Magnetism and Superconductivity in RNi$_2$B$_2$C Compounds (R = Rare-earth and Y)*

J. M. Cadogan

School of Physics, University of New South Wales, Sydney, NSW 2052, Australia.

Abstract

In this paper I will review the RNi$_2$B$_2$C (R = rare-earth and Y) series of compounds. These compounds exhibit a complex interplay between superconductivity and magnetism and are unique in that the characteristic temperatures of these effects are comparable.

1. Introduction

The discovery of a new family of superconducting compounds is always interesting to both experimentalists and theorists alike. It is even more so when the superconductivity is linked with magnetism, as is the case with the recently discovered RNi$_2$B$_2$C (R = rare-earth and Y) compounds which are the subject of this review. I will concentrate mainly on the magnetic behaviour of the RNi$_2$B$_2$C compounds. It is inevitable that many papers on this subject will not be mentioned here but it is hoped that this review will provide the interested reader with enough starting points for a further, more detailed exploration of this fascinating subject.

In general, magnetism and superconductivity are mutually exclusive with magnetism being responsible for breaking the Cooper pairing of electrons in the superconductor (see e.g. Matsumoto and Umezawa 1983; Whitehead et al. 1985). In 1977, the ternary rare-earth compounds RRh$_4$B$_4$ and the Chevrel phases RMo$_6$X$_8$ (X = S, Se) were shown to become superconducting upon cooling, despite the presence of magnetic moments on the rare-earth ions (Fertig et al. 1977; Ishikawa and Fischer 1977). Upon further cooling, these materials re-enter the normal state and a finite magnetisation appears. Most importantly, there exists a small intermediate temperature range in which superconductivity and long-range, modulated magnetic order coexist. In ErRh$_4$B$_4$, for example, the superconducting transition temperature is 8.7 K and the re-entrant temperature is 0.8 K with the coexistence region being 0.8–1.0 K.

The high-$T_C$ materials (HTSC) such as YBa$_2$Cu$_3$O$_{7-\delta}$ show superconducting transition temperatures of order 100 K and magnetic order transitions of order ~few K. Once again, there is at least an order of magnitude difference between

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the characteristic temperatures, with the HTSC materials being superconducting or magnetic depending on the oxygen content.

Recently, Nagarajan et al. (1994) found that the resistivity of YNi$_4$B dropped sharply at 12 K (but did not reach zero). By varying the composition, and in particular with the addition of carbon, they were able to increase substantially the superconducting fraction and they proposed the existence of a phase with composition YNi$_2$B$_3$C$_{0.2}$ as the superconducting phase. They also observed Meissner behaviour (negative susceptibility) and a specific heat anomaly, supporting their conclusion of the formation of a new superconducting material.

Fig. 1. (a) Crystallographic and magnetic structures, commensurate (b) and incommensurate (c), of RNi$_2$B$_2$C compounds. [Reproduced from Grigereit et al. (1995).]

At around the same time, Cava, Siegrist and co-workers (Cava et al. 1994; Siegrist et al. 1994) reported the formation of the intermetallic family RNi$_2$B$_2$C with nearly all the rare-earth elements. The heavy-R compounds showed superconductivity and a maximum superconducting temperature $T_C$ of 16.6 K was observed in LuNi$_2$B$_2$C. The crystal structure of the RNi$_2$B$_2$C compounds is tetragonal layered (cf. the HTSC materials) with alternating planes of R, C and Ni$_2$B$_2$. The space group is I4/mmm and the lattice parameters are $a \sim 3.5$ Å and $c \sim 10.5$ Å (Fig. 1a). On the basis of the large cell contraction in the basal plane with increasing atomic number, these authors suggested that a strong chemical bonding exists between the R and C atoms. Superconducting transitions were found for R = Y, Lu, Ho, Er and Tm, the latter three being magnetic rare-earth ions (Fig. 2); $T_C$ was found to scale with the magnetic de Gennes factor $(g - 1)^2J(J + 1)$ of the R$^{3+}$ ion (Fig. 3a inset). It is now clear that the superconducting phase observed by Nagarajan et al. is the same as that of Cava, Siegrist et al., i.e. RNi$_2$B$_2$C.
The pair-breaking effect of the R$^{3+}$ ions is clearly seen by comparing $T_C$ values. The difference in $T_C$ between LuNi$_2$B$_2$C and YNi$_2$B$_2$C (both are non-magnetic R) is $\sim$1 K for a volume difference of $\sim$3.5%, whereas the $T_C$ difference between YNi$_2$B$_2$C and HoNi$_2$B$_2$C (magnetic R) is $\sim$8 K for a volume difference of only $\sim$0.5%. Susceptibility measurements showed that the R$^{3+}$ ions carry their free-ion
magnetic moment. Cava, Siegrist et al. also observed superconductivity in the isomorphous series RPd$_2$B$_2$C, with $T_C$ reaching as high as 23 K in YPd$_2$B$_2$C.

The first evidence for re-entrant behaviour was found in HoNi$_2$B$_2$C by Eisaki et al. (1994). The superconducting transition was observed at 8 K and at $\sim$5 K HoNi$_2$B$_2$C re-entered the normal state before returning to the superconducting state at $\sim$4·6 K. This unusual behaviour was clearly seen in resistivity and critical field measurements (Fig. 3). Magnetic susceptibility measurements showed that HoNi$_2$B$_2$C orders antiferromagnetically at $T_N \sim 5$ K, the re-entrant temperature, but also gave evidence of ferromagnetism. The suggested magnetic structure consisted of ferromagnetic sheets coupled antiferromagnetically along the $c$-axis. This will be discussed in more detail in the following section.

In the remainder of this paper, I will discuss the following topics: (i) neutron diffraction, (ii) magnetometry, (iii) hyperfine studies (mainly Mössbauer), (iv) band structure calculations and (v) the superconductivity of RNi$_2$B$_2$C.

2. Neutron Diffraction

It is clear that the RNi$_2$B$_2$C compounds show a fascinating interplay between superconductivity and magnetism and it is therefore important to characterise the magnetic behaviour of these compounds. To this end, numerous neutron elastic scattering experiments have been carried out to study the ordering of the $R^{3+}$ moments in RNi$_2$B$_2$C.

The absence of magnetic order in YNi$_2$B$_2$C was confirmed by Sinha et al. (1995) and Lynn et al. (1996). The latter authors also determined the magnetic structure of DyNi$_2$B$_2$C which orders in a simple commensurate, collinear antiferromagnetic structure below 6 K with ferromagnetic layers of Dy$^{3+}$ moments coupled antiferromagnetically along the $c$-axis. The magnetic moments lie in the basal plane (Lynn et al. 1996) and the measured Dy$^{3+}$ moment at 1·7 K was 8·47 $\mu_B$.

TmNi$_2$B$_2$C was studied by Chang et al. (1996). It has $T_C \sim 11$ K and $T_N \sim 1·5$ K and its magnetic structure comprises incommensurate ferromagnetic (110) planes of Tm moments aligned along the $c$-axis with a sinusoidal modulation of moments along [110]. This modulation allows superconductivity to coexist with the magnetic order. Interestingly, TmNi$_2$B$_2$C is the only magnetic RNi$_2$B$_2$C compound whose $R^{3+}$ moments are not in the basal $a$-$b$ plane. The measured Tm$^{3+}$ moment at 50 mK is 4·8 $\mu_B$, quite a bit lower than the value of 7 $\mu_B$ expected for a Tm$^{3+}$ ion with a fully stretched $|J_z| = J$ electronic state.

ErNi$_2$B$_2$C shows a superconducting transition at $T_C = 11$ K and orders magnetically at $T_N \sim 6·8$ K (Sinha et al. 1995; Lynn et al. 1996; Zarestky et al. 1995). It shows no evidence of re-entrant behaviour. Its magnetic structure is an incommensurate modulated antiferromagnet with transverse sinusoidal polarisation along the $a$-axis. The propagation vector is $q_a = 0·553a^*$. This incommensurate magnetic structure coexists with the superconductivity. The Er$^{3+}$ magnetic moment is 7·8 $\mu_B$ at 2 K. Some evidence for a small ($-0·35 \mu_B$) moment on the Ni was suggested by Sinha et al. (1995) but this measurement was made on a powder sample and it would be difficult to resolve such a small moment in the presence of the rather large Er moment. Other factors such as the effect of carbon content (vide infra) further weaken the suggestion of an Ni moment. A small moment on the Ni atoms raises problems since the Ni electrons are presumed to be responsible for the Cooper pairing.
HoNi$_2$B$_2$C has come in for particular attention because it is the only superconducting RNi$_2$B$_2$C compound to exhibit re-entrant behaviour (Lynn et al. 1995; Goldman et al. 1994; Grigereit et al. 1995). HoNi$_2$B$_2$C goes superconducting at $T_C \sim 7.8$ K and re-enters the normal state at $\sim 5–6$ K, before recovering the superconducting state at $\sim 4.7$ K. Magnetically, HoNi$_2$B$_2$C orders in an incommensurate antiferromagnetic structure at $\sim 6$ K in which the Ho$^{3+}$ moments form a $c$-axis spiral with a turn angle of $\sim 165^\circ$ between adjacent Ho planes along the $c$-axis (180$^\circ$ would be commensurate). This incommensurate structure is characterised by modulation along both the $a$ and $c$ axes, with propagation vectors $q_a = 0.585a^*$ and $q_c = 0.915c^*$. Below 4.7 K, the magnetic structure of HoNi$_2$B$_2$C is identical to that of DyNi$_2$B$_2$C, i.e. a commensurate antiferromagnet and the superconducting state is recovered.

Both ErNi$_2$B$_2$C and HoNi$_2$B$_2$C show incommensurate magnetic order but only HoNi$_2$B$_2$C shows re-entrant behaviour which suggests that the re-entrance is a result of pair-breaking by the $c$-axis spiral state since both ErNi$_2$B$_2$C and HoNi$_2$B$_2$C show $a$-axis modulation. One possible explanation for this behaviour is that the incommensurate alignment of the Ho moments results in a net exchange field acting at the intermediate Ni sites, thereby causing the pair-breaking (Grigereit et al. 1994). Once the magnetic structure becomes commensurate upon further cooling there is a cancellation of the exchange fields at the Ni sites from neighbouring Ho planes and the superconducting state is recovered. This point will be re-addressed later in this review when I discuss the Mössbauer work on the RNi$_2$B$_2$C compounds.

If I may speculate at this point: another possible explanation for the unique behaviour of HoNi$_2$B$_2$C relates to the turn angle of 165$^\circ$ which yields a repeat distance of 12 cells along the $c$-axis. This corresponds to $\sim 125$ Å; which is close to the coherence length $\xi$ (a value of $\xi = 135$ Å in ErNi$_2$B$_2$C was determined by Cho et al. 1995). Is it possible that long-wavelength magnons propagating along the $c$-axis cause the pair-breaking?

To finish this review of elastic neutron scattering work we note that the modulated incommensurate magnetic structures along the $a$-axis in ErNi$_2$B$_2$C and HoNi$_2$B$_2$C are nearly identical (0.553$a^*$ and 0.585$a^*$ respectively). Recent band calculations on LuNi$_2$B$_2$C by Rhee et al. (1995) show that a strong Fermi surface nesting occurs for $q \sim 0.6a^*$, consistent with the experimental data.

Inelastic neutron scattering has been carried out on HoNi$_2$B$_2$C, ErNi$_2$B$_2$C and TmNi$_2$B$_2$C by Gasser et al. (1996) and was used to deduce crystal field parameters. These data reproduce the observed magnetic easy directions in these compounds. The parameters also reproduce specific heat and magnetisation anisotropy data.

3. Magnetometry

As mentioned earlier, the first detailed study of the magnetic properties of the RNi$_2$B$_2$C compounds was by Eisaki et al. (1994) who showed that the $T_C$ scales with the de Gennes factor of the R$^{3+}$. They also showed that the $T_C$ of TmNi$_2$B$_2$C was lower than expected, on this basis, and that TbNi$_2$B$_2$C did not show superconductivity. The de Gennes scaling of $T_C$ is a result of the pair-breaking by the R$^{3+}$ moments and is in agreement with the Abrikosov–Gor’kov (1961) theory which gives the decrease in $T_C$ as
\[ \frac{\delta T_c}{T_c} \propto nI^2N(E_F)(g-1)^2J(J+1), \]

where \( n \) is the number of magnetic moments, \( I \) is the exchange constant, and \( (g-1)^2J(J+1) \) is the de Gennes factor of the \( R^{3+} \) ion.

Eisaki et al. also showed that HoNi\(_2\)B\(_2\)C exhibits re-entrant behaviour which they associated with changes in the magnetic ordering of the Ho\(^{3+}\) moments. They also linked susceptibility transitions showing antiferromagnetic ordering to the re-entrance. Interestingly, their susceptibility work on DyNi\(_2\)B\(_2\)C showed antiferromagnetic order but suggested ferromagnetism as well. Their critical field data were interpreted as being evidence for 3D electronic behaviour rather than 2D, despite the layered structure.

Canfield et al. (1994) studied HoNi\(_2\)B\(_2\)C and found that the Ho moments are aligned in the crystal \( a-b \) plane, from susceptibility measurements. Their work produced a magnetic phase diagram for HoNi\(_2\)B\(_2\)C which shows quite vividly the complex variety of magnetic order below 5 K.

One common finding of the magnetometry experiments carried out to date on the RNi\(_2\)B\(_2\)C compounds is the occurrence of field-induced transitions in the magnetisation. Many of these are associated with metamagnetic behaviour and/or crystal-field driven reorientations [Dy (Ku et al. 1996), Ho (Canfield et al. 1994; Ku et al. 1996), Er (Szymczak et al. 1995, 1996; Rao et al. 1996; Canfield et al. 1996) and Tb (Hossain et al. 1995)—see Fig. 4].

![Fig. 4. Single-crystal magnetisation measurement on ErNi\(_2\)B\(_2\)C at 2 K. (Reproduced from Szymczak et al. (1996).)](image)

Tomy et al. (1995) studied the effects of varying the carbon content on the superconductivity of DyNi\(_2\)B\(_2\)C. The stoichiometric DyNi\(_2\)B\(_2\)C phase showed a \( T_c \) of 5.5 K but a slight increase in C content to DyNi\(_2\)B\(_2\)C\(_{1.2}\) was enough to kill the superconductivity (at least down to 1.4 K). This work is particularly significant in that it shows the important role played by the carbon content, a point which seems to have been ignored by most workers.
Canfield et al. (1996) observed a transition to a magnetic state in ErNi$_2$B$_2$C below 2·3 K in which a weak ferromagnetic component of 0·33 $\mu_B$ exists which suggests that the superconductivity may be able to coexist with weak ferromagnetic order.

Eversmann et al. (1996) studied the mixed phase (Ho,Y)Ni$_2$B$_2$C and observed a linear scaling of $T_C$ with the number of R moments and the de Gennes factor, in agreement with the Abrikosov–Gor’kov theory.

Krug et al. (1996) studied HoNi$_2$B$_2$C and claimed that the re-entrant minimum in the critical field is mainly an effect of the antiferromagnetic state which develops at $T_N$ and not of the incommensurate magnetic states vanishing at that temperature. I am more persuaded by the neutron data which show the re-entrance being linked to the c-axis incommensurate structure.

4. Hyperfine Interactions

Mössbauer spectroscopy has been employed mainly as a probe of crystal-field effects at the R sites in RNi$_2$B$_2$C. Mulder et al. (1995) used $^{155}$Gd to determine a value of $-428 K a_0^{-2}$ for the dominant second-order crystal-field lattice summation ($A_{20}$) in GdNi$_2$B$_2$C. The advantage of using $^{155}$Gd is that Gd$^{3+}$ is an S-state ion and therefore the electric field gradient at the $^{155}$Gd nucleus is determined solely by the lattice charge distribution; there is no 4f contribution. GdNi$_2$B$_2$C was found to order magnetically at 21 K; it is not superconducting.

Sanchez et al. (1996) used $^{161}$DyNi$_2$B$_2$C Mössbauer spectroscopy to show that there is significant easy-plane anisotropy in DyNi$_2$B$_2$C. They also found evidence of Dy→C electron transfer in their isomer shift data, in agreement with the suggestion of a strong chemical bonding between the R and C atoms by Cava, Siegrist et al. (1994) mentioned earlier.

Mulders et al. (1996) carried out $^{169}$TmNi$_2$B$_2$C spectroscopy and observed a sharp drop in the quadrupole splitting (QS) at 1 K, close to the magnetic ordering temperature of ~1·5 K. From the temperature dependence of QS they estimated the crystal-field parameters and suggested a singlet ground state for the Tm$^{3+}$ ion with a small induced magnetic moment of ~0·1 $\mu_B$ on the Tm, at odds with the neutron scattering results of Chang et al. (1996).

Bonville et al. (1996) carried out $^{166}$ErNi$_2$B$_2$C spectroscopy and found that the ground state of the Er$^{3+}$ ion is a doublet separated from another doublet by about 10 K. Interestingly, their work gives some evidence to suggest that the conduction electrons which are exchange-coupled to the 4f spin take part in the formation of the superconducting state. This Mössbauer and specific heat work yielded a set of crystal-field parameters which are consistent with inelastic neutron scattering data.

Pulsed NMR measurements were made on YNi$_2$B$_2$C using the $^{11}$B and $^{89}$Y resonances with emphasis on spin-lattice relaxation measurements. Hanson et al. (1995) determined a value of 108 nm for the penetration depth from NMR studies of the temperature dependence of the NMR signal linewidth. Suh et al. (1996) showed that the temperature dependence of the spin-lattice relaxation time fits well to the BCS theory, giving an energy gap of $2 \Delta(T=0) = 3·4 k_B T_C$.

Cywinski et al. (1994) carried out a combined $\mu$SR and magnetometry study of YNi$_2$B$_2$C. Critical field measurements were used to deduce a value of 7·4 nm
for the superconducting coherence length and $\mu$SR gave a value of 124.5 nm for the penetration depth.

![Fig. 5. $^{57}$Fe Mössbauer spectra of (a) TbNi$_2$B$_2$C and (b) HoNi$_2$B$_2$C doped with enriched $^{57}$Fe. The magnetic hyperfine fields at the $^{57}$Fe sites are shown in (c). [Reproduced from Sanchez et al. (1996).]](image_url)

In an attempt to probe directly the magnetism at the Ni sites a number of authors have carried out $^{57}$Fe Mössbauer studies on RNi$_2$B$_2$C compounds doped with enriched $^{57}$Fe isotope (Sanchez et al. 1996; Felner 1996; Zeng et al. 1997). Fe substitutes for Ni in this structure and these studies show that the Ni atoms in RNi$_2$B$_2$C do not carry a magnetic moment. The most interesting result is that of Sanchez et al. (1996) who showed that the only compounds in which a magnetic hyperfine field at the $^{57}$Fe nucleus was observed are TbNi$_2$B$_2$C, which does not superconduct (Fig. 5a), and HoNi$_2$B$_2$C only in the re-entrant
region where it is normal (Fig. 5b). The Ni site in TbNi$_2$B$_2$C experiences a transferred or dipolar magnetic field at the nucleus from the surrounding Tb$^{3+}$ planes (Fig. 5c). This field amounts to $\sim$1 T at $T \to 0$. In HoNi$_2$B$_2$C, a hyperfine field is only observed in the range 3–6 K over which HoNi$_2$B$_2$C is in the normal state. The maximum field is only 0.3 T. Sanchez et al. claim that their data suggest that the Ho$^{3+}$ moments are not fully in the a-b plane but are canted slightly out of this plane towards the c-axis, a point which was not evident in the neutron studies. However, given the smallness of this hyperfine field I think this suggestion should be regarded as speculative at this stage.

The magnetic structure of TbNi$_2$B$_2$C has been studied by neutron diffraction [Tomy et al., unpublished, cited by Chang et al. (1996)]. These authors claim that TbNi$_2$B$_2$C has an incommensurate magnetic structure along the a-axis, similar to ErNi$_2$B$_2$C, but the c-axis structure is presumably commensurate, since no mention of any incommensurate nature along the c-axis is made by Chang et al. (1996). If the c-axis order is commensurate then the explanation of a transferred field at the Ni site from the Tb planes breaks down. Clearly, this point requires detailed study by neutron diffraction.

5. Calculations

Coehoorn (1994) has carried out self-consistent band calculations on LuNi$_2$B$_2$C using the augmented spherical wave method. He concluded that the superconductivity in this series is related to the presence of a narrow peak, with mixed Lu and Ni character, in the density of states (DOS) at the Fermi level. He also showed that ferromagnetic alignment of the R$^{3+}$ moments in RNi$_2$B$_2$C would produce an exchange splitting of this peak which would be at least an order of magnitude larger than the superconducting energy gap, demonstrating that antiferromagnetism rather than ferromagnetism is compatible with the superconductivity.

Pickett and Singh (1994) and Mattheis (1994) showed that the RNi$_2$B$_2$C compounds are strongly 3d-metallic with all atoms contributing to the metallic character, which is quite different from the behaviour of the HTSC materials. The calculations of Pickett and Singh suggest that the peak in the DOS at the Fermi level is dominated by the contribution from the Ni 3d electrons. As pointed out by Mattheis, the RNi$_2$B$_2$C compounds are more likely to be conventional intermetallic superconductors driven by a standard electron-phonon interaction and the enhanced $T_C$ values arise from high-frequency phonons due to the light B and C atoms.

6. Substitution for Ni

It is generally believed that the Ni electrons are responsible for the superconductivity in the RNi$_2$B$_2$C compounds. To study this idea, many groups have prepared compounds with Ni partially replaced by other transition metal elements. These include Fe (Bud’ko et al. 1995; Zhou et al. 1996), Co (Bud’ko et al. 1995; Schmidt et al. 1995; Looney et al. 1995; Gangopadhyay et al. 1995; Gangopadhyay and Schilling 1996), Cu (Looney et al. 1995; Gangopadhyay and Schilling 1996), and Ru (Bud’ko et al. 1995). Most work has concentrated on Co and Cu substitution both of which decrease $T_C$, with Co having a more drastic effect than Cu [$dT_C/dx = -45$ K cf. $-19$ K] (Fig. 6). This impinges on the idea that the superconductivity in RNi$_2$B$_2$C is
Fig. 6. (a) Susceptibility measurements on Y(Ni,Fe)$_2$B$_2$C and (b) superconducting transition temperature in Y(Ni,Co)$_2$B$_2$C. [Reproduced from Zhou et al. (1996) and Schmidt et al. (1994).]

related to the existence of a peak in the DOS at the Fermi level. Looney et al. (1995) studied the substituted systems Y(Ni,M)$_2$B$_2$C with M = Co and Cu as a function of applied pressure. In all cases, i.e. M = Co, Ni, Cu, the $T_C$ decreased with increasing pressure even though the Fermi level lies below the DOS peak for M = Co and above the peak for M = Cu. It is known that the application of pressure causes s→d electron transfer so it was expected that the Fermi level with M = Co would move up in energy, towards the DOS peak, thereby increasing $T_C$. The Fermi level in M = Cu would also increase in energy, moving further away from the DOS peak and $T_C$ would drop. For the unsubstituted
M = Ni, little change in $T_C$ was expected since the Fermi level and the DOS peak would move together. The fact that $T_C$ decreased for all M suggests that the electron–phonon coupling strength is also affected.

Finally, it is clear that the idea of a peak in the DOS at the Fermi level, predicted by band calculations, has been adopted by many workers when analysing the $T_C$ behaviour of their RNi$_2$B$_2$C materials. However, recent photoemission work by Kobayashi et al. (1996) on YNi$_2$B$_2$C seems to suggest that there is no such peak! This discrepancy between theory and experiment may be due to the presence of electron correlation effects not taken into account in the band calculations. In any event, it seems to me imperative that more experiments on the RNi$_2$B$_2$C series are needed to determine the shape of the DOS at the Fermi level.

7. Superconductivity

There are numerous questions about the nature of the superconductivity in the RNi$_2$B$_2$C series of compounds. My reading of the literature suggests that the majority of studies carried out to date tend towards a conventional model of superconductivity. The RNi$_2$B$_2$C compounds appear to be three-dimensional, electron–phonon driven, Type-II, clean-limit superconductors.

Allen et al. (1995) have studied the dependence of $T_C$ in the RNi$_2$B$_2$C series as a function of applied pressure. The function $T_C(P)$ shows a peak for YNi$_2$B$_2$C and ErNi$_2$B$_2$C but a monotonic decrease for TmNi$_2$B$_2$C and HoNi$_2$B$_2$C. These authors explained this behaviour in terms of the pressure sweeping the Fermi level through the peak in the DOS, which was predicted by band structure calculations.

It is clear that electron–phonon coupling is important in determining the $T_C$ values in RNi$_2$B$_2$C. For example, the standard BCS expression for the $T_C$ is

$$T_C = 1.14\theta_D \exp[-1/N(E_F)V],$$

where $\theta_D$ is the Debye temperature, $N(E_F)$ is the DOS at the Fermi level and $V$ is the electron–phonon coupling constant. Recent measurements of $\theta_D$ give 489 K and 345 K for YNi$_2$B$_2$C (Movshovich et al. 1994) and LuNi$_2$B$_2$C (Carter et al. 1994) respectively, while their $T_C$ values are $\sim$15·5 and 16·5, respectively, showing that the simple linear scaling of $T_C$ with $\theta_D$ does not hold.

As mentioned earlier, TmNi$_2$B$_2$C is somewhat unusual in that its $T_C$ is significantly lower than expected from the de Gennes dependence. Recent $\mu$SR work (Cooke et al. 1995; Le et al. 1995) suggests that magnetic correlations are present in TmNi$_2$B$_2$C at temperatures above $T_C$ so the superconducting transition occurs in the presence of magnetic correlations which are not taken into account in the Abrikosov–Gor’kov theory.

Jeong et al. (1995) carried out electron tunnelling experiments on YNi$_2$B$_2$C and LuNi$_2$B$_2$C using point-contact spectroscopy. They determined the energy gaps to lie in the ranges 2·55–3·2 meV and 2·65–3·3 meV for YNi$_2$B$_2$C and LuNi$_2$B$_2$C respectively. The temperature dependence of the energy gap shows BCS behaviour only near $T_C$. The deviation from BCS behaviour was attributed to the temperature dependence of the coherence length of the normal layer.
Hong et al. (1994) used magnetic and specific heat measurements to show that YNi$_2$B$_2$C is a type II superconductor with an upper critical field of 3.7 T ($T \rightarrow 0$) and a coherence length of 9.4 nm. The energy gap in YNi$_2$B$_2$C is in the range

$$3.4 \leq \frac{2\delta(0)}{k_B T_C} \leq 4.9,$$

whereas the value predicted by the BCS model is 3.52. The coherence length is $\lambda \sim 10$ nm and the penetration depth is $\xi \sim 70–160$ nm. A summary of the various superconducting parameters of the RNi$_2$B$_2$C compounds is given in Table 1.

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8. Conclusions

The series of intermetallic compounds RNi$_2$B$_2$C provides a fascinating arena for the study of the interplay of superconductivity and magnetism in that the energy scales of the two, normally competing, effects are comparable. They seem to be more conventional superconductors than the HTSC materials, despite their layered crystal structures, and are clean-limit, Type-II superconductors. Their coherence length is $\sim 10$ nm, roughly a factor of 5 larger than in the HTSC compounds. The magnetic structures of the RNi$_2$B$_2$C materials are either commensurate or incommensurate antiferromagnetic. The development of a c-axis spiral incommensurate structure in HoNi$_2$B$_2$C seems to be linked to the pair-breaking observed in this compound, the only member of the series to exhibit re-entrance and c-axis modulation.
Numerous questions remain, though:

- We need to know why the light rare-earths (lighter than Dy) do not show superconductivity in RNi$_2$B$_2$C. The most likely explanation in the cases of TbNi$_2$B$_2$C and GdNi$_2$B$_2$C is the pair-breaking effect; their de Gennes factors are greater than that of DyNi$_2$B$_2$C. However, the de Gennes factors of NdNi$_2$B$_2$C, PrNi$_2$B$_2$C and SmNi$_2$B$_2$C are all smaller than those of HoNi$_2$B$_2$C and DyNi$_2$B$_2$C yet these three light-R compounds do not superconduct.
- We need to investigate the shape of the density of states at the Fermi level. The results of band calculations showing a peak in the DOS seem to fit in with experiments on the superconductivity, in particular pressure and 3d-doping work, but recent photoemission work throws doubt on this idea.
- There is continuing debate over whether or not the Ni atoms carry a small magnetic moment in this structure. My own opinion is that they do not, given that they are most likely responsible for the Cooper-pairing, but it would be extremely interesting if the Ni atoms were to carry a moment!
- Why is Tm the only rare-earth whose magnetic moment is not aligned in the $a$–$b$ basal plane? Is it simply a crystal-field effect (although Er$^{3+}$ has the same signs of the second- and fourth-order Stevens coefficients as Tm$^{3+}$)?
- If the re-entrance exhibited by HoNi$_2$B$_2$C is in fact related to the $c$-axis incommensurate magnetic structure then what is the mechanism for the pair-breaking?

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**References**


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