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Superconductivity and magnetism in the Ho–Ni–B–C system

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Abstract

We investigated the annealing temperature, the carbon non-stoichiometry and the Fe doping effects on the physical properties of the superconductor $HoNi_2B_2C_x$ ($1 \leq x \leq 1.35$), using X-ray diffraction, magnetisation or electrical resistance measurements and ^{57}Fe Mössbauer spectroscopy. We show that the spontaneous re-entrant behaviour of $HoNi_2B_2C$ which has been attributed to the occurrence of incommensurate magnetic states destructive to superconductivity, is strongly enhanced by quenching or by decreasing the annealing temperature. The re-entrant behaviour also increases with the carbon content and the ^{57}Fe (0.5 at.%) doping. We conclude that the chemical defects introduced by quenching, deviation from stoichiometry or Fe doping, depress superconductivity and favour the appearance of the re-entrant behaviour. Our ^{57}Fe Mössbauer investigation shows that the presence of the incommensurate magnetic orders in the re-entrant region does not lead to the introduction of a hyperfine field at the Fe probe. © 1997 Elsevier Science S.A.

Keywords: $HoNi_2B_2C$; Superconductivity; Magnetism

1. Introduction

The decrease of T_c in RNi_2B_2C [1–3] (16.6 K, 11 K, 10.5 K and 8 K for R = Lu, Tm, Er and Ho, respectively [4]) can be interpreted as due to the pair breaking effect of the magnetic moments carried by the rare-earth ions [5], according to the De Gennes' factor $(g_J - 1)^2 J(J + 1)$, and to changes in the electronic states due to volume effects. In these compounds, the magnetic and the superconducting (SUP) transition temperatures are close and this results in an interesting competition between magnetism and SUP. In particular, $HoNi_2B_2C$ shows a spontaneous re-entrant behaviour which has been attributed to the existence of incommensurate modulated magnetic orders, destructive to superconductivity [6–8].

The aim of this work is to study the SUP and magnetic properties of $HoNi_2B_2C_x$ ($1 \leq x \leq 1.35$) with X-ray powder diffraction (XRD), magnetic or electrical resistance measurements and ^{57}Fe Mössbauer spectroscopy. We investigated the effects of the annealing temperature on the impurity phases stability and on the physical properties of $HoNi_2B_2C$. We also studied the dependence on carbon stoichiometry of the SUP properties in $HoNi_2B_2C_x$ ($1 \leq x \leq 1.15$). Finally, we tried to detect the presence of a transferred hyperfine field on the Mössbauer probe ^{57}Fe diluted (0.5 at.%) in a re-entrant $HoNi_2B_2C_{1.05}$ sample.

2. Experimental

Buttons of 2 g were prepared by the arc-melting method. Appropriate amounts of Ho (99.9%), Ni (99.9%), B (99.7%) and C (99.7%) were arc-melted on a water-cooled copper hearth, under an argon atmo-

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sphere. The total weight loss was less than 1%. Pieces of button were wrapped in Ta foils, sealed in evacuated quartz tubes and annealed at temperatures between 700 and 900°C for 2 weeks or at 1100°C for 6 days. Some buttons, annealed at 1100°C, were quenched in water. Samples were characterised by XRD using a diffractometer with Cu Kα radiation. The magnetisation measurements were investigated with a commercial SQUID magnetometer in zero field cooled (ZFC) conditions (measuring field of 10 G). Four-lead electrical resistance measurements were performed with typical current densities of 10 A/cm^2.

3. Results and discussion

3.1. Samples homogeneity

XRD results show that $HoNi_2B_2C$ is in equilibrium with the ternary compounds HoB_2C_2, $Ho_2Ni_3B_6$ and two unidentified phases. HoB_2C_2 is generally the main impurity phase. Impurities may influence the physical properties of the matrix. In particular, HoB_2C_2 which undergoes a ferromagnetic transition at 7 K [9], could be detrimental to the SUP of $HoNi_2B_2C$. Consequently, we studied the impurities stability depending on the annealing temperature, the carbon content or the Fe doping (for the Mössbauer study sample). Both as-cast and annealed $HoNi_2B_2C$ samples contain a very small amount of impurities (less than 5%) which is minimum when the annealing temperature is 800°C. The non-stoichiometric $HoNi_2B_2C_x$ ($1 \leq x \leq 1.35$) samples, annealed at 800°C, show a volume fraction of HoB_2C_2 which clearly increases with increasing carbon content, and reaches 15% for $x = 0.35$. When doping $HoNi_2B_2C_{1.05}$ with ^{57}Fe (0.5 at.%) and for an annealing temperature of 800°C, we observe a change in the impurities nature. HoB_2C_2 disappears whereas the amounts of $Ho_2Ni_3B_6$ and of another unidentified phase increase up to 5%. The lattice parameters of $HoNi_2B_2C$ (a = 3.517(1)Å; c = 10.525(4)Å) are consistent with the results of Schmidt and Braun [10] and of Godart et al. [11] and do not show any significant change with the annealing treatment, carbon content or Fe substitution.

3.2. Annealing temperature effects on $HoNi_2B_2C$

Fig. 1 shows ZFC magnetisation curves of $HoNi_2B_2C$ samples for various annealing temperatures. Two different types of behaviour are observed: SUP for the as-cast sample with a low T_c (approx. 5 K) and re-entrant behaviour for the annealed samples. Re-entrant behaviour is characterised by a first SUP transition at 8.2 K, followed by a plateau and a second transition around 5 K. The occurrence of the plateau indicates that the compound partially recovers the normal (non-SUP) state, and then returns to the SUP state at lower temperatures. Neutron diffraction studies [6–8] showed that in the re-entrant region, one or several incommensurate spiral magnetic states are formed. These modulated states are destructive to SUP through the increase in the pair breaking properties of the Ho^{3+} moments [6–8]. At the Néel temperature (T_N = 5 K [5,12]), they collapse in favour of the simple antiferromagnetic state which coexists with superconductivity.

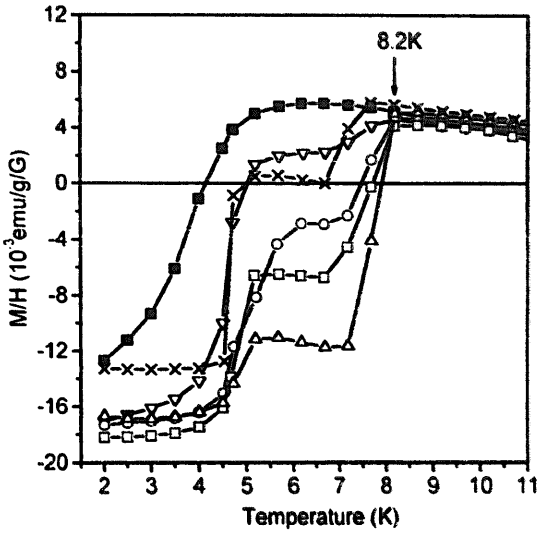

Fig. 1. ZFC magnetisation of $HoNi_2B_2C$ for the as-cast sample (full squares) and the annealed samples (empty symbols) at various temperatures: 700°C (down triangles), 800°C (circles), 900°C (squares), 1100°C (up triangles) and 1100°C + quenching (crosses). Lines are guides for the eye.

According to our magnetisation data, the second transition occurs at T_N which implies that the plateau is the materialisation of the incommensurate magnetic orders. The magnitude of the signal for the first SUP transition clearly increases with the annealing temperature. We observe a zero magnitude value for the as-cast sample and magnitudes of 10, 30, 50 and 75% of the complete diamagnetic signal for annealing temperatures of 700, 800, 900 and 1100°C, respectively. We conclude that high annealing temperatures reinforce SUP against the spiral magnetic states, irrelevant of the amount of impurity phases observed by XRD. These results are also confirmed by our lower critical field H_{c1} study. The values of H_{c1}, that we measured at 2 K, increase from less than 20 G for the as-cast and for the samples annealed below 800°C, to 80 G for annealing temperatures above 900°C. On the sample annealed at 1100°C and quenched, the magnitude of the transition (25%) and H_{c1} (60 G) are smaller than in the non-quenched sample. We assume that quenching is detrimental to SUP as it may favour a higher level of chemical defects. The evolution of

H_{c1} vs. temperature for the best SUP sample ($T_{ann.}$ = 1100°C) is shown in Fig. 2. In the pure SUP region ($T \leq 5$ K), H_{c1} clearly decreases with increasing temperature. This behaviour agrees with the empirical law $H_{c1}(T) \approx H_{c1}(0)[1 - (T/T_c)^2]$ with $H_{c1}(0) \approx 90$ G and $T_c \approx 5.2$ K, showing that the temperature dependence of the critical field is strongly influenced by the re-entrant behaviour.

From our XRD results, we observe that 800°C is the optimum annealing temperature as concerns the impurities content. However, the best SUP properties are obtained with a higher annealing temperature of 1100°C. We also show that quenching has important effects on SUP properties. These results indicate that the effect of the chemical defects is more important than the presence of a low content of the HoB_2C_2 impurity. Next, we investigated the physical properties of several non-stoichiometric samples.

3.3. Non-stoichiometry effects

Fig. 3 shows the electrical resistance vs. temperature curves of annealed $HoNi_2B_2C_x$ ($1 \leq x \leq 1.15$). Surprisingly, the $HoNi_2B_2C$ sample shows zero resistance at approximately 8 K, whereas it exhibits a re-entrant behaviour on the ZFC magnetisation data. From that, we conclude that electrical resistance is less sensitive to the re-entrance behaviour than magnetisation measurements. A similar effect has been reported by Schmidt et al. [13] when comparing electrical resistance and AC susceptibility measurements. As seen in Fig. 3, the onset of T_c rapidly decreases from 8.7 K ($x = 1$) to 7 K for $x = 1.15$. Moreover, compounds with $x \leq 1.05$ show zero resistance below

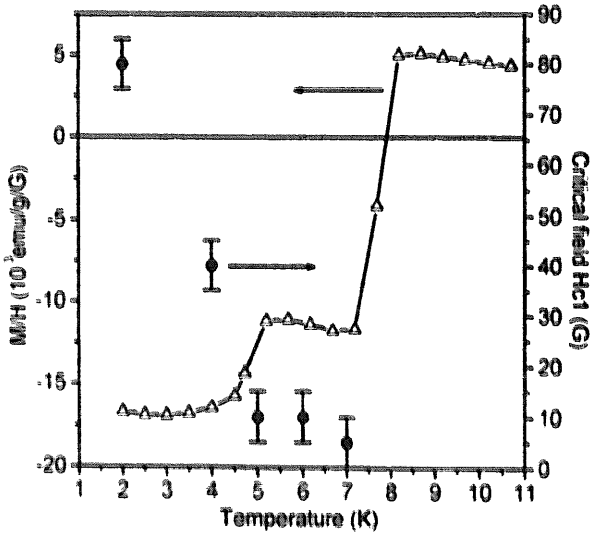

Fig. 2. Lower critical field H_{c1} vs. temperature for $HoNi_2B_2C$ annealed at 1100°C (full circles) and temperature dependence of the ZFC magnetisation (empty up triangles). The line is a guide for the eye.

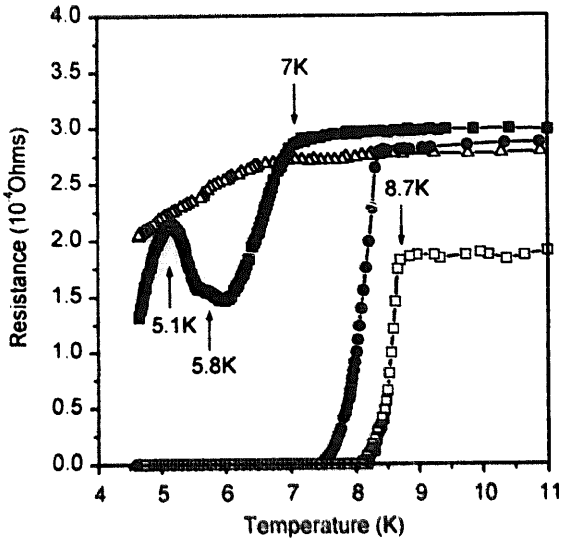

Fig. 3. Electrical resistance vs. temperature curves of $HoNi_2B_2C_x$ ($1 \leq x \leq 1.15$) samples annealed at 700°C for $HoNi_2B_2C$ (empty squares) and 800°C for $x = 1.05$ (full circles), 1.10 (empty triangles) and 1.15 (full squares).

T_c, whereas for greater carbon amounts, the samples exhibit a re-entrant behaviour and the resistance does not go down to zero above 4.5 K. $HoNi_2B_2C_{1.15}$ clearly displays a re-entrant maximum at 5.1 K which corresponds with the end of the plateau in the magnetisation curves. A weak anomaly is also noticed at approximately 5.8 K. This anomaly has been observed in specific heat and magnetisation measurements on a SUP single crystal [12] and in AC susceptibility measurements on polycrystalline samples [13]. It has been assumed that the anomaly is strongly connected with the development of the re-entrant behaviour, implying the existence of two independent incommensurate magnetic states, rather than one.

Our partial study shows that in $HoNi_2B_2C_x$, the re-entrant behaviour essentially appears when $x > 1.05$. The deviation from stoichiometry may introduce chemical site substitutions or vacancies on certain sites of the matrix, which in turn can depress the SUP properties. Surprisingly, Schmidt et al. [13] have reported that pure SUP behaviour was obtained for $x \geq 1.3$. Further investigations are in progress in order to clarify the non-stoichiometry effects.

3.4. ^{57}Fe Mössbauer study

We have performed ^{57}Fe Mössbauer absorption measurements in $HoNi_2B_2C_{1.05}$ doped with 0.5 at.% ^{57}Fe and annealed at 800°C, in order to examine if the presence of the incommensurate magnetic orders in the re-entrant region leads to the introduction of a hyperfine field at the Fe probe. As seen in Fig. 4, our sample shows a re-entrant region between 4.8 and 5.6

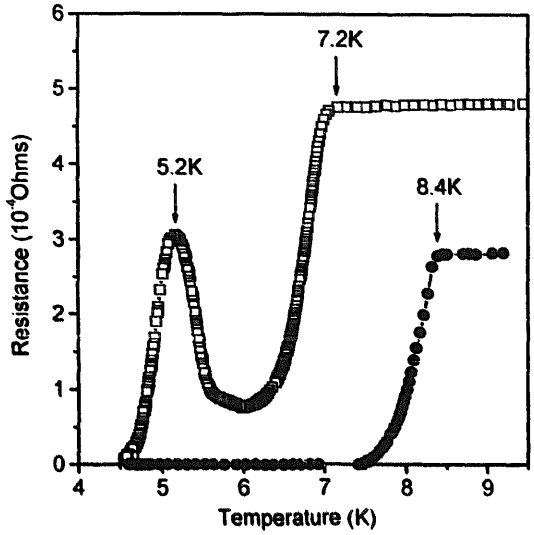

Fig. 4. Electrical resistance vs. temperature curves of the ^{57}Fe doped (open squares) and the undoped $HoNi_2B_2C_{1.05}$ (closed circles) annealed at 800°C.

K with an electrical resistance maximum at 5.2 K. By comparison with the undoped sample, we observe that the Fe substitution, assumed to take place at the Ni sites, creates an important depression of T_c (8.4–7.2 K) and the occurrence of a strong re-entrant behaviour. A slightly smaller effect on T_c has been reported by Sanchez et al. [14] on 1 at.% Fe doped $HoNi_2B_2C$.

The ^{57}Fe Mössbauer absorption spectra recorded in the temperature range 1.5–77 K show little, if any, thermal variation. They consist of two components, a dominant single line (75%) and a weaker spectral doublet (25%), arising from the quadrupolar hyperfine interaction of ^{57}Fe at a non-cubic site. Fig. 5 presents spectra at selected temperatures above, within and below the re-entrant region, and the two-components fits (dashed line for the doublet, thin solid line for the single line). Within experimental uncertainty, all the low temperature spectra are identical. The fits yield the following parameters (the isomer shift δ is given with respect to α-Fe, the quadrupolar splitting of the doublet is Δ and Γ is the HWHM of the lines): for the single line, $\delta = 0.15(1)$ mm/s and $\Gamma = 0.20(1)$ mm/s, and for the doublet, $\delta = 0.175(10)$ mm/s, $\Delta = 0.56(1)$ mm/s and $\Gamma = 0.12(1)$ mm/s. The rather large width of the single line allows an alternative fit in terms of an unresolved quadrupolar doublet: with a fixed value $\Gamma = 0.12$ mm/s, one gets a quadrupolar splitting Δ approximately equal to 0.12 mm/s.

We attribute the dominant component (single line) to Fe substituted for Ni in the $HoNi_2B_2C_{1.05}$ phase. As to the 25% weight quadrupolar doublet, it could be associated either with the 5% impurity phase evidenced in the XRD spectra (then Fe doping would occur preferentially into this phase), or with Fe at an interstitial site in the main phase.

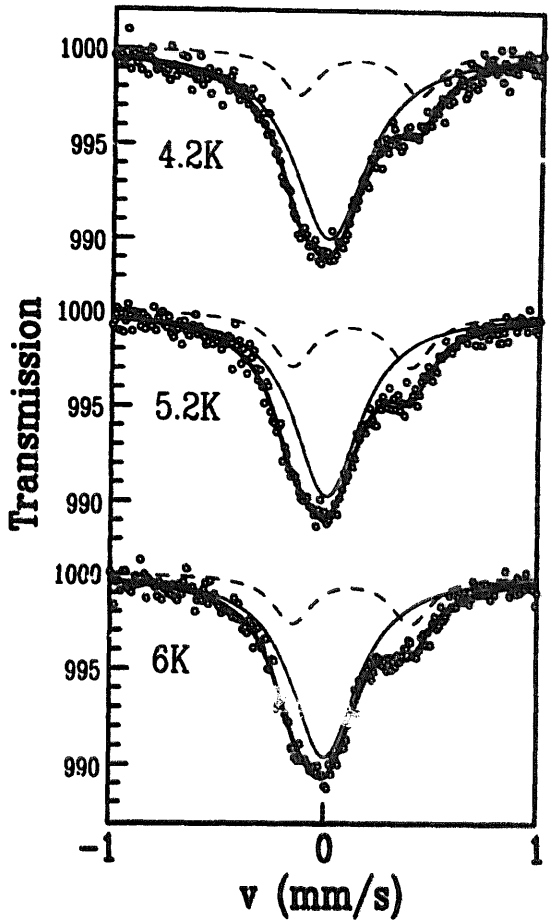

Fig. 5. ^{57}Fe Mössbauer absorption spectra in $HoNi_2B_2C_{1.05}$ doped with 0.5 at.% ^{57}Fe for three temperatures: above (6 K), inside (5.2 K) and below (4.2 K) the re-entrant region.

The main result of this study is that there is no significant difference for the dominant spectra component when the temperature is decreased from 6 K (in the Ho^{3+} paramagnetic phase) to 5.2 K (in the center of the re-entrant region) and to 4.2 K (in the antiferromagnetic phase). In particular, there is no evidence in our spectra of any magnetic field at the ^{57}Fe nucleus in the re-entrant phase. This result is at odds with that obtained in [14], where it is claimed that a pair breaking field of 0.3 T is observed at the Fe substitutional site around 5 K in a $HoNi_2B_2C$ sample doped with 1 at.% Fe.

4. Conclusion

From our partial results, we can conclude that the chemical defects introduced by the sample preparation, deviation from stoichiometry or Fe doping, depress the superconductivity of $HoNi_2B_2C$ and consequently reinforce the apparent weight of the re-entrant behaviour. Further investigations are in progress

in order to complete our study of the non-stoichiometry effects. The spontaneous re-entrant behaviour of $HoNi_2B_2C$ has been attributed to the occurrence of incommensurate spiral magnetic states destructive to superconductivity. We show that the presence of these modulated magnetic orders in the re-entrant region does not lead to the introduction of a hyperfine field at the Fe probe.

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