Magnetic Resonance of ^{160}Tb Oriented in a Terbium Single Crystal at Low Temperatures

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We report the first observation of magnetic resonance of oriented rare-earth nuclei in a rare-earth host. Radioactive ^{160}Tb implanted in a single crystal of ferromagnetic terbium was subjected to magnetic resonance detected by perturbation of the gamma-ray anisotropy. The open Tb $4f$ shell gives rise to a strong electric quadrupole interaction in addition to the magnetic interaction; the resulting resonance signal has six components, of which the first was detected at 480.0(4) MHz. The derived quadrupole interaction frequency is 167.7(2.6) MHz, giving $Q = 3.56(10)$ b.

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Nuclear magnetic resonance on oriented nuclei (NMR-ON) has been in use for about twenty years[1] and has yielded numerous precise determinations of magnetic hyperfine fields, nuclear dipole moments, and information on nuclear spin-lattice relaxation in very dilute alloys. Recently, emphasis has been on the precise determination of the nuclear moments of radioactive nuclei, and several facilities for on-line implantation and nuclear orientation are now operating or are under construction. Implantation techniques have greatly broadened the range of host-impurity combinations which can be studied, and employ the extreme sensitivity of NMR-ON to good advantage.

Nevertheless, it is striking that the great majority of NMR-ON experiments up to now were performed on host-impurity combinations in which orbital angular momentum is effectively absent. As a consequence, quadrupole splittings have been small and generally observable only by indirect methods.[2,3] Nuclei from most of the Periodic Table have been subjected to resonance, with the notable exceptions of the rare-earth and the actinide series.[4] In a recent Letter, Ebeling *et al.*[5] reported the first NMR-ON experiment in a rare-earth host, using oriented ^{111}In implanted in gadolinium. This host, unlike the other heavy rare earths, consists of S-state ions, and the magnetic properties of the metal resemble those of cobalt. However, gadolinium (like cobalt) is noncubic and thus may permit the precise determination of nuclear quadrupole moments; this was a major motivation for the demonstration of NMR-ON in this host, as pointed out in Ref. 5.

Here, we report the first NMR-ON experiment on a rare-earth–rare-earth system, where both the host and the resonant nuclear species (72-d ^{160}Tb) have unfilled $4f$ shells. This gives rise to extremely large magnetic hyperfine fields, to strong electric quadrupole interactions, to large crystalline anisotropies in the host, and to rather short nuclear spin-lattice relaxation times. This host-impurity combination is thus qualitatively different from those studied up to now, and is of particular interest for several reasons.

(i) As a result of the short relaxation times and large quadrupole splittings, Tb is an ideal host for on-line nuclear implantation and orientation experiments, especially for nuclei from the $4f$ and $5f$ series.[6] The present result demonstrates the feasibility of combining such measurements with magnetic resonance, a spectroscopic method of great inherent precision, and in particular of determining electric quadrupole moments of radioactive nuclei. This opens up new perspectives for the study of nuclear systematics in these regions of the Periodic Table.

(ii) This is the first example of NMR-ON in which the electric quadrupole interaction frequency is of the order of hundreds of megahertz, so that the magnetic resonance line is split into widely separated subresonances, which can be observed individually. This provides a genuine two-level system at low temperatures, which may be used, for example, to study population inversion by adiabatic fast passage.[2]

(iii) Finally, as a result of the mixed dipolar-quadrupolar hyperfine interaction in Tb:^{160}Tb, it can be employed as a gamma-ray absolute thermometer over a wide range of temperatures (from below 10 mK to about 80 mK). Moreover, the large magnetic hyperfine field (305 T) makes this thermometer rather insensitive to applied magnetic fields, in contrast to most gamma-ray thermometers now in use.[7]

The NMR of stable ^{159}Tb in terbium was studied some time ago by Sano and Itoh[8] using spin-echo techniques on a polycrystalline powder sample. Here, the nuclear spin is $\frac{3}{2}$ and the quadrupole interaction splits

the resonance into three lines, according to

$$\nu_n = \nu_M - 2(I - n + \tfrac{1}{2})\nu_P, \quad n = 1, 2, \ldots, 2I, \quad (1)$$

where ν_M is the magnetic NMR frequency, equal to $|\mu\mu_N B_{\rm hf}/Ih|$, ν_P is the electric quadrupole frequency defined by $\nu_P = 3e^2qQ/4hI(2I-1)$, and n is an index numbering the $2I$ observable resonance lines at frequencies ν_n, with $n=1$ corresponding to the subresonance between the energetically lowest pair of levels. At low temperatures ($kT < h\nu_M$), only the lowest levels are populated, so that only the first one or two subresonances can be detected. Thus, observation of the ν_1 resonance at low temperatures immediately gives the sign of the electric quadrupole interaction eqQ (where eq is the total electric field gradient and Q the nuclear quadrupole moment). In Ref. 8, the subresonances were rather broad and showed satellites, which were attributed to variations in shape of the Tb powder particles, leading to different demagnetizing fields. The spin-lattice relaxation of the Tb nuclei was also observed, showing that the Weger mechanism[9] dominates and the relaxation is therefore rapid compared to that in the $3d$ ferromagnetic hosts; it is also different for each subresonance.

From the previously reported g factors of the two Tb isotopes[10,11] we predicted ν_M for Tb:^{160}Tb to be near 1320 MHz and ν_1 to be in the range of 440–720 MHz, with an effective relaxation time of about 5 ms. Saturation of the ν_1 resonance equalizes the populations of the lowest two nuclear sublevels and reduces the gamma-ray anisotropy by about 40% (at 15 mK).

Samples were prepared from a terbium single crystal obtained from Ames Laboratories. Rectangular slabs of about 4.5×10 mm^2 and 1-mm thickness were spark machined from the crystal with the basal plane in the plane of the slab, and an easy (b) axis parallel to the long side. Implantations of ^{160}Tb were carried out with use of the Bonn isotope separator at a voltage of 80 kV and total doses between 5×10^{12} and 5×10^{13} ions/cm^2. The ions were implanted in a circular region of about 3-mm diameter near the center of the crystals, so that the demagnetizing field was constant over the active region, which contained 10–15 μCi of ^{160}Tb activity. We expected the fraction f of undisturbed sites to be near 1.00, since the implanted species is chemically identical to the host and has nearly the same mass. However, all the samples showed a considerable reduction in gamma-ray anisotropy [observation of the 299- and 1272-keV gamma rays[12] by Ge(Li) detectors]. A sample whose surface had been electropolished also showed magnetic hardness. A second crystal, implanted under identical conditions, exhibited the magnetization behavior known from bulk measurements,[13] but a site occupation factor of only 0.5. Samples implanted at lower doses and mechanically polished just prior to implantation had occupation factors near 0.25. The reason for this low site occupation is not known, but further experiments at higher accelerating voltage are planned. The crystals, which were indium soldered to Cu strips before implantation, were maintained in argon atmosphere prior to mounting in a dilution cryostat; this was done with a screw joint to the Cu, tinned with In-Ga eutectic. The gamma-ray anisotropy agreed with that seen in bulk samples,[13,14] with allowance for the reduced site occupation.

Figure 1 shows some resonances (ν_1) observed at several applied fields; the sample temperature was 20–25 mK, giving an overall γ-ray anisotropy (relative change in counting rate $\dot{N}$) of about 8.4%. The quantity plotted is the difference in $\dot{N}$ (parallel to the applied field) at constant rf power and frequency, with and without frequency modulation (triangle-wave modulation with $\nu_{\rm FM} = 500$ Hz and 4-MHz bandwidth). This is to first order insensitive to nonresonant rf-heating effects; a residual background due to nonresonant heating was determined at high applied fields, where the resonance effect is small because of the decreased rf enhancement factor, and subtracted from the resonance lines, which were then fitted with Gaussian functions as shown in Fig. 2.

The resulting field dependence of ν_1 is illustrated by Fig. 3, and the relevant quantities, corrected for fre-

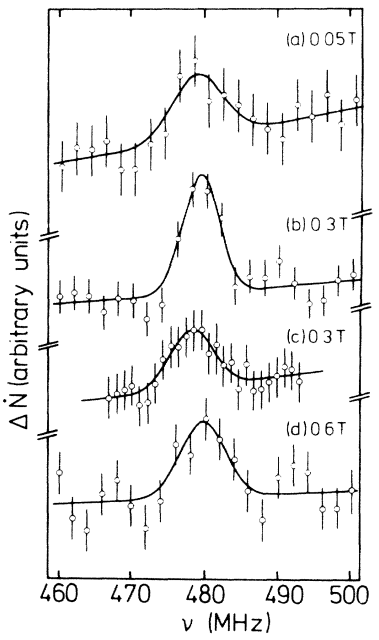

FIG. 1. Four resonance lines (ν_1) from ^{160}Tb oriented in a Tb single crystal, observed near 20 mK and the applied fields indicated. In (a), (b), and (d), the frequency steps were 2 MHz and the FM bandwidth 4 MHz; in (c), the steps were 1 MHz and the bandwidth 3 MHz. The quantity plotted is the difference in counting rates with and without FM, as described in the text. The curves are Gaussians with a linear background.

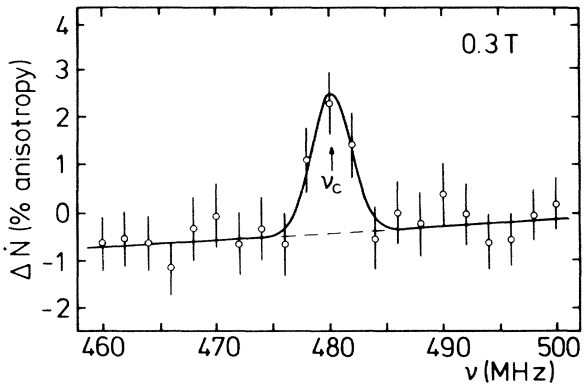

FIG. 2. The resonance line observed at 0.3-T applied field [Fig. 1(b), percent counting-rate change], corrected for nonresonant background and fitted with a Gaussian function. The data in Table I are obtained from such fits.

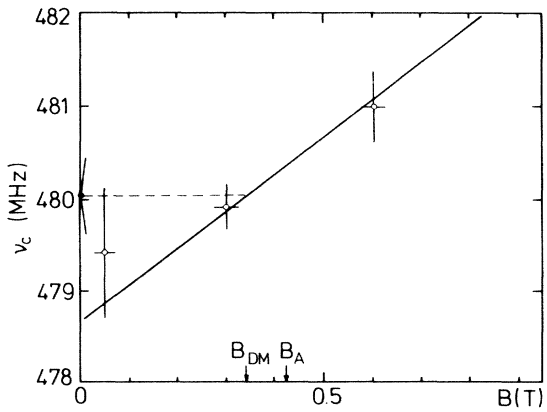

FIG. 3. Field dependence of the NMR frequency ν_1 from Table I. The point shown for $B = 0.3$ T is the weighted average of the two measurements given in the table. The solid line has the expected slope for a magnetically saturated sample and is adjusted to the data at 0.3 and 0.6 T; the dashed line is for a virgin sample with increasing field.

quency modulation, are summarized in Table I. The signal S (fractional reduction of available γ-ray anisotropy, integrated over the resonance line) is consistent with a ferromagnetic enhancement model taking the anisotropy field B_A to be 0.42 T, near the value expected from bulk measurements.[13] The wide line and small S for 0.05-T applied field are typical of magnetically unsaturated samples, where the local quantization axis is not parallel to B for a large fraction of the nuclei.[5,15] The value of S at 0.3-T applied field corresponds to about 85% saturation of the resonance, but the observed change in $\dot{N}$ is small because of the low site occupation of the samples (Fig. 2).

The solid line in Fig. 3 shows the field shift of ν_1, given by

$$\nu_1(B) = \nu_1(0) \pm (1+K)(B - B_{DM}) g\mu_N/h,$$

where K is the Knight shift (here assumed to be small), B_{DM} is the demagnetizing field of the sample, and the positive sign corresponds to a positive B_{hf}, as in the present case. From the ESR value of the ^{160}Tb g factor,[11] we expect a slope of 4.32(2) MHz/T, in agreement with our data. The dashed line indicates the behavior of a virgin sample on increase of the applied field; in this case, B is initially shielded by the domain walls, so that the effective field is constant and equal to B_{hf}. Only when magnetic saturation is reached is a linear relation between ν_1 and B observed. As pointed out in Ref. 5, in an anisotropic crystal host there are two other mechanisms which can cause a deviation from linearity at low applied fields: anisotropy in B_{hf} along different crystalline axes, and variation of the angle between the symmetry axes of the magnetic and electric quadrupole interactions. Both should be small in Tb, since the local moments remain in the basal plane as a result of the large crystalline anisotropy[16]; any anisotropy in B_{hf} between the nearly equivalent crystalline a and b axes should be small, and the angle with the quadrupole symmetry axis remains constant. Upon reduction of the field B below the saturation value (as in our experiments), the resonance may be observed anywhere between the solid and dashed lines in Fig. 3, because of hysteresis effects. The filled circle on the ordinate indicates the extrapolated value of $\nu_1(0)$ (with fit errors), obtained with $B_{DM} = 0.34$ T.

To determine ν_M and ν_P independently, at least two of the subresonances must be observed. Direct observation of ν_2 at low temperatures is difficult because of the small population of the $M_I = +2$ substate, from which it originates; however, if ν_1 is saturated, this population increases considerably, and simultaneous irradiation at ν_2 would destroy 70% of the remaining anisotropy in saturation. We did not attempt this double-resonance experiment on the present samples with low site occupations, but it is planned with samples implanted at higher voltage.

For the present, we adopt the value of 1318(12.9) MHz for ν_M, with errors as quoted in Refs. 8 and 11.

TABLE I. Fitted resonance line parameters, corrected for FM.

B (T)	ν_c (MHz)[a]	FWHM (MHz)[b]	S (%)	S (%), calc.[c]
0.05	479.4(0.7)	7.4	11.3	. . .
0.3	480.1(0.24)	2.95	34.7	38.2
0.3[d]	479.4(0.5)	4.78	29.5	
0.6	481.0(0.4)	3.8	16.4	18.9

[a]Center frequency of fitted Gaussian.
[b]Linewidth corrected for FM.
[c]Calculated assuming enhancement model; see text.
[d]Frequency step 1 MHz; others are 2 MHz.

The quadrupole frequency $\nu_P=(\nu_M-\nu_1)/5$ is then 167.7(2.6) MHz, and the ^{159}Tb/^{160}Tb quadrupole-moment ratio is $R=0.402(9)$, taking ν_P for Tb:^{159}Tb from Ref. 8. With $Q(^{159}\text{Tb})$ equal to 1.432(8) b,[17] we find $Q(^{160}\text{Tb})$ to be 3.56(10) b, in agreement with the (less precise) ESR value.[11] (The errors in R are mostly due to uncertainties in ν_M; if ν_1 and ν_2 were determined independently with comparable accuracies as described above, we could derive R with about 1% uncertainty. The precision of the thermometry using Tb:^{160}Tb depends only on the uncertainties in ν_M and ν_P, and is independent of the nuclear-moment determination.)

In summary, we have observed NMR-ON on ^{160}Tb implanted in a Tb single crystal. The first subresonance of the quadrupole-split line was found at 480.0(4) MHz in zero applied field, with a Gaussian width of about 4 MHz. We are pursuing adiabatic passage and double-resonance experiments which can yield very precise information about the hyperfine interactions in this system. This experiment points the way for the study of short-lived nuclei in the $4f$ and $5f$ series by on-line implantation and NMR-ON, and for the use of the Tb nuclear-orientation thermometer over a wide range of low temperatures and high magnetic fields.

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