Magnetic transitions and nearly reentrant superconducting properties of HoNi$_2$B$_2$C

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A low-temperature phase diagram $H(T)$ of the 7.8-K superconductor HoNi$_2$B$_2$C (with an onset of 8.3 K) is generated through characterization of well-prepared samples by various experimental techniques including ac magnetic susceptibility, superconducting quantum interference device dc magnetic susceptibility, magnetic hysteresis, specific heat, and electrical resistivity measurements. The results yield a superconducting upper critical field $H_c(0)$ of 3.5 kG, a lower critical field $H_{c1}(0)$ of 250 G, and a Ginzburg-Landau parameter $\kappa$ of 3.5. A nearly reentrant deep minimum at 5.2 K with very small $H_c$ of 400 G and $H_{c1}$ of 5 G are observed. Two distinct magnetic transitions are observed with an incommensurate magnetic ordering temperature $T_m$ of 5.7–6 K and an antiferromagnetic Néel temperature $T_N$ of 5.2 K. The magnetic entropy $\Delta (S_m + S_N)$ estimated between 2 and 10 K is 10.4 J/mol K. The effective internal field which causes the nearly reentrant behavior is 2 kG at 5.2 K.

I. INTRODUCTION

Relatively high superconducting transition temperatures $T_c$ up to 23 K have been reported in the quaternary borocarbide $RT_2$B$_2$C compounds ($R$ = Sc, Y, Th, U or a rare earth; $T$ = Ni, Pd, or Pt). The superconducting phase has been identified to be of the body-centered-tetragonal LuNi$_2$B$_2$C type with space group $I4/mmm$. The structure is a three-dimensionally connected framework with LuC layers alternated with Ni$_2$B$_2$ layers, where nickel is tetrahedrally coordinated by four boron atoms.

Among many nonmagnetic compounds in the Ni system, LuNi$_2$B$_2$C exhibits the highest $T_c$ of 16.6 K, followed by 15–16 K for YNi$_2$B$_2$C and metastable ScNi$_2$B$_2$C, 7 K for ThNi$_2$B$_2$C, and no superconducting transition was found down to 2 K for LaNi$_2$B$_2$C. Band-structure calculations on LuNi$_2$B$_2$C (Refs. 12,13) indicate a high density of states $N(E_F)$ at the Fermi level near the top of the almost-filled Ni(3d) band, with only modest admixture from B and C. All characteristics are indicative of a good, three-dimensional metal. A strong-coupled phonon mechanism for the occurrence of superconductivity is deduced with a very large electron-phonon coupling parameter $\lambda$, which is related to an unusual combination of electronic states at the Fermi level and a substantial contribution from the vibration of the light atoms.

For compounds containing magnetic rare earth elements such as $R$ = Dy, Ho, Er, and Tm, lower $T_c$ values were observed due to the magnetic pair-breaking effect. In fact, HoNi$_2$B$_2$C is the most intensively studied compound of the Ni-based system due to its nearly reentrant behavior around 5–6 K below the superconducting transition temperature $T_c$ of 7.5–8 K. However, the reported magnetic transition temperatures are ill defined. For example, while yielding consistently an antiferromagnetic transition temperature $T_N$ around 5 K, two neutron diffraction measurements give two different incommensurately modulated/spiral magnetic transition temperatures $T_m$ of 8 K (Ref. 15) and 6 K (Ref. 16), respectively. Meanwhile, prior specific-heat measurements show vaguely two shoulders around 5.5 and 6 K, in addition to a $T_N$ of 5 K. The temperature dependence of superconducting upper critical field $H_{c2}(T)$ is also ambiguous. The zero-temperature value $H_{c2}(0)$ of 4.5 kG, a local minimum at 5.2 K, and a local maximum at 6.2 K were obtained from field-dependent electrical resistivity measurements in contrast to 1.9 kG, 5–5.2 K, and 6 K, respectively, from magnetic measurements on a single crystal.

In this work, we have characterized a well-prepared HoNi$_2$B$_2$C polycrystalline sample through various experimental techniques including ac magnetic susceptibility, superconducting quantum interference device (SQUID) dc magnetic susceptibility, magnetic hysteresis, specific-heat, and electrical resistivity measurements. A phase diagram of this quaternary compound is thus generated with reference to the temperature dependence of critical magnetic fields.

II. EXPERIMENTS

HoNi$_2$B$_2$C samples were prepared from high-purity elements Ho (99.9%, ingot), Ni (99.9% foil), B (99.9995% chips), and C (99.995% chips) with a stoichiometric ratio
of (1;2;2:1) under an argon atmosphere in a Zr-gettered arc furnace. The Ho, B, and C ingredients were wrapped in the Ni foil and arc melted carefully several times to ensure negligible weight loss and sample homogeneity. The as-melted samples were then wrapped in Ta foils and annealed under argon atmosphere in a sealed quartz tube at 1100°C for three days and then quenched in liquid nitrogen. Crystallographic data were obtained with a Rigaku Rotaflex 18-kW rotating anode powder x-ray diffractometer using Cu Kα radiation with a scanning rate of 1° in 2θ per min. A LAZY PULVERIX PC program was employed for phase identification and lattice parameter calculation.

Electrical resistivity measurements (16 Hz) were carried out by the standard four-probe method in an RMC Cryosystems closed-cycle refrigerator down to 9 K and using single-shot cooling to 6.5 K. ac magnetic susceptibility measurements were made with a Lake Shore Model 7221 susceptometer/magnetometer down to 4.2 K in an ac magnetic field 0.1 or 0.01 G (rms) at 1 kHz. The ac signal can be biased by a dc magnetic field up to 1 T. dc magnetic susceptibility and magnetic hysteresis measurements were made with a Quantum Design MPMS or a Mu-metal shielded MPMS2 SQUID magnetometer down to 2 K in an applied field from 1 G to 1 T. Specific-heat measurements were made with an adiabatic calorimeter from 1.5 to 20 K. The sample was thermally anchored to a copper block containing a germanium thermometer and a manganin wire heater, for which measurements were made separately for addenda correction.

III. RESULTS AND DISCUSSION

In preparing HoNi2B2C samples, a minute amount of Ni3B impurity often prevails,14 which can actually serve as the flux in growing HoNi2B2C single crystals.14 For the annealed samples used in this work, the powder x-ray diffraction pattern in Fig. 1 reflects practically a single phase. The diffraction lines can be well indexed with the LuNi2B2C-type structure having tetragonal lattice parameters \(a = 3.516(3)\) Å, \(c = 10.530(6)\) Å, and unit cell volume \(V = 130.2(1)\) Å³. The excellent sample quality is attributed to the use of Ni foil as the wrap of the high-purity starting materials, followed by liquid nitrogen quench after annealing.

A. Superconducting and magnetic transitions

The low-temperature real and imaginary parts of ac magnetic susceptibilities \(\chi_{ac}(T) = \chi'(T) + i\chi''(T)\) of the annealed HoNi2B2C bulk sample are shown together in Fig. 2, with 0.01 G (rms) ac field at 1 kHz frequency. Three phase transitions around 7.8, 5.7, and 5.2 K can be identified from the imaginary part. The first one at 7.8 K corresponds to a superconducting transition as the transition is accompanied by a diamagnetic, superconducting real part signal. This is consistent with the transport data in Fig. 3, where the temperature dependence of electrical resistivity \(\rho(T)\) shows a superconducting transition with 10% resistivity onset drop \(T_c\) (onset) of 8.3 K, 50% midpoint drop \(T_c\) (mid) of 8.1 K, and zero resistivity \(T_c\) (zero) of 7.8 K. The small extrapolated residual resistivity \(\rho(0)\) of 24 μΩ cm, along with the large metallic resistivity ratio \(\rho(RT)/\rho(9 K)\) of 7.5, are indications of good polycrystalline sample quality. The \(T_c=7.8\) K for

![FIG. 1. Powder x-ray diffraction pattern of annealed HoNi2B2C sample.](image1)

![FIG. 2. Low-temperature real and imaginary parts of ac magnetic susceptibilities \(\chi_{ac}(T) = \chi'(T) + i\chi''(T)\) (0.01 G rms at 1 kHz) for bulk sample. Three distinct transitions were observed.](image2)

![FIG. 3. Low-temperature electrical resistivity \(\rho(T)\).](image3)
HoNi$_2$B$_2$C is 8.8 K lower than the $T_c = 16.6$ K for nonmagnetic LuNi$_2$B$_2$C. Judging from the systematic variation of $T_c$ with Ni-Ni in-plane distance $d = a/\sqrt{2}$ (a is the tetragonal lattice parameter) for the nonmagnetic compounds RNi$_2$B$_2$C ($R =$ Sc, Lu, Y, Th, or La), the $T_c$ depression due to the magnetic pair-breaking effect at $d = 2.468$ Å (for HoNi$_2$B$_2$C with $a = 3.516$ Å) can be estimated as $\Delta T_c(\text{Ho}) = T_{c0}(\text{Ho}) - T_c(\text{Ho}) = 15.8$ K for $g = 8$ K, or about 90% of the observed $T_c$ depression as compared with LuNi$_2$B$_2$C. If the magnetic pair-breaking effect is in the framework of the Abrikosov-Gor’kov theory with $\Delta T_c$ proportional to the de Gennes factor $(g_J - 1)^2 J(J + 1)$, where $J$ is the total angular momentum and $g_J$ is the Landé $g$-factor, then using $\Delta T_c(\text{Ho}) = 8$ K and the calculated Fermi-level density of states $N(E_F)$ of 4.8 states/eV cell or 0.8 states/eV atom for LuNi$_2$B$_2$C, a small exchange-coupling parameter $|J|$ of 8.1 meV between conduction electron and localized 4f moment is derived by using the formula $\Delta T_c = [m^2 N(E_F) / 6 \times 2k_B] |J|^2 (g_J - 1)^2 J(J + 1)$. The tetragonal crystal-field effect (CEF) is neglected for the present crude estimation. The same $T_c(d)$ curve with $\Delta T_c / T_{c0}$ proportional to the de Gennes factor can also be used to predict the superconducting transition temperature of DyNi$_2$B$_2$C using $T_{c0}(\text{Dy})$ of 15.3 K at $d = 2.498$ Å (for DyNi$_2$B$_2$C with $a = 3.532$ Å). The calculated $T_c(\text{Dy}) = 3.1$ K is indeed close to $T_c$ of 3.8 K observed in our preliminary study and is higher than the previously reported $T_c$ onset around 2 K.

The two other transitions observed at 5.7 and 5.2 K from ac magnetic susceptibility data are apparently related to the long-range Ho$^{3+}$ magnetic ordering through the Ruderman-Kittel-Kasuya-Yosida indirect exchange interaction. The real part ac signal indicates a nearly reentrant behavior starting from the magnetic ordering temperature $T_m$ around 5.7 K, reaching to a small positive peak at the antiferromagnetic Néel temperature $T_N$ of 5.2 K, then dropping sharply back to diamagnetic signal below $T_N$. No nearly reentrant behavior can be detected from the resistivity measurement due to the low-temperature limit of 6.5 K. However, these two magnetic transitions can be clearly corroborated by low-temperature specific-heat data $C(T)$ as shown in Fig. 4. Two distinct transition peaks were observed at 5.7 and 5.2 K, respectively. The expected specific-heat discontinuity at $T_c$ would be of the order of $\text{mJ/mol K}$, and is too small to be observed in the presence of large magnetic contributions. Strictly speaking, there should be four contributions to the total heat capacity $C = \gamma T + \beta T^3 + C_m + C_V$, corresponding to the electronic, the lattice, and the two magnetic transition components, respectively. By employing the literature data for nonmagnetic LuNi$_2$B$_2$C (Ref. 21) as the base line representing the electronic and lattice terms, the magnetic entropy between 2 and 10 K can be derived as $\Delta S_N = S_N = \int [(C - 0.0197T - 0.00035T^3)/T]dT = 10.4$ J/mol K. Additional contributions to the magnetic entropy below 2 K and above 10 K are relatively insignificant, judging from the data in Fig. 4. The small difference between 10.4 J/mol K and $\Delta S_N = R \ln 3 = 9.12$ J/mol K, which is expected for the antiferromagnetic ordering of Ho$^{3+}$ with a quasiparticle ground state (locally spaced doublet and singlet levels) in the tetragonal crystal field, could simply be the consequence of the change-over from an antiferromagnetic state to the incommensurate modulated/spiral magnetic structure near $T_m$. Such a transition should be considered as an order-to-order process with a latent heat. In fact, the minor peak at $T_m = 5.7$ K can easily account for such a $\Delta S_N$ value. More importantly, the magnetic transition temperatures are consistent with the results of single-crystal neutron diffraction measurements, where a simple commensurate antiferromagnetic structure was observed with moments aligned in the tetragonal basal plane around 5 K and an incommensurate modulated/spiral magnetic transition was developed around 6 K with the ferromagnetic planes rotating from layer to layer along the c axis with a turn angle of 165°, and the neighboring moments along the a axis are rotated by approximately 104°. The persistence of the neutron satellite peaks up to 8 K from the powder neutron data may be due to the strong short-range magnetic fluctuation.

Identical results are obtained from the low-field (1 G), zero-field-cooled (ZFC), and field-cooled (FC) dc mass magnetic susceptibilities $\chi_g(T)$ as shown in Fig. 5. A powder sample with fine particle size of around $1 \mu$m is used to avoid any unwanted shielding signal and the complex flux-pinning effect which are always observed for bulk borocarbide samples. The superconducting transition temperature $T_c$ of 7.8 K was observed from the merging point of the ZFC and FC curves, which is also the onset deviation from the Curie-Weiss law, with a large ZFC signal of $-1.3 \times 10^{-2}$ emu/g K and FC signal of $-7.1 \times 10^{-3}$ emu/g K at 2 K. Using x-ray density of 4.02 g/cm$^3$, volume susceptibility percentages 4$\chi$ of 66% (ZFC) and 36% (FC) at 2 K are obtained for the powder sample, indicating good sample quality. Nearly reentrant behavior is also observed with a $T_N$ peak of 5.2 K and $T_m$ upturn around 6 K. The large positive $\chi_g$ value of $3.3 \times 10^{-3}$ emu/g K at 5.2 K is still smaller than $4.1 \times 10^{-3}$ emu/g K at $T_c$ of 7.8 K.
B. Superconducting upper critical field \( H_{c2}(T) \) and lower critical field \( H_{c1}(T) \)

Several methods are used to determine the superconducting upper critical field \( H_{c2}(T) \) and lower critical field \( H_{c1}(T) \).

The low-temperature ac magnetic susceptibility \( \chi_{ac}(T) \) in ac field of 0.1 G (rms) at 1 kHz with a dc-biased magnetic field of 100 G is shown in Fig. 6. \( T_c \) decreases from 7.8 K in the zero-field-biased case to 7.5 K in the 100-G-biased case, or \( H_{c2}(7.5 \text{ K}) = 100 \text{ G} \). \( T_m \) of 6 K and \( T_N \) of 5.2 K are observed. A small bump around 4.5 K was observed below \( T_N \). Judging from the shape of the real part signal, these magnetic structures under applied field may be slightly weakly ferromagnetic.

The field-dependent low-temperature ZFC dc mass magnetic susceptibilities \( \chi'_c(T) \) in various applied fields of 100, 500, and 1 kG for bulk samples are shown collectively in Fig. 7. \( T_c \) decreases from 7.8 K in 1 G to 7.5 K in 100 G, 6.8 K in 500 G, and 6.5 K in 1 kG applied field. \( T_m \) and \( T_N \) are almost field independent in these low applied fields. The small bump observed in ac magnetic susceptibility is reflected as a knee at 4.5 K for \( \chi'_c(T) \) in 100 G applied field. This bump is suppressed to 3.5 K in 500 G and is no longer observable in 1 kG. Superconductivity is completely destroyed in 5 kG as shown in Fig. 8, where only the two unchanged magnetic transitions of \( T_m \) and \( T_N \) remain.

Constant-temperature magnetic hysteresis measurements provide more precise information on the temperature dependence of superconducting upper critical field \( H_{c2}(T) \). As in Fig. 9, a \( H_{c2}(T) \) value of 3 kG for 2 K is determined from the merging point of the hysteresis curve as indicated by the arrow. Similarly, \( H_{c1} \) is 1 kG at 4 K. Moreover, each \( M(H) \) curve has a linear, nonhysteretic, paramagnetic-like background due to simple commensurate antiferromagnetic structure with moments aligned in the tetragonal basal plane.\textsuperscript{15,16} The exchange interaction is ferromagnetic in the basal plane with weak antiferromagnetic coupling mediated through the Ni layers.

Figure 10 yields higher-temperature \( H_{c2} \) values of 400 G at 5.2 K (\( T_N \)) and 300 G at 7 K (\( > T_m \)). Finally, it is of particular interest to note that, more than the superconducting hysteretic behavior at 6 K (near \( T_m \)), a non-
linear magnetic background was present in Fig. 11. Meanwhile, a much enhanced $H_{c2}$ of 2.2 kG was obtained at this temperature. This complex background is apparently due to the onset of the incommensurate modulated/spiral magnetic structure.

The temperature dependence of superconducting lower critical field $H_{c1}(T)$ can also be determined from the magnetic hysteresis measurements as shown in Figs. 9–11. The $H_{c1}(T)$ is defined as the deviation from linearity in the initial magnetization in each $M(H)$ curve in Figs. 9–11. The values thus obtained are 10 G at 7 K, 20 G at 6 K, 5 G at 5.2 K, 50 G at 4 K, and 200 G at 2 K.

### C. Low-temperature phase diagram

Based on this work and the data analysis outlined above, the low-temperature phase diagram $H(T)$ of HoNi$_2$B$_2$C is generated and given in Fig. 12. In terms of the temperature dependence of critical fields, the extrapolated $H_{c2}(0)$ value is 3.5 ±0.5 kG while the extrapolated upper limit of $H_{c1}(0)$ is 250 ±100 G. The previously reported $H_{c2}(0)$ value of 1.9 kG from single-crystal magnetic data is apparently too low since a $H_{c2}(2 K)$ value of at least 3.0 kG was already observed experimentally from the hysteresis measurement. On the other hand, the $H_{c2}(0)$ value of 3.5 kG is less than 4.5 kG reported from resistivity data where the $H_{c2}$ values are arbitrarily defined as the midpoint resistivity drop. The resistivity data may yield the surface critical field $H_{c3}$, which is the limit of field in which superconductivity can persist at the surface of the sample, rather than $H_{c2}$.

From $H_{c2}(0)$ and $H_{c3}(0)$, the Ginzburg-Landau parameter $\kappa$ value of 3.5 is evaluated using the formula $H_{c2}/H_{c1} = 2\kappa^2/(\ln\kappa + 0.5)$. As a comparison, $\kappa$ values of 12–15 are reported for nonmagnetic, higher-$T_c$ YNi$_2$B$_2$C and LuNi$_2$B$_2$C. From the local minimum of 400 G at $T_N$ of 5.2 K and the shape of the $H_{c2}(T)$ curve, a maximum effective internal field $H_{int}$ of 2 kG is deduced. The relatively slow recovery of $H_{c2}(T)$ below $T_N$ may be due to the incommensurate magnetic fluctuation where the neutron data indicate that the fluctuation is persisted down to lower temperatures.

The phase diagram with two magnetic transitions below $T_c$ reported for HoNi$_2$B$_2$C is indeed very similar to the previously reported pseudoternary Ho(Rh$_{1-x}$Ir$_x$)$_4$B$_4$...
system\textsuperscript{26–28} with compositions around $0.25 < x < 0.5$. For example, the Ho(Rh$_{0.7}$Ir$_{0.3}$)$_4$B$_2$ compound is superconducting at 5.5 K with two distinct magnetic transitions at 1.12 and 0.86 K from the specific-heat data. Nearly reentrant behavior is expected between these two magnetic transitions. True reentrant behavior was indeed observed for 0.075 $< x < 0.25$. For example, superconductivity of 5.2 K Ho(Rh$_{0.8}$Ir$_{0.2}$)$_4$B$_2$ was completely destroyed by a ferromagnetic ordering with Curie temperature $T_C$ at 2.77 K.

IV. CONCLUSION

Well-prepared HoNi$_2$B$_2$C samples were characterized by various experimental techniques including ac magnetic susceptibility, SQUID dc magnetic susceptibility, magnetic hysteresis, specific-heat, and electrical resistivity measurements. The results yield three distinct phase transitions: a superconducting transition temperature $T_C$ of 7.8 K (with onset of 8.5 K), and incommensurate magnetic ordering temperature $T_m$ of 5.7–6 K, and an antiferromagnetic Néel temperature $T_N$ of 5.2 K. Furthermore, a low-temperature phase diagram of this nearly reentrant magnetic superconductor is generated in terms of temperature dependence of $H_{c1}$, $H_{c2}$, $T_m$, and $T_N$. From the extrapolated $H_{c2}(0)$ of 250±100 G and $H_{c1}(0)$ of 3.5±0.5 kG, the Ginzburg-Landau parameter $\kappa$ value of 3.5 is derived.

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