ELSEVIER

Physica C 248 (1995) 349-352

PHYSICA C

Observation of superconductivity at 6 K in $DyNi_2B_2C$

C.V. Tomy *, G. Balakrishnan, D.McK. Paul

Department of Physics, University of Warwick, Coventry CV4 7AL, UK

Received 21 February 1995; revised manuscript received 3 April 1995

Abstract

We report a systematic study of the intermetallic compound $DyNi_2B_2C$, with variations in the starting compositions of C and Dy. Our results show that for an exact starting composition of 1:2:2:1, the compound forms without any impurity phases and a superconducting transition with an onset as high as 6 K is observed. Excess of C or Dy in the compound is found to be detrimental to the superconducting properties.

1. Introduction

The discovery of superconductivity in the Y–Pd–B–C system [1] and RNi_2B_2C compounds [2] has motivated the search for further superconductors in such intermetallic compounds. Although the phase responsible for superconductivity in the Y–Pd–B–C system is not yet identified, the superconducting phase in the R–Ni–B–C system is now known to be RNi_2B_2C, where R is for rare earth. This phase forms for most of the R ions and superconductivity above 4 K has been reported for R = Y, Lu, Tm, Er and Ho [2]. The structure consists of alternate layers of R–C and Ni_2B_2 [3]. The fact that for non-magnetic rare earths Y and Lu, T_c is of the order of 16 K and decreases for the magnetic rare earths Tm to Ho, suggests a degree of interaction between the rare-earth ions and the conduction electrons. These compounds are further interesting because they show coexistence of magnetism and superconductivity. It is now well established from neutron studies that the magnetic rare-earth ions Ho [4–6] and Er [7,8] order magnetically below T_c and evidence from specific-heat measurements show that Tm also orders magnetically below 2.5 K [9].

$DyNi_2B_2C$ shows evidence for magnetic order at ≈ 10.5 K from magnetic susceptibility measurements [2]. Resistivity measurements [10] show a change in slope at this temperature and a further sharp drop at lower temperatures, suggesting the possible existence of a superconducting phase in this compound. Traces of a superconducting phase found in our samples of $DyNi_2B_2C$ made previously [10], seemed to suggest that the superconducting properties of these RNi_2B_2C compounds are very sensitive to the stoichiometry of the constituents, especially that of carbon. We have investigated the properties of $DyNi_2B_2C$ as a function of varying the starting compositions of both Dy and C, to try and optimise the superconducting phase present in the Dy–Ni–B–C system. Our results show that a superconducting phase with a T_c as high as 6 K can be achieved in $DyNi_2B_2C$ if the stoichiometry is maintained close to the nominal composition, 1:2:2:1. Our studies also show that the superconducting phase is indeed the 1221 phase and not a minor impurity phase present in these compounds.

* Corresponding author.

SSDI 0921-4534(95)00254-5

2. Experimental details

Samples with nominal starting compositions, $DyNi_2B_2C_y$ with $y = 0.5$, 0.8, 0.9, 1.0, 1.1 and 1.2 and $Dy_xNi_2B_2C_{1.0}$ with $x = 0.9$, 1.0 and 1.1, were prepared by the standard arc-melting method. The starting materials were Dy ingot (99.9%), Ni rod (99.99%), B flakes (99.9%) and ultra pure C rods (99.999%). Appropriate amounts of the materials were arc melted under a flow of argon gas on a water-cooled copper hearth. In order to ensure homogeneity, the melted buttons were turned over and melted several times. Great care was taken to minimise the weight losses and the over-all weight loss was less than 0.5% in all the compounds. The samples were then wrapped in Ta foil and annealed in evacuated quartz tubes at 1050°C for 16 h. The phase purity of the samples were determined by X-ray powder diffraction. A standard mutual inductance method was used for the AC susceptibility measurements and a standard four-probe DC method for the resistance measurements. Both the experiments were carried out between 1.4 K and 300 K. The DC magnetisation was measured using a SQUID (Quantum Design) from 2–15 K in an applied field of 10 Oe.

3. Results and discussion

Fig. 1 shows the X-ray powder diffraction patterns for a few of the compounds. It is clear that only the compound with the stoichiometry 1:2:2:1, shows an X-ray pattern with no traces of impurities within the resolution of the instrument. In the carbon-excess compounds, one of the main impurity phases is identified as DyB_2C_2. The carbon-deficient and the Dy rich compounds show the presence of more than one impurity, which we have as yet not identified. In all cases, the majority phase is the 1221 phase.

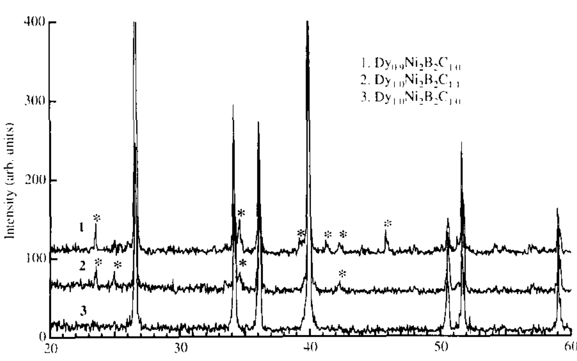

Fig. 1. X-ray powder diffraction patterns for a few of the $Dy_xNi_2B_2C_y$ compounds synthesized. The peaks corresponding to the impurity phases are marked with (∗).

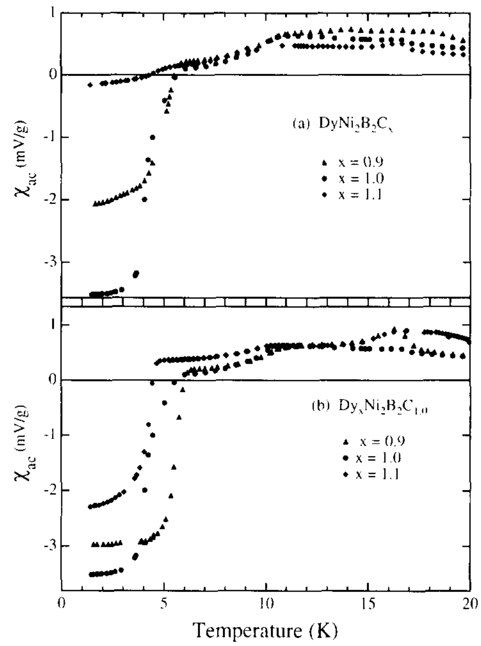

Fig. 2. Real part of the AC susceptibility (χ_{AC}) for the $Dy_xNi_2B_2C_y$ compounds, normalised to their masses, with (a) varying carbon content, (b) varying dysprosium content.

The temperature variation of the AC susceptibility (χ_{AC}), normalised to their masses, for the various compositions are shown in Fig. 2. The anomaly at ≈ 10.5 K in the susceptibility seen in almost all the compounds is associated with the magnetic ordering of the Dy moments. Preliminary analysis of our neutron powder diffraction data taken on the stoichiometric 1:2:2:1 compound shows the presence of antiferromagnetic peaks [11]. Detailed analyses to establish the exact nature of this magnetic ordering are in progress. $DyNi_2B_2C$ appears to be a unique member of the RNi_2B_2C series where the onset of superconductivity takes place in a magnetically ordered state albeit coexistent with antiferromagnetic order. The drop in susceptibility at lower temperatures in Fig. 2 (4.5–6.5 K) corresponds to a diamagnetic signal from the superconducting phase. It is seen that the diamagnetic signal is strongest for nominal starting compositions of carbon close to 1.

Fig. 3 shows the results of the DC magnetisation measurements for the superconducting compound, $DyNi_2B_2C$, in an applied field of 10 Oe. From the zero-field cooled magnetisation (ZFC) curve, the magnetic shielding is estimated to be 100% of that expected for perfect diamagnetism. However, on cooling in the same field, the measured field-cooled magnetisation (FC) lies close to zero which makes it difficult to estimate the Meissner fraction. The Meissner effect observed for the other members of this family of compounds, including the Y and Lu compound show a maximum of about 10% of that expected for perfect diamagnetism [2]. In $DyNi_2B_2C$, there appears to be a strong paramagnetic contribution due to the ordering of the Dy moments above T_c. The FC and the ZFC magnetisation curves do not overlap above the superconducting transition until T_N (at ≈ 10.5 K) even for a small field of 10 Oe. Similar results have been observed in the FC and ZFC magnetisation curves at higher fields as well [11].

The results of the resistance measurements are shown in Fig. 4. The compound with starting compositions $x = 1$ and $y = 1$ shows a drop in resistance at ≈ 6.5 K and zero resistance is obtained at ≈ 5.5 K. T_c decreases as the carbon content is varied above or below $y = 1$. For $y = 0.8$, the compound no longer shows a zero resistance although a small diamagnetic signal is seen in the AC susceptibility, while the compound with $y = 1.2$ does not show either a diamagnetic signal in χ_{AC} or a drop in resistance. It is therefore quite clear that small variations in the starting content of carbon affect the superconducting properties in this compound. Variations in Dy starting content between 0.9 and 1.1 does not appear to drastically affect the superconductivity, T_c being maximum for $x = 0.9$ and 1. The results on all the compounds investigated are summarised in Table 1.

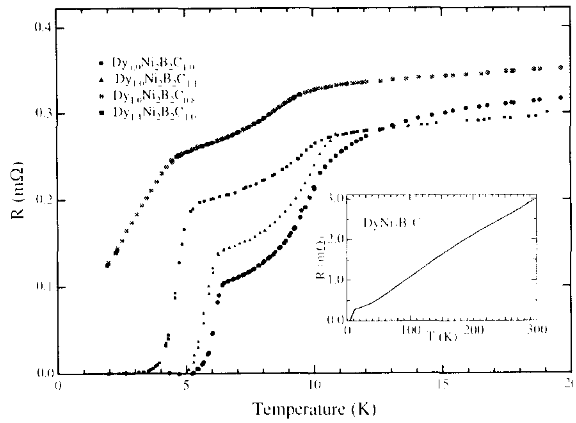

Fig. 4. Resistance vs. temperature curves for some $Dy_xNi_2B_2C_y$ compounds; the inset shows the resistance behaviour of the stoichiometric compound, $DyNi_2B_2C$, from 1.4–300 K.

The structure of the RNi_2B_2C compounds can be viewed as a layered structure where the R–C layers alternate with the Ni_2B_2 layers, the layers being connected by short boron–carbon bonds. The Ni_2B_2 layers are supposed to be crucial for superconductiv-

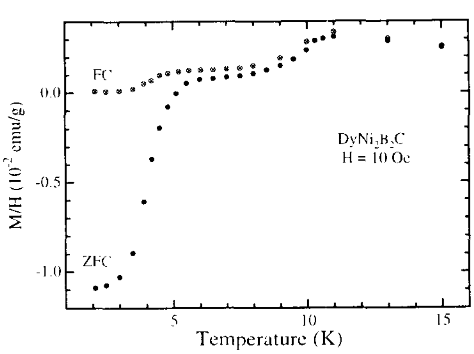

Fig. 3. Zero-field cooled (ZFC) and field-cooled (FC) magnetisation for $DyNi_2B_2C$ measured in an applied field of 10 Oe, showing the superconducting transition at ~ 6 K and the magnetic ordering at ~ 10.5 K.

Table 1
Superconducting properties of the $Dy_xNi_2B_2C_y$ compounds synthesized

Nominal starting compositions	T_c (K) ($R = 0$)	Diamagnetic signal (χ_{AC})
$DyNi_2B_2C_{0.5}$	nsc [a]	No
$DyNi_2B_2C_{0.8}$	< 1.4	Yes, weak
$DyNi_2B_2C_{0.9}$	5.0	Yes, strong
$DyNi_2B_2C_{1.0}$	5.5	Yes, strong
$DyNi_2B_2C_{1.1}$	5.0	Yes, weak
$DyNi_2B_2C_{1.2}$	nsc [a]	No
$Dy_{0.9}Ni_2B_2C_{1.0}$	5.5	Yes, strong*
$Dy_{1.1}Ni_2B_2C_{1.0}$	3.5	Yes, strong

[a] Not superconducting.

ity in these compounds. It is therefore difficult to understand why changing the carbon and/or the rare-earth content is detrimental to superconductivity. One of the factors that is expected to influence the superconductivity is the strain in the Ni_2B_2 layer, which is the least for the smallest rare earth, Lu (T_c of $LuNi_2B_2C$ is 16.5 K) and is not likely to be very different for Dy. The excess carbon introduced and/or the deficiency in carbon content could indirectly affect the superconducting Ni_2B_2 layers or the coupling between the Ni_2B_2 layers in such a way that T_c reduces first and then vanishes. $DyNi_2B_2C$ also appears to be different from the other superconducting members of the series, in that, although the majority phase in all the compounds we have synthesised for this study, is the 1221 phase, superconductivity is not observed in all the compounds. The presence of impurity phases is not favourable to its superconducting behaviour, whilst in compounds containing Ho or Y, for example, superconductivity persists despite the presence of small amounts of secondary phases, as long as the majority phase is the 1221 phase. The 1221 phase which forms as the majority phase in $Dy_xNi_2B_2C_y$ compounds with starting compositions other than 1:2:2:1 therefore appears to be in some way different from the superconducting 1221 phase. Specific-heat measurements will further corroborate our observation of bulk superconductivity in the stoichiometric $DyNi_2B_2C$ compound and these measurements are now in progress.

4. Conclusions

Superconductivity has been observed in $DyNi_2B_2C$ for the first time. We have shown that a superconducting phase with a T_{conset} as high as 6 K, in a magnetically ordered state, can be achieved in $DyNi_2B_2C$, if the stoichiometry is kept close to 1:2:2:1. Our studies emphasise the need for phase purity in order to observe superconductivity in this compound and the role of carbon in particular in determining the superconducting properties. Single crystals of the superconducting $DyNi_2B_2C$ have now been grown and the detailed measurements on the single crystals are to be published.

Acknowledgements

We thank the IRC in Superconductivity, Cambridge, for the use of the SQUID. This work was supported by a grant from the SERC, UK.

References

[1] R.J. Cava, H. Takagi, B. Batlogg, H.W. Zandbergen, J.J. Krajewski, W.F. Peck Jr., R.B. van Dover, R.J. Felder, T. Siegrist, K. Mizuhashi, J.O. Lee, H. Eisaki, S.A. Carter and S. Uchida, Nature (London) 367 (1994) 146.

[2] R.J. Cava, H. Takagi, H.W. Zandbergen, J.J. Krajewski, W.F. Peck Jr., T. Siegrist, B. Batlogg, R.B. van Dover, R.J. Felder, K. Mizuhashi, J.O. Lee, H. Eisaki and S. Uchida, Nature (London) 367 (1994) 252.

[3] T. Siegrist, H.W. Zandbergen, R.J. Cava, J.J. Krajewski and W.F. Peck Jr., Nature (London) 367 (1994) 254.

[4] L.J. Chang, C.V. Tomy, D.McK. Paul, N.H. Andersen and M. Yethiraj (to appear in Physica B)

[5] A.I. Goldman, C. Stassis, P.C. Canfield, J. Zarestky, P. Dervenagas, B.K. Cho, D.C. Johnston and B. Sternlieb, Phys. Rev. B 50 (1994) 9668.

[6] T.E. Grigereit, J.W. Lynn, Q. Huang, A. Santoro, R.J. Cava, J.J. Krajewski and W.F. Peck Jr., Phys. Rev. Lett. 73 (1994) 2756.

[7] J. Zarestky, C. Stassis, A.I. Goldman, P.C. Canfield, P. Dervenagas, B.K. Cho and D.C. Johnston, Phys. Rev. B 51 (1995) 678.

[8] S.K. Sinha, J.W. Lynn, T.E. Grigereit, Z. Hossain, L.C. Gupta, R. Nagarajan and C. Goddart, Phys. Rev. B 51 (1995) 681.

[9] R. Movshovich, M.F. Hundley, J.D. Thompson, P.C. Canfield, B.K. Cho and A.V. Chubkov, Physica C 227 (1994) 381.

[10] C.V. Tomy, L.C. Chang, G. Balakrishnan and D. McK. Paul, Physica C 235–240 (1994) 2551.

[11] C.V. Tomy, L.J. Chang, D. McK. Paul, N.H. Andersen and M. Yethiraj, to be published.