZrRuP	Fe_2P (hexag)	a = 6.4; c = 3.8	13.0	Barz *et al.*[12]
				Muller *et al.*[13]
NbPS	NbPS (ortho)	a = 3.4; b = 11.9; c = 4.7	12.5	Donohue and Bierstedt[14]
$LaRu_4P_{12}$	$LaFe_4P_{12}$ (cubic)	a = 8.1	7.2	Meisner[15]
$LiTi_2O_4$	$MgAl_2O_4$ (spinel)	a = 8.4	13.7	Johnston[16]
$BaPb_{0.8}Bi_{0.2}O_3$	$CaTiO_3$ (perovskite)	a ~ 5.2	13.2	Sleight *et al.*[17]
$Zr_{0.6}Rh_{0.3}O_{0.1}$	Fe_3W_3C (cubic)	a = 12.4	11.8	Matthias *et al.*[18]
$Pb_{0.9}Mo_6S_{7.8}$	$PbMo_6S_8$ (rhombo-hexag Chevrel phase)	a = 9.2; c = 11.48	15.2	Chevrel *et al.*[19]
				Matthias *et al.*[20]
$Cu_{1.8}Mo_6S_8$	$PbMo_6S_8$	a = 9.58; c = 10.25	10.8	Matthias *et al.*[20]
$Mo_6S_6I_2$	Mo_6Se_8 (rhombo-hexag)	a = 9.64; c = 10.44	14.0	Sergent *et al.*[21]
				Perrin *et al.*[22]

structural instabilities exhibited by them. This is followed by a brief discussion of the structural features of the well-studied METS superconductors and the interesting and exotic phenomena exhibited by them. The data are condensed in the form of figures and tables and elaborate discussions are avoided. For a detailed discussion of the METS superconductors the reader is referred to the reviews and books.[23-28]

Empirical Guidelines and Structure-Property Correlations

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. It is not easy to quantify the above parameters (which govern the T_c) in the absence of detailed information on the crystal structure, electronic band structure and low temperature physical properties for a given system.

Matthias[29] and Vandenberg and Matthias[30] and Vandenberg[31] have enunciated a few guidelines for the prediction of superconductivity in binary and ternary systems. These guidelines have been developed empirically but with qualitative theoretical support and successfully applied for the realization of many binary and ternary high T_c superconductors. The T_c of a material is found to be a sensitive function of the crystal symmetry, atomic order and/or stoichiometry, metal atom clustering, lattice instabilities and atomic properties such as average valence electron concentration. Clustering of the metal and/or non-metal atoms is an important feature of the high T_c ternary superconductors. That is, the existence, in the crystal lattice, of metal and/or non metal atom pairs, triangular, tetrahedral or octahedral clusters with short *intracluster* distances (of the same order of magnitude or less than in the parent metal; e.g., $PbMo_6S_8$ with Mo_6 clusters; $LuRh_4B_4$ with tetrahedral Rh_4 clusters and B_2 pairs). In addition, the existence of relatively short *intercluster* distances ($\leqslant$ 20 per cent of the intracluster) is an essential feature since this will ensure conduction band formation and metallic nature of the material while the metal atom clusters ensure the existence of large density of states at the Fermi level. Furthermore, high T_c superconductivity is encountered in systems containing 'isolated' clusters of metal atoms in the crystal lattice. Whenever, there is a 'condensation' or 'fusion' of clusters (by corner, edge or face sharing; e.g., as in $Ag_4Mo_9Se_{11}$, $TlMo_3S_3$, $LaRu_4B_4$), the T_c gets lowered. The important structural features and crystal chemical relationships of METS superconductors are summarized and presented in Table II.[31a]

In binary superconductors, it is well known that certain crystal structures are favourable to high T_c superconductivity (e.g., cubic β-tungsten (A_3B), α-Mn, NaCl and Pu_2C_3 structures). In ternaries, no such favoured structures have yet been found, probably due to lack of sufficient data but generally it is found that high crystal symmetry (cubic, tetragonal, hexagonal or rhombohedral) combined with a 3D-network structure favours high T_c (e.g., $PbMo_6S_8$: rhombohedral; $LuRh_4B_4$:

TABLE II

Structure-property correlations in METS superconductors[102]

Property	Chevrel Phases $LnMo_6Ch_8$	Borides		Stannides LnM_xSn_y (M = Rh; Os) $[Ln_3Rh_4Sn_{12}(I)\ Sn_1(II)]$	ZrRuP(As)
		$LnRh_4B_4$	$LnRuB_2$		
Crystal Structure[a]	Rhombohedral-hexagonal ($a \sim 9.0$Å; $c \sim 11.5$Å)	Tetragonal ($a \sim 5.3$Å; $c \sim 7.4$Å)	Orthorhombic ($a \sim 5.8$Å; $b \sim 5.3$Å; $c \sim 6.3$Å)	Cubic or distorted cubic ($a_0 \sim 9.7$Å or $\sqrt{2}\,a_0$)	Hexagonal (Fe_2P type) ($a \sim 6.5$Å; $c \sim 3.8$Å)
Metal atom clusters[b]	Octahedral Mo_6 clusters	Tetrahedral Rh_4 clusters	Zig-zag chain clusters of Lu	Pairs (Sn_2)	Triangular clusters of Ru
Rare earth atoms or ions[c]	Large concn (~ 7 at%)	Large concn (~ 11 at%)	Large concn (~ 25 at%)	Large concn (~ 15 at%)	—
Role of third element (anion)[d]	S or Se ions	B_2 pairs	B_2 dimers exist which form zig-zag chains	Sn atoms at the site II	P or As ions
Supercond Trans. Temp.[e]	Arises from Mo-4*d* band ($T_c \sim 1$–12 K)	Arises from Rh-4*d* band (5–12 K)	Arises from Ru-4*d* band ($\sim$ 3–10 K)	Most certainly from [Sn-(5s, 5p)] (1–9 K)	Arises from Ru-4*d* band (13 K)
Mag ord temp[f]	Low T_m (0.5–1.0 K)	Reasonable T_m (1–12 K)	Low T_m (1–2 K)	Reasonable T_m (1–11 K)	—

[a]The crystal lattice is a truly 3D network structure. The phases are isostructural for a given ternary but lattice constants vary with the Ln or A atom or non-metal.

[b]The intracluster (or pair) distances are very small ($\sim$ 2.5–3.0Å; same order as in the respective metals) and the intercluster distances are not very large. This leads to strong metal-mtal bonding and also conduction band formation.

[c]Ln forms part of the crystal lattice and hence is distributed uniformly but isolated effectively (Ln-M dist $\geqslant$ 4Å) from the conduction electrons. Also 4f electrons support a large magnetic moment.

[d]The third element aids in the stabilisation of the structure and has the major role of an anion. Detailed structural analysis and Mössbauer study have shown that Sn(II) site differs from Sn(I) site. Ln size (atomic or ionic radius) is not critical except for $LnRh_4B_4$ for the formation of proper phase.

[e]The Mo, Ru and Rh 4*d* conduction bands are narrow. T_c can be high (10–15 K) for nonmagnetic Ln (La, Yb, Lu or Y) or other elements (e.g. A = Pb, Sn or Ca).

[f]Magnetic ordering can be ferromagnetic or antiferromagnetic and is exclusively due to the Ln-ion or atom. No superconductivity is observed at any temperature, when T_m is > 5 K in borides and stannides.

tetragonal; ZrRuP : hexagonal). On the other hand, by trial and error, it has been established that certain crystal structures are *not* favourable to high T_c superconductivity. Examples are : Rare earth ternary rhodium borides and silicides, $LnRh_3X_2$ (X = B or Si) with the undistorted hexagonal structures,[32–34] and borides with the perovskite structure, $LnRh_3B$,[35] ternary phosphides and silicides with the orthorhombic TiNiSi or Co_2P or anti $PbCl_2$ structure, $MM'X$ (X = P or Si; M = transition or rare earth metal and M' = transition metal)[13,13a] and ternary silicides MM'_2Si_2 with the tetragonal ($ThCr_2Si_2$) structure.[36,37]

Yvon[5] pointed out an interesting feature of the high T_c ternary superconductors in that for those systems which do not possess cubic symmetry, the crystallographic c/a axial ratios fall usually close to 'special' values such as 2, $\frac{1}{2}$, $\frac{1}{3}$, $\sqrt{2}$, $\sqrt{3}/2$ etc. The physical origin of this correlation is not yet clear except that it seems to indicate the influence of Brillouin zone effects and simulation of pseudo-cubic symmetry behaviour.

Another important empirical guideline is the role played by electronic charge transfer effects and the electro-negativity of the non-metallic constituent in inducing high T_c superconductivity in ternary systems. This is exemplified by the behaviour of the compounds ZrRuP and ZrRuSi. Both crystallize in the hexagonal Fe_2P structure, which is conducive to high T_c superconductivity. However, while ZrRuP exhibits a T_c of 13 K, ZrRuSi is not superconducting above 1.2 K. Since P or Si atoms are isolated in the structure (no P–P or Si–Si bonds exist) it is reasonable to assume that they are present as P^{3-} and Si^{4-} in ZrRuP and ZrRuSi respectively. Since zirconium is always tetravalent there is no effective charge transfer from Zr to Ru in $Zr^{4+}RuSi^{4-}$ whereas one electron is contributed to Ru conduction band in $Zr^{4+}RuP^{3-}$. Similar arguments can be applied to the isostructural series of compounds NbRuSi, NbRhP, NbReSi, etc. where changes in electronic band structure are effected by changes in X and M atoms and where the M' transition metal atoms act as a source or sink of electrons. Such empirical considerations have led to the recent discovery of superconductivity in ternary silicides, $MM'Si$ (M = Nb, Ta; M' = Ru, Re).[38]

Thus, it appears certain that the existence of isolated transition metal and/or non-metal clusters, and a 3D-network structure with overall simple crystal symmetry give rise to large electron-phonon coupling constants and favourable phonon-density of states and large Debye-temperatures essential for high T_c in METS compounds.

Superconductivity and Structural Instabilities

Lattice instability is a characteristic feature of many high T_c superconductors e.g., A15 structure compounds, transition metal carbides and nitrides.[39] In the AMo_6Ch_8 chalcogenides the A atoms, when small, vibrate anharmonically; many of them undergo structural phase transformations (e.g., Cu, Co and Zn-containing compounds). In particular, the compounds exhibiting the highest T_c's, $PbMo_6S_8$ and $SnMo_6S_8$, have been found to show some structural instability recently.[40]

Many of the other high T_c ternary superconductors also tend to be metastable since they compete with other phases of different structure or of slightly different composition. Thus, there are four different modifications of the $LuRh_4B_4$ borides already known and still more seem likely to exist.[41,42] In the case of the superconducting stannides $Ln_3Rh_4Sn_{13}$, as many as three different phases of almost the same composition have been reported.[43,44] A similar situation occurs with some of the superconducting chalcogenides because slight variations of the metal to non-metal atom ratio can produce a series of closely related (isolated or condensed) cluster compounds, such as $InMo_6Se_8$, $In_{\sim 3}Mo_{15}Se_{19}$, $In_2Mo_{15}Se_{19}$ and $InMo_3Se_3$.[19,45–47]

Structural Aspects of METS Superconductors

Ternary Molybdenum Chalcogenides (Chevrel Phases)

The ternary molybdenum chalcogenides $A_xMo_6Ch_8$ (A = Metal; x = 0.0–4.0; Ch = S, Se, Te) represent a family of isostructural METS compounds with remarkable chemical and physical properties. Many of them are high T_c ($\leqslant$ 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.[2,3,4,23,48–57]

Structure and Stoichiometry—The compounds, $A_xMo_6Ch_8$, possess a hexagonal-rhombohedral crystal structure ($a \sim$ 6.5Å; $\alpha \sim 90°$). The structure essentially consists of a rhombohedral stacking of Mo_6Ch_8 units in such a way that the A atoms occupy the empty channels. Each Mo_6Ch_8 unit consists of an octahedral cluster of Mo-atoms enclosed in a slightly deformed cube of Ch-atoms (Fig. 2). The intracluster and intercluster Mo–Mo distances are small (intra, 2.7Å, same as that in Mo-metal; inter, 3.2Å) with the result that strong metal-metal bonding exists within the cluster and sufficiently strong interactions exist between intercluster Mo–Mo atoms. The A-atoms are mostly the electropositive elements of the Periodic Table. The stoichiometry x in $A_xMo_6Ch_8$ and the site occupancy depends on the ionic radius of the A metal. Small ionic radii elements (e.g., Cu, Ni, Co etc.) occupy the so called off-channel positions (with essentially tetrahedral coordination of Ch-atoms) and x can vary from 0.0 to 4.0. On the other hand, large ionic radii elements (e.g., Pb, Sn, La, Eu, Yb) occupy the central channel positions (Fig. 2; essentially 8-fold coordination) and x is fixed and close to 1.0. The A-atoms effect an electronic charge transfer to the Mo_6Ch_8 unit (in essence, to the Mo-4d conduction band).[48,58–60] Chevrel phases are amenable to a wide variety of chemical substitution at the A, Mo and Ch sites. In addition to $(A_{1-x}A'_x)$ Mo_6Ch_8-type solid solutions, isostructural phases $(Mo_2Re_4)Se_8$, $(Mo_4Ru_2)Se_8$, $(Mo_{6-x}M_x)$ Se_8, (M = Nb, Rh), $Mo_6Ch_6X_2$ (X = Cl, Br, I), $Cu_xMo_6S_6I_2$ and $Li_2Mo_6S_6Br_2$ have been

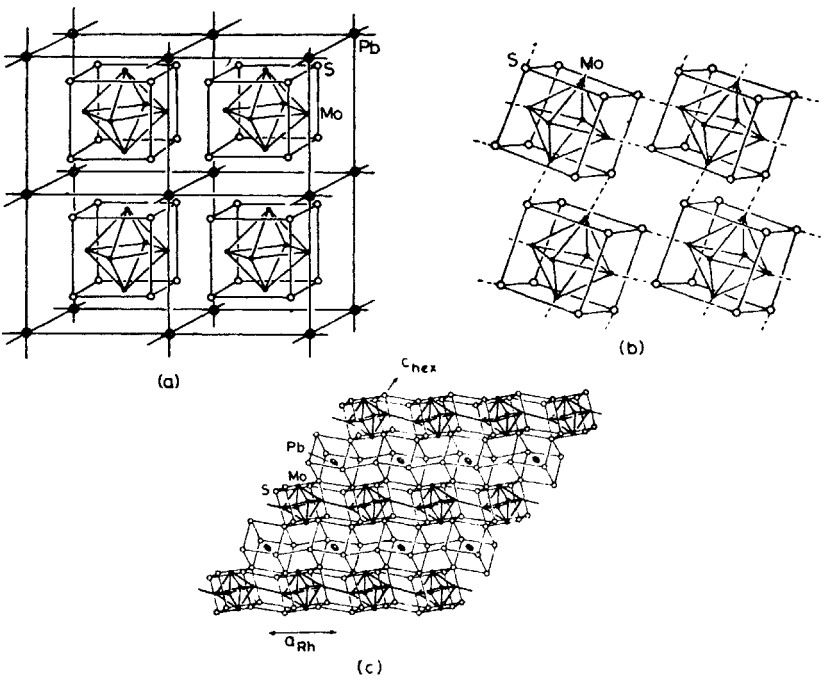

FIG 2 Structure of the Chevrel phases, AMo_6Ch_8 (*a*) Idealized $PbMo_6S_8$ (*b*) Mo_6S_8 units showing the distortion with respect to $\bar{3}$ axis and Mo–S bonding (*c*) Projection along the $(11\bar{2}0)$ plane showing the channels occupied by the Pb-atoms.

isolated and studied.[45,46,48,61–67] Interestingly enough, and true to the nature of the channel structure, the *A*-atoms, when small (e.g., 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.[48,49,66,68,69]

Superconductivity and Related Properties—The binary Mo_6Ch_8 and many ternaries, $A_xMo_6Ch_8$ exhibit metallic behaviour, but with fairly high resistivity ($\sim 10^{-3}$ 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 at 1 K and Mo_6Te_8 does not become superconducting upto the lowest temperatures. $Mo_6S_6X_2$ (X = 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 $A_xMo_6Ch_8$ and the metallic and superconducting behaviour are exclusively due to the Mo-4d electrons.[48,60,70] The number of electrons per Mo_6-cluster (NEC) is an important parameter in determining the properties because it determines the occupancy of the

4*d*-conduction bands. For Mo_6S_8, NEC is 20 ((6 × 6)—(2 × 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 4*d*-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 4*d*-sub-band will be completely filled for an NEC of 24 (assuming Mo–Mo intera-cluster bonding, 12 edges in the Mo_6-octa cluster require 12 × 2 = 24 electrons to form electron-pair bonds) and the material should exhibit semiconductor behaviour (because the upper lying Mo-4*d* sub-band is separated by an energy of 1.0–1.5 eV). Indeed, the compounds $Mo_2Re_4S_8$, $Mo_2Re_4Se_8$, $Mo_4Ru_2Se_8$ and $Cu_4^1{+}Mo_6S_8$ which possess an NEC of 24 are found to exhibit a semiconductor behaviour.

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.[71] The ternary molybdenum chalcogenides exhibit the interesting phenomena of coexistence of superconductivity and magnetic order and also reentrant behaviour. This is discussed in Section devoted to Reentrant Superconductors.

Condensed Molybdenum Cluster Phases—Ternary molybdenum compounds containing (Mo_9Ch_{11}), ($Mo_{12}Ch_{14}$) or ($Mo_{6/2}Ch_{6/2}$) (*Ch* = S, Se, Te) units resulting from a linear condensation of the octahedral Mo_6 clusters have been recently synthesized and studied. Representive compounds are : $Ag_xMo_9Se_{11}$ ($x \sim 4$),[72] $A_2Mo_9S_{11}$ (*A* = K, Tl), $K_2Mo_{15}S_{19}$, $A_2Mo_{15}S_{19}$ (*A* = K, Ba, Tl). $In_xMo_{15}Se_{19}$ (x = 2.9–3.4),[19,54] AMo_3S_3 (*A* = K, Rb, Cs)[73] and AMo_3Ch_3 (*A* = In, Tl; *Ch* = Se, Te).[74] The compounds crystallize with a hexagonal symmetry. The *a* lattice parameter is ~ 9Å but the *c*-parameter varies with the Mo_xCh_y content and decreases to a low value (~ 4.5Å) for $x : y = 3 : 3$. The structure of the $A_xMo_{15}Se_{19}$ phases is characterized by the presence of Mo_6Se_8 and Mo_9Se_{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 (~ 2.7Å as in Chevrel phases) but intercluster distance is large (~ 3.4–3.5Å). The indium and other *A*-atoms are situated in a 3D network of channels similar to the $A_xMo_6Ch_8$ compounds. All the phases examined so far are metallic and superconducting but T_c values are low (⩽ 4.3 K) indicating that such structures are not conducive to high T_c.

Ternary Borides with the Stoichiometry AM_4B_4

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 *a*-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 (Fig. 3). 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) with an alternate arrangement (stacking) of tetrahedra of different orientations along the *c*-axis. The intracluster Rh–Rh distances (2.6–2.8Å) are approximately the same as in rhodium metal (2.69Å) but intercluster distances are large (3.1Å). The *B–B* distances are small (1.80–1.83Å) indicating pair formation whereas the the *A–A* distances are large (~ 5Å) 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 $LuRh_4B_4$-type (Fig. 3).[7,41,75] Thus, the *bct* and orthorhombic structures can be viewed as containing two interpenetrating three-dimensional networks or extended

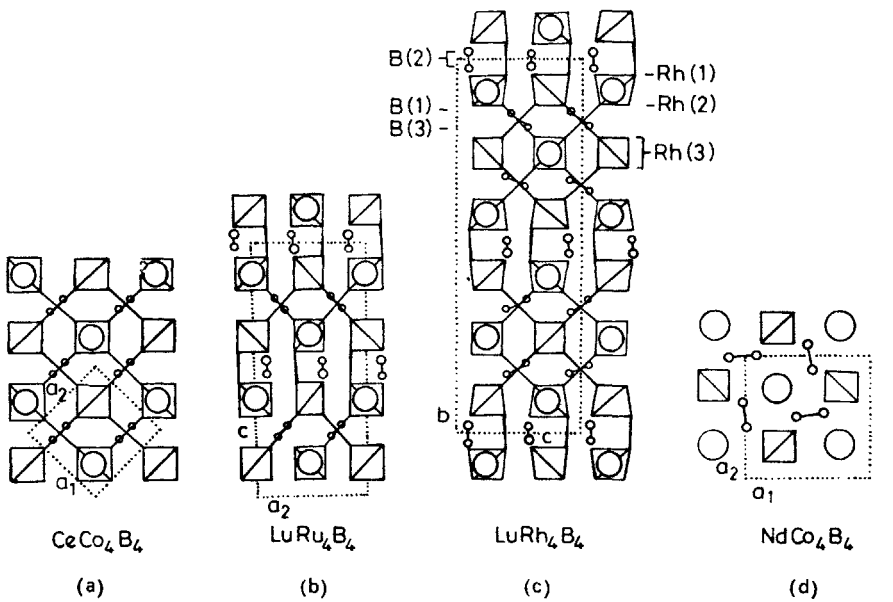

FIG 3 The structure of $LuRh_4B_4$ (*c*) compared with those of the other known AM_4B_4 polytypes.[41]

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 : $\sqrt{2}\ a \approx c$ ($CeCo_4B_4$-type) $\approx a \approx (c/2)$ ($LuRu_4B_4$-type) $\approx a \approx (b/3) \approx c$ ($LuRh_4B_4$-type).

The $NbCo_4B_4$-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 ($\sim$ 3.8Å $\approx$ c-lattice parameter) so that they can be considered to form infinite linear chains along the tetragonal axis (Fig. 3). 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 $\sim$ 1.4 in the former while it is much smaller ($\sim$ 0.53) in the latter. These structural differences play a crucial role in the T_c behaviour of the compounds.

The formation and stability of the AM_4B_4 compounds with different types of structure 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 → Tm, Lu; M = Rh, A = Nd, Sm, Gd → 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 ba stabilized at the nominal AM_4B_4 stoichiometry by substitution with a few atom per cent of Ru. Orthorhombic $LuRh_4B_4$-type compounds are known only for M = Rh and Ln = Ho → 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 = OsLn = La → Eu, Th; M = Ir, Ln = La → Dy, Y and Th. Pseudo-ternary 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.

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. The phases containing non-magnetic rare earths Lu and Y exhibit high T_c values (Table III). 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. The pure compound $ErRh_4B_4$ exhibits a reentrant (metallic) behaviour.[3]

Solid solutions of the type $(Ln_{1-x}Ln'_x)Rh_4B_4$ and $Ln(Rh_{1-x}M_x)B_4$ (M = Ir and Ru) have been examined in detail in the literature and provided a wealth of

TABLE III

T_c data on some representative AM_4B_4 compounds[a]

$CeCo_4B_4$-type		*bct*-$LuRu_4B_4$-type[b]		Orthorh. $LuRu_4B_4$-type	
Phase	T_c, K	*Phase*	T_c, K	*Phase*	T_c, K
$LuRh_4B_4$	11.7	$Lu(Rh_{0.85}Ru_{0.15})_4B_4$	9.0	$LuRh_4B_4$	6.2
YRh_4B_4	11.3	$Y(Rh_{0.15}Ru_{0.15})_4B_4$	9.4	—	—
$ErRh_4B_4$	8.7	$Er(Rh_{0.85}Ru_{0.15})_4B_4$	7.9	$ErRh_4B_4$	4.3
$TmRh_4B_4$	9.8	$Tm(Rh_{0.85}Ru_{0.15})_4B_4$	8.3	$TmRh_4B_4$	5.4

[a]Taken from Johnston and Braun.[42] Phases with the $NdCo_4B_4$-type structure do not exhibit superconductivity above 1 K.

[b]$LuRh_4B_4$ and YRu_4B_4 have a T_c of 2.0 and 1.4 K respectively.

information on the interplay between superconductivity and magnetism in these materials.[3,42]

The interesting and unusual properties of the *Ln* Rh_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 4*d*-electrons are exclusively responsible for superconductivity and participate in the Cooper pair formation. This has been confirmed by the magnetic susceptibility (χ) and other studies[76] and band structure calculations.[60] 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 4*d*-conduction band. This has been confirmed by $\chi - T$,[76] Mössbauer[52] and neutron diffraction.[77] 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 ($\leqslant$ 12 K).

(*iii*) The boron atoms which exist as pairs play the role of anion and stabilize the structure.

The AM_4B_4 phase 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 (Table III). 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 occurence of superconductivity since it

does not contain isolated (M_4B_4) clusters and also, perhaps, because of the small A–A separation.

Ternary Phosphides with MM'X Stoichiometry

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.*,[12] Muller *et al.*[13] and Meisner *et al.*[78] on the equiatomic (1 : 1 : 1) ternary transition metal phosphides and arsenides of the general formula, $MM'X$ (M = Ti, Zr, Hf, Nb, Ta; M' = Ru, Rh, Os; X = P, As). The compound ZrRuP can crystallize either in a hexagonal ZrRuSi (ordered Fe_2P or ZrNiAl)[79] type or in the orthorhombic TiNiSi (ordered Co_2P or anti $PbCl_2$)[80] type. Hexagonal ZrRuP and ZrRuAs show a T_c of 13.0 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 = Nb, Ta and the hexagonal arsenide phases are metastable at low temperatures.

An important structural feature of the hexagonal ZrRuP over that of the orthorhombic polymorph 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, 2.63Å). 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.[13] Recent heat capacity data[81] on the superconducting hexagonal phosphides show that the density of states at the Fermi level is not particularly large (0.76 ± 0.15 states/(eV-atom)) for ZrRuP with a T_c of 13.0 K (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.

Interesting Physical Properties Exhibited by METS Superconductors

Coexistence of Superconductivity and Magnetic Order

Magnetism and superconductivity are usually considered to be two mutually incompatible phenomena because of the following observations : (*i*) None of the magnetic elements or their alloys are superconducting, (*ii*) application of sufficiently strong magnetic field ($\geqslant H_{c2}$) always destroys the superconducting state in a metal and (*iii*) introduction of even a small concentration of magnetic impurity is very detrimental to superconductivity and can destroy it. The latter phenomenon is understood in terms of the well-known magnetic moment-conduction electron exchange interaction Γ. Thus, in principle coexistence of both phenomena in a solid can be observed if Γ is small and the magnetic atoms are uniformly distributed in the crystal lattice; Γ can be small if the concentration of atoms is small and also, when they are situated relatively far away from the superconducting electrons. Further, if the coupling of the magnetic dipoles is antiferromagnetic in nature, then there will be no macroscopic magnetic field to compete with super-

conductivity and the realization of an antiferromagnetic superconductor is more likely than a ferromagnetic one where the associated dipolar field is energetically unfavourable for superconductivity.

The discovery of superconductivity in the rare earth containing METS (e.g., $LnMo_6Ch_8$ and $LnRh_4B_4$) has brought a completely new situation in the field of solid state science. It is the first time a compound with a magnetic ion present in a regular lattice position, has been found to exhibit superconductivity. All the earlier systems studied were with magnetic ions as doped impurities.[82,83] The immediate interest was to find whether magnetic ordering sets in in these compounds and if so what happens to the superconducting state. Extensive studies have been carried out on these aspects by way of χ, ρ, C_p, H_{c2}, thermal conductivity, thermal expansion, Mössbauer effect and neutron diffraction and it is now established that $LnMo_6S_8$ with Ln = Nd, Gd, Tb, Dy, Er and Yb and $LnMo_6Se_8$ with Ln = Gd, Tb and Er and $LnRh_4B_4$ with Ln = Nd, Sm and Tm exhibit antiferromagnetic order below the respective T_c without destroying the superconductivity in zero applied magnetic fields.[3,23,25] It is interesting to note that many of the antiferromagnetic superconductors become normal (reentrant behaviour) at T_N and develop some sort of ferromagnetic order by the application of a magnetic field ($H \lesssim H_{c2}$, the critical field).[53]

The experimentally determined low temperature states (magnetic, superconducting) of 15 distinct ternary phases containing a sublattice of Ln-atoms are summarised in Table IV.[84] The antiferromagnetism exhibited by the ternary systems is exclusively due to the rare-earth ions but the exact type of ordering has been unequivocally established only in few cases. Neutron diffraction measurements[85] on $DyMo_6S_8$ revealed that the magnetic structure is characterized by alternating ferromagnetic (100) planes in the nearly cubic Ln-sublattice in which the magnetic moments are parallel or antiparallel to the rhombohedral (111) axis.

The anomalous depression of H_{c2} in the vicinity of T_N and other properties of antiferromagnetic superconductors have been recently studied.[86] Several mechanisms by means of which superconductivity is modified by antiferromagnetic order have been considered.

Reentrant Superconductors

If the rare-earth spins in the compounds are to order ferromagnetically, the macroscopic dipolar field so created will become strongly competitive with superconductivity and destroy the latter once the critical magnetic field value for the destruction of the superconducting state is reached.

Many METS superconductors have been observed to exhibit reentrant superconductive behavior due to the onset of long range ferromagnetic order (Table IV).[3,52,84,87] The compounds become superconducting at an upper critical temperature T_{c1} and then lose their superconductivity at a second lower critical temperature T_{c2} which is close to the magnetic ordering temperature T_M. The superconducting-to-normal transition at T_{c2} in $ErRh_4B_4$ is thermal hysteretic[88] and

TABLE IV

Superconductivity and magnetic order in METS-rare earth (Ln) phases (after Shelton (1983) with modifications)

PHASE	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Ln Rh_4B_4	-	S	-	-	-	S/A	S/A	-	F	F	F	F	S/F	S/A	-	S
Ln Ru_4B_4	S	S	-	N	N	M	N	N	M	M	M	M	M	N	N	S
Ln Ru_3B_2	-	N	N	N	M	M	M	-	M	M	M	M	M	M	N	N
Ln Os_3B_2	-	S	S	-	-	-	M	-	M	M	M	M	M	M	N	S
Ln Ru B_2	-	S	-	-	-	-	-	-	-	M	M	M	M	M	-	S
$Ln_2Fe_3Si_5$	S	S	-	-	-	-	A	-	A	A	A	A	A	S/M	A	S
Ln Ru_3Si_2	-	S	S	N	N	M	M	M	M	M	M	M	M	M	N	S
$Ln_5Ir_4Si_{10}$	S	S	-	-	-	-	-	-	-	-	M	M	M	M	-	S
$Ln_3Os_4Ge_{13}$	-	S	-	M	M	M	N	M	M	M	M	M	M	M	M	S
$Ln_3Rh_4Sn_{13}$(I)	-	-	S	N	N	N	N	M	M	-	-	-	-	-	S	-
$Ln_3Rh_4Sn_{13}$(II,III)	S	S	-	-	-	-	-	-	-	M	M	M	S/F	S	-	S
$Ln_3Os_4Sn_{13}$(III)	-	-	-	-	-	-	-	-	M	S	M	S	S/F	S/F	-	-
Ln Fe_4P_{12}	-	-	S	A	M	M	N	F	-	-	-	-	-	-	-	-
Ln Mo_6S_8	S	S	S	A	S	S	S	N	S/A	S/A	S/A	S/F	S/A	S	S	S
Ln Mo_6Se_8	S	S	S	F	S	S	S	N	S/A	S/A	S	S	S/A	S	S	S

S, supercond.; A, antiferro.; M, magnetic; F, ferro.; N, neither S nor M

there is a spikeshaped feature in the heat capacity at T_{c2} indicating a first order transition.[89] For $HoMo_6S_8$, T_{c1} and T_{c2} are 1.82 and 0.6 K respectively. The spin structure of $HoMo_6S_8$ is similar to $DyMo_6S_8$ with Ho^{3+} moments (9.06 compared to the free ion value of 10.0 μ_B) aligned parallel along the rhombohedral (111) direction. Careful neutron scattering studies on $HoMo_6S_8$ have shown that an oscillatory magnetic state (with characteristic wavelength 230 $\pm$ 50Å) coexists with the superconducting state in a very narrow temperature interval around T_M.[90,91] Coexistence of ferromagnetism and superconductivity has been demonstrated recently in *bct*-type $ErRh_4B_{3.8}\square_{0.2}$ ($\square$, vacancy).[92]

Heavy Fermion Superconductors

One of the interesting recent developments is the observation of superconductivity in a cerium containing METS compound, $CeCu_2Si_2$.[93,94] The Ce 4f electron in this material is responsible for superconductivity and it is proposed that the compound is a 'Kondo-lattice' heavy Fermion system where the charge carriers exhibit large effective masses ($\sim$ 100–200m_e). The heavy Fermion superconductors are characterized by relatively low values of T_c ($CeCu_2Si_2$, T_c = 0.5 K; UBe_{13} T_c = 0.9 K; UPt_3. T_c = 0.5 K), large values of electronic specific heat coefficient γ — (1000 mJ/mole-K^2), large discontinuity in the specific heat at T_c, and large value of H_{c2} and its initial slope, indicating the high thermodynamic stability of this state.

It has been suggested that $CeCu_2Si_2$ and related f-electron systems (UBe_{13} and UPt_3)[95–97] may represent examples exhibiting triplet paired or *p*-wave superconductivity[98,99] while the singlet (spin) paired state (BCS mechanism) is still favoured by some workers.[100,101] It must be said that no conclusive proof for the *p*-wave superconductivity is as yet forthcoming.

Summary and Conclusions

As a result of intense research activity during the past decade, more than 10 classes of METS superconductors, many with $T_c > 10$ K, have been discovered. Efforts have been mainly concentrated on *Ln*-containing systems to study and understand the interplay between magnetism and superconductivity. In this process, new phenomena like heavy Fermion superconductivity ($CeCu_2Si_2$) and exotic materials ($ErRh_4B_4$ and $ErRh_4B_{3.8}\square_{0.2}$ which exhibit reentrant behaviour and coexistence of itinerant ferromagnetism and superconductivity respectively) have been discovered. Experiment has always been ahead of theory in the area of METS superconductors.

Since T_c is a subtle property dependent on various factors like band structure, phonon density of states, electron-phonon interaction etc., it may not lend itself to a simple correlation with atomic or any structure-dependent property in METS superconductors, because the latter are not simple systems. Thus, Matthias rules, so very successful for binary superconductors, have not been useful for ternaries. However, the essential features of the known high T_c METS superconductors viz., the existence of isolated metal and/or non-metal atom clusters, 3D-network structure combined with cubic or pseudo-cubic symmetry are sufficient guidelines in the search for new high T_c compounds. Structural instabilities and metastable nature of the phases, common in binaries, also appear to be a feature of the METS superconductors. Only a few of the large number of known METS have been examined in detail till to-date. Thus, a detailed and systematic study of even the simplest METS of the type $MM'X$ (X = non-metal) is a worthwhile undertaking in the elucidation of structure-superconductivity relationships.

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