Observation of Oscillatory Magnetic Order in the Antiferromagnetic Superconductor $HoNi_2B_2C$

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The nature of the holmium order in the reentrant superconductor ($T_c = 7.5$ K) $HoNi_2B_2C$ is revealed by neutron scattering. Upon cooling, a transversely polarized oscillatory magnetic state is formed ($T_M \approx 8$ K), characterized by a wave vector $(0,0,q_c)$ where $q_c \approx 0.05$ Å^{-1} is only weakly dependent on temperature and field. At the reentrant superconducting transition ($\sim$5 K) the amplitude of the oscillatory state abruptly decreases in favor of a commensurate antiferromagnet, whereby superconductivity is restored and coexists with antiferromagnetism at low temperatures.

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The interplay between the competing effects of superconductivity and magnetism remains at the forefront of research into the microscopic mechanisms underlying these ordered states of matter. In the well-known ferromagnetic systems $ErRh_4B_4$ [1,2] and $HoMo_6(S,Se)_8$ [3–5], such coupling manifests itself in the appearance of an oscillatory magnetic state ($T \sim 1$ K), often as a precursor to ferromagnetism which then extinguishes the superconductivity at low temperatures. More common for these ternary systems is the coexistence of antiferromagnetism and superconductivity, where anomalies in H_{c2} are often observed near T_N [6], but only $Tm_2Fe_3Si_5$ [7] is reentrant as a result of the antiferromagnetic order. However, no direct effect of the superconductivity on the magnetic order was observed in those systems. The newly discovered rare-earth quaternary nickel boron carbide systems [8–10] are ideal candidates for study as they represent a new class of noncuprate high-T_c superconductors which exhibit coupling of the rare-earth moments with the superconducting order parameter via a de Gennes scaling behavior [11]. The relatively high temperature scale of the magnetism necessitates that exchange interactions dominate the energetics. The most interesting material appears to be $HoNi_2B_2C$, which becomes superconducting at $\sim$7.5 K, reenters the normal conducting state at 5 K, and quickly recovers superconductivity at lower temperature. Here we show that the magnetic order that first forms on cooling is oscillatory in nature and is directly coupled to the superconducting order parameter. In contrast to previously known systems, however, this oscillatory state is detrimental to superconductivity, and the superconducting state only survives at low temperatures because of a first-order transition to a compensated antiferromagnet.

Most of the temperature and field-dependent neutron data were obtained on the BT-2 or BT-9 triple-axis spectrometers, operated with a pyrolytic graphite monochromator in two-axis mode. An incident wavelength of 2.35 Å was chosen so that a graphite filter could be used to suppress higher order wavelength contaminations. Typical collimations of 40′-20′-20′ (FWHM) before and after the monochromator, and after the sample, were used. A 7 g polycrystalline sample was prepared [10] with ^{11}B to reduce nuclear absorption, and was placed in an annular sample holder to reduce further the remaining absorption. A pumpled ^4He cryostat with a low temperature capability of 1.8 K or a 7 T superconducting magnet with a minimum temperature of 4.5 K was used to control the sample environment. Full diffraction patterns were also obtained on the BT-1 high-resolution powder diffractometer [Cu(311) monochromator and a wavelength of 1.5391 Å] at a few selected temperatures, so that complete profile refinements of the nuclear and magnetic structures could be made.

The crystal structure obtained from our profile refinements is in good agreement with the x-ray determination [12] and is shown in Fig. 1(a). Impurity phases in the sample are less than 2%. Details of the results of these refinements will be reported elsewhere [13]; here we simply note that the tetragonal ($I4/mmm$) structure ($a = 3.508\,33$ Å, $c = 10.5268$ Å at 2 K) consists of superconducting Ni_2B_2 layers and separate Ho-C layers, with the Ho ions occupying a body-centered tetragonal lattice. The low-temperature magnetic structure for the Ho moments is shown in Fig. 1(b) and consists of ferromagnetic sheets of spins in the a-b plane, with these sheets being coupled antiferromagnetically along the c axis. This is a simple commensurate antiferromagnetic structure, and, with no frustration involved, it is clear that the net exchange interaction within the Ho-C plane is ferromagnetic. The ordered moment is $(8.7 \pm 0.2)\mu_B$, substantially below the free-ion value of $10\mu_B$, indicating that crystal field effects are important. The entire sample is ordered antiferromagnetically, and this order coexists

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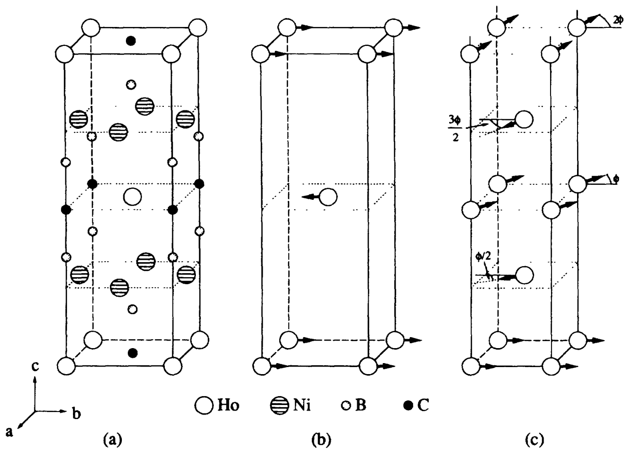

FIG. 1. $HoNi_2B_2C$ (a) crystal structure; (b) commensurate antiferromagnetic structure; (c) spiral magnetic structure.

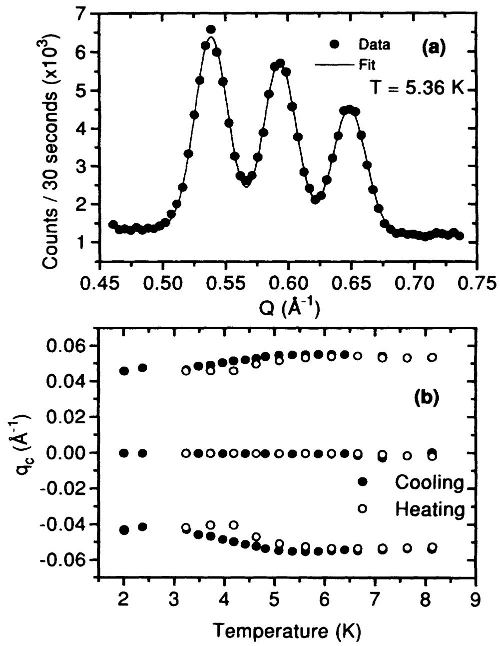

FIG. 2. (a) Observed scattering for the satellite peaks on either side of the (001) commensurate antiferromagnetic peak at $Q \cong 0.59$ Å^{-1}. The satellites have equal intensity after correction for the instrumental Lorentz factor and the magnetic form factor. (b) Satellite position as a function of temperature.

with superconductivity. In addition, our field-dependent studies show that the moments strongly prefer to lie in the *a-b* plane, again presumably due to crystal field effects, and indeed it is quite easy to produce a sample with the *c* axis aligned perpendicular to the field direction by the application of modest fields at low temperatures. Thus an *xy* model with fourfold anisotropy would be suitable to describe the moments at low T. For the exchange interactions an anisotropic three-dimensional exchange model is likely appropriate, with ferromagnetic exchange in the *a-b* plane and a weaker antiferromagnetic exchange being mediated through the Ni layers.

Figure 2(a) shows the observed scattering at 5.3 K in the vicinity of the (001) antiferromagnetic peak position. In addition to the (001) peak in the center, two strong satellite peaks are also observed, indicating that the low-T commensurate antiferromagnetic structure is modulated at this temperature. This is the largest satellite splitting seen, and based on a detailed comparison of ~30 satellites the modulation wave vector is found to be along the *c* axis, with the moments being transversely polarized with respect to the oscillatory wave vector $(0,0,q_c)$. Thus, the RKKY exchange interactions along the *c* axis must be more complicated than inferred from the simple low-temperature magnetic structure. At this temperature $q_c = 0.0543$ Å^{-1}, which corresponds to a wavelength $\lambda = 2\pi/q_c = 115.7$ Å, or about eleven unit cells along the *c* axis. This wave vector is essentially temperature independent above ~5 K [Fig. 2(b)] and weakly temperature dependent below 5 K. q_c is also field independent for the temperature range explored ($T \geq 4.5$ K). In view of the propensity of the moments to lie in the *a-b* plane and the net ferromagnetic interactions within these planes, the most likely model to describe the oscillation is a spiral in which the ferromagnetic planes rotate from layer to layer along the *c* axis, with a turn angle [14] $(\phi/2)$ of 16.4° away from the antiparallel direction for each holmium layer, as in Fig. 1(c). A transversely polarized spin-density wave cannot, however, be ruled out. We also observe a commensurate antiferromagnetic peak in addition to the satellites. If these two types of peaks are coming from the same regions of the sample, then the full magnetic structure would be the coherent superposition of these two structures; above ~5 K the spiral amplitude would be twice as large as the antiferromagnetic component of the moment. Under no circumstances, in particular above 5 K, has either state been observed separately, but it is still possible that the satellites and antiferromagnetic peaks originate from different regions of the sample in this temperature regime. In this case the regions where antiferromagnetic order develop initially would likely not be reentrant, as we discuss below. The superconducting and magnetic properties of nominal $HoNi_2B_2C$ are dependent on sample preparation [15], and different regions of the sample could have different magnetic structures depending on the electronic structure and/or whether they are superconducting.

The temperature dependence of these three peaks is shown in Fig. 3(a) for the commensurate antiferromagnetic peak, and in Fig. 3(b) for the oscillatory peak. On cooling, these peaks first become observable just above 8 K, and initially they increase in intensity at the same rate. This is the same temperature regime where the superconducting state is forming, with $T_c \approx 7.5$ K. The intensities of both types of peaks continue to grow down to

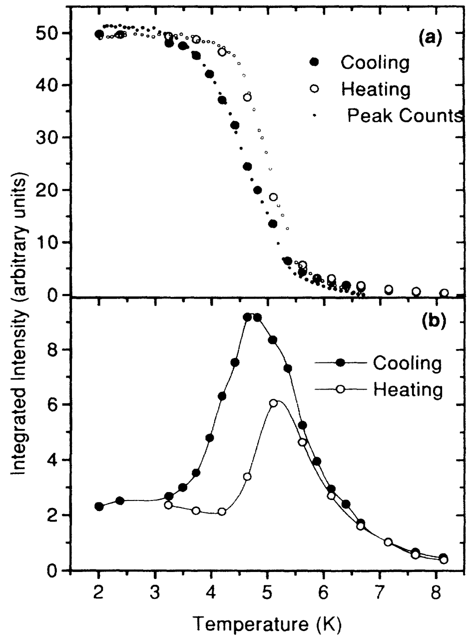

FIG. 3. (a) Integrated intensity of the antiferromagnetic peak as a function of temperature, showing hysteresis. The small dots are the peak counts versus temperature, taken with finer temperature steps. (b) Hysteresis in the temperature dependence of the satellite peaks. The rapid intensity decrease at ~5 K coincides with the reentrant superconducting transition. The solid curves are just a guide.

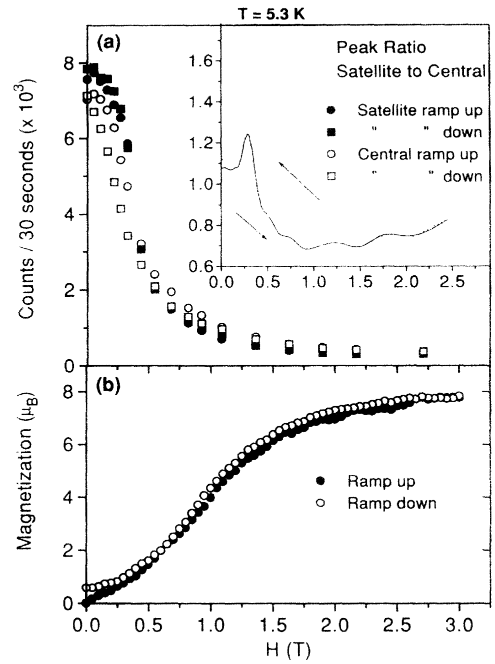

FIG. 4. (a) Field dependence of the satellite and commensurate antiferromagnetic peaks at 5.3 K. The inset shows the ratio of intensities of the satellite to commensurate peaks, where the satellite peak is favored at modest fields. (b) Induced magnetization as determined from the magnetic contribution to the (002) nuclear reflection.

5 K, where the intensity at q_c suddenly begins to drop. This is just in the narrow temperature range where the normal conducting state is reentered [11] and demonstrates that the oscillatory component is directly coupled to the superconductivity. With further decrease of temperature, the oscillatory amplitude rapidly drops, and superconductivity is quickly restored again in the system. The intensity belonging to the commensurate antiferromagnetic state, on the other hand, continues to grow as $T \rightarrow 0$, and this antiferromagnetic state readily coexists with superconductivity at low temperature. However, the intensity at q_c does not go completely to zero, but comprises ~4% of the total intensity at low temperatures, with a somewhat longer and temperature-dependent wavelength. This residual intensity could be from nonsuperconducting domain boundaries or from other nonsuperconducting regions. Indeed, our highest-resolution data [13] reveal a small, temperature independent, intrinsic width to the magnetic Bragg peaks, which we attribute to domain size effects (~2000 Å). Upon warming, strong hysteresis occurs in all the intensities, and to a lesser extent in q_c. These hysteretic properties should be directly reflected in hysteretic superconducting properties.

The field dependence of the magnetic intensities is shown in Fig. 4, taken after cooling from well above the ordered phases in zero field. These data were obtained after an initial field application to orient the particles, with the *a*-*b* plane following the (vertical) field. The position of the oscillatory peaks was found to be essentially field independent, and thus shown here is the intensity observed at the peak positions as a function of field. Figure 4(a) shows the field dependence of the three-peak structure (Fig. 2), along with the intensity ratio of the satellite to the central peak. These data are representative of the field behavior for most temperatures studied. Upon increasing the applied field the intensities of all three peaks decrease, but the central peak decreases faster than the satellites, producing a sharp maximum in their ratio (at ~0.3 T for this temperature). This implies that the oscillatory component is favored for modest fields. With decreasing H there is clear hysteresis, with the intensities below those observed on increasing H, but the maximum in the ratio is higher. Figure 4(b) shows the induced moment (magnetization) as measured at the (002) nuclear Bragg peak, where nearly the full low temperature moment is obtained for fields of a few T. The irreversibility in these data implies that the internal magnetic field from the Ho is somewhat stronger on ramping down than on ramping up. This may explain at least a portion of the hysteresis observed for the antiferromagnetic and satellite peaks.

The overall behavior for $HoNi_2B_2C$ appears at first glance to be similar in some respects to the "ferromagnetic" superconductors such as $HoMo_6S_8$ and $ErRh_4B_4$. In those materials superconductivity is well established, and then the magnetic system tries to order ferromagnetically at low T. Initially a compromise oscillatory state is formed, but the ferromagnetism quickly dominates the energetics, and they lose their superconductivity and are ferromagnetic and normal at low temperature. The behavior in $HoNi_2B_2C$ is similar in that an oscillatory state is also realized at high temperatures, and is suppressed at low temperature. However, the underlying origin of the oscillatory state may be quite different for the following reasons. In the present system the oscillatory state forms at, or slightly above, the superconducting state. Initially the amplitudes of both states are feeble, and it seems unlikely that the superconductivity would be able to force such an oscillatory state to form. Furthermore, such an oscillatory wave vector would be expected to be strongly temperature dependent [5], in contrast to the observed behavior. More importantly, as the oscillatory state is suppressed superconductivity returns, and quite readily coexists with the commensurate antiferromagnetic state at low temperature. We conclude that the oscillatory state itself is preferred by the magnetic system; that is, this is the state that would form if there were no superconductivity in the system. For the superconductivity, however, the misalignment of adjacent ferromagnetic planes destroys the antiferromagnetic compensation on the Ni planes between the holmium and produces a net ferromagnetic component on the Ni layers. Hence, it is the oscillatory state itself that is detrimental to superconductivity and just the opposite behavior as for the ferromagnetic superconductors. Finally, we remark that the π-phase model [16] may provide a description of this material at low temperatures, with an appropriate generalization for the spiral component above 5 K. Anomalies in the critical current along the c axis would be the signature of such a system.

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