Quaternary borocarbides – A new class of superconductors and materials

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Quaternary rare earth transition metal borocarbides are a new class of interesting superconducting and magnetic materials which have their origin in the discovery of superconductivity a decade ago at TIFR, Mumbai, in yttrium–nickel–boron–carbon (Y–Ni–B–C) system – the first quaternary system to exhibit superconductivity ($T_c \sim 13$ K). The single phase material, YNi_2B_2C (T_c = 15.5 K) has a tetragonal structure. A family of materials have been derived from this structure – the quaternary borocarbides. The discovery and the materials have attracted worldwide attention for a variety of reasons. Many members have high T_c (~> 10 K) for intermetallics, with a phase in Y–Pd–B–C having a T_c as high as 23 K which equalled highest T_c then known for intermetallics. In the RNi_2B_2C (R = rare earth) series, a range of other phenomena also occur, such as, valence fluctuation ($CeNi_2B_2C$), heavy fermion behaviour ($YbNi_2B_2C$) and the not-so-common phenomenon of coexistence of superconductivity and magnetism in RNi_2B_2C (R = Dy, Ho, Er, Tm). The high (>~5 K) T_c and T_N of superconductivity and magnetism and their different combinations ($T_c > T_N$, $T_c \sim T_N$ and $T_c < T_N$) in these magnetic superconductors, have given a good scope for understanding the coexistence phenomenon in detail. The field continues to be fertile throwing up new and exciting results. A phase in Sm–Ru–B–C was found to exhibit ferromagnetic order ($T_c \sim 60$ K) with a very large coercive field (H_c) of ~150 kOe at 5 K, which is perhaps the largest reported H_c for a polycrystalline Sm intermetallic. Very recently coexistence of superconductivity and magnetism in $NdPt_2B_2C$ system was established. Currently, the symmetry type of the order parameter of superconductivity and whether superconductivity is of unconventional nature in these materials is being debated. This review describes the discovery and gives an overview of the field with emphasis on materials aspect.

THE family of quaternary borocarbide materials originated from the discovery of superconductivity at an elevated temperature for intermetallic systems (superconducting transition temperature, $T_c \sim 12$–15 K) in yttrium–nickel–boron–carbide (Y–Ni–B–C) system[1–3] at TIFR, Mumbai, in the early nineties. The discovery is a landmark in superconductivity and opened up a new area of research: superconductivity and magnetism in quaternary *f*-element transition metal borocarbide superconductors[4] which continues to hold the interest of researchers internationally[5]. This article describes the experiments that led to the discovery and gives an overview of the subject. The structural aspects and some unique properties of the non-superconducting materials are highlighted. Properties of superconducting borocarbides are only briefly mentioned as their details can be found in other reviews[4,6–12].

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Discovery of superconductivity in Y–Ni–B–C system

The discovery of superconductivity in quaternary borocarbides was an offshoot of the investigations of ternary rare earth boride series RNi_4B (R = Y, or rare earths)[13,14]. Interesting results were observed in this series of materials, such as, anomalous magnetism in $CeNi_4B$[13,14]; anomalously high ferromagnetic ordering temperature in $SmNi_4B$ ($T_m \sim 39$ K)[15] which, contrary to the usual trend in rare earth series, is higher than that of $GdNi_4B$ ($T_m \sim 36$ K)[13,14] and has the possibility of having mono-atomic domain walls[15]. The most surprising result of the investigations was the observation of signatures of superconductivity in the sample of YNi_4B[1,2], which was investigated as a non-magnetic analogue for comparison of properties of members of RNi_4B series.

Samples of YNi_4B were prepared by arc melting the constituent elements (purity: Y and Ni –99.9% and B 99.8%) in argon atmosphere. Powder X-ray diffraction (XRD) pattern (Figure 1, top) showed the sample to be of single

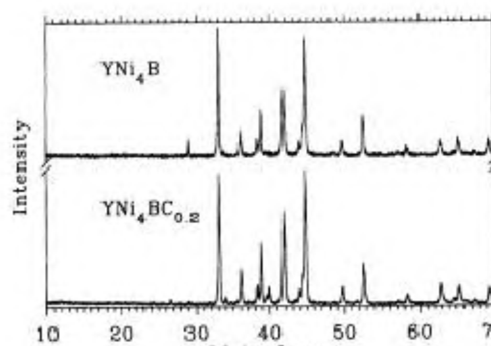

Figure 1. Powder X-ray (Cu-K_α radiation) diffraction patterns of YNi_4B (*top*) and a sample of nominal composition $YNi_4BC_{0.2}$ (*bottom*). Reprinted figure with permission from Nagarajan *et al.*, *Phys. Rev. Lett.*, **72**, 274, 1994. © 1994 by the American Physical Society.

phase. Resistivity and magnetic susceptibility measurements of the sample, produced intriguing results (Figure 2)[2]. Around 12 K, resistivity showed a sharp drop (Figure 2) hinting at the possibility of superconductivity, but did not become zero at further low temperatures. Magnetic susceptibility showed a peak similar to that of an antiferromagnetic transition, around the same temperature (Figure 2), but increased again at lower temperatures. To understand the magnetic response better, the magnetization of the material was investigated as a function of magnetic field, which showed diamagnetism at low fields (Figure 3) and revealed the existence of trace superconductivity in this sample with $T_c \sim 12$ K. The antiferromagnetic-transition-like signature in temperature dependence of magnetic susceptibility (Figure 2) can now be understood in terms of a superconducting signal riding on an over-all paramagnetic signal. The superconducting fraction in the sample was only ~2% (estimated from the strength of diamagnetic response at low field). Powdered sample of the material also showed superconductivity, confirming that the observed superconductivity was not a surface phenomenon. A jump in heat capacity (C) at T_c and its extent is indicative of the bulk nature of superconductivity. In this case, there was no jump in the heat capacity at T_c, but it did not rule out bulk superconductivity, as the jump is proportional to the coefficient of electronic specific heat (the intercept of C/T^2 vs T on the Y-axis) which was nearly zero for this sample[2].

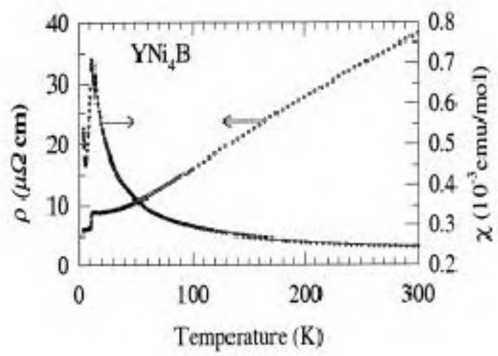

Figure 2. Temperature dependence of magnetic susceptibility (χ) measured at 6 kOe and resistivity (ρ) of a sample of YNi_4B (based on a figure from ref. 2). The anomaly around 12 K is due to a very small quantity of a superconducting phase.

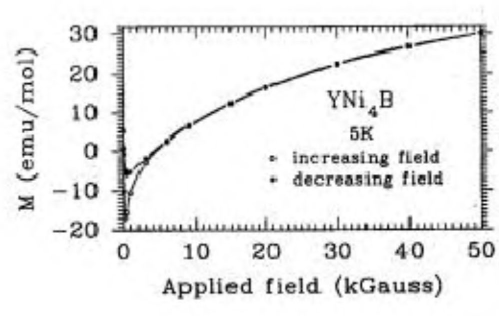

Figure 3. Magnetic field dependence of magnetization (M) of the sample of YNi_4B at 5K. The diamagnetism at low field shows occurrence of superconductivity in the sample. The data were taken first with increasing the field from 0 KOe to 50 kOe (open circle symbols) and then with decreasing the field to 0 kOe (filled circle symbols) (based on figure from ref. 2). The hysteresis is due to trapped magnetic field in the superconductor.

Finding superconductivity with $T_c \sim 12$–15 K in this material was a very surprising and remarkable result for two important reasons. This material contains large proportion of Ni which is normally a magnetic element and is not conducive to superconductivity. Because of its magnetic moment, Ni even in small concentrations, is known to suppress superconductivity, e.g. 2% Ni suppresses T_c of $Lu_2Fe_3Si_5$ from ~6 K to ~2 K[16]. But in certain structures and atomic environments, Ni in a material could lose its moment and superconductivity can survive, as it happens in this case. Only a few Ni-containing superconductors were known then and in all those cases T_c is less than 4.2 K, the boiling point of liquid helium. The T_c observed in the material was high – $T_c > 10$ K is considered high for intermetallics (highest T_c for intermetallics then known being 23 K for *thin film* of Nb_3Ge). Only a few superconducting intermetallics were known with T_c ~> 10 K and most of them contained Nb which was thought to be a necessity for high T_c. In view of these, it was imperative that further work be done to confirm the observation and determine the origin of superconductivity in our samples of YNi_4B.

In order to check the reproducibility of the result and to check whether the origin of superconductivity is from any impurity, several independent batches were prepared using elements from different sources. In all these samples, the superconducting transition was reproducible, but superconducting phase ($T_c \sim 12$–15 K) always remained a minor phase. Optical and electron microscope examinations and element analyses using Energy Dispersive Spectroscopy–Electron Probe Micro Analysis (EDS-EPMA) showed the samples to be highly homogeneous (except for grain-oriented blow holes)[2] and no significant impurity was found. Therefore, initially it was speculated that superconductivity in this material might be related to the crystallographic superstructure of YNi_4B[2].

The extent of resistance drop being different in different batches and variation of T_c (12 K–15 K), hinted at the possibility of superconductivity arising from a minor phase with a composition other than YNi_4B, even though other analyses did not indicate such a possibility. Therefore, many compositions of the type $Y_xNi_yB_z$ reported in the phase diagram of Y–Ni–B, as well as a few which were likely to form (speculated from the knowledge of phases found in ternaries with other similar elements) were synthesized, and were investigated for the occurrence of superconductivity. This resulted in finding three more multiphase samples (YNi_2B_3, YNi_3B_2, YNi_4B_3) exhibiting superconductivity around the same temperature, however, still only as a minor fraction. These results suggested the possibility of superconductivity in the samples arising from a phase, stabilized by the presence of a 'foreign' element. Amongst the likely foreign elements conducive to superconductivity, carbon was thought to be the most likely candidate. In order to test this conjecture, an ingot of YNi_4B was re-melted with 0.2 atom fraction of carbon, deliberately added to the sample. The XRD pattern of this sample of $YNi_4BC_{0.2}$ (Figure 1 bottom)[3] was nearly the same as that of YNi_4B, except for an additional minor peak near $2\theta = 40°$, but superconductivity at ~12 K dramatically resulted in *zero resistance* (Figure 4)[3] and the diamagnetic response of the material also spectacularly *increased by twenty times*[3] that of the sample without carbon. Though Meissner expulsion (diamagnetic susceptibility obtained under field cooled (FC) condition) at 5K and heat capacity anomaly across T_c were small, they did not rule out bulk nature of superconductivity in the material[3]. The possibility that the observed superconductivity could be due to Y_2C_3 (which is also a superconductor having T_c in the range of 5–15 K – but is a high temperature, high pressure phase) was ruled out from careful EDS–EPMA analysis of the material, which showed no Ni free regions[3].

Since a few compositions other than YNi_4B had also exhibited superconductivity, they were also re-melted with 0.2 atomic fraction of carbon and investigated for superconductivity. Of these, the multiphase sample $YNi_2B_3C_{0.2}$ exhibited superconductivity around 13 K with good Meissner expulsion signal and significant and largest (amongst the samples investigated) specific heat anomaly across T_c (Figure 5) which showed that this material had the maximum fraction of the new superconducting phase[3]. Samples with various combinations of the elements were prepared to confirm that all the four elements are required for the formation of this superconducting phase. EDS–EPMA analyses showed that the major phase had Y:Ni ratio as 1:2. (The fraction of B and C in this phase could not be determined due to insensitivity of our EDS–EPMA equipment for lighter elements.) These results established that the system Y–Ni–B–C had a bulk quaternary superconducting phase[3]. This conclusion brought further importance to the work as superconductivity in intermetallic quaternaries (compound with four elements) was not known prior to this work and thus laid the foundation for the new subject – superconductivity and magnetism in quaternary rare earth transition metal borocarbides. At this juncture, it is pertinent to point out that *ternary* borocarbide superconductors, such as, YB_2C_2 (T_c = 3.6 K) were known earlier.

Subsequently, Cava *et al.* reported the single phase superconducting material[17] YNi_2B_2C with $T_c \sim 15.5$ K and having a tetragonal crystal structure[18] (Figure 6). They also reported that the rare earth (R) analogues of the material form, of which Ho-, Er- and Tm compounds exhibit superconductivity (T_c ~8 K, ~10.5 K, ~11 K)[17]. Replacing Ni in this quaternary system by the isoelectronic Pd produced a multiphase material in which superconductivity was found to occur with a T_c as high as ~23 K[19], which was the highest T_c for *bulk* intermetallics known, till the very recent discovery of superconductivity in MgB_2 at 39 K[20]. These developments excited the scientific community[21] with a possibility for new route to High T_c superconductivity and triggered intense work at many laboratories all over the world[5] and revitalized research in intermetallic superconductors, which had been dormant since the discovery of high temperature superconductivity in oxides[22].

Materials in the quaternary borocarbide family and some of the structural considerations

Once the composition and structure of a new material is known (in this case, YNi_2B_2C), it is possible to synthesize new materials with iso-electronic elements. In the quaternary system YNi_2B_2C, Y can be replaced by Sc, rare earth (4*f*-elements La to Lu), Th or U (5*f*-elements); Ni can be replaced by a transition *d* element such as Co, Cu, Pd, Pt,

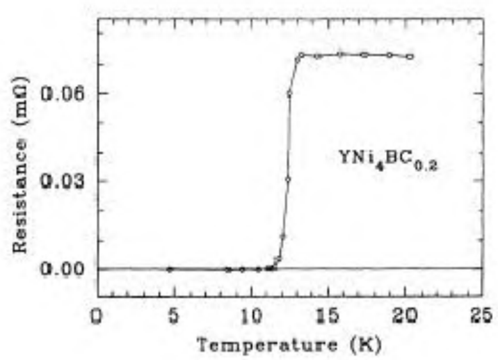

Figure 4. Temperature dependence of resistance of the sample of nominal composition $YNi_4BC_{0.2}$ showing superconducting transition at $T_{c,onset}$ ~13 K with zero resistance below ~11.5 K. Reprinted figure with permission from Nagarajan *et al.*, *Phys. Rev. Lett.*, **72**, 274, 1994. © 1994 by the American Physical Society.

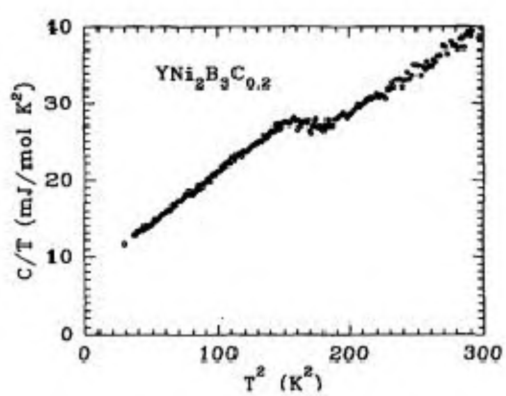

Figure 5. Heat capacity of the multiphase sample with nominal composition $YNi_2B_3C_{0.2}$ shown as *C/T* vs T^2 plot (*C* is molar specific heat, *T* is temperature). The clear step-like behaviour around T_c (13 K) shows bulk superconductivity in the sample. (The jump in heat capacity expected around T_c appears as a step, due to multiphase nature of the sample.) Reprinted figure with permission from Nagarajan *et al.*, *Phys. Rev. Lett.*, **72**, 274, 1994. © 1994 by the American Physical Society.

Rh, Ir, etc.; and B and C be replaced by Si, Ge, N, P, etc. Thus, in this quaternary system, there is potential for synthesizing a large number of new materials. Obviously, all of the combinations would not form, due to reasons of chemical bonding, structural stability, etc. Except for two boronitrides ($La_3Ni_2B_2N_3$ and LaNiBN)[23], all other compounds known so far, are borocarbides. Some silicocarbides, such as RCr_2Si_2C and $R_2Mn_2Si_2C$ are known but they do not have the YNi_2B_2C-type (also referred as 1221-type) structure. So far, no superconductor has been found in silicocarbides. Research in quaternary borocarbides has so far resulted in more than 60 members in the family[10]. Of these, about 20 are superconductors with most of them having $T_c > 5$ K.

Polycrystalline samples of the quaternary borocarbides are usually prepared by arc melting technique followed by annealing at a suitable temperature (around 1000°C) and duration (one to two weeks). It hardly needs emphasis that single crystals are very necessary for investigations of detailed properties of materials. Incongruent melting of RNi_2B_2C phase prevents growth of single crystals by crystal pulling techniques such as, Czochralski technique. It is possible to pick small (thin plates of about 1 mm × 1 mm × 0.05 mm) single crystals of these materials from the arc-melted button. Larger single crystals of the heavier members of RNi_2B_2C series have been grown by flux technique[24] using Ni_2B as flux and by floating zone technique using infrared mirror furnace[25], or RF induction heating furnace[26]. From flux technique, plate-like crystals (approximate size 5 mm × 5 mm × 0.1 mm) have been obtained for RNi_2B_2C (R = Lu to Tb). Very large crystals (about a few cm long and ~6 mm dia.) of YNi_2B_2C are reported to have been obtained by floating zone technique through a self-flux process[25]. The phase diagram in the vicinity of melting point of the borocarbide seem to be significantly different for different members of the family, because, single crystals of all the borocarbides have not been obtained. For example, it has not been possible to grow single crystals of lighter rare earth members, such as, $LaNi_2B_2C$, by either technique. It has been possible to grow single crystals of RNi_2B_2C only for R = Y, Lu, Ho by float zone method. Success is claimed to have been achieved only recently for $ErNi_2B_2C$. Availability of large single crystals and superconductivity occurring at ~>10 K have been notable factors for the large body of works that have emerged on quaternary borocarbides.

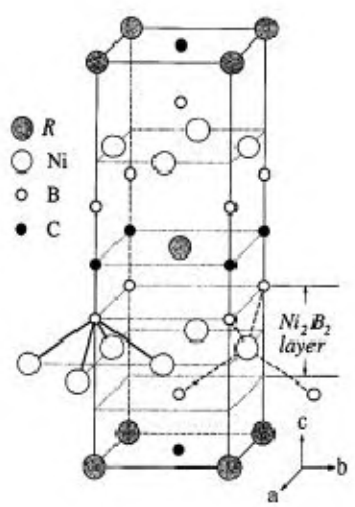

Figure 6. The tetragonal (space group *I4/mmm*) crystal structure of RNi_2B_2C (R = Y, rare earth). Reprinted figure with permission from Lynn, J. W. *et al.*, *Phys. Rev.*, **B55**, 6584, 1997. © 1997 by the American Physical Society.

There has been only a limited success in preparing thin film samples of the quaternary borocarbides. YNi_2B_2C[27,28] and $ErNi_2B_2C$[29,30] have been prepared in thin film form by magnetic sputtering as well as by pulsed laser deposition technique. The fact that quaternary borocarbides are more metallic compared to HTSC oxide superconductors poses some problems in the formation of thin films by laser ablation technique. The quality of the film is also affected to some extent by oxidation from oxygen of the substrate[31].

Some structural/stability considerations

Almost all the quaternary borocarbides are of RNi_2B_2C-type and with tetragonal crystal structure (Figure 6), which is a derivative of the well-known $ThCr_2Si_2$ tetragonal structure with C atoms inserted in Y (or R)-planes giving alternating layers of (Y–C) and (Ni_2B_2) in the structure[18]. The ratio c/a of the two lattice parameters, a, and c of the unit cell is ~3 and anisotropy is seen in the magnetic properties but to much less extent in superconducting properties.

The c-parameter seems to play a crucial role in the stability of the structure. The related materials, YFe_2B_2 and YNi_2Si_2 with $ThCr_2Si_2$ structure form, but the corresponding borocarbides do not form. In contrast, YNi_2B_2 does not form, but as we now know YNi_2B_2C forms! A comparison of the structural parameters of these materials *vis-à-vis* YNi_2B_2C, indicates that the c-parameter for YNi_2B_2 is the smallest amongst these, which perhaps is beyond the stability limit (in terms of the other bond distances) of the structure[32]. Introduction of C in the R-layers modifies the c/a ratio, thereby stabilizing the structure and facilitating the formation of YNi_2B_2C.

In the series of materials RT_2B_2C (R = rare earth, Sc, Y, U, Th; T = transition d-element), the structure appears to be robust for T = Ni, as single phase materials are obtained for entire series of rare earth elements (the Eu-based compound does not seem to form), including, Th and U, even though the (trivalent) ionic radius monotonically decreases (known as lanthanide contraction) across the series La (lightest rare earth) to Lu (heaviest rare earth). The stability is affected for Sc, which has the smallest ionic radius amongst elements iso-electronic to Y, and $ScNi_2B_2C$ forms only as metastable material on quenching the sample[33]. $ScNi_2B_2C$ shows superconductivity (T_c ~15 K) and on annealing both the 1221 phase and superconductivity are lost[33,34]. While the *a* lattice parameter in RNi_2B_2C series exhibits the classic lanthanide contraction (Figure 7), the *c* parameter varies in the opposite direction (i.e. increases)[18]. This shows that the R–R bond dominates the structure, squeezing and distorting the NiB_4 tetrahedron in the structure as the size of R decreases. The deviation of the cell parameters of $CeNi_2B_2C$ from the systematics is notable and indicates non-trivalent state of Ce in this material. This aspect is discussed later on.

For the borocarbides with *d*-element other than Ni, materials of nominal composition, YT_2B_2C (T = Co, Rh, Ir, Os, Cu, Ru, Pd, Pt) are multiphase but do contain 1221 phase. These still require extensive investigations to determine the conditions of phase pure formation. When Y is replaced by other rare earths, the variation of rare earth ion size adds to the complexity of structural stability. Some notable cases in these substitutions are mentioned below.

Samples of nominal composition YCo_2B_2C, are found to form with ~80% 1221-type phase. Considering that Co is a neighbour of Ni in the periodic table, and has no magnetic moment in this structure, one would expect this material to be a superconductor, but surprisingly superconductivity is not found down to 2 K[35]. For Rh, Ir, Pt and Pd systems, the structural stability is systematically affected. In the cases of RRh_2B_2C[36,37] and RIr_2B_2C[36], reasonable phase purity is obtained for R = La, the rare earth with largest ionic radius, but the phase purity decreases drastically with the decrease of the rare earth ion size. In the case of RPt_2B_2C, even for La, the phase purity is affected[38]. In the Pd-system, the phase stability is so severe that 1221 phase is formed for R = Y only as a metastable phase in a multiphase matrix (discussed later).

The RPt_2B_2C series is a good example for the kind of investigations required to determine the conditions to obtain phase pure samples. In this case, considerable amount of efforts have gone in because some of the members exhibit superconductivity at $T_c > 5$ K–YPt_2B_2C ($T_c \sim 10$ K),

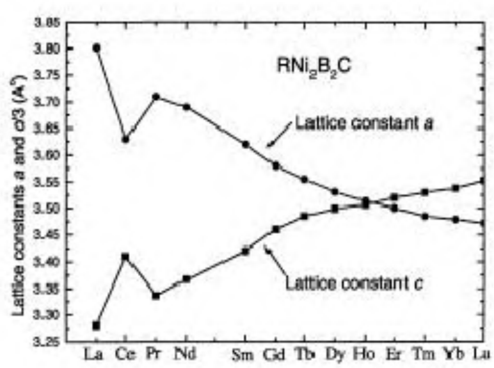

Figure 7. Variation of lattice constants *a* and *c* of the tetragonal unit cell of RNi_2B_2C with R (rare earth) (based on data from ref. 35). There is no data for radioactive Pm. The deviation occurring for Ce is due to valence fluctuation nature of Ce ion in $CeNi_2B_2C$.

$LaPt_2B_2C$ ($T_c \sim 10$ K), and $PrPt_2B_2C$ ($T_c \sim 6$ K)[38]. In this system, synthesis with nominal 1221 starting composition does not give phase pure material. The phase pure sample is obtained if the starting composition is either off-stoichiometric, such as $LaPt_{2.1}B_{2.2}C_{1.1}$ (ref. 39) or if Pt is partially substituted by Au, such as $LaPt_{1.5}Au_{0.6}B_2C$[40]. One reason that is suggested for pure phase formation by partial substitution of Pt by Au, is that it reduces the annealing temperature to a practical value (~1100°C) and that Au does not really enter the structure. However, very recent investigations of $NdPt_2B_2C$ system[41,42] seem to suggest that Au does enter the structure and also has a role in enhancing superconducting properties. It is not clear as to how the excess Pt, B and C stabilize the structure. Investigations of Pt-system[43] show that the structure collapses even with as small as 0.1 substitution of Sm or Gd.

Presence of hydrogen is known to influence T_c of superconductors and large absorption of hydrogen is an important aspect in rare earth nickel alloys due to their potential for applications. Experiments of hydrogenation of YNi_2B_2C show that the material takes hydrogen only to an extent of 0.25 atomic fraction and it neither affects the structure nor the T_c in any significant manner[44].

It has been shown[18] that this family can form in homologous series $(R–C)_m(Ni_2B_2)_n$, with the structure having more sheets of R–C layers between the Ni_2B_2 layers. Most of the known cases form with $m = 1$, $n = 1$. For $m = 2$, $n = 1$ (i.e. RNiBC) only the heavier members (with smaller ionic radius) of the rare earth series form[18,45,46]. In this series, the only known case of substitution of *d* metal is the case of partial substitution of Ni by Cu in $YNi_{1-x}Cu_xBC$. Interestingly, this substitution increases T_c of YNiBC from ~0.8 K to a value as high as 9 K[47].

One compound is known for $m = 3$ and $n = 1$, but it is a nitride $La_3Ni_2B_2N_3$ (ref. 23) and is the only stoichiometric material outside 1221 type (other than YNiBC ($T_c \sim 0.8$ K) and LuNiBC ($T_c \sim 2.9$ K)), which is a superconductor ($T_c \sim 12$ K). Two compounds have been reported for $m = 4$, $n = 1$, i.e. $Lu_4Ni_2B_2C_4$ (or Lu_2NiBC_2)[48] and $Y_4Ni_2B_2C_4$ (or Y_2NiBC_2)[49]. However, later detailed investigations have shown that the four-layer RC structure[50] incorporates a B layer between two pairs of RC layers, giving $Lu_4Ni_2B_3C_4$, suggesting that a four layer RC as a unit, is perhaps unstable as such and needs a B layer for stability. Very recently it has been shown that this is, very likely, a very stable structure and a large number of borocarbide compounds can be formed with many rare earth and *d* metal combinations. This is perhaps the only structure which gives a quaternary borocarbide with Fe. However, the structure has a slight monoclinic distortion – $Lu_4Ni_2B_3C_4$ has the lattice parameters[51]: $a \sim 5$ Å, $b \sim 5$ Å, $c \sim 27.4$ Å, $\beta \sim 93°$.

Formation of a member of the series $m = 3$ and $n = 2$, $Y_3Ni_4B_4C_3$ has been reported and also claimed to be a superconductor with $T_c \sim 12$ K[52]. Our studies confirm the formation of the phase but not in phase pure form. We believe that the reported superconductivity originates from the presence of 1221 phase in their sample. Recently, structures with $m = 5$, $n = 6$ ($Y_5Ni_6B_6C_5$) or with $m = 5$, $n = 8$ ($Y_5Ni_8B_8C_5$) have been reported to exist locally as metastable phases in as cast/annealed samples of $YNi_{2-x}B_{2-x}C$[53]. From the observation of stacking faults, possible occurrence of structures with $m = 2$, $n = 3$ ($Y_2Ni_3B_3C_2$) and $m = 4$, $n = 7$ ($Y_4Ni_7B_7C_4$) have also been claimed[53].

The highest T_c borocarbide: Y–Pd–B–C (T_c ~ 23 K)

The two known Pd borocarbide systems, Y–Pd–B–C[19,54] and Th–Pd–B–C[55,56] deserve special mention as they contain the superconducting phases with very high T_c (~23 K and ~20 K, respectively) which were close to the highest T_c then known (~23 K) for intermetallics.

The structural stability in the case of Y–Pd–B–C is so severe that materials with nominal composition YPd_2B_2C contain only a minority 1221 phase and the superconducting signal is very weak[19,57,58]. A strong signal of superconductivity (T_c ~23 K) is obtained in a multiphase material with a nominal composition around $YPd_5B_3C_{0.3}$ (ref. 19). Even in this multiphase material, the superconducting phase is found to form only as a metastable high temperature phase which is obtained by quenching the melt. On annealing, superconductivity vanishes. This behaviour seems to confirm the belief that in intermetallic superconductors, structural stability is correlated to T_c[59] (higher the T_c, lesser is the stability), as had also been noted from Nb_3Ge, the previously known highest T_c (23 K) system, where also superconducting phase does not form in bulk material with the required nominal composition, but forms only in *thin film* form of Nb_3Ge[60]. (Of course, the recent superconductor[20] MgB_2 with T_c ~ 39 K is an extraordinary exception.) While a systematic study of heat treatment of $YPd_5B_3C_{0.35}$ and correlation of intensities of X-ray diffraction peaks of 1221 phase with strength of diamagnetic signal seems to suggest superconducting phase is cubic[61], recent experiments on micro-grain single phase specimen[62] seem to confirm the phase to be 1221-type tetragonal structure. Interestingly, investigations on the phase diagram of the pseudo quaternary $Y(Ni_{1-x}Pd_x)_2B_2C$ have shown that stable and superconducting tetragonal phase can be obtained on substitution of Ni by Pd only up to $x = 0.4$ and T_c *decreases* on the substitution (T_c ~ 10 K for $x = 0.4$)[58].

Following our work on YNi_4BC_x, we investigated YPd_4BC_x system, and found traces of superconductivity with two transitions (T_c ~22 K and 10 K) in the material with nominal composition, $YPd_4BC_{0.5}$ (ref. 54). Trace superconductivity was found in Lu and Sc analogues (T_c ~ 10 K) also[54]. While the phase with T_c ~22 K may belong to 1221 phase, the superconducting phase responsible for the 10 K transition is yet to be identified.

In the context of high T_c, Th–Pd–B–C system also deserves mention as it has a phase with a high T_c (~20 K) comparable to that found in Y–Pd–B–C. In this case too, samples of nominal composition $ThPd_2B_2C$ do not yield single phase materials. Our samples exhibited two superconducting transitions, one with $T_c = 20$ K (resistance not reaching zero) and another with T_c ~ 14 K (resistance attaining zero)[56]. Sarrao *et al.*[63], reported a phase with $T_c = 21.5$ K (resistance not reaching zero) in a sample of nominal composition $ThPd_3B_3C$. Later investigations using high resolution electron microscopy suggested that the transition around 14 K belongs to 1221 type $ThPd_2B_2C$ phase, whereas the phase with T_c ~ 21 K belongs to a ternary phase, $ThPd_{0.65}B_{4.7}$, with a cubic structure[64].

Before concluding this section on materials, we would like to note that microwave absorption results of our sample of YNi_2B_2C showed an anomaly around 23 K, apart from the one at T_c ~ 15 K, suggesting the presence of a superconducting phase with T_c ~23 K[65]. Interestingly, a similar suggestion has also been made from the observation of magnetic anomalies observed around the same temperature in samples of YNi_2B_2C prepared by the powder metallurgy technique[66]. This is an important and interesting aspect requiring further investigations.

Physical properties of quaternary borocarbides

Quaternary borocarbide family of materials, particularly RNi_2B_2C series, exhibit a wide range of properties and provide examples of superconductivity, magnetism with a variety of magnetic structure, coexistence of superconductivity and magnetism, valence fluctuation, heavy fermion behaviour, etc. Some of these are mentioned below.

Nonmagnetic superconducting borocarbides – RNi_2B_2C (R = Y, Lu)

Amongst the nonmagnetic superconductors in the quaternary borocarbide family, YNi_2B_2C and $LuNi_2B_2C$ have been extensively investigated for the superconducting properties because they easily form single phase materials and single crystals are also available. Only their basic properties are mentioned here.

YNi_2B_2C[32,67,68] and $LuNi_2B_2C$[69] are found to be type-II superconductors with upper critical field $H_{c2}(0)$ ~ 10 T. H_{c2} is found to be almost isotropic in these two materials[70,71]. Initial studies indicated that these are conventional BCS type superconductors. Isotope effect on T_c has been observed[72] (from studies of samples having only ^{10}B or ^{11}B isotopes) supporting the mechanism of pairing of Cooper pairs of electrons to be the well-known electron–phonon interaction. A rare and remarkable direct evidence of electron–phonon interaction comes from inelastic neutron scattering experiments on single crystals of YNi_2B_2C[73] and $LuNi_2B_2C$[74] where a dramatic change has been observed in the phonon spectra on the onset of superconductivity. A narrow phonon peak occurs below T_c. That this peak is associated with superconductivity, is further strengthened by the observation that the intensity of this peak depends on the strength of an external field in a manner similar to the temperature dependence of H_{c2}[73]. While Kawano *et al.*[73] have interpreted the peak as due a new excitation, others[74,75] have interpreted it as due to narrowing of the phonon width as a result of increased life time due to opening up of the superconducting gap.

While initial studies indicated that these materials are conventional superconductors, later studies revealed some deviations from the conventional behaviour. One of the unusual behaviours of superconductivity in YNi_2B_2C, first observed by us[32] and later confirmed by others[69,71,76] in $LuNi_2B_2C$ also, is the positive curvature of $H_{c2}(T)$ near T_c. Initial studies attributed the behaviour to granularity[77]. It has also been possible to explain this behaviour using two-band model with medium coupling between slow and fast electrons[78]. Whether this has a bearing on the superconducting gap function (see below) is not clear. In the ^{11}B NMR investigations of YNi_2B_2C, temperature (T) dependence of the spin lattice relaxation time (T_1) is found to deviate from a simple Korringa relaxation behaviour $1/(T_1T) \propto$ const. Such a behaviour could arise from antiferromagnetically coupled dynamically fluctuating magnetic moment on Ni-atoms which in turn suggests a possibility of magnetically mediated superconductivity in these materials[79,80]. This assumes significance in the light of anisotropic s-wave or non s-wave-like superconducting gap function that has been suggested in recent single crystal experiments (see below). The observation has also been interpreted by other workers[81] as due to increase in the s-band conduction electron spin susceptibility (as inferred from and taking into account the Knight shift of the NMR signal) with decreasing temperature and that there is no need to invoke a magnetic moment on Ni. However, a later NMR study using a single crystal of YNi_2B_2C suggests non s-wave (d-wave) superconductivity in the material, based on the temperature dependence of $1/T_1$ below T_c[82].

Quaternary borocarbides may have boron/carbon vacancies depending on the preparation conditions and superconductivity seems to be somewhat sensitive to these vacancies. Positron annihilation studies[83] in YNi_2B_2C have indicated the presence of carbon vacancies and ^{11}B NMR experiments have shown two sets of signals below T_c, the position of NMR lines in one set shifting with temperature and those in the other set remaining the same as that above T_c. The unshifted signal is perhaps due to those regions which are non superconducting. Sensitivity of superconductivity to boron/carbon stoichiometry/vacancy is severe in the case of the magnetic superconductor members $HoNi_2B_2C$ and $DyNi_2B_2C$ (see below).

At low temperatures and below T_c, there is no change in the structure of RNi_2B_2C[84–86]. In YNi_2B_2C, there is no change in structure under pressure up to 6 GPa at room temperature[87] and T_c does not change much under pressure in YNi_2B_2C ($\sim$+ 0.03 K/GPa)[88]. Maximum rate of change of T_c ($\sim$–0.45 K/GPa) is found in $HoNi_2B_2C$[89].

Theoretical investigations suggest that at the fermi energy, nearly half of the contribution to the density of states (DOS) of electrons comes from Ni 3d electron states and the remaining contribution comes from s and p electron states of C and B and d electron states of Y (or Lu)[90,91]. Isomer shift of ^{161}Dy Mössbauer resonance of superconducting $DyNi_2B_2C$ is similar to that of a non metallic system thereby indirectly suggesting that superconductivity arises from Ni_2B_2 layers[92]. It has been found that both density of states at the Fermi energy and T_c scale the same way as the structural parameter c/a ratio (effectively the B–Ni–B bond angle)[93]. $LuNi_2B_2C$ with near-perfect B–Ni–B bond angles in the NiB_4 tetrahedron of the structure, is superconducting with high T_c whereas $LaNi_2B_2C$ in which the NiB_4 tetrahedron is distorted from ideal bond angles, is non-superconducting (down to 0.3 K). It has been remarked that such a structure-T_c relationship is unusual for intermetallic superconductors[93]. However, it may be noted that the high T_c ($\sim T_{c,onset} \sim$ 16 K) of metastable $ScNi_2B_2C$ significantly deviates from the above structural correlation[93].

Another interesting property of superconductivity in quaternary borocarbides is the occurrence of *square* superconducting vortex flux line lattice (observed through small angle neutron scattering) as against the usually expected hexagonal flux line lattice. At fields higher than ~1 kOe, a square flux line lattice has been observed both in YNi_2B_2C[94] (Figure 8) and in $LuNi_2B_2C$[95]. At low fields or at higher temperatures, the flux line lattice goes over to hexagonal symmetry[95]. Internal magnetic field also changes the symmetry/orientation of the flux line lattice in the magnetic superconductors of these borocarbides (see later). Such a field-driven transition of symmetry of flux line lattice has not been observed before in any superconductor[95]. Presently, the most stimulating and unusual aspect of the nonmagnetic superconducting borocarbides is the question of symmetry of the gap function or the order para-

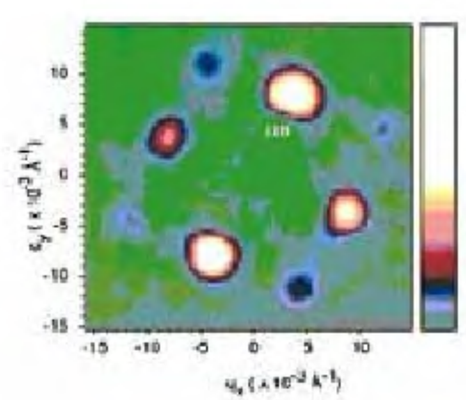

Figure 8. Flux line lattice with square symmetry observed in small angle neutron scattering experiment in a single crystal of YNi_2B_2C with magnetic field of 4 kOe strength applied parallel to the c-axis of the crystal. Reprinted figure with permission from Yethiraj, M. *et al.*, *Phys. Rev. Lett.*, **78**, 4849, 1997. © 1997 by the American Physical Society.

meter of superconductivity. While the initial experiments and interpretations suggested an isotropic *s*-wave symmetry of the function, recent detailed experiments, such as, tunnelling spectroscopy[96], point contact spectroscopy[97], ultra-high resolution photoemission spectroscopy[98], heat capacity[99] and thermal conductivity[100] measurements under magnetic field, etc. on high quality single crystals are increasingly pointing out to clear anisotropy in energy gap. Some of these results seem to point to an unusual $s + g$ type symmetry for the order parameter (Figure 9) and suggest unconventional superconductivity in these quaternary borocarbides[101]. This is still an open question and is the current focus in the field.

Magnetic superconductors – RNi_2B_2C (R = Tm, Er, Ho, Dy) and $NdPt_2B_2C$

As mentioned earlier, under normal circumstances, presence of magnetic ions is detrimental to superconductivity in a material. However, cases such as RRh_4B_4 (R = Pr, Nd, Sm, Tm) are well-known, where superconductivity has been shown to coexist with *antiferromagnetism*[16]. In these cases, the magnetic ordering temperature (T_N) is rather low (< 2 K). One of the remarkable properties of the quaternary borocarbide materials is that the materials, RNi_2B_2C (R = Dy, Ho, Er, Tm) show coexistence of superconductivity and magnetism with high magnetic ordering temperatures ($T_N > 5$ K). With both T_c and T_N being > 4 K, and occurrence of all the three possibilities of competition between T_c and T_N, viz. T_c (11 K) > T_N (1.5 K) in $TmNi_2B_2C$[102]; T_c (11 K) > T_N (6 K) in $ErNi_2B_2C$[32,108]; T_c (8 K) ~ T_N (8 K) in $HoNi_2B_2C$[102]; T_c (6 K) < T_N (11 K) in $DyNi_2B_2C$[103–106], these systems are ideal for detailed investigations of the coexistence property[107]. The presence of bulk (shown by heat capacity[32,108]) and long range magnetic order (shown by elastic neutron scattering[85]) has been confirmed in these materials. High T_Ns imply that unlike the previously known cases, in quaternary borocarbides, the magnetic interaction is mediated by the conduction electrons (through the well-known RKKY interaction in magnetism of metallic systems), possibly by the same electrons which are responsible for superconductivity. This is an exciting possibility, which makes these materials important. The double reentrant behaviour of $HoNi_2B_2C$ in zero external magnetic field (on cooling, first becomes a superconductor at 8.5 K, tends to become normal around 5.5 K and regains superconductivity below ~4.5 K), has not been seen earlier in any other system. Superconductivity occurs in $DyNi_2B_2C$ after the onset of magnetic order. These are fascinating aspects of competition between superconductivity and magnetism in this series. The competition is so delicate that B and C stoichiometry severely affects the superconducting properties of $HoNi_2B_2C$[109] and $DyNi_2B_2C$[104]. In $HoNi_2B_2C$, the reentrance property is critically dependent on the stoichiometry. In $DyNi_2B_2C$, because of superconductivity occurring in an already magnetically ordered lattice, even non-magnetic impurities act as pair breakers[110]. Indeed, due to this reason, discovery of superconductivity was missed in $DyNi_2B_2C$ in the initial studies[17]. Recently, coexistence of superconductivity ($T_{c,onset} \sim 3$ K) and magnetism ($T_N \sim 1.7$ K) has been shown in the $NdPt_2B_2C$ system[41,42].

The unique square superconducting vortex flux lattice observed in the non-magnetic borocarbides[94,95] becomes a microscopic tool for observation of interplay of superconductivity and magnetism in magnetic superconductors at microscopic scale. The flux lattice is found to undergo a rotation on the onset of magnetic order in $ErNi_2B_2C$[111]. Simultaneous transformation of magnetic structure and flux lattice structure has been seen in $TmNi_2B_2C$[112]. Such interesting behaviours have been observed for the first time in magnetic superconductors[113]. More discussion on magnetic superconductors can be found in refs 4, 107, 113.

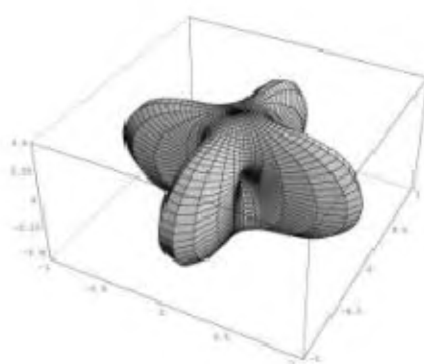

Figure 9. The anisotropic shape of gap function of superconductivity with $s + g$ wave symmetry with four point nodes. Reprinted figure with permission from Maki, P. *et al.*, *Phys. Rev.*, **B65**, 140502, 2002. © 2002 by the American Physical Society.

Borocarbides with hybridization effects

Usually, the valence state of rare earth ions in a rare earth intermetallic is the 3+ state. But, for Ce, Eu and Yb ions, 4+, 2+ and 2+ valence states may also be favoured, as they correspond to empty 4*f*-shell, half filled 4*f*-shell and fully filled 4*f*-shell, respectively. For these three rare earth ions, the *f*-electron wave function can be spatially extended and relatively non-local, resulting in a hybridization of 4*f*-electrons with conduction electrons. Such a *f*-electron hybridization manifests in a variety of anomalous properties which are interesting. Ce-, Yb- and U-based quaternary borocarbides show these effects and are briefly described below.

Valence fluctuating borocarbide – $CeNi_2B_2C$. The lattice parameters of $CeNi_2B_2C$ deviate from the systematic variation in the rare earth series (Figure 7), which indicates that Ce is in non-trivalent state due to hybridization of 4*f* electron with conduction electrons. In this case, the hybridization effect manifests as valence fluctuation (VF) phenomenon[114] where the valence of Ce ion fluctuates in time between 3+ and 4+ states at a time scale of ~10^{-13} s. This is seen from the much reduced magnetic susceptibility of the material at any temperature[114], compared to that expected for a Ce^{3+} compound magnetically ordering at very low temperatures, due to time averaged susceptibility of the two valence states (Ce^{4+} is non-magnetic as there is no *f*-electron). The average valence of $CeNi_2B_2C$ is found to be close to 4+ (ref. 114). X-ray L_{III} edge absorption measurements, having very short probe time (~ 10^{-16} s) compared to the fluctuation time, give the complementary confirmation of VF in $CeNi_2B_2C$ where two absorption edges are seen corresponding to the two valence states (Figure 10)[114]. The material does not show magnetic order down to 2 K, which is consistent with VF behaviour, as the nonmagnetic 4+ state is the ground state for such a system.

In fact, in the CeM_2B_2C (M = Ni, Co, Rh, Ir, Pd, Pt) series, the hybridization increasing in a continuous manner with respect to the *d* element, can be inferred from the average of valence of Ce ion and the magnetic property of the materials[115,116]. Valence of Ce is closer to tetravalent state in the Ni-, Co-compounds; intermediate state in the Rh- and Ir-compounds; and ends up close to 3+ state in the Pd- and Pt-compounds[115–117]. While Ce in the Pd-compound $CePd_2B_2C$ appears to be in the stable 3+ state with Ce-moments ordering magnetically at low temperature (T_N ~ 4.5 K)[118], in the Pt-compound, the hybridization effect is still present, as seen from the moderate heavy fermion behaviour[118].

Spin fluctuation/heavy fermion borocarbide – $YbNi_2B_2C$. $YbNi_2B_2C$, though non-superconducting, is a very important member of the quaternary borocarbide family. Considering that the two neighbouring members of $YbNi_2B_2C$ in the rare earth series are superconducting – $LuNi_2B_2C$ (T_c ~ 16.5 K) and $TmNi_2B_2C$ (T_c ~ 11 K), from the deGennes scaling systematics of T_c of magnetic superconductors of RNi_2B_2C[102] with respect to rare earth, one would expect $YbNi_2B_2C$ to exhibit superconductivity around 12 K. Due to low melting point and high vapour pressure of Yb, although it is difficult to synthesize Yb compounds, $YbNi_2B_2C$ was successfully synthesized[119,120]. Investigation of its properties showed surprising absence of superconductivity down to 2 K. In contrast, it is to be noted that among the members of RMo_6S_8 series, $YbMo_6S_8$ has the highest T_c (~ 9 K). High and temperature independent resistivity of $YbNi_2B_2C$ in the high temperature interval (50 K–300 K)[119] shows that 4*f*-electrons of Yb hybridize with conduction electrons and the material behaves as a dense Kondo system. In this case, at low temperatures, the hybridization brings about a correlation amongst electrons which increases their effective mass by about a hundred fold (as inferred from the coefficient of electronic specific heat (γ) deduced from heat capacity (in the temperature range 12–25 K) of the material which is at least ~200 mJ/mol K^2 (Figure 11)[119] as against a few milli-joules encountered in normal metallic systems) and evolves into what is termed as moderate heavy fermion state. The value of γ obtained from extrapolation of the heat capacity data below 2 K is ~ 600 mJ/mol K^2[119,120]. Thus, strong hybridization of 4*f*-electrons with conduction electrons takes place in $YbNi_2B_2C$. As against the previous example of valence fluctuating $CeNi_2B_2C$, in the case of $YbNi_2B_2C$, the charge on Yb remains stable 3+ as inferred from high temperature susceptibility and temperature independent X-ray L_{III} edge line shape and position[119]. Therefore, $YbNi_2B_2C$ is not a charge fluctuation

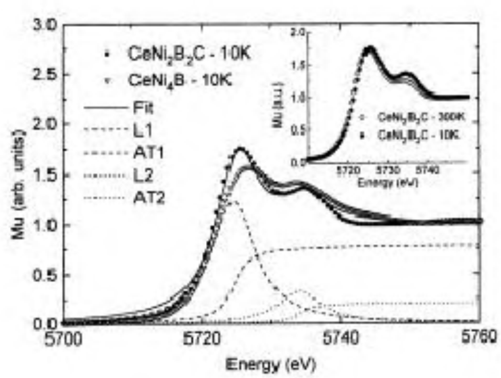

Figure 10. Ce L_{III}-edge X-ray absorption spectrum of $CeNi_2B_2C$ at 10 K. The double edge spectrum (second edge is seen as a shoulder) shows the presence of Ce ion in both 3+ and 4+ valence states in the material due to valence fluctuation (VF) phenomenon. For comparison, the L_{III}-edge spectrum of another known VF material $CeNi_4B$, which has average Ce valence closer to 4+ is also shown. Inset shows the spectrum of $CeNi_2B_2C$ at 300 K and at 10 K indicating temperature dependence of average valence of Ce as often expected in a VF material. Reprinted figure with permission from Alleno, E. *et al.*, *Phys. Rev.*, **B52**, 7428, 1995. © 1995 by the American Physical Society.

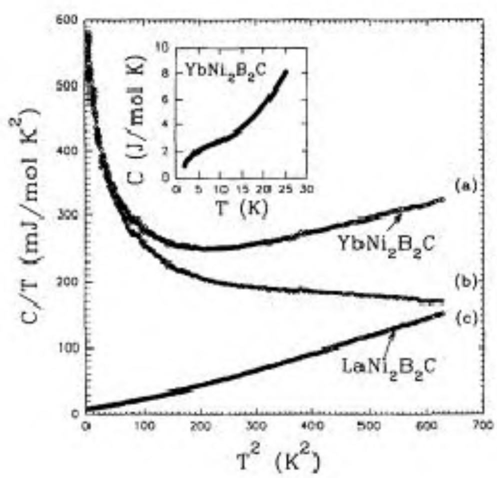

Figure 11. Temperature (T) dependence of heat capacity (C) of $YbNi_2B_2C$ (curve a) plotted in the form of C/T vs T^2. For comparison, T dependence of C of the nonmagnetic analogue $LaNi_2B_2C$ (curve c) is also shown. Curve b is the heat capacity of $YbNi_2B_2C$ after subtracting the non-magnetic contribution using the data of $LaNi_2B_2C$. The large value of the intercept at the *y*-axis of the extrapolation of the curve b indicates the heavy fermion nature of $YbNi_2B_2C$ (see text) (from ref. 119).

system but a spin fluctuation system. Considering that in $YbNi_2B_2C$, the estimated Kondo temperature ($T_K \sim 11$ K)[120], and the expected T_c are comparable, the absence of superconductivity in this material seems to be due to the competition of moderate heavy fermion nature of the material. In fact, the effect of hybridization is so strong that a substitution of even 0.1 atomic fraction of Y by Yb in YNi_2B_2C, depresses its T_c by 12 K[121]. This is the largest suppression of T_c observed for Yb substitution in an intermetallic superconductor. The magnitude of the depression can be contrasted against the depression of T_c by only 4K by the substitution of 0.1 atomic fraction of Y by Gd in YNi_2B_2C[121]. It is to be noted that the substitution by Gd ion is expected to give the largest depression of T_c in a rare earth series of substitution in a superconductor. Considering that heavy fermion superconductors are known to exist, understanding the exact cause of suppression of superconductivity in $YbNi_2B_2C$ would indirectly add to the knowledge of mechanism of superconductivity in these quaternary borocarbides. X-ray absorption studies on Ni edge in RNi_2B_2C show that Ni–*d* band in $YbNi_2B_2C$ is less filled than others. Thus, it appears that Kondo interaction may be causing a reduction in electron density of states at E_F, which in turn can be responsible for loss of superconductivity in $YbNi_2B_2C$[122].

High T_M systems – YbNiBC, UNi_2B_2C, and URh_2B_2C. In another extreme condition of hybridization, it can result in an enhancement of magnetic exchange coupling and to an enhanced magnetic ordering temperature. YbNiBC (with $m = 2$ and $n = 1$ in the homologous series mentioned earlier and one of the compounds synthesized by us for the first time[123]) is an example of this type. It orders magnetically around 4 K[123], which is a relatively high magnetic ordering temperature for a Yb system. The effect is more pronounced in U-based borocarbides, UNi_2B_2C (antiferromagnetic order at 218 K) and URh_2B_2C (ferromagnetic order at 185 K)[124]. These magnetic ordering temperatures are the highest amongst those reported for U compounds with closely related structure[124] of $ThCr_2Si_2$. In these two materials, temperature dependence of resistivity has a T^2 behaviour which is further evidence of hybridization effect[124].

Before we conclude this section, it is noted that non-formation of $EuNi_2B_2C$ may be related to hybridization effects as seen in Ce and Yb systems. In the case of Eu, hybridization effect usually drives Eu ion to divalent state which has a much larger ionic radius which in turn may drive the lattice into instability preventing the formation of the compound.

Magnetic borocarbides – RNi_2B_2C (R = Pr, Nd, Sm, Gd, Tb) and high coercive field Sm–Ru–B–C

The magnetic borocarbides $PrNi_2B_2C$, $NdNi_2B_2C$, $SmNi_2B_2C$, $GdNi_2B_2C$ and $TbNi_2B_2C$ order antiferromagnetically[103] ($T_N \sim 4$ K, 5 K, 10 K, 19 K and 15 K, respectively) with a variety of magnetic spin structures[85]. In addition, the magnetic structure of some of them undergoes a change with temperature or with externally applied magnetic field. For example, $TbNi_2B_2C$ at 5 K, has a spin structure which is antiferromagnetic along *a*-direction and ferromagnetic along *b*- and *c*-directions[85]. On application of magnetic field, the initial antiferromagnetically aligned spin sublattice undergoes a spin reorientation (around 2 kOe), and the material ends up with a ferromagnetic structure (above 20 KOe) (Figure 12)[103]. On the basis of deGennes scaling, from the systematics of T_cs of superconducting members, $TbNi_2B_2C$ is expected to superconduct around 4 K. Absence of superconductivity in this material is attributed to the *ferromagnetic* nature of magnetic order of Tb-magnetic moments below this temperature. Along with the magnetic structure of the magnetic superconductors, RNi_2B_2C (R = Tm, Er, Ho, Dy), this set of materials gives another opportunity to systematically study the magnetism in a rare earth series.

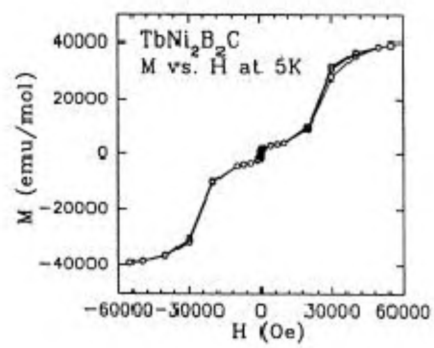

Figure 12. Magnetic field-induced changes in the magnetic structure as reflected in the field (*H*) dependence of magnetization (*M*) of $TbNi_2B_2C$ at 5K (from ref. 35). The step near 0 Oe shows ferromagnetic component of the initial magnetic structure.

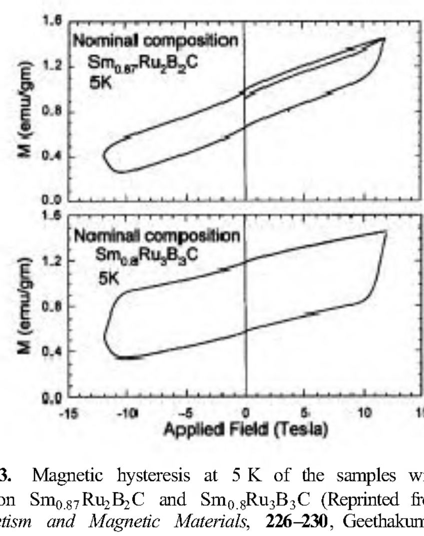

Figure 13. Magnetic hysteresis at 5 K of the samples with nominal composition $Sm_{0.87}Ru_2B_2C$ and $Sm_{0.8}Ru_3B_3C$ (Reprinted from *Journal of Magnetism and Magnetic Materials*, **226–230**, Geethakumary *et al.*, pp. 1437–1439, © 2001, with permission from Elsevier). The complete hysteresis loop is not traceable due to available applied field being smaller than the coercive field (H_c) of the materials. Extrapolation of the 0 to −15 T branch of the top curve indicates that the H_c is ~15 T at 5 K.

The Sm–Ru–B–C system[125] is perhaps the most interesting magnetic borocarbide. Samples of nominal composition $Sm_{0.87}Ru_2B_2C$ (deficiency in Sm is due to high volatile nature of Sm metal during the melting process) give a single phase material, with a *hexagonal* structure instead of the tetragonal structure of other members of RM_2B_2C series. It is noted that the Y-analogue, YRu_2B_2C, forms in the expected 1221 tetragonal structure (though not in phase pure form) and also exhibits superconductivity ($T_c = 9.7$ K)[126]. The hexagonal structure resembles that of $SmRu_3B_2$, but $SmRu_3B_2$ itself does not form readily, showing that C has a role in stabilizing the structure. Samples of nominal composition $Sm_{0.8}Ru_3B_3C$ also give a hexagonal single phase material with slightly different lattice constants. These materials order ferromagnetically ($T_M \sim 50$ K–70 K). An interesting observation is that $Sm_{0.87}Ru_2B_2C$ and $Sm_{0.8}Ru_3B_3C$ show huge magnetic hysteresis at 5 K with a coercive field of ~150 kOe[125] (Figure 13) (extrapolated value, as full hysteresis could not be covered in ± 120 kOe field of the magnetometer), which, perhaps, is the largest observed for a polycrystalline Sm intemetallic.

Summary

In this review, we have described the landmark discovery of superconductivity in first the quaternary intermetallic system at TIFR, Mumbai. The discovery led to a new family of materials, quaternary borocarbides, i.e. rare earth transition metal borocarbides. The members of the family have a variety of interesting properties, superconductivity with $T_c \sim > 10$ K, coexistence of superconductivity and magnetism with high T_c and T_N, valence fluctuation behaviour, heavy fermion behaviour, etc. Apart from high T_c, superconductivity, these materials show other interesting aspects such as, positive curvature of $H_{c2}(T)$ around temperature close to T_c, square flux line lattice and its symmetry having interesting behaviour with respect to external and internal magnetic fields, non *s*-wave symmetry of the superconducting gap function, etc. We have attempted to give an overview of the materials and a flavour of the properties of some of the important members. There are still several open questions in the field. Some of the materials with interesting property are still to be prepared in single phase. Structural instability/phase purity problems of some of the materials could possibly be overcome by appropriate partial substitutions, as it had been found in the case of RPt_2B_2C system. Even in the case of R–Pt–B–C system, the role of excess of Pt, B and C used in some of the synthesis methods of single phase samples is yet to be resolved. From our investigations[42] it was concluded that in the earlier reported single phase material $NdPt_{1.5}Au_{0.6}B_2C$, Au plays a direct role in enhancing the superconducting property of Nd–Pt–B–C system. A systematic investigation of Au substitution in this system would be rewarding. Identification of the superconducting phase with $T_c \sim 10$ K in Y–Pd–B–C system[54] would be fruitful and this would need investigation of phase diagram Y–Pd–B–C system. Though Bitterlich *et al.*[57] did study some aspect of the phase diagram, they did not report any transition with T_c around 10 K. This may be because, their emphasis was on the phase with T_c around 23 K and any superconducting signal from a T_c around 10 K might have got masked in the superconducting signal from the phase with T_c around 23 K. Since it is very difficult to determine a quaternary phase diagram, phase relationship should be attempted at least in the vicinity of 1221 phase, as it had been done in Y–Ni–B–C[127]. The indication of the presence of a superconducting phase with $T_c \sim 23$ K in Y–Ni–B–C from microwave absorption measurements[65] and a similar suggestion from investigations of samples prepared by powder metallurgical route[66] are important and need further investigations and confirmation.

Being quaternary, there is considerable potential for new materials and new phenomenon. For example, the coexistence of superconductivity and magnetism in $NdPt_2B_2C$ ($T_c \sim$ 2.5 K, $T_N \sim 1.5$ K)[42] was established only recently. In Lu–Re–B–C system, a quaternary superconducting phase ($T_c \sim 6$ K) exists[128]. The exact composition and structure of this phase is yet to be identified. Since superconductivity is observed in other members of this system, and in one of them (Tb–Re–B–C, $T_c \sim 4$ K) a magnetic order with relatively high transition temperature ($T_M \sim 30$ K) is also seen[128], identification of superconducting phase in Lu–Re–B–C would be rewarding not only in discovering new superconducting material, it would also enable establishing whether superconductivity and magnetism coexist in the same phase in Tb–Re–B–C. The exact composition and structure of the high coercive field Sm–Ru–B–C is still to be established. If better success is achieved in growing thin films of borocarbides, going by the example of Nb_3Ge, where the superconducting phase exists only in thin film form, it will be worthwhile to investigate whether the high T_c (23 K) phase in multiphase Y–Pd–B–C system could be formed as a single phase YPd_2B_2C in thin film form. Novel physics may be obtained when success is achieved in obtaining multi-layer thin films of appropriate combinations of superconductor/insulator/superconductor/magnetic superconductor/magnetic layers. The symmetry type of the order parameter of superconductivity and whether superconductivity is of unconventional nature in quarternary borocarbides is an on-going fundamental debate.

It is hoped that this review gives a feel for the methods and efforts, which in our opinion represents a piece of classic science, that went into the exciting discovery of superconductivity in quaternary borocarbides. Superconductors with high T_cs, magnetic superconductors with high coexistence temperatures, large number of materials with a variety of physical properties, have all attracted world-wide attention and research. Detailed works with high quality single crystals are revealing further intriguing properties of these exciting superconductors which keeps these materials in the forefront of research in superconductivity[129]. The excitement created by quaternary borocarbides has provided incentive and impetus for the hard task of search for new materials, even going beyond quarternaries to multinary intermetallics.

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