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Reduced-moment antiferromagnetism in single-crystal UNi_4B

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We present an extensive experimental study on a single-crystalline sample of the new hexagonal compound UNi_4B. The magnetic anisotropy as observed in susceptibility and resistivity is huge, with small antiferromagnetically ordered U-moments lying in the (a,b)-plane. Below $T_N = 20$ K, a large, nearly field-independent increase of the linear specific-heat coefficient up to 250 mJ/mol K^2 is observed, comparable to that of heavy-fermion UCu_5.

In a previous paper [1] we have described the unusual magnetic properties of the new compound UNi_4B, a member of the growing class of '1–5' intermetallic compounds, in polycrystalline form. After this initial study of the magnetism, we have prepared a single crystal to investigate the magnetic anisotropy. Here we present the low-temperature properties of oriented UNi_4B, as studied by magnetization, resistivity and specific-heat measurements over a wide range of temperatures (1.3–300 K) and fields (0–35 T). We will conclude by discussing the atypical behavior of these properties in the antiferromagnetic state (Néel temperature $T_N = 20$ K) through a comparison with the well-known 'heavy-fermion' compound UCu_5 [2], and consider possible spin-frustration effects in the hexagonal basal plane.

We have grown a large single crystal of UNi_4B at the FOM-ALMOS facility with the 'tri-arc' Czochralski method. No additional heat treatment was given after the crystal growth. The quality of the crystal was confirmed by X-ray diffraction and electron probe microanalysis (EPMA), which gives a relative composition $U_{1.08(1)}Ni_{4.06(4)}B_{0.86(5)}$, using modern absorption-correction procedures. The lattice parameters are $a = 4.952$ Å and $c = 6.954$ Å, with the proper $CeCo_4B$ crystal structure [1], and agree with those of polycrystalline samples and those obtained by Val'ovka and Kuz'ma [3], who first reported the existence of this compound. A slight mosaic structure of the single crystal was observed by means of X-ray Laue diffraction. The c-axis is constant throughout the entire crystal, but several orientations in the basal plane are present. Therefore, the in-plane anisotropy cannot be resolved in detail. The inter-uranium distances, d_{U-U}, are different in the two principal directions, viz in the (a,b)-plane d_{U-U} is 4.95 Å, while along the c-axis d_{U-U} is only 3.48 Å. This small d_{U-U} should be contrasted with the much larger 4.2 Å of the new HF superconductor UPd_2Al_3, which possesses a sizeable local moment [4].

In fig. 1 we present typical susceptibility data, $\chi \equiv M/H$, as measured with a vibrating-sample magnetometer from 1.6 K up to room temperature, in fields of 0.5 T and 5.0 T. Above 100 K, the susceptibility in the *basal plane* obeys a Curie–Weiss law with $p_{eff} = 2.90\mu_B$ and $\Theta_{CW} = -64.8$ K (not shown), indica-

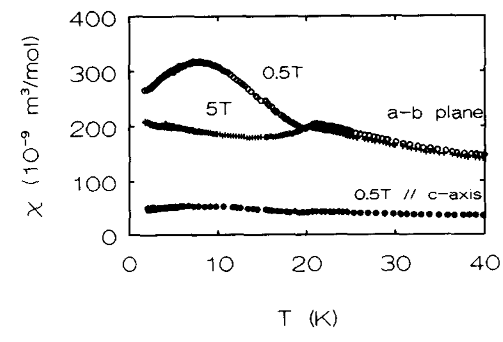

Fig. 1. Susceptibility ($\chi \equiv M/H$) of UNi_4B in the (a,b)-plane (○: $\mu_0 H = 0.5$ T; +: $\mu_0 H = 5$ T) and along the c-axis (●: data taken in 0.5 T). Note the large anisotropy and the suppression of the low-temperature maximum in large applied fields.

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tive of large (high-temperature) uranium moments. A small, but well-defined peak at 21 K signals antiferromagnetic (AF) ordering of uranium moments lying in the basal plane. If we define T_N as the maximum in $\partial(\chi T)/\partial T$, $T_N = 20.0$ K. Note that χ along the c-axis is small and almost independent of temperature and field. The antiferromagnetic character of the transition was established by magnetization versus field sweeps around T_N, which are almost linear and without field remanence. Immediately below T_N, an unexpected *increase* of $\chi(T)$ is observed, especially in low fields ($0.1\,\mathrm{T} < \mu_0 H < 2\,\mathrm{T}$). Here a well-resolved broad maximum develops around $T_0 \simeq 7$ K, which can be suppressed in larger fields applied parallel to the (a,b)-plane.

The large anisotropy and field dependence of the magnetization is further clarified by our high-field magnetization experiments, performed in the Amsterdam high-field installation. In fig. 2 we present data taken at $T = 4.2$ K in fields up to 35 T, with two in-plane field-orientations and with the field along the c-axis, respectively. For fields parallel to the (a,b)-plane, two or three successive transitions are found, depending on orientation. From the results of fig. 2 it is clear that UNi_4B exhibits considerable in-plane anisotropy. For the 'easy' direction in the (a,b)-plane, a single, field-hysteretic, step of $0.17\mu_B$ is observed at $H_1 = 9.3$ T (thin solid line) while for the 'hard' in-plane direction this transition requires two steps at $H_2 = 8.2$ T and $H_3 = 12.5$ T (dashed line) to complete. The small, nonhysteretic step of $0.075\mu_B$, at $H_0 = 20$ T (18.6 T at 1.4 K), for both in-plane directions might well indicate the antiferromagnetic phase boundary, as $\mu_B H_0 \simeq k_B T_N$. However, given the rather small and

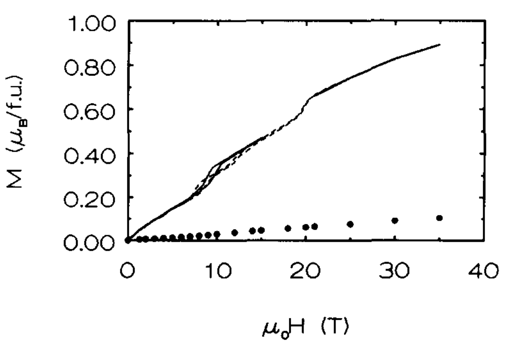

Fig. 2. Magnetization versus field measurements on single-crystalline UNi_4B at $T = 4.2$ K. The thick line represents the low- and high-field data, taken at constant fields (duration ±100 ms) parallel to the (a,b)-plane. The lines represent data taken continuously during smooth field pulses, with two different in-plane crystal orientations (dashed line shows two steps, while the thin solid line displays a single step, see text). The c-axis magnetization (•).

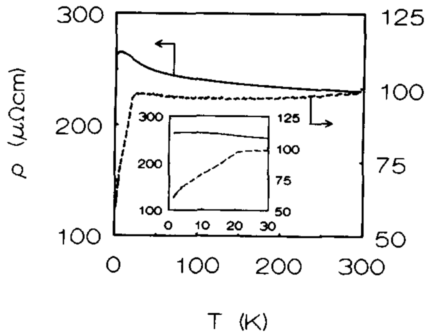

Fig. 3. Resistivity of single-crystalline UNi_4B with current parallel to the (a,b)-plane (—) and along the c-axis (- - -). Note the largely different absolute values of $\rho(T)$ for the two directions. The inset shows the same data from 0 K to 30 K.

not yet saturated moment of $0.89\mu_B$ in 35 T and the decrease of H_0 with decreasing temperature, further magnetization steps cannot be excluded. These magnetization data do show that the magnetically ordered uranium moment should be small, with an upper boundary of $\sim 0.4\mu_B$, estimated from the net step height (see fig. 2). The magnetization process of these small U-moments is rather complicated and requires further investigation. The induced c-axis magnetization is negligibly small, even in 35 T.

The huge magnetic anisotropy is also evident from the resistivity, $\rho(T)$, shown in fig. 3. With the current in the (a,b)-plane, $\rho(T)$ increases monotonically upon cooling from room temperature (RT). The c-axis resistivity, which is much smaller at RT, exhibits a totally different temperature dependence. After an initial decrease, $\rho(T)$ rises a little as T_N is approached and then drops sharply below T_N. The T_0 of 7 K, as determined from the χ-maximum, is reflected by a 'knee' in the c-axis resistivity around this temperature.

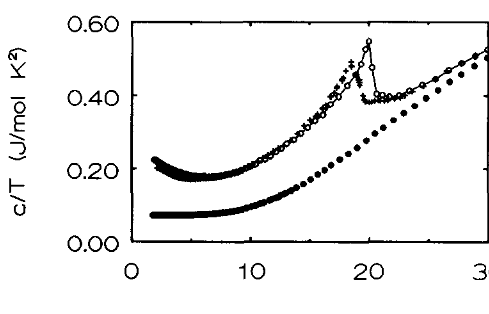

Fig. 4. Specific heat of UNi_4B plotted as c/T versus temperature, measured in zero field (○) and in 6 T parallel to the (a,b)-plane (+). The solid line is a guide to the eye. The zero-field data on nonmagnetic UCo_2Ni_2B (•) are given for comparison.

The absence of superconductivity in UNi_4B, at 1.5 K, was previously reported by Rogl and DeLong [5], who limited their study to the possibility of superconductivity. Our resistivity measurement on a polycrystalline sample did not show superconductivity down to 40 mK (not shown).

The characteristic temperatures T_N and T_0 are further evidenced from our specific-heat measurements, plotted as c/T versus T in fig. 4. Here we have a peak at $T_N = 20.0$ K and a broad maximum in $c(T)$ around $T_0 = 7$ K, that appears as an upturn in c/T below this temperature, reaching 250 mJ/mol K^2 at 1.8 K. While T_N shifts downwards by 1.5 K in an applied field of 6 T parallel to the (a,b)-plane, the low-temperature upturn is hardly affected by this large field, in contrast to the susceptibility. For comparison we also give the results on isostructural UCo_2Ni_2B, with $\gamma_0 = 72.7$ mJ/mol K^2, which does not show magnetic ordering down to 1.3 K. This lack of magnetism supports our supposition of ordered U-moments in UNi_4B. We can estimate the phonon contribution to the specific heat of UNi_4B by the total $c(T)$ of UCo_2Ni_2B, corrected for its constant linear term $\gamma_0 \times T$. A subtraction yields $\gamma = 92$ mJ/mol K^2 for UNi_4B above T_N, which is considerably smaller than that obtained if the phonon-specific heat is approximated by a single Debye function [1]. A definitive value of γ can only be determined by comparing with $ThNi_4B$. The magnetic entropy reaches $0.47R\ln 2$ at 25 K, indicative of reduced-moment ordering.

The huge magnetic anisotropy can be phenomenologically understood by considering the combined hybridization between neighboring uranium 5f electrons, and between 5f- and the (spd)-conduction electrons, donated by nickel and boron. Because of the much smaller distances along the c-axis, this hybridization is much stronger in the c-direction than in the basal plane. As a consequence, the ordered U-moment is reduced to $\sim 0.4\mu_B$, lying in the basal plane. The c-axis resistivity is sensitive to the strong hybridization along the c-axis and drops sharply below T_N. In view of the possible frustration of U-spins on a hexagonal lattice, we suggest that the magnetic moments in the plane are still fluctuating, albeit at a slow rate, thereby causing the large, increasing in-plane resistivity. The gradual drop of ρ below $T_0 = 7$ K and the maximum in χ then follow from 'freezing out' of these fluctuating moments. The upturn in c/T below T_0 is another consequence of these slow processes via the release of a large amount of entropy over a wide temperature range. The multi-step structure in the magnetization shows that different spin states are formed if large fields, which lift the frustration, are applied in the basal plane.

The low-T behavior of *hexagonal* UNi_4B with its anisotropic d_{U-U} bears striking resemblance to that of *cubic* UCu_5, which was claimed to be the first manifestation of the formulation of a heavy-electron ground state *from within* an AF-ordered state ($T_N = 15$ K) [2]. In UCu_5, the existence of at least 4 spin states, depending on the applied field, has been observed [6]. The upturn in c/T below 4 K up to $\sim$400 mJ/mol K^2 is cut off by a first-order, possibly magnetic, transition at 1 K, which results in a drop of the electronic specific-heat coefficient to $\gamma = 86$ mJ/mol K^2, thus showing the instability of the HF state to this phase transition [2].

Both UCu_5 and UNi_4B display long-range antiferromagnetism of reduced moments with a small change of entropy. Below T_N a considerable amount of entropy becomes available over a wide temperature range, giving the large c/T values. In UCu_5 this heavy-electron state is destroyed below 1 K by another phase transition, which cannot occur if the system is doped with silver [2]. These observations are a strong motivation for a detailed low-temperature study by different microscopic techniques on UNi_4B and related compounds.

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