Magnetic and Structural Features of RNi_2B_2C and RNiBC (R=Er, Ho, Dy, Tb, Gd) Superconducting Compounds

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Temperature dependent Mössbauer spectroscopy on ^{57}Fe doped (1 at % of Ni) RNi_2B_2C and RNiBC provided clear evidence of a pair-breaking field at the Ni site for non-superconducting compounds. This field is not present in the superconducting collinear AF $DyNi_2B_2C$, however it appears when this compound is diluted with non-magnetic Lu ($Dy_{1-x}Lu_xNi_2B_2C$). Important local information on the spin structure of the R magnetic moments is obtained for both systems. The local symmetries of RNi_2B_2C and RNiBC compounds, measured through the ΔE_Q, were found to be linearly correlated with the c'/a ratio (c' is the distance of the R-C layers between which the Ni_2-B_2 layers are sandwiched). A scaling of T_c with the local symmetry (c'/a) was found to be the same for all the RNi_2B_2C and RNiBC (except for Y) compounds.

I Introduction

The interplay between superconductivity and magnetically ordered structures, which is the main reason for the great interest in the RNi_2B_2C compounds, essentially does not exist for the RNiBC family [1-5], since with the exception of LuNiBC [3] none of these compounds has been found to be superconducting. In order to understand why this is the case, despite the fact that the structures of both classes of compounds are very similar, except for an additional R-C layer (next section), we have studied in detail crystallographic structure, magnetic ordering and transport properties of RNiBC (R= Er, Ho, Dy, Tb, Gd) compounds. Especially ^{57}Fe Mössbauer Effect (ME) spectroscopy on 1 at % ^{57}Fe-doped RNi_2B_2C and RNiBC has been used to study the local structure at the Fe (Ni) site via the nuclear quadrupole splitting and the magnetic order of the R magnetic moments via the transferred magnetic hyperfine field.

II Structure

The similarities between the RNi_2B_2C and the RNiBC structure are illustrated in Figs. 1(a) and (b): while in RNi_2B_2C [$\equiv(RC)_1(NiB)_2$] there are alternating layers of R-C and Ni_2-B_2, an additional R-C layer exists between the Ni_2-B_2 layers in the RNiBC [$\equiv(RC)_2(NiB)_2$] series. Thus, in both classes of compounds the Ni_2-B_2 layers, which are responsible for superconductivity, are sandwiched between two R-C layers. These Ni_2-B_2 layers are built from NiB_4 tetrahedra with a B-Ni-B bonding angle φ as indicated in figs. 1(a) and (b). In RNiBC series the lattice parameters c and d [see fig 1(a)] turned out to be essentially independent of R with c=7.55Å and d=2.41Å [4,5]. In RNi_2B_2C (see Fig. 1(b)) $(c/a) = 2(c'/a)$, with c' being the distance of the R-C layers between which the Ni_2-B_2 layers are sandwiched and a being the lattice parameter in the basal plane [6]. In the RNiBC compounds c' is given by $c' = c - d$ (Fig. 1(a)).

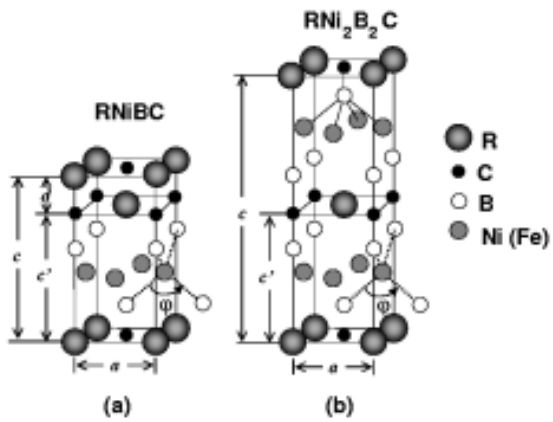

Figure 1. Crystal structures of unit cell of (a) RNiBC and (b) RNi_2B_2C compounds. The relevant lattice parameters a and c′ used in the text are indicated.

The $|\Delta E_Q|$ values for RNiBC (R= Er, Ho, Dy, Tb, Gd) and for RNi_2B_2C (R=Er, Ho, Dy, Tb, Gd, Nd, Pr) [7,8] are plotted in Fig. 2 as a function of the structural parameter (c'/a) which is a measure for the B-Ni-B bonding angle φ [see Figs. 1(a) and (b)].

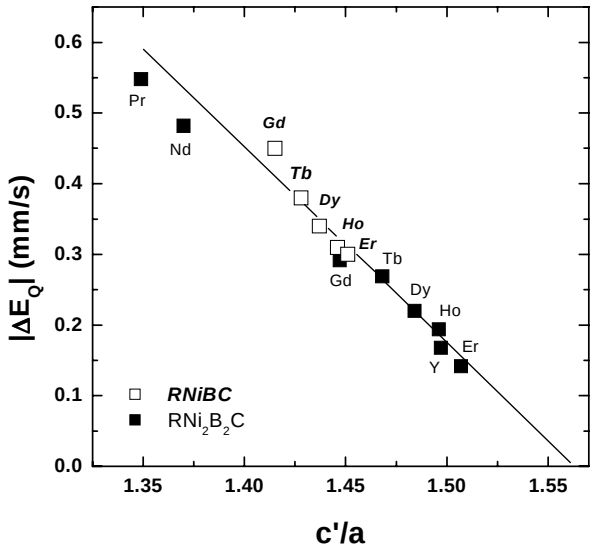

Figure 2. Room temperature quadrupole splitting $|\Delta E_Q|$ observed in RNiBC (R = Gd, Tb, Dy, Ho, and Er) and RNi_2B_2C (R = Pr, Nd, Gd, Tb, Dy, Ho, Er) compounds as a function of the (c'/a)-ratio.

Fig. 2 shows that *all* compounds, RNi_2B_2C as well as RNiBC, have the *same* linear correlation between (c'/a) and $|\Delta E_Q|$. This clearly indicates that both the crystallographic and the electronic structure (which determine ΔE_Q) at the Fe(Ni) site in RNiBC and RNi_2B_2C compounds are very similar for equal structural parameter (c'/a). Furthermore, since $|\Delta E_Q|$ is a measure for the deviation from ideal tetrahedral symmetry, we have to conclude from Fig. 2 that the NiB_4 tetrahedra in RNiBC compounds displays stronger deviation from ideal tetrahedral symmetry than the RNi_2B_2C compounds. Considering the band structure calculations by Mattheiss et al [9], which have shown that ideal tetrahedral symmetry of the NiB_4tetrahedra happens to coincide with a relative high density of states at the Fermi energy, it becomes evident why the structure of the RNiBC compounds is less favorable for superconductivity than that of the RNi_2B_2C compounds (see section IV).

III Magnetism

$HoNi_2B_2C$ orders antiferromagnetically at $T_N = 8.5$ K and becomes superconductor at 8 K. An incommensurate modulated magnetic structure appears at ~6 K, which seems to be responsible for the reentrant behavior, i.e., the suppression of superconductivity between $4.7\,K < T < 6\,K$ (Fig. 3(a)).

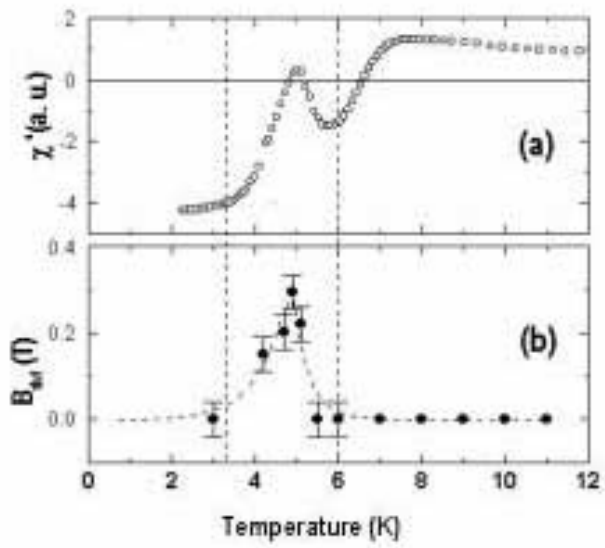

Figure 3. (a) χ_{ac} showing the range of temperature where the reentrant behavior occurs and (b) $\mathbf{B}_{thf}$ at the Ni site obtained for the $H_0(Ni_{0.99}{}^{57}Fe_{0.01})_2B_2C$ compound.

The loss of superconductivity in this range of temperature is attributed to the appearance of a pair-breaking field at the Ni layer, where ^{57}Fe probe is located. The transferred magnetic hyperfine field $\mathbf{B}_{thf}$ at the Ni (^{57}Fe) site, resulting from the four nearest neighbor of Ho atoms (two from the Ho layer above and two from the Ho layer below the Ni plane), will not cancel in the interval $4.7\,K < T < 6$ K, due to the incommensurate antiferromagnetic structure of $HoNi_2B_2C$. The $\mathbf{B}_{thf}$ as a function of the temperature (Fig. 3(b)), shows clearly that such a magnetic pair breaking field indeed exists in the reentrant region for the $HoNi_2B_2C$ compound. A pair-breaking field (transferred hyperfine field) was observed at the Ni site and also suppresses superconductivity in $TbNi_2B_2C$ [10] and $GdNi_2B_2C$ [11]. Such kind of pair breaking field is not observed in case of $DyNi_2B_2C$ and $ErNi_2B_2C$, where superconductivity coexists with magnetic order [12].

The superconductivity in the collinear AF superconductor $DyNi_2B_2C$ relies on the delicate canceling of the ordered magnetic moments on the Ni site. As a consequence, no $\mathbf{B}_{thf}$ was observed at any temperature in this compound. On the other hand, the doping of $DyNi_2B_2C$ with other non-magnetic elements (e.g. Lu), $Dy_{1-x}Lu_xNi_2B_2C$, disturb this balance and would yield to the appearing of a net $\mathbf{B}_{thf}$ at the Ni site, such that Lu should act like a magnetic impurity. So, a decreasing of T_c with the Lu doping, in agreement with the Abrikosov-Gor'kov theory, was observed [13]. Furthermore, these elements introduce disorder in the $4f$-spin system such that simultaneously T_N also decreases with doping concentration. Low temperature Mössbauer experiments on non-superconducting $Dy_{0.8}Lu_{0.2}Ni_2B_2C$ shown that in fact a $\mathbf{B}_{thf}$ exist below T_N and act as

pair breaking field. Fig. 4 shows the Bt_{hf}, as a function of the temperature for $Dy_{0.8}Lu_{0.2}Ni_2B_2C$.

The magnetic ordering temperatures T_M of RNiBC (R=Er, Ho, Dy, Tb, Gd) have been determined by AC susceptibility measurements [5]. We have plotted these values for the different compounds in Fig. 5 together with those of the corresponding RNi_2B_2C and RRh_4B_4compounds as a function of the de Gennes factor. While the T_M values of the RNi_2B_2C compounds nicely follow a linear relation with the de Gennes factor (see Fig. 5) this is not the case for the RNiBC compounds where T_M for Dy and Tb are even higher than that for Gd (see Fig.7). This finding is very similar to that found for *ferromagnetic* (FM) ordered RRh_4B_4 compounds where again the highest T_M does not occur for Gd but for Dy (Fig. 5). Crystal field effects have explained this fact which enhance T_M of FM compounds in such a way that T_M of $TbRh_4B_4$ and $DyRh_4B_4$ is higher than that of $GdRh_4B_4$ [14]. As it is shown below, DyNiBC and TbNiBC have a FM structure just below T_c.

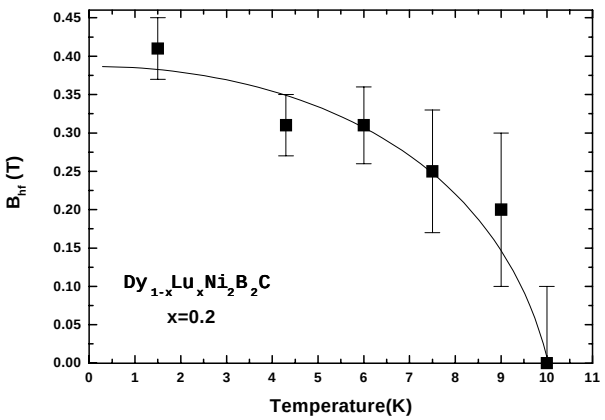

Figure 4. B_{thf} at the Ni site obtained for the $Dy_{0.8}Lu_{0.2}(Ni^{57}_{0.99}Fe_{0.01})_2B_2C$ compound.

From the analysis of magnetoresistance data for RNiBC (R=Er, Ho, Dy, Tb , Gd) [5] one obtains FM coupling for Er, Dy and Tb, corroborated by recently neutron diffraction data [15]. ^{57}Fe ME studies below T_M for RNiBC (R=Er, Ho, Dy, Tb , Gd) show a magnetic hyperfine field at the Fe (Ni) nucleus for Tb and Er, again in agreement with neutron and magnetoresistance data. No magnetic hyperfine field, on the other hand, was observed for Ho, Dy and Gd. While this is in agreement with the other experimental data for Ho and Gd, the absent hf field in DyNiBC is a puzzle.

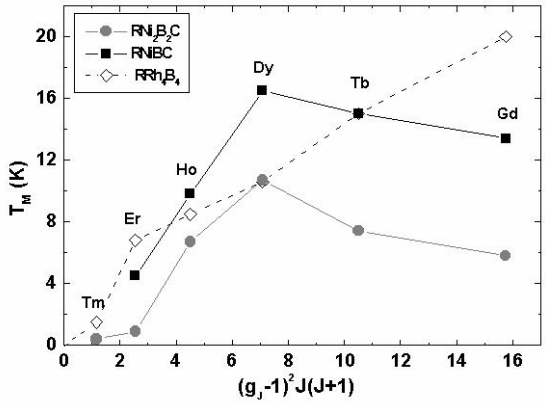

Figure 5. Magnetic transition temperatures T_M for the RNi_2B_2C [6], RNiBC [5] and RRh_4B_4 [14] compounds as a function of the de Gennes factor.

IV Superconductivity

The T_c of the heavy magnetic rare earth RNi_2B_2C has been found to decrease linearly with increasing de Gennes factor $(g_J\text{-}1)^2J(J+1)$ [16]. This correlation pointed the magnetic pair-breaking as the dominant effect in determine the depression of T_c in magnetic RNi_2B_2C compounds but does not explain the behavior of non magnetic Lu, Y and La. However, a different approach, in which the structural effects seem to play an important role in determining the variation of T_c in the rare earth-nickel-borocarbides (including the magnetic and non-magnetic RNi_2B_2C, and their counterparts RNiBC), will be shown below.

A deviation of the ideal tetrahedral symmetry of the NiB_4 of $LuNi_2B_2C$ can be obtained experimentally doping the Lu site with the nonmagnetic La. Being the ionic radius of the La different from Lu the doping will lead to a change in the (c'/a) parameter. Because these samples are nonmagnetic, there is no magnetic influence on superconductivity and the depression of T_c will be determined only by structural effects (change of (c'/a) parameter). The above arguments are also valid for YNi_2B_2C if doped with La. In view of these facts we decided to prepare the $Lu_{1-x}La_xNi_2B_2C$ and $Y_{1-x}La_xNi_2B_2C$ alloys.

In order to see if there is any relation between this structural parameter and the superconducting transition temperature T_c we have plotted in Fig. 6 the T_c value for LuNiBC [3] together with those for the non-magnetic RNi_2B_2C (R=Lu, Sc) compounds, the non-magnetic mixtures $(Lu_{1-x}La_x)Ni_2B_2C$ [17], $(Y_{1-x}La_x)Ni_2B_2C$ [18] and the magnetically ordered RNi_2B_2C (R=Tm, Er, Ho, Dy) compounds. The non-magnetic $LuNi_2B_2C$, $ScNi_2B_2C$, $(Lu_{1-x}La_x)Ni_2B_2C$ and LuNiBC show a linear relation between (c'/a) and T_c (see solid line in Fig. 6). The non-magnetic mixtures $(Y_{1-x}La_x)Ni_2B_2C$ also show a linear relationship

between (c'/a) and T_c (see dashed line in Fig. 6) with a slope which is identical to that for the other non-magnetic compounds. This slope of T_c vs (c'/a), thus is a measure for the decrease of T_c with increasing (c'/a).

The T_c values found for $(Y_{1-x}La_x)Ni_2B_2C$ are higher (for the same (c'/a) value) than those of RNi_2B_2C family of borocarbides. As mentioned in section II, this feature is likely related with the fact that the Y does not behave as a rare earth in these series of compounds, which is also observed in the Chevrel phases [19].

The YNiBC becomes superconducting when doped with Cu [20], and their T_c vs c'/a plot follows quite the same trend observed for the $Y_{1-x}La_xNi_2B_2C$ series (Fig. 9). Despite the fact that in this case there occurs a change in the density of states at the Fermi level it seems that again a structural change is relevant for the change in T_c when the Cu substitutes the Ni in YNiBC.

Quite surprisingly the magnetically ordered RNi_2B_2C (R=Dy, Ho, Er) compounds with T_N close to T_c are on the same line as the non-magnetic compounds. Only T_c of $TmNi_2B_2C$ with $T_N << T_c$ is slightly below the line (see Fig. 6), indicating that there is a clear paramagnetic pair-breaking effect due to exchange scattering in the framework of Abrikosov-Gorkov theory for this compound. Thus, the pair breaking effect of the R magnetic moment seems to be very small for Dy, Ho, Er and it is $\Delta\ T_c \approx$ -2 K for Tm. This finding is quite in contrast to the generally accepted opinion that T_c in all magnetically ordered RNi_2B_2C compounds scales with the de Gennes factor [6,16]. However, it is in perfect agreement with very recent theoretical calculations [21] which have shown that the Ni($3d$), electrons which are mainly responsible for superconductivity, do not feel the R magnetic moments in the case that the R magnetic moments are antiferromagnetically ordered, i.e. for Dy and Ho.

In the $R_{1-x}R'_xNi_2B_2C$ pseudoquaternary alloys, where one of them is magnetic (e.g. R = Lu or Y and R' = Gd [11,22]), T_c will decrease according to Abrikosov-Gorkov theory. In this case, the pair breaking effect is more effective in reduction of T_c than the structural effect (change of c'/a) and cannot be considered in our linear relation of T_c with (c'/a).

Taking into account what was discussed above, the (c'/a) parameter (a measure of the distortion of the NiB_4 tetrahedra) seems to be a relevant parameter, which determines T_c in *all* non-magnetic and antiferro-magnetically ordered RNi_2B_2C and RNiBC compounds. On the other hand, the T_c scale with (c'/a) ratio and the de Gennes factor in a similar way for the heavy rare earth RNi_2B_2C. However, in the Abrikosov-Gorkov framework is not possible to explain the differences in T_c of the nonmagnetic $LuNi_2B_2C$, $ScNi_2B_2C$, YNi_2B_2C, $LaNi_2B_2C$, and the R-C double layer LuNiBC compound.

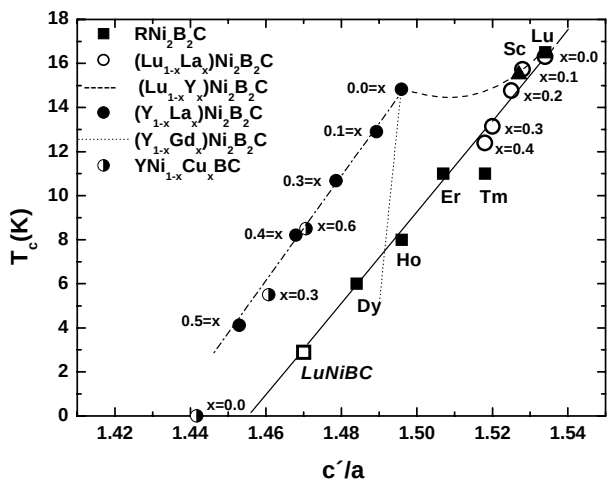

Figure 6. Superconducting transition temperatures of RNi_2B_2C [6], $(Lu_{1-x}La_x)Ni_2B_2C$ [17], $(Y_{1-x}La_x)Ni_2B_2C$ [18], LuNiBC [3], and $YNi_{1-x}Cu_xBC$ [20].

The superconducting properties of the RNi_2B_2C phases are attributed to an electron-phonon mechanism [9]. Although the Fermi electrons in these materials have predominant Ni($3d$) character, the superconductivity occurs only when a special $s-p$ band is optimally aligned relative to the Fermi level (i.e., when the NiB_4 tetrahedra angles are nearly "ideal") and which exhibits strong electron-phonon coupling [9].

Since we expect that the structure by itself can not determine T_c, more work is necessary to elucidate the role of the structural effects on the electron-phonon coupling, which seems to be essential to describe the nature of the depression of T_c in the rare earth-nickel-borocarbides series of compounds.

V Conclusion

^{57}Fe Mössbauer spectroscopy on ^{57}Fe doped RNi_2B_2C show a transferred hyperfine field at the Fe (Ni) nucleus for the compounds where superconductivity is not observed ($TbNi_2B_2C$ and $GdNi_2B_2C$) and where the superconductivity disappears in certain region of temperature ($HoNi_2B_2C$ in the reentrant region) and doping ($Dy_{0.8}Lu_{0.2}Ni_2B_2C$, below T_N). This transferred hyperfine field is interpreted as a field originating from the magnetic moments of the neighboring R atoms, which are in a spin configuration different that commensurate antiferromagnetic, and acts as a pair-breaking field at the Ni site. ^{57}Fe Mössbauer results in RNiBC indicate a ferromagnetic spin structure for TbNiBC and ErNiBC and antiferromagnetic one for HoNiBC. Electrical field gradient measurements at Fe site show that the NiB_4 tetrahedra in RNiBC displays stronger deviation from "ideal" tetrahedral symmetry (as that $LuNi_2B_2C$) than the RNi_2B_2C compounds. The same linear relation between T_c and (c'/a) was found for the magnetic as well as the non-magnetic RNi_2B_2C and the RNiBC series,

indicating that structural effects may be essential for the establishment of the superconducting state in the rare-earth-nickel-borocarbides.

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