# OBSERVATION OF A PAIR - BREAKING FIELD AT THE Ni SITE IN NON-SUPERCONDUCTING $RENi_2B_2C$

Dalber R. Sánchez, H. Micklitz[1], M.B. Fontes, S.L. Bud'ko,
and E. Baggio-Saitovitch
Centro Brasileiro de Pesquisas Físicas, Rua Xavier Sigaud 150 Urca, Rio de Janeiro.
22290-180, Brazil.

## ABSTRACT

$^{57}$Fe Mössbauer spectra of $RENi_2B_2C$ (RE= Tb, Dy, Ho, Er) doped with 1 at. % $^{57}$Fe show a magnetic hyperfine field $B_{hf}$ at the $^{57}$Fe nucleus in $TbNi_2B_2C$ for $T<T_N \sim 15K$ and in $HoNi_2B_2C$ for 5.5K>T>4.2K. *No* $B_{hf}$ is observed in superconducting $DyNi_2B_2C$ and $ErNi_2B_2C$. Since $TbNi_2B_2C$ is not superconducting at all and superconductivity disappears in $HoNi_2B_2C$ for 6K>T>4.7K (reentrant state) we have to conclude that the observed $B_{hf}$ at the $^{57}$Fe nucleus, resulting from the non-collinear antiferromagnetic spin structure of the RE moments, acts as a pair-breaking field at the Ni site.

PACS: 74.70.Ad, 75.25.+z, 76.80.+y

[1]Visitor from II. Physikalisches Institut, Universität zu Köln, D-50937 Köln, Germany

*Accepted for publication in Physical Review Letters.

It is the interplay between magnetism and superconductivity occurring in the rare-earth (RE) nickel borocarbides ($RENi_2B_2C$) which makes this new class of compounds so interesting [1-4]. While all of these intermetallic layered compounds with magnetic RE have one or two magnetic phase transitions at low temperatures, not all of them show superconductivity. Simple de Gennes scaling seems to be appropriate to describe the change of the magnetic transition temperature in the various $RENi_2B_2C$ systems. The same scaling arguments in principle could be used to explain the suppression of superconductivity in $TbNi_2B_2C$ and $GdNi_2B_2C$. However, soon it was realized that collinear as well as non-collinear antiferromagnetic (AF) spin structures appear in the magnetically ordered phases: while there is a ferromagnetic coupling within the RE-C layers, two consecutive RE-C layers can be either aligned in opposite directions (collinear AF, e.g. $DyNi_2B_2C$ [5]) or coupled in a more complicated way (e.g. helical in the case of $HoNi_2B_2C$ [6,7]) leading to an incommensurate modulated magnetic structure. The latter, for example, seems to be responsible for the reentrant behavior, i.e. the suppression of superconductivity in $HoNi_2B_2C$ in the temperature region $4.7K<T<6K$ [6,7]. From this point of view it is rather tempting to attribute the suppression of superconductivity to the appearance of a pair-breaking field in the Ni-layer for the case of a non-collinear AF structure [6,7]. Such a field has not been observed until now. It may be big enough, however, to be detectable by a local probe sitting in the Ni-plane.

Mössbauer spectroscopy on $^{57}Fe$ doped $RENi_2B_2C$ in principle offers the possibility to use $^{57}Fe$ as such a local probe. Since it is well established that Ni has no magnetic moment in $RENi_2B_2C$, it is very likely that Fe sitting at a Ni-site has also no magnetic moment, this is supported by additional $^{57}Fe$ ME experiments we have

*Accepted for publication in Physical Review Letters.

performed on highly doped $Y(Ni_{0.93}Fe_{0.07})_2B_2C$ at low temperatures. No magnetic hf field was seen down to 4.2 K [8]. In this case one has the unique opportunity to study the occurrence of a pair-breaking field in the Ni-layer by the appearance of a magnetic hyperfine (hf) field (either transferred hf field via RKKY interaction or dipolar field) at the $^{57}Fe$ nucleus.

Our $^{57}Fe$ Mössbauer experiments, which are the first ones reported for $RENi_2B_2C$, clearly show that such a magnetic hf field indeed exists for $HoNi_2B_2C$ in the "reentrance" region and for non-superconducting $TbNi_2B_2C$ below $T_N$, but *not* for $DyNi_2B_2C$ and $ErNi_2B_2C$ where coexistence of magnetic ordering and superconductivity has been established.

Polycrystalline samples of $RE(Ni_{0.99}\ ^{57}Fe_{0.01})_2B_2C$, RE= Tb, Dy, Ho, Er, were prepared by melting stoichiometric amounts of high purity elements in arc-furnace in ~300 torr Ar atmosphere and subsequent annealing at ~1000$^o$C for 2 days. X-ray diffraction shows that the expected $ThCr_2Si_2$-like structure is formed as a majority phase with a low (< 10% ) level of impurities, characteristic for the polycrystalline samples of borocarbides. Obtained lattice parameters are consistent with the ones of pure $RENi_2B_2C$ [3]. In addition, samples were characterized by AC susceptibility. No significant changes of magnetic ordering temperatures were induced by the introduction of 1 at. % of Fe, since $T_N$ of 16.2, 8.8, 6.0, and 5.4 K were found for Tb, Dy, Ho and Er respectively. However $T_C$ decreases sligthly with iron doping as expected [9], since $T_C$ of 9.0 and 7.5K were obtained for Ho and Er respectively. $^{57}Fe$ Mössbauer effect (ME) spectra were taken with the $RENi_2B_2C$ samples in a variable temperature helium

[*]Accepted for publication in Physical Review Letters.

cryostat and the $^{57}$Co:Rh source at room temperature, moving in a sinusoidal mode outside of the cryostat.

Fig 1. shows the $^{57}$Fe ME spectra for all studied $RENi_2B_2C$ compounds at room temperature (RT). All spectra were fitted with two quadrupole doublets, one main doublet (~80% of total absorption area) whose quadrupole splitting $\Delta E_Q$ is RE dependent ($\Delta E_Q$ decreases with increasing 4f-electron number from $\Delta E_Q$=0.27(1)mm/s for $TbNi_2B_2C$ to $\Delta E_Q$=0.14(1)mm/s for $ErNi_2B_2C$) and an additional weak doublet whose quadrupole splitting is almost independent of RE ($\Delta E_Q \sim$ 0.40mm/s). We attribute the main doublet to $^{57}$Fe in the $RENi_2B_2C$ phase, while the additional weak doublet is probably due to an impurity phase also seen in the x-ray diffraction data. We want to mention already at this point that the weak doublet caused by the impurity phase was taken into account in all the low-temperature $^{57}$Fe ME spectra shown below without any further discussion of its origin.

Cooling the $RENi_2B_2C$ samples down to 4.2K results in quite different $^{57}$Fe ME spectra for the various compounds. For this reason we will discuss in the following each of these low-temperature spectra separatly.

The $^{57}$Fe ME spectra of $DyNi_2B_2C$ and $ErNi_2B_2C$ taken at 4.2K are given in fig.2. Comparing these spectra with the RT spectra shown in fig.1, there is no obvious difference: the value of the center shift is slightly more negative compared to the center shift at RT, due to second order Doppler shift, the quadrupole splitting is the same within the experimental errors ($\Delta E_Q$=0.23(1)mm/s and 0.14(1)mm/s for $DyNi_2B_2C$ and

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$ErNi_2B_2C$, respectively). Additional spectra were taken at temperatures between the magnetic ordering temperature ($T_N$ = 10K and 6K for $DyNi_2B_2C$ and $ErNi_2B_2C$, respectively) and 4.2K. *No* magnetic hf field was observed at any temperature below $T_N$ ($B_{hf} < 0.1T$).

$TbNi_2B_2C$ is known to show antiferromagnetic order below $T_N \sim 15K$ [2]. As it is evident from the $^{57}Fe$ ME spectra shown in fig. 3, a magnetic broadening begins to appear below 15K resulting in an asymmetrically broadened ME spectrum whose width is increasing with decreasing temperature. The spectra have been fitted using the full hyperfine Hamiltonian including electrical quadrupole and magnetic interaction. Furthermore, the following assumptions have been made : (1) quadrupole asymmetry parameter $\eta=0$, as it is expected for $^{57}Fe$ on a regular Ni site, and (2) absence of spin texture in the polycrystalline powder sample. Linewidth, quadrupole interaction ($\Delta E_Q$ = 0.25mm/s) and center shift (CS= -0.10mm/s relative to $^{57}Co$:Rh at RT), as obtained from the paramagnetic 15K-spectrum, have been kept constant for all spectra between 15K and 3.0K. The sign of $V_{ZZ}$ (main component of electrical field gradient tensor), the magnetic hf field $B_{hf}$ and the angle $\theta$ between the directions of $B_{hf}$ and $V_{ZZ}$ were the only free fitting parameters. This fitting procedure yields : $V_{ZZ} < 0$, $\theta \approx 90 \pm 5^o$ for all ME spectra and a $B_{hf}$ which increases with decreasing temperature from $B_{hf}$ (T=15K) ~0T to $B_{hf}$ (T=3K) ~1.0T. The temperature dependence of $B_{hf}$ is given in fig. 5. The onset of magnetic ordering at $T_N$ ~15K is clearly seen.

*Accepted for publication in Physical Review Letters.

The temperature dependence of the $^{57}$Fe ME spectra in $HoNi_2B_2C$ for $T \leq 5.5K$ is more complicated than those of the spectra for $RENi_2B_2C$ (RE=Er, DY, Tb). In fig. 4 we show the corresponding $HoNi_2B_2C$ spectra: starting with a quite symmetric spectrum at T~5.5K, the spectra change their shape for 5.3K>T>4.2K and again become quite symmetric for T=3K. In order to fit these $^{57}$Fe ME spectra we have made the same assumptions as in the case of $TbNi_2B_2C$ but added one more: since we know that $V_{ZZ}<0$ for $TbNi_2B_2C$ (see above) and assuming that the sign of $V_{ZZ}$ is independent of RE, we have taken $V_{ZZ} < 0$ also for $HoNi_2B_2C$. Comparing the asymmetry of the $TbNi_2B_2C$ spectra with that of the $HoNi_2B_2C$ spectra for 5.3K>T>4.2K, we see that these asymmetries are opposite, from which immediately follows that $\theta \sim 0^o$ for $HoNi_2B_2C$ in this temperature regime. The values of the magnetic hf field obtained from this fitting procedure in the temperature region $T \leq 6K$ are shown in fig. 5. The spectrum taken at the lowest temperature (T=3K) clearly is symmetric. It can be only fitted with a pure quadrupole interaction [$B_{hf}(3K) \leq 0.1T$], however with a slightly increased linewidth [ $\Gamma(3K) \sim 0.32$ mm/s compared to $\Gamma(8K) \sim 0.27$mm/s] which may be caused by vibrations originating from the He-bath pump.

We want to discuss now why the $^{57}$Fe ME spectra at low temperatures are so different in the different $RENi_2B_2C$ systems. Our experiments show that there exists *no* measurable magnetic hf field ($B_{hf} < 0.1T$) at the $^{57}$Fe nucleus for Fe, supposedly sitting at the Ni-site, in the case of $ErNi_2B_2C$ and $DyNi_2B_2C$. For these two compounds the coexistence of superconductivity and magnetic order has been established. In the case of $TbNi_2B_2C$ and $HoNi_2B_2C$, however, the situation is quite different: we observe a magnetic hf field in the case of $TbNi_2B_2C$ below $T_N \sim 15K$ (see fig.5) and for $HoNi_2B_2C$ between the first magnetic phase transition at $T_{N_1} \sim 6K$ and the second one at $T_{N_2} \sim 4.7K$.

*Accepted for publication in Physical Review Letters.

At the same time it is known that superconductivity does not appear at all in $TbNi_2B_2C$ and disappears for $HoNi_2B_2C$ in the temperature region $T_{N_1}>T>T_{N_2}$ (reentrance behavior) [10,11]. Taking these two facts together it is very reasonable to assume that (1) the observed magnetic hf field at the $^{57}Fe$ nucleus is a pure dipolar or a transferred hf field resulting from the neighboring RE moments (i.e. $\mu_{Fe} < 0.01\mu_B$) and (2) this magnetic hf field acts as a pair-breaking field at the Ni site which leads to the suppression of superconductivity in some of the $RENi_2B_2C$ compounds. Such a magnetic hf field obviously does not exist in the case of $DyNi_2B_2C$ due to its simple collinear antiferromagnetic spin structure [5]. It exists, on the other hand , for $HoNi_2B_2C$ with an incommensurate modulated spin structure between ~ 6K and ~ 4.7K and for $TbNi_2B_2C$ which magnetic spin structure to our knowledge has not yet been determined.

The additional fact that the observed $B_{hf}$ in $TbNi_2B_2C$ and $HoNi_2B_2C$ is of the same order of magnitude as the critical magnetic field $B_{c2}$ measured for the superconducting $RENi_2B_2C$ compounds ( $B_{c2}(T=0)$ ~ 0.2, 0.6 and 1.6T for RE=Ho,Dy and Er, respectively [12-14]) is a further support of our interpretation for the suppression of superconductivity as given above.

In the following, we want briefly to discuss why in the incommensurate modulated spin structure of $HoNi_2B_2C$ a magnetic hf field is observed while this is not the case for the incommensurate modulated spin structure in $ErNi_2B_2C$: in $HoNi_2B_2C$ the spin structure is modulated along the c-axis as well as along the a (b)-axis [6,7]. The modulation along the c-axis results in a c-axis spiral with a turn angle of approximately $165^o$ between two successive Ho layers. As a consequence, the magnetic hf field at the

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Fe (Ni) site resulting from the four nearest neighbor Ho atoms (two from the Ho layer above and two from the Ho layer below the Ni plane) will *not* cancel. In $ErNi_2B_2C$, on the other hand, there is only a modulation of the spin structure along the a (b)-axis [15,16]. This modulation seems to result in a much smaller (not measurable) magnetic hf field at the Fe (Ni) site.

Finally, further conclusions about the spin structure in $TbNi_2B_2C$ and $HoNi_2B_2C$ can be drawn from the measured angle $\theta$ between the directions of $V_{ZZ}$ and $B_{hf}$. In $TbNi_2B_2C$, with unknown exact spin structure, we find $\theta=90\pm5^o$. Following symmetry arguments, the direction of $V_{ZZ}$ has to be in c-direction. Thus, we have to conclude that for $TbNi_2B_2C$ $B_{hf}$ lies in (a,b)-plane. Such a field direction is expected for a non-collinear AF spin structure, for example, with the Tb moments aligned parallel in each (a,b)-plane and a helical modulation of their direction along the c-axis. For $HoNi_2B_2C$, on the other hand, we find $\theta=0\pm5^o$ (assuming the sign of $V_{ZZ}$ to be independent of RE), from which follows that now $B_{hf}$ is in c-direction. This conclusion seems to be in contradiction to the spin structure as proposed from neutron scattering data [6,7]. Our result rather suggests that the Ho moments in the incommensurate magnetic phase ($T_{N_1} > T > T_{N_2}$) are slightly canted out of (a,b)-plane. It should be pointed out, however, that from neutron scattering it can only be concluded that the Ho-moments are *very close* to the (a,b)-plane [6,7]. It may be that the magnetic hf field measured in $^{57}Fe$ Mössbauer experiments is more sensitive to a small canting out of (a,b)-plane than neutron scattering.

In conclusion, our $^{57}Fe$ Mössbauer experiments on $^{57}Fe$ doped (~ 1 at. %) $RENi_2B_2C$ (RE=Tb, Dy, Ho, Er) show a magnetic hyperfine field at the $^{57}Fe$ nucleus for

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those two compounds where either no superconductivity is observed at all ($TbNi_2B_2C$) or where superconductivity disappears in a certain temperature region ($HoNi_2B_2C$, with "reentrance" behavior for 6K>T>4.7K). We interpret the observed magnetic hyperfine field as a field originating from the neighboring RE moments and acting as a pair-breaking field at the Ni site. The existence of such a pair-breaking field already has been proposed before by other authors [6,7] in order to explain the reentrance behavior of $HoNi_2B_2C$. While their suggestion is based on the spin structure as obtained from single crystal neutron scattering experiments, our experiments for the first time show that such a magnetic field at the Ni site *indeed exists* not only for $HoNi_2B_2C$ in the "reentrance" region but also for non-superconducting $TbNi_2B_2C$.

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## FIGURE CAPTIONS:

Fig.1 : $^{57}$Fe Mössbauer spectra of $RENi_2B_2C$ (RE=Tb, Dy, Ho, Er) at 300K. For $TbNi_2B_2C$ the two subspectra, corresponding to two doublets, explicitly are shown.

Fig. 2 : $^{57}$Fe Mössbauer spectra of $DyNi_2B_2C$ and $ErNi_2B_2C$ at T=4.2K.

Fig. 3 : $^{57}$Fe Mössbauer spectra of $TbNi_2B_2C$ in the temperature region $15K \geq T \geq 3K$.

Fig. 4 : $^{57}$Fe Mössbauer spectra of $HoNi_2B_2C$ in the temperature region $6K \geq T \geq 3K$.

Fig. 5 : Temperature dependence of magnetic hf field $B_{hf}$ at the $^{57}$Fe nucleus in $TbNi_2B_2C$ and $HoNi_2B_2C$ as obtained from least-squares fittings to the spectra shown in figs. 3 and 4, respectively. The dashed lines through the data points are only a guide for the eyes.

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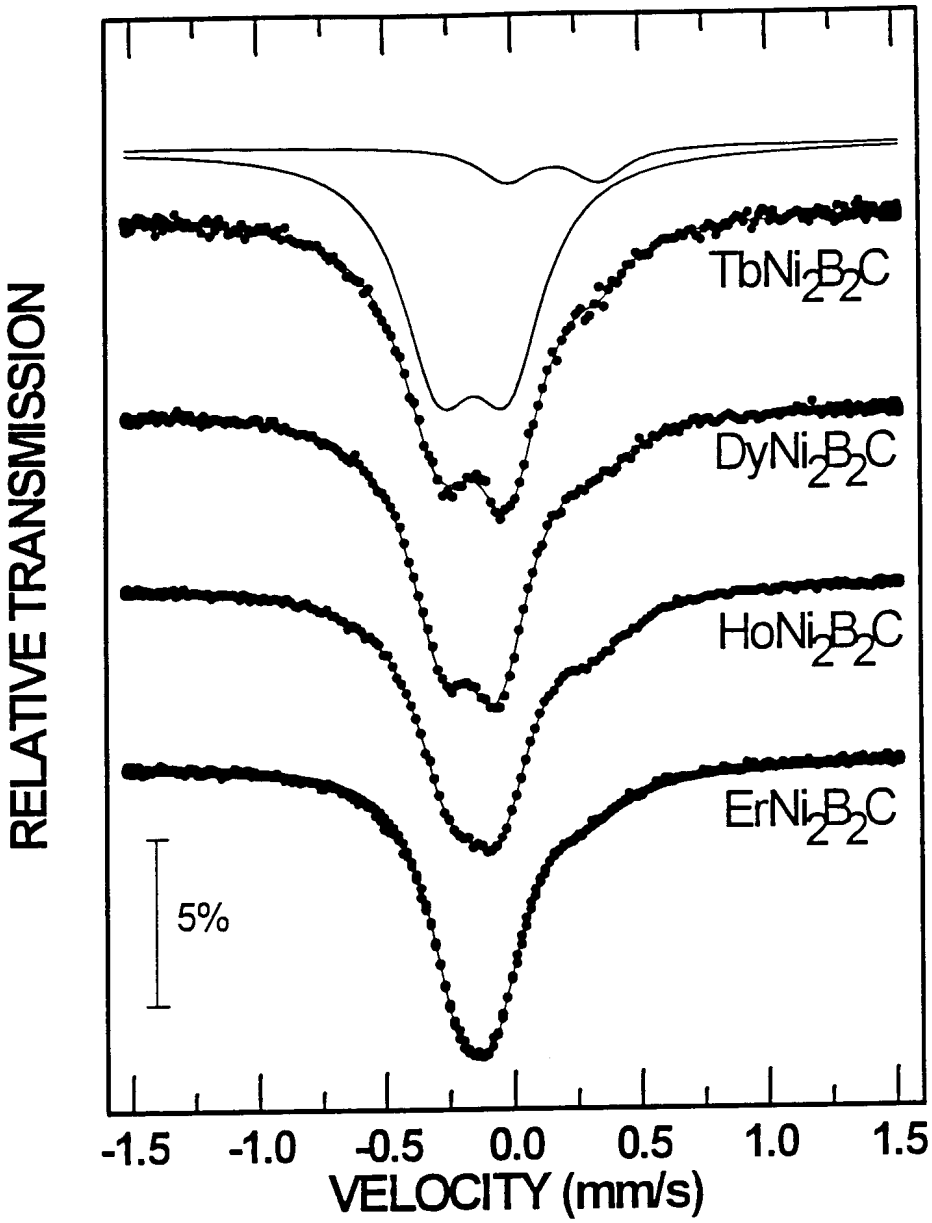


Fig. 1

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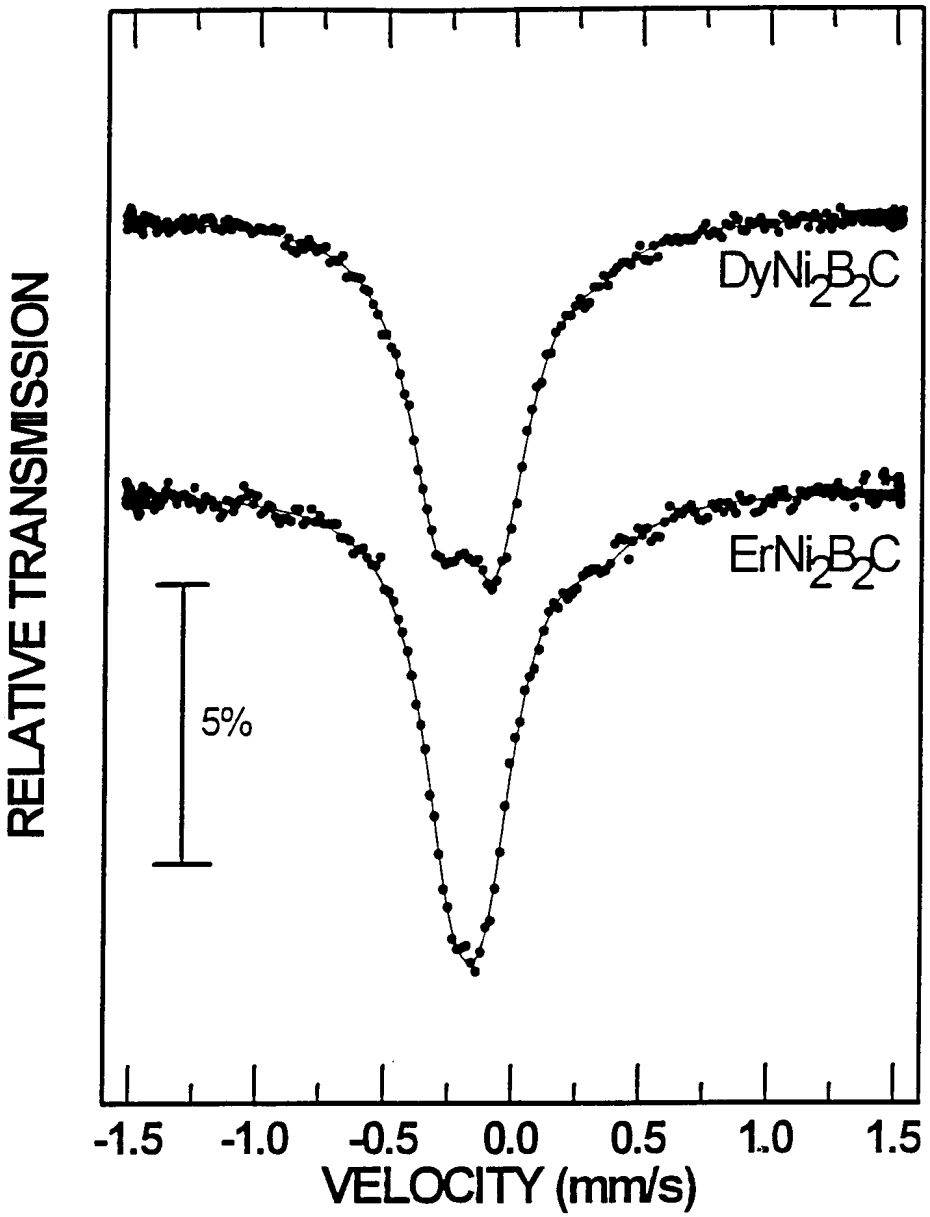


Fig. 2

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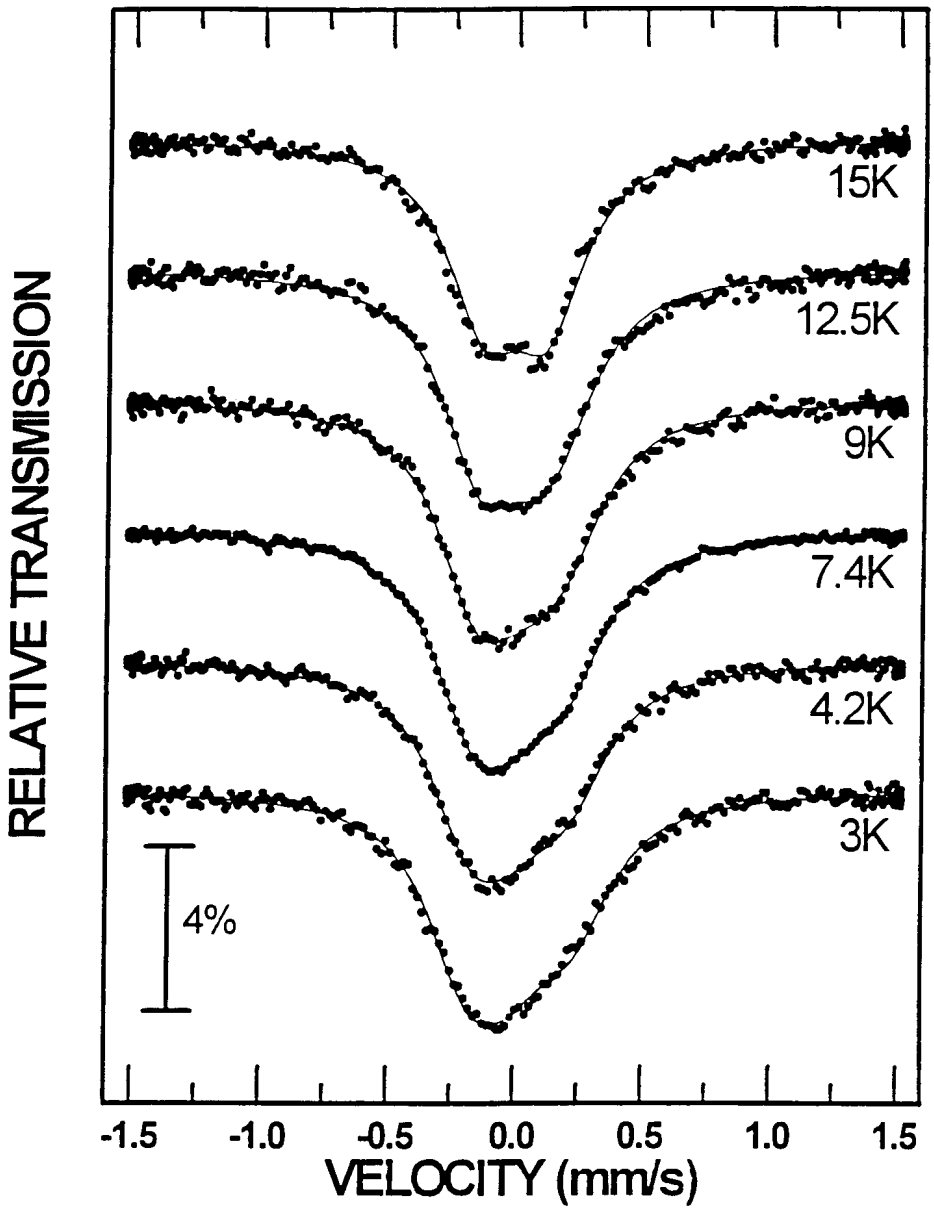


Fig. 3

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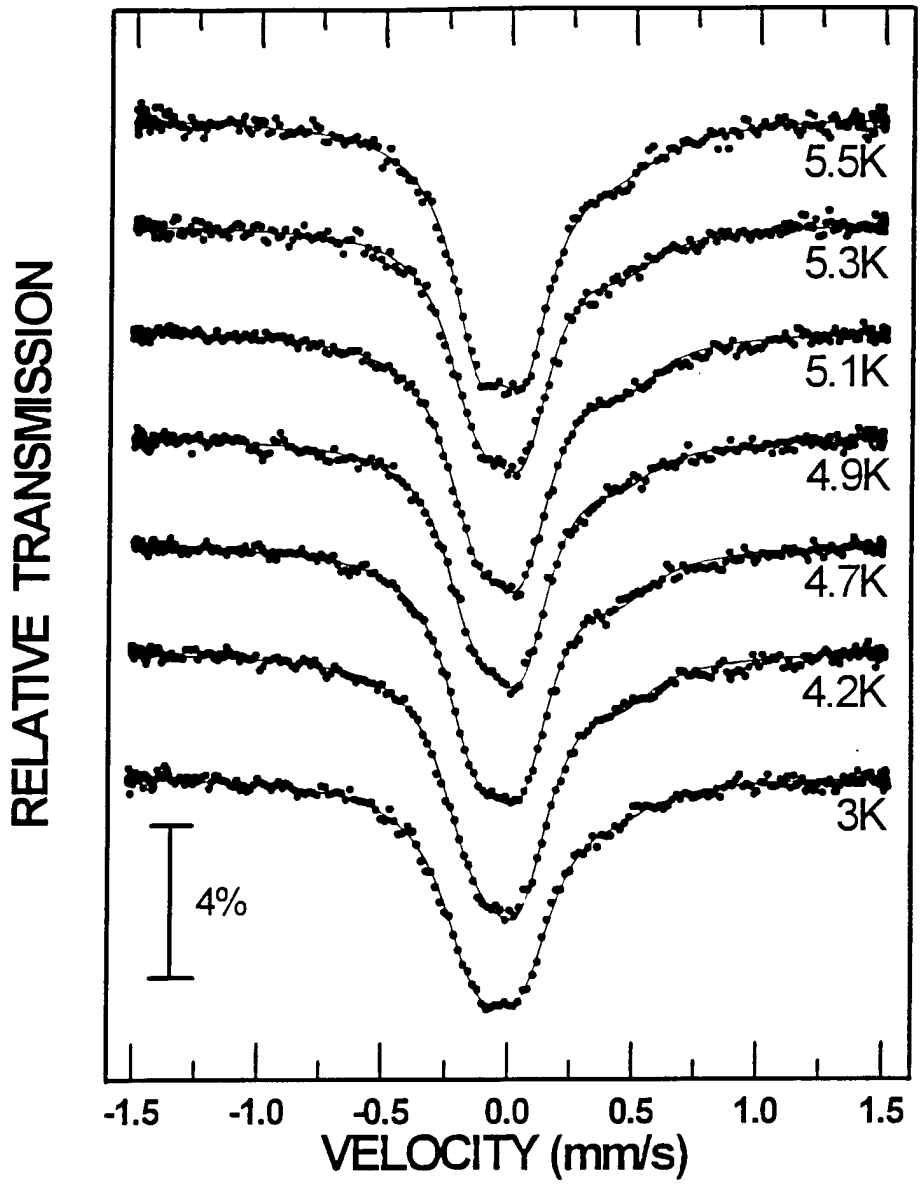


Fig. 4

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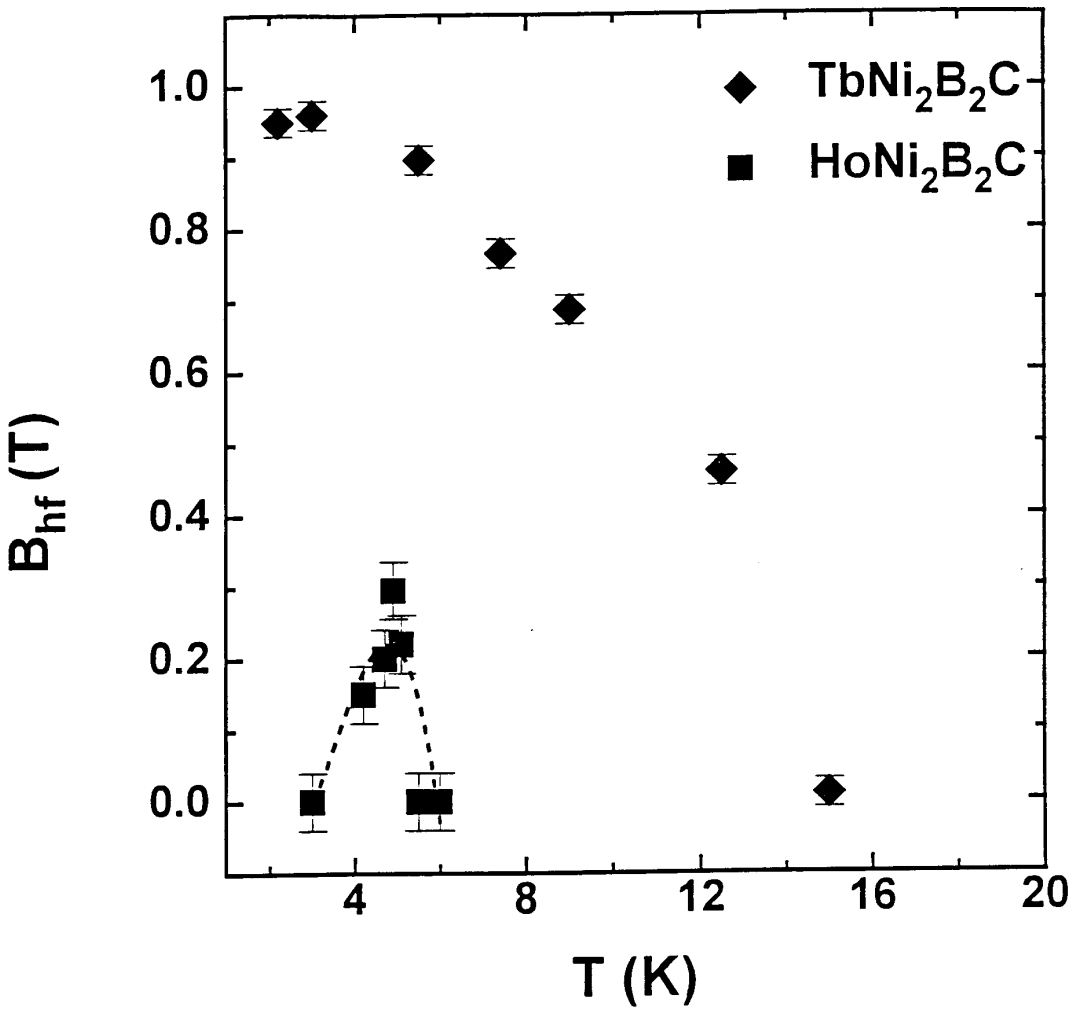


Fig. 5

*Accepted for publication in Physical Review Letters.

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*Accepted for publication in Physical Review Letters.