yielded the following parameters for $(J=1): E_0=51.3$ $\pm 0.2 \text{ eV}, \Gamma_n^0 = 3.28 \pm 0.16 \pm (0.16) \text{ meV}.$

Figure 2 shows the cross section measured in the keV region and the true average cross section as computed taking into account the sample thickness corrections. The value of the spin-averaged strength function is $(0.54\pm0.10)\times10^{-4}$. The principal source of uncertainty stems from the error in R', and is included in the error estimate of 0.10×10^{-4} . The value of $\langle \Gamma_n^0 \rangle / D$ calculated from the resonance parameters from the relation $\langle \Gamma_n^0 \rangle / D = \sum g \Gamma_n^0 / (E_f - E_i)$ is $(0.76 \pm 0.27) \times 10^{-4}$. Garg et al.¹³ have reported a value of $(0.46\pm0.05)\times10^{-4}$ for natural Ag. This result, with the result of the present experiment, implies nearly equal strength functions for the Ag¹⁰⁷ and Ag¹⁰⁹ isotopes.

The value of $R' = 6.3 \pm 0.1$ F is somewhat lower than the value of Sheer and Moore⁴ of 6.6 ± 0.1 F, obtained from a scattering experiment at 5 eV. Zimmerman and Hughes¹⁵ obtained a result of 6.6 ± 0.6 F from totalcross-section data. The present result is obtained by fitting over a much wider energy region that is done in previous work. As noted previously, the value of R' in this A region should be very nearly equal to the radius parameter R of the optical model. For the value of $r_0 = 1.35$ in the relation $R = r_0 A^{1/3}$, a value for Ag¹⁰⁹ of 6.4 F is obtained, which is in excellent agreement with the present result.

ACKNOWLEDGMENT

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¹⁵ R. L. Zimmerman and D. J. Hughes, Bull. Am. Phys. Soc. 3, 176 (1958).

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Nuclear Spin and Moment of Ag^{110m} by Paramagnetic Resonance^{*}

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Paramagnetic resonance was observed in 253-day Ag^{110m}, present as Ag²⁺ in the [(iso-C₃H₇)₂NCS₂]₂Ag complex. Eleven hfs 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 $a_{110m} = (7.108 \pm 0.02)$ $\times 10^{-3}$ cm⁻¹ was determined. A hyperfine anomaly of $\Delta_{107, 109} = -0.40\% \pm 0.1\%$ was observed for stable Ag²⁺ in this complex, indicating that the hfs arises from contact interaction. A nuclear moment of μ_{110m} $=+3.55\pm0.04$ 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 $(g_{9/2})^{\tau}$ proton configuration might be coupled to spin $\frac{7}{2}$. 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

YPERFINE magnetic fields at nuclei of 3d, 4d, H 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 (NMR). 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, $H_{\rm hf}$. In those instances where the nuclear spins and

magnetic moments are known, the hyperfine fields are easily calculated. The quantity $\mu H_{\rm hf}$, 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 (PMR). We report herein the results of paramagnetic resonance measurements.

Pettersson and Vänngård have reported the PMR spectra of Ag²⁺ diisopropyl dithiocarbamate in solution

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^{(1965).}

² G. A. Westenbarger and D. A. Shirley, Phys. Rev. 138, A160

^{(1965).} ³ W. B. Ewbank, W. A. Nierenberg, H. A. Shugart, and H. B. Silsbee, Phys. Rev. 110, 595 (1958).

at room temperature and in frozen glasses.⁴ The roomtemperature spectrum was characterized by narrow lines (approximately 2-G linewidths), and the hyperfine structures of the two naturally occurring Ag isotopes, Ag¹⁰⁷ $(I=\frac{1}{2})$, $\mu=-0.1130$ nm, natural abundance 51.35%), and Ag¹⁰⁹ $(I = \frac{1}{2}, \mu = -0.1299$ nm, natural abundance 48.65%) were resolved. We have measured the hyperfine coupling constants in solutions of Ag¹⁰⁷, Ag¹⁰⁹, and Ag^{110m} complexed with thiuram disulfide, 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 Sec. 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 Ag107-Ag109 hfs anomaly in the thiuram disulfide complex. The nuclear magnetic moment and hyperfine fields are discussed in Sec. IV.

II. EXPERIMENTAL

The radioactive isotope Ag110m was obtained from Oak Ridge National Laboratory as AgNO₃ solution (5.3 ml) containing 0.02 at.% Ag^{110m} in a total of 2.3 mg of Ag¹⁰⁷ and Ag¹⁰⁹ isotopes. This solution was evaporated to dryness and 2 ml of benzene (B and A reagent grade) containing a large excess of tetraisopropyl thiuram disulfide was added to the residue. A blue color characteristic of the divalent Ag complex [(iso-C₃H₇)₂NCS₂]₂Ag formed immediately⁶ 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 Ag¹⁰⁷ (purity 95.7%) and Ag¹⁰⁹ (purity 99.1%) which were obtained from Oak Ridge National Laboratory as Ag metal. With the addition of the benzene solution of thiuram disulfide to the metal, the blue color of the Ag²⁺ 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

TABLE I. Calculated and experimental hyperfine line positions of Ag^{110m} , $a_{110m} = 75.39 \pm 0.2$ G. Lines are numbered arbitrarily: the highest field line is 1, the next highest is 2, etc.

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

below are average values of "up" and "down" field scans.

The spin Hamiltonian appropriate to Ag²⁺ in solution is

$$\mathcal{C} = g_{e}\beta \mathbf{H} \cdot \mathbf{S} + a\mathbf{I} \cdot \mathbf{S}, \qquad (1)$$

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

$$h\nu = g_{e}\beta H + aM_{I} - (a^{2}/2g_{e}\beta H)[I(I+1) - M_{I}^{2}], \quad (2)$$

where $M_I = -I$, -I + 1, ..., $I^{4,7}$ For Ag^{110m}, I = 6, so 13 lines are expected in the spectrum. We have observed 11 of the 13 lines. The remaining two lines were obscured by either the hyperfine structure of the stable Ag²⁺ isotopes or by two unexplained impurity lines. Positions of eight of the Ag^{110m} lines were measured accurately and for Ag^{110m} we found $a_{110m} = 75.39 \pm 0.2$ G, (7.108 ± 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

$$\Delta_{1,2} = \epsilon_1 - \epsilon_2, \qquad (3)$$

where $(-\epsilon_i)$ 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 ± 0.004) %. This constitutes independent

- ⁷ B. Bleaney, Phil. Mag. 42, 441 (1951).
 ⁸ G. Wessel and H. Lew, Phys. Rev. 92, 641 (1953).
 ⁹ P. B. Sogo and C. D. Jeffries, Phys. Rev. 93, 174 (1954).

⁴ R. Pettersson and T. Vänngård, Arkiv Kemi 17, 249 (1961).

⁵ J. Eisinger and V. Jaccarino, Rev. Mod. Phys. 30, 530 (1958).

⁶S. Akerström, Arkiv Kemi 14, 403 (1959).

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 which 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

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

The positive sign was obtained from nuclear-polarization experiments.1

The theory of hfs anomalies was given by Bohr and Weisskopf,¹⁰ and Bohr¹¹ extended it to treat specific nuclear models. Eisinger and Jaccarino⁵ 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, is⁵

$$\boldsymbol{\epsilon} = -\left(\bar{\kappa}_s \alpha_s + \bar{\kappa}_l \alpha_l\right). \tag{4a}$$

The parameters $\bar{\kappa}_s$ and $\bar{\kappa}_l$ 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 have¹⁰

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

where g_s and g_l are the spin and orbital components, respectively, of g.

We may write the contact portion of a for Ag^{110m} in terms of the point-nucleus constant a^{0}_{110m} as

$$a_{110m} = a_{110m}^0 (1 + \epsilon_{110m}) = c (1 + \epsilon_{110m}) g_{110m}, \qquad (5)$$

where c is the same for all Ag isotopes to good approximation. Writing a similar expression for Ag¹⁰⁹ and combining, we find

$$g_{110m} = g_{109} \left(\frac{a_{110m}}{a_{109}} \right) \left(\frac{1 + \epsilon_{109}}{1 + \epsilon_{110m}} \right).$$
(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 $\pi(g_{9/2})^2 \nu(d_{5/2})^5$ (see Sec. IV A) and ϵ_{110m} arises mostly from the proton. Since in the singleparticle model \mathbf{l}_p and \mathbf{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.

 ${\rm Ag^{107}}$ and ${\rm Ag^{109}}$ have $p_{1/2}\text{-}{\rm proton}$ ground states, and ϵ_{107} and ϵ_{109} are expected to be several percent. Brun and Staub¹² 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 $\epsilon_{107(109)}$ = $-(1.01\alpha_s+0.25\alpha_l)\%$. 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 Ag¹⁰⁷ and Ag¹⁰⁹ 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 Ag¹⁰⁷ and Ag¹⁰⁹ 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 $\Delta_{109,110m} \simeq -3.7\%$. 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 Lind-

¹⁰ A. Bohr and V. F. Weisskopf, Phys. Rev. **77**, 94 (1950). ¹¹ A. Bohr, Phys. Rev. **81**, 331 (1951).

 ¹² E. Brun and H. H. Staub, Helv. Phys. Acta 26, 821 (1953).
 ¹³ H. Noya, A. Arima, and H. Horie, Progr. Theoret. Phys. (Kyoto) 12, S33 (1955).

gren's tabulation¹⁴ 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 $\frac{7}{2}$. 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 V⁵¹). The calculated magnetic moment is then

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

in good agreement with experiment. [Note added in proof. Professor L. S. Kisslinger has obtained theoretical evidence for low-lying states of the type $|j^n\rangle_{j-1}$, of threequasiparticle character. This seems to support our interpretation. We thank Professor Kisslinger for helpful discussions.]

B. Hyperfine Fields

The recently reported nuclear polarization experiments² gave the products

$$\mu H = -(10.0 \pm 0.07) \times 10^5$$
 nm G for Ag in Fe,
 $\mu H = -(3.1 \pm 0.03) \times 10^5$ nm G 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 $\bar{\kappa}_s \neq \bar{\kappa}_l$, and $|\alpha_s|$, $|\alpha_l| \gg 1$, subject of course to $\alpha_s + \alpha_l = 1$, that 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



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 $\mu = \frac{2}{3} - \frac{1}{6}g_s$, where g_s is the "effective" intrinsic-spin g factor.

mixing until the cancellation is complete. The nuclear g factor and hfs constant are given by the equations

$$g = g_s \beta_s + g_l \beta_l, \qquad (7a)$$

$$a = cg(1 - \bar{\kappa}_s \alpha_s - \bar{\kappa}_l \alpha_l)$$

= $c(g - \bar{\kappa}_s g_s \beta_s - \bar{\kappa}_l g_l \beta_l).$ (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 $\beta_s = g_l/(g_l - g_s)$, using $\beta_l + \beta_s = 1$. However (except for trivial solutions) this condition will give a=0[Eq. (7b)] only if $\bar{\kappa}_s = \bar{\kappa}_l$, 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

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

in the region $-0.05 \le \mu \le 0.05$. Evidently for $|\mu| \sim 0.01$ an anomaly of $\sim 50\%$ is expected. The ϵ curves were obtained from Eq. (8) and the relation $\epsilon = -(1.01\alpha_s + 0.25\alpha_l)\%$, 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 *negative*. We conclude that moments in the ~ 0.01 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.

¹⁴ I. Lindgren, in *Perturbed Angular Correlations*, edited by E. Karlsson, E. Matthias, and K. Siegbahn (North-Holland Publishing Company, Amsterdam, 1964), Appendix 1.