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Magnetic pair breaking in $HoNi_2B_2C$

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Neutron-diffraction techniques have been used to study the interplay between superconductivity and magnetism in $HoNi_2B_2C$ ($T_c = 8$ K). The experimental results, obtained on *single* crystals, show that below approximately 4.7 K, this compound is in a simple antiferromagnetic state that coexists with superconductivity. Between approximately 4.7 and 6 K, an incommensurate modulated magnetic structure has been found. This observation strongly suggests that pair breaking associated with this incommensurate magnetic structure is responsible for the deep minimum in H_{c2} and the near-reentrant behavior observed in this compound at approximately 5 K.

I. INTRODUCTION

Since the discovery of high-T_c superconductivity considerable effort has been directed towards an understanding of various layered structures containing transition elements. The purpose of such studies is a better understanding of the interplay between magnetism and superconductivity. Among these layered structures, of particular interest is the recently discovered[1–4] family of rare-earth nickel boride carbides, RNi_2B_2C, where R stands for a rare-earth element. The structure[3] of these compounds is tetragonal (space group I_4/mmm) and consists of R-C layers separated by Ni_2B_2 sheets, a layered structure similar to the $ThCr_2Si_2$ structure and reminiscent of the high-T_c oxide superconductors. Perhaps the most interesting feature of these compounds is that superconductivity is observed[2,5] not only for the nonmagnetic rare-earth elements, but also for the magnetic rare-earth elements (Tm, Er, Ho). In this respect, the properties of the magnetic rare-earth nickel boride carbides are reminiscent of the magnetic superconductors RRh_4B_4 and RMo_6S_8.[6–9]

Among the heavy rare-earth nickel boride carbides, $HoNi_2B_2C$ ($T_c = 8$ K) is of particular interest. Resistivity and upper critical field measurements by Eisaki *et al.*,[5] performed on powder samples, demonstrated that this compound exhibits reentrant behavior even under zero field in a small temperature range around 5 K.[10] Their susceptibility measurements[5] and those by Canfield *et al.*[11] however, show that at temperatures below 5 K the compound is in an antiferromagnetic state that coexists with superconductivity. Therefore, it is natural to assume that, in the reentrant (or near-reentrant[10,11]) temperature range, the magnetic structure of $HoNi_2B_2C$ is different from the antiferromagnetic state at low temperatures. This observation motivated us to initiate a systematic study of the magnetic structure of this compound by neutron-diffraction techniques. The measurements were performed on *single* crystals of $HoNi_2B_2C$ grown and characterized as described below.

II. EXPERIMENT DETAILS

Single crystals of $HoNi_2B_2C$ of sufficient size for neutron-scattering experiments were grown at the Ames Laboratory by the high-temperature flux growth technique[12] and characterized by x-ray diffraction and magnetization measurements.[11] The boron used in the sample was isotopically depleted in the heavily absorbing B^{10} nuclei. Single crystal platelets of $HoNi_2B_2C$ with dimensions as large as $2\times4\times0.1$ mm^3 were removed from the flux. X-ray and neutron-diffraction measurements showed that in all cases examined, the platelets were single crystals of high quality (mosaic spread less than 0.2°) with the c axis perpendicular to the flat surface.

Magnetization measurements as a function of temperature and magnetic field were performed[11] on single crystals from the same batch as those used in the present experiments. The low-temperature normal-state magnetic susceptibility is highly anisotropic with a Curie-Weiss temperature dependence for $\mathbf{H}\perp c$ and with practically temperature independent paramagnetic behavior for $\mathbf{H}\|c$. The moment obtained by fitting the data for $\mathbf{H}\perp c$ to a Curie-Weiss law was found[11] to be $10.4\mu_B$ in good agreement with the value obtained by measurements[13] on polycrystalline samples. These observations suggest that the moment is in, or very close to, the basal plane and its magnitude is consistent with that expected for Ho^{3+} ions. A detailed account of these experiments will be published elsewhere.[11]

The neutron-diffraction experiments were performed using the triple-axis spectrometers HB2 and HB1A at the HFIR reactor of the Oak Ridge National Laboratory and H7 at the HFBR reactor of Brookhaven National Laboratory. For all three measurements, pyrolytic graphite (002) was used as monochromator and analyzer and pyrolytic graphite filters were used to minimize the $\lambda/2$ contamination of the incident beam. The measurements were performed with incident neutron energies of 14.7 and 41 meV. Measurements over the 1.7–300 K temperature range were taken for two different crystal orientations, namely, with the scattering plane coincident with the a-b or a-c planes.

III. RESULTS AND DISCUSSION

At temperatures above approximately 7 K, only nuclear reflections (hkl) with $h+k+l=2n$ are observed as expected

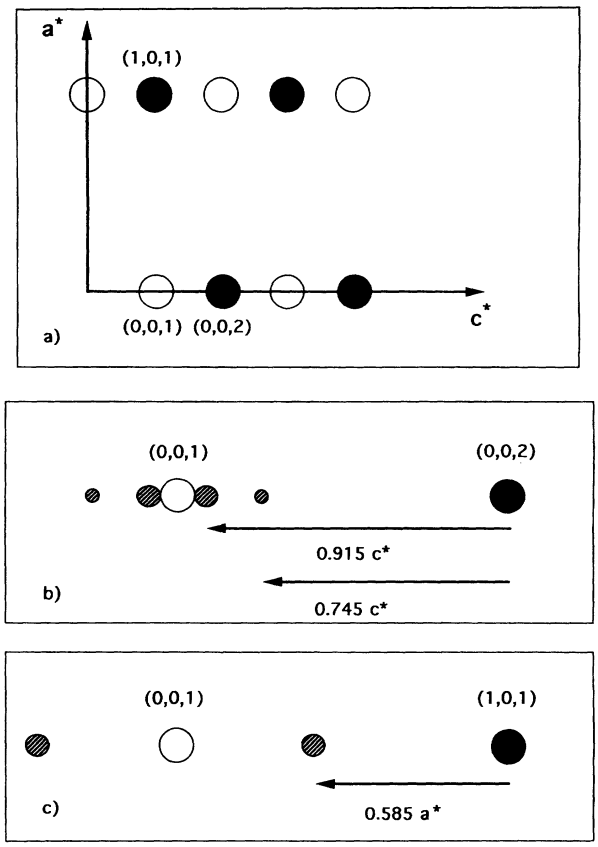

FIG. 1. (a) One quadrant of the $h0l$ reciprocal space plane showing the points associated with nuclear scattering (filled circles) and the commensurate antiferromagnetic Bragg points (open circles); (b) the first- and third-order satellites associated with the modulation wave vector, $\mathbf{K}_1 = 0.915\mathbf{c}^*$ (shaded circles); (c) the satellite positions associated with the modulation wave vector $\mathbf{K}_2 = 0.585\mathbf{a}^*$ (shaded circles).

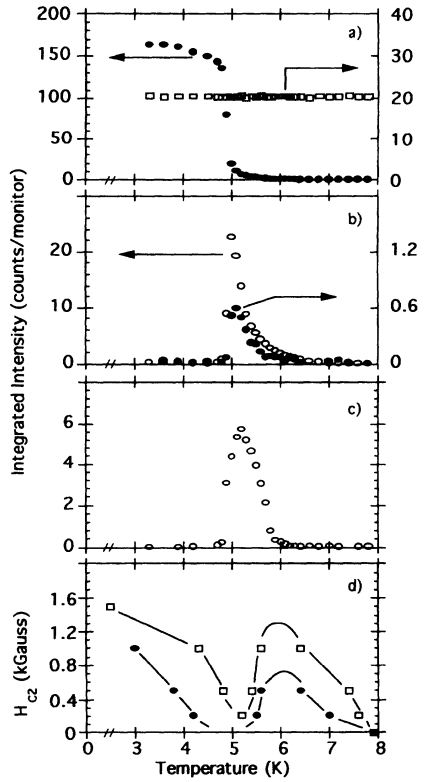

FIG. 2. Temperature dependence of (a) the (003) commensurate antiferromagnetic peak (filled ellipse) and the (101) nuclear Bragg peak (open rectangles); (b) the first- (open ellipse) and third-order (filled ellipse) satellites associated with the modulation wave vector, $\mathbf{K}_1 = 0.915\mathbf{c}^*$; (c) the $\mathbf{K}_2 = 0.585\mathbf{a}^*$ magnetic satellite; and (d) the upper critical field, H_{c2} (Ref. 11) determined via temperature-dependent magnetization measured parallel (open rectangles) and perpendicular (filled ellipse) to the tetragonal c axis. Lines are intended as guides to the eye.

from the crystal structure of the compound. As the temperature is decreased below approximately 6 K three additional types of diffraction peaks start to develop, as shown in the reciprocal space map of Fig. 1. Scattering develops at the positions of the forbidden nuclear reflections (hkl) with $h+k+l=2n+1$ [open circles in Fig. 1(a)]. Pairs of satellites to each allowed nuclear reflection appear with incommensurate wave vectors of approximately (0,0,0.915) [shaded circles in Fig. 1(b)] and (0.585,0,0) [shaded circles on Fig. 1(c)]. In addition, third-order satellites of the (0,0,0.915) reflection are observed.

The temperature dependence of the intensities of the observed satellites are shown in Fig. 2. Below $T_c = 8$ K, but above approximately 6 K, the local moments are paramagnetic. The intensities of the satellites increase as the temperature of the sample decreases below 6 K, reach a maximum at approximately 5 K, and then sharply decrease in intensity, and practically disappear at approximately 4.7 K. The intensity of the magnetic peaks at the commensurate antiferromagnetic positions $(h+k+l=2n+1)$, on the other hand, increase monotonically as the temperature decreases and start to saturate below approximately 4.7 K. These commensurate reflections are observed down to 1.7 K, the lowest temperature reached in these experiments. To within experimental uncertainty, the intensities of the nuclear-diffraction peaks remain constant over the entire temperature range investigated.

The above observations imply that there are three different magnetic regimes for the local moments in this compound in the 300–1.7 K temperature range. Between 300 K and approximately 6 K the local moments are paramagnetic. In this region, only nuclear scattering and critical magnetic scattering are observed. Below approximately 4.7 K down to 1.7 K, the lowest temperature reached in the present experiment, the compound is a commensurate antiferromagnet, since in addition to nuclear scattering, magnetic reflections (hkl) with $h+k+l=2n+1$ are observed. In this temperature range the Ho^{3+} moments are aligned ferromagnetically in each layer (basal plane of the tetragonal structure), with the magnetic moments of two consecutive layers (along the c axis) aligned in opposite directions. The magnetic cell has the same dimensions as the chemical cell, consistent with the absence of magnetic reflections with half-integer indices. Since the structure factors obtained from the intensities of the observed antiferromagnetic peaks are subject to relatively large uncertainties due to secondary extinction effects (especially those obtained from the measurements performed with

an incident neutron energy of 14.7 meV) powder diffraction measurements were also performed at these temperatures. The powder diffraction intensities, and those obtained from the 41 meV single crystal data (although the latter, as mentioned above, are subject to relatively large uncertainties), are consistent with the moment being in the basal plane. The magnitude of the moment was found to be $(10.5\pm1)\mu_B$, a value consistent with that expected from Ho^{3+}.

The most interesting temperature range is between approximately 4.7 and 6 K. Here, in addition to the developing commensurate antiferromagnetic structure described above, a modulated magnetic structure, or structures, characterized by wave vectors $\mathbf{K}_1=0.915\mathbf{c}^*$ and $\mathbf{K}_2=0.585\mathbf{a}^*$ occur. The Ho^{3+} moments, to first order, form a c-axis spiral with a turn angle of approximately 165° (0.915π); this spin arrangement is close to that of the low-temperature collinear antiferromagnetic structure described above. The presence of the third harmonic reflections indicates a "squaring" of the simple spiral. Along the a axis (or the equivalent b axis of the tetragonal structure) the magnetic ordering can be described in terms of a structure where neighboring moments are rotated by approximately 104° (0.58π). Alternatively, the structure can be viewed as a transverse spin wave with propagation vector along $\mathbf{a}^*$ (or $\mathbf{b}^*$). If this structure was commensurate, it would have a magnetic cell twice as large as the chemical cell in the basal plane. Therefore, the modulated structure(s) between 4.7 and 6 K may best be characterized as nearly antiferromagnetic. We point out here that it is not known, at this point, whether the modulations along the a and c axes described above are characteristic of a single domain or two, physically distinct magnetic structures. Indeed, the temperature dependence of the two modulations, shown in Figs. 2(b) and 2(c), exhibit some differences.

The most important result of the present experiment is the observation of this modulated structure between approximately 4.7 and 6 K. This is the same temperature range where there is an anomalously deep minimum in the upper critical field. Further, in this temperature range, features in the temperature-dependent specific heat and magnetization[11] can be associated with the onsets of both the incommensurate and commensurate antiferromagnetic states. The coincidence of the incommensurate ordering with the deep minimum in H_{c2} is clearly illustrated in Fig. 2 where [in Fig. 2(d)] the upper critical field is plotted as a function of temperature for fields parallel and perpendicular to the tetragonal c axis. Since similar anomalies have been observed in the antiferromagnetic superconductors $R\mathrm{Rh}_2\mathrm{B}_4$ and $R\mathrm{Mo}_6\mathrm{S}_8$ (Refs. 14–21) it is natural to attribute their occurrence in $\mathrm{HoNi}_2\mathrm{B}_2\mathrm{C}$ to the interaction between the local moment magnetism and superconductivity in this compound. What is unique, however, in $\mathrm{HoNi}_2\mathrm{B}_2\mathrm{C}$ is that it exhibits reentrant, or in the case of bulk single crystals, nearly-reentrant behavior in the vicinity of 5 K where the satellites characterizing the modulated structure reach their maximum intensity. It is, therefore, reasonable to assume that the deep minimum in the upper critical field is due to the pair-breaking interactions associated with the modulated structure. Compared with the previously known antiferromagnetic superconductors ($R\mathrm{Rh}_4\mathrm{B}_4$ and $R\mathrm{Mo}_6\mathrm{S}_8$) this interaction in $\mathrm{HoNi}_2\mathrm{B}_2\mathrm{C}$ must be particularly strong to bring about the observed deep minimum in H_{c2}.

Although considerable progress has been achieved towards a theoretical understanding of antiferromagnetic superconductors[22] no detailed microscopic theory of the magnetic structures that occur is presently available to assess how the magnetic structure may be influenced by superconductivity. $\mathrm{HoNi}_2\mathrm{B}_2\mathrm{C}$ presents us with an important opportunity to reopen this issue since the strength of the magnetic interactions at low temperature which favor the commensurate antiferromagnetic structure seems close to the strength of those favoring the intermediate modulated phase. Since the difference in energies between these two magnetic ground states appears to be small, the energy associated with the stabilization of the superconducting ground state may be significant in determining the ultimate low-temperature ground state of the coupled electron-local moment system. Indeed, preliminary neutron-scattering work on the magnetic field-temperature phase diagram of $\mathrm{HoNi}_2\mathrm{B}_2\mathrm{C}$ indicates a rich variety of magnetic phases in weak applied fields at low temperature. These results will be presented elsewhere.

In summary, we have observed a modulated magnetic structure in $\mathrm{HoNi}_2\mathrm{B}_2\mathrm{c}$ between 4.7 and 6 K that may account for the near-reentrant behavior of this compound. The particularly strong pair-breaking interaction between conduction electrons and the spin system in $\mathrm{HoNi}_2\mathrm{B}_2\mathrm{C}$ makes this system a particularly promising candidate for the theoretical understanding of the interplay between magnetism and superconductivity.

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