Second Low-Temperature Phase Transition in Frustrated UNi_4B

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Hexagonal UNi_4B is magnetically frustrated, yet it orders antiferromagnetically at $T_N = 20$ K. However, one-third of the U spins remains paramagnetic below this temperature. In order to track these spins to lower temperature, we measured the specific heat C of UNi_4B between 100 mK and 2 K, in applied fields up to 9 T. A sharp kink in C at $T^* \approx 330$ mK is observed at zero field, which we interpret as an indication of a second phase transition involving paramagnetic U. We attribute the rise in $\gamma = C/T$ between 7 K and 330 mK and the absence of a large entropy liberated at T^* to a combination of Kondo screening effects and frustration that strongly modifies the low T transition.

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Frustration, even without disorder, has been a prime ingredient for the study of novel magnetic phenomena. Already a wide variety of multiple phase transitions and critical/spin liquid behaviors have been observed in insulating materials [1]. However, when the frustration is combined with strong interactions, as exist in metallic U-based heavy-fermion (HF) compounds, highly unusual forms of magnetic ordering and/or (quantum) ground states can be expected [2]. As compared to the magnetic insulators, frustrated magnetic metals are much less common in homogeneous ordered crystals, and, therefore, their properties are neither fully known nor understood.

One such intermetallic compound, UNi_4B, has recently become the subject of experimental and theoretical study because of its hexagonal structure and basal-plane antiferromagnetic interactions [3–5]. The main reason for this interest is a highly unconventional ordered state that the compound attains at its Neél temperature of $T_N = 20$ K. Only two-thirds of the U atoms order magnetically, with the rest remaining paramagnetic below T_N [3]. The origin of such behavior must be sought in the frustrating nature of the triangular lattice and antiferromagnetic coupling.

We have followed the behavior of the one-third of the U spins that remain disordered below $T_N = 20$ K into the dilution-refrigerator temperature regime. Specific heat data display an anomaly at $T^* = 330$ mK, which we interpret as an antiferromagnetic ordering transition in the one-third U spin system. The size of the anomaly and its evolution with the applied magnetic field suggest the importance of the Kondo effect, with conduction electrons screening the paramagnetic U spins. It is the interplay between the geometric frustration and the Kondo effect that drives the ordering of the one-third U spins to a temperature 60 times lower than T_N. At such low temperatures the system is close to a $T = 0$ quantum critical point between the heavy-fermion and antiferromagnetically ordered (AF) ground states. One should consider quantum fluctuations out of the AF and HF ground states, together with geometric frustration, in order to gain a full understanding of UNi_4B. This emphasizes the richness of such itinerant frustrated magnetic systems.

The crystal structure of UNi_4B corresponds to the hexagonal $CeCo_4B$-type [6]. The U- and Ni(or B)-containing triangular planes are shown in Fig. 1. Within these planes both nearest (nn) and next nearest neighbor (nnn) interactions are antiferromagnetic, with a-b an easy magnetization plane. Below T_N this highly frustrated system partially orders, with magnetic unit cell containing nine U atoms (see Fig. 1). Six of them form an in-plane vortexlike pattern, with neighboring U spins rotated by 60°. The other three U atoms remain paramagnetic (with the field from the ordered U spins canceling to zero at these sites), and occupy two distinct positions: one is in the center of the vortex; two other are between the vortices and are surrounded by three pairs of antiparallel ordered U spins. The U spins are coupled ferromagnetically along the c axis, creating in 3D an ordered array of ferromagnetic and paramagnetic chains. A number of transport and thermodynamic properties were measured

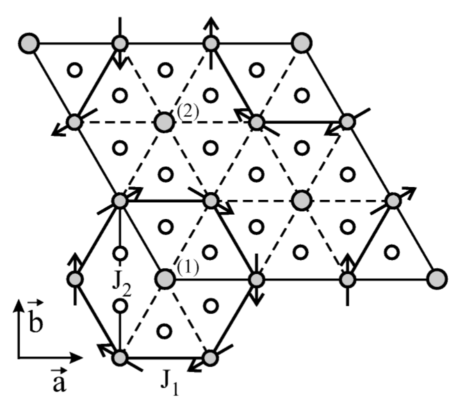

FIG. 1. Magnetic structure of UNi_4B in a-b plane, from Ref. [1]. U atoms at sites (1) and (2) remain paramagnetic below T_N. Open circles: Ni or B atoms.

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to investigate the ordered phase of UNi_4B, both in zero [3] and applied magnetic field [4,7]. Resistivity in the a-b plane continues to rise below T_N, peaks at 5 K, and then drops rather sharply. The specific heat divided by temperature $C/T = \gamma$ initially drops below $T_N = 20$ K, but it starts rising again below 7 K. γ continues to rise to the lowest previously measured temperature of $T = 0.35$ K to ≈ 0.5 J/mol K^2. Application of magnetic field up to 16 T suppressed γ by about a factor of 3. These results were taken as an indication that Kondo effect plays an important role in determining the low-temperature properties of UNi_4B [5,7].

Several theoretical attempts were made to reproduce the unique partially ordered state below T_N and interpret the low-temperature specific heat. Initially [3], ferromagnetic fluctuations in the paramagnetic 1D chains were suggested to explain the low-temperature upturn in γ. The specific heat calculated for a 1D Heisenberg ferromagnetic chain [8] with $S = \frac{1}{2}$ and $J_c = 35$ K gave a rather good representation of the measured low-temperature increase. An alternative viewpoint was taken by Lacroix *et al.* [5], where a model was developed to treat both geometric frustration and a possible Kondo interaction between the paramagnetic U spins and conduction electrons. The starting point of this model postulates that the 1D U chains along the c axis are close to a magnetic-nonmagnetic instability between the ferromagnetic alignment of U spins and a 1D lattice of Kondo-screened zero spin U atoms. Within this model several ground states are possible depending on the strength of the nn and nnn exchange interactions (J_1 and J_2, respectively) as well as the Kondo energy $\triangle$, which it is necessary to overcome to create a magnetic chain. For sufficiently small values of J_1 and J_2, the Kondo effect dominates and results in a nonmagnetic phase, with all U spins Kondo compensated. In the intermediate range of J_1 and J_2, and taking into account the slight lattice distortion found experimentally [9,10], the stable structure is the observed mixed phase described above.

Another approach treats U's as classical Heisenberg spins in the a-b plane [11]. Again, nn and nnn interactions are taken into account, as well as an interhexagon exchange coupling. For the appropriate choices of parameters, quantum fluctuations can destabilize the standard 120° (three sublattice) Neél order, and minimization of the total energy gives the experimentally observed ground state (Fig. 1). The calculated γ has a broad maximum at 2 K, and smoothly decreases to zero as $T \rightarrow 0$, due to the dominant contribution of spin waves. Therefore, this model is unable to reproduce the experimentally observed specific heat.

To distinguish between these scenarios and compare the data with detailed predictions of the 1D ferromagnetic chain and the Kondo models, we performed specific heat measurement at lower temperatures, down to 100 mK. The single crystal of UNi_4B used in this experiment (with a mass of $\approx$173 mg) was grown with the Czochralski technique. Similarly produced samples were evaluated with microprobe analysis and x-ray and neutron diffraction, and were found to be of high quality [3] (no second phase and without disorder). Specific heat data were collected with a quasiadiabatic technique [12], where ruthenium oxide thick film resistors [13] were used for thermometry.

Figure 2 shows the specific heat data collected with magnetic field parallel to the a axis (along the line connecting nearest in-plane U neighbors), where we plot both specific heat (a) and $\gamma = C/T$ (b) for magnetic field up to 9 T. Not all available field data are shown in the figure for the sake of clarity. The anomaly in zero field appears as a clear kink in the specific heat and a sharp peak in C/T at a temperature of $\approx$330 mK. This latter feature is substantially narrower (by about 80% on the high-temperature side) than a best fit Schottky anomaly with the ground and excited states of equal degeneracy. Increasing the degeneracy of the excited state results in a narrower anomaly. Such an approach was used to fit the specific heat of $LiHo_xY_{1-x}F_4$, a dilute Ising system in a "decoupled cluster glass" regime [14]. Thus, the narrowness of the 330 mK anomaly in UNi_4B may be an indication of glassy behavior caused by the frustration. Application of a magnetic field initially moves the anomaly to higher temperature, with the temperature T^* of the peak in γ reaching a maximum at about 3 T. For still larger fields the anomaly first broadens and then shifts to higher temperatures for fields above 4 T.

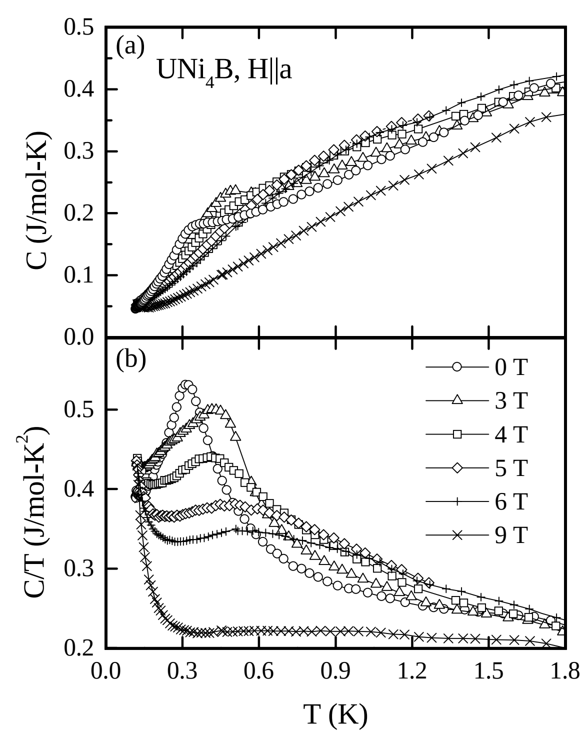

FIG. 2. (a) Specific heat of UNi_4B in magnetic field with $\vec{H} \parallel \vec{a}$. (○) $H = 0$ T; (△) $H = 3$ T; (□) $H = 4$ T; (◇) $H = 5$ T; (+) $H = 6$ T; (×) $H = 9$ T. (b) Specific heat divided by temperature (γ) for the data from (a).

The field of 9 T completely destroys the anomaly and exposes a low-temperature tail, which is dominated by the boron nuclear Schottky anomaly in the applied field, with possible contributions (on the order of 10%) from the hyperfine fields produced by the ordered U spins.

Figure 3 shows specific heat data taken with the field parallel to the b axis (along the line connecting the U next nearest neighbors), where we plot only γ vs temperature. The peak initially moves slightly to higher temperature for fields up to 2 T, before turning around, and is suppressed to $T = 0$ at 6 T. As in the case of $\vec{H} \parallel \vec{a}$, the field of 9 T completely suppresses the anomaly, and reveals a low-temperature nuclear Schottky tail.

To compare the data for different field orientations, we plotted T^* as a function of the magnetic field along both the a and b axes in Fig. 4. For the field along the a axis the dependence is not monotonic, with a break at 4 T. Low-temperature magnetic susceptibility measurements performed at 200 mK as a function of magnetic field in the same orientation ($\vec{H} \parallel \vec{a}$) show a change in slope (a kink) at a field of 4 T [15], corresponding to the peak observed in magnetoresistance [16]. It is likely that the break in the behavior of T^* vs field at 4 T for $\vec{H} \parallel \vec{a}$ is related to the same phenomenon. For both $\vec{H} \parallel \vec{a}$ and $\vec{H} \parallel \vec{b}$, T^* initially rises with field, though this feature is much more pronounced for $\vec{H} \parallel \vec{a}$. For $\vec{H} \parallel \vec{b}$ orientation, T^* is suppressed smoothly to zero by the field of 6 T. Spin reorientation transitions have been previously observed above 7 T via both magnetization and resistivity measurements [14], with the zero-field structure more resilient to the field applied in the b than in the a direction. One of the very surprising features of the ordered phase of UNi_4B below $T_N = 20$ K was the absence of subsequent ordering of the U spins in paramagnetic chains. These chains are coupled by the J_2 exchange interaction which appears to be dominant in the a-b plane. This interaction would be expected to drive the ordering of the paramagnetic chains as the temperature is lowered farther below T_N. There are other examples of magnetic systems that display cascades of ordering transitions, both insulating and itinerant [1,17,18]. For example, the insulating Ising triangular system $CsCoBr_3$ undergoes the first phase transition at 28 K, where, just as in the case of UNi_4B, only two-thirds of the spins participate. The remaining one-third of the spins order antiferromagnetically at 12 K, a temperature $2\frac{1}{2}$ times lower [19,20]. In the case of UNi_4B we can now say that a second ordering does indeed take place. However, the difference between the temperatures of the two observed phase transitions in UNi_4B is much greater, a factor of 60. Yet, we expect the ferromagnetic coupling J_c along the chains and the antiferromagnetic exchange interaction J_2 in a-b planes to drive both high- and low-temperature phase transitions. We believe that the origin of the large difference between the ratios of the phase transition temperatures in the two systems lies in the fact that $CsCoBr_3$ is an insulator and UNi_4B is a metal. Kondo screening of the paramagnetic U spins by the conduction electrons in UNi_4B plays a crucial role in suppressing the second antiferromagnetic ordering temperature T^*.

Within this scenario we can understand several features of the specific heat data, beginning with the size of the anomaly in specific heat associated with the low-temperature phase transition, which is manifested only by a kink in the specific heat. By integrating the available C/T data (after subtraction of the low-temperature Schottky tail and using various extrapolations to $T \rightarrow 0$), we obtain the entropy released at T^* of 0.1 ± 0.01 J/mol K. This value is 40 times less than $0.72R \ln 2 = 4.15$ J/mol K of magnetic entropy recovered at 25 K [16,21]. If we integrate C/T up to 2 K, the entropy grows to 0.57 J/mol K, close to 30% of the $\frac{1}{3}R \ln 2$ of the

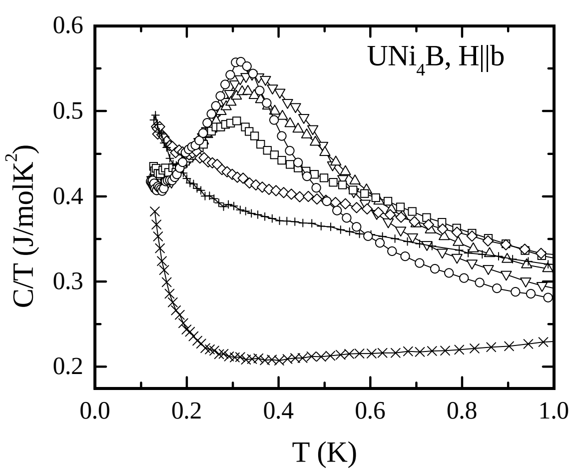

FIG. 3. Specific heat divided by temperature of UNi_4B in magnetic field with $\vec{H} \parallel \vec{b}$. (○) $H = 0$ T; (▽) $H = 2$ T; (△) $H = 3$ T; (□) $H = 4$ T; (◇) $H = 5$ T; (+) $H = 6$ T; (×) $H = 9$ T.

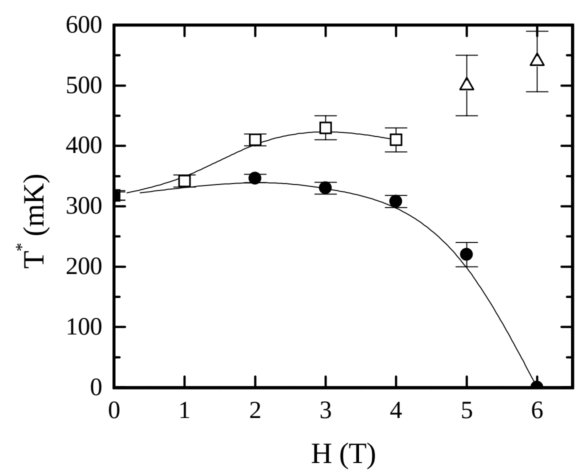

FIG. 4. Phase transition temperature T^* vs field. (□) $\vec{H} \parallel \vec{a}$; (●) $\vec{H} \parallel \vec{b}$. Solid lines are guides to the eye. The △'s indicate the broad maximum in the data about 4 T for $\vec{H} \parallel \vec{a}$.

total entropy one can expect for the U spins in the paramagnetic chains (assuming a doublet ground state).

There are two mechanisms at work which result in a reduced T^* and a limited peak in C/T at the phase transition. (i) Frustration affects both the low (T^*) and high (T_N) temperature ordering transitions. The strongest interaction that couples U spins is ferromagnetic exchange $J_c = 35$ K along the c axis. However, frustration and weak AF exchange (J_2) in the a-b plane hinder magnetic order from taking place. T_N is diminished and only partial ordering occurs at 20 K. Note that below T_N the remaining paramagnetic spins feel no internal field from the surrounding ordered moments (see Fig. 1). Therefore, they can be viewed as a new renormalized triangular lattice with nn exchange J_2, that is inherently frustrated. (ii) Kondo screening and development of the heavy-fermion state are present with characteristic temperature $T_K \approx 9$ K [7,16]. Such screening with this value of T_K alone would be expected to effectively reduce the nonordered U spins at $T^* = 0.33$ K, thereby absorbing most of the spin entropy into γ and greatly weakening the exchange interaction between these paramagnetic moments. Hence, due to frustration and the Kondo effect, T^* is much smaller than T_N and most of the entropy associated with paramagnetic spins is liberated well above T^*, resulting in a small specific-heat feature at T^*.

The unusual evolution of T^* with magnetic field, displayed in Fig. 4, seems to be caused by the field breaking of the Kondo singlet state, increasing the U magnetic moments, and thus increasing T^*. The reversal of this trend at higher magnetic field (especially pronounced for $\vec{H} \parallel \vec{b}$ orientation) is most likely due to the usual tendency of the magnetic field to suppress the antiferromagnetic order. In addition, a larger field creates Ising behavior along the field direction, eliminating the transition entirely [22].

Our observation of a second T^* phase transition, possibly into a three sublattice 120° planar ordered state with greatly reduced moments, is not in accord with calculations of Ref. [5]. While this theory uses a Kondo compensation to account for the 20 K phase transition and its unusual magnetic structure, it does not predict a second low T transition at $T^* \ll T_N$. In any case, the definitive proof of a "weakened" T^* phase transition requires more than specific-heat measurements. Resistivity experiments [23] do exhibit a peak in $d\rho/dT$ at 280 mK. However, anomalies have not been clearly detected in preliminary ac susceptibility [15] and μSR [24] measurements in this temperature regime. Also, neutron diffraction has not yet been performed at such low temperatures. Detailed studies of the above experimental quantities would be most useful in testing our suggestion for explaining the observed specific heat anomaly.

In conclusion, we have discovered a second low-temperature phase transition in magnetically frustrated hexagonal UNi_4B. The low temperature $T^* = 330$ mK with very large ratio $T_N/T^* = 60$, small entropy, and a nonmonotonic field dependence of the specific heat anomaly can be qualitatively explained by a combination of the Kondo screening and geometric frustration.

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