Effect of interstitial C on the antiferromagnetism of UNiB4

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Effect of interstitial C on the antiferromagnetism of UNi$_4$B

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Abstract

We performed measurements of the specific heat, resistance, magnetization and DC-susceptibility of UNi$_4$BC$_x$ with 0 $\leq$ x $\leq$ 0.1. We found that the interstitially substituted carbon strongly affects the magnetism of the UNi$_4$B host matrix. While UNi$_4$B orders antiferromagnetically below 20 K, $T_N$ is reduced to 12 K for UNi$_4$BC$_{0.1}$. We discuss possible mechanisms for this tuning of the antiferromagnetism.

1. Introduction

Within the last few years the physical properties of UNi$_4$B, crystallizing in the hexagonal CeCo$_4$B-structure, have been investigated in detail [1,2]. It was found that UNi$_4$B undergoes an unusual antiferromagnetic transition of U moments below $T_N = 20$ K in zero field. Ni is non-magnetic. Furthermore peculiar spin-wave excitations have been seen below 7 K in the macroscopic measurements.

Recently, the magnetic structure of UNi$_4$B has been determined [3]. The magnetic ordering consists of two arrangements around central U atoms of (i) 6 U spins arranged in the basal plane like a vortex and (ii) 3 pairs of 2 antiferromagnetic spins. In both arrangements the net magnetic exchange interaction at the location of the central U atom is zero and its moment remains paramagnetic. Along the c-axis the spins are ferromagnetically coupled. Thus, at lowest temperatures ferromagnetic spin-waves appear due to the central U atoms.

Apart from the magnetic structure a crystallographic superstructure has been found in UNi$_4$B, and it was argued that this superstructure is related to the magnetic structure. Very recent work [4] has claimed that addition of small amounts of C to isostructural YNi$_4$B destroys the crystallographic superstructure and causes superconductivity at $\approx$12 K. Therefore, we started this examination of UNi$_4$BC$_x$ in order to determine how the magnetism and superstructure would be modified, and if superconductivity would occur.

2. Metallurgical details

Polycrystalline samples have been arc-melted in stoichiometric ratio (U, 3 N; B, 3 N; C, 3 N; Ni, 4 N) under an argon atmosphere. The carbon loaded samples were annealed in evacuated quartz-tubes at 900°C for 5 days. As reference sample we used polycrystalline UNi$_4$B annealed at 700°C for 7 days. All samples were checked by X-ray diffraction and electron probe micro analysis (EPMA). Our EPMA is sensitive to boron, whereas we can only determine carbon directly in the given phase for amounts higher than about 20 at%. Thus the C concentrations are nominal for UNi$_4$BC$_x$.

The results of the metallurgical analysis are summarized in Table 1. The carbonized samples show the presence of minority phases in a matrix of UNi$_4$B-stoichiometry. Only for UNiBC could we resolve the absolute amount of C. For the other second phases, as well as for the matrix, the carbon signal in the EPMA was too low to evaluate the C concentration. However, our data on physical properties and the X-ray...
Table 1
Composition and lattice parameters of UNi$_4$BC$_x$ (the notation ($C_x$) indicates unknown amount of C)

<table>
<thead>
<tr>
<th>$x$</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$V$ (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>98% UNi$_4$B</td>
<td>4.953</td>
<td>6.964</td>
</tr>
<tr>
<td>0.05</td>
<td>2% UNiB</td>
<td>4.936</td>
<td>6.984</td>
</tr>
<tr>
<td>0.1</td>
<td>80% UNi$_4$B($C_x$)</td>
<td>4.934</td>
<td>6.985</td>
</tr>
<tr>
<td></td>
<td>10% UNi$_4$(C$_x$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8% UNi$_4$B</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2% UNi$<em>4$B$</em>{2.4}$(C$_x$)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

analysis indicate that the matrix is loaded with C. Although we cannot determine the exact amount of carbon in the matrix, we note that it will be somewhat lower than the nominal $x$ in UNi$_4$BC$_x$, for the main second phase UNiBC is carbon rich, and consequently, the remaining phases will have a lower C concentration.

X-ray diffraction was used to investigate the effect of C on the structural parameters and on the superstructure. Clearly the $c/a$-ratio is changed by adding C. Unfortunately, even in pure UNi$_4$B the superstructure reflections are quite weak. Hence, we were unable to see the superstructure in any of our samples. We therefore cannot draw a conclusion about the influence of C on the superstructure.

3. Experiments

For measurements of the physical properties we used a standard adiabatic technique to measure specific heat $c_p$ from 2 to 30 K. Magnetization up to 12 T and DC-susceptibility up to 50 K were performed in a Foner-magnetometer. A 4-point AC-technique between 1.3 and 300 K was employed to measure resistance.

In Fig. 1 $c_p/T$ versus $T$ of UNi$_4$BC$_x$ with $x = 0$, 0.05 and 0.1 is plotted. The main features of pure UNi$_4$B, the antiferromagnetism and the low-temperature anomaly due to spin-wave excitations, remain unaffected by C loading apart from the decrease in the Néel temperature. This temperature $T_N$ decreases from 20 K at $x = 0$ to 12 K for $x = 0.1$. Also the minimum in $c_p/T$ versus $T$ below $T_N$ is shifted down in temperature. Further, the electronic contribution to the specific heat $\gamma$, extrapolated from $c_p$ above $T_N$, is significantly lowered with increasing $x$ ($\gamma_{x=0} = 0.24$ J/mol K$^2$; $\gamma_{x=0.05} = 0.17$ J/mol K$^2$; $\gamma_{x=0.1} = 0.12$ J/mol K$^2$).

Minority phases cannot account for these effects. This is evident for the shifts of $T_N$ and the minimum in $c_p/T$. But also the decrease in $\gamma$ cannot be due to secondary phases. Since there are no anomalies in $c_p$ other than those of UNi$_4$BC$_x$, the contributions of the impurity phases should behave as $\gamma_{imp} T + \beta_{imp} T^3$. In the worst case $\gamma_{imp}$ would be zero and $\gamma$ of UNi$_4$BC$_x$ higher than the above reported numbers. However, estimating the effective $\gamma$-values for this case, we only obtain an increase of 10–20% from the values given above for $x = 0.05$ and 0.1. With any non-zero $\gamma_{imp}$ the real $\gamma$ will be lower than this worst case scenario.

A similar shift of $T_N$, determined as minimum of $\partial^2 R/\partial T^2$ (see Fig. 2), which corresponds to the

![Fig. 1. Specific heat divided by temperature as a function of temperature for UNi$_4$BC$_x$.](image1)

![Fig. 2. Normalized resistance of UNi$_4$BC$_x$ as a function of temperature. In the insert $\partial^2 R/\partial T^2$ versus $T$ for $x = 0$, 0.05 and 0.1 is plotted. The minimum in $\partial^2 R/\partial T^2$ corresponds to the antiferromagnetic kink.](image2)
position of the kink in $R$ versus $T$, can be observed in
the normalized resistance of $\text{UNi}_4\text{BC}_x$. The change in
the general shape of the resistance with carbon substitu-
tion as seen in Fig. 2 probably reflects the influence
of the second phases forming low resistance paths in
the samples.

The tuning of $T_N$ is also visible in the susceptibility
(not shown). And in the magnetization versus field
(not plotted) the first spin-flop transition reported for
$\text{UNi}_4\text{B}$ can be identified for all samples. The transition
fields increase with C addition. No superconductivity
was observed in any of our samples down to 1.3 K.
Another sample of nominal composition $\text{UNi}_4\text{BC}_{0.2}$
showed no trace of superconductivity even down to
0.4 K.

4. Discussion

From our data we can construct a $B$-$T$ phase
diagram. Carbonizing $\text{UNi}_4\text{B}$ decreases $T_N$, while the
field of the first spin-flop transition slightly increases.
This behavior probably reflects the increase in crystal-
lographic anisotropy, as found from X-ray diffraction.

A possible model is that adding C to $\text{UNi}_4\text{B}$
simulates the effect of pressure on the $a$- and $b$-axes.
Although no data on elastic constants of $\text{UNi}_4\text{B}$ are
yet available, we can at least roughly estimate the
order of magnitude of pressure. The lattice parameters
$\Delta c/c$ and $\Delta a/a$ change with addition of carbon about
0.3% and $-0.3\%$, respectively. Typically lattice
parameter changes $\Delta x/x$ are about 0.1–0.01% kbar$^{-1}$.
Therefore the shift of $T_N$ could be the result of
chemical pressure of the order of 10 kbar. This is a
comparable large, yet not impossible, pressure effect.
Nevertheless, we are aware that the influence of C on
the band structure should also be taken into account.

In conclusion we have presented data on $\text{UNi}_4\text{B}$
with interstitially substituted carbon up to $x = 0.1$. By
adding small amounts of carbon, the magnetism and
the anisotropy of $\text{UNi}_4\text{B}$ can be tuned. We suggest
that these effects can be explained in terms of chemical pressure. But to verify this, an examination of the
magnetism of $\text{UNi}_4\text{B}$ under pressure will be necessary.

Acknowledgement

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References

Nieuwenhuys and J.A. Mydosh, Physica B 186–188
(1993) 270.
K.V. Gopalakrishnan, L.C. Gupta, C. Godart, B.D.
Padalia and R. Vijayaraghavan, Phys. Rev. Lett. 72
(1994) 274.