Recoil-Free Absorption Hyperfine Spectra of the 90-keV Mixed Transition in Ru^{99}†

O. C. KISTNER
Brookhaven National Laboratory, Upton, New York
(Received 15 December 1965)

The Mössbauer effect was employed to measure hyperfine splittings of the 90-keV transition in Ru^{99}. A fully resolved magnetic hyperfine pattern was obtained with an absorber consisting of a solid solution of 2.3 at.% enriched ruthenium in metallic iron. Partially resolved quadrupole hyperfine spectra were obtained with absorbers of $Ru(C_5H_5)_2$ and RuO_2. A single line source of Rh^{99} in metallic ruthenium was used for these measurements. From these spectra the following information was deduced. The ratio of the magnetic g factors of the 90-keV level to that of the ground state, $g_1/g_0=0.759\pm0.016$. The 90-keV transition is a mixture of dipole and quadrupole ($M1$ and $E2$) radiation with a mixing ratio $E2/M1=\delta^2=2.7\pm0.6$. By using the known spin and magnetic moment of the ground state, we infer that the spin of the 90-keV level is $\frac{3}{2}$, that $g_1=0.19\pm0.05$, and that the field at the nucleus of the ruthenium atom in the iron environment is 500 kG. The ratio of the quadrupole moment of the excited state to that of the ground state, $|Q_1/Q_0|\geq3$, and $|Q_1|\geq0.15$ b. With the use of a 30-kG superconducting solenoid the relative sign of the magnetic field at the ruthenium nucleus in the iron absorber was shown to be negative and an absolute measurement of the nuclear g factors was made with the result that $g_1=0.20\pm0.02$. A measurement of the absorption spectrum of ferromagnetic $GdRu_2$ gave the result that the magnetic field at the ruthenium nucleus in this compound is <10 kG. Hyperfine measurements were made with the ruthenium-iron absorber magnetically polarized both parallel and perpendicular to the direction of the resonant radiation. Under these conditions it was possible to observe, for the first time, the interference between two multipole components for the individual hyperfine components of a radiative transition. From these measurements the sign of the conventional mixing parameter δ was determined to be negative, and an upper limit of 30% could be placed on the time-reversal-odd component of the gamma-decay matrix element. The properties of the 90-keV level, which are not compatible with a simple shell-model description, are compared with the predictions of a core-excitation description. If the latter description is correct, then these results give evidence that the magnitude of the time-average quadrupole moment associated with the 2+ core is ≥0.29 b.

I. INTRODUCTION

THE observation of recoilless resonance absorption employing the 90-keV transition in Ru^{99} has previously been reported.[1] The 90-keV first-excited state of Ru^{99} has a half-life[2] of 2.0×10^{-8} sec and is populated in the electron capture decay of 16-day Rh^{99}. The ground state of Ru^{99} has a spin[3] of $\frac{5}{2}$ and a magnetic moment[4] of -0.63 ± 0.15 nm. The spin of the 90-keV level and the multipole character of its radiative decay, however, cannot be unambiguously determined from previously published data. Temmer and Heydenburg[5] have found an enhanced $E2$ transition rate to the 90-keV level in Coulomb excitation measurements and suggest that the spin of this level is probably $\frac{1}{2}$ or $\frac{3}{2}$ because of the lack of feeding from the long-lived Tc^{99} isotope.

The present paper reports on measurements, employing the Mössbauer effect, of the hyperfine splitting of the 90-keV gamma transition in Ru^{99}. A fully resolved magnetic hyperfine pattern was obtained with an absorber of enriched ruthenium dissolved in iron. The largest quadrupole splittings were observed with absorbers of ruthenocene and ruthenium dioxide and were only partially resolved. These measurements provide a direct determination of the spin of the 90-keV level, the multipole composition of the radiative transition, the ratio of the magnetic dipole moments, and a lower limit of the ratio of the electric quadrupole moment of the 90-keV level to that of the ground state. From an estimated upper limit of the electric field gradient at the ruthenium nuclei in the above compounds, a lower limit for the electric quadrupole moment of the excited state was obtained. With the help of a 30-kG superconducting solenoid the absolute values of the nuclear magnetic moments as well as the relative sign of the magnetic field at the ruthenium nucleus in the iron lattice were determined.

Of particular interest is the multipole character of the 90-keV gamma ray, which was found to be a mixture of comparable parts of dipole and quadrupole ($M1$ and $E2$) radiation. It was possible for the first time by employing the Mössbauer effect to observe the interference terms for the individual Zeeman components of a mixed transition. From these measurements the relative phase between the $M1$ and $E2$ components was determined, and a preliminary limit of time-reversal invariance for the nuclear radiative process was deduced. The results of the nuclear-moment measurements are compared with the predictions of a core-excitation description of the 90-keV level. A collective character for this level is suggested by the relative $M1$ and $E2$ transition rates for the 90-keV gamma ray.

Two independent determinations of the magnetic g

† Work performed under the auspices of the U. S. Atomic Energy Commission.
[1] O. C. Kistner, S. Monaro, and R. Segnan, Phys. Letters **5**, 299 (1963).
[2] O. C. Kistner, S. Monaro, and A. Schwarzschild, Phys. Rev. **137**, B23 (1965).
[3] J. H. E. Griffiths and J. Owen, Proc. Phys. Soc. (London) **A65**, 951 (1952).
[4] K. Murakawa, J. Phys. Soc. Japan **10**, 919 (1955).
[5] G. M. Temmer and N. P. Heydenburg, Phys. Rev. **104**, 967 (1956).

factor of the 90-keV level,[6,7] which employed the precession of an angular correlation in an applied magnetic field, have been reported since preliminary results of the present work have appeared.[8] These two measurements, however, are in considerable disagreement with one another. The present results resolve this disagreement.

II. EXPERIMENTAL APPARATUS AND PROCEDURE

The recoil-free resonance velocity spectra were measured by the conventional gamma-ray transmission method. The continuous velocity sweeping and multichannel-analyzer data storage technique was used in a manner similar to that described in an earlier paper.[9] The electro-mechanical transducer and velocity pickup in this case consisted of a pair of modified loud speakers mechanically coupled together. The impregnated cloth suspensions of the voice coils were replaced by beryllium-copper leaf springs. This device was driven by a sine-wave signal of ~40 cps which was applied to one of the voice coils. Velocity to pulse-height conversion was achieved by driving the pulse-height sensing circuit of a 400-channel pulse-height analyzer with the amplified signal derived from the second voice coil. For moderate amplitudes this signal is directly proportional to the instantaneous velocity. A 3-mm-thick $\times 1\frac{1}{2}$-in.-diameter beryllium window NaI(Tl) scintillation counter was used to detect the 90-keV gamma rays. These counts were stored in one half of the multichannel analyzer. Random counts from an auxiliary source and counter were stored simultaneously in the second half of the analyzer. The resonant spectrum was then both normalized for the nonuniform time distribution of the sine-wave motion and corrected for the dead time effects of the multichannel analyzer, by dividing it, channel for channel, by the nonresonant spectrum stored in the second half.

Both source and absorber for all of the following hyperfine spectrum measurements were maintained at liquid-helium temperature. The arrangement of the helium cryostat is shown in Fig. 1. The motion was transmitted to the bottom of an evacuated tube in the helium Dewar by means of a length of $\frac{1}{4}$-in.-diameter thin-walled stainless steel tubing. The vacuum seal between the drive tube and the inner volume of the helium Dewar was made by means of a pair of very flexible metal bellows placed in opposition so that the forces due to atmospheric pressure were cancelled out.

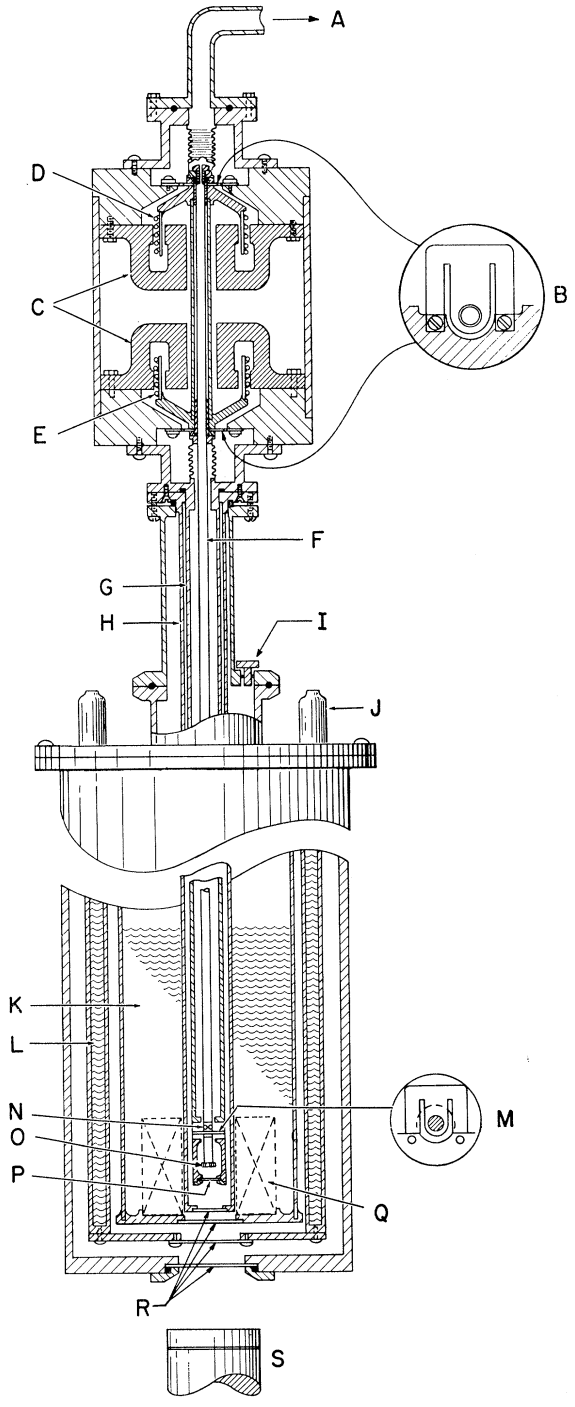

FIG. 1. Arrangement of the Mössbauer transducer and liquid-helium cryostat. A, to vacuum pump or exchange gas. B, beryllium copper leaf support springs. C, loudspeaker magnets. D, driving voice coil. E, velocity pickup voice coil. F, $\frac{1}{4}$-in.-diameter thin-walled stainless steel drive tube. G, $\frac{3}{4}$-in.-diameter absorber support tube. H, 1-in.-diameter vacuum jacket. I, liquid-He fill. J, liquid-N_2 fill. K, liquid-He reservoir. L, liquid-N_2 reservoir. M, thin brass leaf guide spring. N, vent holes. O, source. P, absorber. Q, position of superconducting solenoid. R, thin gamma-ray exit windows. S, gamma-ray detector.

[6] E. Matthias, S. S. Rosenblum, and D. A. Shirley, Phys. Rev. **139**, B532 (1965).

[7] E. Bodenstedt, C. Gunther, J. Radeloff, W. Engels, W. Delang, M. Forker, and H. Luig, Phys. Letters **15**, 296 (1965). The sign of the g factor reported in this paper was reversed (making it negative) in a subsequent erratum, Phys. Letters **15**, 296 (1965).

[8] O. C. Kistner and R. Segnan, Bull. Am. Phys. Soc. **9**, 396 (1964).

[9] O. C. Kistner, A. W. Sunyar, and J. B. Swan, Phys. Rev. **123**, 179 (1961).

Thermal contact of the source and absorber with the liquid helium was made by introducing a small amount of helium gas into the evacuated volume. Beryllium windows were located at the bottom of the Dewar to provide an exit for the gamma rays. The system was velocity calibrated from a measurement of the well-known[10] absorption lines of Fe^{57} in an iron foil. A single line source of Co^{57} in copper was used for this purpose.

III. SOURCE PREPARATION

The sources for these measurements consisted of 16-day Rh^{99} contained in a host lattice of ruthenium metal. They were prepared by (p,n) reaction on metallic ruthenium with 10-MeV protons at the Brookhaven cyclotron. Sources were made both from natural ruthenium and from ruthenium enriched in Ru^{99}. The latter had the advantage of being freer of contaminating activities though the former were quite usable for the limited period between 2 weeks to 4 weeks after bombardment.

The velocity absorption spectra obtained with these sources and an absorber of 100 mg/cm^2 of natural ruthenium metal powder exhibited a single resonance line having a full width at half-maximum of 0.24 mm/sec. This width is 1.6 times that expected from the known lifetime. Part of this broadening can be attributed to self absorption in the ruthenium metal sources. Annealing of this source at 1000°C for 1 h gave no improvement in the width of the resonance line observed. The recoil-free fraction of the ruthenium metal sources was estimated to be approximately 14% at 4.2°K from measurements with different absorber thicknesses at both 4.2° and 77°K. This corresponds to a Debye temperature of ~380°K.

IV. ZEEMAN HYPERFINE SPECTRA

(A) Unpolarized Absorbers

Three ferromagnetic ruthenium absorbers,[11] $Ru_{0.3}Co_{0.7}$, $GdRu_2$, and $Ru_{0.023}Fe_{0.977}$ were examined for magnetic hyperfine splittings. Only the last of these gave a resolvable hyperfine splitting.

The $Ru_{0.3}Co_{0.7}$ absorber was prepared with natural ruthenium and therefore required the relatively large percentage of ruthenium in order to make the recoilless resonance absorption sufficiently large. Ruthenium and cobalt are reportedly completely soluble in one another; the Curie temperature of the mixture decreases with increasing ruthenium concentration passing through 0°C at 33 at.%.[12] The Mössbauer absorption spectrum showed a single, considerably broadened resonance having a full width at half-maximum of ~0.96 mm/sec, or approximately six natural linewidths.

$GdRu_2$ is a cubic laves phase compound which is reported to have a ferromagnetic Curie point of 84°K.[13] The Mössbauer absorption spectrum of this material showed a single resonance which had a width of 0.26 mm/sec, comparable to that obtained with ruthenium metal.

The $Ru_{0.023}Fe_{0.977}$ absorber was prepared with enriched ruthenium so as to keep the concentration of ruthenium required as low as possible. A limited solubility of ruthenium in iron has been observed. At 2.3 at.% ruthenium the α phase is stable up to 850°C and the Curie point is at 750°C.[14] The alloy was made by melting 85 mg of ruthenium metal enriched to 86% in Ru^{99} together with 2 grams of iron. The resulting button was pressed flat to form a disk with a Ru^{99} area density of 58 mg/cm^2. Finally, the sample was annealed in vacuum at 800°C for 4 hours. X-ray examination of this absorber showed little or no preferred orientation either before or after annealing. The annealing, however, did result in a considerable improvement in the resolution of the x-ray diffraction pattern.

A well-resolved magnetic hyperfine pattern was obtained with this absorber. The spectrum shown in Fig. 2(a) was recorded in 230 hours of continuous running time. The pattern consists of 18 nearly equally spaced lines spread over a velocity range of 5.6 mm/sec. The positions of the lines are symmetric with respect to the center of the pattern within the accuracy of the measurement thereby excluding the presence of any significant amount of quadrupole interaction. There is a very small shift of the center of the pattern relative to zero velocity (isomeric chemical shift) of −0.024 mm/sec. A spectrum obtained with this absorber before annealing exhibited a small broad background resonance near the central portion of the pattern.

In order to interpret the spectrum, a visual comparison was made with theoretical graphs showing the relative line positions of the hyperfine pattern *versus* the ratio of the gyromagnetic ratio of the excited state to that of the ground state, g_1/g_0. Because of the uncertainties in both the spin of the excited state and the multipolarity of the 90-keV radiation the possibilities of $\frac{1}{2}$-$\frac{5}{2}$, $\frac{3}{2}$-$\frac{5}{2}$, $\frac{5}{2}$-$\frac{5}{2}$, and $\frac{7}{2}$-$\frac{5}{2}$ transitions with both dipole and quadrupole radiation, when allowed, were considered. In the limit of a thin, nonoriented absorber, a good approximation in this case, the relative intensities of the components are given by the squares of the Clebsch-Gordan coefficients connecting the magnetic sublevels. Furthermore, when the absorber is unpolarized the interference terms (cross terms) for a mixture of multipoles average to zero and the intensities for the mixture are simply the sum of the intensities for the individual multipoles. A unique fit was found to the graph for a $\frac{3}{2}$-$\frac{5}{2}$ transition with a dipole-qudarupole ($M1-E2$)

[10] R. S. Preston, S. S. Hanna, and J. Heberle, Phys. Rev. **128**, 2207 (1962).

[11] These materials were kindly prepared for us by J. H. Wernick of Bell Telephone Laboratories, Murray Hill, New Jersey.

[12] Max Hansen, *Constitution of Binary Alloys* (McGraw-Hill Book Company, Inc., New York, 1958), p. 496.

[13] R. M. Bozorth, B. T. Matthias, H. Suhl, E. Corenzwit, and D. D. Davis, Phys. Rev. **115**, 1595 (1959).

[14] Max Hansen, *Constitution of Binary Alloys* (McGraw-Hill Book Company, Inc., New York, 1958), p. 704.

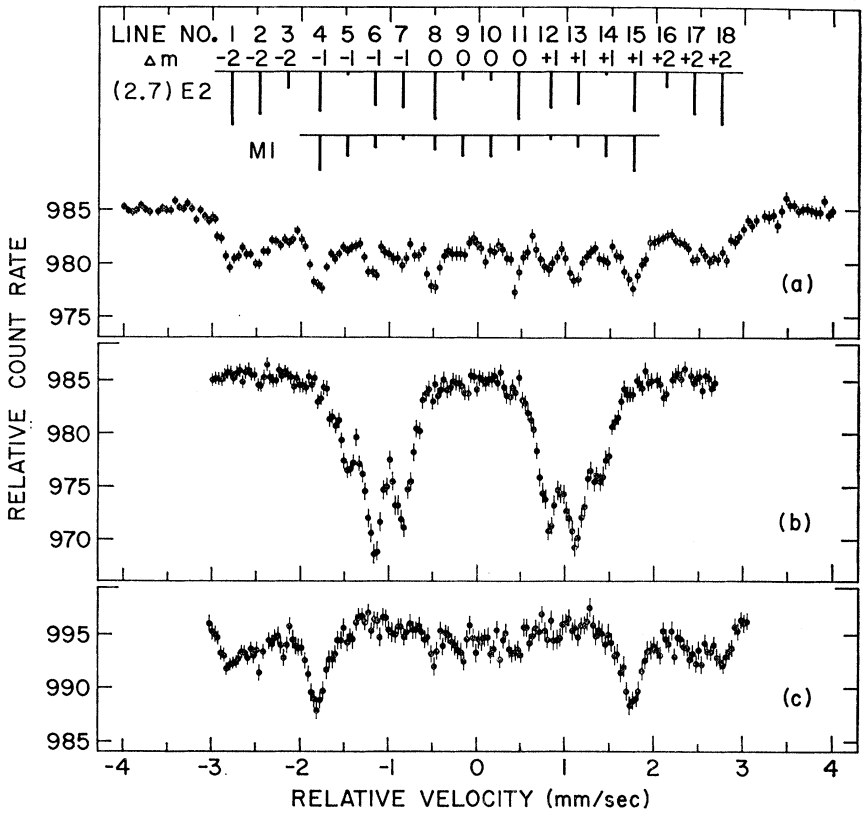

FIG. 2. Recoil-free resonance absorption spectra for the 90-keV transition in Ru^{99} with a source of Rh^{99} in Ru metal and an absorber of 2.3-at.% ruthenium dissolved in metallic iron. (a) Spectrum obtained with unpolarized absorber. The theoretical dipole ($M1$) and quadrupole ($E2$) absorption strengths, and the change in magnetic quantum number, Δm, are indicated for each absorption line. The "line Nos." assigned here correspond to those of Table I. (b) Spectrum obtained with absorber magnetized parallel to incident gamma rays. (c) Spectrum obtained with absorber magnetized perpendicular to incident gamma rays.

mixture.[15] The graph for this case is shown in Fig. 3 where the fit to the experimental data is indicated by the horizontal line. It is fortuitous that the ratio of g factors falls at almost the exact value where all of the hyperfine lines are spaced at equal intervals. The theoretical absorption strengths of each of the components for dipole and quadrupole radiation are indicated in Fig. 2(a) for comparison with the experimental spectrum. The splitting parameters deduced from this spectrum are $g_0H=(1.326\pm0.020)$ mm/sec [(95.8 ± 1.5) Mc/sec] and $g_1H=(1.007\pm0.018)$ mm/sec [(72.8 ± 1.3) Mc/sec] for the ground state[16] and first-excited state, respectively. The resulting ratio of g factors is $g_1/g_0=0.759\pm0.016$. With the known value[3] for u_0 of (-0.63 ± 0.15) nm, the field at the ruthenium nuclei in the iron absorber is deduced as (500 ± 120) kG.

The determination of the relative dipole and quadrupole contributions to the transition was greatly facilitated by making use of another fortunate feature of the hyperfine spectrum, namely, that the six $\Delta m=\pm2$ components, which have no dipole contribution, are

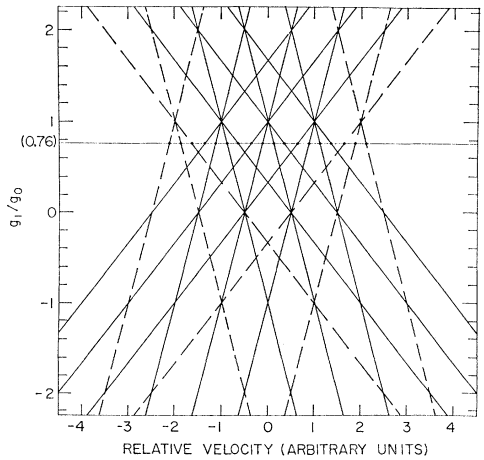

FIG. 3. Plot of relative position of magnetic hyperfine absorption lines as a function of the ratio of the magnetic g factor of the excited state to that of the ground state. This plot is for the case of a quadrupole (broken and solid lines) or dipole (solid lines only) transition between levels of spin $\frac{3}{2}$ and $\frac{5}{2}$. The horizontal line indicates the fit to the experimental spectrum. The magnetic quantum numbers for each line may be obtained from Table I numbering the lines consecutively from left to right at $g_1/g_0=0.76$.

[15] The Mössbauer absorption spectrum does not determine whether a radiative transition is electric or magnetic. The quadrupole component, however, has been identified as electric quadrupole ($E2$) by Coulomb excitation experiments (Ref. 5). This requires that the dipole component be magnetic dipole ($M1$). The $M1$-$E2$ assignment is also required by the systematics of multipole transitions rates.

[16] The $\frac{3}{2}$ spin has been assigned to the 90-keV level based on the previous spin assignment of $\frac{5}{2}$ for the ground state (Ref. 3). The value of g_0H deduced in the present experiment has been subsequently confirmed by J. I. Budnick, R. E. Gegenwarth, and J. H. Wernick, Bull. Am. Phys. Soc. **10**, 444 (1965), with nuclear magnetic resonance measurements, who report a maxima of the hyperfine field distribution at Ru^{99} nuclei in a 2.5% solution of ruthenium in iron of (96 ± 1) Mc/sec. This close agreement is good confirmation of the ground-state spin assignment for Ru^{99}.

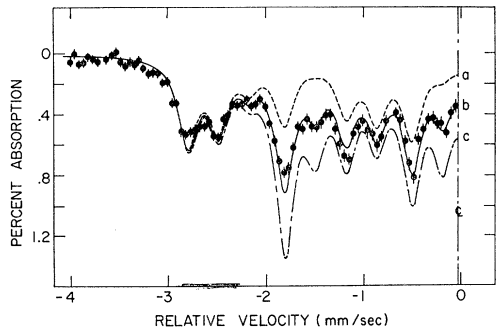

FIG. 4. Comparison of experimental Zeeman spectrum for unpolarized absorber to calculated curves for different values of the $E2/M1$ mixing ratio: (a) $\delta^2=\infty$; (b) $\delta^2=2.50$; (c), $\delta^2=1.25$. Curve b is normalized to area. The positive- and negative-velocity halves of the experimental spectrum have been added together folding about ℄.

located at the ends of the spectrum. (The change in the magnetic quantum number, Δm, corresponding to each absorption line is shown in Fig. 2(a).) The admixture could be simply determined from the ratio of the area under the six outer lines to the area under the remaining 12 central lines. For this analysis, a plot of the area ratio *versus* the $E2/M1$ mixing ratio δ^2 was obtained from a set of synthesized hyperfine spectra. These were computed from the experimental splitting parameters using Lorentz-shaped lines which had a width of 0.24 mm/sec. This width is compatible with the experimental spectrum near zero velocity where the the broadening due to finite velocity resolution is negligible. The thin-absorber approximation could be made in this case. The resulting value for δ^2 is 2.7 ± 0.6. In Fig. 4 the synthesized spectra for the cases of $\delta^2=\infty$ (pure $E2$), 2.50, and 1.25 are compared with the experimental data. In this plot the positive- and negative-velocity halves of the experimental spectrum have been added together folding about the center of symmetry at -0.024 mm/sec, in order to improve the statistical accuracy of the points and allow a more detailed comparison.

The magnetic quantum numbers, the Clebsch-Gordan coefficients (both for dipole and quadrupole components), and the resonance velocities for each of the hyperfine lines are listed in Table I for convenient reference.

(B) Magnetized Absorber

The interference between the dipole and quadrupole components of the radiation may be observed when the ruthenium iron absorber is magnetically polarized. The details of the interference will depend upon the relative phase angle between the two multipole amplitudes. The relative absorption strengths (which are the same as the corresponding emission intensities) for given $\Delta m=m_1-m_0$ hyperfine transitions in the magnetically aligned absorber are given by the following expressions[17]:

$$I(\theta)_{\Delta m=0}=\tfrac{3}{2}\sin^2\theta|C(J_11J_0;m_1,0,m_0)|^2+(15/8)\sin^2 2\theta|C(J_12J_0;m_1,0,m_0)|^2\delta^2,$$

$$I(\theta)_{\Delta m=\pm1}=\tfrac{3}{4}(1+\cos^2\theta)|C(J_11J_0;m_1,\mp1,m_0)\mp\tfrac{1}{2}(\sqrt{15})\cos\varphi(\cos^2\theta+\cos2\theta)\times C(J_11J_0;m_1,\mp1,m_0)\times C(J_12J_0;m_1,\mp1,m_0)+(5/4)(\cos^2\theta+\cos^2 2\theta)\times|C(J_12J_0;m_1,\mp1,m_0)|^2\delta^2,$$

$$I(\theta)_{\Delta m=\pm2}=(5/4)(\sin^2\theta+\tfrac{1}{4}\sin^2\theta)\times|C(J_12J_0;m_1,\mp2,m_0)|^2\delta^2.$$

$C(J_11J_0;m_1,-\Delta m,m_0)$ and $C(J_12J_0;m_1,-\Delta m,m_0)$ are the Clebsch-Gordan coefficients for the dipole and quadrupole components, respectively. J_1, m_1 and J_0, m_0 denote the spin and magnetic quantum number for the excited state and ground state, respectively. θ is the angle between the incident gamma ray and the direction of magnetization and φ is the relative phase angle between the dipole and quadrupole amplitudes. If the electromagnetic interaction with the nucleus is invariant with respect to time reversal, φ must be either 0° or 180°.[18] Note that an interference term is present only for the $\Delta m=\pm1$ components.

Absorption spectra were obtained with the Ru-Fe absorber magnetized both parallel and perpendicular to

TABLE I. Recoil-free hyperfine spectrum information for the 90-keV transition in Ru^{99}. Column 1, line Nos. corresponding to those of Fig. 2(a). Column 2, resonance velocities for a ruthenium metal source and $Ru_{0.023}Fe_{0.977}$ absorber. Column 3, magnetic quantum numbers m_1 and m_0 for the excited and ground states, respectively. Column 4, $\Delta m=m_1-m_0$. Columns 5 and 6, Clebsch-Gordan coefficients for dipole and quadrupole radiation, respectively.[a]

Line No.	Position (mm/sec)	m_0, m_1	Δm	$C(J_11J_0;$ $m_1,-\Delta m,m_0)$	$C(J_12J_0;$ $m_1,-\Delta m,m_0)$
1	−2.84	$\frac{5}{2}$, $\frac{1}{2}$	−2	0	0.756
2	−2.52	$\frac{3}{2}$, $-\frac{1}{2}$	−2	0	0.676
3	−2.20	$\frac{1}{2}$, $-\frac{3}{2}$	−2	0	0.414
4	−1.83	$\frac{5}{2}$, $\frac{3}{2}$	−1	1.000	0.655
5	−1.51	$\frac{3}{2}$, $\frac{1}{2}$	−1	0.775	−0.169
6	−1.19	$\frac{1}{2}$, $-\frac{1}{2}$	−1	0.548	−0.598
7	−0.871	$-\frac{1}{2}$, $-\frac{3}{2}$	−1	0.316	−0.621
8	−0.503	$\frac{3}{2}$, $\frac{3}{2}$	0	−0.632	−0.717
9	−0.184	$\frac{1}{2}$, $\frac{1}{2}$	0	−0.775	−0.293
10	0.136	$-\frac{1}{2}$, $-\frac{1}{2}$	0	−0.775	0.293
11	0.455	$-\frac{3}{2}$, $-\frac{3}{2}$	0	−0.632	0.717
12	0.823	$\frac{1}{2}$, $\frac{3}{2}$	1	0.316	0.621
13	1.14	$-\frac{1}{2}$, $\frac{1}{2}$	1	0.548	0.598
14	1.46	$-\frac{3}{2}$, $-\frac{1}{2}$	1	0.775	0.169
15	1.78	$-\frac{5}{2}$, $-\frac{3}{2}$	1	1.000	−0.655
16	2.15	$-\frac{1}{2}$, $\frac{3}{2}$	2	0	−0.414
17	2.47	$-\frac{3}{2}$, $\frac{1}{2}$	2	0	−0.676
18	2.79	$-\frac{5}{2}$, $-\frac{1}{2}$	2	0	−0.756

[a] From A. H. Wapstra, G. J. Nijgh, and R. Van Lieshout, *Nuclear Spectroscopy Tables* (North-Holland Publishing Company, Amsterdam, 1959), p. 124.

[17] H. Frauenfelder, D. E. Nagle, R. D. Taylor, D. R. F. Cochran, and W. M. Visscher, Phys. Rev. **126**, 1065 (1962) and more recently, J. T. Dehn, J. G. Marzolf, and J. F. Salmon, Phys. Rev. **135**, B1307 (1964). The form given here is from J. Weneser (unpublished).

[18] S. P. Lloyd, Phys. Rev. **81**, 161 (1951).

the direction of the incident γ rays. The simplest hyperfine pattern is obtained when the absorber is magnetized along the direction of the incident gamma rays. In this direction all but the $\Delta m=\pm 1$ components vanish. This requires magnetization of the absorber along the difficult direction of magnetization, i.e., perpendicular to the plane of the disk. The applied field must be sufficiently large to overcome the demagnetizing field induced in the sample which for pure iron can be as large as $\sim$22 kG. This was conveniently accomplished with a superconducting solenoid which provided an axial field of some 30 kG at the center of a one-inch-diameter bore. The spectrum shown in Fig. 2(b) was obtained with the source located on the axis of the solenoid in a fringe field of $\sim$5 kG and the absorber located near the center of the solenoid in a field of 29 kG. The complete absence of the $\Delta m=\pm 2, 0$ lines indicates essentially complete polarization of the absorber. Magnetization of the absorber in the transverse direction, i.e., in the plane of the absorber disk, was achieved with the use of a small permanent magnet. The spectrum obtained in this case is shown in Fig. 2(c).

Theoretical absorption spectra were calculated with the above expressions for comparison with the experimental spectra. The splitting parameters and mixing ratio determined in the previous sections were used. For these spectra a more exact calculation was made which took into account the finite absorber thickness. This was necessary because the effective cross sections for some of the lines in the polarized absorber are many times enhanced over those of the nonpolarized absorber, thereby making the approximation of a thin absorber no longer applicable.

The calculated spectra are compared to the experimental spectra in Figs. 5(a) and 5(b), for parallel and perpendicular polarization, respectively. As before, the positive, and negative-velocity halves of the spectra have been added together folding about the center of symmetry. Consider the case of parallel polarization, i.e., $\theta=0$. The difference in the spectrum for the two possible choices of φ is very pronounced. The fit of the experimental spectrum to the curve calculated for $\cos\varphi=-1.00$ is excellent and clearly establishes that the relative phase of the dipole and quadrupole components is such that the sign of the conventional mixing parameter δ is negative.[19] It should be noted that lines No. 4 and 15, which are the strongest lines in the unpolarized spectrum, are nearly completely extinguished by the interference. The dipole and quadrupole amplitudes for these components are opposite in phase and nearly equal in magnitude at $\theta=0°$. The intensities of these lines are therefore sensitive to the exact value of $\cos\varphi$. The curves calculated with $\cos\varphi=-0.90$ and -0.95 are shown in Fig. 5(a) in the region of the line of interest. The present experimental data are consistent with $\cos\varphi\leq-0.95$. The experimental spectrum for the case of perpendicular polarization shows some deviation from the calculated spectrum which can be accounted for by incomplete polarization of the absorber in the $\theta=\pi/2$ direction. The essential features of the dipole-quadrupole interference, however, are well displayed. The interference terms for the $\Delta m=\pm 1$ components have changed sign, and the lines which are extinguished at $\theta=0$ are now strongest.

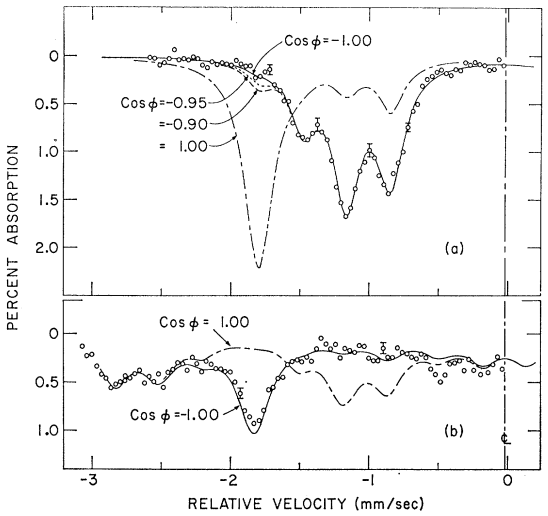

FIG. 5. Comparison of experimental Zeeman spectra to calculated curves for absorber magnetized (a) parallel and (b) perpendicular to incident gamma rays. φ is the relative phase angle between the dipole and quadrupole components of the radiation. The positive- and negative-velocity halves of the experimental spectrum have been added together folding about ℄.

It is of interest to determine the sign of the magnetic field which exists at the nuclei of the ruthenium atoms contained in the iron host lattice relative to the direction of the externally applied field. Analysis of the spectrum obtained with the absorber located in the longitudinal magnetic field of 29 kG showed no change in the magnetic field at the nucleus to within $\pm 0.6\%$, or ± 3 kG based on an effective field of 500 kG. Most of the cancellation of the applied field can be accounted for by the demagnetizing field which for pure iron would amount to approximately 22 kG over most of the volume of the absorber. In order to determine the sign of the field unambiguously, an experiment was performed which made use of the sense of circular polarization (helicity) of the gamma rays emitted along the direction of an applied magnetic field by the $\Delta m=\pm 1$ transitions. The hyperfine spectrum was measured with both source and absorber located in the central field of the solenoid. Analysis of this spectrum, which is similar to that of Fig. 2(b), showed an *increase* in the separation between the two triplets of lines (actually 4 lines of which one is nearly extinguished) by a measureable amount, Δv. The sign of this change in "separation" is related to the sign of the field in the following way: The "triplet"of lines lying on the negative-velocity half of the absorption spectrum of Fig. 2(b) all represent

[19] The sign convention is that adopted by L. C. Biedenharn and M. E. Rose, Rev. Mod. Phys. **25**, 729 (1953), where the sign of δ applies to a gamma-gamma angular correlation where the mixed transition is the *second step* in the cascade.

$\Delta m=-1$ transitions. Likewise, the corresponding "triplet" on the positive-velcoity half of the spectrum all represent $\Delta m=+1$ transitions. It is reasonable to assume that the magnetic field at the nuclei in the ruthenium metal source has the same sense as the applied field. The recoil-free spectrum emitted by the source in a direction parallel to the applied magnetic field is a compressed version of the spectrum in Fig. 2(b) which can be approximated by a closely spaced doublet; the negative-velocity member of the doublet consists of gamma rays circularly polarized antiparallel to the direction of the field and the positive-velocity member consists of gamma rays circularly polarized parallel to the direction of the field. If the field at the ruthenium nuclei in the absorber is parallel to the applied field, then the gamma rays circularly polarized antiparallel can be absorbed only by the $\Delta m=-1$ transitions and those circularly polarized parallel can be absorbed only by the $\Delta m=+1$ transitions. The net effect is that the separation of the two "triplets" in the absorption spectrum will be decreased. If the field is directed opposite to the applied field, the above argument is reversed and the separation of the "triplets" will be increased by the same amount. The experiment therefore shows that the field is negative.

The above analysis provides us with a technique for measuring the magnitude of the otherwise unresolved splitting of the single line source in the externally applied magnetic field. For splittings sufficiently small compared to the linewidth, Δv is equivalent to the spacing between the centroids of the two groups of lines of opposite helicity emitted by the source along the direction of the applied magnetic field. This splitting parameter is readily related to the products of the magnetic g factors and the applied field. For a difference in field at the two source positions of (26.3±1.0) kG, Δv was measured as (0.125±0.011) mm/sec. The resulting value of g_1 is 0.20±0.02.[20]

It should be noted that by the above analysis the fringe field of 5 kG present at the source for the spectrum of Fig. 2(b) accounts for the remainder of the *apparent* complete cancellation of the applied field at the absorber nuclei not accounted for by the demagnetizing field.

QUADRUPOLE HYPERFINE SPLITTINGS

A search was made for a ruthenium compound which gave a resolved quadrupole hyperfine spectrum. The largest nuclear quadrupole interaction was found in ruthenocene, $Ru(C_5H_5)_2$. This, however, was still insufficient for complete resolution of all six lines. The Mössbauer spectrum for this compound has two slightly broadened lines of approximately equal intensity separated by (0.46±0.04) mm/sec or (33±3) Mc. A similar

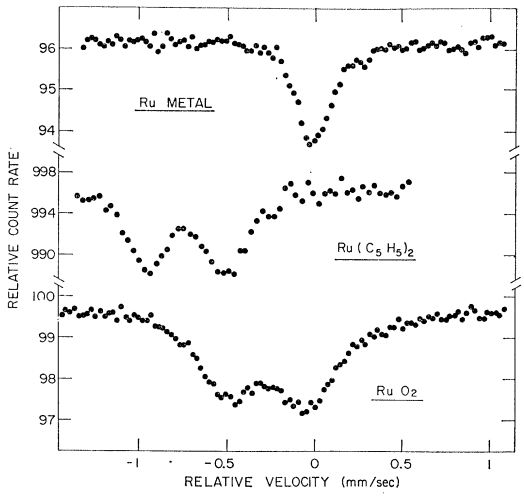

FIG. 6. Recoil-free resonance absorption spectra for the 90-keV transition in Ru^{99} with a source of Rh^{99} in Ru metal and absorbers of 97 mg/cm² ruthenium metal powder, 1800 mg/cm² $Ru(C_5H_5)_2$ and 750 mg/cm² RuO_2.

spectrum exhibiting approximately the same splitting but with a poorer peak-to-valley ratio was found with RuO_2. The spectra for these two compounds are shown in Fig. 6 together with the single line spectrum of metallic ruthenium. The slightly greater intensity of the line near zero velocity in the RuO_2 spectrum is probably due to the presence of some metallic ruthenium impurity. An examination of several samples, of RuO_2 showed varying degrees of line broadening. X-ray analysis of these samples showed that the broadening of the Mössbauer lines was correlated with poor definition of the x-ray diffraction pattern and could therefore be attributed to poor crystalization of the sample. This doublet is characteristic when the quadrupole splittings of the excited $\frac{3}{2}$ state dominates; each member of the doublet consists of an unresolved triplet. From a comparison of the experimental spectrum for $Ru(C_5H_5)_2$ with a series of synthesized spectra, computed with the previously determined parameters, a lower limit was established for the ratio of the quadrupole moment of the excited state to that of the ground state, $|Q_1/Q_0|\geq 3$.

A reliable calculation of the electric field gradient (EFG) existing at the nuclei of atoms in compounds is in general very difficult. A useful upper limit, however, may be obtained. For the case of RuO_2 the maximum EFG that may be expected is that due to the four $4d$ valence electrons on the Ru^{4+} ion. Cubic and lower symmetry crystal fields split the $4d$ shell levels and affect their occupancy in a predictable way.[21] The maximum EFG of the resulting configuration is given

[20] A possible correction due to paramagnetic shielding effects has been neglected. According to Matthias *et al.* (see Ref. 6) these corrections are expected to be no larger than a few percent in metals.

[21] F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry* (Interscience Publishers, Inc., New York, 1962). RuO_2 has an octahedral structure which results in a t_{2g}^4 electron configuration. Three of the $4d$ electrons will fill the three t_{2g} orbitals with their spins parallel, forming a system which has cubic symmetry and zero EFG. The fourth electron will occupy the lowest lying orbital (zx or yz) with opposite spin and contribute the EFG given in the text.

by[22,23]

$$q=-(2/7)\langle r^{-3}\rangle_{4d},$$

where the free-ion value $\langle r^{-3}\rangle_{4d}\simeq 7.1$ atomic units (a.u.) may be obtained by extrapolation from the Hartree-Fock calculations of Freeman and Watson.[24] The quadrupole splitting of the $\frac{3}{2}$ state may be simply expressed as

$$\Delta\epsilon=\tfrac{1}{2}e^2qQ_1.$$

A lower limit of 0.15 b is then obtained for $|Q_1|$ from the observed splitting of the $\frac{3}{2}$ state in RuO_2.

Ruthenocene is a covalent compound which has a crystal structure fairly similar to that of ferrocene.[25] The EFG at the nucleus of the iron atom in ferrocene has been considered by Erickson[26] who estimates the contributions from the $3d$ electrons to be $\sim+0.6(4/7)\langle r^{-3}\rangle_{3d}$. A similar distribution of the $4d$ electrons in ruthenocene would therefore give an EFG which is approximately the same as the maximum estimate made for RuO_2 above, but of opposite sign. The magnitude of the experimental quadrupole splittings for the two compounds *are* observed to be nearly equal.

The isomeric chemical shifts for $Ru(C_5H_5)_2$ and RuO_2 relative to the ruthenium metal source are (-0.76 ± 0.04) mm/sec and (-0.24 ± 0.05) mm/sec, respectively. These relatively large shifts are readily apparent in Fig. 6. Similarly large isomeric chemical shifts, both positive and negative, were observed in most of the nonmetallic compounds examined. These data will not be further elaborated upon in the present paper.

CONCLUSIONS AND DISCUSSION

The measurements of the magnetic hyperfine splittings of the 90-keV ground-state transition in Ru^{99} show conclusively that this transition proceeds between levels of spin $\frac{3}{2}$ and $\frac{5}{2}$, and that it consists of a mixture of dipolar ($M1$) and quadrupolar ($E2$) components which are "out of phase" relative to one another. On the basis of the previous spin assignment of $\frac{5}{2}$ for the Ru^{99} ground state, the spin of the 90-keV state is therefore established as $\frac{3}{2}$. The $E2/M1$ mixing ratio δ[2] was determined to be 2.7 ± 0.6,[27] where the sign of the conventional mixing parameter δ is negative.[19] The partial $M1$ and $E2$ transition rates deduced from this mixing ratio and the lifetime of the 90-keV level are $\sim2\times10^{-4}$ and 50 times[2] the Weisskopf single-particle estimate, respectively.

The ratio of the magnetic g factor of the 90-keV state to that of the ground state as deduced from the magnetic hyperfine splittings is $g_1/g_0=0.759\pm0.016$. This ratio, when taken together with the known value of the ground-state magnetic moment of (-0.63 ± 0.15)nm.,[4] gives a magnetic moment for the 90-keV state, $\mu_1=(-0.29\pm0.07)$ nm or a g factor, $g_1=-0.19\pm0.05$. Measurements of the splitting of a single line source in an externally applied field gives $g_1=-0.20\pm0.02$ which is in good agreement with the above value (a possible paramagnetic shielding correction[20] is expected to be small compared to the assigned error). These results are to be compared with the conflicting determinations of g_1 recently made by the method of precessed angular correlations: There is excellent agreement with the value $g_1=-0.189\pm0.004$ reported by Matthias *et al.*,[6] but there is definite disagreement with the value $g_1=-0.261\pm0.008$ reported by Bodenstedt *et al.*[7]

The analysis of partially resolved quadrupole hyperfine spectra yields a *lower* limit for the ratio of the quadrupole moment of the excited state to that of the ground state $|Q_1/Q_0|\geq3$ and a lower limit for $|Q_1|$ of 0.15 b.

These results lead to some interesting implications concerning the character of the 90-keV excitation. Ru^{99} is an even-odd nucleus with 55 neutrons. The ground-state spin and magnetic moment are consistent with a $d_{5/2}$ neutron orbital. The spin and magnetic moment of the 90-keV level, however, is not readily explained by any of the available single-particle states. The $d_{3/2}$ orbital is not expected to be found at so low an excitation energy and, furthermore, has the opposite sign magnetic moment. The $M1$ rate is remarkably retarded whereas the enhancement of the $E2$ rate is comparable to the enhancements of the lowest $2+$ to $0+$ transitions in the neighboring even-even ruthenium isotopes. These facts suggests that the 90-keV state may be described by a core excitation model such as discussed by Lawson and Uretsky[28] and de-Shalit.[29] The 90-keV level would then be one member of a multiplet of five levels formed by the coupling of the $\frac{5}{2}+$ ground-state orbital to a $2+$ excited core. Definite predictions relating the nuclear moments may be made using the relations given by de-Shalit.[29] The g factor of the $\frac{3}{2}$ state is given by

$$g_1=(13/15)g_0+(2/15)g_c.$$

Here g_c is the gyromagnetic ratio for the core which may be approximated by Z/A or ≈0.5. With the above value for the ground-state magnetic moment,[4] the model gives $g_1=-0.15$ or $g_1/g_0=0.60$ which is in reasonable agreement with experiment. The above relation (for

[22] Contributions due to the lattice are expected to be small compared to this upper estimate and have therefore been neglected. Covalent effects will lower $\langle r^{-3}\rangle_{4d}$ from the free-ion value. The free-ion Sternheimer antishielding factor R [R. M. Sternheimer, Phys. Rev. **84**, 244 (1951), **95**, 736 (1954); **105**, 158 (1957)] may affect this estimate by $\pm20\%$.

[23] For a discussion of the EFG due to d valence electrons see R. L. Ingalls, Phys. Rev. **133**, A787 (1964).

[24] A. J. Freeman and R. E. Watson in *Magnetism*, edited by Suhl-Rado (Academic Press Inc., New York, 1965), Vol. IIA, p. 291.

[25] G. L. Hardgrove, D. H. Tempelton, University of California Radiation Laboratory Report 8141, 1957 (unpublished).

[26] N. E. Erickson, thesis, University of Washington, 1964 (unpublished).

[27] This value is in good agreement with a recent measurement by P. Connors and A. Schwarzschild (to be published) of the relative l-subshell internal conversion coefficients. The conversion electron spectrum confirms the $M1$-$E2$ assignment.

[28] R. D. Lawson and J. L. Uretsky, Phys. Rev. **108**, 1300 (1957).

[29] A. de-Shalit, Phys. Rev. **122**, 1530 (1961).

this particular case) is relatively insensitive to the exact value of g_c.

Similarly, the quadrupole moment of the $\frac{3}{2}$ state is given by this model as[29]

$$Q_1 = -(2/25)Q_0 - \tfrac{1}{2}Q_c,$$

where Q_c is the static quadrupole moment of the 2+ core. If the 2+ excitation is taken to be a pure quadrupole oscillation of a spherical core which produces no time-average quadrupole moment, then

$$Q_1/Q_0 = -2/25.$$

The experimental results, however, are $|Q_1/Q_0| \geq 3$ and $|Q_1| \geq 0.15$ b, which when inserted into the above expression give $|Q_c| \geq 0.29$ b. If the hypothesis of a 2+ vibrational excitation of the core is correct, then these results show that there is an appreciable static quadrupole moment associated with this excitation.[30] A more quantitative determination of these quadrupole moments would be of considerable interest.

Unfortunately little has been learned about the properties of other levels in Ru^{99} from radioactive decay studies. It would be interesting to learn more about this nucleus through Coulomb excitation experiments in order to test further the hypothesis of a core excitation multiplet. It would be especially interesting if it were feasible to measure the reorientation effect in Coulomb excitation[30] for some of the levels in the multiplet.

The magnitude of the magnetic field at the ruthenium nuclei in the iron host lattice based on the known ground-state moment[4] is 500±120 kG. If the more accurate measurement of the 90-keV state g factor of Matthias *et al.*[6] is used the result is (500±10)kG. The sign of this field was shown to be negative relative to an externally applied field. These results are consistent with the investigation of the systematics of hyperfine fields in an iron host lattice reported by Shirley and Westenbarger.[31]

An upper limit of 10 kG is established for the field at the ruthenium nucleus in the ferromagnetic laves phase compound $GdRu_2$, from the width of the resonance observed. Jaccarino[32] has suggested that the small magnitude of this field is consistent with observations of small Knight shifts in laves phase compounds of 4*d* transition elements with rare earths. Both of these observations indicate that the conduction-electron wave functions which have a significant amplitude at the ruthenium sites have a small amplitude at the rare-earth sites and vice versa.

The fact that the 90-keV transition consists of comparable parts of $M1$ and $E2$ multipoles makes it especially suitable for investigating the possible violation of time-reversal invariance of the electromagnetic interaction recently suggested by Bernstein, Feinberg and Lee.[33] These authors have suggested that nuclear gamma decay matrix elements may contain an admixture of T noninvariant amplitude which is of the order of 10^{-2} to 10^{-3} .The fraction F of the Hamiltonian which is T noninvariant is proportional to the sine of the relative phase angle φ between the $M1$ and $E2$ amplitudes. In the present experiment we have shown that $\cos\varphi \leq -0.95$. This corresponds to $F \leq 0.30$. If the limit on $\cos\varphi$ were lowered to -0.99, the upper limit on F would only be reduced to 0.15. In order to lower this limit to the region of interest, it is clearly necessary to make a measurement which determines $\sin\varphi$ directly. Henley and Jacobsohn[34] have discussed in detail the possible ways of making a measurement which is proportional to $\sin\varphi$. These measurements require the selection of various degrees of polarization of the initial and final states and the gamma ray of the mixed transition. This is generally accomplished by multiple coincidence measurements of β rays and γ rays which are in cascade with the mixed transition.[35] By employing the Mössbauer effect with individually polarized source and absorber it is possible to make such a measurement with a singles counting experiment. The resulting increase in couuting rate allows a corresponding increase in the ultimate accuracy that may be achieved. Such an experiment is presently in progress and will be reported on at a later date.

ACKNOWLEDGMENTS

The author is grateful to numerous colleagues for helpful discussions, especially M. Blume, N. E. Erickson, G. T. Emery, V. Jaccarino, A. Z. Schwarzschild, R. E. Watson, and J. Weneser. I am indebted to R. Segnan for his contributions at the beginning of these experiments.

I wish to thank J. H. Wernick and Bell Telephone Laboratories for the preparation and analysis of the metallic absorbers and P. P. Craig for the use of his superconducting solenoid. I wish to express my appreciation to C. P. Baker and the Brookhaven cyclotron operating staff for their cooperation in the many bombardments.

[30] J. deBoer, R. G. Stokstad, G. D. Symons, and A. Winther, Phys. Rev. Letters **14**, 564 (1965), have recently found evidence for a quadrupole deformation of the first 2+ state in the vibrational nucleus Cd^{114}. These authors have deduced a quadrupole moment of (−0.70±0.21) b for this state from a measurement of the reorientation effect in Coulomb excitation. P. H. Stelson, W. T. Milner, J. L. C. Ford, Jr., F. K. McGowan, and R. L. Robinson, Bull. Am. Phys. Soc. **10**, 427 (1965) and P. H. Stelson, Proceedings of Brookhaven Summer Study Group (on Physics of the Emperor Tandem Van de Graaff Region), 1965 (unpublished), confirm the Coulomb reorientation measurements of J. deBoer *et al.* on Cd^{114} and in addition report similar observations for the first 2+ levels in Cd^{112} and Cd^{116} as well as the $\frac{3}{2}$+ and $\frac{5}{2}$+ levels in Ag^{107} and Ag^{109}. These latter levels in the odd-A silver isotopes have been considered by de-Shalit (Ref. 29) as examples of 2+ core excitation doublets built on the spin-$\frac{1}{2}$ ground states.

[31] D. A. Shirley and G. A. Westenbarger, Phys. Rev. **138**, A170 (1965).

[32] V. Jaccarino (private communication).

[33] J. Bernstein, G. Feinberg, and T. D. Lee, Phys. Rev. **139**, B1650 (1965).

[34] Boris A. Jacobsohn and Ernest M. Henley, Phys. Rev. **113**, 234 (1959).

[35] E. Fuschini, V. Gadjokov, C. Maroni, and P. Veronesi, Nuovo Cimento **33**, 1309 (1964) have obtained an upper limit for F of approximately 4% from a $\beta-\gamma_1-\gamma_2$ correlation experiment on Rh^{106}.