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# Competition between magnetism and superconductivity in $TmNi_2B_2C$ observed by muon-spin rotation

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We report muon-spin-rotation measurements of the internal field in the rare-earth nickel boride carbide superconductor $TmNi_2B_2C$ from 100 mK up to well above the superconducting transition temperature ($T_c$=9.5 K). An oscillatory muon response indicates that the muon is affected by a quasistatic local field that follows a $T^{-1}$ dependence over a wide temperature range and without interruption at the superconducting transition. The corresponding relaxation rate remains constant in the normal state, but begins to rise very sharply with decreasing temperature below $T_c$ scaling approximately with the local field down to its maximum at 2.5 K. The quasistatic internal field may be attributed to a spiral structure or slow three-dimensional correlations of the Tm moments. Decoupling experiments reveal a dynamic depolarization mechanism which may tentatively be ascribed to fast two-dimensional correlations of the Ni moments, slowed by the onset of superconductivity.

The competition between superconductivity and magnetism has been a central topic of study for both experimentalists and theorists for many years. Local magnetic moments usually strongly suppress superconductivity, destroying the spin-singlet Cooper pairs even if the magnetic impurity concentration is extremely low.[1] However, in certain compounds (e.g., $RRh_4B_4$, $R$=rare earth[2]), where the crystallographic site of the magnetic ion is well isolated from the conduction path, this pair-breaking interaction is weakened and magnetism and superconductivity can coexist. The recent discovery of a family of high-$T_c$ boride carbides $RNi_2B_2C$ (Refs. 3–5) has provided renewed impetus to understand this problem since these materials show a varying competition between the $R$ magnetism and superconductivity as the $R$ element is varied.[6] For example, as the $R$ varies across the series Ho, Er, and Tm, the superconducting transition temperature $T_c$ and upper critical field $H_{c2}$ increase, whereas the susceptibility and effective moment per $R$ ion both decrease.[6]

The crystal structure of $RNi_2B_2C$ is $ThCr_2Si_2$ type with the nickel boride framework modified by the insertion of a carbon atom in the $R$ layer.[7] It contains $R$-C layers separated by $Ni_2B_2$ layers. It has been suggested that the $R$ spins are strongly ferromagnetically coupled within the $R$-C layers, with weak antiferromagnetic interlayer coupling, giving rise to long-range order.[6]

Muon-spin rotation/relaxation ($\mu^+$SR) (Ref. 8) is an ideal technique to study the local development of magnetic order in these materials since it provides direct information about the local internal field and can be used equally well on samples in both the normal and superconducting state. The technique has already been applied to a number of materials in this family.[9–11] In this paper, we report measurements of the internal field of $TmNi_2B_2C$ from 100 mK to temperatures well above $T_c$.

Samples of $TmNi_2B_2C$ were prepared by simultaneous arc melting of correct weights of nickel rod, thulium den-

 

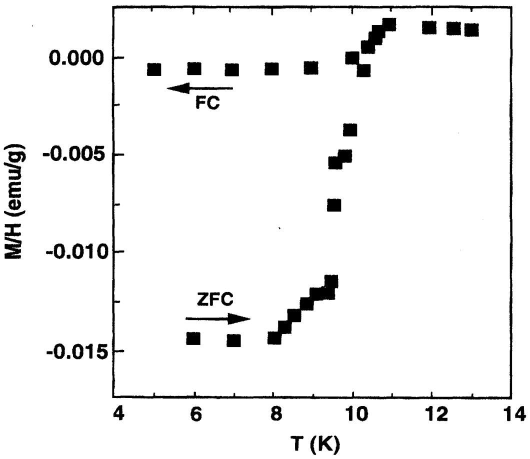


FIG. 1. Temperature dependence of the magnetization for $TmNi_2B_2C$. Arrows indicate the direction of the temperature scan after applying a magnetic field of 1 mT.

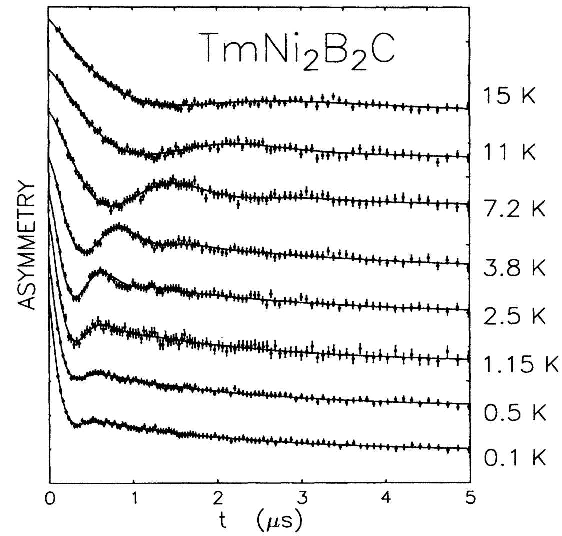


FIG. 2. Representative data of zero-field $\mu^+$ asymmetry for $TmNi_2B_2C$ for various temperatures on either side of the superconducting transition, $T_c = 9.5$ K. (For representative asymmetry scales, see Fig. 4; here the asymmetry scales are staggered for clarity.)

drites, carbon spectrographic rod, and amorphous boron pellets. The samples were turned and melted nine times, broken into tiny pieces, and melted seven additional times. Weight loss (which was not replaced and was mainly thulium vapor) for the ~8 g samples was 3.2% for $TmNi_2B_2C$. After a final very hot melting of the samples, the environment was evacuated so that the large samples cooled slowly, and no subsequent annealing was performed. X-ray analysis showed only a few faint lines due to an impurity crystallographic phase that could represent a few percent of the sample. The superconducting transition, shown in the susceptibility data of Fig. 1, is quite sharp and represents 100% diamagnetism with an uncertainty in the absolute value due only to an incomplete knowledge of the correct demagnetization factor. Using the 10% to 90% points and defining $T_c$ as the midpoint temperature, we deduce $T_c = 9.5$ K.

$\mu^+$SR measurements were performed with a pulsed beam of positive muons at ISIS (Rutherford Appleton Laboratory, UK) using the MUSR beam line and both a pumped $He^4$ cryostat and a dilution refrigerator. Zero- and longitudinal-field data were collected in the forward ($F$) and backward ($B$) positron telescopes utilizing the standard time-differential technique and plotted as muon decay asymmetry $G(t) = [B(t) - F(t)]/[B(t) + F(t)]$ which is proportional to the $\mu^+$ polarization $P_z(t)$. For zero-field measurements, the stray field was compensated to less than 2 $\mu$T.

Representative zero-field $\mu^+$SR data are shown in Fig. 2. An oscillatory signal is visible below 20 K, demonstrating that the muons sense an internal field which is characterized by a component which is either static or quasistatic (i.e., any fluctuations are slow compared with the measured frequency). The data were therefore fitted to the functional form

$$P_z(t) = a_\parallel \exp(-\lambda_\parallel t) + a_\perp \exp(-\lambda_\perp t)\cos(\omega_\mu t), \quad (1)$$

where $\omega_\mu$ is the muon precession frequency ($\omega_\mu = \gamma_\mu B_\mu$, with $\gamma_\mu = 2\pi \times 0.1355$ MHz/mT the muon gyromagnetic ratio and $B_\mu$ the local magnetic field at the muon site), and $a_\parallel$, $a_\perp$, $\lambda_\parallel$, $\lambda_\perp$ are constants to be determined; the first term describes the relaxation of polarization parallel to the quasistatic local field; the second term describes the precession and relaxation of *transverse* components. In a polycrystalline material (as used here), we expect $a_\perp / a_\parallel = 2$. A third constant (nonrelaxing) term is added to Eq. (1) to model the signal resulting from muons stopped in the silver sample mount and the cryostat. Because two different cryostats were used to cover the required temperature range, this constant is different for these two cases. It is difficult to separate the longitudinal relaxation from the constant background reliably, but we estimate $\lambda_\parallel \sim 0.2$–$0.4\ \mu s^{-1}$. The parameters for the precession frequency and transverse relaxation could be determined much more reliably from the fitted data and are plotted as a function of temperature in Fig. 3.

The precession frequency $\omega_\mu$ increases as $T^{-1}$ down to a temperature $T_M = 2.5$ K where it reaches a maximum value corresponding to a local field of about 11 mT. It then falls very slightly as the temperature is lowered and reaches a value of about 80% of this maximum local field at 100 mK. The relaxation rate $\lambda_\perp$ is approximately constant down to the superconducting transition temperature region, and then rises quite dramatically at lower temperature. Below $T_c$, but above $T_M$, it scales approximately with the precession frequency, i.e., approximately as $T^{-1}$; below $T_M$ it increases more slowly with decreasing temperature.

The maximum local field is two orders of magnitude larger than typical nuclear dipolar fields and must therefore be due to electronic moments, with Tm being the obvious candidate. Susceptibility measurements estimate the effective moment per Tm ion to be 7.7 $\mu_B$, very near the free trivalent ion value.[6] It is possible that the local field develops from the correlation of neighboring Tm moments and consequent slowing down of their fluctuations, an idea previously developed to describe $R$-moment behavior in $RRh_4B_4$.[12,13] This idea is supported by the failure to observe any indication that the local field collapses to zero above some transition temperature, as would be expected for a conventional

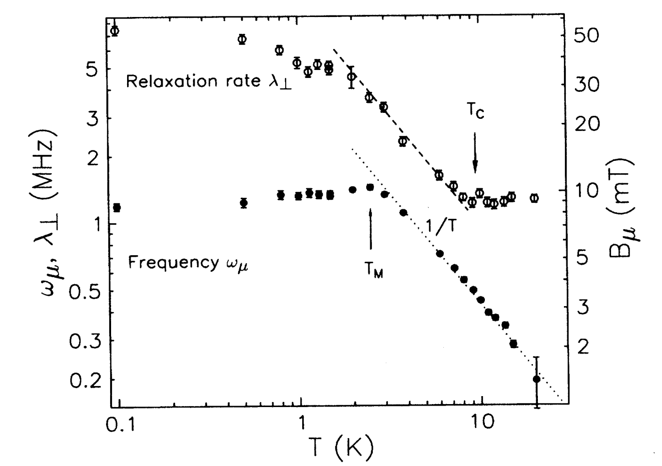


FIG. 3. Zero-field $\mu^+$ relaxation rate (open circles) and precession frequency (filled circles) as a function of temperature for $TmNi_2B_2C$. Both data sets are plotted in MHz. The right-hand scale shows the values of magnetic field corresponding to the precession frequencies.

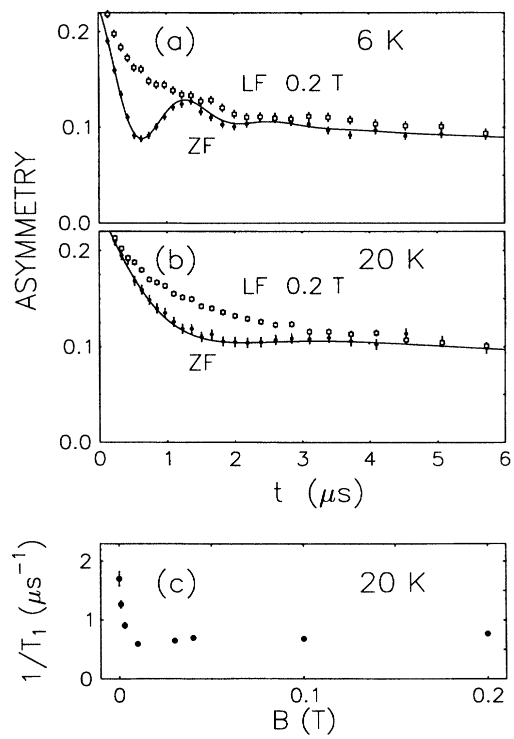


FIG. 4. Representative comparison of zero- and longitudinal-field $\mu^+$ data at (a) $T=6$ K and (b) 20 K for $TmNi_2B_2C$. (c) The fitted longitudinal relaxation rate as a function of longitudinal field at 20 K.

order parameter. However, the relaxation rate is roughly constant in the region 10–20 K; if the $T^{-1}$ dependence of the precession frequency is due simply to fluctuations, then it is difficult to understand why this would not have a strong effect on the relaxation rate, unless some other weakly temperature-dependent relaxation mechanism were to dominate above $T_c$.

The fact that the precession frequency exhibits no discontinuity at $T_c$ may be taken as evidence that the quasistatic local field is due to the Tm ions, whose electrons are not involved in superconductivity. It also raises a question as to the nature of the Tm spin structure: specific heat measurements[14] suggest a phase transition near 1.5 K but our own data reveal that the internal field peaks at 2.5 K and remains quasistatic to much higher temperatures.

The spatial arrangement of the Tm spin structure is not known, but we note that in one closely related material, $HoNi_2B_2C$, superconductivity is seen below 7.5 K but disappears below 5 K and then quickly recovers at lower temperature. This reentrant behavior is thought to be connected with the development of a spirally modulated magnetic structure which has been detected by neutron measurements.[15] Such spiral arrangements of the magnetic moments can arise as a direct result of the competition between superconductivity and magnetic order.[16] It is not yet known whether such a modulated magnetic state develops in $TmNi_2B_2C$, but it is noteworthy that a spiral structure is perfectly compatible with an oscillatory muon response, i.e., with a local field at the muon sites which takes a well defined and nonzero *magnitude* irrespective of *direction.* A strongly canted magnetic arrangement could explain why the local field in $TmNi_2B_2C$ is an order of magnitude smaller than that observed in other $R_2Ni_2B_2C$ materials[10,11] even though the size of the rare earth is comparable to that of the other rare earths. In this model, which could be tested by diffraction techniques, the $T^{-1}$ dependence of the internal field would represent a temperature-dependent effective interplanar exchange interaction which controls the pitch of the spiral magnetic order.

We now discuss the origin of the muon relaxation rate. For the transverse polarization components [$a_\perp$ in Eq. (1)] it is necessary to distinguish a spread of values of the local field, causing a dephasing of the muon precession, from the effect of fluctuations, i.e., a dynamical depolarization mechanism. [For the longitudinal components ($a_\parallel$), the relaxation can only be dynamic in origin.] A static or quasistatic field distribution should normally *narrow* as the order parameter increases, whereas the observed precession signal exhibits a relaxation rate which *increases* for decreasing temperature below $T_c$. In addition, the relaxation is exponential (suggesting fluctuations) rather than Gaussian (which would suggest static broadening). The coexistence of magnetism and superconductivity raises the question as to whether the field distribution might be broadened by superconducting screening, but this can reasonably be excluded on the following grounds: a recent $\mu^+$SR study of $YNi_2B_2C$ (Ref. 9) showed that the penetration depth $\lambda$ and coherence length $\xi$ were both much larger than the $RC$ interplane spacing $c/2$ [$c\sim1$ nm, $\xi\sim1$ nm, $\lambda(T\rightarrow0)\sim100$ nm]. If similar values apply to $TmNi_2B_2C$, then it is clear that if the superconductivity is primarily due to the $Ni_2B_2$ sheets, the screening effect will only weakly affect the distribution of local fields since length scales characterizing the superconducting state are much greater than the unit-cell size.

These considerations lead to the conclusion that the additional relaxation below $T_c$, related to the evolution of the superconducting state, must be dynamical in origin, a hypothesis which may be tested in decoupling experiments. We find that, whereas application of longitudinal fields as small as 30 mT quench the oscillations in the muon response, a monotonic depolarization persists even at applied fields of up to 0.2 T (see Fig. 4). Complete quenching of the relaxation would be expected in the case of quasistatic moments. Thus partial quenching is very suggestive of the existence of a dynamic local field, perhaps associated with rapid, small-amplitude fluctuations as suggested in the NMR work of Kohara *et al.*[17] We therefore suggest that the local field measured by the muon $B_\mu$ is composed of both a quasistatic and dynamic component, i.e., $B_\mu(t) \sim B_{qs} + \delta B(t)$. The first term we assign to the time-averaged Tm moments. The physical origin of the dynamic second term is not clear, although one could speculate that it derives from fluctuating components of the Tm moments, from fluctuating Ni moments, or indeed from correlated fluctuations of Tm and Ni. We would argue that while the Tm moments are responsible for the magnetism, which is independent of superconductivity, it is fluctuation of the Ni moments which is the main source of the increased muon relaxation below $T_c$. We also have an indication that Ni-moment fluctuation may be important in $LuNi_2B_2C$ in which the rare earth is nonmagnetic, and this is supported by NMR studies of another member of the family, namely $YNi_2B_2C$.[17] Because the spatial extent of the superconducting electronic wave function is predominantly confined to the Ni layers, the frequency spectrum of the Ni moment fluctuation is altered in the superconducting state and the muon relaxation rate (which picks out the spectral density at the origin) is changed accordingly. Application of a longitudinal field would dominate the static local field from the three-dimensional (3D) array of Tm moments but would not strongly affect the rapidly fluctuating 2D correlations of Ni moments. Further work is required to assess the merits of these models.

In summary, we have shown using $\mu^+$SR that magnetism and superconductivity coexist in $TmNi_2B_2C$. A quasistatic local field sensed by the implanted muons follows a $T^{-1}$ dependence down to 2.5 K without interruption at the superconducting transition. We speculate that this may be due to a modulated ordering or correlated fluctuations of the Tm moments. The corresponding relaxation rate is relatively temperature independent above $T_c$ but rises sharply below $T_c$ and continues to rise even below the magnetic ordering temperature. We tentatively attribute this relaxation to fluctuating Ni moments, with a spectral density enhanced by the onset of superonductivity.

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