June 8, 1994

International Conference on Strongly Correlated Electron Systems
Amsterdam, The Netherlands, August 15-18, 1994

μ^+SR Studies of Magnetic Properties of Boron Carbide Superconductors

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Positive-muon spin relaxation (μ^+SR) has been carried out in the recently-discovered rare-earth boron carbide superconductors RNi_2B_2C, R = Ho, Er and Tm. For R = Ho and Er zero-field μ^+SR measurements showed a well-defined internal field below the Néel temperatures of 5.5 K coexisting with the superconducting state down to 0.1 K. The observed temperature dependence of the order parameter for Ho is consistent with a 2-dimensional Ising model. For R = Tm a spontaneous internal field appears above 30 K, whose magnitude saturates below about 3 K at a value corresponding to a rare earth moment much smaller than for Ho and Er. Transverse-field μ^+SR measurements in R = Tm showed a superconducting penetration depth λ = 1,200 Å. The temperature dependence of λ is consistent with conventional s-wave pairing.

Keywords: superconductivity, magnetism, μ^+SR

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Recently, superconductivity has been discovered in several intermetallic boron carbide compounds, with the highest T_c being above 20 K [1,2]. In the series $R\mathrm{Ni_2B_2C}$, superconductivity is depressed gradually with increasing de Gennes factor G of the rare-earth element R, and is quenched completely for R = Dy and Tb, which have the largest G. For the systems with middle-ranged G (R = Ho, Er and Tm), magnetic order is found to coexist with superconductivity [3]. These features are reminiscent of the rare-earth rhodium borides $R\mathrm{Rh_4B_4}$ and Chevrel phases $R\mathrm{Mo_6S_8}$ [4]. In order to understand their magnetic nature, as well as the interplay between superconductivity and magnetism in these systems, we performed μ^+SR studies [5] in $R\mathrm{Ni_2B_2C}$, with R = Ho, Er and Tm.

The μ^+SR experiments were performed at the Paul Scherrer Institute (PSI) in Villigen, Switzerland, using the Low Temperature Facility and the General Purpose Spectrometer. Polycrystalline samples of $R\mathrm{Ni_2B_2C}$ were prepared as previously described [2], and then powdered and pressed into pellets which were attached to the cryostat cold finger.

The zero-field μ^+SR spectra were well described by

$$A(t) = A\,[\,(1/3)\exp(-\lambda_1 t) + (2/3)\exp(-\lambda_2 t)\cos(2\pi\nu_\mu t)\,]. \qquad (1)$$

The first term corresponds to the relaxation of the muon polarization parallel to the internal field and thus the relaxation rate λ_1 reflects the dynamic properties of the host moments. The second term describes muon precession transverse to the internal field and therefore λ_2 represents relaxation due both to dynamic effects and static field inhomogeneities. In a polycrystalline specimen the ratio of the amplitudes is 1:2.

For R = Ho and Er a well-defined muon-spin precession frequency ν_μ is observed below the Néel temperatures $T_N \approx 5.5$ K. The observation of ν_μ in zero external field indicates the onset of magnetic order, where the spontaneous magnetization is proportional to ν_μ. The frequency is 59 MHz for Ho and 40 MHz for Er at the lowest measured temperature of 0.1 K and 3 K, respectively. The large values of ν_μ (about 10 times larger than observed in $\mathrm{La_2CuO_4}$ [6]) indicate a frozen moment of several μ_B, consistent with that expected from Ho and Er.

As shown in Fig. 1, for R = Ho, ν_μ remains almost constant from 0.1 K up to 5 K and then drops rapidly. The weak temperature dependence of ν_μ below 5 K indicates a strong suppression of low-energy excitations, and the rapid change of ν_μ around T_N indicates an abrupt and possibly first-order transition. However, neither our ZF-μ^+SR nor susceptibility measurements show signs of thermal hysteresis near T_N.

We are able to fit $\nu_\mu(T)$ quite well using a 2-dimensional (2D) Ising model, for an intra-plane ferromagnetic exchange interaction J / k_B = 2.4 K (solid line in Fig. 1). This yields a sharp but second-order phase transition at T_N. Such a temperature dependence of the sublattice magnetization is not unreasonable considering the crystal structure and the possible effects of the crystal field splitting. $HoNi_2B_2C$ has a 2D crystal structure, where the HoC layers alternate with the Ni_2B_2 layers [7]. A strong anisotropy has been observed in the normal-state susceptibility on a single crystal, which leads to the frozen Ho moments in the basal *ab*-plane [8]. Crystal field parameters have not been determined for this system. We note, however, that the Ho-ion ground state in $HoRh_4B_4$, also possessing a tetragonal structure, exhibits an Ising behavior due to crystal field splitting [9].

Figure 1 also shows the temperature dependence of ν_μ in $TmNi_2B_2C$. A muon precession frequency appears at the rather high temperature of 30 K. Between 20 and 3 K, ν_μ is inversely proportional to temperature, $\nu_\mu = C / T$, where C = 4.3 MHz·K (dashed line in Fig. 1), consistent with previous ZF-μ^+SR studies by Cooke *et al.* [10]. Below 3 K, ν_μ starts to saturate, reaching a maximum of 1.6 MHz near 1.5 K, which corresponds to T_N obtained by the specific heat [11] and resistivity measurements [3]. In comparison with R = Ho and Er, $\nu_\mu(T)$ for R = Tm is distinctively different. No abrupt onset of magnetic order is observed. Furthermore, the local field below T_N is 25 − 35 times smaller for R = Tm than for Ho and Er.

The magnitude of ν_μ found below 3 K in $TmNi_2B_2C$ corresponds to a local field of about 120 G. Assuming dipolar μ^+-Tm coupling, this corresponds to a frozen moment of order 0.1 μ_B, much smaller than the free-ion value for Tm (7.7 μ_B) deduced from the susceptibility [3]. If one associates this internal field with Tm ordering, the reduced frozen-moment could be due to crystal-field effects and/or rapid, limited-amplitude fluctuations. Longitudinal field measurements at 0.83 K were performed to elucidate the spin dynamics. At H_L = 1 kG, the precession signal disappears, but significant μ^+ relaxation is still observed. This relaxation rate was changed only slightly in applied field up to 10 kG, indicating fluctuation rates at least as large as $\gamma_\mu H_L \sim 10^9$ s^{-1}. The simultaneous occurrence of precession in a local field of 120 G and fluctuation rates of order 10^9 s^{-1} can only occur if the fluctuations are of limited amplitude (giving rise to a small frozen moment), or if there are two independent sources for the local field sensed by the muon: one producing precession and the other relaxation. Further experiments and analysis will be undertaken to explore these possibilities.

It is generally difficult to investigate the superconducting properties of these magnetic superconductors because the relaxation rate from the magnetic ions is often too large and temperature dependent to permit a clear observation of field broadening due to the superconducting vortex lattice. For R = Ho we found it even impossible to determine the superconducting transition temperature T_c using μ^+SR. The strong internal magnetic fields apparently cause the same problems for other techniques. The superconducting penetration depth λ, for instance, has not yet been determined for the Ho or Er compounds.

Here we report TF-μ^+SR measurements in $TmNi_2B_2C$, where we are able to separate the superconducting signal from large magnetic background. The spectra were fitted with

$$A(t) = A \exp[-(\sigma_s t)^2/2] \exp(-\lambda_s t) \cos(2\pi\nu_\mu t). \quad (2)$$

The temperature dependence of $\sigma_s(T)$ (solid circles) and $\lambda_s(T)$ (open triangles) under a transverse field of 1 kG is shown in Fig. 2. A rather sudden enhancement of σ_s is found below 10.5 K (which corresponds to the reported T_c [2]), while λ_s varies smoothly with temperature. We thus attribute σ_s to superconductivity and λ_s to magnetism. Multiplication of Gaussian and exponential relaxation functions in Eq. (2) indicates that muons see both relaxation processes due to superconductivity and magnetism simultaneously. The values of λ_s are comparable with the zero-field relaxation rates attributed to magnetic relaxation.

In a type-II superconductor, a field broadening ΔB due to the formation of the vortex lattice reflects the superconducting penetration depth λ as $\sigma \propto \Delta B \propto \lambda^{-2}$. Since σ_s above T_c is nearly temperature independent, we assume that this residual relaxation rate also remains unchanged below T_c. Thus $\sigma^2(T) = \sigma_s^2(T) - \sigma_s^2(T_c)$. We then find that $\sigma(T)$ can be best described by the weak-coupling BCS theory (solid line in Fig. 2). This is consistent with a conventional s-wave pairing in $TmNi_2B_2C$. The extrapolated relaxation rate $\sigma(0) = 7.5\ \mu s^{-1}$ yields a powder-averaged λ = 1,200 Å, comparable with the in-plane λ = 1,500 Å obtained in the non-magnetic superconductor YNi_2B_2C [12]. Using the upper critical field $H_{c2} \approx 2.5$ Tesla [3], we further calculate the Ginzburg-Landau parameter $\kappa \approx 10$ and the lower critical field $H_{c1} \approx 250$ G.

In conclusion, we have investigated magnetic properties of RNi_2B_2C, where R = Ho, Er and Tm. We observed spontaneous magnetic order in all three systems below T_N. The temperature dependence of sublattice magnetization can be understood partially by the 2-dimensional crystal structure and possible effects of the crystal-field splitting in these systems. In $TmNi_2B_2C$ the appearance of oscillation frequency well above T_N with a reciprocal temperature dependence is not clear at the moment. Further studies of magnetism in these rare-earth boron carbide systems should stress the difference between the Tm and Ho compounds, and the interplay between magnetic and superconducting order parameters.

The authors acknowledge the FOM-ALMOS center for preparing $ErNi_2B_2C$, J.D. Thompson for susceptibility measurements on $HoNi_2B_2C$ and $TmNi_2B_2C$, Stefen Süllow for resistivity measurements on $ErNi_2B_2C$, J.D. Thompson and M. Xu for useful discussions. Work at Los Alamos was performed under the auspices of USDOE, and at

UC Riverside was supported in part by the USNSF (DMR-9114911). Ames Laboratory is operated for the USDOE by Iowa State University under Contract no. W-7405-ENG-82.

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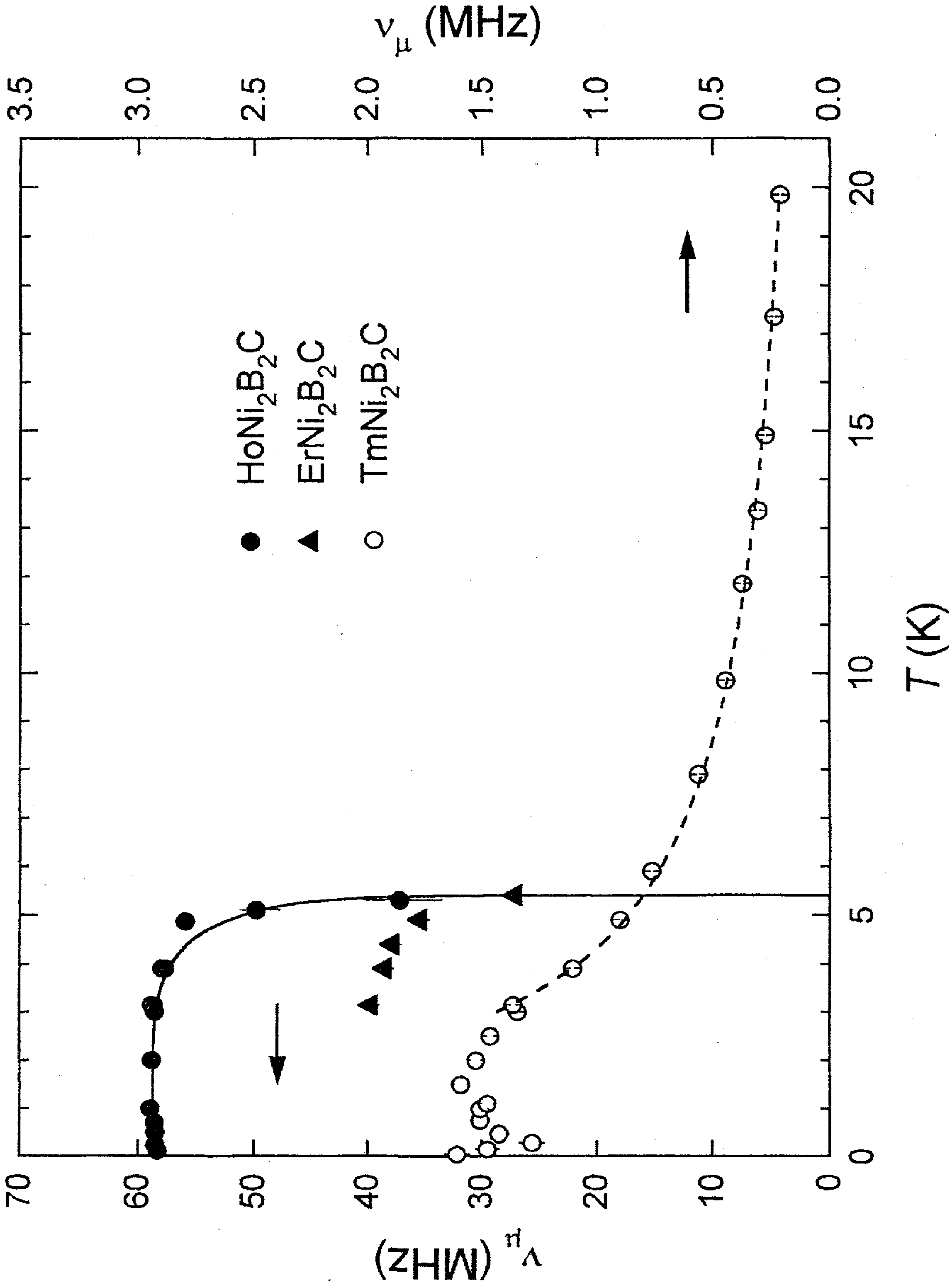
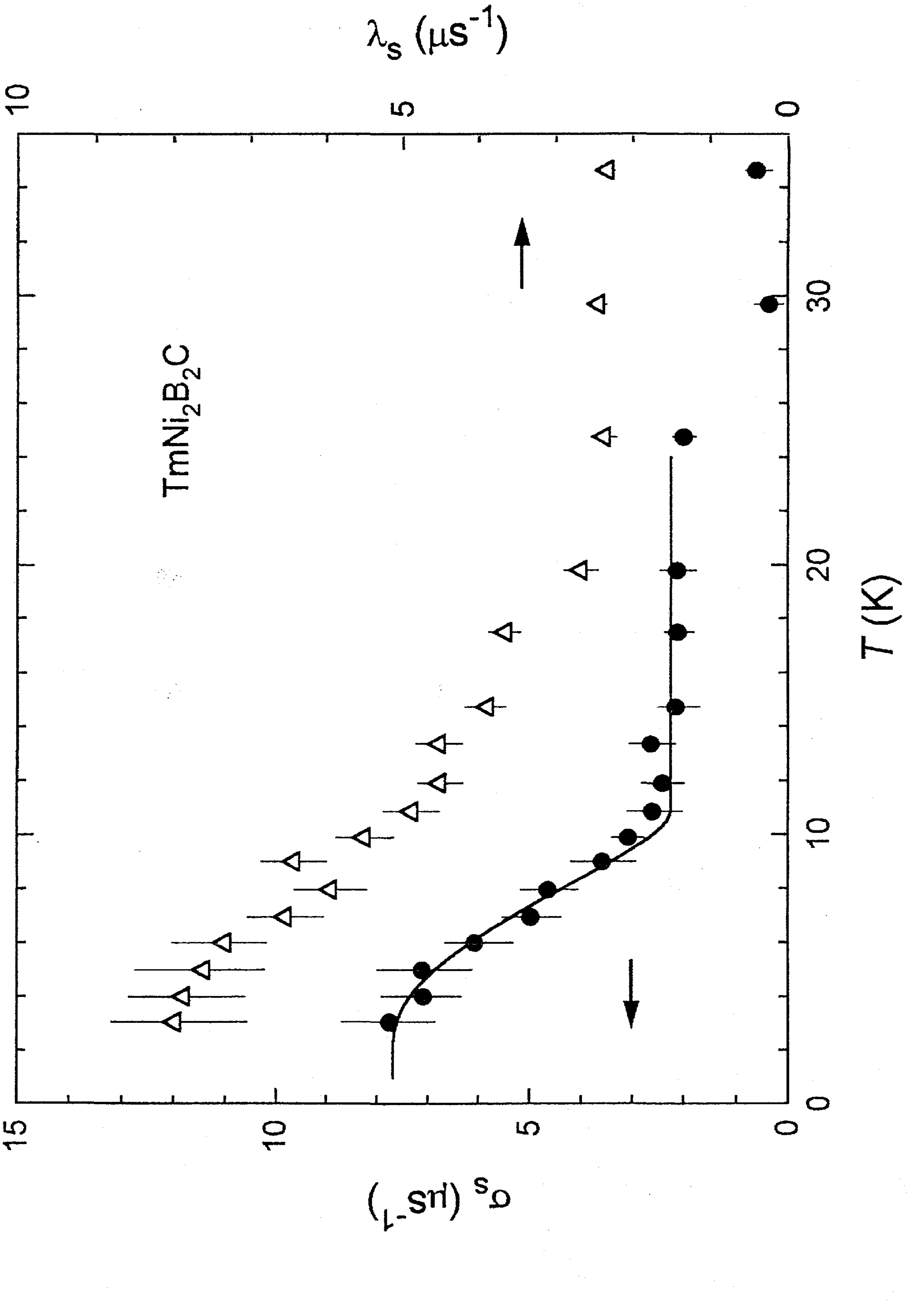
Figure Captions

Fig. 1. Temperature dependence of zero-field muon-spin precession frequency observed in $HoNi_2B_2C$, $ErNi_2B_2C$ and $TmNi_2B_2C$. The solid line denotes 2-dimensional Ising model, and the dashed line denotes a reciprocal temperature dependence.

Fig. 2. Temperature dependence of transverse-field Gaussian and exponential relaxation rate observed in $TmNi_2B_2C$. The solid line refers to weak-coupling BCS theory.



ν_μ (MHz)
ν_μ (MHz)
T (K)
$HoNi_2B_2C$
$ErNi_2B_2C$
$TmNi_2B_2C$



TmNi2B2C
λs (μs-1)
σs (μs-1)
T (K)
0
10
20
30
0
5
10
15
0
5
10