^{169}Tm Mössbauer-spectroscopy study of the magnetic superconductor $TmNi_2B_2C$

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The magnetic properties of $TmNi_2B_2C$ were measured with ^{169}Tm Mössbauer spectroscopy at temperatures from 0.3 to 700 K. A clear transition in the quadrupole splitting (QS) near 1 K is observed, which might be due to magnetic ordering or to quadrupole ordering. Although a possible small magnetic Tm moment of $\sim 0.1(1)\mu_B$ is found below $\sim$1 K, the change in QS is larger than expected due to magnetic ordering only. Therefore the nature of the transition is unclear at this moment. From the temperature dependence of QS is deduced that the crystal-field ground-state level most likely equals the singlet $a|-4\rangle + b|0\rangle + a|+4\rangle$.
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Over the past few years, the RNi_2B_2C compounds (R=rare earth) have been the subject of different studies including magnetization,[1] specific heat,[2] inelastic neutron scattering,[3] and μ^+SR.[4–6] In some of these compounds (R =Tm, Er, and Ho) these studies revealed 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.[7] For $TmNi_2B_2C$ it is believed that the Tm sublattice orders magnetically at T_N=1.52(5) K (Ref. 2) with the Tm moments aligned along the c axis.[1] The Tm moments are ferromagnetically coupled in the TmC plane and antiferromagnetically between the TmC planes.[2] Such a magnetic structure produces an approximately zero magnetic field at the superconducting NiB layers and is therefore able to coexist with the superconducting phase of the compound [T_c=10.8 K (Ref. 1)].

Surprisingly, μ^+SR measurements on $TmNi_2B_2C$ (Refs. 4–6) reveal that a spontaneous internal field is present until $\sim$30 K which is far above T_N. This spontaneous field saturates below $\sim$2.5 K. If this internal field is caused by only the Tm moments, the saturation value corresponds to a Tm moment of $\sim 0.1\mu_B$. As superconductivity is believed to be concentrated in the NiB layers[8] and even small magnetic Ni moments would tend to destroy the correlations between the Cooper electrons, magnetism caused by the Ni atoms is not very likely. Furthermore, no antiferromagnetic correlations between the Ni atoms have been observed in YNi_2B_2C.[9]

In order to obtain more information about the magnetic properties of this compound, $TmNi_2B_2C$ is studied by ^{169}Tm Mössbauer spectroscopy. This technique 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, Mössbauer spectroscopy is not sensitive to the superconducting properties. In this paper we present the results of this study.

The polycrystalline sample of $TmNi_2B_2C$ was prepared by arc melting from starting materials of at least 99.9% purity. X-ray diffraction showed the desired crystal structure combined with a second unknown phase of $\sim$10%. This second phase did not contain Tm and is therefore invisible to the ^{169}Tm Mössbauer technique. A superconducting quantum interference device (SQUID) measurement showed the superconducting transition at T_c=10.3 K.

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 γ rays emitted by ^{169}Er obtained after neutron irradiation of $^{168}ErAl_3$ grains in an Al matrix.

The ^{169}Tm Mössbauer spectra of $TmNi_2B_2C$ were recorded at various temperatures between 0.3 and 773 K. Because the Ni atoms partially absorb the 8.4 keV γ rays (K absorption edge), the ^{169}Tm Mössbauer effect is rather small and therefore long measurement times were needed for reasonable spectra statistics. All spectra showed a quadrupole doublet, including the spectra recorded at low temperatures, and were analyzed on the basis of a single subspectrum. Two spectra, measured at T=0.45 and 8 K, are plotted in Fig. 1. The quadrupole doublet 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 (V_{zz}^{4f}) and the crystal field of the lattice (V_{zz}^{latt}). 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. At first sight there are no clear signs of magnetic ordering in the 0.45 K spectrum. However, a precise analysis of this low-temperature spectrum shows a slightly broadened left Mössbauer absorption line (Fig. 1) which is likely due to a small magnetic moment of the Tm atoms. In that case the hyperfine interaction is a small perturbation on the electric quadrupole splitting. We were able to deduce from the 0.45 K spectrum a Tm moment of $0.1(1)\mu_B$.

Figure 2 shows the deduced quadrupole splitting ($QS \propto V_{zz}$) as a function of temperature. We observe a clear change in QS at 1 K. A transition from a paramagnetic phase to a magnetically ordered phase is usually accompanied by a change in QS because the exchange interaction influences

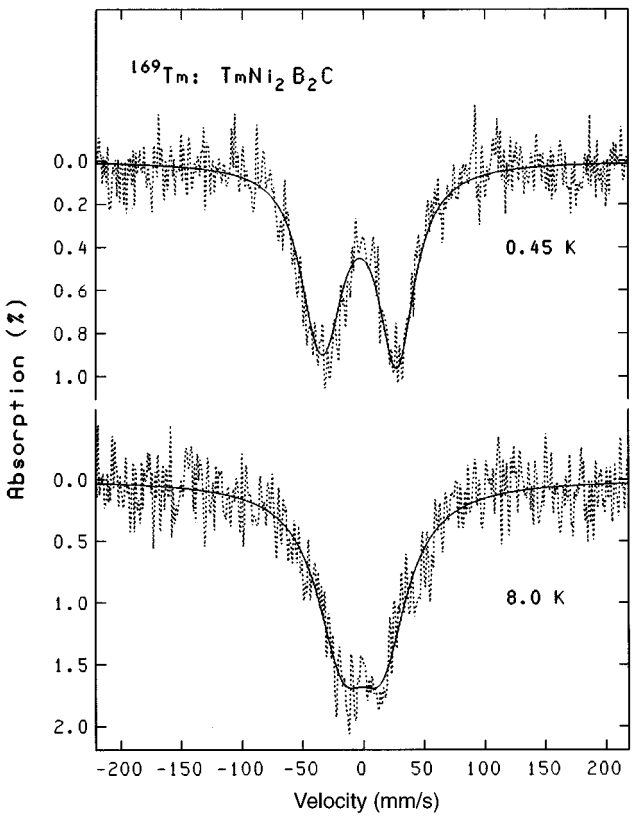

FIG. 1. Two spectra recorded below (0.45 K) and above (8 K) the transition temperature of 1 K. The 0.45 K spectrum shows a slightly broadened left Mössbauer peak indicative of a small Tm moment in the order of $0.1\mu_B$. Note that the QS at 0.45 K is clearly larger than at 8 K. Above 1 K a broadening of the quadrupole doublet lines is observed.

the relative position of the energy levels of the crystal-field split $2J+1$ manifold of the $4f$ shell. As the change in QS is abrupt and rather large it is not obvious that this change is related to magnetic ordering. Another possibility is that the transition observed at 1 K is indicative of quadrupole ordering as observed in, for example, TmZn (Jahn-Teller transition).[10] Specific-heat measurements[2] show a magnetic transition at 1.5 K and no signs of quadrupole ordering at lower temperature. As small differences in sample quality might be responsible for the difference in transition temperature the precise transition temperature of our sample will be determined by specific-heat measurements in the near future. This experiment might show the nature of the transition.

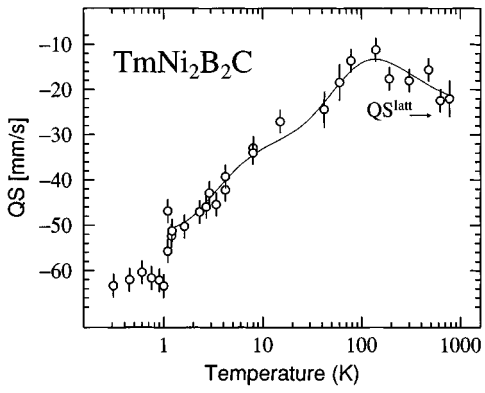

FIG. 2. The quadrupole splitting $QS=(1/2)eV_{zz}Q$ as observed by ^{169}Tm Mössbauer spectroscopy as a function of temperature. The sudden change at 1 K is related to magnetic or to quadrupolar ordering (see text). The solid curve is obtained from the crystal field parameters $B_2^0=-1.16$ K, $B_4^0=4.61\times10^{-3}$ K, $B_4^4=-0.173$ K, $B_6^0=-1.44\times10^{-5}$ K, and $B_6^4=-1.11\times10^{-3}$ K but can be considered only as a guide to the eye (see text).

Above the transition at 1 K line broadening [Fig. 1(b)] is observed which decreases with increasing temperature and persists up to about 40 K. At present, its origin is not yet obvious. It might correspond to the phenomenon seen in μ^+SR studies[4–6] where the μ^+ precession frequency persists up to high temperatures compared with T_N. Magnetic relaxation of the Tm moments above T_N could explain our Mössbauer spectra as well as the μ^+SR data if the relaxation is sufficiently slow ($>10^{-6}$ s). In that case the Tm moments appear to be static to the muon and a precession signal will be observed.

From the temperature dependence of QS (Fig. 2) it is, in principle, possible to determine the crystal-field parameters of the Tm $4f$ shell. QS can be decomposed into two components, QS^{latt} and QS^{4f}:

$$QS(T)=QS^{4f}(0)\langle 3J_z^2-J(J+1)\rangle_{4f}+QS^{latt} \qquad (1)$$

with $\langle\ \rangle_{4f}$ indicating the thermal average over the $4f$ crystal-field levels and J,J_z, the total angular momentum and its z component. QS^{latt} is constant and determined by the crystal structure of the compound. The second term is temperature dependent and becomes negligible at high temperature because $\langle 3J_z^2-J(J+1)\rangle_{4f}^{T\to\infty}=0$. Using this high-temperature approximation QS^{latt} is found to be equal to $-22(4)$ mm/s.

QS^{latt} is related to V_{zz}^{latt} by

$$QS^{latt}=\tfrac{1}{2}|e|V_{zz}^{latt}Q, \qquad (2)$$

where e is the electronic charge and Q is the quadrupole moment of the Tm nucleus. With Eq. (2) V_{zz}^{latt} is calculated to be equal to $10(2)\times10^{21}$ V/m^2 which is in good agreement with $V_{zz}^{latt}=11.9\times10^{21}$ V/m^2 obtained with ^{155}Gd Mössbauer spectroscopy on $GdNi_2B_2C$,[11] where $V_{zz}^{4f}=0$ because the Gd $4f$ shell is spherical.

Although the crystal-field parameter B_2^0 is related to the electric-field gradient experienced by the $4f$ shell and V_{zz}^{latt} is measured at the nucleus, there is an empirical relation between the two. Using this relationship $V_{zz}^{latt}=-4cB_2^0/\alpha_J\langle r^2\rangle$ with $c=185$,[12] α_J the second-order Stevens parameter and $\langle r^2\rangle$ the radial integral of the $4f$ electron cloud, we calculated $B_2^0=-2.8(5)$ K. The sign of B_2^0 corresponds to a c-axis anisotropy as also observed by susceptibility and μ^+SR measurements.[1,4–6] Its strength, however, is twice as large as the value derived from the susceptibility measurements. The reason for this discrepancy will be discussed later.

The crystal-field Hamiltonian $\mathcal{H}_{cf}$ for the tetragonal point symmetry ($I4/mmm$) of the Tm $4f$ shell can be written as

$$\mathcal{H}_{cf}=B_2^0O_2^0+B_4^0O_4^0+B_4^4O_4^4+B_6^0O_6^0+B_6^4O_6^4, \qquad (3)$$

where B_l^m are the crystal-field parameters and O_l^m represent Stevens operators. This Hamiltonian describes the splitting of the $J=6$ ground multiplet. The thermal population of the different crystal-field levels of this multiplet determines $\langle 3J_z^2-J(J+1)\rangle_{4f}$ and therefore QS(T).

Because there are five crystal-field parameters involved in the calculation of QS(T), there are different sets of parameters which describe the data presented in Fig. 2. One set of B_l^m corresponds to the solid curve in Fig. 2 but because these parameters do not describe the inelastic neutron-scattering data of Gasser *et al.*,[3] it can be considered only as a guide to the eye. The crystal-field parameters determined from inelastic neutron scattering[3] do not describe the QS data. Still, we believe that a unique set of crystal-field parameters may be found which describes both experiments as well as magnetization and specific-heat results.[1,2] Although until now this goal was not achieved, some conclusions can be drawn from the temperature dependence of QS.

First, the crystal-field ground-state level most likely equals the singlet $a|-4\rangle+b|0\rangle+a|+4\rangle$. If this ground state is in energy only a few Kelvin separated from a magnetic crystal-field level, say a doublet with the eigenfunctions $c|\pm 5\rangle+d|\pm 1\rangle+e|\mp 3\rangle$, this explains the small magnetic moment of Tm in the antiferromagnetic state, which is then induced by the magnetic crystal-field doublet into the nonmagnetic ground state. It also might explain the saturation moment of $\sim 5\mu_B$ observed in an external field of 5 T by Cho *et al.*[1] In that case, the magnetic field changes the relative position of the magnetic crystal-field level and a Tm moment of $\sim 5\mu_B$ will be observed. Furthermore, it explains the μ^+SR depolarization data of Amato *et al.*,[6] where an enhanced μ^+SR depolarization rate is observed when a small external field (up to 0.7 T) is applied. The applied field will influence the relative position of the magnetic crystal-field level(s) and will enlarge the Tm moment. This, in turn, will increase the muon depolarization rate. A last argument in favor of the proposed crystal-field levels is suggested by Cho, Canfield, and Johnston.[13] These authors observe that $TmNi_2B_2C$ is as effective in magnetic pair breaking as $GdNi_2B_2C$ and they conclude that the crystal-field levels in $TmNi_2B_2C$ are close together so they all contribute to the pair-breaking process.

μ^+SR established the magnetic c-axis anisotropy in $TmNi_2B_2C$.[4–6] The temperature dependence of QS(T) also indicates that B_2^0 is negative, that is approximately -1 to -1.7 K. This value is smaller than $B_2^0=-2.8(5)$ K as it is calculated above. Most likely, the empirical relation $V_{zz}^{\mathrm{latt}}=-4cB_2^0/\alpha_J\langle r^2\rangle$ with $c=185$, is not valid in this compound due to the carbon atoms which are interstitially present in the crystal nearby the Tm atoms. We therefore believe that the empirical constant c equals approximately 4×10^2 in $TmNi_2B_2C$.

The small magnetic moment of Tm along the c axis as well as the maximum in the temperature dependence of QS at 140 K (Fig. 2) both indicate that crystal-field effects play an important role in $TmNi_2B_2C$. Strong crystal-field effects are also observed in $ErNi_2B_2C$, where they cause a change in magnetic anisotropy at ~ 150 K.[14] Although a negative B_2^0 is responsible for c-axis anisotropy at high temperature in $ErNi_2B_2C$, a basal plane anisotropy is observed at low temperature due to higher-order crystal-field parameters. We believe a more detailed analysis of QS(T) combined with further specific-heat measurements might resolve the nature of the transition observed at 1 K in in $TmNi_2B_2C$.

In summary, we have presented results of a ^{169}Tm Mössbauer study on $TmNi_2B_2C$. Although we are not yet able to fully understand our data we have observed remarkable features. First, a possible small Tm moment is observed below 1 K of $0.1(1)\mu_B$ which corresponds with the μ^+SR result of $0.1\mu_B$. Second, an abrupt change in QS is observed at 1 K. This change may be indicative of magnetic ordering as well as of quadrupolar ordering. Although the small Tm moment at low temperature indicates a magnetic transition, the change in QS is larger than expected from magnetic ordering only. A detailed analysis of QS(T), combined with specific-heat measurements, may turn out to be conclusive. Third, line broadening is observed above 1 K, persisting up to ~ 40 K. This line broadening might correspond to μ^+ SR results, where a muon precession signal is observed up to ~ 30 K.[4,5] Both these features indicate slow magnetic relaxation above the Néel temperature.

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