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Journal of Alloys and Compounds 323–324 (2001) 477–480

Journal of ALLOYS AND COMPOUNDS

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Magnetic features of the $(U_{0.50}Tm_{0.50})Ni_2B_2C$ solid solution

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Abstract

The quaternary borocarbides $TmNi_2B_2C$ and UNi_2B_2C crystallize in the body-centered tetragonal $LuNi_2B_2C$-type structure, and exhibit antiferromagnetic order below 1.53 and 218 K, respectively. The magnetic structure of $TmNi_2B_2C$ is characterized by incommensurate, long-range, spin-density-wave in the basal plane, with Tm moments along the *c*-axis, and does not involve ferromagnetic basal planes, while that of UNi_2B_2C is assumed to contain U moments along the *c*-axis in ferromagnetic basal planes. In the system $(U,Tm)Ni_2B_2C$ the different magnetic structures of the end compounds result in a frustration of magnetic moments, which is not just directional. Indeed, the newly-prepared intermediate solid solution $(U_{0.50}Tm_{0.50})Ni_2B_2C$ is paramagnetic down to 2 K, for both as-cast and annealed samples, with no indication for any cooperative phenomenon. The paramagnetic values of the annealed sample [$\theta=-5.6(5)$ K, $\mu_{eff}=5.4(1)$ μ_B] are compatible with those of the end compounds.

Keywords: $(U_{0.50}Tm_{0.50})Ni_2B_2C$; Pseudoquaternary borocarbides; Antiferromagnetism; Frustration

1. Introduction

The quaternary borocarbides ANi_2B_2C [A=Y, lanthanide (Ln), or actinide (An)] crystallize in the body-centred tetragonal $LuNi_2B_2C$-type structure (space group *I4/mmm*) [1,2]. The lattice parameters of the ANi_2B_2C compounds vary in the ranges $a=347$–380 pm, $c=986$–1066 pm. The ANi_2B_2C borocarbides can be classified into four groups: (a) A=La, Ce, Yb: normally-conducting and nonmagnetic. (b) A=Y, Lu, Th: superconducting (SC) and nonmagnetic. (c) A=Pr, Nd, Gd, Tb, U: normal conductors of various antiferromagnetic (AF) structures. (d) A=Dy, Ho, Er, Tm: superconducting with various antiferromagnetic structures.

The $(A,A')Ni_2B_2C$ solid solutions crystallize generally in the same $LuNi_2B_2C$-type structure of the end compounds. The magnetic features of the hitherto-known $(A,A')Ni_2B_2C$ solid solutions are discussed in a separate paper [3].

UNi_2B_2C is isostructural with the $LnNi_2B_2C$ compounds (see lattice parameters in Table 1). Its DC and AC magnetic susceptibilities and magnetization [2] indicate AF ordering below $T_N=218$ K. The magnetic data above 350 K follow a Curie–Weiss law with a paramagnetic Curie temperature $\theta=-280$ K and effective magnetic moment $\mu_{eff}=3.31$ μ_B/fu. The magnetic structure of this AF compound has not yet been determined. However, as in other uranium tetragonal systems, the ordered moments are expected to be along the *c*-axis, forming ferromagnetic basal planes.

$DyNi_2B_2C$, studied recently with as-cast and annealed polycrystalline samples, yielded RT lattice parameters [4–6] (see Table 1) and paramagnetic values [5,6] (see Table 2) close to the previously published data. A recent study by magnetization [5,6] indicated an initial, presumably two-dimensional (2D), ordering at $T_N=16.3(3)$ K, and a final, full three-dimensional (3D), ordering at $T_o=10.4(3)$ K. A third transition, to the SC state, was observed at $T_c\cong 6$ K.

$TmNi_2B_2C$, studied earlier on polycrystalline sample [7], had paramagnetic values of $\theta=-10.8$ K and $\mu_{eff}=7.7$ μ_B/fu. A study of a single crystal [8] yielded powder averages of $\theta=-11.6(4)$ K and $\mu_{eff}=7.54(2)$ μ_B/fu. The latter study [8] yielded magnetic ordering at $T_N=1.52(5)$ K, close to the neutron diffraction value of $T_N=1.53$ K [4]. The lattice parameters of $TmNi_2B_2C$ are given in Table 1 and averaged values of the above paramagnetic values in Table 2.

Indeed, neutron diffraction measurements were performed by Lynn et al. [4] on annealed polycrystalline $LnNi_2^{11}B_2C$ samples of most lanthanides (excluding Gd, La, and Lu).

The commensurate AF structure of $DyNi_2B_2C$, the 'AF-I-related' structure, is characterized by a wavevector

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0925-8388/01/$ – see front matter
PII: S0925-8388(01)01129-X

Table 1
R.T. $LuNi_2B_2C$-type tetragonal-cell parameters and volumes in $DyNi_2B_2C$, UNi_2B_2C, $TmNi_2B_2C$, and their intermediate solid solutions[a]

Borocarbide	a (pm)	c (pm)	V (10^{-30} m^3)	Refs.
$DyNi_2B_2C$	353.61(2)	1049.13(8)	131.18(2)	[5,6]
$(U_{0.50}Dy_{0.50})Ni_2B_2C$	352.3(1)	1051.0(3)	130.45(7)	[9]
UNi_2B_2C	351.3	1054.0	130.02	[2]
$(U_{0.50}Tm_{0.50})Ni_2B_2C$	**350.1(1)**	**1055.8(3)**	**129.38(5)**	PW
$TmNi_2B_2C$	348.66(2)	1058.60(5)	128.68(2)	[7,8]

[a] PW = present work.

(0,0,1) and alternate stacking along the c-axis of ferromagnetic basal (a–b) planes with Dy moments lying in these planes (aligned along the [110] direction in $DyNi_2B_2C$, as deduced from magnetization). The magnetic structure of $TmNi_2B_2C$ involves incommensurate, long-range, spin-density-wave in the basal plane [with a wavevector (0.093,0.093,0) at 0.65 K] below T_N, but with Tm ordered moments along the c-axis. The latter structure has been modified slightly in more recent single-crystal neutron-diffraction studies.

$(U_{1-x}Dy_x)Ni_2B_2C$ and $(U_{1-x}Tm_x)Ni_2B_2C$ solid solutions are expected to be formed, since the lattice parameters of the end compounds, listed in Table 1, differ by less than 1%.

In the end compounds of the $(U_{1-x}Dy_x)Ni_2B_2C$ system U ordered moments are aligned (presumably) along the c-axis while Dy ordered moments are perpendicular to the c-axis. Intermediate compositions in this system are expected to exhibit directional frustration of the ordered moments. Indeed, AC-susceptibility and magnetization study of the solid solution $(U_{0.50}Dy_{0.50})Ni_2B_2C$ [9] show paramagnetic behaviour down to 6.5 K, with deduced values $\theta = -5(5)$ K and $\mu_{eff} = 7.7(1)$ μ_B, compatible with those of the end compounds, indicating possible cooperative phenomena at lower temperatures. The observed paramagnetic behaviour, at variance with the AF order in $(Pr_{0.50}Dy_{0.50})Ni_2B_2C$ [5], was attributed to a directional frustration of the magnetic moments on the (U,Dy) site [9], which should be less pronounced for out-of-the-middle compositions [10].

Table 2
Paramagnetic values in $DyNi_2B_2C$, UNi_2B_2C, $TmNi_2B_2C$, and their intermediate solid solutions

Borocarbide	T_N (K)	θ (K)	μ_{eff} (μ_B)	Refs.
$DyNi_2B_2C$	16.3(3)	+0.6(5)	10.21(1)	[5,6]
$(U_{0.50}Dy_{0.50})Ni_2B_2C$	none	−5(5)	7.7(1)[a]	[9]
UNi_2B_2C	218	−280	3.31	[2]
$(U_{0.50}Tm_{0.50})Ni_2B_2C$	**none**	**−5.6(1)**	**5.4(1)**[b]	PW
$TmNi_2B_2C$	348.66(2)	−11(1)	7.6(1)	[7,8]

[a] Calculated value 7.6 μ_B.

[b] Calculated value 5.8 μ_B.

We present here magnetization study of the intermediate solid solution $(U_{0.50}Tm_{0.50})Ni_2B_2C$.

2. Experimental details

A polycrystalline sample of the $(U_{0.50}Tm_{0.50})Ni_2B_2C$ solid solution, weighing 2 g, was prepared by arc melting stoichiometric amounts of the constituents in an argon atmosphere. A titanium piece was used as a getter for oxygen. The weight loss in the melting process was less than 1%. Part of the as-cast sample, weighing 1 g, was then annealed in vacuum at 1323 K for 4 weeks. The as-cast and annealed samples were characterized by powder X-ray diffraction at room temperature (RT = 295 K). The annealing entailed samples with high content of the major $LuNi_2B_2C$-type phase. Minority phases, detected by X-ray-diffraction measurements, amounted to less than 5%.

Magnetic measurements were done on the as-cast and annealed polycrystalline samples (weighing 50–150 mg), using a MAGLAB System 2000 (Oxford Instruments), in applied magnetic fields, low (LF, 5–25 mT) and medium (MF, 0.05–1 T), in the temperature range 1.5–300 K.

3. Results

The intermediate solid solution $(U_{0.50}Tm_{0.50})Ni_2B_2C$ adopts the $LuNi_2B_2C$-type structure of the end compounds. Refinement of the RT lattice parameters from the X-ray diffractogram of the annealed sample (with content of the major-phase above 95%) down to a residual of $R = 0.030$, yields the values $a = 350.1(1)$ pm and $c = 1055.8(3)$ pm. These lattice parameters and the calculated tetragonal cell volume, $V = 1219.38(5) \times 10^{-30}$ m^3, are shown in bold in Table 1. With respect to the parameters of the end compounds $TmNi_2B_2C$ and UNi_2B_2C there is a slight shift from Vegard's law, negative for a and positive for c, while V obeys this law.

LF magnetization of both samples of $(U_{0.50}Tm_{0.50})Ni_2B_2C$ (Fig. 1) shows a normal low-temperature paramagnetic increase on both curves.

The magnetization of the annealed $(U_{0.50}Tm_{0.50})Ni_2B_2C$ sample, measured in various MF (shown for B = 1 T in Fig. 2) magnetic fields, also shows normal low-temperature paramagnetic increase, with no change in curvature down to 2 K, and with no indication of any kind of cooperative phenomena. The straight inverse molar DC-susceptibility line (Fig. 2) in the temperature range 10–300 K**,** obtained for applied magnetic fields up to 1 T, leads to a paramagnetic Curie temperature $\theta = -5.6(5)$ K, and an effective magnetic moment $\mu_{eff} = 5.4(1)$ μ_B (shown in bold in Table 2), close to the value calculated from the effective magnetic moments of the end compounds, namely 5.8 μ_B (see Discussion).

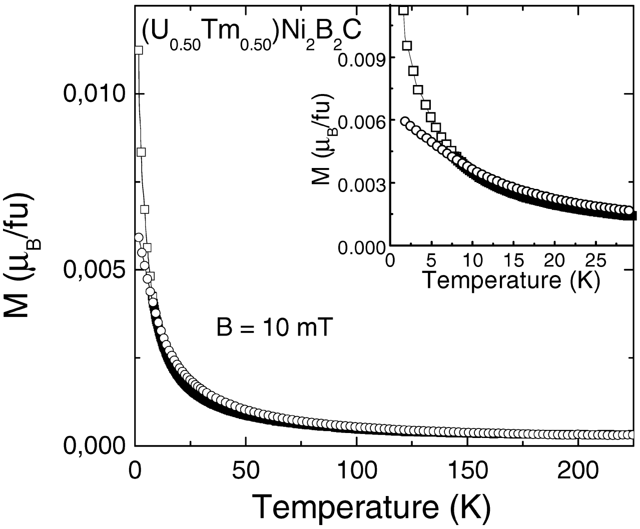

Fig. 1. Magnetization curves (in B = 10 mT) of as-cast (black curves) and annealed (gray curves) polycrystalline samples of $(U_{0.50}Tm_{0.50})Ni_2B_2C$ in the temperature range 1.5–225 K. Inset: Magnetization curves for 1.5–25 K.

4. Discussion

The lattice parameters of $(U_{0.50}Tm_{0.50})Ni_2B_2C$ are placed well between those of UNi_2B_2C and $TmNi_2B_2C$, confirming the intermediate nature ($x \approx 0.50$) of the composition.

The effective magnetic moment, $\mu_{eff} = 5.4(1)\mu_B$, measured for $(U_{0.50}Tm_{0.50})Ni_2B_2C$, should be compared with the value calculated from the effective magnetic moments of the end compounds, via their squares. For a general composition, $(U_{1-x}Tm_x)Ni_2B_2C$, the relation is:

$$[\mu_{eff}]^2 = x[\mu_{eff}(TmNi_2B_2C)]^2 + (1-x)[\mu_{eff}(UNi_2B_2C)]^2$$

while for the intermediate composition it is:

$$[\mu_{eff}]^2 = 0.5[\mu_{eff}(TmNi_2B_2C)]^2 + 0.5[\mu_{eff}(UNi_2B_2C)]^2$$

It turns out that the value on the thulium side is:

$$[\mu_{eff}(TmNi_2B_2C) = 7.6\ \mu_B] \approx [\mu_{eff}(Tm^{+3}) = 7.56\ \mu_B]$$

and is not going to change with the varying environments in all solid solutions in this system. On the uranium side:

$$[\mu_{eff}(UNi_2B_2C) = 3.3\ \mu_B] < [\mu_{eff}(U^{+4}/U^{+3}) = 3.58/3.62\ \mu_B]$$

and the value in the solid solutions is reduced even more, due to their random character. Indeed, the experimental value of $5.4(1)\mu_B$ can be accounted for by the above thulium value, a more-reduced uranium value of $\approx 2.7\ \mu_B$, and a slightly reduced thulium content, $x \approx 0.45$.

In order to understand the paramagnetism encountered in the $(U_{0.50}Tm_{0.50})Ni_2B_2C$ solid solution, we turn to the results in parallel intermediate solid solutions, $(Pr_{0.50}Dy_{0.50})Ni_2B_2C$ [5] and $(U_{0.50}Dy_{0.50})Ni_2B_2C$ [9], obtained in studies of the magnetic properties of the systems $(Pr,Dy)Ni_2B_2C$ and $(U,Dy)Ni_2B_2C$, respectively. These solid solutions also adopt the $LuNi_2B_2C$-type structure of the end compounds ($PrNi_2B_2C$, $DyNi_2B_2C$, UNi_2B_2C).

The magnetic structure of annealed polycrystalline $PrNi_2^{11}B_2C$, determined also by the neutron-diffraction study of Lynn et al. [4], is an AF-I-related structure, with Ln ordered magnetic moments lying in ferromagnetic basal planes, stacked antiferromagnetically (alternate stacking), similar to the structure of $DyNi_2^{11}B_2C$. At T = 1.7 K the Pr moments in the basal plane are $m = 0.81(3)\ \mu_B$, and are probably aligned along the [110] direction.

The recent study of $PrNi_2B_2C$ [5,6] yielded RT lattice parameters (see Table 1) and paramagnetic values (see Table 2) close to the previously published data. The magnetization measurements [5,6] also indicated an initial, presumably 2D ordering at $T_N = 15.0(3)$ K, and a final, full 3D ordering at $T_0 < 1.8$ K.

As the end compounds in the $(Pr,Dy)Ni_2B_2C$ system have similar AF-I-related structures [4], with Ln ordered moments aligned along the *c*-axis in ferromagnetic basal planes, stacked antiferromagnetically (+ − + −), their solid solutions are expected, and indeed found [5,6], to have AF ordering, below intermediate ordering temperatures. The planar magnetic ordering could be established, although the ferromagnetic moments of Dy (known to be along a [110] direction) and of Pr (exact direction unknown) may not be exactly along the same direction. The intermediate solid solution $(Pr_{0.50}Dy_{0.50})Ni_2B_2C$ was found to have mean lattice parameters (see Table 1), an appropriate effective magnetic moment $\mu_{eff} = 7.67(1)\ \mu_B$, and an intermediate 3D-ordering temperature, 5.0(2) K (see Table 2).

The different behavior of the intermediate solid solutions $(Pr_{0.50}Dy_{0.50})Ni_2B_2C$ and $(U_{0.50}Dy_{0.50})Ni_2B_2C$ is

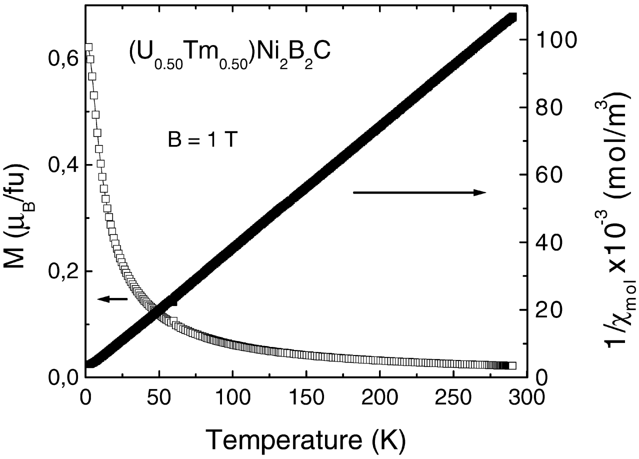

Fig. 2. Magnetization and inverse molar DC-susceptibility of $(U_{0.50}Tm_{0.50})Ni_2B_2C$, measured in B = 1 T in the temperature range of 2–300 K.

clear from the magnetic data accumulated in Table 2. In the former both Pr and Dy ordered moments lie in the basal plane, and eventually a common alignment direction is reached, allowing AF-I-related ordering, similar to the one in the end compounds, to take place. On the contrary, in $(U_{0.50}Dy_{0.50})Ni_2B_2C$ two uncompromised moment directions are involved, of the Dy ordered magnetic moments in the basal plane (along the [110] direction) and of the U ordered magnetic moments, presumably along the [1] axis, perpendicular to the basal planes.

It is this directional frustration of the magnetic moments on the (U,Dy) site that does not allow magnetic ordering and imposes paramagnetism in $(U_{0.50}Dy_{0.50})Ni_2B_2C$. In case of Dy and U ordered moments with a common alignment direction the ordering temperature in an intermediate solid solution should be close to the average of those of the end compounds, i.e. around 110 K. However the directional frustration of the U and Dy magnetic moments imposes paramagnetism down to low temperatures, as described in Table 2.

From the magnetic data accumulated in Table 2 it is clear that the behaviour of the intermediate $(U_{0.50}Tm_{0.50})Ni_2B_2C$ and $(U_{0.50}Dy_{0.50})Ni_2B_2C$ solid solutions is quite similar. In both cases the ordered magnetic moments are frustrated, resulting in nonordered systems. However, in the present material this frustration is not just directional, since the end compounds have totally different magnetic structures, as mentioned above. The more complex frustration eliminates the possibility of any cooperative phenomenon, hinted for in the case of $(U_{0.50}Dy_{0.50})Ni_2B_2C$ [9].

Acknowledgements

This work was partially supported by the exchange program 2000-ICCTI/CNRS. The stay of MK at ITN was supported by a PRAXIS XXI fellowship.

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