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Journal of Alloys and Compounds 275–277 (1998) 642–645

Journal of ALLOYS AND COMPOUNDS

Effect of chemical composition on magnetic properties of $GdNi_2B_2C$

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Abstract

We report on effects of non-stoichiometry in $Gd_tNi_xB_yC_z$ samples annealed at 800°C, with $t=16.67\%$ and $t+x+y+z=100\%$. Every sample shows a peak at 12–13 K in the zero field cooled branch of the susceptibility curve merging with the field cooled branch at the same Néel temperature $T_N(Gd)=20.0(5)$ K. The magnetization at 5 K, M(H), and the paramagnetic behavior for all materials have been measured and in the limit of uncertainty all look the same. We conclude that the non-stoichiometry, up to 5%, on Ni, B and C sites does not affect magnetic ordering in this material and that the annealing temperature is very crucial for magnetic impurity phases. © 1998 Elsevier Science S.A.

Keywords: Magnetic properties; $GdNi_2B_2C$

1. Introduction

The discovery of superconductivity in quaternary based borocarbides [1,2] has received great attention due to various behaviors such as: existence of high critical temperature T_c (up to 16 K) in the Ni-based materials $LnNi_2B_2C$ [3], the highest T_c (23 K) for an intermetallic system (in a Pd-based phase) [4], coexistence of magnetism and superconductivity in $LnNi_2B_2C$ [5] (with the magnetic Ln ions: Dy, Ho, Er, Tm) on the same energy scale ($T_{mag}\sim T_c$). Magnetic moments have been shown to decrease T_c roughly as expected from the de Gennes' scaling in pure $LnNi_2B_2C$. In these systems, superconducting properties are also always depressed by various substituents on the Ni site [6]. They are also very sensitive to changes in initial compositions in B and C, as shown in the case of Ho- and Dy-based $LnNi_2B_2C$ [7,8]. Other $LnNi_2B_2C$ with magnetic Ln ions (Pr–Tb) are magnetic and non-superconducting materials [9–12]. Out of these, $GdNi_2B_2C$ is of special interest as crystalline field effects do not occur, but also because various magnetic transitions were reported both intrinsic (19–20 K [13,14] and 13–14 K [15,16]) or probably due to impurity phases at 45 K [17], 7 K [18] or at ~2.6 K [19,20]. In order to check to which extent, the magnetic properties of $GdNi_2B_2C$ are also sensitive to chemical composition, we studied various starting compositions of the magnetic non superconducting $Gd_tNi_xB_yC_z$ system with $t=16.67\%$ and $t+x+y+z=100\%$. In these samples, we report on lattice parameters, phase coexistence and magnetic susceptibility measurements on both as-cast and annealed samples.

2. Experimental and results

Seven samples with composition $GdNi_\alpha B_\beta C_\gamma$, with (α,β,γ) as given in Table 1, were prepared using the following procedure. Stoichiometric amounts of the elements (Gd and Ni 99.9% pure, B 99.7% and C 99.7%) were melted in an arc furnace under a protective argon atmosphere in a three-step procedure: Ni and B were first melted together. Any weight loss during this melting process was considered to arise from boron losses and was compensated accordingly. Next, the required amount of gadolinium was added and melted two times. No weight loss was observed at this stage. Finally, carbon was added to prepare the Gd–Ni–B–C alloy and the resulting ingot was melted and flipped over six times to ensure a good homogeneity. The final ingots were cut in two parts of which one was sealed in an evacuated quartz tube and was annealed at 800°C for 3 weeks.

X-ray Powder Diffraction of the samples was performed on a Philips automatic X-ray diffractometer using Cu

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0925-8388/98/$19.00
PII: S0925-8388(98)00410-1

Table 1
Results of X-ray diffraction and magnetic measurements in Gd–Ni–B–C system (see text)

Initial Compositions	*a* (Å)	*c* (Å)	Vol. (Å)	% GdB_2C_2	% $GdNi_4B$	Other 2θ(°)	μ_{eff} (μ_B)	Θp (K)
$GdNi_2B_2C$	3.577	10.363	132.6	3	3	31.62	7.95	6.6
$GdNi_{2.1}B_{1.9}C$	3.576	10.363	132.5	6	6		7.98	8.4
$GdNi_{1.9}B_{2.1}C$	3.580	10.369	132.9	9	<8		8.20	8.8
$GdNi_{1.9}B_2C_{1.05}$	3.577	10.366	132.6	4	<8		8.13	5.4
$GdNi_{2.1}B_2C_{0.9}$	3.578	10.362	132.7	6	3		7.82	12.1
$GdNi_2B_{1.9}C_{1.1}$	3.576	10.372	132.6	5	<7		8.46	10.9
$GdNi_2B_{2.1}C_{0.9}$	3.578	10.360	132.6	8	<8	31.54	8.29	8.9

radiation: as-cast and annealed samples essentially crystallise in the body-centred tetragonal structure of a 'filled' variant of the $ThCr_2Si_2$-type (space group I4/mmm) [21]. The lattice parameters evaluated from least-squares fit of the X-ray line positions, within experimental errors, were found to be similar in every samples (see Table 1). Faint extra lines corresponding to GdB_2C_2 [22,23], a classical impurity of RNi_2B_2C samples [24], were observed in all samples with an intensity ranging from 3 to 9%, the intensity content being estimated from the ratio of the lines intensities. The highest GdB_2C_2 content is observed for the highest initial boron content. Other faint lines belonging to $GdNi_4B$ (2 to 8%) [25,26] were also observed. An unknown line is observed, for two samples, at $2\theta=31.6°$ which do not belong to GdNiBC [27], nor to $Gd_2Ni_3B_6$. Let us notice that our XRD results show that the phases $GdNi_2B_2C$, GdB_2C_2 and $GdNi_4B$ co-exist in as cast samples as well as after annealing at 800°C, irrelevant of initial changes in compositions. This behavior is different from what we recently observed in $HoNi_2B_2C$ [28] in which non-stoichiometry favours the appearance of (HoB_2C_2 or of $Ho_2Ni_3B_6$) [29] and $HoNi_4B$, but not of both.

A Quantum Design SQUID magnetometer was employed for the dc magnetic susceptibility measurements in the temperature range 4.2 K–300 K. In the high temperature range, samples show a Curie–Weiss behavior with an effective magnetic moment ~8.0 μ_B (see Table 1), as expected from Gd^{3+} in the $4f^7$ configuration, and a small Curie paramagnetic temperature Θ_p (see Table 1). We observe that the Θ_p values are positive in contrast to materials with dominant antiferromagnetic interactions. This is the result of the different impurity phases, each of them has its own Curie–Weiss characteristics and we measure the total paramagnetic behavior. Therefore we cannot derive from our data the exact interaction in the majority phase; even though the global behavior is similar in different samples.

Zero field cooled (ZFC) and Field Cooled (FC) measurements, in the low temperature range, were performed from low fields (<10 Oe) up to 10 kOe. Surprisingly, the curves are very much dependent on the intensity of the field as shown in Fig. 1 and Fig. 2. As an example, Fig. 1 shows the ZFC and FC susceptibility of $GdNi_{2.1}B_2C_{0.9}$

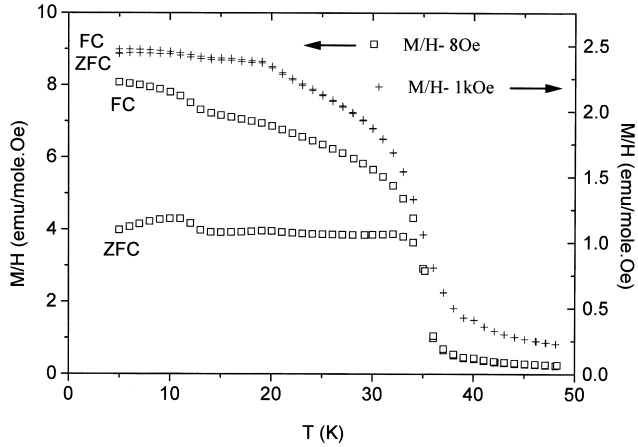

Fig. 1. ZFC and FC susceptibility of $GdNi_{2.1}B_2C_{0.9}$ versus temperature under 8 Oe (left scale) and 1 kOe (right scale).

under 8 Oe and 1 kOe. With a very low field, the antiferromagnetic transition of GdB_2C_2 (at ~45 K) is not seen, but a strong transition seems to exist at ~35 K which we interpret as due to the ferromagnetism of $GdNi_4B$ [25,26] (as we don't observe GdNiBC (T_{mag}~33 K [27]). The transition of $GdNi_2B_2C$ at ~20 K [13,18] is not observed whereas the spin re-orientation transition of $GdNi_2B_2C$ [16] is easily seen at ~13 K. With higher field

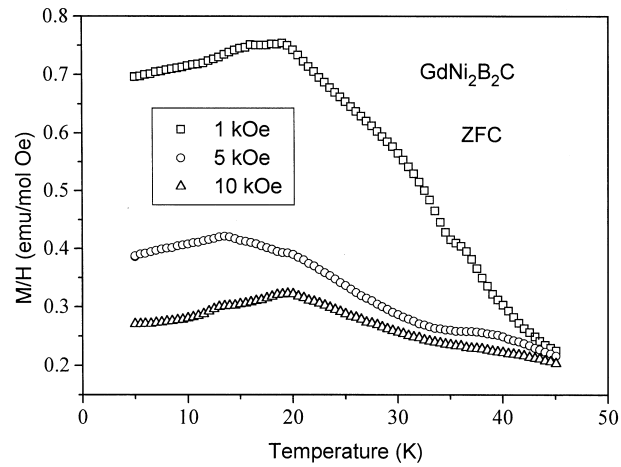

Fig. 2. ZFC susceptibility of $GdNi_2B_2C$ versus temperature under 1–5 and 10 kOe.

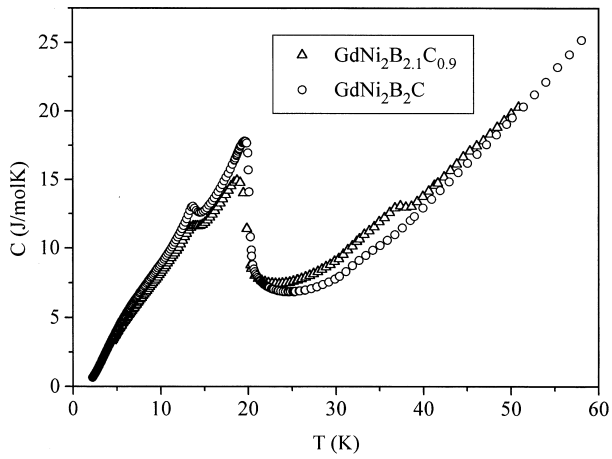

Fig. 3. Specific heat versus temperature of $GdNi_2B_{2.1}C_{0.9}$ annealed at 800°C and of $GdNi_2B_2C$ annealed at 1020°C.

(1 kOe), as illustrated in $GdNi_2B_2C$, the transition at ~20 K becomes prominent and as expected the ZFC and FC branches merge at this temperature corresponding to the main antiferromagnetic transition of $GdNi_2B_2C$ and the transition at ~13 K apparently vanishes. As seen on Fig. 2, with increasing field (1–5 and 10 kOe) the extrinsic transition at ~35 K progressively vanishes and intrinsic transitions are seen (both at 20 and 13 K). The same behaviors are observed for all the samples.

In order to establish that the impurity contents, as estimated from X-ray diffraction results, are reasonable, we perform specific heat measurements (zero field measurement) on a $GdNi_2B_{2.1}C_{0.9}$ sample (with the highest impurity content) and on a sample of $GdNi_2B_2C$ annealed at 1020°C for two weeks. The three transitions are clearly seen, in Fig. 3, at ~35 K which corresponds to T_c of $GdNi_4B$, at ~20 K for $GdNi_2B_2C$ and at ~13 K for the spin re-orientation in $GdNi_2B_2C$. From the amplitude of the jump in specific heat at 35 K and from the reduction of the peak at 20 K we estimate that roughly 15% of $GdNi_4B$ contribute to the specific heat, in reasonable agreement with X-ray data.

Mössbauer experiments on that series would be of interest to check sensitivity of the technique to the various magnetic impurities, even though the technique is not sensitive to spin re-orientation [14].

3. Discussion

Every sample shows a peak at 12–13 K in the zero field cooled branch of the susceptibility curve merging with the field cooled branch at the same Néel temperature T_N ~20.0(5) K. The magnetisation at 5 K, M(H), and the paramagnetic behavior for all materials have been measured and in the limit of uncertainty they all look the same. We conclude that the non-stoichiometry, up to 5%, on Ni, B and C sites in $GdNi_2B_2C$ (and probably in other $LnNi_2B_2C$) does not affect the magnetic ordering temperature and the global magnetic properties in these materials. In the case of superconducting $LnNi_2B_2C$, in which superconducting properties strongly depend on composition, characterization using measurements of magnetic properties alone is consequently inadequate.

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