ducers alone was investigated in a number of experiments. In one experiment, a 25-MHz transducer was bonded back to back to a 12.5-MHz pick-up transducer. When power was supplied to the 25-MHz transducer in the vicinity of its fundamental resonance, half-frequency oscillations could be observed having distinct excitation thresholds as low as a few volts. They could be observed discontinuously over a range of several MHz when the input frequency was changed. Neither the different amplitudes nor thresholds were observed to have a direct relationship to the measured mechanical resonance of the system. Furthermore, the excitation of the fractional harmonics did not depend critically upon the fundamental resonance frequency of the pick-up transducer. For example, a 10-MHz transducer could also be used to detect the 12.5-MHz oscillations. One of the most interesting observations was that other frequencies, fractionally related to the input frequency (e.g., $p/q=\frac{3}{2}$, $\frac{3}{8}$, 13/22, etc.), could be detected by changing the tuning of the pick-up transducer output or by using different transducer combinations. The output signal was observed to have a fixed phase relationship to the input. Furthermore, some fractional harmonics could also be detected across a single 25-MHz transducer suspended in air only by its leads. The amplitude of the observed fractional harmonics was typically of the order of a few millivolts. Following an initial increase above threshold, raising the input voltage an order of magnitude produced no significant increase in the fractional harmonic output, which also differs from common parametric behavior.

These experiments have shown that the transducer alone can produce fractional harmonics but of insufficient amplitude to cause the nuclear-spin saturation. In order to explain the remarkable nuclear-spin saturation of Fig. 1, one is led to assume that the sample can also generate fractional harmonics (or parametrically amplify the one supplied by the transducer[4]) as soon as a critical energy density is reached.

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OBSERVATION OF THE Pr^{141} AND Tm^{169} NUCLEAR MAGNETIC RESONANCES IN THE PARAMAGNETIC STATES OF RARE-EARTH INTERMETALLIC COMPOUNDS*

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The first observations of the Pr^{141} and Tm^{169} nmr in rare-earth intermetallic compounds are described. The calculated and observed values for the nmr frequency shifts are in good agreement.

The possibility of observing the nuclear magnetic resonance (nmr) of the nucleus of a paramagnetic ion whose ground state in a crystalline field is a singlet, has been discussed in the literature for about ten years.[1-5] The basis for such an observation is that when a paramagnetic ion is in a singlet ground state, the hyperfine interaction is zero. Recently, the Pr^{141} nmr has been observed in a single crystal of $Pr_2(SO_4)_3 \cdot 8H_2O$ at 1.5°K by Al'tshuler and Teplov.[6] Because of a large nuclear quadrupolar interaction, the Pr^{141} nmr spectrum was complicated. However, the analysis of the nmr data indicated that the nuclear hyperfine interaction was indeed small.

In rare-earth metals and rare-earth intermetallic compounds the crystal field splitting of the $(2J+1)$-fold degenerate spin-orbit J state is about an order of magnitude smaller than found in insulators such as $Pr_2(SO_4)_3 \cdot 8H_2O$.

The consequence of this smaller crystal field interaction is that the magnetic-field–induced Van Vleck susceptibility in the singlet ground state will be an order of magnitude larger than found in insulators. Since orbital hyperfine fields have a magnitude of approximately 5×10^6 Oe, a very large nmr frequency shift $(\Delta H/H)$ is expected. Hence, the observation of the nmr of a rare-earth nucleus in metallic compounds (where the singlet ground state is a result of a crystal field interaction) will occur in very weak magnetic fields.

We wish to report the first successful observation of the nmr of a nucleus of a paramagnetic rare-earth ion in rare-earth metals and rare-earth intermetallic compounds. In this Letter we will present and discuss the Pr^{141} nmr in PrP and PrAs, and the Tm^{169} nmr in TmP, TmAs, and TmSb, where we find that the nmr frequency shifts are extremely large ($\approx$1000 %) in agreement with theoretical predictions.

The NaCl-type intermetallic compounds PrP, PrAs, TmP, TmAs, and TmSb have been studied extensively by paramagnetic susceptibility measurements.[7-9] The P^{31}, As^{75}, and Sb^{121} nmr have also been observed in these compounds.[10,11] These investigations have shown that the sixfold cubic crystal field interaction gives rise to a singlet (Γ_1) ground state for both the $\mathrm{Pr}^{3+}\,({}^3H_4)$ and $\mathrm{T}_m^{3+}\,({}^3H_6)$ ions. The over-all crystal field splitting parameters Δ for these compounds are tabulated in Table I.

The Pr^{141} and Tm^{169} nmr were observed in powdered samples in the range of 1.5-77°K and 1.5-27°K, respectively, using a variable-frequency induction spectrometer and a conventional laboratory electromagnet. The nmr frequency-shift measurements were made at a fixed frequency by measuring the magnetic field for which resonance occurred with the proton nmr in $\mathrm{H_2O}$. The nmr frequency shifts were determined to be frequency independent in the range of 5-16 MHz. The Pr^{141} and Tm^{169} nmr linewidths were found to vary linearly with magnetic field at 4°K. The Pr^{141} nmr linewidth was found to be temperature independent between 1.5 and 27°K, while the Tm^{169} nmr linewidth doubled between 4 and 27°K even though the paramagnetic susceptibility of the thulium compounds decreased by approximately a factor of 2 in the same temperature range. This phenomenon is associated with the thermal excitation of higher lying crystal field states. Because of the large hyperfine interaction in these states, the fluctuations of the electronic spin system in the excited states give rise to a large nmr linewidth. The effective gyromagnetic ratios γ_{eff} at 4°K are tabulated in Table I for each compound. The error estimates for γ_{eff} are due to the uncertainty in measuring the center of the nmr spectrum. In calculating the measured nmr frequency shifts $(\Delta H/H)$, the nuclear moments used were $+4.28(8)\mu_N$[12] for Pr^{141} and $-0.227(3)\mu_N$[13] for Tm^{169} corresponding to gyromagnetic ratios of 1.31(2) kHz/Oe and 0.346(4) kHz/Oe, respectively. The measured nmr frequency shifts at $T=4$°K in PrP and TmP were found to be $(\Delta H/H)^{141}=6.38\pm0.12$ and $(\Delta H/H)^{169}=+(76.7\pm1.0)$. In terms of the more customary usage these represent nmr frequency shifts of 638 and 7670 %, respectively. The measured nmr frequency-shift data are tabulated in Table II. The error estimates for the nmr frequency-shift data are due to the uncertainty in the values of the Pr^{141} and Tm^{169} nuclear moments.

An analysis[11,14] of the P^{31} and As^{75} Knight-shift data in these intermetallic compounds has shown that these Knight shifts are proportional to the paramagnetic susceptibility of the rare-earth ion [e.g., Eq. (4)]. Thus, we

Table I. Various parameters used in the analysis of the Pr^{141} and Tm^{169} frequency-shift data. The effective gyromagnetic ratio is for $T=4.0$°K.

	PrP	PrAs	TmP	TmAs	TmSb
$\chi_M(4°\mathrm{K})^{\mathrm{a}}$	$3.1\times10^{-2\,\mathrm{a}}$	$3.1\times10^{-2\,\mathrm{a}}$	0.46^{b}	0.42^{b}	0.51^{b}
$\chi_M(27°\mathrm{K})$	3.0×10^{-2}	$3.0\times10^{-2\,\mathrm{a}}$	0.24^{b}	0.24^{b}	0.24^{b}
$\chi_M(77°\mathrm{K})$	1.8×10^{-2}	...	...	...	...
$\Delta(°\mathrm{K})$	400^{a}	400^{a}	$300^{\mathrm{b,c}}$	$275^{\mathrm{b,c}}$	$220^{\mathrm{b,c}}$
$\langle r^{-3}\rangle$(a.u.)	5.0	5.0	11.7	11.7	11.7
$(\gamma_{\mathrm{eff}}/2\pi)$(kHz/Oe)	9.66(4)	9.82(4)	26.9(2)	24.9(2)	31.1(2)

[a] Ref. 14. [b] Ref. 7. [c] Ref. 18.

Table II. Calculated and observed values of the Pr^{141} and Tm^{169} nmr frequency shifts.

	$(\Delta H/H)_{\text{orb}}$	$(\Delta H/H)_{\text{core}}$	$(\Delta H/H)_{\text{ce}}$	$(\Delta H/H)_{\text{tot}}$	$(\Delta H/H)_{\text{obs}}$
		PrP			
4.0°K	+5.7	+0.1	+0.3	+6.1	+6.38 ± 0.12
27°K	+5.5	+0.1	+0.3	+5.9	+6.30 ± 0.12
77°K	+3.3	+0.1	+0.2	+3.6	+3.93 ± 0.07
		PrAs			
4.0°K	+5.7	+0.1	+0.3	+6.1	+6.50 ± 0.12
27°K	+5.5	+0.1	+0.3	+5.9	+6.37 ± 0.12
		TmP			
4.0°K	+80.7	−1.3	−0.7	+78.7	+76.7 ± 1.0
27°K	+42.1	−0.7	−0.4	+41.1	+41.2 ± 0.5
		TmAs			
4.0°K	+73.7	−1.2	−0.6	+71.9	+70.9 ± 1.0
27°K	+42.1	−0.7	−0.4	+41.1	+37.9 ± 0.5
		TmSb			
4.0°K	+89.5	−1.4	−0.8	+87.3	+88.7 ± 1.2

are able to compare the temperature dependences of the P^{31} and As^{75} Knight shifts in PrP, PrAs, and TmAs with the Pr^{141} and Tm^{169} nmr frequency-shift data (the P^{31} and Sb^{121} nmr have not been observed in TnP and TmSb at at 4°K). The ratio R of the 4 and 27°K Knight shifts and nmr frequency shifts are $R^{31} = 1.03$, $R^{141} = 1.02$ for PrP, $R^{75} = 1.04$, $R^{141} = 1.03$ for PrAs and $R^{75} = 1.87$, $R^{169} = 1.87$ for TmAs, while for the ratio between the 4 and 77°K PrP data, $R^{31} = 1.60$ and $R^{141} = 1.62$. Thus, within experimental error, the temperature dependences of the Pr^{141} and Tm^{169} nmr frequency shifts are identical to those of the P^{31} and As^{75} Knight-shift data.

There are three contributions to the total nmr frequency shift $\Delta H/H$. The first and largest, $(\Delta H/H)_{\text{orb}}$, is the contribution from orbital and spin dipolar hyperfine field. The second and third contributions are the core-polarization frequency shift $(\Delta H/H)_{\text{core}}$ and the s-f exchange enhanced conduction-electron spin-polarization Knight shift $(\Delta H/H)_{\text{ce}}$. Even though the orbital contribution $(\Delta H/H)_{\text{orb}}$ essentially accounts for the observed nmr frequency shift, the core polarization and conduction-electron contributions are included for completeness. Thus, the total nmr frequency shift is

$$\Delta H/H = (\Delta H/H)_{\text{orb}} + (\Delta H/H)_{\text{core}} + (\Delta H/H)_{\text{ce}}. \quad (1)$$

We will now proceed to estimate the magnitudes and signs of these three contributions.

The orbital and spin dipolar hyperfine fields have been discussed by Elliott and Stevens[15] and a straightforward calculation for this shift in terms of the paramagnetic susceptibility gives

$$(\Delta H/H)_{\text{orb}} = 2\langle r^{-3}\rangle\langle J\|N\|J\rangle\chi/Ng_J, \quad (2)$$

where r is the $4f$ electron radius, $\langle J\|N\|J\rangle$ is the operator-equivalent factor for the orbital and spin dipolar hyperfine field operators, χ is the paramagnetic susceptibility of the crystal-field-split energy-level system and is expressed in units of emu per mole, N is Avogadro's number, and g_J is the Lande g factor. The most recent values for $\langle r^{-3}\rangle$ have been tabulated by Watson and Freeman[16] and are given in Table I for the Pr^{3+} and Tm^{3+} ions. The operator-equivalent factor $\langle J\|N\|J\rangle$ is 296/225 for Pr^{3+} and 7/9 for Tm^{3+}. Using the susceptibility data given in Table I, $(\Delta H/H)_{\text{orb}}$ is calculated for each compound and the results are given in Table II.

The core-polarization nmr frequency shift can be calculated in terms of the paramagnetic susceptibility χ and is

$$(\Delta H/H)_{\text{core}} = (g_J - 1)H_{\text{core}}\chi/N\beta, \quad (3)$$

where $H_{\text{core}} \simeq -90$ kOe per Bohr magneton β.[17] Table II gives the values of $(\Delta H/H)_{\text{core}}$ for each compound.

The conduction-electron spin-polarization Knight shift is difficult to estimate. However, we can obtain an order-of-magnitude estimate by using the uniform conduction-electron spin-polarization model which has been used[11] in the analysis of the P^{31} Knight-shift data in these compounds. The expression for $(\Delta H/H)_{\rm ce}$ is

$$(\Delta H/H)_{\rm ce} = K_0[1+\Gamma(g_J-1)\chi/2Ng_J\beta^2], \qquad (4)$$

where K_0 is the Pr^{141} or Tm^{169} Knight shift in the absence of any s-f exchange interaction and Γ is the s-f exchange energy. We estimate $K_0 \simeq 0.3\,\%$ by using the La^{139} Knight-shift value in LaP.[10] The values of the s-f exchange energy Γ which we will use are those obtained[11] by the P^{31} nmr data and are $\Gamma(\mathrm{Pr}) \simeq -0.7$ eV and $\Gamma(\mathrm{Tm}) \simeq -0.2$ eV. The calculated values for $(\Delta H/H)_{\rm ce}$ are given in Table II. It is evident that this contribution is small compared to $(\Delta H/H)_{\rm orb}$. Thus any errors introduced in $(\Delta H/H)_{\rm ce}$ which are caused by using the unsophisticated uniform conduction-electron spin-polarization model for the Knight shift probably are not significant.

Inspection of Table II shows that the total calculated nmr frequency shifts are in good agreement with the experimentally observed values. Better agreement could have been achieved by adjusting the values for $\langle r^{-3}\rangle$ and for χ, which are probably accurate, at best, to about 5%. When more accurate values for the Pr^{141} and Tm^{169} nuclear moments become available, these nmr frequency shift data can be used to obtain good experimental estimates for $\langle r^{-3}\rangle$.

In conclusion, we have observed the Pr^{141} and Tm^{169} nmr in the paramagnetic states of PrP, PrAs, TmP, TmAs, and TmSb. To our knowledge, these frequency-shift data are, to date, the largest measured in a paramagnetic medium. We have also made preliminary measurements of the Pr^{141} nmr in praseodymium metal, and these results will be presented in a future publication.

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