PHYSICAL REVIEW VOLUME 165, NUMBER 2 10 JANUARY 1968

Nuclear Magnetic Resonance and Relaxation in Iridium Metal: The Nuclear Magnetic Dipole Moments of ^{191}Ir and ^{193}Ir[†]

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(Received 7 August 1967)

The nuclear magnetic resonances of ^{191}Ir and ^{193}Ir have been detected by pulsed NMR techniques in iridium metal in the temperature range $T=1$–$4°$K and in external magnetic fields between 50 and 60 kOe. The observed frequency-field ratios for these isotropes are $\nu^{(191)}/H=0.074127(18)$ kHz/Oe and $\nu^{(193)}/H=0.080725(6)$ kHz/Oe. By combining the measured spin-lattice relaxation times $T_1^{(193)}T=2.8\pm0.2$ sec °K with known values of the magnetic susceptibility and electronic specific heat, the Knight shift in iridium metal is estimated to be $K=+(1.3\pm0.4)\%$. Applying this shift to the experimental frequency-field ratios yields the nuclear magnetic dipole moments (uncorrected for diamagnetic shifts) $\mu^{(191)}=0.1440(6)\mu_N$ and $\mu^{(193)}=0.1568(6)\mu_N$.

I. INTRODUCTION

PREVIOUSLY available nuclear moment data for ^{191}Ir and ^{193}Ir were derived from optical hyperfine structure studies of atomic iridium.[1,2] Because of their extremely small magnetic dipole moments μ, the nuclear magnetic resonances (NMR) of these isotopes have not been detected previously. Fortunately, the difficulties which are inherent in NMR experiments involving isotopes with small nuclear moments can be greatly reduced by performing the experiments at low temperatures and by taking advantage of the intense, uniform magnetic fields which can currently be produced in compensated NbZr superconducting solenoids. This has been demonstrated, for example, by the recent observation of the ^{197}Au NMR in metallic gold.[3] The purpose of the present paper is to report the first accurate determination of the iridium dipole moments $\mu^{(191)}$ and $\mu^{(193)}$ based on a successful application of high-field NMR techniques to a study of the ^{191}Ir and ^{193}Ir resonances in metallic iridium.

A metallic host was chosen for the present investigation since the full utilization of the $1/T$ dependence of the resonance intensity requires reasonably short spin-lattice relaxation times at low temperatures. For the determination of nuclear magnetic dipole moments, the metallic state has the disadvantage, of course, that the resonance frequency is perturbed by conduction-electron-induced hyperfine shifts (Knight shift) which can be particularly large for heavy isotopes. In many cases, the magnitude of the Knight shift can be estimated, however, from the experimental spin-lattice relaxation rates since the latter are generally dominated by hyperfine interactions with the conduction electrons. In transition metals, the relationship between Knight shift and spin-lattice relaxation rate is unfortunately complicated by the simultaneous presence of several hyperfine coupling mechanisms.[4–6] It may nevertheless be possible to obtain a reliable Knight-shift estimate by utilizing the measured spin-lattice relaxation rates together with experimental values of the electronic specific heat and magnetic susceptibility. Iridium represents a particularly favorable case for such an analysis since its electronic properties are not strongly influenced by collective-electron effects.[7]

Our experimental techniques are described briefly in Sec. II. Results of measurements of the frequency-field ratios for ^{191}Ir and ^{193}Ir as well as spin-spin and spin-lattice relaxation times for ^{193}Ir are presented in Sec. III. A partitioning of the net hyperfine interaction in iridium metal is accomplished in Sec. IV. The resulting estimate of the Knight shift permits accurate values of the nuclear magnetic dipole moments to be obtained from the experimental frequency-field ratios. A summary of this work is offered in Sec. V.

II. EXPERIMENTAL DETAILS

The iridium nuclear magnetic resonances were detected near 4 MHz in 300-mesh powdered samples[8] by means of crossed-coil spin-echo techniques. The experiments were carried out in the temperature range 1–4°K and in external magnetic fields between 50 and 60 kOe. The experimental apparatus used in the present study was essentially identical to that utilized in our earlier work on gold.[3] Magnetic fields to ~60 kOe with a homogeneity of a few parts in 10^5 over a sample volume of approximately 1 cm^3 were produced by a 1-in.-diam bore, compensated NbZr solenoid which was usually operated in the persistent mode. Magnetic field strengths were determined from measurements of the ^{109}Ag NMR in silver metal ($\nu^{109}/H=0.199133$ kHz/Oe).[3]

Transient excitation of the nuclear resonances was

[†] This work was supported by the U.S. Atomic Energy Commission.

[1] K. Murakawa and S. Suwa, Phys. Rev. **87**, 1048 (1952).

[2] W. v. Siemens, Ann. Physik **13**, 136 (1953).

[3] A. Narath, Phys. Rev. **163**, 232 (1967).

[4] J. Korringa, Physica **16**, 601 (1950).

[5] Y. Obata, J. Phys. Soc. Japan **18**, 1020 (1963).

[6] Y. Yafet and V. Jaccarino, Phys. Rev. **133**, A1630 (1964).

[7] M. A. Jensen and K. Andres, J. Appl. Phys. **38**, 1255 (1967).

[8] United Mineral and Chemical Corp., N.Y., 99.999% iridium sponge; according to the supplier the principal impurities in ppm were Si-5, Na-2, and Ca-1.

accomplished with a phase-coherent 15-kW gated transmitter capable of producing rotating rf field strengths H_1 of at least 200 Oe within a volume of ≈ 2 cm^3. Echos were produced by two equal-width rf pulses. After synchronous detection, the signals were either displayed on an oscilloscope and recorded photographically or averaged by means of a "boxcar" integrator.

Frequency-field ratios were determined at fixed fields by analyzing the interference patterns between the nuclear and reference signals. Spin–spin relaxation times were obtained from the variation of the spin-echo amplitude with pulse separation. Spin-lattice relaxation times were obtained from measurements of the echo recovery following saturation of the nuclear resonance. Results obtained with conventional rf saturation techniques were verified by experiments in which the specimen was initially withdrawn from the magnet with a motor driven hoist to achieve demagnetization after which it was quickly reinserted into the magnet.[9] The subsequent recovery of the longitudinal nuclear magnetization was monitored in the usual way by measurements of the echo amplitude.

III. EXPERIMENTAL RESULTS

From optical hyperfine studies,[1,2] it is known that ^{191}Ir and ^{193}Ir possess identical nuclear spins ($I=\frac{3}{2}$), and approximately equal magnetic dipole moments ($\mu \approx 0.2\mu_N$) and electric quadrupole moments.[10] As a result of the large quadrupole moments, the strain-induced broadening of the two iridium resonances was sufficiently large in our powdered samples to make the observation of free-induction decays difficult. All measurements were therefore carried out on spin echos produced by a two equal-width rf pulse sequence. Typical ^{193}Ir echos obtained at 4.2 MHz are shown in Fig. 1. Although the observed echos were sharply peaked near the center, the wings were always sufficiently broad to allow the central resonance frequencies to be determined within 1 kHz for ^{191}Ir and 0.3 kHz for ^{193}Ir. The sign of both nuclear dipole moments was ascertained to be positive on the basis of phase comparisons between the iridium echos and those of ^{109}Ag, ^{183}W, and ^{197}Au. Several determinations of the resonance frequencies near 1.5°K gave

$$\nu^{(191)}/H = 0.074127(18) \text{ kHz/Oe}, \tag{3.1}$$

$$\nu^{(193)}/H = 0.080725(6) \text{ kHz/Oe}, \tag{3.2}$$

where the numbers in parentheses indicate the estimated uncertainty in the last quoted digit. The identification of the two resonances was based on a comparison of the observed echo amplitudes with the known natural abundances of ^{191}Ir and ^{193}Ir (38.5 and 61.5%, respectively[11]). In view of the relatively severe strain broadening, as revealed, for example, by the narrow echo widths (Fig. 1), it was deemed important to establish the magnitude of possible systematic errors in (3.1) and (3.2) arising from second-order quadrupole shifts of the iridium resonances. Figure 2 shows the observed variation of the echo intensity with applied magnetic field strength at 4.2 MHz. The presence of a large first-order spread in the resonance fields of the $\pm\frac{1}{2}\leftrightarrow\pm\frac{3}{2}$ transitions is clearly indicated by the broad wings on each side of the much narrower central $+\frac{1}{2}\leftrightarrow-\frac{1}{2}$ transitions. From the width of the first-order spectrum, the average strength of the strain-induced quadrupole interaction can be estimated to be approximaltey $\nu_Q=$

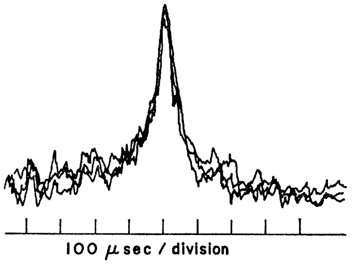

FIG. 1. Spin echos at 4.2 MHz for ^{193}Ir in iridium metal. The observations were made at 1.5°K using two 10- μsec rf pulses separated by 0.9 msec.

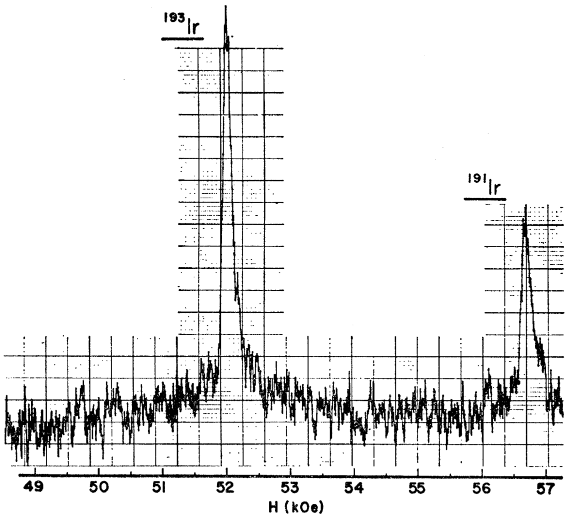

FIG. 2. Variation of spin-echo amplitudes for ^{193}Ir and ^{191}Ir in iridium metal with applied magnetic field strength. The spin-echo spectrum was obtained with a boxcar integrator (0.3 msec time constant) at 1.8°K. The echos were produced with a two 50-μsec rf pulse sequence (4.200 MHz) whose repetition rate was 0.5 sec^{-1}.

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[9] This technique is described more fully in A. Narath, Phys. Rev. **162**, 320 (1967).

[10] Murakawa and Suwa in Ref. 1 have reported

$$Q^{(193)} = +(1.0\pm0.5)\times10^{-24} \text{ cm}^2,\ Q^{(191)}/Q^{(191)} = 1.2\pm0.4,$$

whereas v. Siemens in Ref. 2 has given

$$Q^{(193)} = +(1.5\pm1)\times10^{-24} \text{ cm}^2,\ Q^{(193)}/Q^{(191)} = 1.0\pm0.3.$$

[11] M. B. Sampson and W. Bleakney, Phys. Rev. **50**, 732 (1936).

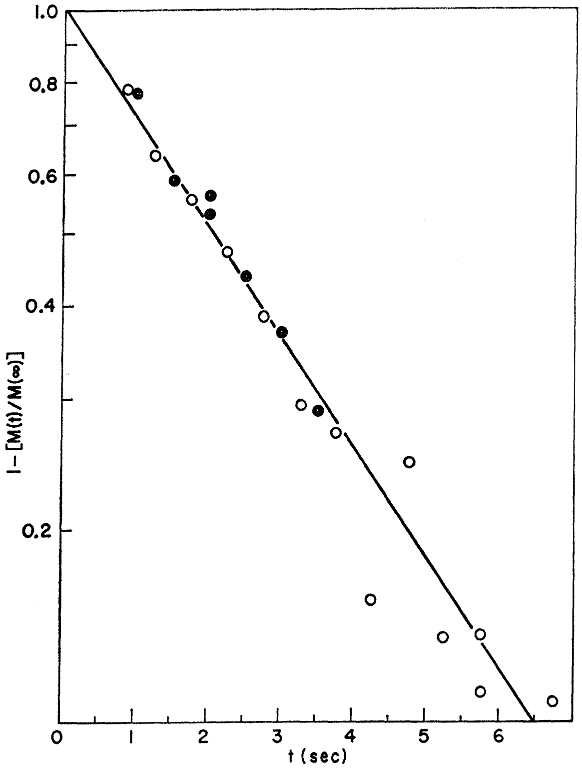

FIG. 3. Spin-lattice relaxation curves for ^{193}Ir in iridium metal at 1.78°K. The data points represent amplitudes of spin echos following two 10-μsec 4.2-MHz pulses separated by 0.9 msec. The signals were recorded by means of a boxcar integrator. The two sets of data correspond to two different saturation techniques. Open circles: rf saturation using fifty 10-μsec pulses during a time interval of 2 sec. Closed circles: demagnetization by removal of sample from the magnet (the time scale has been adjusted to correct for the 0.5-sec insertion time).

$3h^{-1}e^2qQ[2I(2I-1)]^{-1}\approx 0.16$ MHz, where q is the major principal component of the electric field gradient tensor. For an axially symmetric field gradient and $I=\frac{3}{2}$, the second-order shift of the central transition is approximately given for a powdered sample by $7\nu_Q{}^2/96\nu_L$, where ν_L is the Larmor frequency.[12] Thus, the expected shift is of the order of 0.4 kHz which is comparable to the experimental uncertainty in (3.2) and smaller than that given in (3.1). In view of the small magnitude of these shifts together with the fact that the beat method of determining resonance frequencies tends to weight heavily the narrowest part of an inhomogeneously broadened resonance (corresponding in the present case to those regions of the sample exhibiting the smallest second-order quadrupole broadening), we may conclude that the effects of quadrupole interactions on (3.1) and (3.2) can be safely ignored.

Measurements of the nuclear spin relaxation times were restricted to the ^{193}Ir resonance because of its greater intensity. The observed decays of the ^{193}Ir echo phase memory were nearly exponential with a time constant $T_2\approx 6$ msec. The ^{193}Ir spin-lattice relaxation times were inversely proportional to the absolute temperature ($T=1$–4°K) with

$$T_1T=2.8\pm 0.2 \text{ sec °K}. \tag{3.3}$$

Typical recovery curves for the two different saturation techniques are compared in Fig. 3. Within the experimental uncertainty, the two sets of data yield identical relaxation times. This provides convincing evidence that complete saturation was achieved with the rf comb technique despite the large inhomogeneous width of the resonance. The observed recovery rates in Fig. 3 are therefore the true spin-lattice rates $T_1^{-1}=2W$, where W is the usual transition probability for $I=\frac{1}{2}$. It should be noted that attempts to determine T_1 by the rf saturation technique with pulse widths of 30–50 μsec (rather than 10 μsec as used above) yielded significantly faster relaxation rates. These results imply that the $\pm\frac{1}{2}\leftrightarrow\pm\frac{3}{2}$ satellites were only partially saturated by the wider pulses (i.e., smaller H_1 fields).[13]

IV. DISCUSSION

The linear dependence of the observed spin-lattice relaxation rate on temperature indicates that the dominant low-temperature spin-lattice relaxation processes in iridium metal arise from hyperfine interactions between the nuclear spins and the conduction electrons. In the following, we partition the total hyperfine interaction into its principal contributions on the basis of the measured relaxation rate. The results of this analysis make it possible to establish the approximate magnitude of the Knight shift.

In a cubic transition metal such as iridium, the total spin-lattice relaxation rate $R\equiv(T_1T)^{-1}$ can be represented by a sum of several terms.[5,6] The most important of these are believed to arise from s-contact, d-spin core polarization, and d-orbital interactions which, in the tight-binding approximation, are given by

$$R_s=2hk_B\gamma_n{}^2\rho^2[N(0)H_{\text{hfs}}{}^{(s)}]^2, \tag{4.1}$$

$$R_d=2hk_B\gamma_n{}^2(1-\rho)^2[N(0)H_{\text{hfs}}{}^{(d)}]^2q, \tag{4.2}$$

$$R_{\text{orb}}=2hk_B\gamma_n{}^2(1-\rho)^2[N(0)H_{\text{hfs}}{}^{(\text{orb})}]^2p, \tag{4.3}$$

respectively, where γ_n is the nuclear gyromagnetic ratio and $N(0)$ is the total bare-electron density of states at

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[12] For a discussion of nuclear electric quadrupole effects in solids see M. H. Cohen and F. Reif, in *Solid State Physics,* edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5.

[13] For extensive discussions of the effects of incomplete saturation of quadrupolar broadened nuclear resonance lines on the apparent relaxation times see E. R. Andrew and D. P. Turnstall, Proc. Phys. Soc. (London) **78,** 1 (1961); W. W. Simmons, W. J. O'Sullivan, and W. A. Robinson Phys. Rev. **127,** 1168 (1962); as well as the paper cited in Ref. 9.

the Fermi level for one direction of the spin. The fractional s character at the Fermi level is denoted by

$$\rho = N_s(0)/N(0). \tag{4.4}$$

The effective s-contact and d-spin core-polarization hyperfine fields per electron are denoted by $H_{\text{hfs}}^{(s)}$ and $H_{\text{hfs}}^{(d)}$, respectively. The orbital hyperfine field $H_{\text{hfs}}^{(\text{orb})}$ per unit orbital angular momentum can be related to the expectation value of r^{-3} for the d orbital:

$$H_{\text{hfs}}^{(\text{orb})} = |\gamma_e \hbar| \langle r^{-3} \rangle, \tag{4.5}$$

where γ_e is the electronic gyromagnetic ratio. Finally, the reduction factors p and q are given for cubic symmetry by[5,6]

$$p = (2/3)f[2-(5/3)f], \tag{4.6}$$

$$q = (1/3)f^2 + (1/2)(1-f)^2, \tag{4.7}$$

where f is the fractional Γ_5 character of the d functions averaged over the Fermi surface.

In addition to the three mechanisms mentioned above, magnetic dipolar[5] and electric quadrupolar[14] relaxation mechanisms may also be important in exceptional cases.[15] To a good approximation, the corresponding relaxation rates may be related to the orbital rate (4.3) as follows.

$$R_{\text{dip}} = (3/98)[6/(6f-5f^2)-1]R_{\text{orb}}, \tag{4.8}$$

$$R_Q = \frac{\pi}{\hbar^2}\left(\frac{e^2 Q_{\text{eff}}}{\gamma_n \gamma_e I \hbar}\right)^2 \times \left(\frac{3(2I+3)[(5/3)f^2-2f+2]}{245(2I-1)\{(2/3)f[2-(5/3)f]\}}\right) R_{\text{orb}}, \tag{4.9}$$

where Q_{eff} is the effective electric quadrupole moment of the nucleus which may differ from the actual moment Q because of antishielding effects. Despite the fact that R_Q has been inferred to be quite small in all other metals studied to date, the quadrupolar rate may be very important in iridium metal because of the unusually small magnetic dipole moments and large electric quadrupole moments of ^{191}Ir and ^{193}Ir.

TABLE I. Variation of the fractional s character (ρ) and spin-lattice relaxation rates (R_i in units of sec^{-1} °K^{-1}) with the fractional Γ_5 character at the Fermi level (f) and the effective electric quadrupole moment (Q_{eff} in units of 10^{-24} cm^2). Values in parentheses are for $f=1$; others for $f=\frac{3}{5}$.

Q_{eff}	0.0	1.5	2.5
ρ	0.263(0.262)	0.241(0.236)	0.185(0.155)
R_s	0.340(0.340)	0.287(0.275)	0.169(0.118)
R_d	0.007(0.011)	0.007(0.012)	0.008(0.014)
R_{orb}	0.009(0.005)	0.009(0.006)	0.011(0.006)
R_{dip}	0.001(0.001)	0.001(0.001)	0.001(0.001)
R_Q	0	0.053(0.063)	0.168(0.218)

TABLE II. Summary of parameters used in the analysis of hyperfine effects in iridium metal.

$H_{\text{hfs}}^{(s)}$ (10^6 Oe)	10.6
$H_{\text{hfs}}^{(d)}$ (10^6 Oe)	−1.19
$H_{\text{hfs}}^{(\text{orb})}$ (10^6 Oe)	0.95
$N(0)$ (10^{11} erg^{-1} atom^{-1})	3.12
χ_{spin} (10^{-6} emu/mole)	40
χ_{VV} (10^{-6} emu/mole)	15
χ_{dia} (10^{-6} emu/mole)	−35

Combining the above results yields the total relaxation rate

$$R = R_s + R_d + R_{\text{orb}} + R_{\text{dip}} + R_Q. \tag{4.10}$$

Because of the cubic symmetry no interference terms arise between the various contributions to the relaxation even in the presence of s-d mixing at the Fermi level. Since $N(0)$ can be estimated from the known electronic specific-heat coefficient ($\gamma_{\text{el}} = 3.1$ mJ/deg^2 mole [16]) and the hyperfine fields from their free-atom values as well as from previous analyses of hyperfine interactions in platinum metal[17] (which has one more d electron per atom than iridium), the least known parameter in (4.10) is the fractional s character ρ. We therefore treat ρ as an adjustable parameter. Table I lists the values of ρ which yield agreement between calculated and observed relaxation rates for two different choices of f and three choices of Q_{eff}.

All of the results listed in Table I are based on values of the hyperfine fields and the bare-electron density of states which are summarized in Table II. The s-contact hyperfine field was obtained by adjusting the $6s$ atomic hyperfine field[1] of iridium by a factor of 0.7 [17] to approximate the reduced field in the metal, the core-polarization field was assumed to have the same magnitude as in platinum metal,[17] and the orbital hyperfine field was obtained by reducing the corresponding field in platinum in accordance with known trends of $\langle r^{-3} \rangle$ for the $3d$ and $4d$ neutral atoms.[18] The bare-electron density of states was taken from the work of Jensen and Andres,[7] who analyzed the bulk electronic properties of iridium with due consideration for many-body effects. Their value $N(0) \approx 3.1 \times 10^{11}$ erg^{-1} atom^{-1} may be compared with the

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[14] Y. Obata, J. Phys. Soc. Japan **19**, 2348 (1964).

[15] A. Narath and D. W. Alderman, Phys. Rev. **143**, 328 (1966).

[16] N. M. Wolcott, in *Conference de Physique des Basses Temperatures, Paris, 1955* (Centre National de la Recherche Scientifique, Paris, 1956), p. 286.

[17] A. M. Clogston, V. Jaccarino, and Y. Yafet, Phys. Rev. **134**, A650 (1964).

[18] See, for example, the tabulation of $\langle r^{-3} \rangle$ values (based on Hartree–Fock calculations) by A. J. Freeman and R. E. Watson, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1965), Vol. IIA, Chap. IV.

value 4.2×10^{11} erg^{-1} atom^{-1} calculated directly from the electronic specific-heat coefficient on the basis of the independent-particle approximation. The enhancement of the electronic specific heat due to many-body effects is therefore only approximately 30%. That the electronic properties of iridium metal conform reasonably well to the independent-particle model can also be seen from the small magnitude of the low-temperature susceptibility ($\chi=20\times10^{-6}$ emu/mole [19]). The individual contributions to the measured susceptibility have been estimated by Jensen and Andres[7] and are listed in Table II. Their estimate of the spin susceptibility ($\chi_{\text{spin}}=40\times10^{-6}$ emu/mole) corresponds to 3.9×10^{11} erg^{-1} atom^{-1}, which is only slightly larger than the value of $N(0)$ given above.

An inspection of Table I reveals that the fractional s character obtained from the experimental relaxation rate is essentially independent of the choice of f. Furthermore, the *magnetic* hyperfine contributions to the relaxation rate are seen to be dominated by the s-contact interaction. This result appears to apply quite generally to transition metals with small energy densities at the Fermi level (e.g., tungsten[20] and molybdenum[15]) and is due to (1) the relative strengths of the s- and d-hyperfine fields ($H_{\text{hfs}}^{(s)}\gg|H_{\text{hfs}}^{(d)}|$), and (2) the inhibition factors, e.g., (4.6) and (4.7), which make the d-electron relaxation processes relatively less effective than the s-contact relaxation process. The most interesting feature of the results shown in Table I is the large magnitude of R_Q for reasonable values of Q_{eff}. In fact, $R_Q>(R_d+R_{\text{orb}}+R_{\text{dip}})$ provided that $Q_{\text{eff}}\gtrsim 1.0\times10^{-24}$ cm^2. Thus, if a metallic host could be found in which ρ is sufficiently small, the odd iridium isotopes ^{191}Ir and ^{193}Ir might provide the first example of nuclear resonances whose spin-lattice relaxation rates are determined primarily by quadrupolar interactions with conduction electrons. In the present case the uncertainty in the exact value of Q_{eff} for ^{193}Ir unfortunately introduces a major uncertainty into the determination of ρ. Since antishielding effects are probably unimportant for quadrupolar hyperfine interactions with d conduction electrons,[21] it is reasonable to make the assumption $Q_{\text{eff}}=Q$. Thus, on the basis of the optical hyperfine determinations[10] of $Q^{(193)}$, we conclude that

$$\rho(\text{Ir})=0.24(+0.2,\,-0.7). \tag{4.11}$$

We now turn our attention to the iridium Knight shift which can be expressed in the usual manner as a sum of s-contact, d-spin core-polarization, and orbital contributions.[17]

$$K=K_s+K_d+K_{VV}, \tag{4.12}$$

where

$$K_s=(2/|\gamma_e\hbar|)H_{\text{hfs}}^{(s)}\chi_s, \tag{4.13}$$

$$K_d=(2/|\gamma_e\hbar|)H_{\text{hfs}}^{(d)}\chi_d, \tag{4.14}$$

and

$$K_{VV}=(2/|\gamma_e\hbar|)H_{\text{hfs}}^{(\text{orb})}\chi_{VV}. \tag{4.15}$$

The s- and d-spin susceptibilities can be obtained from the total spin susceptibility in the following way.

$$\chi_s=\rho\chi_{\text{spin}}, \tag{4.16}$$

and

$$\chi_d=(1-\rho)\chi_{\text{spin}}. \tag{4.17}$$

This method of partitioning χ_{spin} is not valid, of course, if the exchange enhancements of the s and d contributions to the spin susceptibility are different. Fortunately, this complication can be ignored in iridium since the enhancement of χ_{spin} is small. Combining (4.11)–(4.17) with the hyperfine fields and magnetic susceptibilities listed in Table II yields the Knight shifts shown in Table III. The calculated total shifts are quite insensitive to variations in Q_{eff} for $Q_{\text{eff}}\lesssim 1.5\times10^{-24}$ cm^2 but decrease rather rapidly for larger values of Q_{eff}. Since an effective quadrupole moment as large as 2.5×10^{-24} cm^2 seems somewhat unlikely, it appears reasonable to take

$$K=+(1.3\pm0.4)\%, \tag{4.18}$$

where the error limits are based on the estimated uncertainty in Q_{eff}. In view of the importance of the contact interaction, one might ask to what extent an error in the contact hyperfine field estimate would affect the value of K given in (4.18). Actually, the effect would be small as can be seen from the following argument. The s-contact relaxation rate is directly proportional to ρ^2; on the other hand, the various d relaxation rates are proportional to $(1-\rho)^2$ and are thus only weakly dependent on ρ since the latter is small compared to unity. A small variation in $H_{\text{hfs}}^{(s)}$ would therefore change ρ in such a way as to keep the product $H_{\text{hfs}}^{(s)}\rho$, and hence K_s, nearly constant.

Correcting the experimental frequency-field ratios according to (4.18) yields the nuclear moments (uncorrected for diamagnetic shifts)

$$\mu^{(191)}=+0.1440(6)\mu_N, \tag{4.19}$$

TABLE III. Summary of Knight shifts (in percent) for iridium metal computed for several possible values of ρ.

ρ	0.26	0.24	0.17
K_s	+1.97	+1.82	+1.29
K_d	−0.63	−0.64	−0.71
K_{VV}	+0.125	+0.25	+0.25
K	+1.59	+1.43	+0.83

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[19] D. W. Budworth, F. E. Hoare, and J. Preston, Proc. Roy. Soc. (London) **257**, 250 (1960).

[20] A. Narath and A. T. Fromhold, Jr., Phys. Rev. **139**, A794 (1965).

[21] R. E. Watson, A. C. Gossard, and Y. Yafet, Phys. Rev. **140**, A375 (1965).

and

$$\mu^{(193)} = +0.1568(6)\mu_N, \qquad (4.20)$$

where $\mu_N = 5.0505 \times 10^{-24}$ erg G^{-1} is the nuclear magneton. Since the Knight shifts are identical for the two isotopes (except for possible hyperfine structure anomalies which are, however, quite negligible for the present purpose), the ratio of the two moments is given directly by (3.1) and (3.2).

$$\mu^{(193)}/\mu^{(191)} = +1.0890(1). \qquad (4.21)$$

Finally, it is possible to correct the moments for core diamagnetism,[22] giving

$$\mu^{(191)}(\mathrm{corr}) = +0.1453(6)\mu_N, \qquad (4.22)$$

and

$$\mu^{(193)}(\mathrm{corr}) = +0.1583(6)\mu_N. \qquad (4.23)$$

Our results may be compared with the earlier optical hfs values obtained by Murakawa and Suwa[1] ($\mu^{(193)} = +0.17 \pm 0.03\mu_N$, $\mu^{(193)}/\mu^{(191)} = 1.04 \pm 0.04$) and by v. Siemens[2] ($\mu^{(193)} = +0.2 \pm 0.1\mu_N$, $\mu^{(193)}/\mu^{(191)} = 1.0 \pm 0.1$). Within the quoted uncertainties, the agreement is seen to be good.

V. SUMMARY

The first observation of the ^{191}Ir and ^{193}Ir NMR has been reported. The experiments were performed on iridium metal at low temperatures and in high magnetic fields using high-power pulsed NMR techniques. An estimate of the Knight shift in iridium metal based on the observed spin-lattice relaxation rate of ^{193}Ir allowed the ground-state nuclear magnetic dipole moments of the two odd iridium isotopes to be determined with an uncertainty of about ±0.4%. The results of the present analysis provide evidence that the hyperfine interactions in iridium metal are dominated by the *s*-contact interaction. The results also suggest that the principal *d*-conduction electron contribution to the spin-lattice relaxation rate is associated with the electric quadrupole interaction.

ACKNOWLEDGMENT

The author is greatly indebted to D. C. Barham for his valuable technical assistance.

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[22] N. F. Ramsey, *Nuclear Moments* (John Wiley & Sons, Inc., New York, 1953), p. 86.

PHYSICAL REVIEW VOLUME 165, NUMBER 2 10 JANUARY 1968

Nonlinear Excitation of Density Fluctuations in Anisotropic Semiconductors by Electromagnetic Radiation

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(Received 10 May 1967)

A nonlinear (parametric) mechanism for the excitation of electron-density fluctuations by a long-wavelength radiation field is discussed, for anisotropic many-valley semiconductors. Here the electron distribution function is given by many Fermi ellipsoids of revolution not parallel to one another. This gives rise to multimode density oscillations which can be excited nonlinearly by external electric fields. The threshold field for this phenomenon is calculated for realistic semiconductor models.

I. INTRODUCTION

With the development of high-intensity radiation sources in the microwave and optical spectrum, the study of nonlinear interactions of electromagnetic radiation with matter stimulates considerable theoretical and experimental interest.[1] One area of interest is the nonlinear excitation of plasma and ion-acoustic waves by a strong radiation field.[2–8] Here the ion-acoustic wave is driven by the plasma wave and the radiation field. Conversely, the plasma wave is driven by the ion-acoustic wave and the radiation field.

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[1] N. Bloembergen, *Nonlinear Optics* (W. A. Benjamin, Inc., New York, 1965).

[2] D. F. DuBois and M. V. Goldman, Phys. Rev. Letters **14**, 544 (1965).

[3] V. P. Silin, Zh. Eksperim. i Teor. Fiz. **48**, 1679 (1965) [English transl.: Soviet Phys.—JETP **21**, 1127 (1965)].

[4] D. Montgomery and I. Alexeff, Phys. Fluids **9**, 1362 (1966).

[5] R. A. Stern and N. Tzoar, Phys. Rev. Letters **17**, 903 (1966).

[6] Y. C. Lee and C. H. Su, Phys. Rev. **152**, 129 (1966).

[7] E. Atlee Jackson, Phys. Rev. **153**, 230 (1967).

[8] T. H. Geballe, in *Semiconductors*, edited by N. B. Hannay (Reinhold Publishing Corp., New York, 1960).