Bulk Superconductivity at an Elevated Temperature ($T_c \approx 12$ K) in a Nickel Containing Alloy System Y-Ni-B-C

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We report here our discovery of bulk superconductivity at rather high T_c in samples having nominal compositions $YNi_4BC_{0.2}$ ($T_c \approx 12.5$ K) and $YNi_2B_3C_{0.2}$ ($T_c \approx 13.5$ K). While $YNi_4BC_{0.2}$ seems to be a single phase material, $YNi_2B_3C_{0.2}$ is a multiphase system. Our experimental results show that the two materials are distinct superconductors. Discovery of superconductivity in these materials is of significance since not only is their T_c high (> 10 K) but they also have nickel in large proportions. No nickel-based ternary superconductor was previously known.

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We have been studying the magnetic properties of several systems of the series $RENi_4B$ (*RE* denotes rare earth) and reported recently [1] on possible superconductivity in samples of nominal composition YNi_4B. A sharp drop in resistance, but not zero resistance, was observed in this system at $\approx$12 K. Attempting to improve superconducting properties, we tried various chemical compositions $Y_xNi_yB_z$. To some of the samples, carbon was also added in small quantities, which dramatically enhanced their superconducting volume fraction (see below). Our results are very significant because generally, superconductors with ferromagnetic elements such as Fe, Co, or Ni as one of the constituents have rather low T_c. Further, only a few nickel-containing binary superconductors are known in the literature and their T_c are less than 5 K [2]. No Ni-based ternary superconductor was previously known. Thus identifying superconducting ternary alloys containing as much as 60 at. % nickel is of general interest. In this Letter, we present our results on systems having nominal composition $YNi_4BC_{0.2}$ (essentially single phase) and $YNi_2B_3C_{0.2}$.

Materials were prepared by standard arc-melting techniques. Overall loss in weight of the samples in the entire melting process was < 2%. The powder x-ray diffraction pattern of $YNi_4BC_{0.2}$ (Fig. 1) was indexed on the basis of hexagonal-type structure (space group *P6/mmm*) having $a = 4.982$ Å and $c = 6.948$ Å . Direct-current resistivity of $YNi_4BC_{0.2}$ clearly shows a superconducting transition with $T_{onset} = 12.5$ K and $T_{zero} = 11.2$ K; see Fig. 2. Alternating-current (313 Hz) susceptibility measurements using an rms field of $\approx$1.5 G show a sharp diamagnetic response around the same temperature. Several independently prepared samples were examined which gave similar results thereby confirming the occurrence of superconductivity in the material.

The homogeneity of the material and its elemental composition were examined using energy dispersive x-ray analysis (EDAX). The electron microscopic images, a typical example of which is shown in Fig. 3, suggest that the material has a uniform composition with some small, isolated inclusions (white spots in Fig. 3). Yttrium and

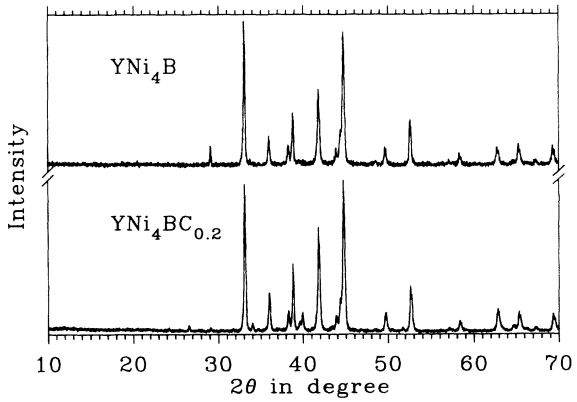

FIG. 1. Room temperature powder x-ray diffraction patterns of YNi_4B and $YNi_4BC_{0.2}$ using Cu $K\alpha$ radiation.

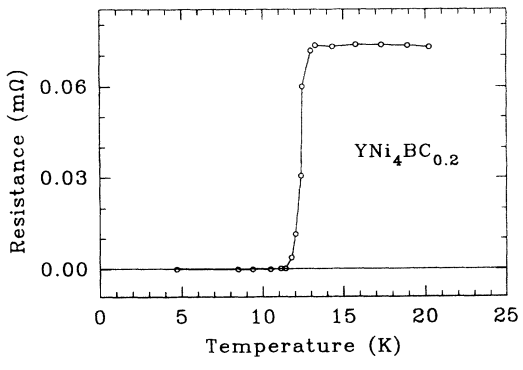

FIG. 2. dc electrical resistance as a function of temperature for the sample $YNi_4BC_{0.2}$.

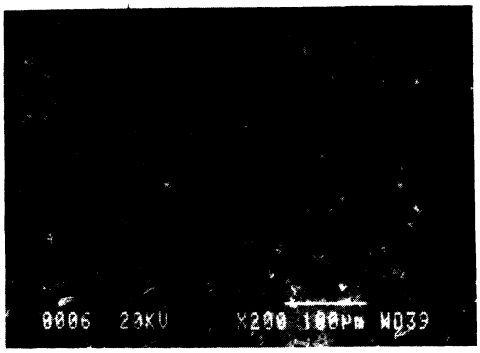

FIG. 3. Typical electron microscope image of a polished surface of $YNi_4BC_{0.2}$.

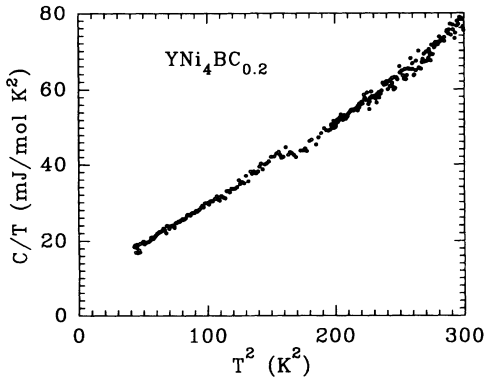

FIG. 4. Specific heat (C/T vs T^2) of $YNi_4BC_{0.2}$.

nickel are distributed homogeneously in the ratio Y:Ni = 20:80 (±3%). Concentration of boron and carbon could not be determined in our EDAX facility. However, considering that there was negligible loss in weight in the synthesis, the material should have boron and carbon as in the starting composition. The material has a tendency to be porous. The inclusions have a Y:Ni ratio as 1:2. The fraction of the material belonging to inclusions as estimated from the electron microscopic studies is $< 5\%$. It is important to point out that these inclusions are unconnected (Fig. 3) and, therefore, they are not responsible for zero resistance and superconductivity. Additional weak lines in the x-ray pattern of $YNi_4BC_{0.2}$ (Fig. 1) are most likely due to the presence of these inclusions.

We point out that Y_2C_3 is reported to be a superconductor with T_c in the range of 6 to 11.5 K [3]. We rule out the presence of Y_2C_3 because (i) the x-ray diffraction pattern (Fig. 1) of $YNi_4BC_{0.2}$ does not have major lines corresponding to Y_2C_3. (ii) It is well known that the formation of Y_2C_3 requires rather stringent conditions of high temperature and pressure while our samples were prepared under flowing argon gas at atmospheric pressure. (iii) We added carbon to YNi_4B. Thus there was no free yttrium to react with carbon. (iv) Careful EDAX analysis of the material did not reveal any nickel free region that could be associated with the presence of Y_2C_3. (v) A sample of yttrium and carbon having the composition Y:C = 2:3, melted under identical conditions of synthesis, was found to be unstable, turning into a white material on exposure to air. Further, a piece of this sample which was protected from air with a coating of silicone grease did not exhibit any diamagnetism down to 5 K.

The specific heat of $YNi_4BC_{0.2}$ shows a small anomaly δC in the neighborhood of T_c (Fig. 4). γ, the temperature coefficient of electronic specific heat, obtained from the data in the range 13–18 K is quite small ≈ 1 mJ/mole K^2. According to the relationship $\delta C/\gamma T_c = 1.43$, δC at T_c in $YNi_4BC_{0.2}$ should also be small. Thus, the small δC observed in $YNi_4BC_{0.2}$ is not inconsistent with bulk superconductivity in this material.

Figure 5 shows magnetization of $YNi_4BC_{0.2}$, below T_c at 5 K as a function of externally applied field as measured using a SQUID magnetometer. The diamagnetic response at low field is comparable to that of a piece of lead of similar volume. The observed hysteresis behavior is typical of a type-II superconductor. The lower critical field (H_{c1}), defined as the applied field (while increasing the field) at which $M(H)$ deviates from linearity, is rather small ($\approx$20 G). The diamagnetic response attains a maximum at $\approx$100 G. The upper critical field H_{c2}, taken as the field at which $M(H)$ crosses zero, is $\approx$9000 G. This is, however, only a lower estimate of H_{c2} as due to the presence of a small paramagnetic impurity, $M(H)$ becomes positive and continues to increase beyond 9000 G. The diamagnetic response measured in a field of 20 G at 5 K is 82% of perfect diamagnetism. It is difficult to estimate the Meissner fraction from flux expulsion from the field-cooled M vs T curve because of considerable flux trapping. Diamagnetism is observed at 5 K in powdered samples as well (Fig. 5 inset). However, the strength of the diamagnetic response is reduced to 9.5% of perfect

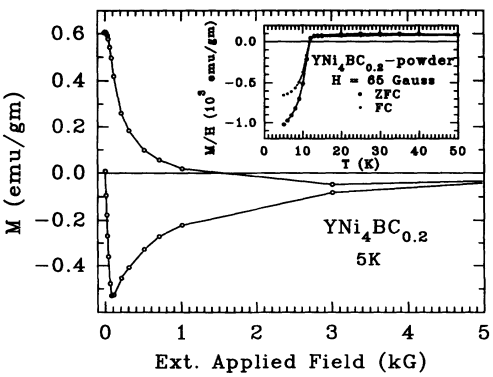

FIG. 5. Field dependence of magnetization of $YNi_4BC_{0.2}$ after cooling in zero field to 5 K. The magnetization data have been recorded both while increasing the field (up to 50 kG) and decreasing the field. The inset shows the temperature dependence of magnetic susceptibility of powdered $YNi_4BC_{0.2}$ at the field of 65 G both at zero field cooled (ZFC) and field cooled (FC) conditions.

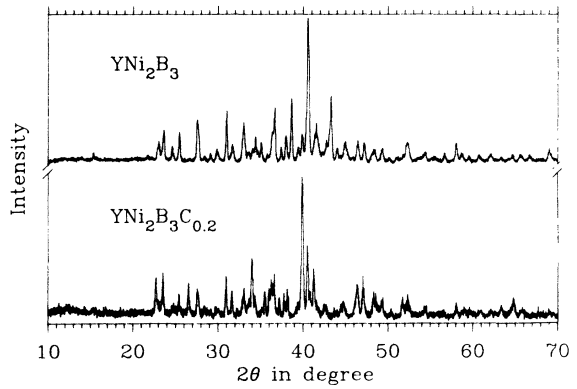

FIG. 6. Room temperature powder x-ray diffraction patterns of the material with nominal compositions YNi_2B_3 and $YNi_2B_3C_{0.2}$ using Cu $K\alpha$ radiation.

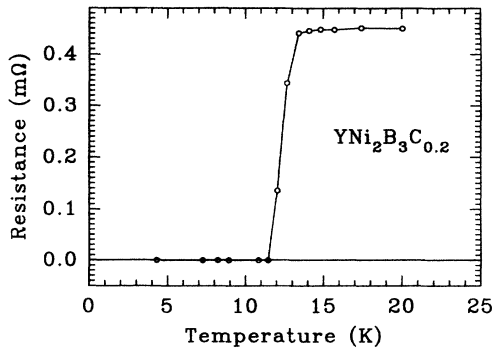

FIG. 7. dc electrical resistance as a function of temperature for the sample with nominal composition $YNi_2B_3C_{0.2}$.

diamagnetism at 5 K in a field of 65 G. A reduction of the diamagnetic signal on powdering a material is not unusual and has been reported to be so in other superconducting materials. The Meissner fraction deduced from the field expulsion is ≈6%, which is much better than that observed in a solid piece of $YNi_4BC_{0.2}$. This reconfirms the bulk nature of superconductivity in $YNi_4BC_{0.2}$.

We now comment upon the bulk nature of superconductivity in $YNi_4BC_{0.2}$ *vis-à-vis* the possibility of its relationship with the crystallographic superstructure of YNi_4B. As mentioned earlier, addition of carbon to YNi_4B leads to a dramatic enhancement of superconducting properties. Carbon seems to modify the superstructure of YNi_4B as well; see Fig. 1. The major difference in the x-ray patterns of the samples with and without carbon is that the line at $d = 3.060$ Å, attributed to the superstructure in YNi_4B, is suppressed in the carbon-doped material. The primary structure, however, remains unchanged. This means that addition of carbon retards the formation of superstructure and increases the fraction of the sample that is free from superstructure. We are led to conclude that the fraction of the sample $YNi_4BC_{0.2}$ with primary structure is responsible for the superconductivity. We point out here that electronic properties do depend on superstructure [4].

In view of the fact that the Y-Ni-B phase diagram is known to contain many other phases, we investigated several other nominal compositions of $Y_xNi_yB_zC_{0.2}$. The material with nominal composition $YNi_2B_3C_{0.2}$ turned out to be a superconductor exhibiting a large δC.

We would like to emphasize that superconductivity in samples of this composition does not arise from $YNi_4BC_{0.2}$ or Y_2C_3. A powder x-ray diffraction pattern of $YNi_2B_3C_{0.2}$ is shown in Fig. 6. Note that this is quite different from that of $YNi_4BC_{0.2}$ (Fig. 1). In the literature, YNi_2B_3 has been suggested to be isostructural with tetragonal $CeNi_2B_3$ [5], but the structural details have not been worked out. The pattern does contain certain lines which correspond to the phase $YNi_4BC_{0.2}$, but the intensity of such lines, in relation to the intensity of other diffraction lines, suggests that $YNi_4BC_{0.2}$, even if present, cannot be the major phase in the material. Further δC, at T_c, is larger in this material (see below), and the major x-ray diffraction lines reported for Y_2C_3 are also not observed in the x-ray pattern.

Our EDAX results indicate that the material $YNi_2B_3C_{0.2}$ is multiphase with three prominent phases. Since, as mentioned above, our EDAX equipment cannot determine boron and carbon concentrations, we comment upon the composition of phases only in terms of yttrium and nickel concentrations. Phase boundaries are not well demarcated in the electron microscopic image. This makes it difficult to quantify the relative amounts of different phases present in the material. We estimate that the major phase has a Y:Ni ratio of 1:2. Some regions have a phase with a Y:Ni ratio as 1:4 and some other regions have a Y:Ni ratio as 4:1. A noteworthy aspect of this analysis is that no nickel-free region was

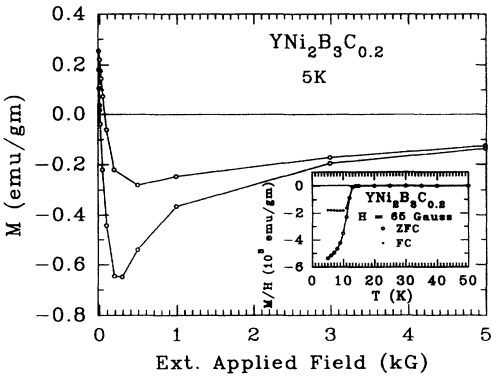

FIG. 8. Field dependence of magnetization of the material with nominal composition $YNi_2B_3C_{0.2}$ after cooling in zero field to 5 K. The magnetization data have been recorded both while increasing the field (up to 50 kG) and decreasing the field. The inset shows the temperature dependence of magnetic susceptibility of a piece of the material with nominal composition $YNi_2B_3C_{0.2}$ at the field of 65 G both at zero field cooled (ZFC) and field cooled (FC) condition.

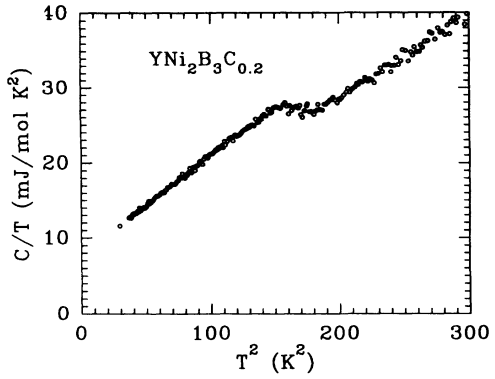

FIG. 9. Specific heat (C/T vs T^2) of the material with nominal composition $YNi_2B_3C_{0.2}$.

detected excluding the presence of Y_2C_3 in the material.

The temperature dependence of resistance of the material with the nominal composition $YNi_2B_3C_{0.2}$ exhibits a rather sharp transition to zero resistance at 11.5 K (Fig. 7). Onset of superconductivity occurs at $\approx$13.4 K. Alternating-current susceptibility measurements show a diamagnetic response confirming the superconducting nature of the transition.

The dc magnetization measurements were carried out on a piece of the material using the SQUID magnetometer. Figure 8 shows that this material also behaves like a type-II superconductor with an H_{c2} of about 30 kG. The diamagnetic response at 5 K and in a field of 65 G in the field-cooled condition is about 50% of that expected for perfect diamagnetism (inset Fig. 8). The Meissner fraction estimated from the flux expulsion in the field-cooled condition at 5 K in a field of 65 G is about 16.5%. Powdered material also exhibits diamagnetism. All these results confirm that a good fraction of the material is a bulk superconductor.

Results of specific heat measurements of this material are shown in Fig. 9. γ obtained from these data T_c is $\approx$7 mJ/(mol K^2), which is substantially larger than that of $YNi_4BC_{0.2}$. From the value of γ and the observed δC, we estimate that about 1/3 of the sample $YNi_2B_3C_{0.2}$ superconducts. These results lead us to conclude that there is a major superconducting phase in $YNi_2B_3C_{0.2}$ and that this phase is distinct from $YNi_4BC_{0.2}$.

In conclusion, we have shown that the nickel-based compound $YNi_4BC_{0.2}$ exhibits superconductivity with a rather high T_c, $\approx$12 K. Addition of carbon to the system introduces a crucial modification in its structure; namely, superstructure is suppressed. The primary structure, which favors superconductivity, is essentially unaffected. We have discussed results of our measurements of superconductivity in another nickel-based system of nominal composition $YNi_2B_3C_{0.2}$ ($T_c\approx$13 K). We have argued that this material has a superconducting phase which is distinct from $YNi_4BC_{0.2}$. We believe that there are other compounds in the phase diagram of the alloy system Y-Ni-B-C that exhibit superconductivity at $T_c > 10$ K.

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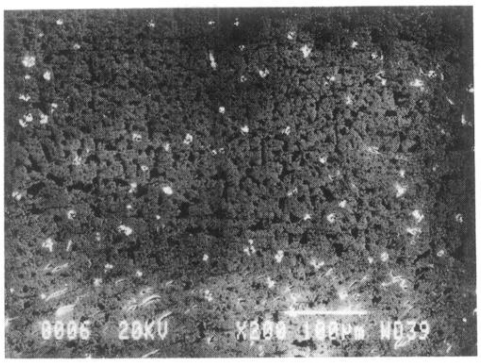

FIG. 3. Typical electron microscope image of a polished surface of $YNi_4BC_{0.2}$.