Heavy-electron behavior in single-crystal $YbNi_2B_2C$

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We have measured the magnetic susceptibility, specific heat, and electrical resistivity on single crystals of the intermetallic borocarbide $YbNi_2B_2C$. An enhanced linear contribution is observed in the specific heat with a Sommerfeld coefficient of 530 mJ/mol K^2, indicative of a heavy-electron system with a Kondo temperature $\sim$10 K. The magnetic susceptibility, which is anisotropic and Curie-Weiss-like at high temperatures, is also consistent with our interpretation of a strongly correlated ground state at low temperatures and crystal-electric-field excitations at higher temperatures. At $T=1.8$ K, the Wilson ratio is determined to be 0.85 using the high-temperature effective moment. The resistivity shows a quadratic temperature dependence below 1.5 K with a T^2 coefficient of 1.2 $\mu\Omega$ cm K^{-2}. Unlike the other members of the series RNi_2B_2C (R=Y, Gd–Lu), $YbNi_2B_2C$ does not order above our lowest measurement temperature of 0.34 K. The suppression of superconductivity in $YbNi_2B_2C$ is consistent with a significantly enhanced hybridization between the conduction electrons and the $4f$ states. [S0163-1829(96)51130-6]

An interesting interplay between superconductivity and local-moment magnetism was recently discovered in the series of intermetallic borocarbides RNi_2B_2C (R=Y, Gd–Tm, and Lu).[1–3] For R=Lu and Y, the compounds are moderately high-temperature superconductors with $T_c\sim$16.0 and 15.0 K, respectively. As one moves across the lanthanide series from Tm to Ho, T_c monotonically decreases, and below the superconducting transition, the compounds also antiferromagnetically order.[2,4–8] The magnetic transition temperature increases in going from Tm to Gd,[3,9] and for Dy,[3] the $T_N>T_c$. Both $TbNi_2B_2C$ (Ref. 10) and $GdNi_2B_2C$ (Ref. 9) magnetically order with no indications of superconductivity at low temperatures. The variations of T_c and T_N described above for the whole series are qualitatively consistent with de Gennes scaling.[3,9] While the coexistence of magnetism and superconductivity has been studied in other series such as $RMo_6(S,Se)_8$ and RRh_4B_4,[11] the lanthanide-nickel-borocarbide series has attracted a great deal of interest because the transition temperatures are relatively high and the crystal structure has alternating layers of Ni_2B_2 and R–C. The crystalline-electric-field (CEF) splitting of the lanthanide orbitals leads to large anisotropies in the magnetic and superconducting properties.[3,5–10,12] In this paper, we report the discovery of a heavy Fermi-liquid ground state at low temperatures in the Yb member of this series. Only a few classes of materials offer such a diverse range of phenomena as a result of changing the lanthanide element. The RNi_2B_2C series provides the scientific community with a unique opportunity for studying the interaction between magnet, superconducting, and now enhanced correlated-electron ground states.

Single crystals of $YbNi_2B_2C$ were grown using a modification of the Ames Lab Ni_2B flux growth technique.[6,13] (Polycrystalline $YbNi_2B_2C$ was synthesized by arc melting together powders of the constituent elements. Excess Yb was used to compensate loss due to the high vapor pressure of Yb at elevated temperatures.) The single crystals grown by this technique are flat plates, which can be as large as $7\times7\times0.2$ mm^3, with the crystallographic c axis perpendicular to the plate surface. Powder x-ray-diffraction spectra taken on a ground single crystal gave $a=$ 3.575 Å and $c=$10.606 Å. These values are consistent with the lattice parameters reported by Seigrist *et al.*,[14] and indicate that at room temperature Yb is close to trivalent.

A Quantum Design superconducting quantum interference device magnetometer was used to determine the static magnetization of a crystal with approximate dimensions of $2\times2\times0.2$ mm^3. The anisotropic susceptibilities were measured from 1.8 to 350 K with an applied field of 1 kOe aligned either perpendicular or parallel to the c axis. The specific heat was obtained with a thermal relaxation technique where a single crystal weighing $\sim$16 mg was attached to a thermometer/heater sapphire platform with a small amount of Apiezon grease.[15] In order to cover the temperature range from 0.34 to 40 K, two calorimeters with different platform thermometers were used. The low-temperature calorimeter, which was cooled with an evaporative helium-3 system, used a germanium thermometer from TRI Research. For temperatures above 2 K, the platform thermometer was a Cernox from LakeShore. The absolute uncertainty in the specific heat is approximately $\pm$1%, and in the temperature range where the calorimeters overlap, the data agree within the absolute uncertainty. A Linear Research LR400 four-wire ac resistance bridge was used to measure the resistivity from 0.57 to 300 K. Platinum wires with a diameter of 0.003 in. were attached to the crystal in a four-probe configuration using Epotek H20E silver epoxy. The contact resistance was $\sim$1 Ω. No joule heating was observed when the measurement current was increased by a factor of 10.

In Fig. 1(a), the magnetic susceptibilities, $\chi_\perp=M/H_\perp$, $\chi_\parallel=M/H_\parallel$, and $\chi_{av}=2\chi_\perp(T)/3+\chi_\parallel(T)/3$ are displayed as a function of temperature from 1.8 to 350 K for $\mathbf{H}\perp\mathbf{c}$, $\mathbf{H}\parallel\mathbf{c}$, and

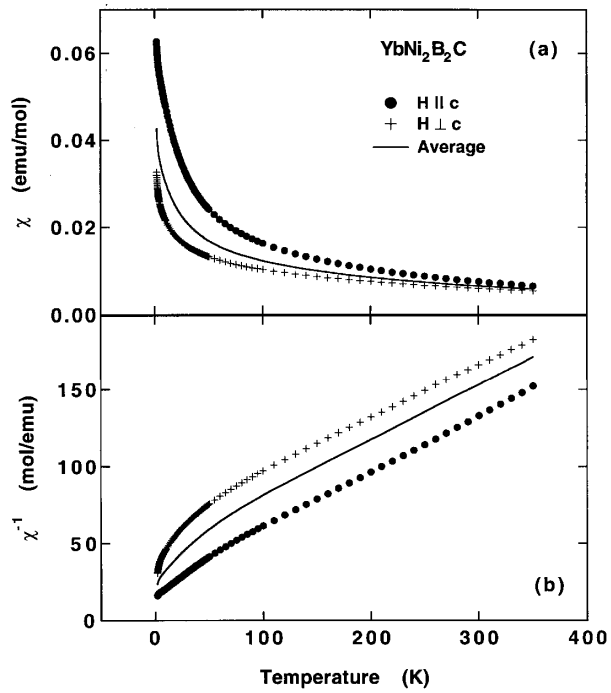

FIG. 1. (a) Anisotropic magnetic susceptibility χ, normalized per mole Yb, versus temperature for $YbNi_2B_2C$. The measurement was performed with a field of 1 kOe applied parallel (circles) and perpendicular (crosses) to the crystallographic c axis. The solid line is the polycrystalline average. (b) Inverse magnetic susceptibility χ^{-1} as a function of temperature for the data in (a).

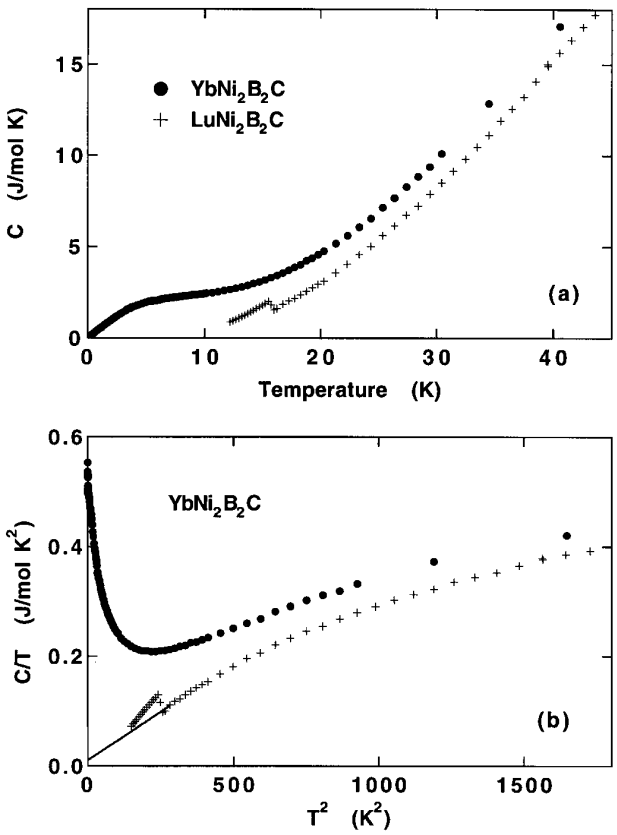

FIG. 2. (a) The specific heat C versus temperature and (b) C/T as a function of T^2 for $YbNi_2B_2C$ (solid circles). The crosses are the data for $LuNi_2B_2C$ with a superconducting transition at 16 K. The solid line in (b) is the extrapolation below the superconducting transition (see text for details) that was used for the phonon subtraction. The specific heat is normalized per mole lanthanide.

the crystallographic average. Notice that the susceptibility is larger when the applied field is aligned parallel to the c axis. As anticipated, this is the same anisotropy found in $TmNi_2B_2C$.[5] When the temperature dependence of the inverse susceptibility is plotted [Fig. 1(b)], Curie-Weiss behavior is observed above $\sim$150 K, and from the high-temperature slopes, the effective moments are 4.85 μ_B, 4.67 μ_B, and 4.72 μ_B for $\mathbf{H}\perp\mathbf{c}$, $\mathbf{H}\|\mathbf{c}$, and the powder average, respectively. These values are slightly larger than 4.54 μ_B calculated for the Hund's rule ground state of Yb^{3+}. The Weiss temperatures are $\theta_\perp=-191.0$ K, $\theta_\|=-63.6$ K, and $\theta_{av}=-129.6$ K, indicating antiferromagnetic correlations are important in this compound.

As the temperature is reduced below $\sim$100 K, the data deviate from the high-temperature Curie-Weiss behavior. The temperature dependence of the data shown in Fig. 1(b) is significantly different from that found for the other members of the RNi_2B_2C series. For R=Dy, Ho, Er, and Tm, $\chi_{av}(T)$ follows a Curie-Weiss law to a temperature comparable to the antiferromagnetic ordering temperature, and the magnitude of the Weiss temperature is close to T_N.[3,5–7] Deviations from Curie-Weiss behavior and the large Weiss temperature for χ_{av} indicate that the Yb $4f$ levels may be significantly hybridizing with the conduction electrons. If this is true, an approximation of the Kondo temperature is given by $\theta/10\leqslant T_K\leqslant\theta$.[16] Anomalies associated with superconducting or magnetic order were not observed throughout the measured temperature range.

To further explore the possibility that $YbNi_2B_2C$ is a heavy fermion, the specific heat C was measured, and the data, which are normalized per mole Yb, are plotted in Fig. 2(a) as a function of temperature. The rapid increase above $\sim$20 K is due in part to phonons as illustrated by our data on $LuNi_2B_2C$ in the same figure. By plotting C/T versus T^2 in Fig. 2(b), the deviation from a straight line shows that the low-temperature T^3 approximation of the Debye model for acoustic phonons inadequately describes the higher-temperature specific heat. Our data extend to high enough temperatures where departures from the T^3 behavior along with Einstein contributions for the optical phonons may become noticeable. In addition, thermal excitations of crystal-electric-field levels will contribute to the specific heat at higher temperatures.

A shoulder is observed in the specific heat below 10 K that we believe is a consequence of magnetic spin fluctuations. After plotting the low-temperature data in Fig. 3, a large low-temperature linear contribution to the specific heat is apparent. A fit to the data below $\sim$1 K yields a Sommerfeld coefficient γ of 530 mJ/mol K^2. The low-temperature saturation of γ at 530 mJ/mol K^2 is evident when the data are plotted as C/T versus T in the inset of Fig. 3. This enhanced electronic specific heat is large enough to classify $YbNi_2B_2C$ as a new Yb heavy-fermion compound (a system with $\gamma>400$ mJ/mol K^2), and using the single impurity relation, $T_K=w_N\pi^3R/6\gamma$ where $w_N=0.4107$ is the Wilson number

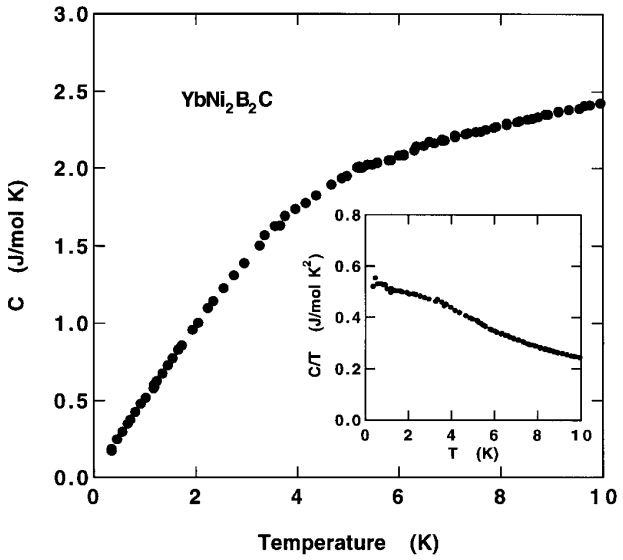

FIG. 3. Specific heat, normalized per mole Yb, at low temperatures for $YbNi_2B_2C$. In the inset, the data are plotted as C/T versus temperature.

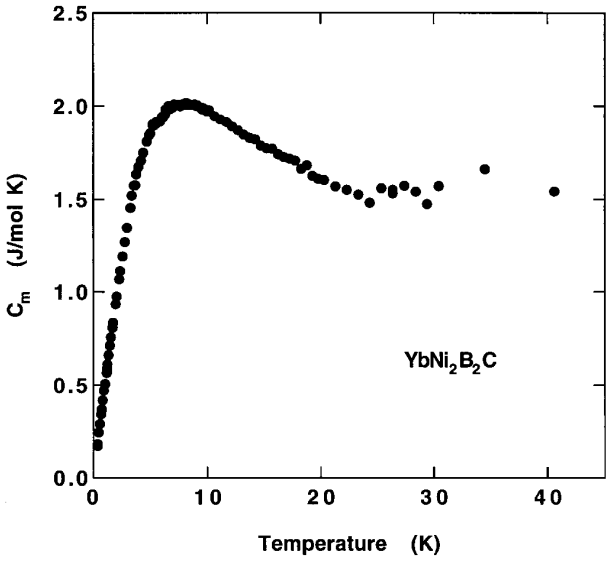

FIG. 4. The magnetic contribution of the specific heat versus temperature for $YbNi_2B_2C$. The plot was obtained by subtracting the specific heat measured for $LuNi_2B_2C$ from the data in Fig. 2(a) (see text).

and R is the gas constant,[17] the Kondo temperature is estimated to be 11 K. The magnetic and thermal excitations are comparably enhanced, and with χ and γ determined at $T=1.8$ K, the Wilson ratio, $\chi\pi^2k_B^2/\gamma\mu_{\rm eff}^2$, is 0.85 using the high-temperature effective moment.[17] Below 100 K, $\mu_{\rm eff}$ decreases with decreasing temperature, and this yields a Wilson ratio that exceeds 1. It should be noted that the sample manifests no feature that can be associated with a superconducting phase transition above 0.34 K, our lowest measured temperature.

To ascertain the nonmagnetic contribution of the specific heat, the isostructural compound $LuNi_2B_2C$ was measured, and the data are presented in Fig. 2. At high temperatures, a deviation from the Debye T^3 law is evident. Below the superconducting transition at 16 K, the specific heat of $LuNi_2B_2C$ is approximated by $\gamma T+\beta T^3$ [solid line in Fig. 2(b)] with the coefficients determined from a fit to the data between the transition and 20 K. A reasonably good fit was found with $\gamma=11\pm5$ mJ/mol K^2 and $\beta=0.35\pm0.01$ mJ/mol K^4 for 16 K$<T<$20 K. Our value for β is the same as that found for single crystals of $HoNi_2B_2C$ (Ref. 7) and $TmNi_2B_2C$,[18] and it is $\sim$30% larger than that reported for polycrystalline $LuNi_2B_2C$.[19] The discrepancy may be a consequence of higher purity or reduced strain in our single crystals. The specific heat discontinuity at the superconducting transition, ΔC, is approximately 600 mJ/mol K, and this yields a ratio of $\Delta C/\gamma T_c\sim3.4$, implying $LuNi_2B_2C$ is a strongly coupled superconductor. After subtracting off the nonmagnetic contribution, the magnetic contribution to the specific heat, C_m, of YbN_2B_2C is plotted in Fig. 4. The pronounced peak at $T\sim7$ K is similar to the prediction of the Coqblin-Schrieffer model;[20] however, the maximum value of the peak falls between those calculated for $J=1/2$ and 1. In $YbNi_2B_2C$, the tetragonal crystal-electric fields should split the $J=7/2$ manifold into four doublets, and thermal excitations of these levels are seen in the specific heat above the peak. After accounting for the spin-fluctuation term, the first excited crystal-electric-field level is estimated from the remaining magnitude of the specific heat to be well above 100 K.

The electrical resistivity in the a-b plane is displayed as a function of temperature in Fig. 5. The resistivity monotonically decreases with decreasing temperature in a manner similar to UPt_3,[21] and no indication of a coherence peak is observed. Using the resistivities at 300 and 0.57 K, the residual resistivity ratio is $\sim$8.6, a value which supports the high quality of our sample. Significant deviations from the Bloch-Grüneisen law may be associated with crystal-electric-field levels. In the inset of Fig. 5, the low-temperature resis-

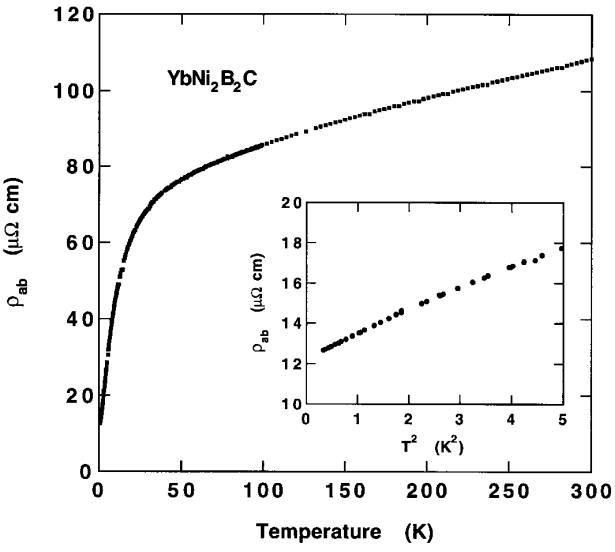

FIG. 5. The temperature-dependent resistivity in the a-b plane for $YbNi_2B_2C$. The inset shows the low temperature data plotted as a function of T^2. Note that the resistivity axis is offset from zero.

tivity is plotted versus T^2. A quadratic temperature dependence is apparent up to $\sim$1.5 K, consistent with the coherent effects of an enhanced Fermi-liquid ground state. The coefficient of the quadratic term $A=1.2\ \mu\Omega$ cm K^{-2}, which gives 4.3 $\mu\Omega$ cm mol^2 K^2 J^{-2} for the ratio of A/γ^2. This is close to the value of 3.9 $\mu\Omega$ cm mol^2 K^2 J^{-2} found for UPt_3 along the hexagonal axis, which as mentioned above has a similar temperature-dependent resistivity.[22] This indicates that the strong-electron correlations renormalize both the thermodynamic and transport properties.

In summary, we report the discovery of a Yb heavy-fermion compound with $\gamma=530$ mJ/mol K^2. Correlated-electron behavior is also exhibited in the magnetic susceptibility and electrical resistivity. No long-range order is observed down to 0.34 K, and the temperature dependences of these properties are prototypical of a correlated-electron system where the spin-fluctuation temperature is well separated from the other energy scales that characterize the CEF and vibrational excitations. Only a couple Yb heavy-fermion compounds have been discovered,[23] and unlike compounds such as YbBiPt,[24] the largely separated energy scales ($T_N, T_c < 0.34\ \mathrm{K} \ll T_K \ll T_{\Delta\mathrm{CEF}}$) in $YbNi_2B_2C$ makes this an ideal system for studying correlated-electron behavior and comparing experimental results with theoretical predictions. What is truly unique about this Yb heavy-fermion material is that it is a member of the RNi_2B_2C series. This class of materials has attracted much interested recently because of the coexistence of relatively high-temperature superconductivity and long-range magnetism in the other heavy lanthanide members. The absence of superconductivity above 0.34 K in $YbNi_2B_2C$ deviates greatly from the Abrikosov-Gorkov prediction with de Gennes scaling for the pair-breaking strength[3] (i.e., the adjacent compounds $TmNi_2B_2C$ and $LuNi_2B_2C$ superconduct at 10.8 and 16.3 K, respectively). This greatly enhanced pair breaking is consistent with the strong electron hybridization in this compound. Based on the de Gennes scaling of T_N for the trivalent members of this series,[3,9] $YbNi_2B_2C$ should order magnetically at approximately 0.4 K, which is much lower than the Kondo temperature of $\sim$10 K. Clearly, further measurements on $YbNi_2B_2C$ are needed to see if any phase transition exists below our minimum obtainable temperature of 0.34 K. Possibilities include an ordering of partially screened moments removing a small part of the total magnetic entropy, heavy-fermion superconductivity, or a density wave associated with the $\mathbf{k}=0.55\ \mathbf{a}^*$ nesting seen in RNi_2B_2C with R=Lu, Er, Ho, Tb, and Gd.[25–29] Substitutional studies between $YbNi_2B_2C$, which has a heavy-fermion ground state with $T_K\sim$10 K, and $LuNi_2B_2C$, which superconducts at 16 K, will allow us to study the transition from pair weakening when strongly hybridized moments are present to pair breaking caused by long-lived moments. Such studies can be compared to the extensive work on Th:U and La:Ce alloys and pseudobinary compounds.[30]

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