Knight Shift and Quadrupole Interaction in Tc Metal

WILLIAM H. JONES, JR., AND FREDERICK J. MILFORD
Battelle Memorial Institute, Columbus, Ohio

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The nuclear magnetic resonance of the Tc^{99} nucleus in technetium metal has been observed. The shape and position of the resonance are due to combinations of isotropic and anisotropic Knight shifts, first and second order quadrupole interactions, and dipolar broadening. The various contributions have been separated by studying the characteristics of the resonance as a function of frequency.

INTRODUCTION

NUCLEAR magnetic resonance has been observed in the hexagonal metals beryllium,[1,2] magnesium,[2] lanthanum,[3] and scandium.[3] Since the hexagonal crystal structure allows an axial electrical field gradient as well as anisotropy of the Knight shift, and since further each of the nuclei in question has a spin greater than $\frac{1}{2}$ and thus generally possesses a quadrupole moment, one might expect to observe a combination of isotropic and anisotropic Knight shifts and first- and second-order quadrupole effects. In none of the reports on hexagonal metals, however, were all four effects observed. Beryllium has a small quadrupole moment and a negligible Knight shift. As a result, observations on beryllium show only the first-order quadrupole splitting. Magnesium, on the other hand, shows both a Knight shift and a second-order quadrupole broadening; the signal to noise ratio is so poor for metallic magnesium, however, that it is not possible to observe the quadrupole satellites, nor is it possible to experiment at a variety of frequencies in an attempt to separate the anisotropic Knight shift from the second-order quadrupole effect. In the case of scandium and lanthanum, only, the Knight shift was observed. First-order quadrupole satellites, anisotropic Knight shift, and second-order quadrupole effect were not observed. Observations on another class of materials, namely the cubic Laves phase rare-earth aluminum compounds,[4–6] have shown the simultaneous effects of all four interactions. In the present paper we report the observation of the nuclear magnetic resonance of Tc^{99} in technetium metal. Each of the effects noted above has been observed, and by making measurements at a number of frequencies they have been separated.

EXPERIMENTS

The technetium sample used in these experiments consisted of one gram of powdered technetium metal obtained from Oak Ridge National Laboratory. Observations were made using a Varian model V4200 wide-line nuclear magnetic resonance spectrometer with field sweep. The field was measured by a simple NMR gaussmeter using either the Li^7 or the H^1 resonance. The gaussmeter probe contained LiCl in an aqueous solution with $MnSO_4$ added to reduce the relaxation time. Frequencies were measured with a Hewlett-Packard model 524D frequency counter. A typical trace at approximately 10 Mc/sec displaying the central resonance and satellites is shown in Fig. 1. Similar recordings were made at a number of frequencies between 3 and 10 Mc/sec as specified in Table I. At the lower frequencies the second-order quadrupole splitting leads to a pronounced asymmetry in the shape of the central resonance. These effects may be seen

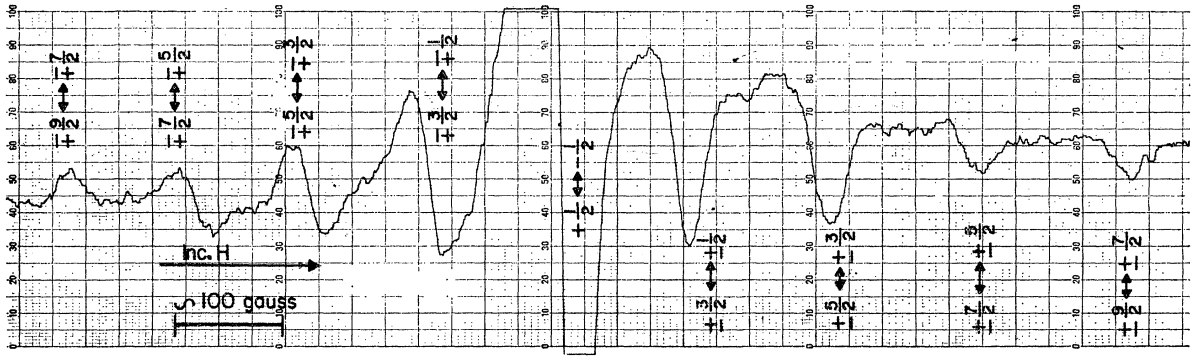

FIG. 1. Tc^{99} nuclear resonance at approximately 10 Mc/sec, showing central resonance and eight satellites.

[1] W. D. Knight, Phys. Rev. **92**, 539 (1953).
[2] T. J. Rowland (to be published).
[3] W. E. Blumberg, J. T. Eisinger, V. Jaccarino, and B. T. Matthias, Phys. Rev. Letters **5**, 52 (1960).
[4] R. G. Barnes, W. H. Jones, Jr., and T. P. Graham, Phys. Rev. Letters **6**, 221, 506(E) (1961).
[5] V. Jaccarino, B. T. Matthias, M. Peter, H. Suhl, and J. H. Wernick, Phys. Rev. Letters **5**, 251 (1960).
[6] V. Jaccarino, J. Appl. Phys. **32**, 102S (1961).

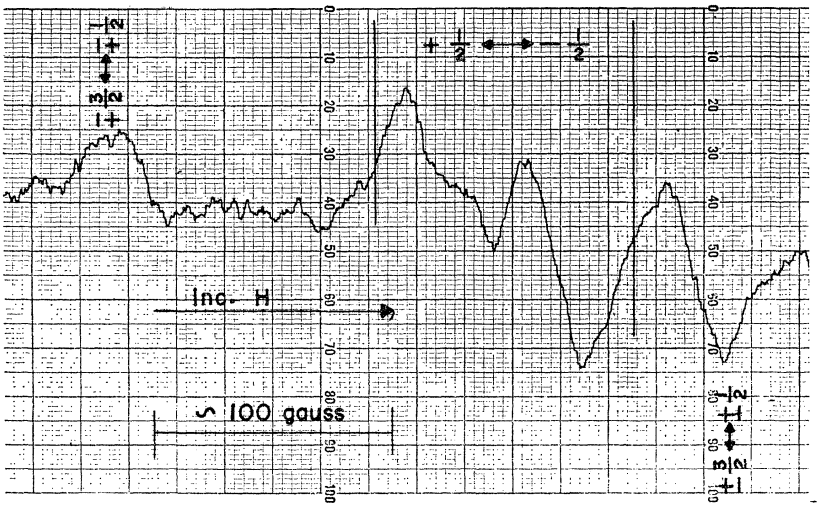

FIG. 2. Tc^{99} nuclear resonance at approximately 3 Mc/sec, showing the shape of the central resonance when anisotropic Knight-shift and second-order quadrupole effects are comparable.

plainly in the trace of Fig. 2 which was recorded at approximately 3 Mc/sec. At three frequencies the positions of the $\pm\frac{1}{2}$ to $\pm\frac{3}{2}$ transition were measured. In addition, for two of the higher frequencies the positions of the $\pm\frac{3}{2}$ to $\pm\frac{5}{2}$ resonance were measured. Poor signal-to-noise ratio precluded this latter measurement at the lower frequencies. Accurate field-frequency positions were determined for the two major peaks in the central resonance at each frequency. From these, the average shifts of the resonance and the peak-to-peak linewidths were determined. Since no observations were made on nonmetallic Tc-containing materials, all shifts reported are relative to the observations of Walchli *et al.*[7] (without diamagnetic correction) on NH_4TcO_4. To check the accuracy of the measuring technique the Na^{23} resonance was observed in an aqueous solution of NaCl. The result, a resonance frequency of 11.262 Mc/sec in a field of 10 000 gauss, is in excellent agreement with previously published results[8] and convincingly demonstrates the accuracy of the techniques which were used.

TABLE I. Line shift, linewidth, and quadrupole coupling constants for Tc^{99} nuclear resonance in Tc metal at various frequencies.

ν_0 (Mc/sec)	K (%)	ΔH (gauss)	Quadrupole coupling constant from satellites $\pm\frac{3}{2}\leftrightarrow\pm\frac{1}{2}$	$\pm\frac{5}{2}\leftrightarrow\pm\frac{3}{2}$
3.4036	+0.405	77.1	5.821	...
4.3612	+0.501	61.5	...	...
5.9277	+0.589	46.5	...	...
6.9676	+0.622	39.3	...	...
8.0176	+0.610	33.0	5.851	5.675
10.2072	+0.629	25.2	...	...
10.2083	+0.620	24.3	5.902	5.715

[7] H. Walchli, R. Livingston, and W. J. Martin, Phys. Rev. **85**, 479 (1952).

[8] T. Kanda, Y. Masuda, R. Kusaka, Y. Yamagat, and J. Itoh, Phys. Rev. **85**, 938 (1952).

DISCUSSION

The data obtained above can be used to obtain values for the quadrupole coupling, the isotropic Knight shift, and the anisotropic Knight-shift parameter in technetium metal. The most directly interpretable data are the splittings of the satellites. From these, through the use of the appropriate second-order perturbation formulas, one may obtain the quadrupole interaction frequency ν_Q, which is defined by

$$\nu_Q=\frac{3e^2qQ}{2I(2I-1)h}(1-\gamma_\infty). \tag{1}$$

In this expression eQ is the nuclear electric quadrupole moment, eq is the electric field gradient parameter, $eq=V_{zz}=\partial^2V/\partial Z^2$, and γ_∞ is the Sternheimer antishielding constant[9] which takes into account the polarizability of the technetium ion. The results obtained in this way for the quadrupole interaction, $(e^2qQ/h)(1-\gamma_\infty)$, are given in Table I. It is worth noting that the conversion from gauss to Mc/sec which is made in Table I for the quadrupole interaction frequency must be made using 9.6522×10^{-4} Mc/sec per gauss rather than 9.5837×10^{-4} Mc/sec per gauss in order to take into account the effect of the Knight shift on field-sweep results. This difference, however, has only about a 0.7% effect on ν_Q and thus does not contribute substantially to the uncertainty in this quantity even though the Knight shift is not known with extreme accuracy.

The shape and position of the central resonance reflect the simultaneous effects of the anisotropic Knight shift and second-order quadrupole interactions. One may recognize four regions according to the values of the parameter $a\nu^2/b$, with a and b as defined below. In each of these regions there is a distinctly different

[9] R. Sternheimer, Phys. Rev. **80**, 102 (1950) and subsequent publications.

line shape and a different dependence of the line shift on frequency. A detailed discussion of the line shapes and shifts will appear in a forthcoming paper by Branes and Jones.[10] For the discussion of the Knight shift and quadrupole effects in technetium it will be sufficient to restrict ourselves to the range $-8/3<a\nu^2/b<1/3$ where the quadrupole interaction dominates and the line shape consequently has the well-known second order quadrupole shape. It should be noted that for the 8- and 10-Mc/sec observations $a\nu^2/b>\frac{1}{3}$; however, assuming that the derivative maxima which were measured correspond to true singularities in the unbroadened line shape is sufficient to insure the validity of expressions (2) and (5) used below for values of ν that correspond to $a\nu^2/b<10/3$.[10] If δ_1 and δ_2 are defined as the positions of the derivative maxima of the central resonance with respect to the Larmor frequency of a Tc^{99} nucleus in the external field H_0, we have for the linewidth, $\delta_1-\delta_2$, the following expression:

$$\delta_1-\delta_2=\sigma-\frac{5}{3}a\nu+\frac{25}{9}\frac{b}{\nu}+\frac{1}{4}\frac{a^2}{b}\nu^3, \tag{2}$$

with σ the width due to dipolar broadening and

$$b=\tfrac{1}{16}\nu_Q^2[I(I+1)-\tfrac{3}{4}], \tag{3}$$

$$a=\tfrac{1}{3}[(\Delta\nu_{11}-\Delta\nu_\perp)/\nu]. \tag{4}$$

In (4), $\Delta\nu_{11}$ and $\Delta\nu_\perp$ are the anisotropic Knight shift in the direction parallel and perpendicular to the symmetry axis in a situation of axial symmetry as defined by Bloembergen and Rowland.[11] It is convenient to recall that $\Delta\nu_{11}=-2\Delta\nu_\perp$. Subject to the same restriction on $a\nu^2/b$, the average shift in position of the central resonance with respect to the same resonance in the reference compound is given by

$$K=\frac{\delta_1+\delta_2}{2\nu}=(k-\tfrac{1}{6}a)-\frac{7}{18}\frac{b}{\nu^2}-\frac{1}{8}\frac{a^2}{b}\nu^2, \tag{5}$$

with k the isotropic Knight shift. Outside of the indicated range different expressions apply for the linewidth and the line shift. We may note that in Eqs. (2) and (5) four parameters, namely σ, a, b, and k occur. Given sufficiently accurate data, all four of these parameters may be determined.

Using $1/\nu$ as the independent variable, a least-squares fit of (2) to the experimental data can be made. The fact that the coefficient of ν^3 depends on the coefficients of ν and $1/\nu$ introduces some complexity in the least-squares procedure and prevents the exact minimization of the sum of the squared deviations in a simple way. It might be expected that an iterative procedure could be used, however, straightforward iteration seems to be a divergent procedure for our data and the functional

[10] W. H. Jones, Jr., T. P. Graham, and R. G. Barnes (to be published).

[11] N. Bloembergen and T. J. Rowland, Acta. Met. **1**, 731 (1953).

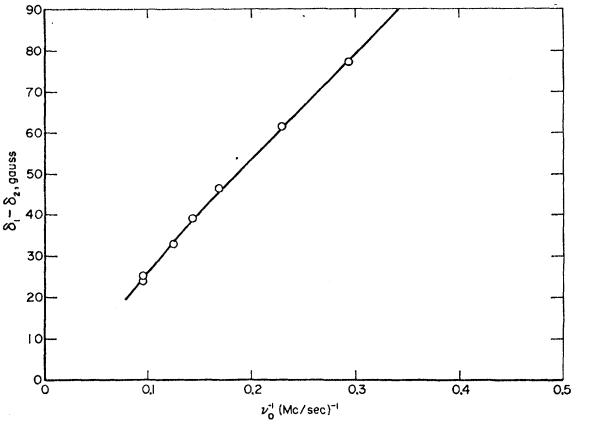

FIG. 3. Width of central resonance as a function of reciprocal frequency. Experimental points and least-squares fit.

form (2).[12] This difficulty can be circumvented, however, by an inelegant procedure which is convergent and which ultimately minimizes the sum of the squared deviations. The results of carrying through this procedure are $\sigma=13.0\pm0.5$ gauss, $b=84.06\pm0.2$ gauss Mc/sec, and $a=0.72\pm0.06$ gauss (mc/sec)$^{-1}$. The experimental data and the least-squares fit to it are shown in Fig. 3. Figure 4 shows the same results plotted in a different way namely $\nu(\delta_1-\delta_2)$ vs ν^2. Reasonable agreement is to be expected but nonetheless the fact that it is achieved in spite of a major change in weighting factor is reassuring. The motive for plotting the data as is done in Fig. 4 is that the slope of the curve for large values of ν^2 is just $-(5/3)a$. It is apparent that a larger value of a would fit the data better when weighted this way.

The line-shift data can also be treated by least-squares fitting. For these data the functional form (5) is appropriate and the fitting parameters may be taken

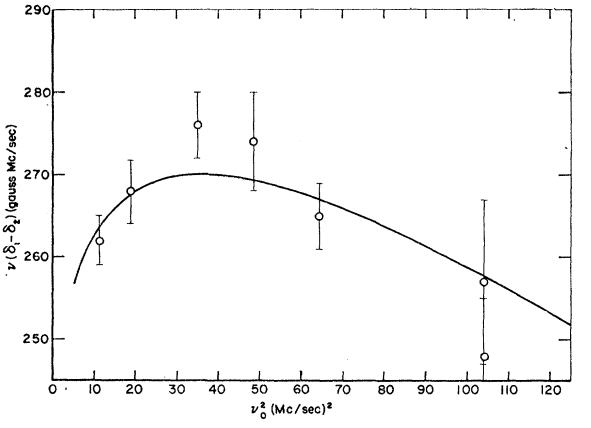

FIG. 4. Frequency times linewidth as a function of frequency squared. Experimental points and curve calculated from least-squares fit shown in Fig. 3. Vertical bars are error estimates for observation.

[12] Z. Kopal, *Numerical Analysis* (John Wiley & Sons, Inc., New York, 1955), p. 111.

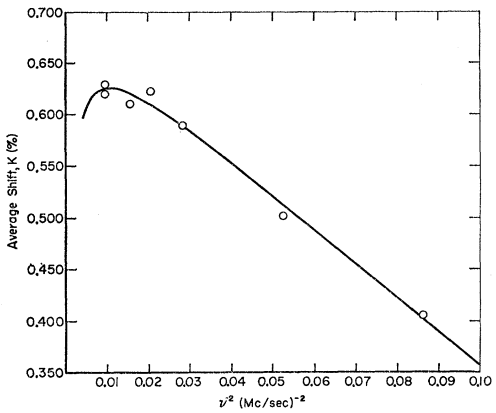

FIG. 5. Average shift of central resonance as a function of reciprocal frequency squared. Experimental points and least-squares fit.

as $k-a/6$, b, and a^2/b. This set of parameters enters linearly in (5) and thus the least-squares fitting can be accomplished exactly by solving a single set of three simultaneous linear equations. The results of this fitting are $k-a/6=0.00696$, $b=0.08678=(\text{Mc/sec})^2$, $a=1.626\times10^{-3}$. The experimental data and the least-squares fit to them are shown in Fig. 5.

The results obtained by the three methods described above have been converted to a common set of units and tabulated in Table II. Also given are weighted averages which represent our best estimates of the true values.

TABLE II. Quadrupole coupling constants, dipolar width, anisotropic Knight shift parameter, and isotropic Knight shift for Tc^{99} resonance in Tc metal as obtained by various methods.

Method	Coupling constant (Mc/sec)	σ (gauss)	a	k %
First-order satellites	5.793	...	...	...
Linewidth	5.582	13.0	0.695×10^{-3}	...
Line shift	5.772	...	1.626×10^{-3}	0.723
Average	5.716	13.0	1.160×10^{-3}	0.715

SUMMARY

The nuclear magnetic resonance of the Tc^{99} nucleus in metallic technetium has been observed. This resonance displays the full first-order quadrupole splitting into a central resonance and eight satellites, four on either side. Furthermore, the central resonance displays the anisotropic Knight shift and quadrupole effects. The accuracy of the data has been sufficient to obtain values for the quadrupole interaction frequency; the Knight shift; the anisotropic Knight-shift parameter; and the dipolar linewidth. In addition to these features of the technetium resonance, there are a number of others which will be interesting to study. Among these we note the temperature dependence of the Knight shift and the characteristics of the resonance in technetium alloys. Work on these topics is continuing.

ACKNOWLEDGMENTS

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