Quaternary Borocarbides - New Class of Intermetallic Superconductors


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Abstract

Our recent discovery of superconductivity (SC) in the four-element multiphase Y-Ni-B-C system at an elevated temperature ($T_c$=12K) has opened up great possibilities of identifying new superconducting materials and generating new physics. Superconductivity with $T_c$ (> 20 K) higher than that known so far in bulk intermetallics has been observed in multiphase Y-Pd-B-C and Th-Pd-B-C systems and a family of single phase materials RENi$_2$B$_2$C (RE = Y, rare earth) have been found. Our investigations show YNi$_2$B$_2$C to be a strong coupling hard type-II SC. $H_{c2}(T)$ exhibits an unconventional temperature dependence. Specific heat and magnetization studies reveal coexistence of SC and magnetism in RENi$_2$B$_2$C (R = Ho, Er, Tm) with magnetic ordering temperatures ($T_m$~5 K, 11 K and Tm~7 K respectively) that are remarkably higher than those in known magnetic superconductors. μ-SR studies suggest the possibility of Ni atoms carrying a moment in ThNi$_2$B$_2$C. Resistivity results suggest a double re-entrant transition (SC-normal-SC) in HoNi$_2$B$_2$C. RENi$_2$B$_2$C (RE = Ce, Nd, Gd) do not show SC down to 4.2K. The Nd- and Gd- compounds order magnetically at ~4.5 K and ~19.5 K respectively. Two SC transitions are observed in Y-Pd-B-C ($T_c$ = 11K, ~10 K) and in Th-Pd-B-C ($T_c$ = 20 K, ~14 K) systems, which indicate that there are at least two structures which support SC in these borocarbides. In our multiphase ThNi$_2$B$_2$C we observe SC at ~6 K. No SC was seen in multiphase UNi$_2$B$_2$C, UPd$_2$B$_2$C, UOs$_2$Ge$_2$C and UPd$_{1.35}$B$_2$C down to 4.2K. $T_c$ in YNi$_2$B$_2$C is depressed by substitutions (Gd, Th and U at Y-sites and Fe, Co at Ni-sites).

1. Introduction.

Our recent discovery of superconductivity in Y-Ni-B-C [1-4], with $T_c$ ~12 K to 15 K, which is relatively high superconducting critical temperature for intermetallics, has triggered an intense activity in the areas of superconductivity and magnetism. This discovery came about as a result of our on going investigations in Ni-based systems [5, 6]. An extension of Y-Ni-B-C system - going from a 3d- to 4d-element - led to the observation of record $T_c$ (~32K) in multiphase Y-Pd-B-C system. It may not be out of place to remark that a similar situation occurred during the initial phase of the discovery of high-$T_c$ superconductivity. Superconductivity was observed in a multiphase material La-Ba-Cu-O with a relatively low $T_c$ (~30K) [9] and later, superconductivity was reported in a multiphase material Y-Ba-Cu-O with a much higher $T_c$ (~93 K) [10].

We have been investigating Ni-based intermetallics for more than a decade in search of new valence fluctuation (VF) systems, besides our being interested in their magnetic and transport properties. We succeeded in identifying a number of new Ni-based VF systems such as EuNi$_2$P$_2$ [11], EuNi$_2$Si$_2$ [12], Eu$_2$Ni$_2$Si$_5$ [13], Ce$_2$Ni$_2$Si$_5$ [14]. Discovery of the above Eu-based VF compounds is particularly significant, as not many stoichiometric Eu-compounds exhibiting VF are known even today. After the discovery of high-$T_c$ superconductors, Ni-based materials acquired additional significance. All high-$T_c$ oxide superconductors, except Ba$_{1-x}$K$_x$BiO$_3$ [15], contain Cu as an essential component. As is well known, Ni-based oxides such as NiO and La$_2$NiO$_4$ are Mott-Hubbard insulators (just as CuO and La$_2$CuO$_4$ are), and attempts to induce SC in the nickel oxides failed. Moreover, partial Ni-substitution in cuprate superconductors suppressed $T_c$. Thus, nickel did not seem to favour superconductivity in oxides. On the other hand, in most Ni-based intermetal-
ics, Ni-moment is quenched and, therefore, they are potential candidates for superconductivity.

Ni-containing boride series RNi$_4$B (R=rare earth) was taken up by us for investigation, as many ternary rare earth-transition metal borides were known to support SC. Some of them are even magnetic superconductors, exhibiting coexistence of SC and magnetism. RNi$_4$B series turned out to be remarkable as we observed various phenomena in the same series, viz., VF in CeNi$_4$B [16], anomalously high ferromagnetic ordering temperature (= 39K) in SmNi$_4$B$_2$ [5, 6, 17] as compared to that of GdNi$_4$B$_2$ (= 36 K) [5, 6, 17] and weak signals of superconductivity in our samples of YNi$_4$B$_2$ [1]. Our further work showed that superconductivity in YNi$_4$B$_2$ originated due to the presence of carbon which stabilizes a SC phase in the material. We present below further details of our discovery of superconductivity in Y-Ni-B-C system and some of our recent results on the borocarbide superconductors.

2. Discovery of Superconductivity in Y-Ni-B-C System.

YNi$_4$B crystallizes in the hexagonal CeCo$_4$B type structure (space group P6/mmm) [18] and is also reported to have a superstructure ($a' = 3a_0; c = c_0$) in its lattice [19]. We synthesized YNi$_4$B by standard arc melting technique. Powder x-ray diffraction (XRD) pattern of the material confirmed the formation of the material in single phase belonging to the above mentioned structure. The lattice constants obtained from Rietveld analysis, including a superstructure, of our XRD pattern yielded lattice parameters as: $a = 14.96(5)$ Å, $c = 6.95(2)$ Å [1], which agree well with the published values [19].

Magnetic susceptibility of our sample of YNi$_4$B, measured as a function of temperature in a field of 4000 G, showed a sharp drop near 12 K [1, 6] (Fig. 1). This drop is not that of a typical antiferromagnet because, the drop is rather sharp and susceptibility increases on further cooling of the sample. Resistivity of our sample as a function of temperature (Fig. 1) also shows a sharp drop (but does not go to zero) around 12 K, the same temperature where the drop in susceptibility is seen [1]. The two observations together indicated the possibility of occurrence of superconductivity in this sample. M Vs H measurements clearly showed diamagnetism at low field, confirming occurrence of superconductivity. Reproducibility of drop in resistivity was confirmed by studying many independent batches (for one of them, the starting materials were obtained from a different source) of YNi$_4$B [1].

M Vs. T measurements (Fig. 3) at 65 G on a single piece of YNi$_4$BC$_{0.2}$ showed shielding and the Meissner fractions to be 4% and 1% respectively. Powdered material also showed diamagnetic response and Meissner effect. Annealing of the sample, though decreased the shielding fraction, improved Meissner fraction and $T_c$ (~15 K) (Fig. 2). As the SC fraction was small, the sample was examined for impurity phases by energy dispersive analysis of x-rays (EDAX) and electron microprobe analysis. The sample was essentially homogeneous except for some small inclusions which appeared to be Y$_2$O$_3$ and YNi$_5$ (both are non superconducting). No binary or ternary alloys of Y, Ni, B are known to be superconducting with such a high $T_c$. Thus, observation of superconductivity at 12 K was a new and surprising result.

Low volume fraction of superconductivity implied that the entire sample was not superconducting and it was necessary to understand the origin of observed superconductivity. We considered the possibility of crystallographic superstructure [1] being responsible for this behaviour. However, we also considered the possibility of the origin of SC being due to a minority phase stabilized by the presence of a fourth element. Carbon was considered to be one possible fourth element which got introduced in the system unintentionally. In order to check this, 0.2 atom fraction of carbon was deliberately added to YNi$_4$B, remelted and the material was studied. On addition of carbon, resistance dropped to zero around 12 K (Fig. 3) and the superconducting shielding fraction dramatically enhanced to nearly 80% of perfect SC [4]. These results were confirmed on many independently prepared batches. It became clear that carbon plays the crucial role in the observed superconductivity. Presence of carbon introduces structural changes as well; XRD pattern of YNi$_4$BC$_{0.2}$ indicated that superstructure of YNi$_4$B gets suppressed as carbon is introduced in the material [4]. Thus, one could argue that carbon does not play any chemical role, it brings in structural changes that in turn are responsible for the observed superconductivity. The observed SC being due to possible formation of Y$_2$C$_3$, which is a known superconductor [20], was ruled out on the basis of EDAX analysis of the material and on other considerations [4].
Encouraged by this observation, carbon was also added to many other compositions \( Y_{x}Ni_{y}B_{2z} \). Of all these materials, the material with the nominal composition \( YNi_{2}B_{2}C_{0.2} \) (multiphase) exhibited superconductivity at \( \sim 13.5 \) K with large specific heat anomaly across \( T_c \) (Fig. 4) [4]. The material showed large Meissner fraction (\( \sim 15\% \)) even in the powdered condition (Fig. 5). From these results we concluded that \( YNi_{2}B_{2}C \) system has a bulk superconducting phase with an elevated transition temperature (\( \sim 12 \) K) [4]. We presented these results at the two International Conferences, LT20, Eugene, U.S.A., Aug. 1993 [2] and SCES'93, San Diego, U.S.A., Aug. 1993 [3] and also communicated for publication [4].

3. Superconductivity and magnetism in \( RENi_{2}B_{2}C \) (\( R E = Y, Er, Ho, Tm \)).

3.1 \( YNi_{2}B_{2}C \)

EDAX analysis of multiphase \( YNi_{2}B_{2}C_{0.2} \) indicated that majority phase in the material has \( Y: Ni \) ratio as 1:2 [4]. It was difficult to ascertain boron and carbon contents by EDAX analysis as these are low Z elements. While our efforts to isolate the SC phase by varying concentration of B and C were in progress, Cava et al. [21] reported SC in single phase materials, \( RENi_{2}B_{2}C \) (\( R E = Y, Ho, Er, Tm \) and Lu), \( T_c = \sigma_{15.6 K}, 8 K, 10.5 K, 11 K, 16.6 K \) respectively), and Siegrist et al. [22] reported crystal structure of \( LuNi_{2}B_{2}C \). Thus, the concentration of B:C in the SC phase turned out to be 2:1. We have prepared \( RENi_{2}B_{2}C \) (\( R E = Y, Ho, Er, Tm \)) and studied in detail their superconducting and magnetic behaviour. Our preliminary results were reported earlier [23]. Some of the results are given below.

We carried out detailed structural studies of \( YNi_{2}B_{2}C \), using electron diffraction and x-ray diffraction on single crystals picked up from the arc-melted button of one of our samples [24]. Results of the analysis of the data were in agreement with those reported by Siegrist et al. [22]. Figure 6 shows a unit cell of the structure of \( YNi_{2}B_{2}C \). The tetragonal structure belongs to the centro-symmetric space group \( P4/mmm \) and is a 'filled-in' version of the well known \( ThCr_{2}Si_{2} \)-type structure. We shall refer to this structure as 1221-structure in the rest of this paper. Carbon atoms are located in the \( Y(Th) \)-planes. Remarkable features of this structure are: rather short B-C distance, nearly ideal Ni-B4 tetrahedra and Ni-Ni bond length shorter than that in Ni-metal, implying that Ni-Ni bonds are strong. The \( c/a \) ratio \( (c = 10.545(5) \AA) \) is 2.99, suggesting that the structure is highly anisotropic. The results further showed that (i) there is no superstructure in \( YNi_{2}B_{2}C \) (ii) free parameter \( z \) of boron atoms is 0.358 (iii) C-atoms have a rather large amplitude of thermal vibration, especially in the \( Y-C \) plane [24]. Our XRD studies did not show any crystallographic phase transition down to 50 K. Further, lattice constants at 50 K are almost unchanged (\( a = 3.521 \) A and \( c = 10.549 \) A).

Magnitude of the room temperature resistivity, \( R(T) \), of our sample of \( YNi_{2}B_{2}C \) is large (\( > 100 \mu \text{ohm cm} \)) [24] for a metallic system. This implies that the electron-phonon interaction may be large. Superconductivity occurs at 15.3 K with a width \( \delta T_c \) (90% - 10%) of the resistive transition of about 0.5 K. \( R(T) \) is linear in temperature down to 40 K. High-\( T_c \) cuprates also exhibit \( R(T) \) proportional to \( T \) behaviour in the normal state. Scattering of the carriers from 2D-antiferromagnetic fluctuations of \( Cu \)-spins has been suggested to be one possible mechanism of this behaviour [25]. In this context, it may be mentioned that evidence of antiferromagnetic spin fluctuations in \( YNi_{2}B_{2}C \) has been found in the anomalous nuclear spin relaxation rate of boron (1/\( T_1 \)) increases with decrease of temperature) [26, 27]. Considering the highly anisotropic structure of \( YNi_{2}B_{2}C \), it is conceivable that these fluctuations could also be anisotropic. Also possibility of Ni-atoms carrying a moment has been indicated in \( \mu \)-SR measurements in, e.g., \( TmNi_{2}B_{2}C \) [28]. To what extent these fluctuations influence the \( R(T) \) of the material is worth investigating, preferably on single crystals.

In the normal state, susceptibility of our sample of \( YNi_{2}B_{2}C \) exhibits paramagnetic behaviour over the temperature range 15-300 K. From a Curie-Weiss fit to the data and assuming that paramagnetic behaviour arises due to moments on Ni ions only (as there are no other magnetic ions), we get a value of 0.18 \( \mu_B/\text{Ni} \) ion. However, caution is to be exercised in this conclusion as susceptibility from minority impurity phases may influence this value.

Diamagnetic response of our sample (bulk, as well as powder) below \( T_c \), both in field cooled (FC) and zero field cooled (ZFC) conditions, is shown in Fig. 7. Both bulk (annealed and as-cast) and powder samples exhibit nearly 100% shielding signal (ZFC). The Meissner fraction (FC) of the as-cast material is
about 10%. In the annealed bulk sample, the Meissner fraction is even smaller (5%). However, in the powdered sample of the annealed material (after powdering, this sample was not annealed), we observe a Meissner fraction of 50%.

We measured molar heat capacity $C_p$ of annealed and unannealed samples of YNi$_2$B$_2$C in the temperature range $5K < T < 22K$. In the annealed sample, anomaly in $C_p$, observed in going through the superconducting transition, is narrower, and occurs at a higher temperature, suggesting that the quality of the sample improves on annealing. This is reflected in the x-ray diffraction pattern of the material as well and also in its diamagnetic response. From the analysis of the data we obtain $\Gamma = 8.9$ mJ/mole K$^2$ and $\beta = 0.163$ mJ/mole K$^4$, where $\Gamma$ and $\beta$ are the temperature coefficients of the electronic and the lattice specific heat capacities respectively. The ratio $\delta C_p/\Gamma T^2$ is calculated to be 3.6 which is much higher than 1.43, the BCS value for the weak-coupling limit. It is, however, to be emphasized that considering that the observed transition is broad, this figure may be taken to suggest the trend. In fact, recent specific heat measurements on a single crystal sample [29] yield this number to be $\sim 1.8$ which still implies strong-coupling in YNi$_2$B$_2$C. From the value of $\beta$, Debye temperature ($T_D$) is estimated to be 415 K. Large value of the ratio $T_c/T_D$ also is consistent with this conclusion.

$C_p/T$ Vs. $T^2$ in YNi$_2$B$_2$C, below the SC transition down to 5 K, follows a linear relationship. It should be interesting to extend these measurements, below 5 K, to check and confirm this temperature dependence of $C_p$. It may be pointed out that the power-law behaviour of the heat capacity in the SC state of heavy fermion systems has been taken as an indication of unconventional superconductivity where the symmetry of the superconducting energy gap is lower than the symmetry of the Fermi surface. More detailed studies are needed to investigate such possibilities in borocarbide quaternary superconducting materials.

Magnetization $M(H)$ measurements of YNi$_2$B$_2$C at 5K, as function of applied field, H, show the material to be a hard type-II superconductor. The temperature dependence of $H_{c2}(T)$, determined from the studies of $R(H,T)$ under applied field [30], is unconventional [24]. The slope, $dH_{c2}(T)/dT$ is close to zero at $T_c$ and increases with decrease of temperature below $T_c$ [24] whereas, in a conventional type-II superconductor, $dH_{c2}(T)/dT$ is non zero at $T_c$ and is nearly constant for a considerable range of temperature below $T_c$ [31]. It would be of interest to investigate this unconventional behaviour of $H_{c2}(T)$ in YNi$_2$B$_2$C. From $H_{c2}(T)$ measurements we estimate the coherence length in this material to be $\sim 80 \AA$ at 5 K.

Magnetic history effects in YNi$_2$B$_2$C [32] also confirm the material to be a hard type-II superconductor [32]. Temperature dependence of $M_{rem}$, $M_{zfc}$ and $M_{fc}$ (symbols have their usual meaning [32]) at 50 G were measured over the temperature $5K < T < T_c$. These magnetizations do not satisfy the relation $M_{rem} = M_{fc} - M_{zfc}$ even at 5 K and 50 G. We have $M_{rem} < M_{fc} - M_{zfc}$ even below $T_c$ [31]. This implies that $H_{c1}$ at 5 K is less than 50 G [32].

The value of lower critical field $H_{c1}$ of YNi$_2$B$_2$C estimated from magnetic-field-modulated low-field microwave absorption measurements is $\sim 20G$ at 10K [33]. An interesting aspect of our preliminary results of direct microwave absorption (with no field modulation) measured as a function of temperature at 9.3 GHz is that it exhibits a drop at $\sim 23 K$ in addition to the expected drop due to SC at $\sim 15$K [33]. Though one may associate the drop near 23 K to onset of SC, the exact origin of this is not clear at present.

$^{11}$B Nuclear magnetic resonance (NMR) experiments on YNi$_2$B$_2$C [26, 27] show that the relaxation rate (1/T$_1$) increases with decrease of temperature, unlike in a metal where 1/T$_1$ is proportional to T. Antiferromagnetic fluctuations on Ni-atoms may be responsible for this behaviour as there are no other magnetic atoms. An interesting feature of the NMR results is that below $T_c$, instead of one line (there is only one crystallographic B-site in the unit cell), two lines are observed [26]: Observation of the second line implies that there are normal regions in the material, even below $T_c$. We believe that variation of stoichiometry at microscopic level, could be the cause of the normal state regions below $T_c$. Such aspects are being looked into in our NMR investigations.

3.2 ErNi$_2$B$_2$C

Our sample of ErNi$_2$B$_2$C shows a sharp superconducting resistive transition ($\delta T$ of transition (90%
- 10% resistivity) is 0.5 K at $T_c = 10.3$K [24]. Resistivity of ErNi$_2$B$_2$C is higher than that in YNi$_2$B$_2$C which we attribute to magnetic scattering of the carriers from Er-spins. In the normal state, magnetic susceptibility of ErNi$_2$B$_2$C follows a Curie-Weiss behaviour with $\mu_{\text{eff}} = 9.32$ $\mu_B$ per formula unit and paramagnetic Curie temperature ($\Theta_p$) $\sim$ 2 K [24]. The value of $\mu_{\text{eff}}$ is less than that of Er$^{3+}$-free ion (9.59 $\mu_B$). One possibility of the reduced magnetic moment is that Er- and Ni- moments are antiferromagnetically correlated even in the paramagnetic state. It should be of interest to investigate these and other related aspects by neutron diffraction measurements.

In the ZFC-configuration, bulk and powder samples of ErNi$_2$B$_2$C exhibit shielding signals that are nearly 100% and 50%, respectively, of the perfect diamagnetism. However, noteworthy is the fact that in both cases, in the FC-configuration, the material exhibits paramagnetic response down to the lowest temperature. This is an indication of sufficient field penetration and field trapping, even at a field as low as 30 G. Paramagnetic contribution from Er-spins in the flux-lines in the interior of the material masks the superconducting diamagnetic response.

Specific heat of ErNi$_2$B$_2$C shows a large anomaly around 5.8 K (Fig. 8) which we interpret as due to the magnetic ordering of Er-spins. Since the resistivity does not show any re-entrant behaviour below this temperature, and the material continues to exhibit diamagnetic response down to ~5 K, we conclude that SC and magnetic ordering coexist in this system.

Coexistence of SC and magnetic ordering occurs, for example, in ternary rare earth rhodium boride and molybdenum chalcogenide superconductors. In the ternary system ErRh$_4$B$_4$ ($T_c = 8.2$K), a reentrant transition to the normal state is observed below the magnetic ordering temperature (~1.2 K). This is because in ErRh$_4$B$_4$, Er-spins undergo a ferromagnetic ordering and superconductivity is destroyed below the magnetic ordering temperature. On the other hand, in cases like TmRh$_4$B$_4$, where Tm ions are known to order antiferromagnetically, superconductivity is not destroyed due to magnetic ordering. These results suggest that it is very likely that Er-spins in ErNi$_2$B$_2$C order antiferromagnetically. Preliminary results of neutron investigations [34] confirm magnetic ordering below 7 K. To investigate the magnetic interactions at the microscopic level, we plan to carry out Er-Mossbauer measurements in ErNi$_2$B$_2$C.

3.2 HoNi$_2$B$_2$C and TmNi$_2$B$_2$C

In the case of HoNi$_2$B$_2$C and TmNi$_2$B$_2$C also, coexistence of superconductivity and magnetism has been observed [23]. Resistivity and diamagnetic response show that superconductivity occurs in both the materials ($T_c \sim$ 8 K and 11 K respectively). Heat capacity measurements show a large anomaly around 4.5K and 4 K in HoNi$_2$B$_2$C (Fig. 8) and TmNi$_2$B$_2$C, respectively, originating from the magnetic ordering of Ho and Tm ions. $\mu$-SR measurements suggest magnetic ordering of Tm- moments taking place at ~2.5 K [28]. In our sample of HoNi$_2$B$_2$C, we see two SC transitions (Fig. 9) [30]. The resistivity starts dropping around 9 K ($T_{c1}$), and continues to drop till 7 K but does not go to zero. On further cooling it starts rising. This is similar to reentrant behaviour seen, for example in ErRh$_4$B$_4$. The unique feature of this material is that resistivity starts dropping again below 5.5 K ($T_{c2}$) signaling a second SC transition. This is the first material which exhibits such a double reentrant, superconducting-normal-superconducting, behaviour. The observed feature is seen even at applied fields up to 1 KG (Fig. 9) [30]. The magnetic response of the material measured at 20 G is primarily paramagnetic. It does show a reduction near 8 K, which is due to the onset of superconductivity. The Meissner fraction however is poor. It is possible that $H_{c1}$ for this material is very small. Therefore, it may be necessary to study the magnetic response in rather low applied magnetic fields. Even after annealing, the material did not show zero resistance, though, the XRD pattern showed some improvement. Coexistence of SC and magnetism in these materials have also been reported by Eisaki et al. [35].

4. Non-superconducting materials - RENi$_2$B$_2$C (RE = Ce, Nd, Gd).

Cava et al. [21] have reported the formation of other RENi$_2$B$_2$C materials (RE = La, Ce, Sm, Tb, Dy) also which do not show SC down to 4.2K. From the lattice parameters, it was concluded that CeNi$_2$B$_2$C is a mixed valence material [22]. We have synthesized and investigated the magnetic properties of RENi$_2$B$_2$C (RE = Ce, Nd and Gd). We find that NdNi$_2$B$_2$C and GdNi$_2$B$_2$C also crystallize in the 1221-type structure. The lattice parameters of Ce-, Nd- and Gd- compounds, respectively, are: a = 3.634 Å, 3.686 Å, 3.583 Å; c =
Meissner signa measurements of materials. We observe YCo₂B₂ forms in ThCr₂Si₂ structure [36] and carbon can be incorporated, in wev HYPd₄B₂C₀.₂. superconductivity at -9 K although the strength of this is near 23 K, in a multiphase material YPd₅B₃Cₓ (0.3 < x < 0.4) [7].

nducting phases. R superconductivity at -10 K only. Magnitude of magnetic response of this sample is about one-third of the sample. Thus, it appears that physical properties of the end-products depend on whether the starting components were taken as powders or pieces.

Sample of the composition YPd₄B₂C₀.₅ exhibits two superconducting transitions, one near 22 K and the other near 9 K (Fig. 10) [8]. It is clear from these measurements that the Y-Pd-B-C system has at least two superconducting phases. Relative proportions of the two phases depend upon not only whether the elements are taken as powders or small pieces but also on the amount of carbon in the system. Cava et al., reported superconductivity at Tc ~ 23 K, in a multiphase material YPd₅B₃Cₓ (0.3 < x < 0.4) [7].

To study the effect of rare earth substitution on the superconducting properties of YPd₄B₂C₀.₂, we have studied superconducting behaviour of LuPd₄B₂C₀.₂ and ScPd₄B₂C₀.₂ [8]. Both the materials exhibit superconductivity at ~9 K although the strength of the superconducting signals is much weaker than in YPd₄B₂C₀.₂.

We also synthesized the materials YT₂B₂C (T = Ir, Rh, Os, Co). All of them were multiphase. However, in the XRD pattern of YCo₂B₂C, a set of lines could be indexed on the basis of the 1221-type phase (a = 3.513Å, c = 10.581Å). None of these was found to be SC down to 4.2 K. It is interesting to point out that YCo₂B₂ forms in ThCr₂Si₂ structure [36] and carbon can be incorporated in the lattice to form YCo₂B₂C but does not exhibit SC down to 4.2 K. On the other hand, YNi₂B₂ does not form [24], but YNi₂B₂C forms and superconducts. Crystal chemistry aspects of this are being looked into.

6. A-M-B-C (A = Th and U; M = transition elements).

We also investigated the existence of SC in various Th- and U-, the 5f- element based borocarbide materials. We observe SC in Th-Pd-B-C and Th-Ni-B-C systems [37]. Sarrao et al. have also reported SC in these materials [38].

We observe two superconducting transitions (Tc ~17 K and 12 K) in our resistance and magnetic measurements of multiphase ThPd₄BC. Resistance of the sample does not go to zero even below the lower transition temperature ~12 K. Shielding signal, measured at 20 G, is low (~10%); however, one does see a Meissner signal (~1%). The superconducting phases are minority phases in this multiphase material. A
number of samples of the composition ThPd$_2$B$_2$C were synthesized and studied. These samples were also
multiphase. Our results show that there are two superconducting transitions in this composition as well
($T_c ~ 20$ K, 14 K) (Fig. 11). Zero resistance is acheived below 14 K (Fig. 11). The strength of the shielding signal
and the Meissner signal are sample dependent. These results show that the system Th-Pd-B-C also has at
least two superconducting phases just as the system Y-Pd-B-C has.

Our samples of ThNi$_2$B$_2$C are multiphase but do contain the 1221-type phase ($a = 3.699\text{Å}$, $c = 10.192\text{Å}$). Resistance of this sample goes to zero below 6 K. Diamagnetic shielding signal at 4.2 K is close
to what one expects for perfect diamagnetism. Thus there is a superconducting phase in the sample with $T_c ~ 6$ K. Magnetic response in the field cooled condition, however, is positive below ~6 K.

If in our multiphase ThNi$_2$B$_2$C, 1221-type phase is the SC phase, then it is interesting to compare
the reduced $T_c$ in ThNi$_2$B$_2$C (in relation to YNi$_2$B$_2$C) with that in ThRh$_4$B$_4$ (in relation to YRh$_4$B$_4$). ThRh$_4$B$_4$ has $T_c ~ 4.5$ K which is much lower than $T_c$ of YRh$_4$B$_4$ (~10.5 K) [39]. In the case of ThRh$_4$B$_4$,
this drop in $T_c$ has been explained as a consequence of change of the electron/atom ratio on replacing triva-
lent Y by tetravalent Th. Subtle changes in the density of states at the Fermi level, which can occur due to the
concomitant variation in the cell constants, also may be responsible, at least partly, for this large change of
$T_c$ [39, 40].

We synthesized ThM$_2$B$_2$C ($M =$ Co, Ir, Os) and also several compositions of U-based materials,
such as, UNi$_2$B$_2$C, UPd$_2$B$_2$C, UOs$_2$Ge$_2$C and UPd$_3$B$_2$C$_{0.35}$. All these samples were multiphase. a.c.
susceptibility investigations of these materials did not show SC down to 4.2K.

7. Dilute substitution studies: $Y_{1-x}A_xNi_{2-y}M_yC$ ($A =$ U, Th, Gd; $M =$ Co, Fe; $x = 0$ and $y = 0.1$; $x = 0.1$
and $y = 0$).

In order to get an insight into the mechanism of SC in these borocarbides, we investigated the effect
of partial substitution at the Y-site and the Ni-site on superconducting properties of YNi$_2$B$_2$C.

In $Y_{0.9}Th_{0.1}Ni_{2}B_2C$, $Y_{0.9}Gd_{0.1}Ni_{2}B_2C$ and $Y_{0.9}Ce_{0.1}Ni_{2}B_2C$ which are essentially single
phase, resistance and susceptibility results show that $T_c$ is depressed by about ~5 K in all the cases (Fig. 12),
even though Th-ions are non-magnetic, Gd-ions are magnetic and Ce-ions are mixed valent and are weakly
magnetic. This is an interesting result, if effects such as variation in cell constants or difference in valence
state (Th is tetravalent and Gd is trivalent) do not play an important role in the depression of $T_c$. It implies
that pair-breaking is not influenced much by the magnetic state of the impurity ions. Similar effects have
been observed in heavy fermion superconductors [41]. This has certain implications with respect to the nature
of pairing ($s$- vs non-$s$). Further work on this aspect is desirable. We have also observed that substitution of
0.05 atomic fraction of Y by U depresses $T_c$ (onset) by 3 K, but major drop in resistance occurs at ~5 K and
$T_c$(zero) is depressed by ~10 K. It would be interesting to ascertain if U-atoms have magnetic moment in this
dilute limit.

In single phase YNi$_1.9Fe_{0.1}B_2C$ and YNi$_{0.9}Co_{0.1}B_2C$, resistance and a.c. susceptibility results
show that $T_c$ is depressed by about ~5 K in Co- and ~7 K in Fe- cases, respectively. It would be interesting to
examine the magnetic state of Fe and Co in dilute limits in borocarbides.

8. Conclusions.

Weak signal of superconductivity at an elevated temperature, $T_c ~ 12$ K - 15 K, that we observed in
YNi$_2$B led us to the discovery of bulk superconductivity in multiphase four-element borocarbid system Y-
Ni-B-C. This discovery laid the foundation of new field of superconductivity and magnetism in quaternary
borocarbides. Y-Pd-B-C and Th-Pd-B-C systems have a phase with $T_c$'s (> 20 K) higher than that observed in
bulk intermetallics known so far. Further, in these two systems there are at least two phases that support
superconductivity. The borocarbide RENi$_2$B$_2$C series, besides having superconducting members, also has
members which are not superconducting. They exhibit a variety of magnetic behaviour.
Our structural investigations on single phase superconductor YNi$_2$B$_2$C suggest that carbon atoms have large and highly anisotropic thermal vibrations and that there is no structural change down to 50 K. From our specific heat and magnetization studies, we conclude that this material is a strong-coupling superconductor and the temperature dependence of $H_{c2}(T)$ is rather unusual. Our $^{11}$B nuclear relaxation measurements suggest short lived moments on Ni-ions in the normal state of YNi$_2$B$_2$C. Microwave absorption measurements in YNi$_2$B$_2$C indicate $H_{c1}$ to be ~20 G at 10 K and exhibit a change in slope at ~23K, origin of which is not clear at present.

Single phase materials, RENi$_2$B$_2$C (RE = Ho, Er, Tm), exhibit coexistence of superconductivity and magnetism. double reentrant transition HoNi$_2$B$_2$C, anomalously high magnetic ordering temperatures, possibility of moment on transition metal ions are some of the phenomenon that distinguish these magnetic superconductors from all other known magnetic superconductors, including high-$T_c$ cuprates.

Thus, borocarbides are not only new superconductors, but they have also provided hopes for new physics and higher $T_c$'s in intermetallics. It is evident that this discovery will motivate efforts not only to identify quaternary systems with other elements such as Al, N, Si and Ge etc. but also multicomponent intermetallic superconductors with still higher number of elements. Our own efforts in this direction are in progress.

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References.

Conference on Magnetism and Magnetic Materials, Abstract No. BP14, Houston, Texas, U.S.A., 
B.D. Padalia and R. Vijayaraghavan, International Conference on Advances in Physical Metallurgy, 
24. C. Godart, L.C. Gupta, R. Nagarajan, S.K. Dhar, H. Noel, M. Potel, Zakir Hossian, Chandan Mazumdar, 
31. See for example, Gerald Burns, in High-Temperature superconductivity: An Introduction, (Academic 
therein.
32. S.B. Roy, Zakir Hossain, A.K. Pradhan, Chandan Mazumdar, P. Chaddah, R. Nagarajan, L.C. Gupta and 
33. R.M. Kadam, M.D. Sastry, Zakir Hossain, Chandan Mazumdar, R. Nagarajan, L.C. Gupta, C. Godart and 
34. S.K. Sinha, L.W. Lynn, T.E. Grigereit, Z. Hossain, L.C. Gupta, R. Nagarajan and C. Godart, 
S. Uchida (pre-print).
38. J.L. Sarrao, M.C. de Andrade, J. Hermann, S.H. Han, Z. Fisk, M.B. Maple and R.J. Cava, High Tc Update, 
1 June, 1994.
39. C.B. Vining and R.N. Shelton in Ternary Superconductors, Proc. Int. Conf. on Ternary Superconductors, 
(1988).
Figure 1.- Resistivity and magnetic susceptibility of our sample of YNi$_4$B as a function of temperature. Solid line is the Curie-Weiss fit in the range 12K to 300 K (from Ref.1).

Figure 2.- Zero field cooled (shielding signal) and filed cooled (Meissner signal) diamagnetic response as function of temperature for as cast and annealed samples of YNi$_4$B.
Figure 3.- a.c. magnetic susceptibility (top) and d.c. resistance (bottom) as a temperature for the sample $\text{YNi}_4\text{BC}_{0.2}$. Inset shows the resistance over the temperature range 4.2 K to 300 K.

Figure 4.- Specific heat ($C/T$ Vs.$T^2$) of the material with nominal composition $\text{YNi}_2\text{B}_3\text{C}_{0.2}$ (from Ref. 4).
Figure 5.- Zero field cooled (shielding signal) and field cooled (Meissner signal) diamagnetic response as a function of temperature for bulk and powdered samples of YNi$_2$B$_3$C$_{0.2}$ (top). Bottom figure show resistance as a function of temperature for the bulk sample of YNi$_2$B$_3$C$_{0.2}$.

Figure 6.- Powder x-ray diffraction pattern of YNi$_2$B$_2$C. Lines corresponding to the impurity phase YB$_2$C$_2$ are indicated by solid circle above those lines. Results of our intensity calculations are shown by cross mark. Inset shows the structure of YNi$_2$B$_2$C determined from single crystal diffraction studies. Note the rather large thermal amplitude of C-atoms in the Y-C plane (represented as ellipsoids) (from Ref. 24).
Figure 7.- Zero field cooled (shielding signal) and field cooled (Meissner signal) diamagnetic response as a function of temperature for bulk and powdered samples of annealed \( \text{YNi}_2\text{B}_2\text{C} \). The solid lines are guide to the eye.

Figure 8.- Specific heat \((C)\) of \( \text{ErNi}_2\text{B}_2\text{C} \) and \( \text{HoNi}_2\text{B}_2\text{C} \) as a function of temperature. The large peaks are due to magnetic ordering in these materials. In \( \text{ErNi}_2\text{B}_2\text{C} \), the anomaly due to SC is seen just below 10 K. In the case of \( \text{HoZNi}_2\text{B}_2\text{C}_2 \) it is below the limit of our observations.
Figure 9.- Resistance as a function of temperature at various externally applied fields of HoNi$_2$B$_2$C. Note the double reentrant behavior for fields upto 1 KG.

Figure 10.- Zero field cooled (shielding signal) and field cooled (Meissner signal) diamagnetic response as a function of temperature for material of nominal composition YPd$_4$BC$_{0.5}$. Solid lines are guide to the eye. Inset shows resistance ($r$) of the sample as a function of temperature (from Ref. 8). Note two superconducting transitions.
Figure 11.- Zero field cooled (shielding signal) and field cooled (meissner signal) diamagnetic response as a function of temperature for material of nominal composition ThPd$_2$B$_2$C. Inset shows resistance ($r$) as function of temperature. Note two superconducting transitions.

Figure 12.- a.c. susceptibility as a function of temperature for $Y_{0.9}M_{0.1}Ni_2B_2C$ ($M =$ Th, Gd, Ce).