it is attributed to the isomer shift, the sense indicates again an increase in electron density in going above the Curie temperature.

D. Debye Temperature

The measurements indicate that the Debye temperature is not constant in iron. It should be noted that at low temperatures the best value of θ probably comes from measurements of the temperature shift, while at high temperatures it is necessary to rely on absorption measurements. However, the shift measurements involve $\langle v^2\rangle_{\text{av}}$ [Eq. (2a)] while the absorption measurements involve $\langle r^2\rangle_{\text{av}}$ [Eq. (7a)]. The degree of agreement to be expected between the effective Debye temperatures calculated from these two quantities depends on the extent to which iron approximates a Debye solid. On the other hand, both methods appear to agree in the low-temperature region (Table V). More refined measurements will be needed to test this agreement further.

ACKNOWLEDGMENTS

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Comparison of the Rubidium-87 and Proton Zeeman Transition Frequencies in the Earth's Magnetic Field

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Alternate measurements of the earth's magnetic field have been made at the same location with a dc rubidium-87 magnetometer and with a proton free-precession magnetometer. The accuracy of the measurements is believed to be 1 μG in terms of the rubidium-87 frequency and 3 μG in terms of the proton frequency. The ratio of the g factors for rubidium electrons and for protons in a spherical water sample is found to be 658.234±0.004. The rubidium electron g factor is thus 27±6 parts per million higher than the g factor for electrons in the hydrogen ground state.

I. INTRODUCTION

A COMPARISON of the rubidium electronic g factor and the proton g factor has been obtained at a field of about $\frac{1}{2}$ G. The Zeeman transitions in an optically pumped rubidium-87 sample were observed by Dehmelt's method.[1–4] The intensity of circularly polarized rubidium $D-1$ radiation (7947 Å) transmitted along the earth's magnetic field H_e through the sample was observed as a function of the frequency of a weak rf field applied perpendicular to H_e. All components of the Zeeman transitions were well resolved despite splittings of only 46 cps between transitions within the same hyperfine level. The measurements were made at the Fredericksburg Magnetic Observatory of the U. S. Coast and Geodetic Survey in order to obtain good magnetic field stability and homogeneity. A proton free-precession magnetometer which was available at the Observatory[5] was used to measure the proton resonance frequency.

The dc rubidium magnetometer[6] was designed to be as nonmagnetic and as free from systematic errors as possible. Direct interchanges of the proton resonance head and the rubidium sample were made. The main limitation on the experimental accuracy came from possible weak paramagnetism of the proton resonance coil. It was unfortunately not possible to remove the water sample from the proton magnetometer and observe the rubidium frequency inside the proton resonance coil. A self-oscillating rubidium magnetometer[7,8]

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[1] H. G. Dehmelt, Phys. Rev. **105**, 1487 (1957).

[2] W. E. Bell and A. L. Bloom, Phys. Rev. **107**, 1559 (1957).

[3] T. L. Skillman and P. L. Bender, J. Geophys. Research **63**, 513 (1958).

[4] P. L. Bender, Compt. rend. 9e Colloq. Ampere, Librairie Payot, Geneva (1960).

[5] L. Hurwitz and J. H. Nelson, J. Geophys. Research **65**, 1759 (1960).

[6] The phrase "dc rubidium magnetometer" is used for convenience to denote a magnetometer in which the observed changes in optical absorption coefficient for the sample are slow compared with the Larmor precession frequency.

[7] H. G. Dehmelt, Phys. Rev. **105**, 1924 (1957).

[8] A. L. Bloom, Appl. Optics **1**, 61 (1962).

was used to track the earth's field during the proton magnetometer measurements. The accuracy achieved is believed to be one microgauss (two parts per million) for the values of H_e at the sample in terms of the rubidium Zeeman frequency and six parts per million for the over-all comparison of the rubidium and proton g factors.

II. RUBIDIUM MAGNETOMETERS

The components of the dc rubidium magnetometer were mounted in a long wooden trough. A commercial rubidium spectral lamp with built-in 100-Mc/sec excitation was used at a distance of 50 cm from the sample. Light from the lamp passed along H_e to the sample through a circular polarizer and an interference filter which passed only the D-1 line at 7947 Å. The transmitted light was focused with a lens about 10 cm behind the sample onto a 1-cm square silicon solar cell which served as the detector. The lens and detector and the lamp could be moved with respect to the sample and such changes in position indicated that the component of the field at the sample from these sources which was parallel to H_e was not more than a few microgauss. Movement of the sample with the other parts fixed indicated that the gradient in H_e was about 0.4 μG/cm.

The sample used for most of the measurements was spherical, about 5 cm in diameter, with a 3-mm-thick Pyrex wall and a thin layer of eicosane[9] ($C_{20}H_{42}$, a straight chain saturated hydrocarbon) on the inside surface. The sample was baked under vacuum, a small amount of eicosane was distilled into the main part of the sample, and then rubidium-87 was distilled into a side tube. At operating temperatures of about 30°C the phase (spin-spin) relaxation time for this sample was 0.2 sec and the signal strength was larger than for samples of the same size containing buffer gases. The larger signal is expected when the probability of disorienting collisions while the rubidium atoms are in the optically excited state is small. Tests of the eicosane-coated sample with externally applied magnetic field gradients showed much less broadening due to field inhomogeneity than for buffer gas samples of the same size. This particular eicosane sample has operated reproducibly for over 2 yr, but our occasional attempts to make larger eicosane-coated samples have been much less successful.

The rf frequency for the sample was derived from a self-oscillating rubidium magnetometer which was located in another building. A weak 5-cps sinusoidal magnetic field and a variable dc bias field at the self-oscillator provided frequency modulation and frequency control for the rf applied to the dc magnetometer sample. With this arrangement the self-oscillator frequency could be set accurately on the center of the strongest resonance line for the sample. The observed linewidth was about 10 cps and the signal-to-noise ratio about 20 with a 1-cps bandwidth. The relative contributions of light intensity and modulation broadening to the linewidth are not known. However, even for 10-cps-wide Lorentz lines, the observed ratio of intensities for the strongest and next strongest lines of about 3:1, and a separation between lines of 46 cps, the shift in the apparent center of the strongest line would be only 0.3 μG. The rf field strength was kept low enough so that multiple quantum transitions were barely observable and did not contribute appreciably to the shift.

The self-oscillating magnetometer was constructed from components on hand and no attempt was made to engineer it properly. Circularly polarized D-1 light from a commercial rubidium lamp was passed at 45 deg to H_e through a 10-cm-diam sample containing rubidium-87 and a neon buffer gas at a pressure of 30 Torr. The transmitted light was focused by a lens onto a square array of four 0.5-cm square silicon solar cells connected in series. With this arrangement the detector response was nearly an order of magnitude worse at the operating frequency of about 400 kc/sec than at lower frequencies but was considerably better than for a single 1-cm square cell. The preamplifier for both the self-oscillator and the dc magnetometer consisted of a single battery-operated type-6922 tube with a plate supply voltage of 28 V. The drift rate of this particular rather crude self-oscillator during magnetically quiet periods when measurements were made was usually 1 or 2 μG/h.

III. PROTON MAGNETOMETERS

Two proton magnetometers were made available by the Fredericksburg Magnetic Observatory for use in this work. One was the instrument normally used by the Observatory.[5,10] The other was a commercial unit purchased by the U. S. Coast and Geodetic Survey for use at the College Magnetic Observatory in Alaska. Both resonance heads were run at the end of long cables and could be interchanged with the rubidium sample in the dc rubidium magnetometer. All final results are based on the Observatory proton magnetometer.

Careful magnetization checks were made by observing the effect on the rubidium sample resonance when the proton resonance heads were placed about 11 cm away in a direction perpendicular to H_e. Magnetic field changes as small as 0.5 μG could be measured. The Observatory resonance head gave a maximum field of 4 μG at the 11-cm distance. The dependence of the observed field on orientation of the head showed that the field was caused by a permanent magnetization which was axially symmetric about the instrument axis. It thus seems probable that the many turn coil of copper wire serving as both polarizing and sensing coil contains tiny ferromagnetic impurities which were highly polarized by repeated sudden applications of the

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[9] H. G. Robinson, E. S. Ensberg, and H. G. Dehmelt, Bull. Am. Phys. Soc. 3, 9 (1958).

[10] J. L. Bottum, R. E. Gebhardt, and J. B. Townshend, J. Geophys. Research 66, 4319 (1961).

polarizing field to the sample. Since the field due to the impurities is nearly perpendicular to H_e under normal operating conditions, measurements made with the instrument are probably not appreciably affected.

The maximum field at an 11-cm distance observed with the commercial proton resonance head was 3 μG. The symmetry of the field indicated that both permanent and induced fields were present. Shortly after the measurements reported here it was found that a brass plug at one end of the head was quite paramagnetic. When the plug was replaced by one of aluminum, no traces of magnesium were seen in either resonance head as judged by deflection of a carefully suspended magnet with one end placed close to the object being checked.[11] The field pattern for the commercial head as observed with the rubidium magnetometer was consistent with a permanent magnetization in the direction of the magnetizing field for the head and an induced magnetization of the plug by H_e. This head gave 12 ppm (7 μG) higher magnetic field measurements than the Observatory instrument when the brass plug was still in place, with an increase in field being consistent with the actual position of the plug during the measurements. The above results indicate that a suspended magnet, while quite sensitive for finding concentrated paramagnetic impurities which may cause trouble in the earth's field, does not have adequate sensitivity for finding distributed ferromagnetic impurities. Measurements with the commercial head were unfortunately not repeated after replacement of the plug, and thus could not be used in obtaining the final results.

IV. COMPARISON PROCESS

The frequency of the rubidium self-oscillator was measured to 0.1 cps during alternate 10-sec periods. It was confirmed that the presence of a weak 5-cps modulation of the field did not affect the results. Between rubidium counts the Observatory proton sample was polarized and the period for 2000 cycles of the proton free-precession signal was measured. The decay time was about 3 sec, but a shorter measuring period was more reliable because of occasional noise pulses. The same crystal oscillator provided the time base for both measurements.

A run consisted of setting the self-oscillator against the $(F=2, M_F=-2)\rightarrow(F=2, M_F=-1)$ Zeeman transition for the dc rubidium magnetometer, replacing the rubidium sample in the dc apparatus by the proton resonance head, taking approximately 10 min of alternate readings with the self-oscillator and the proton apparatus, replacing the rubidium sample, and checking the self-oscillator against it to correct for drifts during the run. Care was taken to center the proton resonance head with respect to the rubidium sample to minimize the effect of field gradients. Alternate runs were made with the resonance head turned over in order to cancel the effect of any permanent magnetic field component along H_e. Control runs were made using 1000 and 4000 cycles of the proton frequency in order to obtain an estimate of possible shifts due to the electronics.

V. RESULTS

The final data were obtained from four runs taken between 12:50 p.m. and 2:05 p.m. EST on October 9, 1961. The value of H_e during this period was 0.5648 G, corresponding to proton and rubidium-87 frequencies of 2405 and 395 200 cps, and the variation during each run was less than 10 μG. An average of results for the 4 runs gives a raw value of

$$\nu_{87}(-2,-1)/\nu_p=164.3416$$

for the ratio of the $(F=2, M_F=-2)\rightarrow(F=2, M_F=-1)$ rubidium-87 Zeeman transition frequency to the proton frequency for the Observatory water sample. The rms scatter was 2 parts per million (ppm). Other sets of runs on June 6 and October 6, 1961 gave the same result to within 2 ppm but could not be used because adequate control measurements were not made. At about 1:35 a.m. EST on October 6 the earth's field was found to be constant during a 5-min period to ±0.3 μG and constant during a 2-min period to the 0.1-μG limit imposed by a 0.1-cps uncertainty in the frequency as measured over a 10-sec period.

From the Breit-Rabi formula,[12] writing all g factors used as positive, $\nu_{87}(-2,-1)$ is given by

$$\nu_{87}(-2,-1)=-g_{87}(\mu_0/h)H+\tfrac{1}{2}\nu_H \times[(1-X+X^2)^{1/2}-(1-X)],$$

where

$$X=(1/\nu_H)(g_{\mathrm{Rb}}+g_{87})(\mu_0/h)H.$$

Here g_{Rb} and g_{87} are the g factors for the rubidium electron and nucleus (uncorrected for diamagnetism), μ_0 is the Bohr magneton, h is Planck's constant, $\nu_H=6\,834\,682\,614\pm1$ cps is the rubidium-87 ground-state hyperfine splitting,[13] and H is the magnetic field. Also,

$$\nu_p'=g_p'(\mu_0/h)H,$$

where g_p' is the proton g factor for a spherical water sample and ν_p' is the corresponding Larmor frequency. For the observatory proton resonance head the correction for the bulk susceptibility of the water[14] is estimated to be less than 1 ppm and will be neglected.

Combining the above expressions, we obtain

$$\frac{\nu_{87}(-2,-1)}{\nu_p'}=-\left(\frac{g_{87}}{g_p'}\right)+\frac{1}{2}\left(\frac{\nu_H}{\nu_p'}\right) \times[(1-X+X^2)^{1/2}-(1-X)].$$

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[11] L. R. Alldredge, U. S. Coast and Geodetic Survey (private communication).

[12] J. M. B. Kellogg and S. Millman, Revs. Modern Phys. **18**, 323 (1946); see p. 343.

[13] L. Essen, E. G. Hope, and D. Sutcliffe, Nature **189**, 298 (1961).

[14] S. H. Koenig, A. G. Prodell, and P. Kusch, Phys. Rev. **88**, 191 (1952); see p. 198.

Setting

$$f=\left(\frac{\nu_{87}(-2,-1)}{\nu_p'}+\frac{g_{87}}{g_p'}\right)$$

and solving for X, we have

$$(\nu_H/\nu_p')X=4f\left[\frac{1+(\nu_p'/\nu_H)f}{1+4(\nu_p'/\nu_H)f}\right].$$

Since

$$(\nu_H/\nu_p')X=(g_{\mathrm{Rb}}/g_p')+(g_{87}/g_p'),$$

we have

$$(g_{\mathrm{Rb}}/g_p')=4f\left[\frac{1+(\nu_p'/\nu_H)f}{1+4(\nu_p'/\nu_H)f}\right]-(g_{87}/g_p').$$

Substituting[15,16] $(g_{87}/g_p')=0.3272$ and $(\nu_p'/\nu_H)=0.3519\times10^{-6}$ gives

$$(g_{\mathrm{Rb}}/g_p')=658.234.$$

The rubidium frequency probable error is estimated to be 2 ppm (1 μG), with the major uncertainties due to possible shifts by nearby transitions (0.5 ppm), noise limitations in setting on the center of the transition (0.5 ppm), drift in the self-oscillator (0.5 ppm), and miscellaneous possible shifts due to the light intensity, collisions with the wall, tubulations on the sample, etc. (estimated as 1 ppm). For the proton measurements the estimated probable error is 5.5 ppm (3 μG), with the largest uncertainties due to possible magnetism of the resonance coil (4 ppm), noise and electronics limitations (3 ppm), and possible effects of magnetic field inhomogeneity in the apparatus (2 ppm). The main part of the uncertainty due to magnetism of the coil comes from possible induced magnetism. This effect was found to give a shift in magnetic field of less than 1 ppm at a distance of 11 cm from the resonance head, but a calculation of the ratio of the field at this distance to the field at the center for the normal east-west orientation of the sample axis showed that the shift in field at the center of the sample would be larger by a factor of between 3 and 4. Combining the uncertainties in the rubidium and proton measurements gives a probable error of 6 ppm, or a final experimental result of

$$(g_{\mathrm{Rb}}/g_p')_{\mathrm{exp}}=658.234\pm0.004.$$

A more accurate measurement in a 12-G magnetic field is presently being completed by R. L. Driscoll at the National Bureau of Standards.

The above ratio is normally expected to be independent of the magnetic field up to very high field strengths. The present measurement is intended, when combined with more accurate experiments at higher fields, to provide a check of the magnetic field independence over a wider range than had previously been possible. However, we can also combine this ratio with Lambe's value[17] of $(g_{\mathrm{H}}/g_p')=658.21591\pm0.00004$ obtained at about 3000 G, where g_{H} is the electron g factor for the ground state of hydrogen. The result is

$$(g_{\mathrm{Rb}}/g_{\mathrm{H}})_{\mathrm{exp}}=1+(27\pm6)\times10^{-6}.$$

This is in good agreement with the theoretical estimate made by Phillips.[18] Also, if we assume the correctness of Phillips' conclusion that the g factors for the alkali atoms lighter than potassium should be close to the values obtained from the relativistic and diamagnetic corrections alone, which give[19]

$$(g_{\mathrm{Na}}/g_{\mathrm{H}})_{\mathrm{Th}}=1+5\times10^{-6},$$

then the present result is in disagreement by 28±12 ppm with the ratio of rubidium and sodium electron g factors measured by Kusch and Taub[20] at about 400 G,

$$(g_{\mathrm{Rb}}/g_{\mathrm{Na}})_{\mathrm{KT}}=1+(5\pm1)\times10^{-5}.$$

It is a pleasure to express my thanks to the U. S. Coast and Geodetic Survey for permission to use their proton magnetometers and to R. E. Gebhardt and the members of the Observatory staff for their assistance in the measurements. I would also like to thank T. L. Skillman, now with the National Aeronautics and Space Administration, and E. C. Beaty of the National Bureau of Standards for their contributions to the early parts of the experiment.

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[15] W. E. Blumberg, J. Eisinger, and M. P. Klein, Phys. Rev. **124**, 206 (1961).

[16] S. Penselin, T. Moran, V. W. Cohen, and G. Winkler, Phys. Rev. **127**, 524 (1962).

[17] E. B. D. Lambe, thesis, Princeton University, 1959 (unpublished).

[18] M. Phillips, Phys. Rev. **88**, 202 (1952).

[19] P. Kusch and V. W. Hughes, in *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, 1959), Vol. 37, Part 1.

[20] P. Kusch and H. Taub, Phys. Rev. **75**, 1477 (1949).