Strong magnetic pair breaking and weak magnetic exchange interaction among R ions in $(Y,R)Pd_2B_2C$

G. Ghosh,[1] A. D. Chinchure,[1,*] R. Nagarajan,[1] C. Godart,[2] and L. C. Gupta[1]
[1]*Department of Condensed Matter Physics and Materials Science, Tata Institute of Fundamental Research, Mumbai 400 005, India*
[2]*C.N.R.S., UPR209, ISCSA, F-94320 Thiais, France*
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In multiphase material $YPd_5B_3C_{0.35}$ of the Y-Pd-B-C system, YPd_2B_2C (space group *I4/mmm*) is believed to be the superconducting phase ($T_c \approx 23$ K). Despite the nonavailability of the superconducting phase YPd_2B_2C in pure form, we have been able to obtain crucial information on the magnetic pair breaking and magnetic exchange interaction among R ions in the RPd_2B_2C ($R=$Y, rare-earth elements) system by studying multiphase $Y(R)Pd_5B_3C_{0.35}$ materials. Strong pair-breaking effects are observed in $Y_{0.9}R_{0.1}Pd_5B_3C_{0.35}$; for instance, ΔT_c—the depression of the superconducting transition temperature T_c—is ≈ 8 K for $R=$Gd. $\Delta T_c(R)$, except for $R=$Ce, Eu, and Yb, nearly follows the de Gennes scaling $\Delta T_c \propto (g_J-1)^2 J(J+1)$, both for light as well as heavy rare-earth atoms. ΔT_c (≈ 8.5 K) is anomalously large for $R=$Ce. Magnetic exchange interaction among R ions is rather weak in RPd_2B_2C as is inferred from our studies in $DyPd_5B_3C_{0.35}$, which does not exhibit a magnetic transition down to 1.7 K. Our present investigations bring out striking dissimilarities in the superconducting and magnetic properties of the materials of RPd_2B_2C vis-à-vis those of RNi_2B_2C.

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I. INTRODUCTION

Immediately after the discovery of superconductivity at an elevated T_c (≈ 13 K) in the multiphase quaternary borocarbide system Y-Ni-B-C (Ref. 1) there has been continued and increasing interest in borocarbide quaternary superconducting materials. The superconducting phase YNi_2B_2C (Refs. 2 and 3) in the Y-Ni-B-C system belongs to a tetragonal structure related to the well-known $ThCr_2Si_2$ structure (*I4/mmm*). Tremendous progress has been made in the studies of RNi_2B_2C, particularly on several aspects of interplay of the superconductivity and long-range magnetic order.[4] This was possible essentially because RNi_2B_2C materials are available as single phase in all three physical forms, namely, polycrystalline, single crystals, and thin films.

In sharp contrast, not much is known on the superconducting properties in the Pd-containing multiphase superconducting system $YPd_5B_3C_{0.35}$ having a high $T_c \approx 23$ K (Ref. 5), the highest reported in bulk intermetallics. This is because it has not yet been possible to synthesize the superconducting phase in pure form though it has been shown[6] that YPd_2B_2C with $LuNi_2B_2C$-type tetragonal structure is responsible for superconductivity. Single phase material YPd_2B_2C ($T_c=22$ K) has been isolated only in micrograin-sized samples.[7] Nonavailability of bulk samples of YPd_2B_2C has been a rather serious obstacle in making progress towards a deeper understanding of the superconducting phase in the Y-Pd-B-C system.

Notwithstanding this difficulty, in our present work, we have obtained crucial information on the magnetic pair-breaking effects and superconducting and magnetic properties of RPd_2B_2C by investigating samples of $Y_{1-x}R_xPd_5B_3C_{0.35}$ ($R=$rare earth ions; $x=0.1$) and $DyPd_5B_3C_{0.35}$. In these investigations we make the assumption that the substitution of Y by R ions takes place proportionally in all the phases belonging to the multiphase sample $YPd_5B_3C_{0.35}$.[8]

II. EXPERIMENT

Samples of nominal compositions $Y_{0.9}R_{0.1}Pd_5B_3C_{0.35}$ (R $=$La through Yb) and $RPd_5B_3C_{0.35}$ ($R=$Y, Dy), each ~ 500 mg, were prepared using a standard arc-melting technique. The samples were fast cooled by shutting off the arc abruptly, since it is known that annealing destroys superconductivity in $YPd_5B_3C_{0.35}$. Such as-cast samples were used in all the measurements. X-ray-diffraction measurements were made on powder samples using Siemens D-500 or Philips PW1510 automatic diffractometers. The superconducting transition temperature T_c was determined for all samples by measuring ac susceptibility $\chi_{ac}(T)$ (frequency = 313 Hz and rms field ≈ 1 G) as a function of temperature in the interval 4-35 K. Dc resistivity also was measured as a function of temperature in selected samples using a four-probe method in the same temperature interval. Dc magnetization was studied in a field of 5 kG as a function of temperature over the interval 1.7–300 K using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design).

At least two batches of each sample were prepared and measured to check the reproducibility of T_c, which was found to be better than 1 K.

III. RESULTS AND DISCUSSION

A. X-ray diffraction

Figure 1 shows the powder x-ray-diffraction pattern of the sample $YPd_5B_3C_{0.35}$ which, as reported by Cava *et al.*[5] is multiphase. It contains YPd_2B_2C, the $LuNi_2B_2C$-type body-centered-tetragonal phase; the diffraction lines corresponding to YPd_2B_2C are marked in the figure with the corresponding indices. YPd_7B_4, having a centered orthorhombic structure,[6] is the majority phase. Lattice parameters, calculated from the diffraction pattern, for the two phases are a = 3.757 and c = 10.739 Å for YPd_2B_2C and a = 8.481, b = 9.056, and c = 16.518 Å for YPd_7B_4. Values of the 1221 phase are con-

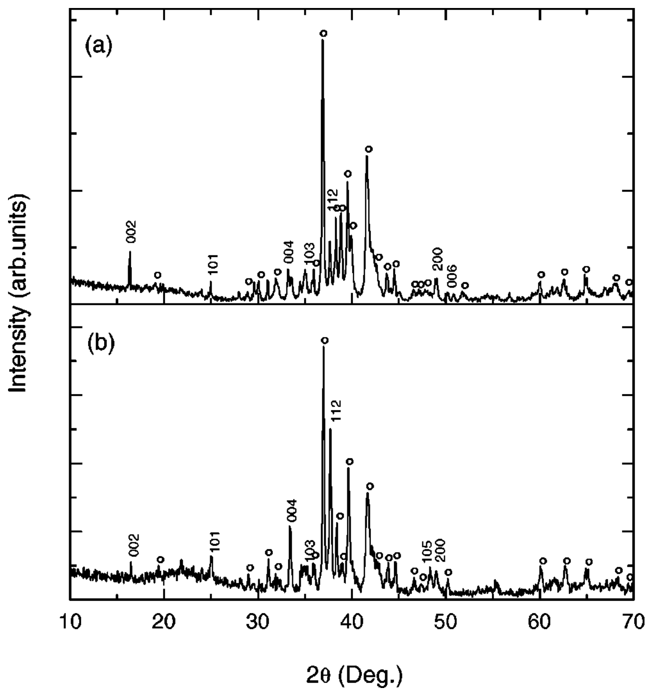

FIG. 1. X-ray-diffraction patterns of $R\mathrm{Pd_5B_3C_{0.35}}$; (a) $R=\mathrm{Y}$ and (b) $R=\mathrm{Dy}$. The indexed lines correspond to the tetragonal phase $R\mathrm{Pd_2B_2C}$ and open-circle-marked lines correspond to the orthorhombic $R\mathrm{Pd_7B_4}$ phase.

sistent with those reported in the single phase, micrograin-sized sample.[7] Figure 1 also shows the x-ray-diffraction pattern of $\mathrm{DyPd_5B_3C_{0.35}}$. Just as in $\mathrm{YPd_5B_3C_{0.35}}$, lines corresponding to the 1221 phase are easily discerned. We obtain the lattice constants of $\mathrm{DyPd_2B_2C}$ as a = 3.756 and c = 10.682 Å.

The lattice parameters of $\mathrm{Y_{0.9}}R_{0.1}\mathrm{Pd_2B_2C}$ as derived from the x-ray-diffraction data of $\mathrm{Y_{0.9}}R_{0.1}\mathrm{Pd_5B_3C_{0.35}}$ are shown in Table I. The a parameter (R-R distance) shows the trend of the lanthanide contraction as it is observed in the $R\mathrm{Ni_2B_2C}$ series and in $R\mathrm{Pd_2B_2C}$ [$R=$La, Ce(3+), and Y]. A trend is not discernible in the c parameter.

TABLE I. Lattice parameters a and c of $\mathrm{Y_{0.9}}R_{0.1}\mathrm{Pd_2B_2C}$ (R = rare-earths elements) as inferred from x-ray-diffraction patterns of $\mathrm{Y_{0.9}}R_{0.1}\mathrm{Pd_5B_3C_{0.35}}$.

Rare-Earth elements	a (Å)	c (Å)
La	3.788	10.724
Ce	3.779	10.687
Pr	3.769	10.687
Nd	3.771	10.689
Sm	3.765	10.712
Eu	3.756	10.689
Gd	3.763	10.735
Tb	3.763	10.745
Dy	3.753	10.691
Ho	3.750	10.723
Er	3.748	10.754
Tm	3.748	10.709
Yb	3.750	10.721
Y	3.757	10.739

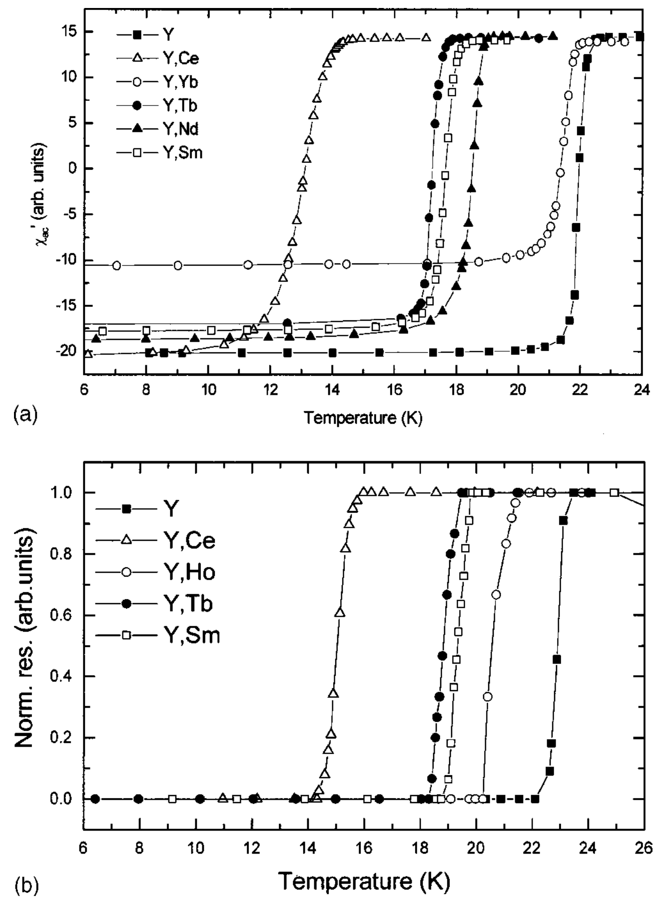

FIG. 2. (a) ac susceptibility χ_{ac} and (b) dc resistivity for $\mathrm{Y_{0.9}}R_{0.1}\mathrm{Pd_5B_3C_{0.35}}$ as a function of temperature; different symbols correspond to different R ions as indicated in figures. The lines are guides for the eye.

B. Strong magnetic pair breaking and large depression of T_c by magnetic impurity in $\mathrm{YPd_2B_2C}$

$T_c(R)$ was determined for the samples $\mathrm{Y_{0.9}}R_{0.1}\mathrm{Pd_5B_3C_{0.35}}$ ($R=$La, Ce, Pr, Sm, Eu, Gd, Tb, Dy, Er, Ho, Tm, and Yb) from $\chi_{ac}(T)$ measurements. Resistivity also was measured for selected samples ($R=$Y, Ce, Ho, Tb, and Sm). Figure 2(a) shows the $\chi_{ac}(T)$ of the samples with $R=$Y, Ce, Nd, Sm, Tb, and Ho (others are not shown for reasons of clarity) while Fig. 2(b) shows results of the dc-resistivity measurements. Figure 3 shows measured ΔT_c [$=T_c(\mathrm{Y})-T_c(R)$] and also ΔT_c calculated on the basis of the de Gennes scaling [$G=(g_J-1)^2J(J+1)$] and normalized with respect to the experimentally observed ΔT_c in $\mathrm{Y_{0.9}Gd_{0.1}Pd_5B_3C_{0.35}}$. These results do establish that the rare-earth ions are incorporated in the superconducting phase, which we take as $\mathrm{Y_{0.9}}R_{0.1}\mathrm{Pd_2B_2C}$ in these materials.

From the data shown in Fig. 3, it is clear that there is an appreciable depression of T_c due to nonmagnetic effects (ex-

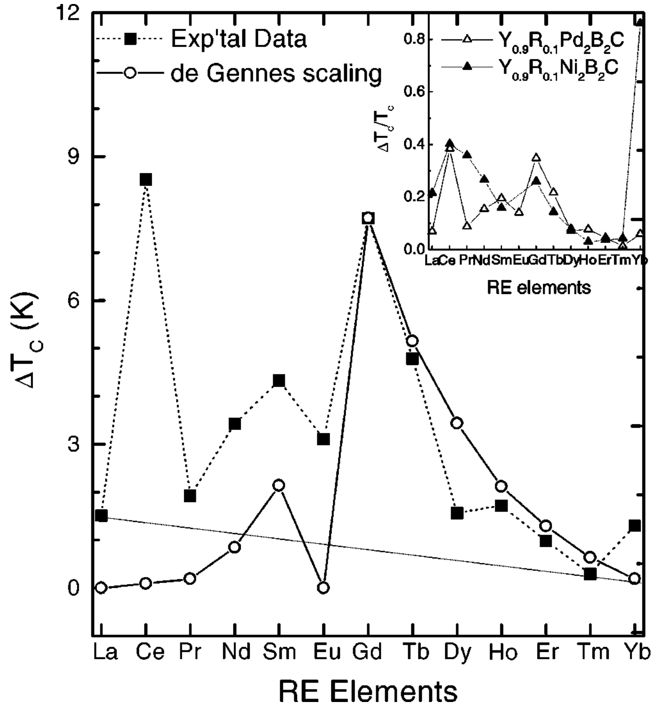

FIG. 3. ΔT_c $[=T_c(\mathrm{Y})-T_c(R)]$ vs the rare-earth atoms. $T_c(\mathrm{Y})=T_c$ in $YPd_5B_3C_{0.35}$ and $T_c(R)=T_c$ in $Y_{0.9}R_{0.1}Pd_5B_3C_{0.35}$. The filled squares are experimental values. The open circles are theoretical values obtained using de Gennes scaling factor (G, see text). The inset shows the comparison of $\Delta T_c(R)/T_c(\mathrm{Y})$ in $Y_{0.9}R_{0.1}Pd_5B_3C_{0.35}$ (open triangles, this work) and $Y_{0.9}R_{0.1}Ni_2B_2C$ (filled triangles, Ref. 10). The lines are guides for the eye. The dashed line represents the depression due to nonmagnetic effects (see text).

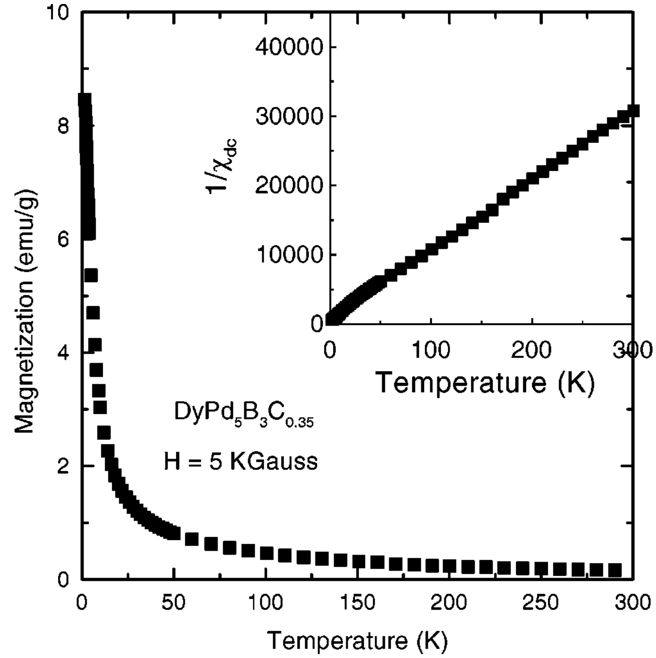

FIG. 4. dc magnetization versus temperature for $DyPd_5B_3C_{0.35}$. The inset shows the inverse of dc susceptibility ($1/\chi_{dc}$) versus temperature for the two materials.

emplified by ΔT_c measured for nonmagnetic La ions) such as a mismatch of the size of the dopant rare-earth ion and the resulting variation of lattice constants and band structure. Such effects have been observed, for example, in $LuRh_4B_4$.[9] In Fig. 3, the line drawn between the data points of La and Tm (Yb is not considered as its T_c is rather anomalous) gives an estimate of the depression of T_c due to the nonmagnetic effect for different R ions.

In order to bring out the difference of magnetic pair breaking in YPd_2B_2C and YNi_2B_2C, we show in Fig. 3 $\Delta T_c(R)/T_c(\mathrm{Y})$ for $Y_{0.9}R_{0.1}Pd_2B_2C$ as measured in our present studies and in $Y_{0.9}R_{0.1}Ni_2B_2C$ as reported in Ref. 10. There is a number of striking dissimilarities between the two cases [we abbreviate Y(Pd) and Y(Ni), respectively for brevity].

(i) ΔT_c due to magnetic R ions (estimated with respect to the line representing nonmagnetic effect in Fig. 3) introduced as impurity ions in YPd_2B_2C nearly follows de Gennes scaling. The trend of pair breaking by magnetic light rare-earth elements Pr, Nd, and Sm in Y(Pd) is consistent with the de Gennes scaling. However, as shown in the inset of Fig. 3, these elements show strong deviation from de Gennes scaling in Y(Ni).

(ii) $\Delta T_c(\mathrm{Ce})/T_c(\mathrm{Y})$ is nearly the same in the two cases. However, if the proper allowance is made for the nonmagnetic effect, it is clear that pair breaking effect of Ce ions is much stronger in Y(Pd) than in Y(Ni).

(iii) Gd causes stronger pair breaking in Y(Pd) than in Y(Ni). This has implications with respect to the difference in band structure and density of states at the Fermi level E_F in the two cases.

(iv) The effect of Yb in Y(Pd) is higher than that expected from de Gennes scaling. This may be suggestive of a hybridization effect of the Yb ion. However, the observed effect is much smaller than in Y(Ni).

(v) Eu ions lead to a depression that is somewhat more than that expected from de Gennes scaling (taking Eu to be trivalent, $J=0$ in a nonmagnetic state). Considering the anomalous behavior of substitutions of Ce and Yb, it is possible that some effect of hybridization is present in this case also. It will be interesting to investigate the valence of Eu in this material by ^{151}Eu Mössbauer spectroscopy.

C. Low T_N in RPd_2B_2C

In order to infer about magnetic and superconducting (possible) properties of RPd_2B_2C (R=magnetic rare-earths metals), we investigated the material $DyPd_5B_3C_{0.35}$. This material was chosen considering that $DyNi_2B_2C$ has the highest T_N among the magnetic superconducting Ni-containing materials RNi_2B_2C (R=Dy, Ho, Er, and Tm).

As mentioned earlier, the multiphase sample of $DyPd_5B_3C_{0.35}$ does contain a 1221 tetragonal phase (Fig. 1). We measured the dc magnetic susceptibility (χ_{dc}) of this sample in the temperature interval 1.7–300 K in an applied field of 5 kG (in zero-field-cooled mode). No magnetic transition was observed in this sample down to 1.7 K (Fig. 4). It, therefore, follows that none of the phases, including

$DyPd_2B_2C$, which is relevant with respect to the present investigations, undergoes a magnetic transition at $T<2$ K. Further, the plot of $1/\chi_{dc}$ versus temperature (see the inset, Fig. 4) is a straight line with θ_P, the paramagnetic Curie temperature nearly zero. μ_{eff} is estimated to be $\approx 9.9\mu_B$, which is close to the free-ion value of Dy ions. Much reduced T_N (<2 K) and $\theta_P \approx 0$ in $DyPd_2B_2C$ clearly suggests that indirect exchange interaction [Ruderman-Kittel-Kasuya-Yosida (RKKY)] among R ions is much weaker in RPd_2B_2C than in RNi_2B_2C. There seems to be a drastic modification of the conduction-electron polarization at the rare-earth sites in the Pd system compared to the Ni-containing materials RNi_2B_2C.

Further, no diamagnetic response is seen down to 1.7 K in zero-field-cooled state low dc-field magnetic susceptibility (applied magnetic field ≈ 10–20 G), suggesting absence of superconductivity down to 1.7 K in $DyPd_2B_2C$. This must be compared with $T_c \approx 6$ K in $DyNi_2B_2C$.

IV. CONCLUSION

We have investigated superconductivity in $Y_{0.9}R_{0.1}Pd_5B_3C_{0.35}$ and have looked for magnetic and superconducting transitions in $DyPd_5B_3C_{0.35}$, studied as a typical magnetic RPd_2B_2C material. Even though the samples are multiphase, we have argued and shown that it is possible to get useful results. We find that ΔT_c in YPd_2B_2C due to light and heavy rare-earth elements introduced as impurities follows nearly de Gennes scaling. T_c and T_N are less than 1.7 K in any of the phases in $DyPd_5B_3C_{0.35}$. These results reveal strong magnetic pair breaking and rather weak RKKY interaction among R ions in RPd_2B_2C. This important result brings in focus the basic difference in magnetic and superconducting properties of the two series RNi_2B_2C and RPd_2B_2C. The present work provides a strong motivation to synthesize RPd_2B_2C in pure bulk form. Because of strong pair breaking and weak RKKY interaction, these materials may reveal certain new aspects of interplay of superconductivity and magnetism.

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*Present address: Kammerlingh Onnes Laboratory, Leiden University, 2300 RA Leiden, The Netherlands.

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