g Factor of the 90-keV Level in Ru^{99} and the Paramagnetic Correction in Transition Atoms*

E. MATTHIAS, S. S. ROSENBLUM, AND D. A. SHIRLEY
Lawrence Radiation Laboratory and Department of Chemistry, University of California, Berkeley, California
(Received 19 March 1965)

Using the decay of 16.1-day Rh^{99}, the half-life of the 90-keV state in Ru^{99} has been measured by observing delayed coincidences for the (354–90)- and the (529–90)-keV cascades. The result, $t_{1/2}=(20.7\pm0.3)$ nsec, is very suitable for a measurement of the Larmor precession in this level by means of the time-differential angular-correlation technique. To overcome the difficult problem of correcting for paramagnetic shielding, the g factor was determined with the Ru atoms in three magnetically different environments: (1) with a liquid source, (2) with Ru embedded in a copper lattice, and (3) with Ru dissolved in Ni. In the last case the product gH_{eff} was measured as a function of an external polarizing field, yielding both the g factor and the magnetic hyperfine field of Ru in Ni. The method of using cubic metal lattices [case (2) above] is demonstrated to be a reliable way of measuring g factors of excited nuclear states, as there are no interfering perturbation effects due to time-dependent and/or static quadrupole interactions. The final result for the g factor is $g=-0.189\pm0.004$, which gives, with a spin of $\frac{3}{2}$ for the 90-keV level, a magnetic moment of $\mu=-0.284\pm0.006$ nm. Paramagnetic shielding in liquid sources of transition elements is discussed, and g factors previously determined for such sources are shown to be in doubt by 5 to 10%.

I. INTRODUCTION

THE isotope Ru^{99} has recently been the subject or Mössbauer studies.[1,2] By using an iron absorber containing 2.3 at.% of Ru^{99}, Kistner and Segnan[2] were able to observe the hyperfine splitting from which they obtained the spin $I=\frac{3}{2}$ for the 90-keV level and the ratio of the magnetic moments for the ground and the excited state, $\mu_1/\mu_0=+0.455\pm0.010$. With a ground-state moment of $\mu_0=-0.63\pm0.15$ nm,[3] the moment for the 90-keV excited state is then $\mu_1=-0.29\pm0.07$ nm. Using this value, Kistner and Segnan deduced a magnetic hyperfine field of 500 kG at the Ru nucleus in the iron lattice. The fact that the half-life of the 90-keV state is 20 nsec[1,4] offers the possibility of measuring the g factor of this state with good accuracy by studying the rotation of the angular-correlation pattern in an external magnetic field. This is interesting especially because the ground-state moment is not accurately known while the ratio μ_1/μ_0 is.[2] This nucleus lies in a region of the periodic table where nuclear properties are neither thoroughly explored nor well understood. Also, the knowledge of this g factor will permit the determination of magnetic hyperfine fields at the nuclei of Ru atoms embedded in ferromagnetic lattices.

In this paper we report measurements of the half-life and g factor of the 90-keV level and of the hyperfine field of Ru in Ni. We also discuss in some detail the nuances of magnetic hyperfine structure effects on precession measurements in transition-series elements, calling attention to a paramagnetic correction which has been mistakenly ignored until now. Preliminary results of this investigation have been reported earlier.[5] During the completion of the experiments we learned about a very recent measurement of the 90-keV state g factor by Bodenstedt *et al.*[6] performed with the same technique as that used in our work. However, both the sign and magnitude of their result for the g factor is in striking disagreement with the results of the Mössbauer measurements[2] and with our preliminary reported g-factor value.[5]

II. SOURCE PREPARATION

The activity was produced by a (p,n) reaction on Ru^{99}. Samples of approximately 10 mg of Ru^{99} metal powder enriched to 80.9% and 98.8% were irradiated with 13-MeV protons at the Berkeley 88-in. cyclotron for about 20 μA-h. The procedure used for dissolving the Ru metal was essentially that used by Gile, Garrison, and Hamilton, as summarized in the pamphlet *The Radiochemistry of Rhodium.*[7] The ruthenium powder was fused with 10 g Na_2O_2 for 30 min at 300°C in a nickel crucible. The fused mass was dissolved in *aqua regia* and the solution made basic with KOH. After volatilizing RuO_4 by passing Cl_2 gas through the mixture and heating to 100°C, the residual solution was centrifuged. The Rh was carried quantitatively on the $Ni(OH)_2$ precipitate. The Rh was then separated from the large amount of Ni by dissolving the precipitate in dilute HNO_3, adding 5 mg of Fe^{+++} carrier and making the solution basic with 14M NH_4OH. The $Fe(OH)_3$ precipitate carried the Rh, and the $Ni(NH_3)_6^{++}$ remained in solution. The Fe was separated from the Rh

* Work preformed 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 and R. Segnan, Bull. Am. Phys. Soc. **9**, 396 (1964), and private communication.

[3] I. Lindgren, in *Perturbed Angular Correlations*, edited by by E. Karlsson, E. Matthias, and K. Siegbahn (North-Holland Publishing Company, Amsterdam, 1964), p. 379.

[4] O. C. Kistner, S. Monaro, and A. Schwarzschild, Phys. Rev. **137**, B23 (1965).

[5] E. Matthias, S. S. Rosenblum, and D. A. Shirley, Bull. Am. Phys. Soc. **9**, 741 (1964).

[6] E. Bodenstedt, C. Günther, J. Radeloff, W. Engels, W. Delang, M. Forker, and H. Luig, Phys. Letters **13**, 330 (1964).

[7] G. R. Choppin, Natl. Acad. Sci.–Natl. Res. Council Nucl. Sci. Ser. NAS-NS 3008.

by dissolving the precipitate in $6M$ HCl and passing the solution through a small bed of Dowex AG1×8 anion exchange resin, the Fe^{+++} being held strongly as a chloride complex, and the Rh eluting rapidly. After elution the solution was evaporated to dryness and taken up in a few drops of water. The oxidation state of the Rh is almost certainly +3 or Rh(III). We use the Roman numeral convention, in accordance with the usual practice in inorganic chemistry, to indicate the oxidation state without implying that the Ru atom has become a tripositive ion. If there were Rh(IV) present it would have remained on the anion exchange column.[7] It is unlikely that it is Rh(II) since no simple compounds of this oxidation state have been convincingly demonstrated[7] although several complex compounds, such as $[Rh(CO)_2Cl]_2$ are well known but unlikely to be formed in our chemical procedure. The Rh(III) is most likely to be in the form of an octahedral complex of either $[RhCl_6]^{-3}$ or $[RhCl_5(H_2O)]^{-2}$.[8]

For the studies discussed in Sec. VI B, C, we made metallic sources by dissolving small amounts of the Ru targets in Cu and Ni lattices. This was accomplished by melting the host metals in an argon atmosphere in the presence of the Ru powder. Solutions of less than 1 at.% Ru were thus obtained. These samples were studied with applied polarizing magnetic fields, and, for the Ni source, with no applied field.[9]

III. THE γ-RAY SPECTRUM

The decay of 16-day Rh^{99} is not very well investigated. A detailed decay scheme is given in the Nuclear Data Sheets with reference to a conference report.[10] However, when studying the gamma-ray spectrum of the 16-day Rh^{99} activity with Ge(Li) detectors we were not able to reproduce the decay scheme of Ref. 10, except for the lowest four excited levels. In Fig. 1 the spectrum up to 550 keV is shown as recorded with a Ge(Li) detector. These lines fit the lowest levels of the decay scheme of Ref. 10 with the energies slightly modified (Fig. 2). We observed a large number of gamma rays in the region between 600 and 2700 keV, but the detailed study of all transitions was outside the scope of this work.

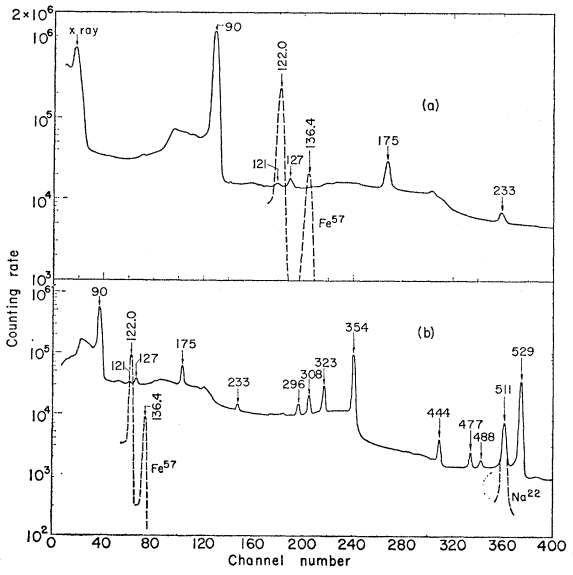

FIG. 1. γ-ray spectrum of the 16-day Rh^{99} as recorded with a 1×2 cm² Ge(Li)-detector of 3-mm thickness. The dashed lines are calibration lines.

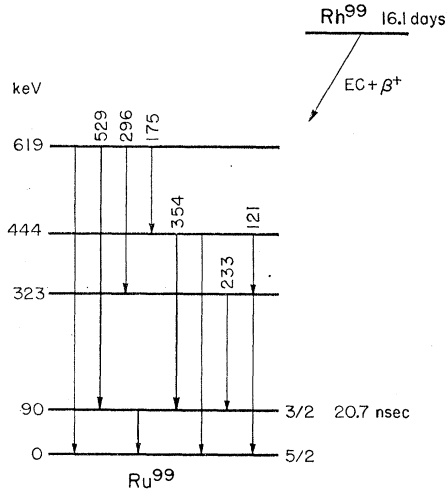

FIG. 2. Lowest part of the Ru^{99} decay scheme. The energies have been determined from the γ spectrum shown in Fig. 1.

IV. THE HALF-LIFE MEASUREMENT

In connection with the Mössbauer experiments on Ru^{99} Kistner *et al.*[1,4] reported a half-life of $t_{1/2}=20\pm1$ nsec for the 90-keV level. Recently, in connection with their *g*-factor investigation, Bodenstedt *et al.*[6] redetermined the half-life and obtained $t_{1/2}=19.7\pm0.4$ nsec. We measured this half-life by observing delayed coincidences for both the (354–90)- and (529–90)-keV γ-ray cascades. NaI(Tl) crystals mounted onto 56 AVP photomultipliers were used as detectors. The anode pulses were shaped by limiters and a clipping device, giving square-formed pulses of 250-nsec length. These were fed into a time-to-height converter working on the overlap principle. Time calibration was done with a set of carefully calibrated delay cables. The over-all accuracy of the time calibration was 1.5%. Half-life measurements have been carried out with both a liquid source, prepared as described above, and a Ru metal source. Great care was exercised to avoid any distortion of the half-life by time-dependent angular correlation effects.[11] This means the detectors were either moved as

[8] F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry* (Interscience Publishers, Inc., New York, 1962), p. 838.
[9] E. Matthias, S. S. Rosenblum, and D. A. Shirley, Phys. Rev. Letters **14**, 46 (1965).
[10] J. D. Kurbatov, C. W. Townley, B. Feigley, and M. H. Kurbatov, Bull. Am. Phys. Soc. **5**, 240 (1960).
[11] P. C. Simms and R. M. Steffen, Phys. Rev. **108**, 1459 (1957).

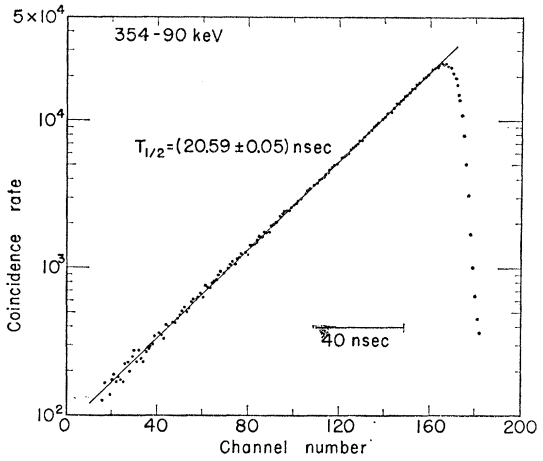

FIG. 3. Half-life measurement of the 90-keV level in Ru^{99}. The data shown represent run 2 in Table I.

close as possible to the source, giving a solid angle of almost 2π for each detector, or they were placed at an angle of 144° with a source-detector distance of about 1 in. In Fig. 3 a typical time spectrum is shown. A summary of all half-life measurements is given in Table I. As a final value we give the weighted average over all individual results:

$$t_{1/2}=(20.7\pm0.3)\text{ nsec}.$$

The final error is composed of the statistical error and an uncertainty of 1.5% in the time calibration. This result is in good agreement with the value reported by Kistner *et al.*[1,4] but disagrees with the half-life reported by Bodenstedt *et al.*[6] which lies somewhat outside the limits of error of our value.

V. THE *g*-FACTOR MEASUREMENTS

For a *g*-factor determination there must be a cascade exhibiting an anisotropic angular correlation. Leonard and Jha[12] reported angular-correlation measurements on both the (529–90)-keV cascade and the (354–90)-keV cascade. With a solid source of Ru metal they obtained for these cascades the coefficients $A_2=-0.20$ and $A_2=-0.082$, respectively. Both values are not corrected for the solid angles of the detectors.

To assure both the sign and the magnitude of the anisotropies we repeated the angular-correlation measurements with a liquid source. The anisotropies obtained were

$$A=-(15\pm2)\%\text{ for the (354–90)-keV cascade,}$$

and

$$A=-(19\pm2)\%\text{ for the (529–90)-keV cascade.}$$

[12] R. F. Leonard and S. Jha, Bull. Am. Phys. Soc. **9**, 484 (1964). The results reported by these authors at the Washington meeting of the APS, 1964, differ from the data given in the abstract. We refer to the values presented at the meeting.

TABLE I. Summary of the results of four independent half-life measurements. Runs 1 and 2 were done with the (354–90)-keV cascade, while for runs 3 and 4 the (529–90)-keV cascade was used.

Run no.	$T_{1/2}$ (nsec)	$\Delta T_{1/2}$ statistical error
1	20.99	0.07
2	20.59	0.05
3	20.70	0.08
4	20.42	0.40
Weighted average:	20.73	0.10

No solid angle or background correction has been applied to these values. The angular-correlation measurements performed with NaI(Tl) detectors are not conclusive enough to determine spin assignments for the 90-, 444-, and 619-keV levels. As is obvious from Fig. 1 the photopeak around 340 keV detected with NaI(Tl) crystals actually consists of four different γ rays. This compound peak in addition rides on a heavy Compton background from both annihilation radiation and higher energy transitions. The situation is similar for the photopeak at about 520 keV which is composed of the 511- and the 529-keV radiation. As the fraction of the positron decay feeding the 90-keV level is not reliably known, it is difficult to obtain the true anisotropy from the measurements. One way to obtain the real angular-correlation coefficients would be to evaluate them from the amplitude of the Larmor-precession measurement. As there is no other half-life known in the decay of Rh^{99}, the background makes only prompt coincidences and does not interfere for delay times larger than the instrumental time resolution. Such an evaluation of the coefficients, however, requires the exact unfolding of the delay curve with the prompt curve. The best way to determine the anisotropies of the two cascades is to measure the angular correlations with Ge(Li) detectors. This, however, is a very time-consuming procedure because of the very low efficiency of these detectors on the high-energy side. Thus any attempt to interpret the angular correlation coefficients, measured with NaI(Tl) detectors, in terms of spins and multipolarities is unattractive.

The anisotropies of the photopeaks at 340 and 520 keV, however, may be used to measure the *g* factor of the 90-keV level in Ru^{99}. This was done by observing the rotation of the angular-correlation pattern in an external magnetic field in the conventional way, described elsewhere.[13] The γ_2 detector was placed at an angle of 135° with respect to the detector for γ_1. The time spectrum of the coincidences was measured for a magnetic field pointing upward ($C_{i\uparrow}$) and downward ($C_{i\downarrow}$) and the ratio

$$R_i=2(C_{i\downarrow}-C_{i\uparrow})/(C_{i\downarrow}+C_{i\uparrow})$$

[13] E. Matthias, L. Boström, A. Maciell, M. Salomon, and T. Lindquist, Nucl. Phys. **40**, 656 (1963).

TABLE II. Summary of the results of all independent g-factor measurements performed with a liquid source. The amplitudes of the cosine waves are given to emphasize the consistency between the different runs and no conclusions are drawn from the values of a. The external magnetic field was in all cases 41.6±0.4 kG.

Run no.	Cascade (keV)	g	Δg statistical error	a Amplitude (%)
1	354–90	−0.1851	0.0041	10.3±0.5
2	354–90	−0.1810	0.0034	10.9±0.4
3	354–90	−0.1775	0.0064	10.5±0.6
4	354–90	−0.1770	0.0054	11.3±0.6
5	354–90	−0.1791	0.0050	11.1±0.6
6	529–90	−0.1760	0.0033	13.7±0.5
7	529–90	−0.1930	0.0055	12.8±0.6
8	529–90	−0.1859	0.0051	13.2±0.6
	Weighted average:	−0.181	0.002	

was formed for each channel number i. For $A_4 \ll A_2$ the ratio R_i can be described by the function[13]

$$R_i = a\cos 2(\omega_L t_i - \phi) + c,$$

where ω_L is the Larmor precession frequency,

$$\omega_L = -gH(\mu_N/\hbar).$$

The four parameters a, ω_L, ϕ, and c are obtained from a least-squares fit of the experimental data R_i. Several measurements with two different liquid sources have been performed for both the (354–90)- and the (529–90)-keV cascade. The results of all runs with liquid sources are summarized in Table II. A typical set of data for each cascade obtained with a liquid source is displayed in Figs. 4 and 5.

Judging from the results of the measurements performed with a liquid source there is no doubt left that both cascades have the same intermediate level. For the runs with the copper alloy source we therefore took the photopeaks at 340 and at 520 keV together in the window of the high-energy channel in order to gain statistical accuracy. The results obtained in this way with the Ru-Cu alloy source are listed in Table III and the experimental points together with the corresponding least-squares fit for a typical run are shown in Fig. 6.

TABLE III. Summary of the results of all independent g-factor mesurements performed with a Ru-Cu alloy source. The amplitudes of the cosine waves are given to emphasize the consistency between the different runs and no conclusions are drawn from the values of a. The external magnetic field was in all cases 41.5±0.4 kG.

Run No.	Cascade (keV)	g	Δg statistical error	a Amplitude (%)
1	(354,529)–90	−0.1914	0.0041	15.4±0.5
2	(354,529)–90	−0.1933	0.0041	14.6±0.4
3	(354,529)–90	−0.1876	0.0024	16.0±0.3
4	(354,529)–90	−0.1862	0.0035	15.2±0.4
	Weighted average:	−0.189	0.002	

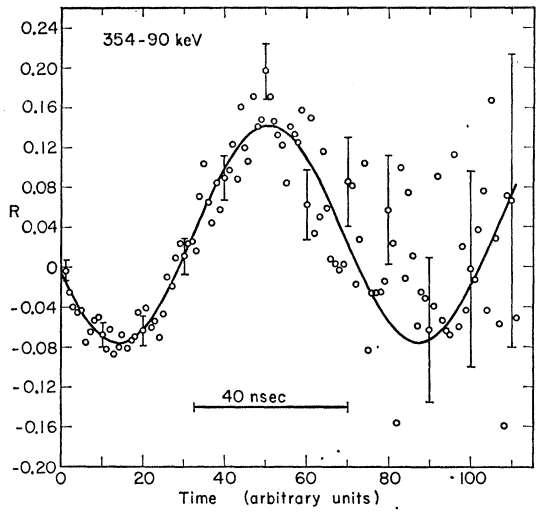

FIG. 4. Measurements of the time-pattern of the angular-correlation precessing in an external magnetic field of 41.6 kG using a liquid source. The 354- and 90-keV gamma rays were both detected with 1½×1-in. NaI(Tl) crystals at a distance of 6 cm. The data shown represent run 2 in Table II.

The results of the various runs given in Tables II and III are independent of each other in the sense that each run was completed with its own time calibration and magnetic-field measurement. It should be noted that in Tables II and III the error for the g factor of each individual run is the statistical error as obtained from the least-squares fit. Correspondingly, the error of the weighted average is the statistical error only. To obtain the final total error for the average g factor, we have to add systematic errors such as the uncertainty of the magnetic field (1%), including its inhomogeneity, and the error of the time calibration (1.5%).

The sign of the g factor can be obtained from the sign of the anisotropy and the sign of the first half-wave of R,[13] keeping in mind that the magnetic-field direction "upward" and "downward" refers to the detector plane in which the angle between the γ_1 detector and the γ_2 detector, $\Theta_0 = 225°$, reads clockwise from γ_1 to γ_2. From Figs. 4, 5, and 6 it can be seen that R starts with $C_{i\downarrow} - C_{i\uparrow} < 0$, which gives with $\Theta_0 = 225°$ and a negative anisotropy: sign (g) = −1. The negative sign of the g factor has independently been checked by observing the rotation direction of the integral angular correlation in an external magnetic field.

VI. HYPERFINE STRUCTURE CONSIDERATIONS

The directly measurable quantity in an angular-correlation-precession experiment is the rotation frequency of the correlation pattern ω_R which is simply related to the Larmor-precession frequency, ω_L. For these experiments on Ru^{99} we have $\omega_R = 2\omega_L$. To determine the nuclear g factor it is necessary to know the effective magnetic field at the nucleus, $\mathbf{H}_{\text{eff}}$, and to use the relation $\hbar\omega_L = -g\mu_N H_{\text{eff}}$ (here μ_N is the nuclear

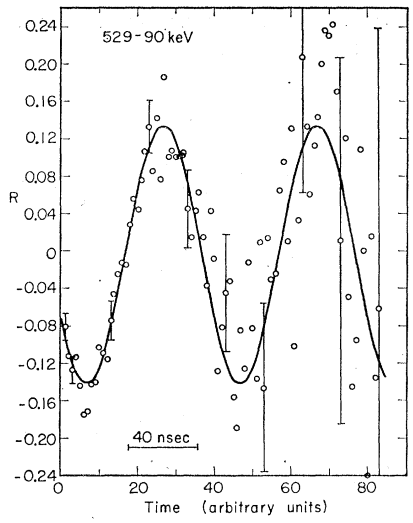

FIG. 5. Measurement of the time-pattern of the angular-correlation precessing in an external magnetic field of 41.6 kG using a liquid source. The 529- and 90-keV gamma rays were both detected with $1\frac{1}{2}\times 1$-in. NaI(Tl) crystals at a distance of 5 cm. The data shown represent run 6 in Table II.

magneton). In a transition-series atom a substantial hyperfine structure may be present, modifying the effect of the external magnetic field, $\mathbf{H}_0$. In certain particularly simple cases including those discussed here, the magnetic hfs may be represented by an internal magnetic field $\mathbf{H}_i$. Then we may write

$$\mathbf{H}_{\text{eff}}=\mathbf{H}_0+\mathbf{H}_i. \quad (1)$$

In each specific case some estimate must be made of the magnitude of the product $\omega_L\tau$, where τ is the electronic relaxation time. For $\omega_L\tau\ll 1$ (cases A and B below), Eq. 1 may be written in the form

$$\mathbf{H}_{\text{eff}}=\beta\mathbf{H}_0, \quad (2)$$

where β is the "paramagnetic correction factor." Here $\mathbf{H}_0$ is described as inducing a (collinear) internal field $(\beta-1)\mathbf{H}_0$ through polarization of electrons near the nucleus under study. For cases in which the hfs is a weak effect β is near unity. Strongly magnetic rare earths may have β's near 10 even at room temperature (and much larger below). These measurements on Ru^{99} constitute the first example of $\beta<1$. Cases should exist (e.g., negative hyperfine fields at low temperatures: Fe^{3+} at 10°K) for which β is zero or negative.

In the limit $\omega_L\tau\gg 1$ (case C below) the two fields $\mathbf{H}_0$ and $\mathbf{H}_i$ simply add vectorially, though the correlation pattern, averaged over an ensemble of nuclei, depends sensitively on the orientation of the magnetization $\mathbf{M}$ of the domains (or ions) producing $\mathbf{H}_i$ with respect to $\mathbf{H}_0$.[9]

A. Measurements on Solutions

There is a formal analogy between "rapid exchange" among several chemical sites in nmr spectroscopy[14] and angular-correlation precession in paramagnetic environments, although the latter case is usually treated by the specific method of a paramagnetic correction.[15] In either technique the observed correlation pattern is characteristic of that expected for a weighted average of several quantum states.

Until now the "paramagnetic correction" has been formulated only for the weak-crystal-field case of rare-earth ions,[15] and discussions of β have been limited to this rather special series. Angular-correlation-precession g-factor measurements have been reported for the d-shell transition-series nuclei V^{51},[16] Tc^{99},[17] Ru^{99},[6] Hf^{177},[18] Hf^{178},[19,20] Hf^{180},[21] Ta^{181},[13,23] W^{182},[23] Os^{186},[24] Re^{187},[25,26] and Os^{188},[27] all measured in aqueous solutions, except for V^{51} where a gaseous source was used. In all of these cases paramagnetic corrections were either simply ignored or were omitted on the basis of incorrect arguments. While in some cases accuracies of a few percent have been claimed for these g-factor measurements, these must, in light of arguments presented below, be regarded as expressions of precision only. Until the paramagnetic effects have been dealt with either empirically, as discussed in Sec. B below for Ru^{99}, or theoretically (an alternative for which there are presently not enough data available), the reported g factors for the above cases must be regarded as being in doubt by approximately 5–10%. This figure is derived below. A complete discussion of paramagnetic corrections for the $3d$, $4d$, and $5d$ series elements in aqueous solution is beyond the scope of this paper, but we give below the bare outlines of those considerations that are relevant to paramagnetic corrections.

First it is necessary to know the oxidation state of the daughter atom during the lifetime of the nuclear state after the (usually beta or electron-capture) decay of the parent nuclear species. The fates of oxidation states following nuclear decay are studied in the discipline of "hot-atom chemistry." A survey of the available data[28]

[14] For a discussion of nmr see J. A. Pople, W. G. Schneider, and H. J. Bernstein, *High-resolution Nuclear Magnetic Resonance* (McGraw-Hill Book Company, Inc., New York, 1959).

[15] C. Günther and I. Lindgren, in *Perturbed Angular Correlations*, edited by E. Karlsson, E. Matthias, and K. Siegbahn (North-Holland Publishing Company, Amsterdam, 1964), p. 357.

[16] Ingrid Y. Krause, Phys. Rev. **129**, 1330 (1963).

[17] E. Bodenstedt, E. Matthias, and H. J. Körner, Z. Physik **153**, 423 (1959).

[18] E. Matthias, E. Karlsson, and C. A. Lerjefors, Arkiv Fysik **22**, 139 (1962).

[19] E. Bodenstedt *et al.*, Z. Physik **168**, 103 (1962).

[20] E. Karlsson, E. Matthias, and S. Ogaza, Arkiv Fysik **22**, 257 (1962).

[21] E. Bodenstedt *et al.*, Z. Physik **165**, 57 (1961).

[22] E. Bozek, A. Z. Hrynkiewicz, and J. Styczen, Phys. Letters **1**, 126 (1962).

[23] H. J. Körner, J. Radeloff, and E. Bodenstedt, Z. Physik **172**, 279 (1963).

[24] E. Bodenstedt *et al.*, Z. Physik **163**, 1 (1961).

[25] S. Koicki, A. Koicki, and G. T. Wood, Nucl. Phys. **49**, 161 (1963).

[26] H. K. Walter, A. Weitsch, and P. Kienle, Z. Physik **175**, 520 (1963).

[27] E. Karlsson, C. A. Lerjefors, and E. Matthias, Nucl. Phys. **25**, 385 (1961).

[28] M. Haissinsky, *Nulcear Chemistry and its Applications*, translated by D. G. Tuck (Addison-Wesley, Publishing Company Inc., Reading, Massachusetts, 1964).

makes us pessimistic about the prospect of reliably predicting the oxidation states in question. In beta decay the Migdal effect[29,30] can lead to higher oxidation states and in electron-capture decay the Auger effect plays the same role. Highly oxidized recoiling atoms can be reduced by water to the lowest stable states available to these atoms. Evidence for this effect was obtained by Burgus and Kennedy[31] in studies of the decay of $Mn^{51}O_4^-$ to $Cr^{51}O_4^{2-}$ and Cr^{3+}, wherein the latter two species were obtained in approximately equal abundances. Thus it is incorrect to assume that only a particular ionic species is present after decay. This case is rather similar to the decay of W^{187} in the WO_4^{2-} ion to Re^{187}. Although it is certainly true that WO_4^{2-} is diamagnetic,[32] it does not follow that no paramagnetic effects are present in the daughter Re^{187}, because this nuclide may not be present entirely as perrhenate ion, ReO_4^-, during the first 10^{-6} sec. Similar arguments can be made for the other cases mentioned above.

The method of differential angular correlations provides a means of studying the chemistry of a complex during the intermediate state. If two chemical species with substantially different paramagnetic effects are present, a periodic amplitude modulation should appear at the beat frequency of the two precession rates. If one species is present and is undergoing rapid chemical change, a single modulation of the amplitude, accompanied by a change in frequency, will appear.

Ruthenium can exist in the seven oxidation states II through VIII, with 0–6 4d electrons.[33] Both electron-capture and β^+ decay occur, and we can offer no unassailable arguments to eliminate any of the seven states. Unfortunately too few cycles could be observed to decide from the criteria mentioned above. We therefore disagree with the assumption of Bodenstedt *et al.*[6] that Ru^{99} is present only as Ru^{3+} after the decay of Rh^{99} in $RhCl_6^{3-}$. The 2+ oxidation state is more likely on the basis that it is isoelectronic with the parent,[28,31] but it is probably only one of several species present.

In those cases for which the oxidation state is known one must next determine the effect on the electronic state of the various interactions present. We discuss this problem for Ru very briefly below.

The exact approach would be to make use of the ligand field theory which is quite thoroughly worked out for the d shells.[34] Under cubic symmetry the d shell is split, in the strong-field case, into a high-lying doublet e_g and a lower triplet t_{2g} spaced by $10\ Dq \cong 2\times 10^4$ cm^{-1}. We need consider only t_{2g}. As a three-dimensional representation of the octahedral group t_{2g} is formally equivalent to a p shell. This equivalence may be employed in estimating hfs effects. For Ru(II)$4d^6t_{2g}^6$, for example, we have a closed shell and diamagnetism, while for Ru(V)$4d^3t_{2g}^3$, a half-filled shell leads to spin paramagnetism. For brevity we now restrict the discussion to the case for which we shall make a quantitative estimate, Ru(III)$4d^5t_{2g}^{-1}$.

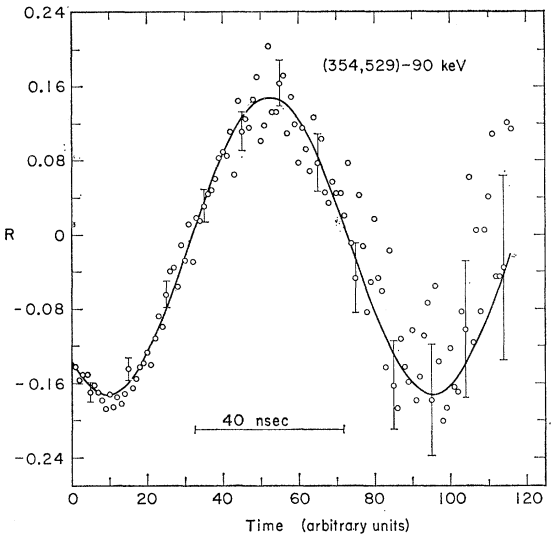

FIG. 6. Measurement of the time-pattern of the angular correlation precessing in an external magnetic field of 41.5 kG, using a Ru-Cu alloy source. Both the (529–90)- and the (354–90)-keV cascade were used together in this measurement. The (354,529)- and 90-keV gamma rays were detected with 2-×2-in. (distance 7 cm) and 1½-×1-in. (distance 5 cm) NaI(Tl) crystals, respectively. The data shown represent run 3 in Table III.

The strong ligand field of Ru(III) in octahedral coordination tends to quench the orbital angular momentum, but spin-orbit coupling acts to lift this quenching. The p-shell analogy for t_{2g} may be extended to strong spin-orbit coupling, where a quartet (analogous to $p_{3/2}$) and a lower doublet (analogous to $p_{1/2}$) are produced for t_{2g}^{-1}. These two levels are spaced by $\frac{3}{2}\xi \cong 1500$–$2000$ cm^{-1},[35] and at room temperature the states are somewhat mixed. Even if we should solve the eigenvalue problem for Ru(III) in t_{2g}^{-1} representation, it would not be practicable to estimate the hyperfine structure effects because of the unknown contribution of core polarization. Fortunately paramagnetic resonance data are available[36] for $Ru(NH_3)_6Cl_3$, from which we may take $A \cong 0.005$ cm^{-1} as an average value for the hfs parameter in the spin Hamiltonian $\mathcal{H} \cong A\vec{I}\cdot\vec{S}$, with an effective spin $S=\frac{1}{2}$. Here $S=\frac{1}{2}$ arises from the t_{2g}^{-1} term rather than the lowest level of a $^6S_{5/2}$ term. Actually the Hamiltonian is anisotropic and there are

[29] E. L. Feinberg, J. Phys. (U.S.S.R.) 4, 424 (1941).
[30] A. Migdal, J. Phys. (U.S.S.R.) 4, 449 (1941).
[31] W. H. Burgus and J. N. Kennedy, J. Chem. Phys. **18**, 97 (1950).
[32] K. Venkateswarlu and K. Rarmanathan, Current Sci. (India) **24**, 83 (1955).
[33] P. J. Durrant and B. Durrant, *Introduction to Advanced Inorganic Chemistry* (John Wiley & Sons, Inc., New York, 1962), p. 1032.
[34] See, for example, Carl J. Ballhausen, *Ligand Field Theory* (McGraw-Hill Book Company, Inc., New York, 1962) for a clear discussion of the relevant ligand field theory.
[35] B. N. Figgis, J. Lewis, R. S. Nyholm, and R. D. Peacock, Discussions Faraday Soc. **26**, 103 (1958).
[36] J. H. E. Griffiths, J. Owen, and I. M. Ward, Proc. Roy. Soc. (London) **A219**, 526 (1953).

several inequivalent sites for the crystal in question. For high magnetic fields we may take the Hamiltonian as

$$\mathcal{H}=g_e\mu_B H_0 S_z+AS_zI_z-g_N\mu_N H_0 I_z \quad (3)$$

to terms of order $A/g_e\mu_B H$, if we take the z axis along $\mathbf{H}_0$. We may then write the *nuclear* spin Hamiltonian as

$$\mathcal{H}_N=A\bar{S}_zI_z-g_N\mu_N H_0 I_z \quad (4a)$$

$$\mathcal{H}_N=-g_N\mu_N\beta H_0 I_z, \quad (4b)$$

taking $\beta=(1-A\bar{S}_z/g_N\mu_N H_0)$. Now we may evaluate $\bar{S}_z$, the average projection of electron spin along $\mathbf{H}_0$, as $\bar{S}_z\cong-g_e\mu_B H_0/4kT$, assuming $S=\frac{1}{2}$. Except for the hfs anomaly the ratio A/g_N is independent of the nuclear state. Thus using $A=0.005$ cm^{-1} and $\mu=0.63$ nm, $I=\frac{5}{2}$ for natural ruthenium,[3] together with $g_e\cong2.0$, we find for $T=300°$K,

$$\mathbf{H}_{\text{eff}}=\mathbf{H}_0(1\pm0.087). \quad (5)$$

Thus a correction of $\sim9\%$, with uncertain sign would be necessary if Ru^{99} were in the Ru(III) state, as assumed by Bodenstedt *et al.*[6] There is no way at present to decide on a theoretical basis the sign of A and thus of this correction. We might expect the above estimate to represent an upper limit for the magnitude of the correction because several of the other oxidation states, which are probably also present, are diamagnetic or only weakly paramagnetic. This expectation is borne out, as discussed below.

B. Measurements in a Copper Lattice

The necessarily approximate nature of the above estimate for β is a result of two formidable difficulties: In a liquid source we cannot determine the oxidation state(s) of Ru during the precession experiment, and too little is known about hyperfine structure in $4d$ transition-series compounds to allow a reliable estimate of the relevant hfs constants. At the same time the calculation for Ru(III) indicates that errors of the order of 10% must be associated with g-factor measurements in the transition series in case the paramagnetism cannot be accounted for.

Fortunately one may greatly diminish the uncertainties of paramagnetism for transition-series atoms, by using metallic sources. The rigid solid lattice and the reducing action of conduction electrons combine to bring the daughter atom into chemical equilibrium in a very short time ($\ll10^{-9}$ sec) following decay of the parent. The Pauli principle allows only a fraction $\sim kT/E_F$ (E_F is the energy at the Fermi surface) of conduction electrons to participate in paramagnetism[37] and the paramagnetic correction is accordingly reduced by this factor, which has a numerical value of $\sim10^{-2}$. The resulting fractional shift, $(H_{\text{eff}}-H_0)/H_0$, of $\sim10^{-4}$–10^{-2} is the same phenomenon that is responsible for the Knight shift for nuclear magnetic resonance in metals.

The cubic copper lattice was chosen for this experiment on Ru^{99} because the target Ru has a hexagonal lattice, which could create quadrupole interaction and complicate the measurement. The results for a copper lattice are given in Table III. The weighted-average result

$$g=-0.189(2)$$

includes statistical errors only, and is to be compared with the value

$$g=-0.181(2),$$

which also includes only statistical errors, determined for liquid sources. The comparison yields an empirical paramagnetic correction

$$\beta=0.958(15).$$

This is the first case for which a β of less than 1 has been found. The $(4.2\pm1.5)\%$ correction agrees well with the estimates made in Section VI A. This experiment demonstrates the feasibility of precession-correlation measurements in a cubic metallic lattice and at the same time indicates the existence of a substantial paramagnetic effect in solutions. We conclude that cubic metallic sources should be used whenever accuracy is sought in g-factor measurements.

C. Measurements in a Nickel Lattice

The magnetic fields induced at impurities in ferromagnetic lattices comprise a subject of considerable theoretical, as well as practical, interest. No rigorous theory dealing specifically with solid-state properties has been developed to deal with this phenomenon, but several calculations[38] involving atomic properties have had considerable (though hardly quantitative) success. For Ru in ferromagnetic lattices the largest contributions to hyperfine fields probably arise from contact interaction between spin-polarized s electrons and the nucleus. This interaction can arise from two sources, core polarization of the closed s atomic shells of Ru (CP), or polarization of $5s$ conduction electrons of Ru (CEP). A recent survey of all available data on induced fields in iron lattices[39] indicates that while CP is dominant in the $3d$ series (which was well known), there is good evidence for CEP in the $5d$ series. It is then of considerable interest to study the $4d$ series, in which CP and CEP might compete on a somewhat equal basis. The latter mechanism might be expected to be larger in Ag, than in Ru because of the larger value of $\psi_{5s}^2(0)$ for atomic Ag. On the other hand, CP effects induced via an open d shell would favor a larger field for Ru. For an Fe host the field at a Ru nucleus is in-

[37] W. Pauli, Z. Physik **41**, 81 (1927).

[38] R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 2027 (1961).

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

TABLE IV. Results of the g-factor measurements performed with sources of different magnetic properties.

Source structure	Cascade (keV)	Magnetic field	$g\beta$
Dilute acid solution, paramagnetic	354–90 529–90	41.6±0.4 kG	−0.181±0.004
Ru dissolved in Cu, Pauli paramagnetic	(354,529)–90	41.5±0.4 kG	−0.189±0.004
Ru dissolved in Ni, ferromagnetic	354–90 529–90	$\mathbf{H}_0+\mathbf{H}_i$	−0.184±0.010

deed larger (by 505 to 272 kG) than for Ag.[39] Our work on Ru in Ni was undertaken to extend this comparison. We were also interested in testing the possibility that "shielding" might cause deviations from the relationship

$$\mathbf{H}_{\text{eff}}=\mathbf{H}_0+\mathbf{H}_i$$

and in determining the sign of $\mathbf{H}_i$, which is in our case the magnetic hyperfine field for Ru in Ni.

The results of these measurements are shown in Fig. 7, where (gH_{eff}) is plotted against H_0. The straight line through the data is valid for a magnetically saturated lattice. It is obvious from the slope that the hyperfine field is negative, i.e., opposite to the external polarizing field. It further appears from Fig. 7 that there is no deviation of the data from a straight line within the experimental errors. We can therefore conclude that there is no magnetic shielding present in the sample which would affect our result within the limits of the accuracy given. The result of the least-squares fit is

$$|g|=0.184\pm0.010 \quad \text{and} \quad H_i=-180\pm10 \text{ kG}.$$

This value for the magnetic hyperfine field is consistent with the result $|H_i|=178\pm8$ kG which is obtained from the zero-field measurement only, using a g factor of $|g|=0.189\pm0.004$ (result of the copper alloy source). The hyperfine field is about twice as large as the value −84(5) kG reported for Ag in Ni, thus supporting the CP mechanism for this case.

VII. THE g FACTOR: DISCUSSION

The results of all g-factor measurements performed with sources of different magnetic properties are summarized in Table IV. We adopt the result obtained with the copper-alloy sources as the best value for the g factor. Taking into account all sources of error we obtain

$$g_1=-0.189(4)$$

for the 90-keV state of Ru^{99}. This is in good agreement with Kistner and Segnan's result for g_1/g_0, which, when combined with the rather inaccurate ground-state moment, gives $g_1=-0.191(46)$. The recent result of Bodenstedt *et al.*,[6] $g_1=+0.261(8)$, seems thus to be wrong in sign. Our present result also calls into question their reported magnitude, which is 38% higher than ours. A large systematic error in their measurement or ours is indicated. It seems very unlikely that the discrepancy can be attributed to paramagnetic effects in liquid sources for three reasons: (1) The liquid sources used by the two groups were ostensibly identical chemically; (2) a paramagnetic effect of 38% is very much out of line with the theoretical estimates mentioned in Sec. VIA; and (3) the available evidence (Sec. VIB) indicates that β is less than 1.

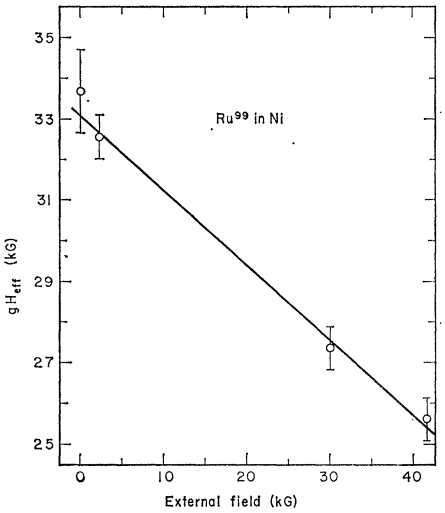

FIG. 7. Measurement of the g factor and the magnetic hyperfine field of Ru in Ni. The sign of the slope clearly tells that the external magnetic field is opposite to the hyperfine field. The slope of the fitted line yields the g factor, presuming that magnetic shielding effects are negligible.

Our result, combined with Kistner and Segnan's ratio, gives a ground-state magnetic moment of

$$\mu=-0.623(19)$$

for Ru^{99}.

Too few data are as yet available for a comprehensive discussion of the g factor of the 90-keV state in terms of nuclear structure, but it is clear that the simplest shell-model picture is not adequate to explain either the spin or the moment. Kistner[2] has suggested core excitation in this nucleus. If the 90-keV state is a $d_{5/2}$ quasiparticle coupled to a 2+ phonon the g factor is given by

$$g(\tfrac{3}{2})=(2/15)g(\text{ph})+(13/15)g(\tfrac{5}{2}). \qquad (6)$$

Using $g(\frac{5}{2})\cong-0.25$ (from the ground-state moment), Eq. 6 can be brought into agreement with experiment for $g(\text{ph})=0.21$.

ACKNOWLEDGMENTS

One of us (EM) gratefully acknowledges a fellowship from the Miller Institute for Basic Research in Science, University of California. The help of Miss Claudette Rugge who performed the least-squares fit calculations on the computer is greatly appreciated. We thank O. C. Kistner for communicating his results and discussing this problem.