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Competition between magnetism and superconductivity in rare-earth nickel boride carbides

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The competition between magnetism and superconductivity was investigated for the recently discovered $R\mathrm{Ni_2B_2C}$ superconductors with the magnetic rare-earth elements R=Tm,Er,Ho,Dy. The systematic decrease of T_c, approximately scaled by the de Gennes factor, implies a very weak coupling between the rare-earth magnetic moments and the conduction electrons due to a small conduction-electron density at the rare-earth site. Associated with the antiferromagnetic order of the rare-earth moments, a pronounced dip structure in the upper critical field $H_{c2}(T)$ was observed; a similar structure has been seen in the previously known magnetic superconductors $R\mathrm{Rh_4B_4}$ and $R\mathrm{Mo_6S_8}$. For $\mathrm{HoNi_2B_2C}$, the pair-breaking associated with the magnetic transition is strong enough to bring about a resistive reentrant behavior even under zero field, an effect which, to our knowledge, has not previously been observed in antiferromagnetic superconductors.

The discovery of a family of high-T_c boride carbides, $R\mathrm{Ni_2B_2C}$ (R=Lu,Tm,Er,Ho,Y, T_c=16.6 K for $\mathrm{LuNi_2B_2C}$), as well as mixed-phase Y-Pd-B-C (T_c=23 K) has provided fresh incentive to drive superconductivity research.[1–4] Initial characterization of their superconducting parameters[5] has revealed that a moderately high density of states at the Fermi level, comparable to that of $A15$ compounds, is part of the reason for the high T_c. The question of whether or not any exotic mechanism plays a role in these high-T_c superconductors, however, still remains to be settled. One of their fascinating features is that superconductivity is observed not only for the nonmagnetic rare-earth elements, but also for the heavy magnetic rare earths, Tm, Er, and Ho.[1] Information on the interaction between the rare-earth magnetic moment and the conduction electrons is of benefit in elucidating the character of the conduction electrons. The discovery of these magnetic superconductors furthermore leads one to expect the occurrence of a variety of exotic phenomena associated with the competition between magnetism and superconductivity.

Competition between superconductivity and magnetism has been one of the main topics of study in the field of superconductivity research. In conventional s-wave superconductors, local magnetic moments break up spin singlet cooper pairs and hence strongly suppress superconductivity, an effect known as magnetic pair-breaking. Because of the pair-breaking effect, in most superconductors the presence of only a 1% level of magnetic impurity can result in the almost complete loss of superconductivity.[6] In a very limited number of compounds, however, superconductivity occurs even though magnetic ions with a local moment occupy all of one specific crystallographic site. This can occur when the crystallographic site for the magnetic ions is well isolated from the conduction path and therefore the interaction between the local magnetic moment and the conduction electrons is substantially weak. The study of this class of magnetic superconductors was initiated by the discovery of $R\mathrm{Rh_4B_4}$ (Ref. 7) and $R\mathrm{Mo_6S_8}$ (Ref. 8) (R=magnetic rare-earth elements), followed by further discoveries of materials with similar behavior. The coexistence of superconductivity and a very high density of local moments in these compounds results in a number of exotic phenomena associated with the long-range order of local magnetic moments, such as reentrant superconductivity and anomalous upper critical field behavior.[9] In this paper, we demonstrate that the boride carbide superconductors with magnetic rare-earth elements belong to the same class of magnetic superconductors as do $R\mathrm{Rh_4B_4}$ and $R\mathrm{Mo_6S_8}$, and show the coexistence of antiferromagnetism and superconductivity.

The $R\mathrm{Ni_2B_2C}$ (R=Ho, Er, Tm, Dy, and Tb) samples used in this study were prepared by arc-melting and subsequent annealing, as described in our previous paper.[1] The powder x-ray diffraction patterns demonstrate that the polycrystalline materials are single-phase $R\mathrm{Ni_2B_2C}$. Bar-shaped samples were cut from the ingots for resistivity and magnetic susceptibility measurements. The resistivity measurements were performed by the conventional four-probe technique, and the magnetic susceptibility measurements were performed in a commercial SQUID magnetometer.

In Fig. 1, temperature-dependent resistivities for $R\mathrm{Ni_2B_2C}$ are shown. As reported previously,[1] a systematic decrease of resistive superconducting transition temperature is observed for $R\mathrm{Ni_2B_2C}$ on going from Lu (T_c=16.6 K) to Ho (T_c=7.5 K). We observe a small resistivity drop for Dy, likely due to superconductivity around 2 K, and no trace of superconductivity for Tb. A noticeable change in the temperature dependence of resistivity can be seen for Dy and Tb at around 10 and 15 K, respectively. Resistivity measurements under magnetic field and with much higher applied current indicate that they are not due to superconductivity.

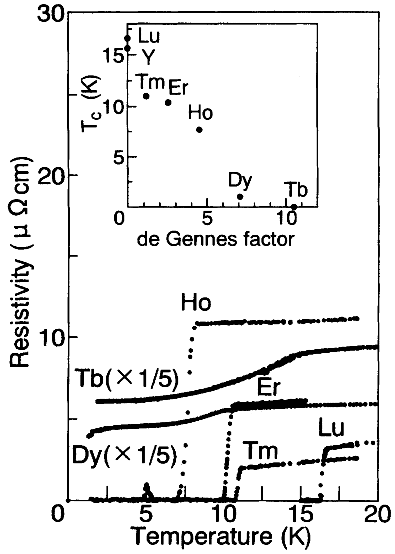

FIG. 1. Temperature-dependent resistivities for $R\mathrm{Ni_2B_2C}$ (R =Lu, Tm, Er, Ho, Dy, and Tb). Inset: Superconducting transition temperature T_c versus de Gennes factor for $R\mathrm{Ni_2B_2C}$.

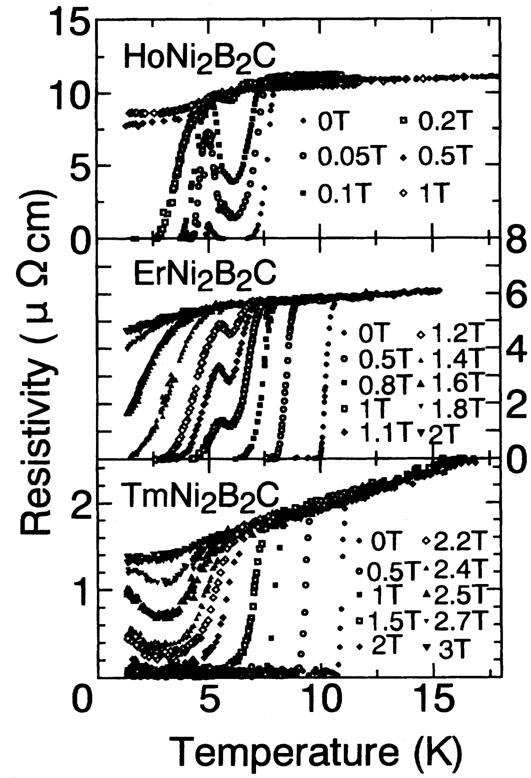

FIG. 2. Temperature-dependent resistivities under various magnetic fields for $\mathrm{HoNi_2B_2C}$, $\mathrm{ErNi_2B_2C}$, and $\mathrm{TmNi_2B_2C}$.

Indeed, the magnetic susceptibility measurements on these samples indicate that the resistive anomalies are associated with antiferromagnetic ordering.

In the inset to Fig. 1, the transition temperatures are plotted as a function of the de Gennes factor DG= $(g-1)^2J(J+1)$, demonstrating that the decrease of T_c is roughly scaled by DG. This gives evidence for the dominance of the magnetic pair-breaking effect in the systematic change of T_c with rare-earth element. In Abrikosov-Gor'kov theory, which quantitatively describes the magnetic impurity effect in superconductors, the initial depression of T_c due to magnetic pair-breaking, $\Delta T_c/T_c$, is essentially given by $nI^2N(0)\mathrm{DG}$ [n is the number of magnetic moments, I is the exchange constant, and $N(0)$ is the density of states at the Fermi level]. Assuming that I is constant for all the compounds and using the density of states $\gamma \sim 35$ mJ/mol K^2,[5] an exchange constant $I \sim 13$ meV is estimated from the T_c slope, $dT_c/d\mathrm{DG}$, seen in the inset to Fig. 1. This exchange constant is almost comparable to those of $R\mathrm{Rh_4B_4}$ and $R\mathrm{Mo_6S_8}$, and is appreciably smaller than is found in the rare-earth binary intermetallics.[10] This implies that the conduction electron density at the R site is as small as those for the magnetic cluster compounds. The single-crystal x-ray study has revealed that $R\mathrm{Ni_2B_2C}$ has a layered structure, with alternative stacking of Ni two-dimensional (2D) squared lattice sandwiched by B layers, and rocksalt-type RC layers.[2] Anisotropic upper critical field measurements on single crystals of the Lu- and Y-based compounds indicate, however, that the new boride carbide superconductors are, despite their layered structure, electronically three dimensional rather than two dimensional.[11] We may therefore infer that three-dimensional conduction between Ni layers is primarily achieved through B and C $2p$ orbitals.

Due to the coexistence of superconductivity and rare-earth magnetic moments, exotic transition behaviors, as are observed in the existing antiferromagnetic superconductors, can indeed be seen under a magnetic field for all of the new magnetic superconductors studied here. Figure 2 shows the resistive transitions under magnetic field for Tm, Er, and Ho nickel boride carbides. The most pronounced anomaly is observed in the Ho compound. Under fields below 0.2 T, the first resistive transition to a superconducting state is seen above 5 K. Below this first transition temperature, a sharp resistivity peak suddenly emerges around 5 K. This indicates that the compound recovers the normal state, and then returns to the superconducting state again at lower temperatures. It is natural to ascribe the observed anomaly to a long-range ordering of the rare-earth moments. Since the magnetic ordering coexists with superconductivity at low temperatures, the ordering is very likely to be antiferromagnetic. Similar anomalies can be seen below 2.5 K and around 5.5 K, for the Tm and the Er compounds, respectively, but only under a modest field. For the Tm compound, the resistivity shows a continuous recovery towards the normal state and does not show any sign of coming back to the superconducting state down to the lowest temperature measured, 1.3 K.

These anomalous transition behaviors can be summarized, as shown in Fig. 3, by plotting the upper critical field $H_{c2}(T)$ curve. The resistive transition temperature at each field was defined as the midpoint of the transition. For comparison we also plot the upper critical field data for the nonmagnetic Y and Lu compounds,[5] illustrating the very strong suppression of the upper critical field in the magnetic compounds. In addition to the overall suppression of upper critical fields, a clear dip in $H_{c2}(T)$ can be seen around 5, 5.5, and 2.5 K for Ho, Er, and Tm, respectively, reflecting a sudden resistivity recovery below the first transition tempera-

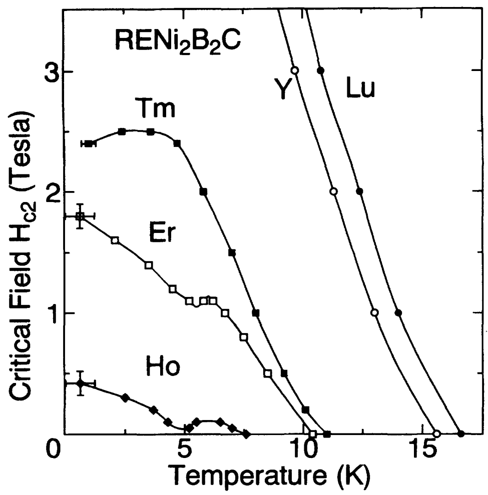

FIG. 3. The upper critical field $H_{c2}(T)$ as a function of temperature for $HoNi_2B_2C$, $ErNi_2B_2C$, and $TmNi_2B_2C$. The superconducting temperature at each field is defined as the midpoint of the resistive transition in Fig. 2.

ture. In most antiferromagnetic superconductors, the magnetic transition manifests itself as a dip in the $H_{c2}(T)$ curve as seen in Fig. 3, indicating the presence of strong pair-breaking near the Néel temperature. The origin of the strong pair-breaking has been a subject of longstanding debate.[9] It is worth noting that the depression of superconductivity observed for the Ho compound, seen as the dip in the $H_{c2}(T)$ curve, is particularly significant when compared to the previously known antiferromagnetic superconductors. For $HoNi_2B_2C$, the resistivity peak in Fig. 2 below the first transition is seen even under zero field though the resistivity does not recover to the normal state completely likely due to sample inhomogeneity. To our knowledge, none of the previously known antiferromagnetic superconductors show any resistive reentrant behavior under zero field.

The temperature-dependent susceptibilities for the boride carbides are plotted as $1/\chi - T$ in Fig. 4. At high temperatures, the inverse susceptibility is linear in T, obeying the Curie-Weiss law $\chi = C/(T+\Theta_{CW})$. From the Curie constant C, the effective moment per rare-earth ion, p_{eff}, is estimated as $7.7\mu_B$, $9.8\mu_B$, $10.4\mu_B$, $11.1\mu_B$, and $9.9\mu_B$ for Tm, Er, Ho, Dy, and Tb, respectively, in good agreement with those expected for free trivalent ions. The extrapolation of the high-temperature linear part in Fig. 4 gives a positive $\Theta_{CW} \sim 10.8$ K for Tm and negative $\Theta_{CW} \sim -2.2$, -1.5, -9.8, and -10.2 K for Er, Ho, Dy, and Tb, respectively. This implies that, for Er, Ho, Dy, and Tb compounds, the dominant interaction between the rare-earth moments is ferromagnetic. Indeed, at low temperatures, the inverse susceptibility commonly deviates downward from the high-temperature linear behavior, indicating the development of ferromagnetic correlation. In the Dy compound which does not superconduct down to 2 K, the susceptibility decreases down 10 K as shown in the inset to Fig. 4, indicating antiferromagnetic ordering despite the negative Θ_{CW}. In the superconducting Ho compound, when a magnetic field higher than H_{c2} is applied, a similar decrease in the magnetic susceptibility is observed below 5 K. This indication of antiferromagnetic order occurs exactly at the temperature where the resistive reentrant behavior appears. This gives strong evidence that the observed reentrant behavior is indeed associated with antiferromagnetic ordering.[12] The observed antiferromagnetic ordering temperatures are roughly scaled by the de Gennes factor DG, as are the superconducting T_c's.

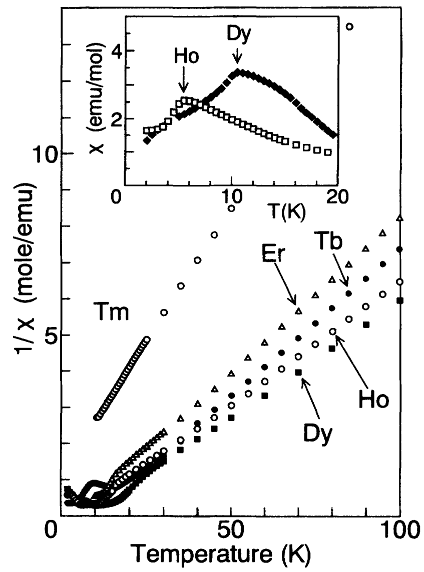

FIG. 4. The inverse susceptibility as a function of temperature for $TbNi_2B_2C$, $DyNi_2B_2C$, $HoNi_2B_2C$, $ErNi_2B_2C$, and $TmNi_2B_2C$. The applied magnetic field is 500 G. Inset: The susceptibility as a function of temperature for $DyNi_2B_2C$ and $HoNi_2B_2C$. For $HoNi_2B_2C$, a magnetic field of 5 kG, which is higher than the upper critical field H_{c2}, is applied to eliminate the diamagnetic contribution from superconductivity.

The observed anomalous behavior of the magnetic susceptibility, antiferromagnetic ordering despite the negative Θ_{CW}, strongly resembles what has been observed in metamagnets like $CoCl_2$,[13] where 2D ferromagnetic layers are weakly coupled antiferromagnetically. We therefore speculate that the rare-earth spins are strongly coupled ferromagnetically within the R-carbon layer and that a weak antiferromagnetic coupling between the ferromagnetic layers gives rise to long-range antiferromagnetic order. The presence of 2D ferromagnetic layers associated with the layered structure may be part of the reason for the unusually strong pair-breaking observed near the Néel temperature.

In summary, we have demonstrated competition between rare-earth magnetism and superconductivity in the new boride carbide superconductors $HoNi_2B_cC$, $ErNi_2B_2C$, and $TmNi_2B_2C$. This happens due to a small interaction between the conduction electrons and the rare-earth magnetic moments, comparable to those found for previously known magnetic superconductors such as RRh_4B_4 and RMo_6S_8, implying a very low conduction electron density at the R site. An anomalous depression of superconductivity has been observed at low temperatures, as has been commonly observed near the Néel temperature in antiferromagnetic superconductors. Compared with the previously known antiferromagnetic superconductors, the observed suppression is very significant. In $HoNi_2B_2C$, the suppression is strong enough to bring about resistive reentrant behavior even under zero field. We speculate that a very anisotropic spin-spin interaction, associated with the layered structure, in-plane ferromagnetic coupling, and antiferromagnetic coupling between planes, gives rise to the complicated temperature dependence of the magnetic susceptibility, and possibly the strong pair-breaking effect near the Néel temperature. A detailed examination of spin structure is needed to clarify this point. Because of their layered structure, these materials may be viewed as naturally occurring "magnet-superconductor superlattices," distinctly different from the previously known magnetic superconductors. Whether or not this feature, specific to these compounds, brings about any exotic phenomena in the competition between magnetism and superconductivity, is worthy of further exploration.

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