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Quaternary borocarbides: Relatively high T_c intermetallic superconductors and magnetic superconductors

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ABSTRACT

Discovery of superconductivity in Y–Ni–B–C ($T_c \sim 13$ K) gave rise to the class of quaternary rare earth transition metal borocarbide superconductors. Before the discovery of Fe-based arsenide superconductors, this was the only class of materials containing a magnetic element, *viz.*, Ni, yet exhibiting T_cs > 5 K. Many members of this class have high T_c (>10 K). T_c of ~23 K in Y–Pd–B–C system equaled the record T_c known then, for intermetallics. Another feature that sets this class apart, is the occurrence of the exotic phenomenon of coexistence of superconductivity and magnetism at temperatures >5 K. Availability of large and electronically 'clean' single crystals and large Ginzburg-Landau (*G–L*) parameter, κ, have enabled detailed investigation of nonlocal effects of superconductivity. Intermediate value of upper critical field H_{c2}, has enabled detailed investigation of superconductivity in this class, over the complete *H–T* plane. This has revealed details of anisotropy of superconductivity (*e.g.*, a fourfold symmetry in the square *a–b* plane is found) and raised questions on the symmetry of order parameter. After a brief outline of the discovery, this article gives a summary of the materials and highlights of superconducting properties of this class of materials. Interesting results from studies, using various techniques, on YNi_2B_2C ($T_c \sim 15$ K) and $LuNi_2B_2C$ ($T_c \sim 16$ K) are presented, including observation of unusual square vortex lattice and its structural transformation with *H* and *T*. With conduction electrons involved in the magnetic order of this class of superconductors, the interplay of superconductivity and magnetism is intimate in these magnetic superconductors. With T_c (~11 K) > T_N (~6 K) in $ErNi_2B_2C$, T_c (~8 K) = T_N (~8 K) in $HoNi_2B_2C$ and T_c (~6 K) < T_N (~11 K) in $DyNi_2B_2C$, and with other parameters being favorable as mentioned earlier, this class of magnetic superconductors have become ideal materials to investigate the coexistence phenomenon. A few major results on these are presented.

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1. Introduction

Amongst superconductors, quaternary rare earth transition metal borocarbides/nitrides (QBC) superconductors form a class of superconductors distinguished by relatively high T_c for intermetallics and magnetic superconductors with relatively high coexistence temperatures. Discovery of superconductivity in quaternary borocarbides originated with the observation of trace superconductivity with transition temperature (T_c) ~15 K in a sample of YNi_4B (Fig. 1) [1] which was being investigated as a part of our investigations of RNi_4B (R = Y, Rare earth) series of materials [2–5]. Though resistance was not zero, superconductivity was confirmed by the diamagnetic response at low magnetic fields. Considering that the resistance was not zero in the superconducting state, many samples were prepared and studied to check the reproducibility of superconductivity. Superconductivity with $T_c \sim 15$ K was confirmed, but remained trace with the fraction being different in different samples. The maximum observed superconducting fraction was ~2% [1]. The 'high' T_c (for intermetallics, $T_c > 10$ K is considered high) and that too for a Ni containing material was a surprise as, Ni–as element is magnetic. Only a few Ni containing binary superconductors were then known and their T_cs were <5 K. Thus, it was important to identify the phase of superconductor.

Many compositions of the type $Y_xNi_yB_z$ were synthesized and examined for superconductivity. A few of the compositions showed superconductivity around the same T_c, but still only as a trace. The results suggested that the superconductivity very likely arose from a phase having a fourth element. Due to a variety of reasons, carbon was thought to be the most likely candidate and a sample of $YNi_4BC_{0.2}$ was prepared and studied. The sample exhibited zero resistance with dramatic increase in diamagnetic signal by a factor of about twenty [6]. Other compositions of Y–Ni–B which had shown trace superconductivity were also prepared with addition of C and studied. These investigations showed that multiphase material of nominal composition $YN_2B_3C_{0.2}$ with major phase having Y:Ni as 1:2 (C and B being light elements were not amenable to composition analysis in standard EDAX equipment) is a bulk superconductor (indicated by extent of heat capacity anomaly at T_c (Fig. 2)) with $T_c \sim 15$ K [6]. Our investigations also confirmed that all four elements are required for the superconducting phase, thus giving rise to the subject of quaternary borocarbide (QBC) superconductors. Cava *et al.* reported superconductivity in single phase materials, RNi_2B_2C with R = Y, Lu, Tm, Er, and Ho with $T_c \sim 15.5$ K, 16.5 K, 11 K, 11 K, and 8 K respectively [7]. Siegrist et al. [8] showed the structure to be a filled variant of the well known $ThCr_2Si_2$ type tetragonal structure with C atoms being in the plane of R atoms (Fig. 3). Cava et al. also showed that the multiphase Pd borocarbide (nominal composition $YPd_5B_3C_{0.3}$) is a superconductor with $T_c \sim 23$ K which was equal to the then known highest T_c for intermetallics [9] (prior to MgB_2 [10] and Fe based pnictide and chalcogenide superconductors [11]). Soon after, it was shown that amongst the above materials, RNi_2B_2C (R = Tm, Er, Ho) are magnetic superconductors with superconductivity coexisting with magnetic order (T_N = ~1.5 K, ~6 K, ~8 K, respectively) [12]. All these findings excited the scientific community [3,4,13] triggering an intense research activity, which resulted in revealing many new aspects of superconductivity, including those in magnetic superconductors. This short review, not necessarily up to date, attempts to present a few highlights in the subject giving a flavor of the fascinating aspects of QBC superconductors. Details may be found in other extensive reviews [14–21], and in other references given at the appropriate places. Though some of the recent Fe based pnictide 'high-T_c' superconductors have similarities with QBC, no attempt has been made to compare them in this review. A review of Fe- pnictide and chalcogenide superconductors can be found in Ref. [11].

2. Synthesis of the materials

Most of the investigations in QBC are carried out on RNi_2B_2C (R = Y, rare earth), as they form with phase purity. Polycrystalline samples of these materials (except for Yb-based members and the nitride) are synthesized by argon arc melting technique. The nitride samples are prepared by arc melting the components in nitrogen atmosphere [22]. Yb-based members are prepared by solid state reaction in a Mo crucible [23]. The availability of relatively large single crystals, which made detailed studies possible, has been one of the attractions to study these materials. Single crystal of about mm size can be picked from the as melted sample. Larger size (about 5 mm × 5 mm × 0.1 mm) plate-like crystals of RNi_2B_2C (R = Lu to Tb) have been grown by flux growth technique in Ni_2B flux [24]. Very large single crystals of YNi_2B_2C have been grown by floating zone technique in a 'self-flux' process [25,26]. Thin films samples have been reported only for YNi_2B_2C [27,28]

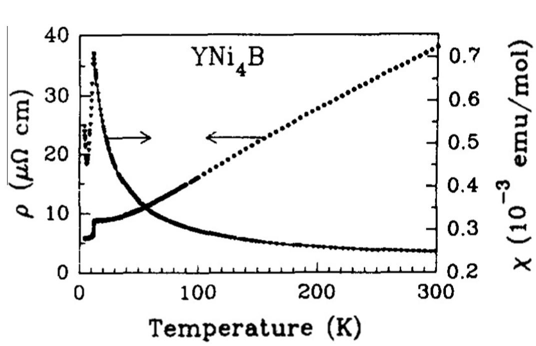

Fig. 1. (a) Resistivity ρ and (b) magnetic susceptibility χ of YNi_4B as a function of temperature. Solid line is the Curie–Weiss fit for χ in the range 12–300 K (figure reproduced from Ref. [1]).

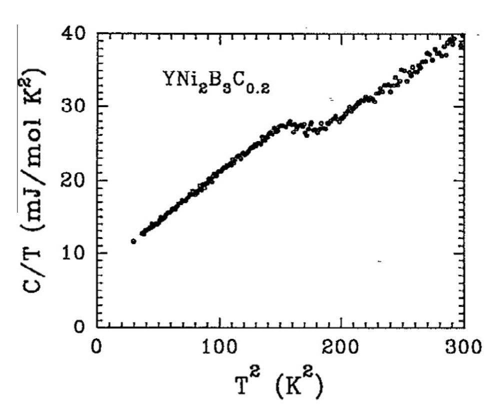

Fig. 2. Temperature dependence of specific heat (C/T vs T^2) of the sample with nominal composition $YNi_2B_3C_{0.2}$ (figure reproduced from Ref. [6]).