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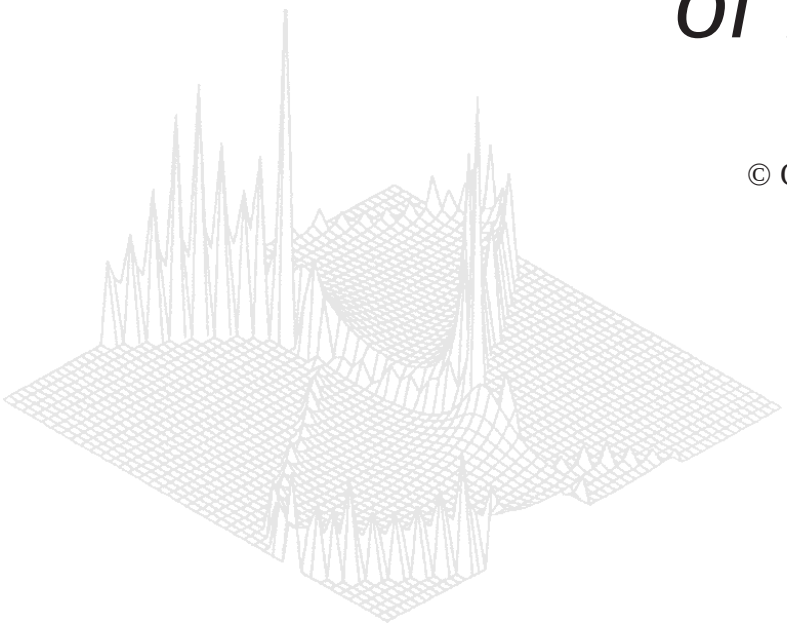
Australian Journal of Physics

Volume 50, 1997



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Aust. J. Phys., 1997, **50**, 1103–17

Magnetism and Superconductivity in RNi_2B_2C Compounds (R = Rare-earth and Y)*

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Abstract

In this paper I will review the RNi_2B_2C (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_2B_2C (R = rare-earth and Y) compounds which are the subject of this review. I will concentrate mainly on the magnetic behaviour of the RNi_2B_2C 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_4B_4 and the Chevrel phases RMo_6X_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 $ErRh_4B_4$, for example, the superconducting transition temperature is $8{\cdot}7$ K and the re-entrant temperature is $0{\cdot}8$ K with the coexistence region being $0{\cdot}8$–$1{\cdot}0$ K.

The *high-*T_C materials (HTSC) such as $YBa_2Cu_3O_{7-\delta}$ 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

* Refereed paper based on a contribution to the Sixth Gordon Godfrey Workshop on Recent Developments in Magnetism and Magnetic Materials, held at the University of New South Wales, Sydney, in October 1996.

 10.1071/PH97029 0004-9506/97/061103$05.00

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_4B 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 $YNi_2B_3C_{0\cdot2}$ 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.

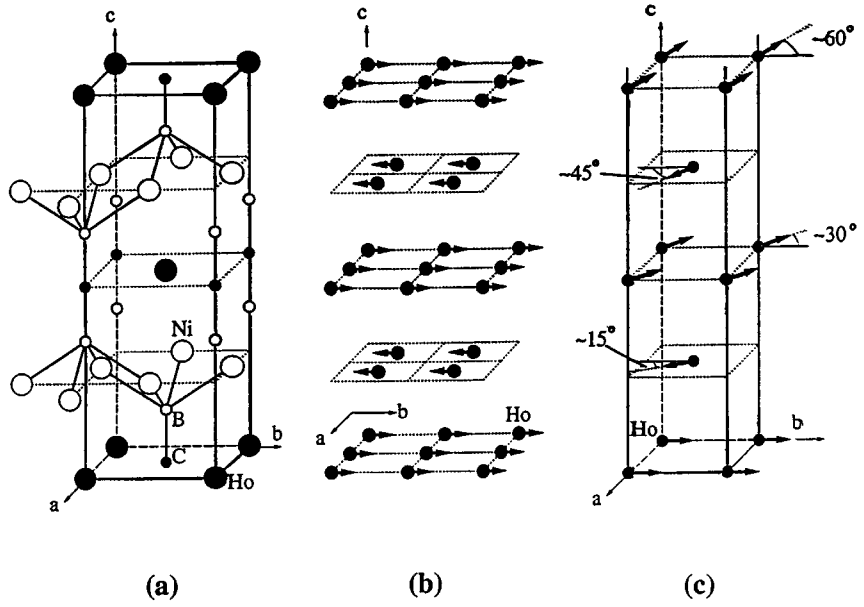

Fig. 1. (*a*) Crystallographic and magnetic structures, commensurate (*b*) and incommensurate (*c*), of RNi_2B_2C compounds. [Reproduced from Grigereit *et al.* (1995).]

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_2B_2C with nearly all the rare-earth elements. The heavy-R compounds showed superconductivity and a maximum superconducting temperature T_C of $16\cdot6$ K was observed in $LuNi_2B_2C$. The crystal structure of the RNi_2B_2C compounds is tetragonal layered (cf. the HTSC materials) with alternating planes of R, C and Ni_2B_2. The space group is I4/mmm and the lattice parameters are $a \sim 3\cdot5$ Å and $c \sim 10\cdot5$ Å (Fig. 1*a*). 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. 3*a* 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_2B_2C.

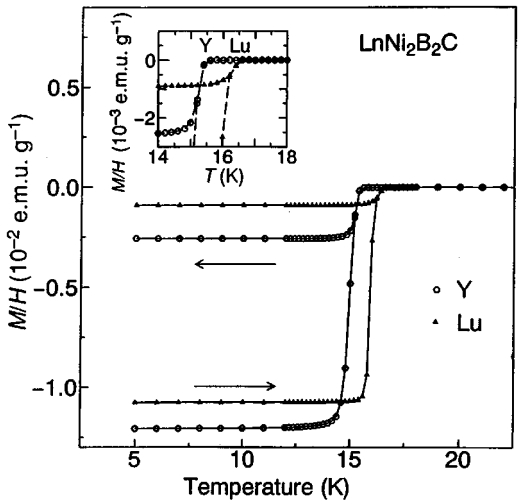

Fig. 2. Susceptibility measurements on YNi_2B_2C and $LuNi_2B_2C$. [Reproduced from Cava *et al.* 1994).]

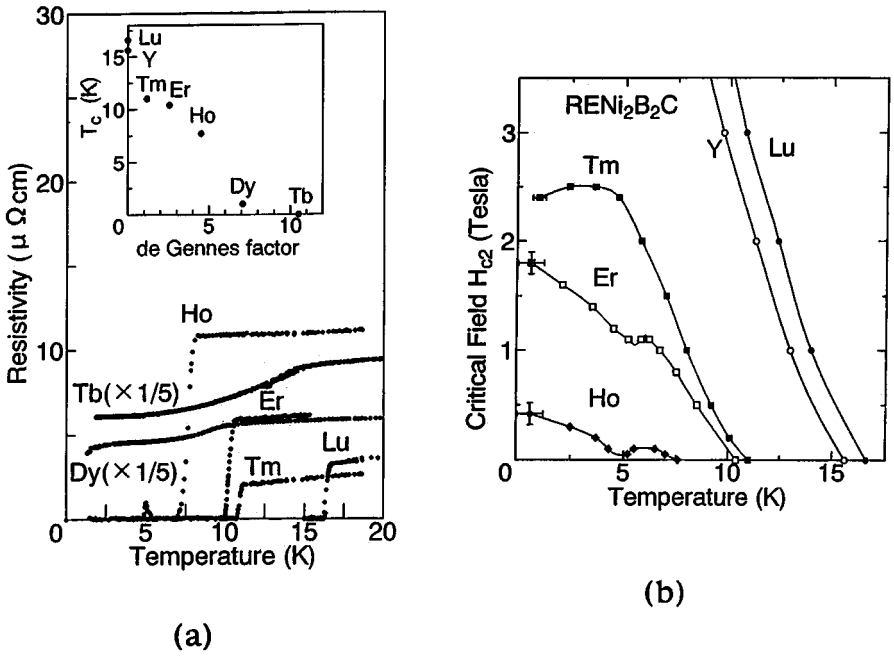

Fig. 3. Resistivity (*a*) and critical field (*b*) measurements on RNi_2B_2C. [Reproduced from Eisaki *et al.* (1994).]

The pair-breaking effect of the R^{3+} ions is clearly seen by comparing T_C values. The difference in T_C between $LuNi_2B_2C$ and YNi_2B_2C (both are non-magnetic R) is $\sim$1 K for a volume difference of $\sim 3 \cdot 5\%$, whereas the T_C difference between YNi_2B_2C and $HoNi_2B_2C$ (magnetic R) is $\sim$8 K for a volume difference of only $\sim 0 \cdot 5\%$. 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_2B_2C, with T_C reaching as high as 23 K in YPd_2B_2C.

The first evidence for re-entrant behaviour was found in $HoNi_2B_2C$ by Eisaki *et al.* (1994). The superconducting transition was observed at 8 K and at ∼5 K $HoNi_2B_2C$ re-entered the normal state before returning to the superconducting state at ∼4·6 K. This unusual behaviour was clearly seen in resistivity and critical field measurements (Fig. 3). Magnetic susceptibility measurements showed that $HoNi_2B_2C$ 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_2B_2C.

2. Neutron Diffraction

It is clear that the RNi_2B_2C 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_2B_2C.

The absence of magnetic order in YNi_2B_2C was confirmed by Sinha *et al.* (1995) and Lynn *et al.* (1996). The latter authors also determined the magnetic structure of $DyNi_2B_2C$ 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 μ_B.

$TmNi_2B_2C$ was studied by Chang *et al.* (1996). It has $T_C \sim 11$ K and $T_N \sim 1{\cdot}5$ 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, $TmNi_2B_2C$ is the only magnetic RNi_2B_2C compound whose R^{3+} moments are *not* in the basal *a*-*b* plane. The measured Tm^{3+} moment at 50 mK is 4·8 μ_B, quite a bit lower than the value of 7 μ_B expected for a Tm^{3+} ion with a *fully stretched* $|J_z| = J$ electronic state.

$ErNi_2B_2C$ shows a superconducting transition at $T_C = 11$ K and orders magnetically at $T_N \sim 6{\cdot}8$ 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 $\boldsymbol{q_a} = 0{\cdot}553\boldsymbol{a}^*$. This incommensurate magnetic structure coexists with the superconductivity. The Er^{3+} magnetic moment is 7·8 μ_B at 2 K. Some evidence for a small (−0·35 μ_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.

$HoNi_2B_2C$ has come in for particular attention because it is the only superconducting RNi_2B_2C compound to exhibit re-entrant behaviour (Lynn *et al.* 1995; Goldman *et al.* 1994; Grigereit *et al.* 1995). $HoNi_2B_2C$ goes superconducting at T_C $\sim 7{\cdot}8$ K and re-enters the normal state at $\sim$5–6 K, before recovering the superconducting state at $\sim 4{\cdot}7$ K. Magnetically, $HoNi_2B_2C$ 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 $\sim 165°$ between adjacent Ho planes along the c-axis (180° would be commensurate). This incommensurate structure is characterised by modulation along *both* the a and c axes, with propagation vectors $\boldsymbol{q}_a = 0{\cdot}585\boldsymbol{a}^*$ and $\boldsymbol{q}_c = 0{\cdot}915\boldsymbol{c}^*$. Below $4{\cdot}7$ K, the magnetic structure of $HoNi_2B_2C$ is identical to that of $DyNi_2B_2C$, i.e. a commensurate antiferromagnet and the superconducting state is recovered.

Both $ErNi_2B_2C$ and $HoNi_2B_2C$ show incommensurate magnetic order but only $HoNi_2B_2C$ shows re-entrant behaviour which suggests that the re-entrance is a result of pair-breaking by the c-axis spiral state since both $ErNi_2B_2C$ and $HoNi_2B_2C$ 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_2B_2C compounds.

If I may speculate at this point: another possible explanation for the unique behaviour of $HoNi_2B_2C$ relates to the turn angle of 165° 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 ξ (a value of $\xi = 135$ Å in $ErNi_2B_2C$ 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 $ErNi_2B_2C$ and $HoNi_2B_2C$ are nearly identical ($0{\cdot}553\boldsymbol{a}^*$ and $0{\cdot}585\boldsymbol{a}^*$ respectively). Recent band calculations on $LuNi_2B_2C$ by Rhee *et al.* (1995) show that a strong Fermi surface nesting occurs for $\boldsymbol{q} \sim 0{\cdot}6\boldsymbol{a}^*$, consistent with the experimental data.

Inelastic neutron scattering has been carried out on $HoNi_2B_2C$, $ErNi_2B_2C$ and $TmNi_2B_2C$ 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_2B_2C 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 $TmNi_2B_2C$ was lower than expected, on this basis, and that $TbNi_2B_2C$ 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

$$\frac{\delta T_c}{T_c} \propto nI^2 N(E_F)(g-1)^2 J(J+1)\,,$$

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

Eisaki *et al.* also showed that $HoNi_2B_2C$ 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 $DyNi_2B_2C$ 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 $HoNi_2B_2C$ 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 $HoNi_2B_2C$ 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_2B_2C 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].

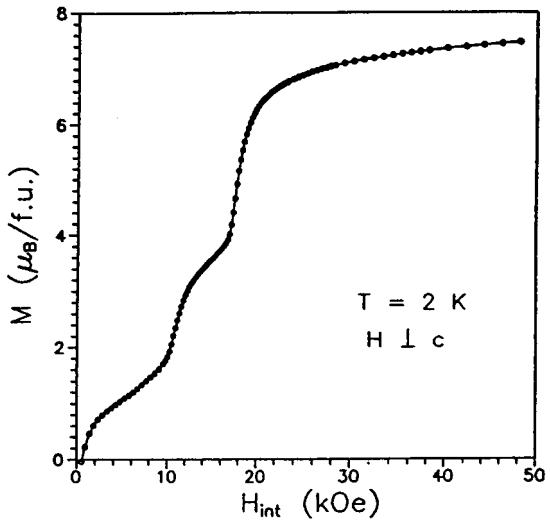

Fig. 4. Single-crystal magnetisation measurement on $ErNi_2B_2C$ at 2 K. [Reproduced from Szymczak *et al.* (1996).]

Tomy *et al.* (1995) studied the effects of varying the carbon content on the superconductivity of $DyNi_2B_2C$. The stoichiometric $DyNi_2B_2C$ phase showed a T_C of $5{\cdot}5$ K but a slight increase in C content to $DyNi_2B_2C_{1\cdot2}$ was enough to kill the superconductivity (at least down to $1{\cdot}4$ 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 $ErNi_2B_2C$ below $2 \cdot 3$ K in which a weak ferromagnetic component of $0 \cdot 33\ \mu_B$ exists which suggests that the superconductivity may be able to coexist with weak ferromagnetic order.

Eversmann *et al.* (1996) studied the mixed phase $(Ho, Y)Ni_2B_2C$ 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 $HoNi_2B_2C$ 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_2B_2C. Mulder *et al.* (1995) used ^{155}Gd to determine a value of $-428\ Ka_0^{-2}$ for the dominant second-order crystal-field lattice summation (A_{20}) in $GdNi_2B_2C$. 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. $GdNi_2B_2C$ was found to order magnetically at 21 K; it is *not* superconducting.

Sanchez *et al.* (1996) used $^{161}DyNi_2B_2C$ Mössbauer spectroscopy to show that there is significant easy-plane anisotropy in $DyNi_2B_2C$. 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 $^{169}TmNi_2B_2C$ spectroscopy and observed a sharp drop in the quadrupole splitting (QS) at 1 K, close to the magnetic ordering temperature of $\sim 1 \cdot 5$ 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 $\sim 0 \cdot 1\ \mu_B$ on the Tm, at odds with the neutron scattering results of Chang *et al.* (1996).

Bonville *et al.* (1996) carried out $^{166}ErNi_2B_2C$ 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_2B_2C 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 $2\Delta(T{=}0) = 3 \cdot 4 k_B T_C$.

Cywinski *et al.* (1994) carried out a combined μSR and magnetometry study of YNi_2B_2C. Critical field measurements were used to deduce a value of $7 \cdot 4$ nm

for the superconducting coherence length and μSR gave a value of $124 \cdot 5$ nm for the penetration depth.

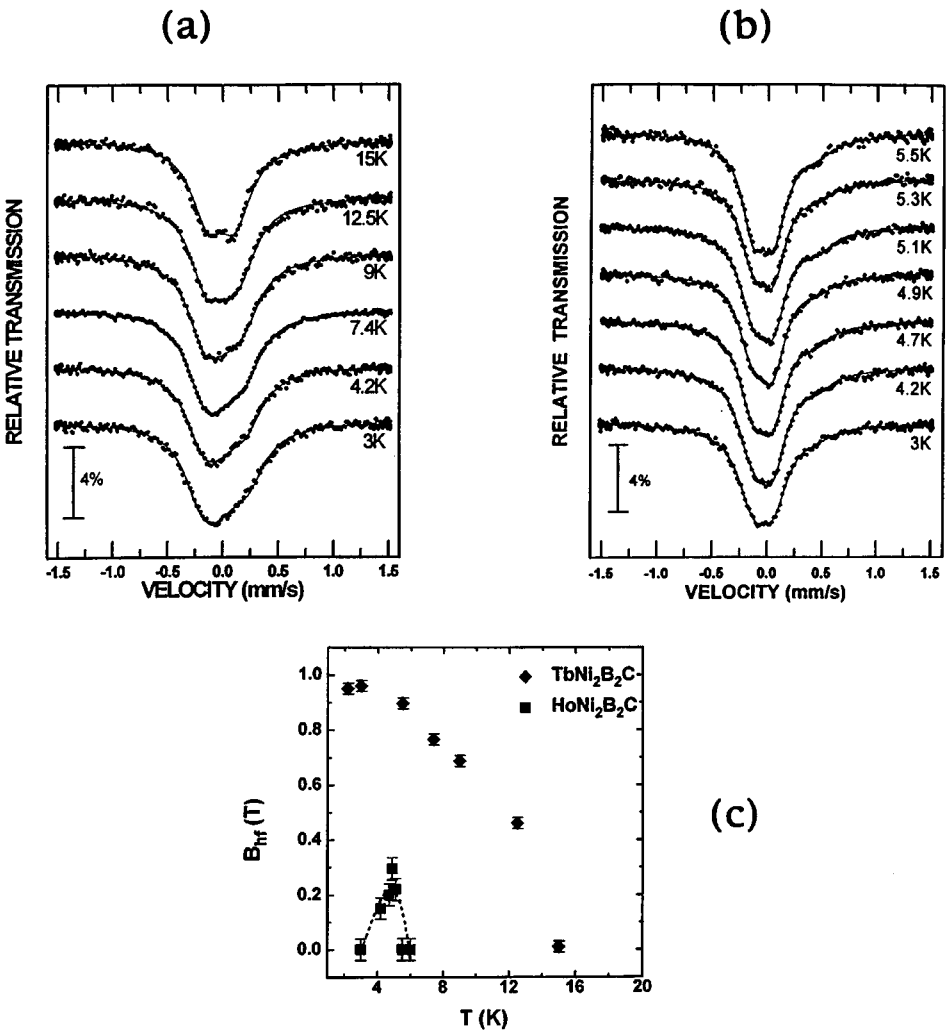

Fig. 5. ^{57}Fe Mössbauer spectra of (*a*) $TbNi_2B_2C$ and (*b*) $HoNi_2B_2C$ doped with enriched ^{57}Fe. The magnetic hyperfine fields at the ^{57}Fe sites are shown in (*c*). [Reproduced from Sanchez *et al.* (1996).]

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_2B_2C 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_2B_2C 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 $TbNi_2B_2C$, which does not superconduct (Fig. 5*a*), and $HoNi_2B_2C$ only in the re-entrant

region where it is normal (Fig. 5*b*). The Ni site in $TbNi_2B_2C$ experiences a transferred or dipolar magnetic field at the nucleus from the surrounding Tb^{3+} planes (Fig. 5*c*). This field amounts to ∼1 T at $T \to 0$. In $HoNi_2B_2C$, a hyperfine field is only observed in the range 3–6 K over which $HoNi_2B_2C$ 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 $TbNi_2B_2C$ has been studied by neutron diffraction [Tomy *et al.*, unpublished, cited by Chang *et al.* (1996)]. These authors claim that $TbNi_2B_2C$ has an incommensurate magnetic structure along the *a*-axis, similar to $ErNi_2B_2C$, 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 $LuNi_2B_2C$ 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_2B_2C 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_2B_2C 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_2B_2C 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_2B_2C 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 *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_2B_2C is

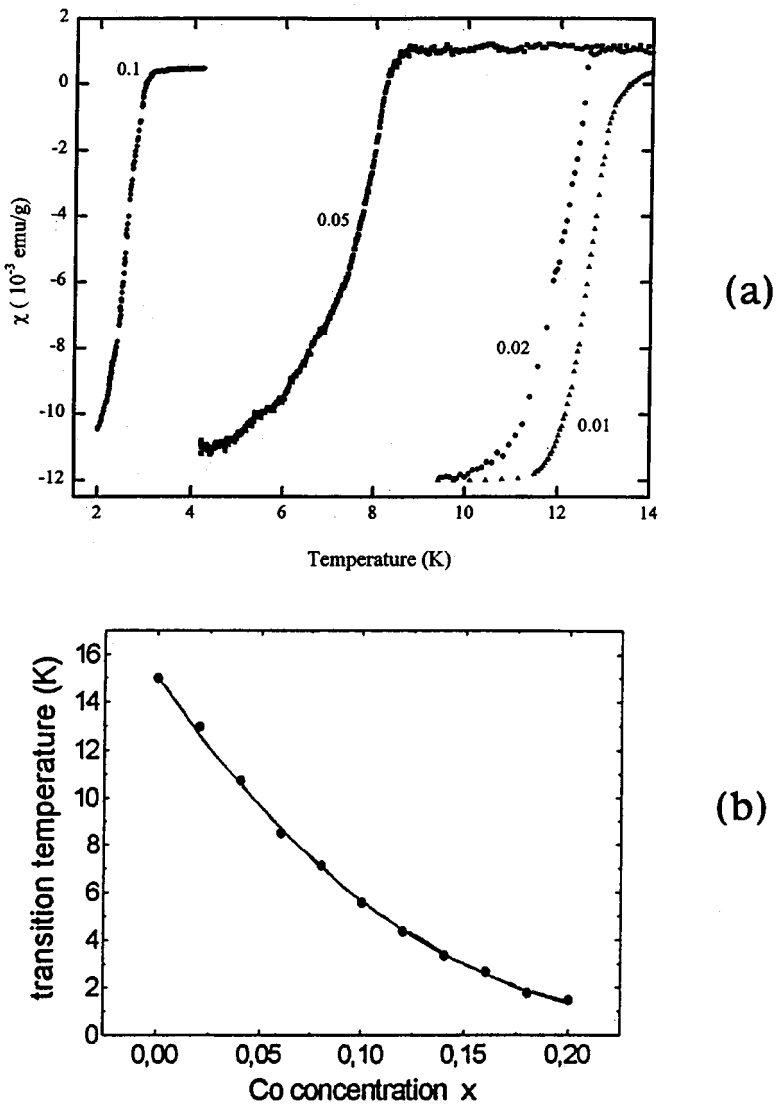

Fig. 6. (*a*) Susceptibility measurements on $Y(Ni, Fe)_2B_2C$ and (*b*) superconducting transition temperature in $Y(Ni, Co)_2B_2C$. [Reproduced from Zhou *et al.* (1996) and Schmidt *et al.* (1994).]

related to the existence of a peak in the DOS at the Fermi level. Looney *et al.* (1995) studied the substituted systems $Y(Ni, M)_2B_2C$ 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_2B_2C materials. However, recent photoemission work by Kobayashi *et al.* (1996) on YNi_2B_2C 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_2B_2C 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_2B_2C 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_2B_2C compounds appear to be three-dimensional, electron–phonon driven, Type-II, *clean-limit* superconductors.

Alleno *et al.* (1995) have studied the dependence of T_C in the RNi_2B_2C series as a function of applied pressure. The function $T_C(P)$ shows a peak for YNi_2B_2C and $ErNi_2B_2C$ but a monotonic decrease for $TmNi_2B_2C$ and $HoNi_2B_2C$. 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_2B_2C. For example, the standard BCS expression for the T_C is

$$T_C = 1{\cdot}14\theta_D \exp[-1/N(E_F)V]\,,$$

where θ_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 θ_D give 489 K and 345 K for YNi_2B_2C (Movshovich *et al.* 1994) and $LuNi_2B_2C$ (Carter *et al.* 1994) respectively, while their T_C values are $\sim 15{\cdot}5$ and $16{\cdot}5$, respectively, showing that the simple linear scaling of T_C with θ_D does *not* hold.

As mentioned earlier, $TmNi_2B_2C$ is somewhat unusual in that its T_C is significantly lower than expected from the de Gennes dependence. Recent μSR work (Cooke *et al.* 1995; Le *et al.* 1995) suggests that magnetic correlations are present in $TmNi_2B_2C$ 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_2B_2C and $LuNi_2B_2C$ using point-contact spectroscopy. They determined the energy gaps to lie in the ranges $2{\cdot}55$–$3{\cdot}2$ meV and $2{\cdot}65$–$3{\cdot}3$ meV for YNi_2B_2C and $LuNi_2B_2C$ 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_2B_2C 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_2B_2C is in the range

$$3{\cdot}4 \leq \frac{2\delta(0)}{k_B T_C} \leq 4{\cdot}9\,,$$

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_2B_2C compounds is given in Table 1.

Table 1. Superconducting parameters of the RNi_2B_2C compounds

T_C and T_N are the superconducting and magnetic transition temperatures, respectively; $B_{C_2}(0)$ is the upper critical field, extrapolated to $T = 0$; λ is the penetration depth; ξ is the coherence length; and κ is the Ginzburg–Landau parameter. The energy gap parameter shown corresponds to $2\Delta(0)/k_B T_C$. (The critical temperatures shown represent averages of numerous determinations by many authors. It should be noted that there is, in some cases, a significant spread in measured values.)

R ion	T_C (K)	T_N (K)	$B_{C_2}(0)$ (T)	λ (nm)	ξ (nm)	κ	E_{gap}	Ref.
Y	15·6	—	3·2–6	108–163	6–10	10·5–20·4	3·4–4·9	a–k
Dy	4	10	0·3–0·5	—	—	3·7	—	l, m
Ho	7·5	5	0·75–0·8	—	—	—	—	n, o
Er	10·5	7	1·5–1·9	116	13·1–15	8·8–9·2	—	l, p
Tm	11	1·5	—	—	—	—	—	q, r
Lu	16·6	—	9·0	71	6	11·8	—	g
Pr	None	?						s
Nd	None	5						t
Sm	None	10						s
Gd	None	19						t
Tb	None	15						s

(a) Hanson *et al.* (1995), (b) Suh *et al.* (1996), (c) Cywinski *et al.* (1994), (d) Movshovich *et al.* (1994), (e) Jeong *et al.* (1995), (f) Hong *et al.* (1994), (g) Takagi *et al.* (1994), (h) Xu *et al.* (1994), (i) Chandrasekhar Rao *et al.* (1995), (j) Michor *et al.* (1995), (k) Fkino *et al.* (1994, 1996), (l) Cho *et al.* (1995), (m) Lin *et al.* (1995), (n) Krug *et al.* (1996), (o) Schmidt *et al.* (1996), (p) Rao *et al.* (1996), (q) Cava *et al.* (1994), (r) Siegrist *et al.* (1994), (s) Hossain *et al.* (1995), (t) Gupta *et al.* (1995).

8. Conclusions

The series of intermetallic compounds RNi_2B_2C 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 ∼10 nm, roughly a factor of 5 larger than in the HTSC compounds. The magnetic structures of the RNi_2B_2C materials are either commensurate or incommensurate antiferromagnetic. The development of a *c*-axis spiral incommensurate structure in $HoNi_2B_2C$ 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_2B_2C. The most likely explanation in the cases of $TbNi_2B_2C$ and $GdNi_2B_2C$ is the pair-breaking effect; their de Gennes factors are greater than that of $DyNi_2B_2C$. However, the de Gennes factors of $NdNi_2B_2C$, $PrNi_2B_2C$ and $SmNi_2B_2C$ are all smaller than those of $HoNi_2B_2C$ and $DyNi_2B_2C$ 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 $HoNi_2B_2C$ is in fact related to the c-axis incommensurate magnetic structure then what is the mechanism for the pair-breaking?

Acknowledgments

I am grateful to the Australian Research Council for its continuing support.

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Manuscript received 23 April, accepted 4 June 1997