

## Two types of magnetism in the magnetic superconductor $\text{TmNi}_2\text{B}_2\text{C}$ related to the degree of carbon-site occupancy

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A combined  $^{169}\text{Tm}$  Mössbauer spectroscopy and  $\mu^+\text{SR}$  (muon spin rotation) study is presented on a polycrystalline sample of  $\text{TmNi}_2\text{B}_2\text{C}$ . The first experimental technique shows the coexistence of two types of Tm  $4f$  magnetism at 0.3 K, one related to a magnetic Tm moment of  $4.3(1)\mu_B$  and the other to a small Tm moment of  $\sim 0.1\mu_B$ . This second type of magnetism is suggested to be caused by carbon vacancies present in  $\text{TmNi}_2\text{B}_2\text{C}$ . These C vacancies locally modify the crystalline electric field and therefore the Tm  $4f$  magnetism. Since these vacancies are ideal cavities in which muons can reside, it is suggested that  $\mu^+\text{SR}$  only probes this  $\sim 0.1\mu_B$  magnetism. [S0163-1829(98)05217-5]

The discovery of the quaternary rare earth nickel boron carbides  $R\text{Ni}_2\text{B}_2\text{C}$  in 1994 started an intensive study of their combined magnetic and superconducting properties. In some of these compounds ( $R = \text{Tm}, \text{Er}, \text{Ho},$  and  $\text{Dy}$ ) these studies reveal the coexistence of superconductivity and magnetism. As the strength of the exchange interaction between  $R$  atoms increases (de Gennes scaling) the transition to the superconducting state occurs at lower temperatures, due to the increase of magnetic Cooper pair breaking.<sup>1</sup> Because of this variation in magnetic strength, the boron carbides are an ideal system to study the interplay between magnetism and superconductivity and they are therefore the subject of continuing scientific interest.

The magnetically ordered state of  $R\text{Ni}_2\text{B}_2\text{C}$  shows a variety of magnetic structures.<sup>2</sup> The nonsuperconducting compounds  $\text{PrNi}_2\text{B}_2\text{C}$  and  $\text{NdNi}_2\text{B}_2\text{C}$  show a commensurate antiferromagnetic structure with an in-plane easy magnetization axis whereas  $\text{GdNi}_2\text{B}_2\text{C}$  and  $\text{TbNi}_2\text{B}_2\text{C}$  show a sine modulated incommensurate antiferromagnetic structure with  $\delta \sim (0.55, 0, 0)$ . Similar magnetic structures are observed in the superconducting  $R\text{Ni}_2\text{B}_2\text{C}$ .  $\text{DyNi}_2\text{B}_2\text{C}$  ( $T_N \sim 10.6$ ,  $T_C \sim 6$  K) and the low-temperature phase of  $\text{HoNi}_2\text{B}_2\text{C}$  ( $T \leq 5$  K) show a commensurate antiferromagnetic structure but  $\text{ErNi}_2\text{B}_2\text{C}$  and the reentrant phase of  $\text{HoNi}_2\text{B}_2\text{C}$  ( $5 \leq T \leq 6.3$  K) show a sine-modulated structure with  $\delta$  similar to  $\text{GdNi}_2\text{B}_2\text{C}$ . In contrast to all these planar magnets, an easy  $c$  axis is observed in  $\text{TmNi}_2\text{B}_2\text{C}$ . For this compound it is shown that  $T_N = 1.52(2)$  K (Ref. 3) and  $T_C = 10.8$  K (Ref. 4). Recent neutron diffraction studies revealed an incommensurate antiferromagnetic structure with  $\delta = (0.093, 0.093, 0)$  i.e., a modulation in the  $[110]$  direction with a clear onset at 1.5 K.<sup>2,5</sup> The sine-modulated mag-

netic moments with a maximum of  $3.78\mu_B$  are pointing along the  $c$  axis and become squared at lower temperature.

$\mu^+\text{SR}$  on  $\text{HoNi}_2\text{B}_2\text{C}$  and  $\text{ErNi}_2\text{B}_2\text{C}$  (Ref. 6) shows a muon precession frequency of the size expected for the magnetic Ho and Er moments [ $\sim 10.4\mu_B$  (Ref. 7) and  $8.4\mu_B$  (Ref. 8)] and confirms the magnetic ordering temperatures of  $\sim 8$  K and 6.8 K. Surprisingly,  $\mu^+\text{SR}$  measurements on  $\text{TmNi}_2\text{B}_2\text{C}$  (Refs. 6, 9, and 10) contradict the magnetic behavior of the Tm atoms as measured by neutron techniques. They reveal that a spontaneous internal field is present up to  $\sim 30$  K which is far above  $T_N$ . This spontaneous field saturates below  $\sim 2.5$  K and shows an inexplicable  $1/T$  dependence above this temperature. The saturation value of this internal field corresponds to a Tm moment of  $\sim 0.1\mu_B$ . Remarkably, this small Tm moment of  $\sim 0.1\mu_B$  is also observed by  $^{169}\text{Tm}$  Mössbauer spectroscopy.<sup>11</sup> Furthermore, the Mössbauer spectra show a line broadening above the magnetic transition temperature up to  $\sim 40$  K which might correspond to the internal field observed by  $\mu^+\text{SR}$ .

Because of the very large difference in magnetic Tm moments between the different experimental techniques, we extended our  $^{169}\text{Tm}$  Mössbauer study<sup>11</sup> to a second sample of  $\text{TmNi}_2\text{B}_2\text{C}$  which was used for inelastic neutron scattering (INS) measurements by Gasser *et al.*<sup>12</sup> From these INS measurements crystal field parameters (CFP's) are deduced which describe not only the INS data but also magnetization,<sup>4</sup> specific heat,<sup>3</sup> and neutron diffraction data.<sup>2,5</sup> These CFP's predict a Tm  $4f$  magnetic moment of  $\sim 4.3\mu_B$  in the magnetically ordered state. In this paper we report on the differences between this sample and the sample used for the previous  $^{169}\text{Tm}$  Mössbauer spectroscopy study<sup>11</sup> and the implications of these differences on the Tm  $4f$  magnetism.

Also a possible explanation will be given for the large discrepancy between the results obtained by neutron techniques and  $\mu^+$ SR.

The behavior of the asymmetric  $4f$  shell of the  $R$  atoms in  $RNi_2B_2C$  is strongly influenced by crystal field effects. The crystal field Hamiltonian  $\mathcal{H}_{cf}$  for the tetragonal point symmetry ( $I4/mmm$ ) of the  $R$   $4f$  shell can be written as

$$\mathcal{H}_{cf} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^4 O_4^4 + B_6^0 O_6^0 + B_6^4 O_6^4, \quad (1)$$

where  $B_l^m$  are the crystal field parameters and  $O_l^m$  represent Stevens operators. This Hamiltonian describes the splitting of the rare earth ground multiplet  $J$  and therefore the magnetism of the  $4f$  shell.

Both polycrystalline samples of  $TmNi_2B_2C$  which were studied by  $^{169}Tm$  Mössbauer-technique were prepared by arc melting from starting materials of at least 99.9% purity. The initial ratio between the starting materials was different for the two samples. Whereas for the sample of Mulders *et al.*<sup>11</sup> a ratio of  $Tm:Ni:B:C = 1.1:2:2:1$  was used, the sample of Gasser *et al.*<sup>12</sup> was prepared in a ratio of  $1:2:2:1.1$ . In this paper we refer to these samples as sample A and sample B, respectively. X-ray diffraction on both samples showed the desired crystal structure combined with a second unknown phase. This second phase was different for the two samples and less than 10%. Superconducting quantum interference device (SQUID) measurements showed the superconducting transition at  $T_C = 10.3(3)$  K and  $T_C = 10.8(3)$  K for samples A and B, respectively.

$^{169}Tm$  Mössbauer spectroscopy uses the  $^{169}Tm$  nucleus as a probe and its quadrupole splitting is very sensitive to the behavior of the electronic  $4f$  shell of the Tm atom. Since the properties of the conduction electrons are screened by the core electrons,  $^{169}Tm$  Mössbauer spectroscopy is not sensitive to the superconducting properties. The  $^{169}Tm$  Mössbauer spectra were recorded on an acceleration-type spectrometer in sinusoidal mode, the measured spectra being plotted on a linear scale. An absolute velocity calibration was obtained with a laser Michelson interferometer. The  $^{169}Tm$  Mössbauer effect was measured using 8.4 keV gamma rays emitted by  $^{169}Er$  obtained after neutron irradiation of  $^{168}ErAl_3$  grains in an Al matrix.

The  $^{169}Tm$  Mössbauer spectra of sample A of  $TmNi_2B_2C$  were recorded at various temperatures between 0.3 K and 700 K and the results of this study are published in Ref. 11. The spectra of sample B were recorded between 0.3 K and 8 K. The spectrum recorded at 0.3 K and the spectrum of sample A at that temperature are plotted in Fig. 1. The spectra show that the Tm magnetism is different in the two samples. In general, a quadrupole doublet, as is observed in sample A, is due to the electrostatic interaction between the quadrupole moment of the Tm nucleus ( $Q$ ) and the electric field gradient caused by the asymmetric  $4f$  shell and the crystal field of the lattice. If there is also a local magnetic field present at the Tm nucleus, the hyperfine interaction gives rise to six absorption lines in the  $^{169}Tm$  Mössbauer spectrum. A small hyperfine field, as, for example, due to a small Tm  $4f$  moment of  $\sim 0.1\mu_B$ , just causes a perturbation on the electric quadrupole splitting.

Sample A shows a single quadrupole doublet at 0.3 K and a spectrum measured with a velocity scale of 200 mm/s [see

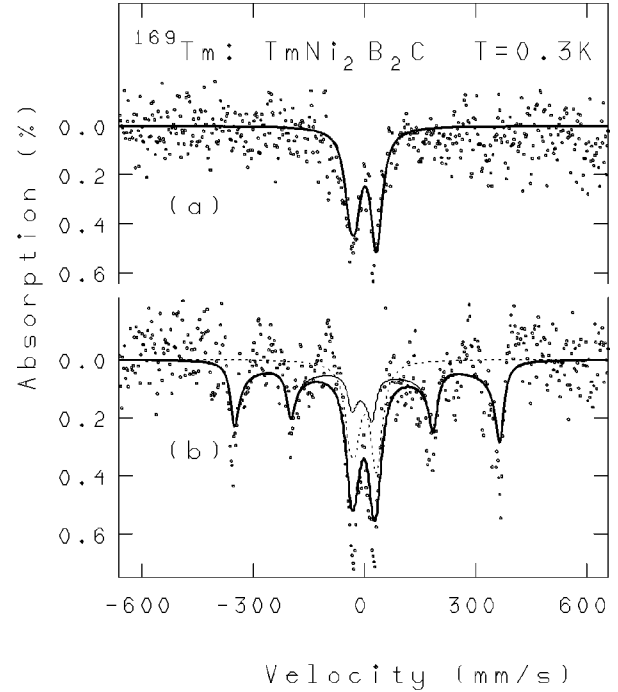


FIG. 1.  $^{169}Tm$  Mössbauer spectrum of sample A ( $Tm_{1.1}Ni_2B_2C$ ) and sample B ( $TmNi_2B_2C_{1.1}$ ) measured at 0.3 K. Whereas sample A shows a single quadrupole doublet, sample B shows two subspectra, a doublet, and a sextuplet. The sextuplet is analyzed with the spin density wave (SDW) modulation determined by Lynn *et al.* (Ref. 2) ( $q+3q+5q$ ) and a maximum Tm  $4f$  moment of  $4.3\mu_B$ . Note that the unequal population of the Zeeman-split nuclear ground state is taken into account. The doublets are shown in more detail in Fig. 2.

Fig. 2(a)] clearly shows asymmetric broadening of the quadrupole doublet which is interpreted as a Tm  $4f$  moment of  $\sim 0.1\mu_B$ . Recent specific heat measurements confirmed a transition of magnetic origin in sample A at 1.15 K. In contrast to this, the spectrum of sample B measured at 0.3 K shows two different subspectra. The sextuplet corresponds to a magnetically ordered Tm  $4f$  moment of  $4.3(1)\mu_B$  and in the center of the spectrum a doublet is observed. Since only a small amount of contamination is observed by x rays, we believe these two subspectra both originate from  $TmNi_2B_2C$ . Apparently, two types of Tm  $4f$  magnetism coexist in sample B. At 0.7 K the sextuplet shows strongly broadened absorption lines which may be a result of the sine-modulated magnetic structure as measured by neutron diffraction.<sup>2,5</sup> At 1.7 K the sextuplet is replaced by a second quadrupole doublet in the Mössbauer spectrum, indicating the paramagnetic state. The quadrupole splittings (QS's) of the two doublets above the magnetic ordering temperature differ substantially from each other, which made it possible to separate the two different contributions in the  $^{169}Tm$  Mössbauer spectrum of sample B. This analysis showed that the QS of the first doublet subspectrum (present in sample B also below 1.7 K) is identical to the QS of sample A within the experimental error between 0.3 and 4 K. For higher temperatures it was not possible to separate the two contributions in sample B. Because the quadrupole splitting is sensitive to the crystal field levels of the Tm  $4f$  shell, this does suggest that the doublet subspectrum of sample B originates from the same type of

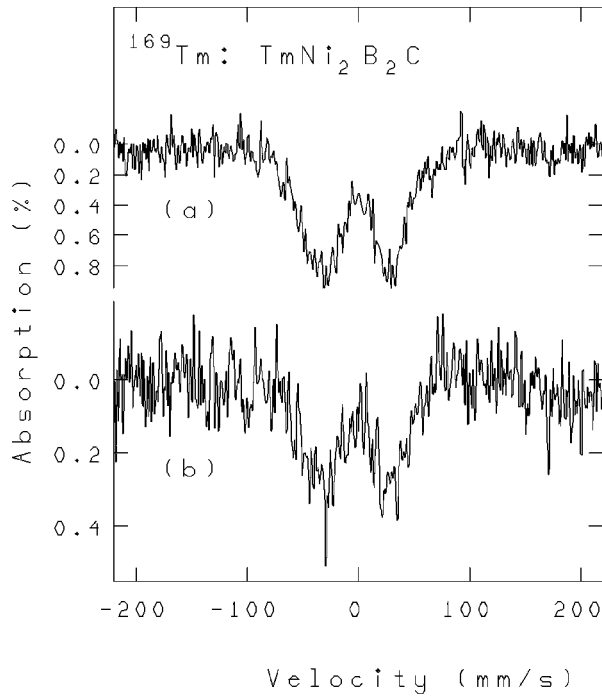


FIG. 2.  $^{169}\text{Tm}$  Mössbauer spectrum of sample A ( $\text{Tm}_{1.1}\text{Ni}_2\text{B}_2\text{C}$ ) and sample B ( $\text{TmNi}_2\text{B}_2\text{C}_{1.1}$ ) measured with a velocity scale of 200 mm/s. These spectra contain the central part of the spectra presented in Fig. 1. The sextuplet is subtracted from the spectrum of sample B. Note that the asymmetric broadened doublet of sample A is also observed in sample B. Since the doublet of sample A is interpreted as a small Tm moment, this suggests that small Tm moments of  $0.1\mu_B$  are also present in sample B.

Tm  $4f$  magnetism as in sample A. Figure 2(b) shows a spectrum of sample B measured at 0.3 K with a velocity scale of 200 mm/s. The sextuplet is subtracted from the spectrum in order to observe the central doublet in more detail. An asymmetric broadening is visible which resembles the spectrum of sample A [Fig. 2(a)] and confirms the hypothesis that the doublets in samples A and B have the same origin.

For the analysis of the sextuplet we used two different approaches. In Fig. 1(b) we used the moment modulation of the magnetic SDW as determined by Lynn *et al.*<sup>2</sup> from neutron diffraction experiments at 0.65 K. To calculate the magnetic moment modulation the wave vectors  $q$ ,  $3q$ , and  $5q$  were used. Because this modulation was measured at 0.65 K, the possibility exists that the magnetic modulation is more squared at 0.3 K. Therefore we also calculated the Mössbauer spectrum corresponding to a fully squared Tm moment modulation. The sextuplet of sample B is equally well described by either one of these analysis. The percentage of Tm atoms which take part in the modulated magnetic structure varies from  $\sim \frac{2}{3}$  in the first analysis to  $\sim \frac{1}{2}$  in the last analysis.

Since a different quantity of carbon was used for the preparation of the two samples, differences in the amount of C interstitials can be responsible for the difference in magnetic behavior of the Tm  $4f$  shell. Although carbon stabilizes the  $R\text{Ni}_2\text{B}_2\text{C}$  compounds, the exact amount of carbon necessary for a stable  $\text{TmNi}_2\text{B}_2\text{C}_x$  is unknown. A study of  $\text{DyNi}_2\text{B}_2\text{C}_x$  (Ref. 13) shows that superconductivity is not influenced drastically for  $0.9 < x < 1.1$ . Since x-ray diffraction is not very sensitive to the amount of C in the sample, a

deficiency in carbon ( $x < 1$ ) is possible. Because a lower C:Tm ratio is used for the preparation of sample A, there will be more carbon vacancies in this sample. We therefore believe that the  $4.3\mu_B$  moment of  $\text{TmNi}_2\text{B}_2\text{C}$  corresponds to Tm atoms surrounded by four carbon atoms as is expected for the  $R\text{Ni}_2\text{B}_2\text{C}$  structure. The  $0.1\mu_B$ , however, may correspond to Tm atoms situated near a C vacancy. This C vacancy reduces the symmetry at the Tm site and modifies the crystal field and therefore the Tm  $4f$  magnetism. The hybridization of the Tm valence electron states with the C valence electrons will decrease when C vacancies are present. This reduction in hybridization is expected to decrease the absolute value of  $B_2^0$ .

In  $\mu^+$ SR the muons localize interstitially in the lattice where they probe the magnetism of their host. C vacancies are an ideal cavity for muons to reside in. It is shown that in  $\text{CeRu}_2\text{Si}_2$ ,<sup>14</sup> a compound with the same tetragonal structure but without interstitial carbon, the muons localize at the  $(\frac{1}{2}, \frac{1}{2}, 0)$  site, i.e., the site of the carbon atoms in  $R\text{Ni}_2\text{B}_2\text{C}$ . Assuming that all samples of  $\text{TmNi}_2\text{B}_2\text{C}$  which were used for  $\mu^+$ SR experiments contain some amount of C vacancies, this explains why  $\mu^+$ SR spectroscopy only measures  $\mu_{\text{Tm}} \sim 0.1\mu_B$ . Based on these arguments there is a fair chance that the muons localize in the C vacancies. For this reason they only probe Tm atoms that are situated in the modified crystal field of the  $0.1\mu_B$  magnetism. The exact muon location site can be verified by  $\mu^+$ SR Knight shift measurements on a single crystal of  $\text{TmNi}_2\text{B}_2\text{C}$ .

Since sample B is polycrystalline, this experiment could not be done but another way to check this muon location hypothesis is muon spin rotation spectroscopy. Since the  $^{169}\text{Tm}$  Mössbauer spectrum at 0.3 K of sample B established a magnetic moment of  $4.3\mu_B$  for approximately half of the Tm atoms, this moment should be observed by  $\mu^+$ SR if the muons localize at the  $(0,0,0.20)$  site as expected from Knight shift measurements on  $\text{HoNi}_2\text{B}_2\text{C}$ .<sup>15</sup> In that case about half of the muons localize near a  $4.3\mu_B$  Tm moment and a partial muon precession signal is then expected which corresponds to this moment size. However, if the muons localize exclusively at the unoccupied C sites  $(\frac{1}{2}, \frac{1}{2}, 0)$  and the Tm magnetic moments near that C vacancy equal  $\sim 0.1\mu_B$ , only a single low muon precession frequency is expected.

The result of the  $\mu^+$ SR measurement performed at 0.3 K on polycrystalline sample B is plotted in Fig. 3. This spectrum is analyzed with

$$A(t) = A \left[ \frac{1}{3} \exp(-\lambda_1 t) + \frac{2}{3} \exp(-\lambda_2 t) \cos(2\pi\nu_\mu t) \right], \quad (2)$$

where  $A$  is the asymmetry,  $\lambda$  the relaxation rate, and  $\nu_\mu$  the muon precession frequency. The first and second terms correspond to the relaxation of the muon polarization parallel and perpendicular to the internal field. In the case of a polycrystalline sample the ratio of the amplitudes is 1:2. As is shown in Fig. 3 a single muon precession signal of  $\sim 1.8$  MHz is observed just as in previous  $\mu^+$ SR measurements performed on other samples of  $\text{TmNi}_2\text{B}_2\text{C}$ .<sup>6,9,10</sup> Although the internal field probed by  $\mu^+$ SR depends on the muon site and on the magnetic size and structure of the rare earth atoms, it is remarkable that the observed muon fre-

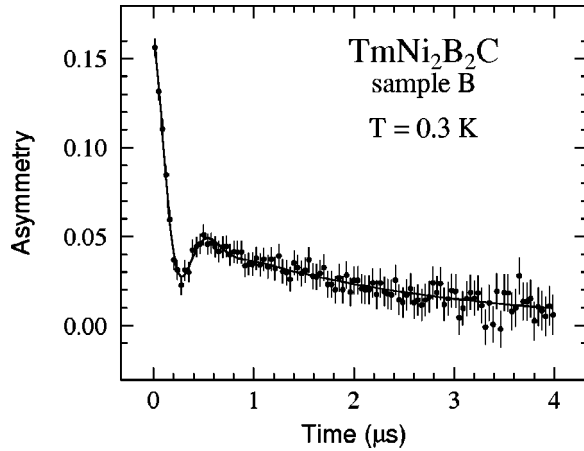


FIG. 3. Zero-field  $\mu$ SR spectrum measured at 0.3 K in polycrystalline sample B. A single muon precession frequency is observed of 1.8 MHz which corresponds to a Tm moment of  $\sim 0.1\mu_B$ .

quency in  $\text{TmNi}_2\text{B}_2\text{C}$  is about 30–40 times smaller than in  $\text{ErNi}_2\text{B}_2\text{C}$  and  $\text{HoNi}_2\text{B}_2\text{C}$ .<sup>6,9,10</sup> The magnetic structure of  $\text{TmNi}_2\text{B}_2\text{C}$  as deduced from neutron diffraction experiments<sup>2,5</sup> predicts a muon precession frequency even larger than observed in the Ho and Er compounds. In fact, dipolar calculations show that the observed muon frequency of  $\sim 1.8$  MHz is only compatible with muon-site locations at  $(0,0,0.20)$  or  $(\frac{1}{2}, \frac{1}{2}, 0)$  near Tm moments of  $\sim 0.1\mu_B$ . However, if the muons would occupy the  $(0,0,0.20)$  sites near Tm atoms with moments of  $4.3\mu_B$ , the corresponding muon frequency would be equal to 64.5 MHz. The localization of the muon near a small Tm moment is therefore a tempting explanation for the observed muon precession signal. Except

for  $^{169}\text{Tm}$  Mössbauer spectroscopy there are no other experimental results to support this small moment. On the other hand, the amount of C vacancies will depend strongly on the sample preparation and small quantities of  $\sim 0.1\mu_B$  Tm moments magnetism are easily disregarded.

In a  $^{166}\text{Er}$  Mössbauer spectroscopy study on  $\text{ErNi}_2\text{B}_2\text{C}$ ,<sup>8</sup> a “secondary phase” of  $\sim 10\%$  is observed which the authors attribute to the  $\text{ErNi}_2\text{B}_2\text{C}$  itself. This also could be due to the presence of vacancies in the sample. From the  $\mu$ SR point of view described above, this is possible because the Er moment of the secondary phase is similar to the moment of the Kramers ion Er in the rest of the sample. Therefore it may pass unnoticed if the muons probe the Er magnetism distorted by vacancies.

It would be interesting to determine the crystal fields of both types of Tm magnetism to see if it is indeed possible that C vacancies are responsible for the observed small Tm moment. The QS is related to the angular momentum ( $J, J_z$ ) and population of the different crystal field levels of the Tm  $4f$  shell. From its temperature dependence different sets of CFP’s can be deduced that are able to describe the experimental results.<sup>11</sup> Because more sets of CFP’s describe the same  $\text{QS}(T)$ , there is no unique solution. The same argument holds for INS, specific heat, and susceptibility. Furthermore, the abundance of the small Tm moment phase depends strongly on the sample preparation. Therefore the deduction of the crystal field for both types of Tm  $4f$  magnetism is not simple. A future study where the carbon content of the  $\text{TmNi}_2\text{B}_2\text{C}$  is varied systematically might elucidate this problem.

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