

Ytterbium NMR: Yb¹⁷¹ Nuclear Moment and Yb Metal Knight Shift*

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The nuclear magnetic resonance of Yb¹⁷¹ has been found in two nonmagnetic ytterbium (ous) compounds, YbCl₂ and YbS, from which a value of $\mu^{171} = +0.4926 \pm 0.0004 \mu_N$ is determined. From the Yb³⁺ electron paramagnetic resonance measurements of the ratio of the hfs constants A^{171}/A^{173} we deduce $\mu^{173} = -0.6772 \pm 0.0025 \mu_N$. Observations of Yb¹⁷¹ NMR in elemental Yb metal and in the intermetallic compound YbAl₂ at temperatures of 1.8, 4.2, and 20.4°K yield values of the Knight shift of $(0.0 \pm 0.1)\%$, and $(7.76 \pm 0.05)\%$, respectively. The absence of any detectable temperature dependence of the field for resonance indicates that the low-temperature increase in the magnetic susceptibilities of these metals is caused by isolated, localized magnetic impurities. In YbAl₂, a constant susceptibility of 7.6×10^{-4} emu/mole remains at higher temperatures. The electronic contribution to the specific heat is found to be $\gamma \cong 4 \times 10^{-3}$ cal/mole °K². The nuclear spin-lattice relaxation time $T_1 \cong 0.12/T$ sec at $T = 1.8^\circ\text{K}$. From these latter two measurements, in conjunction with the large positive Knight shift, we conclude that the larger part of the high-temperature χ does not arise from spin paramagnetism of the band electrons, but is orbital in origin.

INTRODUCTION

IT is somewhat surprising to find that the nuclear moments of the nuclei of rare-earth ions with incomplete 4*f* shells are known to an accuracy of only $\pm 10\%$ —a situation in marked contrast to the nuclei of most other stable elements. The reasons for this are clear. Ordinarily nuclear magnetic resonance (NMR) techniques are applied to nuclei of nonmagnetic ions—that is so-called “closed-shell” configurations. However, it is well known that the 4*f* shell remains incomplete in compounds of the rare-earth group. Magnetic moment determinations have relied on hfs measurements which measure the *product* of the hyperfine field H_{HF} of the 4*f* electrons with the nuclear moment μ_N . Although this product may be known in a particular case with great accuracy, neither H_{HF} nor μ_N can be determined separately. It is generally assumed¹ that H_{HF} may be estimated to a precision of $\pm 10\%$ and so μ_N remains in doubt by this amount.

Fortunately, Yb provides an exception to the rule. Although Yb most often occurs in the trivalent (*ic*) state, in which the 4*f* shell contains one hole, it also exists in the divalent (ous) state with a full 4*f* shell. This circumstance combined with a reasonable magnitude for the Yb¹⁷¹ nuclear moment ($I = \frac{1}{2}$) makes possible the NMR experiment which we now report. Use may then be made of previous Yb¹⁷¹ hfs measurements of the Yb³⁺ ion ($4f^{13} {}^2F_{7/2}$) to determine the hyperfine field with considerable accuracy as was first pointed out by Elliott.²

Yb¹⁷¹ NUCLEAR MAGNETIC MOMENT

Yb¹⁷¹ resonances were found in two divalent compounds: YbCl₂ and YbS. It was necessary to work with the solid salts because the Yb²⁺ ions oxidize rapidly to the trivalent state in water, while they cannot be dissolved in sufficient concentration for NMR experiments in nonoxidizing polar liquids. The experiments were performed with a Varian wide-line nuclear resonance spectrometer.

In searching for resonance, the spectrometer rf probe was balanced to detect the dispersion (χ') mode of the resonance, the maximum possible rf magnetic field (~ 1.0 G) being applied to the sample. Redfield³ has observed that the nuclear magnetic resonance dispersion mode in a solid saturates at a much higher rf field than the absorption mode. Thus it is possible to obtain a larger dispersion-mode signal than absorption-mode signal. The resonance line, although much broadened with this technique, is not proportionately reduced in intensity. One of the distinct advantages of this method is that the allowed rate of scan of the dc magnetic field is increased, making possible a much more rapid search for a weak resonance absorption.

Yb¹⁷¹ NMR signals were observed in both YbCl₂ and YbS at 1.8, 4.2, and 20.4°K. No signal was observable at 77°K or above, nor was any signal observable in aqueous solutions. The intensities of the resonances depended strongly on temperature, being greatest at hydrogen temperature for the chloride and greatest at helium temperature for the sulfide. The resonance frequency was measured relative to the Cl³⁵ NMR in a sodium chloride solution, with the result, in both

* A preliminary report of this work was given at the Seattle A. P. S. Meeting, Bull. Am. Phys. Soc. **7**, 482 (1962).

¹ B. Bleaney, Proc. Phys. Soc. (London) **A68**, 937 (1955).

² R. J. Elliott, Proc. Phys. Soc. (London) **B70**, 119 (1957).

³ A. G. Redfield, Phys. Rev. **98**, 1787 (1955).

YbCl₂ and YbS that

$$\frac{\nu(\text{Yb}^{171})}{\nu(\text{Cl}^{35})} = 1.7874 \pm 0.0015.$$

Applying a +0.804% correction⁴ for the atomic diamagnetic shielding, we obtain an Yb¹⁷¹ ($I = \frac{1}{2}$) nuclear moment of $+0.4926 \pm 0.0004 \mu_N$. No correction for any chemical shift has been made. From the above and Low's⁵ Yb³⁺ electron paramagnetic resonance (EPR) measurement of the ratio of the hfs constants of Yb¹⁷¹ and Yb¹⁷³, we find $\mu^{173} = -0.6772 \pm 0.0025 \mu_N$. A small part (<10%) of the Yb³⁺ hyperfine interaction arises from core polarization of inner *s* electrons. Because of this, the measured ratio of the hfs interaction constants could differ from the ratio of nuclear *g* values for the two isotopes because of the hyperfine structure anomaly. A reasonable estimate of the hyperfine anomaly indicates that the difference between the ratios will be at least an order of magnitude smaller than the uncertainty of the EPR measurement and can be neglected.

The shell model predicts that the odd neutron in Yb¹⁷¹ occupies a $3p_{3/2}$ state for which the Schmidt limit value of $\mu(p_{3/2})$ is $0.63 \mu_N$. The configuration interaction theory of Blin-Stoyle⁶ and Arima and Horie⁷ which successfully accounts in sign and magnitude for the observed deviations of many of the nuclear moments from the Schmidt limits, in the case of nuclei for which collective modes are not important, does in fact allow for no deviations from the Schmidt limits for $p_{3/2}$ nuclei. However, this is a consequence of the assumed δ -function interparticle interaction required to produce the configuration mixing of single-particle states. For $p_{3/2}$ nuclei deviations of the observed sign and magnitude may be obtained from an interaction of finite range.

Having determined μ^{171} directly, it is now possible to obtain from the EPR-hfs measurements the field per unit spin, H_{HF} , acting at the nuclei in free Yb³⁺ ions. The magnetic electron-nuclear interaction may be expressed as $\mathcal{H} = A\mathbf{I} \cdot \mathbf{J}$, in which case $A = g_I \mu_n H_{\text{HF}}$. From the observed value $A^{171}/g = 2.587 \times 10^{-2} \text{ cm}^{-1}$,⁸ we compute for the free Yb³⁺ ion $H_{\text{HF}} = 1.18 \times 10^6$ Oe per spin.

The value of the field at the nucleus in rare-earth atoms is of interest in the theory of atomic wave functions since $H_{\text{HF}} \sim \langle 1/r^3 \rangle_{4f}$ for the *f* electrons.² Recent new approaches for computing $\langle 1/r^3 \rangle_{4f}$ and reviews of

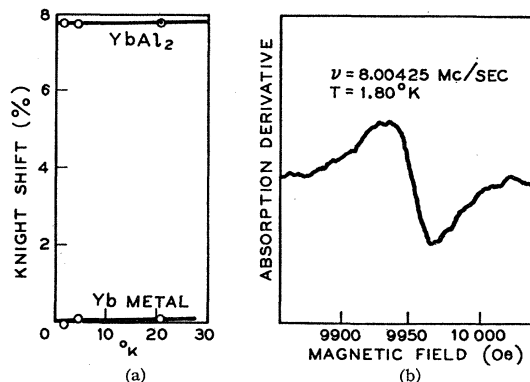


FIG. 1. (a) Knight shift versus temperature for Yb¹⁷¹ NMR in powdered Yb metal and in the powdered intermetallic compound YbAl₂. (b) Resonance absorption derivative of Yb¹⁷¹ in YbAl₂ at 1.8°K.

former calculations have been given by Freeman and Watson⁹ and by Lindgren.¹⁰

KNIGHT SHIFT OF YTTERBIUM METAL AND YbAl₂

We have also observed Yb¹⁷¹ NMR and measured Knight shifts in ytterbium metal and in the cubic Laves phase intermetallic compound YbAl₂. A finely divided sample of ytterbium metal was made by filing an ingot of 99.9% pure ytterbium metal in an argon atmosphere. Again using the induction spectrometer with the technique described above, resonances were observed at temperatures between 1.8 and 20.4°K. The ytterbium metal Knight shifts (*K*) observed relative to the Yb¹⁷¹ NMR frequency in the reference compounds of YbCl₂ and YbS are displayed in the lower curve of Fig. 1(a), and are seen to be zero within the accuracy of the measurements ($\pm 0.1\%$). The susceptibility of ytterbium metal as measured by Lock¹¹ was temperature-dependent with an approximate $1/T$ temperature dependence, in marked contrast with the temperature-independent Knight shift. The Knight-shift results indicate that this $1/T$ contribution to susceptibility arose from isolated localized magnetic impurities, probably other rare-earth atoms. Resonances from nuclei on these impurity sites would not be visible, and the resonance from the aggregate of nuclei on neighboring sites would be broadened rather than shifted in first approximation.¹² Recent susceptibility measurements on purer specimens of Yb metal have shown a greatly reduced $1/T$ contribution, in agreement with this analysis. Specific heat measurements of Yb metal by Lounasmaa¹³ have indicated that paramagnetic impurities also contribute to the specific heat of ytterbium metal and that in purer samples this contribution disappears. The re-

⁴ W. C. Dickinson, Phys. Rev. **80**, 563 (1950).

⁵ W. Low, Phys. Rev. **117**, 1608 (1960).

⁶ R. J. Blin-Stoyle and M. A. Perks, Proc. Phys. Soc. (London) **A67**, 885 (1954).

⁷ A. Arima and H. Horie, Progr. Theoret. Phys. (Kyoto) **11**, 509 (1954). H. Noya, A. Arima, and H. Horie, Suppl. Progr. Theoret. Phys. (Kyoto) **8**, 33 (1958).

⁸ See Ref. 5. The EPR measurements of A^{171} and A^{173} were made on Yb³⁺ ions in the cubic field of CaF₂. Since in CaF₂ the Yb³⁺ ground state is spanned by the $J = 7/2$ manifold, A^{171}/g and A^{173}/g should have the same values in the CaF₂ environment as in the free ion.

⁹ A. J. Freeman and R. E. Watson, Phys. Rev. **127**, 2058 (1962).

¹⁰ I. Lindgren, Nucl. Phys. **32**, 151 (1962).

¹¹ J. M. Lock, Proc. Phys. Soc. (London) **70B**, 476 (1957).

¹² A. C. Gossard, V. Jaccarino, and J. H. Wernick, J. Phys. Soc. Japan **17**, Suppl. B-I, 88 (1962).

¹³ O. V. Lounasmaa, Phys. Rev. **129**, 2460 (1963).

sidual susceptibility of pure Yb is of the order of a free-electron susceptibility. This would be expected to produce a Knight shift of approximately 0.8%. We are thus surprised to find the $(0.0 \pm 0.1)\%$ Knight shift in ytterbium metal.

A sample of YbAl₂ for NMR was prepared by crushing and screening a brittle ingot of the intermetallic compound. An extensive search was made for the NMR of Yb¹⁷¹ in this compound between 1.8 and 20.4°K. The only resonance found was shifted by +7.76% from the Yb¹⁷¹ resonance in YbCl₂ and YbS. A recording of the resonance absorption derivative is shown in Fig. 1(b). The measured Knight shifts are displayed in the upper curve of Fig. 1(a) and are again temperature-independent within the accuracy of our determination ($\pm 0.05\%$). Care was taken to observe both dispersion and absorption modes of the resonance, and measurements were made at several rf frequencies to check that the resonance was not spurious. The resonance frequency and field are not harmonically related to the Al²⁷ resonance. It was therefore concluded that the observed resonance is the Yb¹⁷¹ resonance, and that its Knight shift is indeed +7.76%. The Al²⁷ NMR was also observed, and confirmed the earlier results of Jaccarino *et al.*¹⁴ that the Al²⁷ resonance in YbAl₂ has a small temperature-independent Knight shift of +0.07%, close to the value in LaAl₂ and LuAl₂.

In view of this unusual Knight-shift behavior, further related measurements have been made on YbAl₂. Williams and Sherwood have measured the magnetic susceptibility, and Maita and Scott have measured the low-temperature specific heat. A strikingly large temperature-independent component of the magnetic susceptibility of 7.6×10^{-4} emu/mole appears in YbAl₂. Temperature-dependent components of the susceptibility are again greatly reduced in samples made with purer ytterbium. To determine whether the temperature-independent component arises from spin paramagnetism of band electrons we have analyzed the low-temperature specific heat C to find the density of states at the Fermi level $N(E_F)$. The $N(E_F)$ deduced from $C = 40 \times 10^{-4}$ cal mole⁻¹ deg⁻² yields a value of the susceptibility $\chi = 2\mu_B^2 N(E_F) = 214 \times 10^{-6}$ emu/mole, which is only 28% of the observed susceptibility. From this we conclude that the bulk of the observed susceptibility arises from a source other than band spin paramagnetism.

The total observed susceptibilities (χ) then should contain contributions from the band spin paramagnetism of the 6s and 5d or 4f electrons (χ_{6s}^{spin} and $\chi_{5d \text{ or } 4f}^{\text{spin}}$, respectively); the Kubo-Obata orbital paramagnetism¹⁵ to be expected in partially filled, degenerate-band metals ($\chi_{5d \text{ or } 4f}^{\text{orb}}$), which has been shown to be important in understanding the electronic properties, Knight shifts and relaxation times of the NMR

of *d*-band superconductors,¹⁶ and the Landau diamagnetism and the diamagnetism of the ion cores (χ^{dia}).

$$\chi = \chi_{6s}^{\text{spin}} + \chi_{5d \text{ or } 4f}^{\text{spin}} + \chi_{5d \text{ or } 4f}^{\text{orb}} + \chi^{\text{dia}}. \quad (1)$$

The measured Knight shifts should contain contributions from each of these terms.

$$K = (1/2A\mu_B)[\chi_{6s}^{\text{spin}}H_{\text{HF}}^{6s} + \chi_{5d \text{ or } 4f}^{\text{spin}}H_{\text{HF}}^{5d \text{ or } 4f}] + (2/A)\chi_{5d \text{ or } 4f}^{\text{orb}}\langle 1/r^3 \rangle_{5d \text{ or } 4f}. \quad (2)$$

It is difficult to judge *a priori* the relative 5d and 4f character of the conduction band, so we shall examine the consequences of assuming first exclusively 5d and then exclusively 4f character for the non-6s part of the conduction band. H_{HF}^{6s} , H_{HF}^{5d} , and H_{HF}^{4f} are the hyperfine fields per unit spin of unpaired 6s, 5d, and 4f electrons. The diamagnetic terms contribute negligibly to the measured Knight shifts. $\langle 1/r^3 \rangle$ is the average of $1/r^3$ for the electrons contributing to the orbital paramagnetism, and A is Avogadro's number. Estimates of the contributions to the susceptibility and Knight shift of YbAl₂ are presented in Tables I and II for the 5d

TABLE I. Calculated contributions to the susceptibility and Knight shift of YbAl₂, assuming only 6s and 4f bands. The spin and orbital contributions to K are derived from the following relations: from spin $K = (1/2A\mu_B)\chi_{\text{mol}}H_{\text{HF}} = 0.89 \times 10^{-4}\chi_{\text{mol}}H_{\text{HF}}$; from orbit, $K = (2/A)\chi_{\text{mol}}\langle 1/r^3 \rangle_{4f} = 22.6\chi_{\text{mol}}\langle 1/r^3 \rangle$ (a.u.).

	$\chi_{\text{mol}} \times 10^6$	$H_{\text{HF}}(\text{Oe}) \times 10^{-6}$	$K(\%)$
Spin, 6s	+15.8	+6.05	+0.85
4f	+214	-0.90	-1.73
Orbit, ^a 4f	+566		+15.88
Diamagnetic	-35.5		0.00
Total	+760		+15.00
Observed	+760		+7.76

^a $\langle 1/r^3 \rangle_{4f} = 12.4$ a.u.

and 4f cases, respectively. χ_{6s}^{spin} is estimated on the basis of the free-electron model with one 6s electron per ytterbium atom. χ_{5d}^{spin} and χ_{4f}^{spin} are estimated from the specific heat $N(E_F)$ after subtracting the free-electron 6s contribution to $N(E_F)$. χ^{dia} is taken to consist of an ionic contribution of -29×10^{-6} emu/mole¹⁷

TABLE II. Calculated contributions to the susceptibility and Knight shift of YbAl₂, assuming only 6s and 5d bands.

	$\chi_{\text{mol}} \times 10^6$	$H_{\text{HF}}(\text{Oe}) \times 10^{-6}$	$K(\%)$
Spin, 6s	+15.8	+6.05	+0.85
5d	+214	-2.40	-4.60
Orbit, ^a 5d	+566		+3.19
Diamagnetic	-35.5		0.00
Total	+760		-0.56
Observed	+760		+7.76

^a $\langle 1/r^3 \rangle_{5d} = 2.5$ a.u.

¹⁴ V. Jaccarino, B. T. Matthias, M. Peter, H. Suhl, and J. H. Wernick, Phys. Rev. Letters **5**, 251 (1960).

¹⁵ R. Kubo and Y. Obata, J. Phys. Soc. Japan **11**, 547 (1956).

¹⁶ A. M. Clogston, A. C. Gossard, V. Jaccarino, and Y. Yafet, Phys. Rev. Letters **9**, 262 (1962).

¹⁷ W. R. Angus, Proc. Roy. Soc. (London) **A136**, 569 (1932).

and a $6s$ free-electron contribution of -6.5×10^{-6} emu/mole. χ_{5d}^{orb} and χ_{4f}^{orb} are then taken to be the difference between the observed susceptibility and these calculated contributions from the other sources. H_{HF}^{6s} is obtained from the hyperfine field measured by optical hfs spectroscopy in the $^2S_{1/2}$ state of the free Yb^{+1} ion.¹⁸ This must be reduced by a factor of approximately 0.5 to account for the reduced amplitude of the $6s$ electron wave function at the nucleus in the metallic environment.¹⁹ A further reduction by a factor of 0.7 results from the change of H_{HF} with ionicity. H_{HF}^{5d} is an estimate of the core polarization hyperfine field of $5d$ electrons based on NMR results in Pt metal.²⁰ H_{HF}^{4f} is based on hyperfine interactions observed in EPR measurements of Gd^{3+} ions. We take $\langle 1/r^3 \rangle_{5d} = 2.5$ a.u. as a reasonable estimate for the $5d$ electrons.²¹ For $4f$ electrons, the EPR hyperfine interaction of Yb^{3+} , taken with our measured Yb^{171} nuclear magnetic moment value, indicates $\langle 1/r^3 \rangle_{4f} = 12.4$ a.u. As seen from Tables I and II, the observed Knight shift lies between the predicted values for exclusively $4f$ character and exclusively $5d$ character. Inclusion of $4f$ and $5d$ bands simultaneously would improve the agreement with ex-

periment. Rocher²² has suggested that the $4f$ levels in pure Yb metal may lie very near the Fermi level. Our results indicate that in YbAl_2 such $4f$ levels may actually form part of the conduction band and have important effects on the magnetic properties.

An approximate value of the nuclear spin-lattice relaxation time T_1 was also measured in YbAl_2 by observing the saturation of the resonance absorption. At 1.8°K , we find $T_1 T = 0.12$ sec $^\circ\text{K}$. A Knight shift of 0.85% arising from $6s$ conduction electrons would be expected²³ to produce a $T_1 T$ of 0.13 sec $^\circ\text{K}$, nearly enough to account for the observed relaxation. Core polarization and orbital hyperfine interactions should also produce relaxation, but will likely be less effective than the direct contact interaction of $6s$ electrons.

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²³ J. Korringa, *Physica* **16**, 601 (1950).

¹⁸ K. Krebs and H. Nelkowski, *Z. Physik* **141**, 254 (1955).

¹⁹ W. D. Knight, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 2, p. 93.

²⁰ A. M. Clogston and V. Jaccarino, *Bull. Am. Phys. Soc.* **7**, 293 (1962).

²¹ F. R. Petersen and H. A. Shugart, *Phys. Rev.* **126**, 252 (1962).

Production of Displacement Radiation Effects by Recoils from Photoneutron Reactions*

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The photoneutron method of producing displacement radiation effects has been established. The displacement effects produced by recoils from $\text{Si}(\gamma, n)$ reactions have been detected by measurement of the change in excess-carrier lifetime. The change in the reciprocal of the lifetime is approximately proportional to the total number of primary reactions at various irradiating bremsstrahlung energies between 15 and 38 MeV, with a proportionality constant of $(2.0 \times 10^{-4} \pm 25\%) \text{cm}^3 \text{sec}^{-1}$. The data can be explained on the basis that the primary energy loss of the recoil atoms is due to ionization. Other possible explanations are offered and a comparison of the results with those of 30-MeV electron irradiations is made.

I. INTRODUCTION

A PHOTONUCLEAR reaction resulting in the emission of a neutron imparts a significant recoil energy to the residual nucleus. If this residual nucleus is in a crystal lattice, it will be displaced from its lattice position and will subsequently displace a large number

of other atoms before its energy is dissipated. The resulting cascade of displacing collisions is very similar to that produced by elastic scattering of high-energy (~ 1 MeV) neutrons from the same nucleus. Hence, the defects introduced are expected to be similar to those produced by nuclear reactor irradiation.

The purpose of the work described here was to measure the relative rates of defect production in silicon by various energy bremsstrahlung spectra and, hence, to

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