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NUCLEAR SPIN AND MOMENT OF Ag^{110m}
BY PARAMAGNETIC RESONANCE

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ABSTRACT

Paramagnetic resonance was observed in 253d Ag^{110m}, present as Ag^{2+} in the $[(iso\text{-}C_3H_7)_2NCS_2]_2Ag$ complex. Eleven hfs (hyperfine structure) lines were observed, the positions of the other two lines being obscured by other absorptions present in the sample, and the nuclear spin of 6 was confirmed. A hfs constant $a_{110m} = (7.108 \pm .02) \times 10^{-3}$ cm^{-1} was determined. A hyperfine anomaly of $\Delta_{107,109} = -0.40\% \pm 0.1\%$ was observed for stable Ag^{2+} in this complex, indicating that the hfs arises from contact interaction. A nuclear moment of $\mu_{110m} = +3.55 \pm 0.04$ nm was derived after a 3.7% hyperfine-anomaly correction. It is pointed out that hyperfine anomalies can be infinitely large for very small moments, and that the anomaly may cause a finite moment to exhibit vanishing hyperfine structure or conversely. The nuclear moment does not agree with shell-model predictions using empirical g factors, being low by 1 nm. It is suggested that the $(g_{9/2})^7$ proton configuration might be coupled to spin 7/2. This yields a moment of + 3.54 nm. The hyperfine fields for Ag in Fe and Ni are corrected to -282 ± 20 kG and -87 ± 8 kG respectively.

I. INTRODUCTION

Hyperfine magnetic fields at nuclei of 3d, 4d, and 5d transition-group metals in iron, nickel, and cobalt hosts have been the subject of several recent investigations.[1] These fields are measured by means of the Mössbauer effect, nuclear orientation, low-temperature specific heats, perturbed angular correlations, or nuclear magnetic resonance. Irrespective of the method employed, the measured parameter gives the product of either the nuclear gyromagnetic ratio or the magnetic moment times the hyperfine magnetic field, H_{hf}. In those instances where the nuclear spins and magnetic moments are known, the hyperfine fields are easily calculated. The quantity μH_{hf}, in Ni and Fe lattices, and the nuclear spin of Ag^{110m} have been measured.[2,3] In this paper we report measurements of the nuclear moment of Ag^{110m}.

The quantities of Ag^{110m} available and safe to handle excluded the possibility of a direct NMR measurement of the gyromagnetic ratio. The two most feasible techniques are atomic beam magnetic resonance and paramagnetic resonance. We report herein the results of paramagnetic resonance measurements.

Pettersson and Vänngard have reported the PMR spectra of Ag^{2+} diisopropyl dithiocarbamate in solution at room temperature and in frozen glasses.[4] The room-temperature spectrum was characterized by narrow lines (approximately 2 gauss linewidths), and the hyperfine structures of the two naturally occurring Ag isotopes Ag^{107}, (I=1/2, μ=-.1130 nm, natural abundance 51.35%) and Ag^{109}, (I=1/2, μ=-.1299 nm, natural abundance 48.65%) were resolved. We have measured the hyperfine coupling constants in solutions of Ag^{107}, Ag^{109}, and Ag^{110m} complexed with thiuram disulphide, as described in Sec. II. From the ratio of the hyperfine coupling constant of either stable isotope to that of Ag^{110m}, and the known nuclear moment of the stable isotope, the nuclear moment of Ag^{110m} can be approximately calculated. Since the hyperfine structure observed is due

to the finite s-electron density at the nucleus, the measured coupling constants include the effect of the hyperfine anomaly, and the value of the nuclear moment of Ag^{110m} obtained in this way will be uncorrected for this effect. We estimate in Sect. III the magnitude of the hyperfine anomaly by use of the modified Bohr-Weisskopf theory.[5] In the course of this experiment we have also measured the Ag^{107}-Ag^{109} hfs anomaly in the thiuram disulfide complex. The nuclear magnetic moment and hyperfine fields are discussed in Sect. IV.

II. EXPERIMENTAL

The radioactive isotope Ag^{110m} was obtained from Oak Ridge National Laboratory as $AgNO_3$ solution (5.3 ml) containing 0.02 atom percent Ag^{110m} in a total of 2.3 mg of Ag^{107} and Ag^{109} isotopes. This solution was evaporated to dryness and 2 ml of benzene (B and A reagent grade) containing a large excess of tetraisopropyl thiuram disulphide was added to the residue. A blue color characteristic of the divalent Ag complex $[(iso\text{-}C_3H_7)_2NCS_2]_2Ag$ formed immediately[6] and the intensity of the color increased upon stirring. This solution was degassed in a quartz sample tube by repeated freeze-pump-thaw cycles in order to remove O_2 and was then used for the experiment.

Measurements were also made on the enriched isotopes Ag^{107} (purity 95.7%) and Ag^{109} (purity 99.1%) which were obtained from Oak Ridge National Laboratory as Ag metal. With the addition of the benzene solution of thiuram disulphide to the metal, the blue color of the Ag^{2+} complex formed; the samples were also degassed before use.

The PMR measurements were made at room temperature at a frequency of 9.5 Gc/sec with a superheterodyne spectrometer employing magnetic-field modulation and synchronous detection. The magnetic field was measured with a Varian F-8 NMR fluxmeter whose frequency was measured with a Hewlett-Packard 524-B frequency counter. The line positions reported below are average values of "up" and "down" field scans.

The spin Hamiltonian appropriate to Ag^{2+} in solution is

$$\mathcal{H} = g_e\beta\vec{H}\cdot\vec{S} + a\vec{I}\cdot\vec{S} \qquad (1)$$

where g_e and a are the spectroscopic splitting factor and the hyperfine structure constant, respectively. The transition energies, including second

order terms, are given by

$$h\nu = g_e\beta H + aM_I - \frac{a^2}{2g_e\beta H}[I(I+1)-M_I^{\,2}] \qquad (2)$$

where $M_I = -I, -I+1, \ldots, I$.[4,7] For Ag^{110m}, I=6, so thirteen lines are expected in the spectrum. We have observed eleven of the thirteen lines. The remaining two lines were obscured by either the hyperfine structure of the stable Ag^{2+} isotopes or by two unexplained impurity lines. Positions of eight of the Ag^{110m} lines were measured accurately and for Ag^{110m} we found a_{110m} = 75.39 ± .2 gauss, $(7.108 \pm 0.02) \times 10^{-3}\,cm^{-1}$. In Table I the calculated and experimentally determined magnetic fields for the transitions are listed. The hyperfine lines are listed arbitrarily.

III. THE HYPERFINE ANOMALY AND THE NUCLEAR MOMENT

The hyperfine anomaly for two isotopes 1 and 2 is defined as

$$\Delta_{1,2} = \epsilon_1 - \epsilon_2, \tag{3}$$

where ϵ_i is the fractional hyperfine interaction reduction, for isotope i, from that expected for a point nucleus. Hyperfine anomalies are present only when the hfs is caused by s(or in heavy elements $p_{1/2}$) electrons. Our observed anomaly for $Ag^{107,109}$,

$$\Delta_{107,109} = -0.40 \pm 0.1\%$$

is in excellent agreement with the atomic beam value[8,9] of $(-0.412 \pm 0.004)\%$. This constitutes independent evidence for the observation by Pettersson and Vänngård that the hfs of Ag^{2+} in the complex arises almost entirely from contact interaction. We cannot decide from this anomaly <u>which</u> s electrons cause the hfs, because all s electrons have the same distribution within the nucleus and produce the same anomaly.[10]

For reasons discussed below we believe the $Ag^{107,110m}$ (or $Ag^{109,110m}$) anomaly to be large, and we make a correction of 3.7% for it. Using the approximate relation $g_{110m}/g_{109} \cong a_{110m}/a_{109}$, we obtain

$$\mu_{110m} \cong +3.68 \text{ nm} \quad .$$

The positive sign was obtained from nuclear polarization experiments.[1]

The theory of hfs anomalies was given by Bohr and Weisskopf,[10] and Bohr[11] extended it to treat specific nuclear models. Eisinger and Jaccarino[5] have extended the treatment to higher-order terms and have tabulated relevant

coefficients. The essence of the hfs anomaly is that the density of an s (or a $p_{1/2}$) electron varies over the nuclear volume, rendering the hfs constant sensitive to the distribution of nuclear magnetism. The intrinsic spin and orbital moments of a proton contribute differently to the hfs. The fractional change in a, relative to a point nucleus, is[5]

$$\epsilon = -(\overline{\kappa}_s \alpha_s + \overline{\kappa}_\ell \alpha_\ell) \quad . \tag{4a}$$

The parameters $\overline{\kappa}_s$ and $\overline{\kappa}_\ell$ are functionally dependent on both nuclear and electron distributions, and they may be evaluated from Eisinger and Jaccarino's tables. The parameters α_s and α_ℓ are the fractional contributions of intrinsic spin and orbital moments to g. For a simple shell-model state we have[12]

$$\alpha_s = \frac{g_s}{g}\left(\frac{g - g_\ell}{g_s - g_\ell}\right) \tag{4b}$$

where g_s and g_ℓ are the spin and orbital components, respectively, of g. The relation $\alpha_s + \alpha_\ell = 1$ must be satisfied, but α_s and α_ℓ may exceed unity by any amount. Thus Δ may take any value, including infinity. For a nominally $p_{1/2}$ proton state with a certain deviation from the Schmidt limit, for example, the magnetic moment could be zero, yet magnetic hfs could be observed. Other examples are easily conceived, especially in odd-odd and deformed nuclei. It is therefore certainly not safe to regard Δ as a 1% effect, especially for small magnetic moments.

We may write the contact portion of a for Ag^{110m} in terms of the point-nucleus constant a^{o}_{110} as

$$a_{110m} = a^{o}_{110m}(1 + \epsilon_{110m}) = c(1 + \epsilon_{110m})g_{110m} \tag{5}$$

where c is the same for all Ag isotopes to good approximation. Writing a similar expression for Ag^{109} and combining, we find

$$g_{110m} = g_{109}\left(\frac{a_{110m}}{a_{109}}\right)\left(\frac{1 + \epsilon_{109}}{1 + \epsilon_{110m}}\right) . \tag{6}$$

Now we must estimate ϵ_{109} and ϵ_{110m} from a nuclear model.

For Ag^{110m} the nucleon configuration is probably to first approximation $p(g_{9/2})n(d_{5/2})$ (see Sect. IV A) and ϵ_{110m} arises mostly from the proton. Since in the single-particle model $\vec{\ell}_p$ and $\vec{s}_p$ are coupled "parallel," both α_s and α_ℓ are less than unity. The detailed structure of the 6+ state will affect ϵ_{110m} somewhat, but it cannot be very different from -0.5% for any likely combination of nucleon configurations. This figure is the result of several quantitative estimates based on different assumptions about the 6+ state.

Ag^{107} and Ag^{109} have $p_{1/2}$-proton ground states and ϵ_{107} and ϵ_{109} are expected to be several percent. Brun and Staub[12] calculated $\Delta_{107,\,109}$ = -0.41%, in excellent agreement with experiment, by using "effective" intrinsic g factors for the $p_{1/2}$ protons. Eisinger and Jaccarino pointed out that configuration mixing should be taken into account for such calculations. It is now clear that pairing forces should also be considered. For $Ag^{107,109}$ these refinements are not warranted by our present knowledge of the nuclear structure. In particular, configuration mixing is relatively unimportant for a $p_{1/2}$ particle, vanishing for δ forces.[13] The observed moments are correspondingly close to the Schmidt limits. Using tabulated parameters,[5] we find $\epsilon_{107(109)} = -(1.01\,\alpha_s + .25\,\alpha_\ell)\%$. For α_s and α_ℓ calculated from

the Schmidt-limit value of the magnetic moment of a $p_{1/2}$ proton, this gives $\epsilon = -2.51\%$. This is a rather large reduction, but probably represents a lower limit for the magnitude of ϵ, because the real moments lie closer to zero than does the Schmidt limit and α_s and α_ℓ are probably correspondingly larger in magnitude. Evaluating "effective" intrinsic g-factors, after Brun and Staub, from the empirical moments, we find $\epsilon_{107} = -5.49\%$, $\epsilon_{109} = -4.92\%$. The calculated anomaly is then too large, $\Delta_{107,\ 109} = -0.57\%$, and assuming that the ground states of Ag^{107} and Ag^{109} are similar (in the sense of consisting of slightly different admixtures of the same configurations into the $p_{1/2}$ proton state), we may regard these estimates of ϵ_{107} and ϵ_{109} as somewhat too large. Perhaps the best estimate of $\epsilon_{107(109)}$ is obtained by adjusting α_s and α_ℓ for Ag^{107} and Ag^{109} to fit $\Delta_{107,109}$. Even this adjustment is arbitrary, but we assume that the two nuclei are sufficiently similar that we may move the two values of α_s proportionally toward the Schmidt limits until $\Delta_{107,109}$ agrees with experiment. Then we have $\epsilon_{109} = -4.24\%$, and $\Delta_{109,110m} \cong -3.7\%$. We trust this estimate to $\pm 1.0\%$. From Eq. (6) the final value for the moment becomes

$$\mu_{110m} = +3.55 \pm 0.04 \text{ nm}.$$

IV. DISCUSSION

A. The Nuclear Moment

The single-particle shell model configuration for Ag^{110m} is $\pi(g_{9/2})^2 \nu(d_{5/2})^5$. It is profitable, in estimating theoretical magnetic moments for odd-odd nuclei, to use empirical g factors of the nucleon configurations, obtained from neighboring odd-A nuclei. From Lindgren's tabulation[14] it is clear that the magnetic moments of $g_{9/2}$ proton ($d_{5/2}$ neutron) states vary systematically with proton (neutron) number. By interpolation we can estimate $g_p = +1.24$, $g_n = -0.32$ for the $g_{9/2}$ proton and $d_{5/2}$ neutron in Ag^{110m}. The moment is then calculated as

$$\mu_{110m} = +1.24(29/7)-0.32(13/7) = +4.54 \text{ nm}$$

almost one unit too high. This difference is far outside what would be expected from the regularity of the empirical single-nucleon g factors. This method of estimating the moment should account for pairing and configuration-mixing effects in the configurations of the two types of nucleons.

An attractive explanation for the low moment is the coupling of the proton configuration to spin 7/2. The 6+ state would then be described as $|\pi(g_{9/2})^7{}_{7/2}\nu(d_{5/2})^5{}_{5/2}\rangle_6$. There are precedents for such higher-seniority coupling (for example in V^{51}). The calculated magnetic moment is then

$$\mu = +1.24(7/2) - 0.32(5/2) = +3.54 \text{ nm},$$

is good agreement with experiment.

B. Hyperfine Fields

The recently reported nuclear polarization experiments[2] gave the products

$$\mu H = -(10.0 \pm 0.07) \times 10^5 \text{ nm-gauss for Ag in Fe}$$

$$\mu H = -(3.1 \pm 0.03) \times 10^5 \text{ nm-gauss for Ag in Ni.}$$

An approximate value $\mu_{110m} = +2.9 \pm 1.3$ was also deduced. These fields have been already discussed, and the new value of μ_{110m} has little effect on that discussion. The new values for the fields are

$$H = -282 \pm 20 \text{ kG (Ag in Fe)}$$

$$H = -87 \pm 8 \text{ kG (Ag in Ni).}$$

C. Hyperfine Anomalies in Isotopes with Very Small Moments.

It is evident from the structure of Eq. (4) that for $\bar{\kappa}_s \neq \bar{\kappa}_\ell$, and $|\alpha_s|$, $|\alpha_\ell| \gg 1$, subject of course to $\alpha_s + \alpha_\ell = 1$, the fractional reduction in hfs ϵ may be arbitrarily large. In practice this can happen for a proton state with sufficient configuration mixing to produce a magnetic moment near zero, or it may happen for odd-odd or collectively-excited nuclei in various ways. The first case is easily visualized as a nominal $p_{1/2}$ or $d_{3/2}$ proton state, in which the orbital and spin contributions to the moment tend to cancel, modified by configuration mixing until the cancellation is complete. The nuclear g factor and hfs constant are given by the equations

$$g = g_s\beta_s + g_\ell\beta_\ell \tag{7a}$$

$$a = cg(1-\bar{\kappa}_s\alpha_s - \bar{\kappa}_\ell\alpha_\ell)$$

$$= c(g-\bar{\kappa}_s g_s\beta_s - \bar{\kappa}_\ell g_\ell\beta_\ell). \tag{7b}$$

Here β_s and β_ℓ represent fractional contributions of spin and orbital g factors to the nuclear g factor. Clearly $\alpha_s = \beta_s g_s/g$, and similarly for α_ℓ. We can see formally that g and a vanish separately. From Eq. (7a) we have $g=0$ for $\beta_s = g_\ell/(g_\ell-g_s)$, using $\beta_\ell+\beta_s = 1$. However this condition will give $a=0$ (Eq. 7b) <u>only</u> if $\bar{\kappa}_s=\bar{\kappa}_\ell$, which is in fact never the case.

Clearly the possibility of a large hfs anomaly makes the determination of very small nuclear moments by hyperfine-structure techniques a very hazardous procedure in terms of percentage (but not absolute) accuracy. To give an estimate of the magnitudes of errors involved we show in Fig. 1 the calculated values of ϵ for nominally $p_{1/2}$ proton states (as in $Ag^{107,109}$) but with an "effective" g_s, such that the moment is given by

$$\mu = 2/3 - (1/6)g_s \ , \tag{8}$$

in the region $-.05 \leq \mu \leq .05$. Evidently for $|\mu| \sim .01$ an anomaly of ~50% is expected. The ϵ curves were obtained from Eq. (8) and the relation $\epsilon = -(1.01\alpha_s + 0.25\alpha_\ell)\%$, discussed above. Also plotted is μ', the nuclear moment that would be derived from comparison of hfs constants with an isotope with known moment and no anomaly. The separate vanishing of μ and μ'(or a) are evident. Also between the vanishing points the ratio μ'/μ is <u>negative</u>. We conclude that moments in the ~.01 nm region determined by hfs techniques only, can be in error

by tens or even hundreds of percent and could actually be zero. Direct measurement of these moments would be very interesting.

Table I.

Line	Calculated (Gauss)	Experimental (Gauss)
1	3752.2	3752.0
2	3667.4	3666.9
3	3584.2	3583.8
4	3502.8	3502.5
5	3423.2	
6	3345.2	
7	3268.9	
8	3194.4	3194.5
9	3121.6	3121.6
10	3050.5	3050.5
11	2981.1	2981.0
12	2913.5	
13	2847.5	

Calculated and experimental hyperfine line positions of Ag^{110m}, $a_{110m} = 75.39 \pm .2$ gauss. Lines are numbered arbitrarily; the highest field line is 1, the next highest is 2, etc.

FOOTNOTES AND REFERENCES

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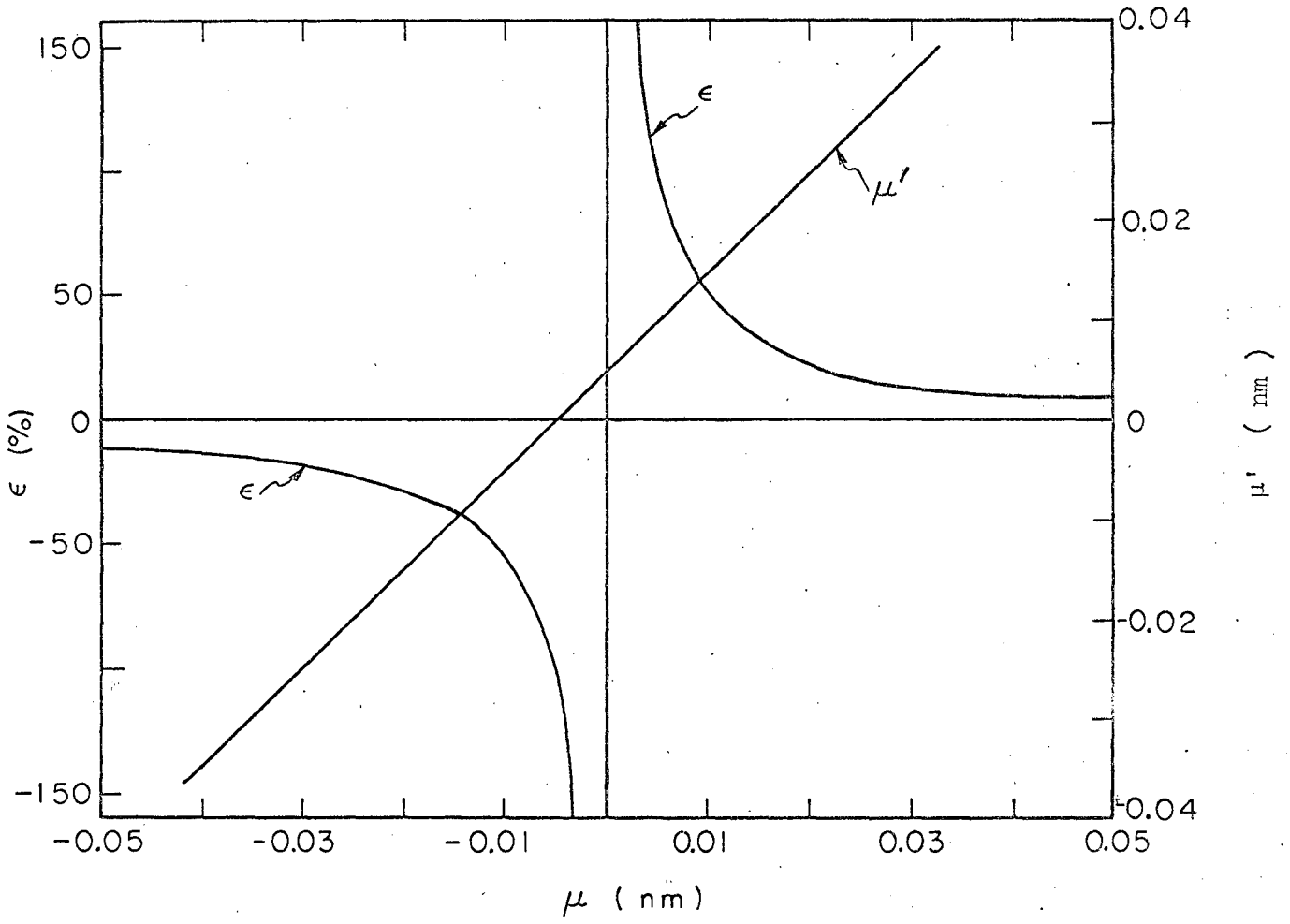
FIGURE CAPTIONS

Fig. 1. Fractional hyperfine-interaction reduction and apparent nuclear moment (deduced without correcting for hfs anomaly) versus nuclear moment, for nominally $p_{1/2}$ proton states with moments given by $\mu = 2/3 - 1/6g_s$, where g_s is the "effective" intrinsic-spin g factor.


150
50
0
-50
-150
ε (%)
0.04
0.02
0
-0.02
-0.04
μ' (nm)
-0.05
-0.03
-0.01
0.01
0.03
0.05
μ (nm)
ε
ε
μ'

MUB-6908

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