Influence of structural parameters on T_c in superconducting RNi$_2$B$_2$C compounds

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The superconducting transtition temperature T_c in nonmagnetic $Lu_{1-x}La_xNi_2B_2C$ ($x \leqslant 0.1$) linearly decreases with the structural parameter c'/a as $dT_c/d(c'/a) = 210(20)$ K. The same decrease of $dT_c/d(c'/a)$ has been observed for the other nonmagnetic series $Lu_{1-x}Y_xNi_2B_2C$ ($x \leqslant 0.1$) [J. Freudenberger, S. L. Drechsler, G. Fuchs, A. Kreyssig, K. Nenkov, S. V. Shulga, K.-H. Müller, and L. Schultz, Physica C **306**, 1 (1998); J. Freudenbenger, Paarbrechung in Seltenerd-Übergangsmetall-Borkarbiden, Thesis, TU, Dresden, 2000]. The decrease in T_c for the antiferromagnetically (AF) ordered compounds RNi_2B_2C (R=Dy,Ho,Er,Tm) and for nonmagnetic LuNiBC again scales as $[dT_c/d(c'/a)] = 200(10)$K. This is a strong indication that in nonmagnetic and AF ordered RNi$_2$B$_2$C as well as RNiBC compounds T_c is determined by c'/a which is a measure for the deviation of the NiB_4 tetrahedra from ideal tetrahedral symmetry.

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I. INTRODUCTION

Since the discovery of superconductivity in the quaternary rare earth (R) nickel borocarbides RNi$_2$B$_2$C in 1994 (Refs. 1 and 2) the main interest in the study of these compounds was to understand the interplay between superconductivity and magnetism occurring in this class of materials. In order to understand the variation of the superconducting transition temperature T_c within the series of RNi$_2$B$_2$C compounds, for example, attempts have been made to correlate T_c with the de Gennes scaling parameter $G = (g_J - 1)^2 J(J+1)$ (g_J and J being the Lande g factor and total angular momentum of the R^{3+} ion, respectively).[3–5] We will not discuss this point any further for the moment but will come back to it at the end of this paper.

The variation of T_c for *non*-magnetic RNi$_2$B$_2$C compounds, on the other hand, e.g., the fact that $LuNi_2B_2C$ has the highest T_c of all superconducting RNi$_2$B$_2$C compounds while $LaNi_2B_2C$ is not superconducting at all or the change of T_c within the series $Y_{1-x}La_xNi_2B_2C$ (Ref. 6) or $Lu_{1-x}Y_xNi_2B_2C$ (Ref. 7), definitely has other reasons. Band structure calculations by Mattheiss *et al.*[8] explain why $LuNi_2B_2C$ has such a high T_c and $LaNi_2B_2C$ is not superconducting: in $LuNi_2B_2C$ the Fermi energy has its position at a relatively high density of states (DOS), while it is at a low value of the DOS for $LaNi_2B_2C$. As it was further pointed out in this paper, high DOS at the Fermi energy happens to coincide with ideal tetrahedral symmetry of the NiB_4 tetrahedra forming the Ni_2-B_2 layers which are responsible for the superconductivity. Recent calculations by Diviš *et al.*[9] essentially come to the same conclusion about the DOS. In order to confirm the idea that deviations from the ideal tetrahedral symmetry of the NiB_4 tetrahedra are responsible for the variation of T_c in *non*-magnetic RNi$_2$B$_2$C compounds more experimental data for T_c in such compounds are needed. It is for this reason that we have studied the system $Lu_{1-x}La_xNi_2B_2C$. Furthermore, such studies offer the possibility to compare this system with the series $Lu_{1-x}Y_xNi_2B_2C$ (Ref. 7) that we have already studied. Preliminary results already have been published elsewhere.[10]

II. SAMPLE PREPARATION AND CHARACTERIZATION

Polycrystalline $Lu_{1-x}La_xNi_2B_2C$ samples were prepared by conventional arc melting of stoichiometric amounts of pure elements in an Ar atmosphere.[6] The room temperature x-ray diffraction measurements were performed on powdered samples with a Rigaku Miniflex diffractometer using Cu Kα radiation. Rietveld analysis was used to obtain the lattice parameters of the samples. Alternating current (ac) susceptibility measurements were done in a Quantum Design superconducting quantum interference device magnetometer in the temperature range between 4.2 and 30 K. Four probe resistance measurements were made using a Linear Research ac bridge (model LR700) in the temperature range $2K \leqslant T \leqslant 300$ K.

The x-ray analysis of $Lu_{1-x}La_xNi_2B_2C$ was done in a similar way as previously made for the $Y_{1-x}La_xNi_2B_2C$ system.[6] Single phase (less than 3% impurity phase) with good crystallinity only was found for samples with compositions close to the Lu and La ends (Fig. 1). For La concentrations between 0.02 and 0.9 (miscibility gap) two phases with $LuNi_2B_2C$ type of structure were found which we assign to a Lu-rich and a La-rich phase, respectively. A similar miscibility gap has been reported for other La diluted RNi$_2$B$_2$C compounds.[6,11] Figure 1 shows the results of the Rietveld analysis assuming the presence of the earlier-mentioned two phases for the samples with $x = 0.02$, 0.07, and 0.9, which correspond to nominal concentrations of 0.1, 0.6, and 0.9, respectively (see later, and Table I). As expected, the analysis shows that the La-rich phase increases with increasing lanthanum concentration.

The reduction of the superconducting transition temperature T_c with La substitution can be seen in Fig. 2. Taking into account that $LaNi_2B_2C$ is not superconducting, it is natural to suppose that T_c of $LuNi_2B_2C$ is reduced by substitution of Lu by La. Therefore, we attribute the superconducting transition observed by ac susceptibility and ac resistance measurements (see Fig. 2) to the Lu-rich phase. An apparent nonsystematic change of T_c with increasing nominal La concentration would be seen if the mismatch between nominal and real concentration is not taken into account. In fact, *real*

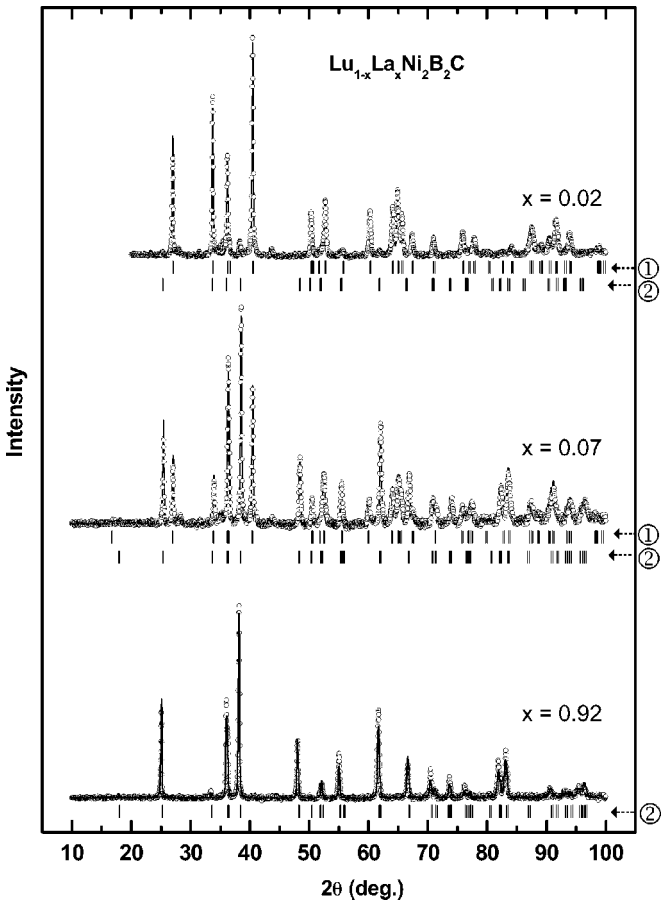

FIG. 1. Cu $K\alpha$ x-ray diffraction pattern of the samples $(Lu_{1-x}La_x)Ni_2B_2C$ with La concentration of 0.02, 0.07, and 0.92. The Bragg peaks, corresponding to the Lu-rich phase (① vertical lines) and La-rich phase (②), obtained after Rietveld analysis, are indicated.

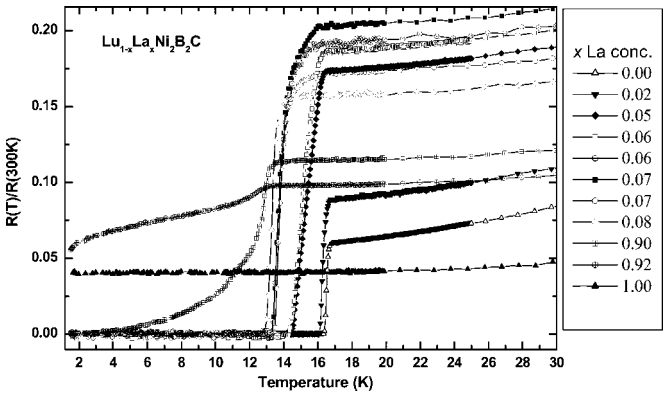

FIG. 2. ac resistivity data, given as a function of temperature for the $Lu_{1-x}La_xNi_2B_2C$ series with different La concentrations.

concentration in the Lu-rich phase does not correspond to the nominal La concentration due to the presence of the earlier-mentioned two phases in the sample. The real La concentration x in the Lu-rich phase has been calculated (see Table I) by making the assumption that the lattice parameters linearly vary, going from pure $LuNi_2B_2C$ to pure $LaNi_2B_2C$ (see Ref. 6). It is important to mention that the calculated values of the real concentration are not relevant for the main conclusion of this paper drawn from the data in Fig. 5. The room-temperature normal-state resistivities are between ~100 and 200 $\mu\Omega$ cm, somewhat higher than what is observed in single crystal[12] but agree with that for polycrystalline samples.[2]

III. EXPERIMENTAL RESULTS AND DISCUSSION

The parameter c'/a (c' is the distance of the two R-C layers between which the NiB_4 tetrahedra are sandwiched and a is the lattice parameter in the basal plane) has been found to be the relevant parameter determining the tetrahe-

TABLE I. Nominal and real x concentrations, a and c lattice parameters and superconducting transition temperatures T_c as obtained from resistance (R) and susceptibility (χ') measurements for the $Lu_{1-x}La_xNi_2B_2C$ series. Labeled parameters for nominal $x \leqslant 0.7$ correspond to Lu-rich phases and for $x > 0.8$ to La-rich phases.

x				T_c(K)	
Nominal	Real	a (Å)	c (Å)	R	χ'
0.0	0.00	3.463(1)	10.626(3)	16.5(2)	16.4(3)
0.1	0.02	3.470(1)	10.615(3)	16.2(3)	16.1(7)
0.2	0.05	3.480(2)	10.605(5)	15.3(8)	14.3(9)
0.3	0.06	3.484(3)	10.601(4)	15.1(7)	14.2(8)
0.4	0.06	3.485(2)	10.595(4)	13.6(3)	13.4(7)
0.5	0.07	3.486(3)	10.596(4)	13.6(5)	13.3(8)
0.6	0.07	3.487(2)	10.590(4)	13.6(6)	13.1(5)
0.7	0.08	3.491(3)	10.583(4)	13.3(6)	13.0(7)
0.8	0.90	3.764(3)	9.894(5)	⋯	⋯
0.9	0.92	3.771(1)	9.865(3)	⋯	⋯
1.0	1.00	3.793(1)	9.824(2)	⋯	⋯

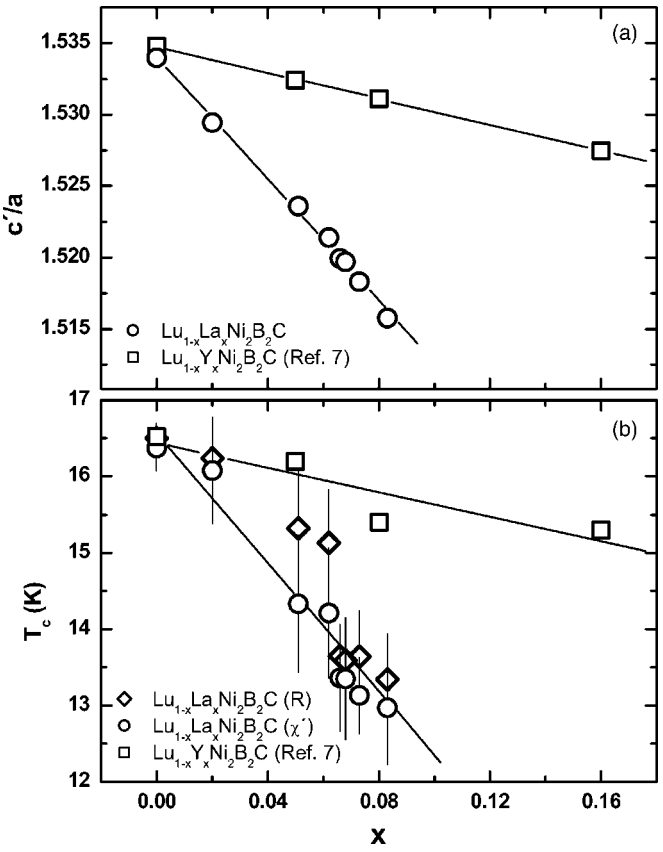

FIG. 3. (a) c'/a parameters for $Lu_{1-x}R'_xNi_2B_2C$ (R'=La and Y) as a function of the concentration x. (b) Superconducting transition temperatures [from resistance (R) and susceptibility (χ') measurements] as a function of x for $Lu_{1-x}R'_xNi_2B_2C$ (R'=La and Y). All the data for R'=Y were taken from Ref. 7.

dral symmetry at the Ni site in RNi_2B_2C as well as RNiBC compounds. This finding results from ^{57}Fe Mössbauer effect studies of various RNi_2B_2C (R=Y, Er, Ho, Dy, Tb, Gd, Nd, Pr) and RNiBC (R=Y, Er, Ho, Dy, Tb, Gd) compounds.[13] The quadrupole splitting $|\Delta E_Q|$ at the ^{57}Fe (Ni) site linearly scales with c'/a for *all* compounds studied. Since $|\Delta E_Q|$ is a measure for the deviation from ideal tetrahedral symmetry (ΔE_Q=0 for ideal tetrahedral symmetry) this linear correlation between $|\Delta E_Q|$ and c'/a clearly proofs that it is indeed the (c'/a) parameter which determines the deviation from ideal tetrahedral symmetry. In Fig. 3(a) we have plotted c'/a for $Lu_{1-x}La_xNi_2B_2C$ as a function of the real La concentration x obtained from the lattice parameters (see earlier) together with c'/a for $Lu_{1-x}Y_xNi_2B_2C$ given in Ref. 7. As can be seen from this figure the change of c'/a with x is a factor of about 4.5 larger for La doping compared to that for Y doping $[d(c'/a)/dx=-0.20$ and -0.045 for La and Y doping, respectively]. This is what one would expect, since the difference in the ionic radii between Lu and La is Δr(Lu−La) $=-0.0223$ nm which is about a factor of 4 larger than the corresponding Δr for Y doping $[\Delta r(\text{Lu}-\text{Y})=-0.0057$ nm].

Figure 3(b) shows the T_c values as obtained from resistance (R) as well as susceptibility (χ') measurements as a function of x for $Lu_{1-x}La_xNi_2B_2C$. As can be seen from this figure, the agreement between the results of the two measuring methods is quite good. In addition we have plotted in Fig. 3(b) the T_c values as given for $Lu_{1-x}Y_xNi_2B_2C$ in Ref. 7. It shows that the influence of La doping on T_c again is a factor of about 4.5 larger than that for Y doping (dT_c/dx $=-42$ K and -8.5 K for La and Y doping, respectively).

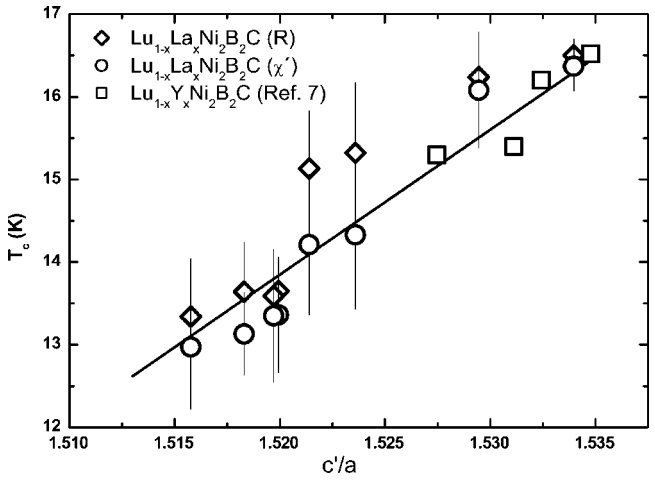

FIG. 4. Superconducting transition temperatures, given as a function of c'/a parameter, for $Lu_{1-x}La_xNi_2B_2C$ and $Lu_{1-x}Y_xNi_2B_2C$ (Ref. 7) systems.

If we now plot T_c vs c'/a, we find that the T_c reduction ΔT_c in *both* systems $Lu_{1-x}La_xNi_2B_2C$ and $Lu_{1-x}Y_xNi_2B_2C$ scales with c'/a in exactly the same way (see Fig. 4). The straight line drawn through the data points in Fig. 4 is a least-square fit with the slope $[dT_c/d(c'/a)]=210(20)$K.

This is quite a remarkable result since it shows that the T_c reduction just scales with c'/a or with the deviation from ideal tetrahedral symmetry of the NiB_4 tetrahedra, independent of the size of the doping atom. Usually it is assumed[14] that the T_c reduction is caused by local lattice distortions due to the different sizes of the host and doping rare earth ion. Since this effect usually scales as $\propto\Delta r^2$ (Refs. 14–16) one would expect that the T_c reduction for a given x should be a factor of about 20 larger for La doping than in the case of Y doping. This, however, is not observed: the experiments clearly show that ΔT_c scales approximately with Δr and *not* with Δr^2. We should mention at this point that magnetic dilution of *antiferromagnetically ordered* (AF) $DyNi_2B_2C$ with La and Y, respectively, indeed reduces T_c by a factor which scales with Δr^2 (Refs. 14–16). This reduction, however, is due to a *magnetic pair-breaking* effect[17] which is not relevant in the nonmagnetic systems we are discussing here.

In the following we want to bring another argument why the T_c reduction in $Lu_{1-x}La_xNi_2B_2C$ and $Lu_{1-x}Y_xNi_2B_2C$, respectively, is not caused by local lattice distortions due to different ionic radii but rather due to the deviation of the NiB_4 tetrahedra from ideal tetrahedral symmetry. Fuchs *et al.*[18] analyzing all existing experimental data for the series $Lu_{1-x}Y_xNi_2B_2C$, suggest that the local lattice distortions due to different sizes of the Y and Lu ions mainly reduces the electron-phonon coupling constant $\lambda_{e\text{-ph}}$. The change in the DOS at the Fermi level, on the other hand, is too small to explain the measured change in the Sommerfeld constant. Whereas it is not quite clear how local lattice distortions will

reduce $\lambda_{e\text{-ph}}$, our finding, namely, that the T_c reduction scales with c'/a can explain the reduction of $\lambda_{e\text{-ph}}$: as it has been pointed out by Mattheiss *et al.*,[8] the NiB_4 tetrahedra in $LuNi_2B_2C$ have almost ideal tetrahedral symmetry. This fact also is "ideal" for superconductivity since in this case an *s*-*p* band, which exhibits strong electron-phonon coupling, happens to coincide with the Fermi level. Changing c'/a, i.e., changing the B-Ni-B bonding angles in the NiB_4 tetrahedra, therefore, will shift this *s*-*p* band and reduces the electron-phonon interaction.

Having discussed in detail the reason for the variation of T_c in nonmagnetic RNi_2B_2C superconductors, we now will switch to the nonmagnetic superconductor LuNiBC and to the AF ordered superconductors RNi_2B_2C with R=Dy, Ho, Er, and Tm. We will ask the question, how much of the T_c reduction in these systems is caused by the deviation of the NiB_4 tetrahedra from ideal tetrahedral symmetry. For that reason we have plotted in Fig. 5 the T_c values of all these compounds as a function of the (c'/a) parameter together with the data points of the nonmagnetic RNi_2B_2C compounds already displayed in Fig. 4. Most surprisingly *all* data points fall on the same line, i.e., for *all* of these compounds the relation between T_c and c'/a is the same. The straight line through the data points of nonmagnetic LuNiBC and the AF ordered RNi_2B_2C compounds in Fig. 5 is a least-squares fit with $[dT_c/d(c'/a)]$=220(10)K. This value is within the experimental errors the same as that found for the nonmagnetic $Lu_{1-x}R'_xNi_2B_2C$ (R'=La, Y) compounds (see Fig. 4). For that reason we can make the following two conclusions:

(i) the difference in T_c between nonmagnetic LuNiBC and $LuNi_2B_2C$ is due to the change of c'/a or the deviation of the NiB_4 tetrahedra in LuNiBC from the ideal tetrahedral symmetry and

(ii) T_c in AF ordered RNi_2B_2C compounds (R=Dy, Ho, Er, and Tm) essentially is determined by c'/a or by the deviation of the NiB_4 tetrahedra from ideal tetrahedral symmetry; the influence of the R magnetic moments on T_c seems to be very small. An exception is Tm where there is a reduction in T_c (see Fig. 5) caused by the fact that only for Tm we have $T_c \gg T_N$, i.e., superconductivity occurs in the paramagnetic state.

Conclusion (i) gives a natural explanation for the missing superconductivity in all the other *R*NiBC compounds: c'/a in all other *R*NiBC compounds is smaller than in LuNiBC and smaller than $(c'/a)_{\text{crit}}$=1.457 (see Fig. 5). We are aware of the fact that conclusion (ii) is in clear contradiction with the generally accepted opinion that de Gennes scaling is the reason for the decrease of T_c with increasing R magnetic moment in these compounds. Nevertheless, the striking agreement in the correlation between T_c and c'/a for the nonmagnetic and AF ordered RNi_2B_2C superconductors should be taken as an experimental fact which cannot be overlooked.

One of the strongest arguments against the plot shown in Fig. 5 is the fact that the data point for YNi_2B_2C is far above the line drawn in Fig. 5, i.e., the T_c value for this compound is much higher than expected from its (c'/a) parameter.

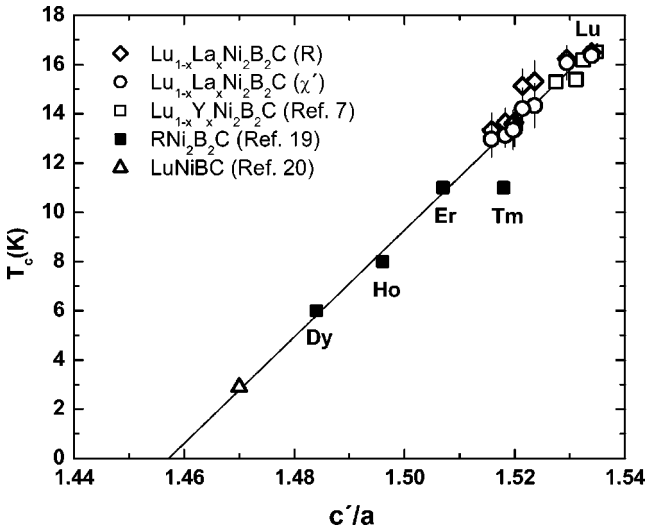

FIG. 5. T_c values for the magnetically ordered superconductors RNi_2B_2C with R=Dy, Ho, Er, and Tm (Ref. 19), given as a function of the (c'/a) parameter, together with the data points corresponding to the nonmagnetic $Lu_{1-x}R'_xNi_2B_2C$ (R'=La and Y) and LuNiBC (Ref. 20).

Even if we have no really satisfactory explanation for this fact, we want to bring up two points: (i) in another family of magnetic superconductors, namely, the Chevrel phases RMo_6S_8, T_c essentially scales with the volume V; again Y is *not* fitting in the T_c vs V relation obtained for all rare earth atoms;[21] (ii) the change of T_c in the nonmagnetic series $Y_{1-x}La_xNi_2B_2C$ is $[dT_c/d(c'/a)]$=293 K (Ref. 6); this value is even somewhat larger than that found for the other nonmagnetic RNi_2B_2C compounds, again indicating that T_c in YNi_2B_2C is too high if compared with the other RNi_2B_2C compounds.

As a final conclusion, we have clear experimental evidence that T_c in nonmagnetic, superconducting $Lu_{1-x}La_xNi_2B_2C$ and $Lu_{1-x}Y_xNi_2B_2C$ (Ref. 7) is determined by the structural parameter c'/a. This indicates that it is the deviation from the ideal tetrahedral symmetry of the NiB_4 tetrahedra which reduces T_c in $Lu_{1-x}R'_xNi_2B_2C$ (R'=La, Y) relative to $LuNi_2B_2C$. There seems to be additional experimental evidence that the T_c reduction in AF ordered RNi_2B_2C compounds is *not* due to the R magnetic moments but rather caused by deviations of the NiB_4 tetrahedra from ideal tetrahedral symmetry. This last finding is rather controversial, but we hope that it will trigger more theoretical work on the subject of T_c in nonmagnetic and AF ordered superconducting RNi_2B_2C compounds.

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