Pressure effects and specific heat in superconducting $HoNi_2B_2C$

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(Received 23 August 1994; revised manuscript received 27 December 1994)

We have studied the interaction of superconductivity ($T_c = 8.4$ K) and magnetism ($T_N = 5$ K) in the $HoNi_2B_2C$ system. Specific-heat measurements at 0 and 2 T indicate that the antiferromagnetic ground state involves a Ho $4f$ doublet, with the entropy shifting to higher temperatures, $T \gg T_N$, with increasing magnetic field. The heat-capacity anomaly at T_c, $\Delta C/T_c$, is 10 (2) mJ/mole K^2, similar to the values found for other borocarbide superconductors where the density of states at the Fermi level is comprised primarily of metal d states. Magnetic susceptibility and resistivity measurements under hydrostatic pressure P reveal that $dT_c/dP \sim 0.07$ (0.04) K/kbar and $dT_N/dP \sim 0.25$ (0.03) up to 7 kbar. These results reveal that the structure has an important influence on the superconducting and magnetic properties of $HoNi_2B_2C$.

Since the discovery of the coexistence of magnetism and superconductivity in rare-earth ternary compounds RMo_6X_8 (X = S, Se) (Ref. 1) and RRh_4B_4,[2] much debate has ensued on the role that magnetism plays in suppressing superconductivity. Traditionally, the magnetic impurities are thought to break up the Cooper pairs because the exchange interaction between the spins of the impurity ions affects the two electrons which form the Cooper pair differently. More recently, research on the heavy-fermion and high-T_c superconductors has shown that antiferromagnetism is not only prevalent in these superconducting systems by may serve to mediate the superconductivity, forcing us to readdress our understanding of the effect of magnetic order on superconductivity.

The recently discovered intermetallic borocarbide superconductors have moderately high T_c's, up to 23 K,[3,4] and long-range antiferromagnetic order,[5] providing a novel system to pursue the interplay between magnetism and superconductivity. Neutron-scattering results on the reentrant superconductor $HoNi_2B_2C$ reveal that incommensurate oscillatory spin fluctuations start to be observed just above the first superconducting transition $T_c \sim 8$ K. As these oscillations grow in intensity, the system loses its superconductivity until the commensurate long-range antiferromagnetic order locks into place at $T_N \sim 5$ K below which the oscillations decrease and the system reenters the superconducting state. The low-temperature magnetic structure for the Ho moments consists of ferromagnetic sheets of spins in the *a-b* plane, with the sheets being antiferromagnetically aligned along the c axis.[6] In this paper, we investigate this system through heat-capacity and hydrostatic pressure measurements. We find that the conduction electrons involved in the superconductivity are primarily Ni $3d$, while the antiferromagnetic ground state is composed of a Ho^{3+} doublet. Our pressure results reveal that the long-range-ordering temperature T_N increases faster than the superconducting temperature T_c with pressure, consistent with expectations on how changes in the crystallographic structure affect the rare-earth moment interaction and the density of states (DOS) at the Fermi surface.

Polycrystalline $HoNi_2B_2C$ was prepared by arc melting and annealing as described elsewhere.[7] Both T_N and T_c are strongly dependent on sample preparation;[8] samples prepared by the same process as ours were characterized by neutron-scattering[6] and resistive H_{c2} measurements.[5] A standard dc pulse-relaxation technique was used to measure the specific heat of the 65-mg sample at 0 and 2 T where the magnetoresistance of the Cermac thermometer and the sample heater are both less than 0.3%. A carbon-chip resistor monitored the sample temperature and was calibrated against the Cermac thermometer during every run. Magnetic susceptibility and resistivity up to 7 kbar were measured simultaneously on a sample of typical dimensions 2mm×1mm×0.5 mm in a BeCu piston clamp pressure cell. An ac coil technique, with a typical measuring field of 1 G and frequency of 400 Hz, and a lockin amplifier were employed to measure the ac magnetic susceptibility. The secondary coil was wound inside the Teflon bucket such that the background was flat and featureless below 20 K and could be easily subtracted. The electrical resistivity was measured using a standard four-probe dc technique and silver paint contacts. $(V_{0.99}Ti_{0.01})_2O_3$ served as the manometer; at ambient pressure, it has a first-order metal-insulator transition at 141 K which decreases at a rate of 5.8 K/kbar.

Resistivity and magnetic susceptibility measurements at ambient pressure reveal the salient features of $HoNi_2B_2C$ (Fig. 5). The system first goes superconducting at $T_c = 8.4$ (0.1) K, below which a rise in the susceptibility is observed as long-range order is approached. The magnetic susceptibility indicates that the antiferromagnetic ordering temperature, T_N, is 5.0 (0.1) K. In the main part of Fig. 1, the specific heat versus temperature at 0 and 2 T is shown. The sharp anomaly at 5 K is indicative of a first-order antiferromagnetic transition. Neutron measurements reveal hysteresis in the magnetic order parameter at T_N, consistent with a first-order transi-

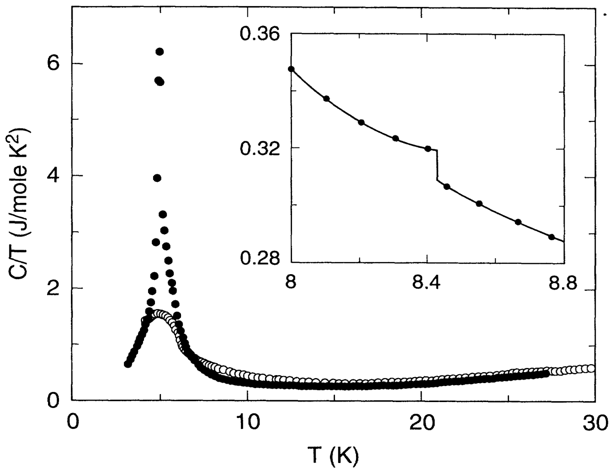

FIG. 1. The heat capacity, C/T, for $HoNi_2B_2C$ at 0 and 2 T (solid and open symbols, respectively). The sharp transition at 5 K is first-order long-range antiferromagnetic ordering composed of a Ho^{3+} doublet. The inset shows the anomaly in the specific heat, $\Delta C/T_c$, at the superconducting transition, T_c.

tion, which presumably arises from a hysteresis in the internal magnetic field from the Ho (Fig. 5).[6] The neutron measurements further show that by 2 T the antiferromagnetic peak is almost completely suppressed. This result implies that initial rise in the heat capacity around 7 K, and the rounded peak near 6 K at 2 T (Fig. 2), are due to magnetic contributions from the oscillatory spin fluctuations and a corresponding Schottky anomaly expected from crystal-field effects of the degenerate Ho^{3+}

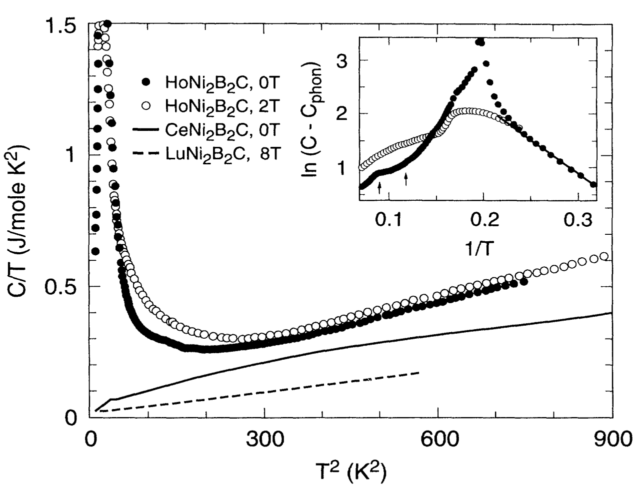

FIG. 2. C/T vs T^2 for $HoNi_2B_2C$ at 0 and 2 T (solid and open symbols, respectively) and for $CeNi_2B_2C$ (solid line) and $LuNi_2B_2C$ (dashed line) driven normal with magnetic field. The inset shows $\ln(C\text{-}C_{phon})$ vs $1/T$ for $HoNi_2B_2C$, where C_{phon} is the T^3 contribution to the specific heat. The arrows indicate the impurity ordering and the superconducting transition temperatures, respectively.

multiplet.[9] The lack of any superconducting or antiferromagnetic anomalies in the heat capacity at 2 T indicates that moderate magnetic field leads to suppression of both the antiferromagnetic order and superconductivity.

In the inset to Fig. 1, we have enlarged the area around T_c to show the superconducting transition anomaly at 8.4 K. The critical field for the Ho compound is 0.5 T so that by 2 T no superconducting transition is observed. The superconducting specific-heat jump $\Delta C/T_c$ is on the order of 10 (2) mJ/mol K^2. Using the values of $1.43 < \Delta C/\gamma T_c < 2.0$ found for the borocarbide superconductors,[10,12] we estimate a γ of 6 (2) mJ/mol K^2, similar to the Ni metal γ of 7 mJ/mol K^2.[13] This result is also on the same order as the γ of 7.5 mJ/mol K^2 found for $LaPt_{1.7}Au_{0.3}B_2C$ with a T_c of 10.2 K.[10] The DOS at the Fermi surface in the $HoNi_2B_2C$ is considerably less enhanced than in $LuNi_2B_2C$ ($\gamma \sim 19$ mJ/mol K^2), implying that the decrease in T_c from 16.4 to 8.4 K may be due to a decrease in the DOS. The BCS critical temperature relation $T_c \sim 0.85\Theta_D \exp[-1/N(0)V]$ suggests a smaller decrease in the DOS at the Fermi surface than we observe.[14]

The graph in Fig. 2 shows C/T versus T^2 for $HoNi_2B_2C$ at 0 and 2 T (solid and open circles, respectively) and for superconducting $LuNi_2B_2C$ driven normal with magnetic field (dashed line) (Ref. 10) and nonmagnetic $CeNi_2B_2C$ (solid line) for comparison.[11] The magnetism dominates the heat capacity such that the phonon and electron contribution to the specific heat are small in comparison. The Debye temperature Θ_D of 348 K is estimated from the $LuNi_2B_2C$ data with the appropriate scaling of the molar masses. After subtraction of this lattice term, a large heat capacity remains which is associated with the magnetism from the Ho^{3+} spins. In the inset to Fig. 2, the plot of $\ln(C\text{-}C_{phon})$ versus $1/T$ shows the range of exponential behavior in the long-range-ordered state (solid line). The entropy associated with the transition of 5.5 (0.3) J/mol K is on the order of R ln2, indicating that the ground state is a doublet. Above T_N, the entropy is mostly due to the magnetism from the remaining Ho^{3+} spins. Only 50% of the magnetic entropy (R ln17) expected for the full Ho^{3+} multiplet is recovered by 30 K in the specific-heat measurement, suggesting that the crystal-field energy levels consist of high-temperature (> 60 K) excited-state multiplets. In the 2-T data, the entropy associated with the Ho^{3+} doublet ground state has shifted to higher temperatures with the suppression of T_N, and it is not fully recovered within the measurement range of 30 K. The broad peak around 12 K observed in the inset to Fig. 2, also seen in susceptibility measurements, is sample dependent and appears to be due to a small percentage of a minority phase.

In summary, the heat-capacity measurements show that bulk superconductivity and local long-range magnetic order coexist in $HoNi_2B_2C$. Band-structure calculations, combined with the heat-capacity results, suggest that the electronic density of states derived from the superconducting transition is mainly comprised of the Ni 3d states.[15] The antiferromagnetic ground state involves a Ho^{3+} doublet. With increasing magnetic field, the system favors the incommensurate oscillatory magnetism with the suppression of both the superconductivity and antiferromagnetic order. Through the course of this work, we became aware of specific-heat data by Michor *et al.* on $(Y_{1-x}Er_x)Ni_2B_2C$ who observe similar results for $ErNi_2B_2C$.[16]

To elucidate the effect that magnetism has on the superconductivity, we measured resistivity and magnetic susceptibility as a function of hydrostatic pressure. Resistivity measurements on a series of rare-earth borocarbides by Eisaki *et al.* show that T_c increases as the rare-earth size decreases.[5] This effect may be accounted for in terms of the de Gennes factor which suggest that the magnetic pair breaking dominates the change in T_c. Alternatively, recent work by Mattheiss *et al.* indicates that T_c is determined by the *s-p* states involved in the B-Ni-B angled bond.[15] Hydrostatic pressure should affect the B-Ni-B bond and the de Gennes factor differently and allow us to address these two different influences on T_c.

In Fig. 3, the resistivity is graphed as a function of temperature. At ambient pressure, the reentrant behavior is not observed in the resistivity, implying that the Cooper pairs remain coherent even in the presence of the long-range order and the oscillatory spin fluctuations (Fig. 4). Other groups have observed reentrant resistivity behavior at ambient pressure and magnetic field;[5,8] however, this is typically on lower T_c samples where impurities might be expected to help break up the superconducting state. By 4.5 kbar, T_N has increased 1 K, and the reentrant behavior is observed in both the magnetic susceptibility and the resistivity at the same temperature. The superconducting transition temperature, T_c, increases on the order of 0.07 (0.04) K/kbar with increasing pressure, P, qualitatively consistent with the result that decreasing the rare-earth size leads to a higher T_c. This pressure dependence is stronger than that observed in RRh_4B_4 superconductors which is in agreement with the

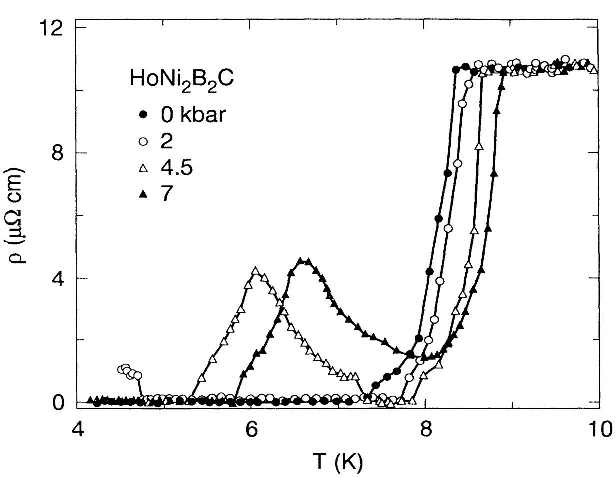

FIG. 3. Pressure-dependent resistivity, ρ, of $HoNi_2B_2C$ shows that T_c weakly increases with pressure, P. The peak in ρ at higher pressures marks the antiferromagnetic ordering temperature, T_N.

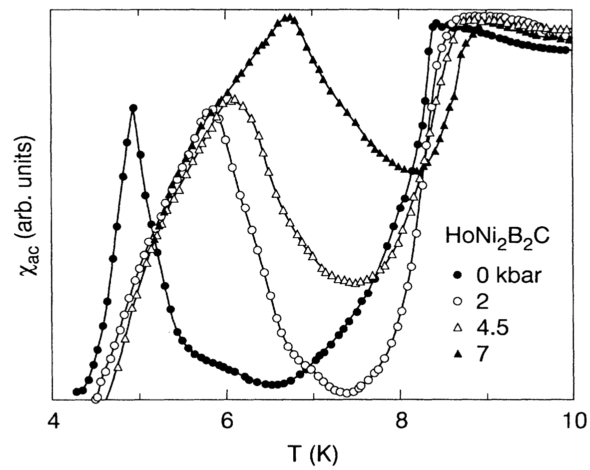

FIG. 4. Pressure dependence of the magnetic susceptibility, χ, reveals that $dT_c/dP \sim 0.07$ (0.04) K/kbar and $dT_N/dP \sim 0.25$ (0.04) for $HoNi_2B_2C$ up to 7 kbars.

observation that T_c changes with rare-earth radius twice as fast in RNi_2B_2C than in RRh_4B_4.[17] Other groups have observed a small decrease in T_c with increasing pressure. These differences may be related to differences in sample preparation and in the anisotropic nature of the material, and we do not discount the possibility for negative dT_c/dP being observed in all samples under sufficiently high pressure.[18]

In Fig. 4, the magnetic susceptibility reveals that the long-range-ordering temperature, T_N, increases faster [$dT_N/dP \sim 0.25$ (0.04) K/kbar] than the superconducting transition, T_c, with pressure. A smaller percentage of the sample is initially superconducting below T_c as the pressure in increased, and by 7 kbar the resistivity no longer drops to zero with the onset of the superconducting behavior. Because T_N and the reentrant superconducting temperature coincide, the magnetic long-range order is not expected to be detrimental to the superconductivity; therefore, we propose that the temperature for the formation of the oscillatory spin is also increasing with pressure and that it is this magnetism which breaks up the formation of the Cooper pairs resulting in finite resistance below T_c. This interpretation agrees with the neutron-scattering data which suggest that it is the oscillatory state itself, not the local antiferromagnetic order, which is detrimental to the superconductivity.[6]

The effects of pressure can be qualitatively understood by considering the crystal structure consisting of HoC NaCl-type layers and Ni_2B_2 layers. Previous results have shown that the *a* axis increases and the *c* axis weakly decreases as larger rare-earth ions are substituted into the lattice.[19] The superconductivity is stabilized by the shrinkage of the *a* axis due to a reduced distortion of the B-Ni-B tetrahedron.[14] In contrast, T_N depends on the antiferromagnetic coupling between the rare-earth spins which is mediated via the RKKY interaction[6] and increases upon shrinkage of the *c* axis.[5] The *a* axis, which is determined mostly from strong metallic bonding be-

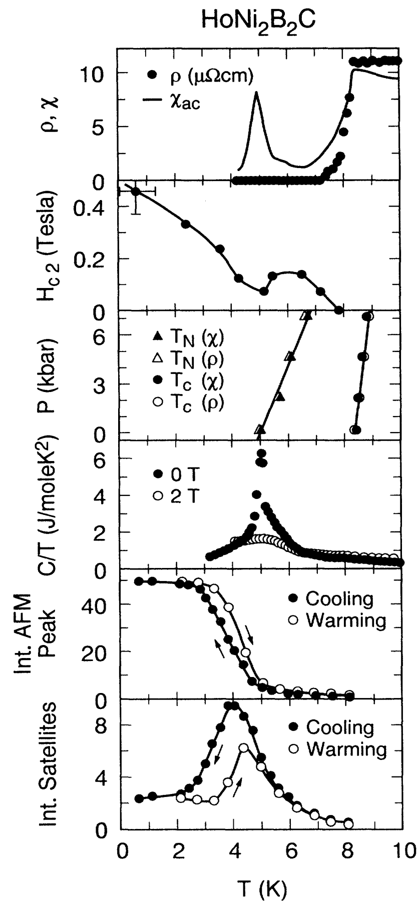

FIG. 5. Summary of results on $HoNi_2B_2C$ for $0<T<10$ K: resistivity, ρ, and magnetic susceptibility, χ, at ambient pressure and field, resistive H_{c2} measurements (from Ref. 5), pressure dependences of T_N and T_c, heat capacity C/T at zero and 2 T, and neutron-scattering results showing the intensity in arbitrary units of the central antiferromagnetic ordering peak and of the satellite oscillatory spin-fluctuation peaks (from Ref. 6).

tween the Ni's, is weakly compressible, and the c axis, formed indirectly via the short boron-carbon bonds, should be more compressible. As observed, pressure should strongly increase T_N by shrinking the c axis and increasing the RKKY interaction between the Ho-Ho spins, and it could also increase T_c by weakly shrinking the a-axis leading to less distortion of the Bi-Ni-B angled bond and a larger DOS at the Fermi surface. Such an interpretation would need to be supported by measurements of the bulk modulus and changes in the DOS with pressure. Nonetheless, the increase in the long-range-ordering temperature, T_N, does not initially decrease T_c, which argues against the coupling between rare-earth moments being the main contribution in determining T_c. An alternate explanation for the determination of T_c depends on the oscillatory spins breaking up the superconducting Cooper pairs. Although our data supports that the oscillatory spins are responsible for the finite resistivity below T_c, we do not know how this model would account for the changes in T_c with pressure.

In Fig. 5, we summarize our heat-capacity data and pressure results along with resistive H_{c2} data by Eisaki *et al.*[5] and magnetic order-parameter data from neutron measurements by Grigereit *et al.*[6] Together, the results show that long-range local moment magnetism and bulk superconductivity coexist in $HoNi_2B_2C$, with the Ho^{3+} $4f$ rare-earth magnetic moments and the superconducting Ni^{3+} $3d$ conduction electrons weakly coupled. This situation of superconductivity coexisting with long-range order, but detrimentally affected by oscillatory spin fluctuations, has been encountered in the magnetic superconductors RRh_4B_4, the details of which have been worked out previously.[2,9] While magnetic field is detrimental to T_c and T_N, pressure enhances both T_c and T_N for pressure less than 7 kbar. These results indicate that, in addition to the rare-earth magnetism, the crystallographic structure has an important influence on the superconducting and magnetic properties of the rare-earth borocarbides.

We are pleased to acknowledge valuable discussions with H. Eisaki and T. Grigereit. After completion of this work, we became aware of neutron-scattering results by Goldman *et al.* and co-workers on single-crystal $HoNi_2B_2C$, which give additional insight into the coupling between the superconductivity and rare-earth magnetism.[20]

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0.85∗345 K)/ln(8.4 K/0.85∗348 K) = 0.8, where $N(0)$ is the DOS for one spin direction at the Fermi surface and V is comprised of the attractive electron-electron interaction mediated by phonons and the screened Coulomb repulsion. Our results give an estimate of $N(0)_{\mathrm{Ho}}/N(0)_{\mathrm{Lu}} \sim \frac{1}{3}$, suggesting that the interaction V is significantly different for the two materials, the full superconducting state is not contributing to $\Delta C/T_c$ at T_c, or magnetic pair breaking also influences T_c, as implied in Ref. 5.

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