

## Nuclear Spin Relaxation in Metals: Rhodium, Palladium, and Silver\*

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The nuclear spin-lattice ( $T_1$ ) and spin-spin ( $T_2$ ) relaxation times have been studied by means of transient nuclear magnetic resonance techniques in metallic rhodium, palladium, and silver in the temperature range  $1 \leq T \leq 4^\circ\text{K}$ . The spin-lattice relaxation rates are dominated by conduction-electron processes, as evidenced by the observation of temperature-independent rates  $R \equiv (T_1 T)^{-1}$  in all three metals. The measured values, in  $(\text{sec}^\circ\text{K})^{-1}$ , are  $R(^{103}\text{Rh}) = 0.10 \pm 0.02$ ,  $R(^{105}\text{Pd}) = 9 \pm 2$ ,  $R(^{107}\text{Ag}) = 0.083 \pm 0.008$ , and  $R(^{109}\text{Ag}) = 0.111 \pm 0.010$ . The relaxation rate in silver is approximately one-half of the rate predicted by the Korringa relation on the basis of the known Knight shift. This discrepancy is attributed to an enhancement of the conduction-electron susceptibility due to collective-electron effects. Since the contact Knight shift is proportional to the product of the  $s$  conduction-electron susceptibility and the contact hyperfine field, this result implies that the average  $5s$  hyperfine field in metallic silver may be substantially smaller than has been assumed generally. In rhodium the principal contributions to the spin-lattice relaxation are shown to arise from both  $5s$  contact and  $4d$  orbital interactions. The magnitude of the measured  $^{103}\text{Rh}$  rate is in satisfactory agreement with estimates based on the results of a published Knight-shift study. In palladium, on the other hand, the measured rate exceeds the estimated rate by a factor of about 10. Possible reasons for this large difference in palladium are discussed. The spin-spin relaxation processes in rhodium and silver, as measured by the decay of the spin-echo envelope, exhibit Gaussian time dependences with characteristic times, in msec,  $T_2(^{103}\text{Rh}) = 10.5 \pm 1.0$ ,  $T_2(^{107}\text{Ag}) = 10.4 \pm 0.2$ , and  $T_2(^{109}\text{Ag}) = 9.1 \pm 0.2$ . The palladium spin-spin relaxation process has an exponential time dependence with  $T_2(^{105}\text{Pd}) = 5.6 \pm 0.5$  msec. These transverse relaxation rates give evidence for weak conduction-electron-coupled spin-spin interactions in these metals.

### I. INTRODUCTION

THE hyperfine coupling of nuclear and conduction-electron spin systems has three important effects on the nuclear magnetic resonance (NMR) in metals. The most frequently studied and best understood of these effects is the Knight shift,<sup>1</sup> which results from the field-induced magnetization of the conduction electrons. The various hyperfine interactions which produce the Knight shift also provide mechanisms for the thermal relaxation of the nuclear spin system.<sup>2-4</sup> A third manifestation of the electron-nucleus interaction is the indirect coupling of nuclear spins via the conduction electrons. The resulting indirect-exchange and pseudo-dipolar contributions to the transverse relaxation process are believed to be the dominant sources of NMR line broadening in heavy metals.<sup>5,6</sup> The extent to which the nuclear resonance is perturbed in a given case by these interactions is a sensitive function of the electronic structure of the metal. For this reason nuclear magnetic resonance experiments have proved capable of yielding important insight into the electronic properties of metals.

In this paper we present the results of a low-temper-

ature transient NMR investigation of spin-spin ( $T_2$ ) and spin-lattice ( $T_1$ ) relaxation processes in the face-centered cubic metals rhodium ( $Z=45$ ), palladium ( $Z=46$ ), and silver ( $Z=47$ ). These elements terminate the second transition series, silver having a single  $5s$  electron outside a filled  $4d$  shell. The Knight shifts have been studied in all three metals. In rhodium<sup>7</sup> and palladium<sup>8</sup> these studies led to a detailed identification of the spin and orbital contributions to the Knight shift and magnetic susceptibility. In both metals the  $d$ -band magnetization contributes significantly to the measured quantities. The Knight shift in silver,<sup>9</sup> on the other hand, can be accounted for entirely on the basis of an  $s$  band containing one nearly free electron per atom. To date, no nuclear spin relaxation data have been reported for rhodium and palladium. Moreover, the only previously available relaxation data for silver were derived from steady-state measurements.<sup>10,11</sup> The present work was undertaken to investigate (1) the relationship between the Knight shifts and spin-lattice relaxation rates, and (2) the importance of conduction-electron coupled spin-spin interactions in these metals.

### II. EXPERIMENTAL METHODS

The samples used in this study were obtained from commercial sources and were in the form of 325-mesh powders. The nominal purity levels were 99.94% for

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<sup>2</sup> J. Korringa, Physica **16**, 601 (1950).

<sup>3</sup> Y. Obata, J. Phys. Soc. Japan **18**, 1020 (1963).

<sup>4</sup> Y. Yafet and V. Jaccarino, Phys. Rev. **133**, A1630 (1964).

<sup>5</sup> M. A. Ruderman and C. Kittel, Phys. Rev. **96**, 99 (1954).

<sup>6</sup> N. Bloembergen and T. J. Rowland, Phys. Rev. **97**, 1679 (1955).

<sup>7</sup> J. A. Seitchik, V. Jaccarino, and J. H. Wernick, Phys. Rev. **138**, A148 (1965).

<sup>8</sup> J. A. Seitchik, A. C. Gossard, and V. Jaccarino, Phys. Rev. **136**, A1119 (1964).

<sup>9</sup> P. B. Sogo and C. D. Jeffries, Phys. Rev. **93**, 174 (1954).

<sup>10</sup> P. B. Sogo and C. D. Jeffries, quoted by M. A. Ruderman and C. Kittel in Ref. 5.

<sup>11</sup> J. Poitrenaud and J. M. Winter, J. Phys. Chem. Solids **25**, 123 (1964).

rhodium,<sup>12</sup> and 99.999% for palladium<sup>13</sup> and silver.<sup>14</sup> Because of the strong dependence of the low-temperature magnetic susceptibility of palladium on paramagnetic impurities,<sup>15</sup> experiments were carried out on samples taken from two different lots whose spectrographic analyses are given in Table I. No discernible differences were found in their respective relaxation rates. The rhodium and silver powders were suspended in paraffin. The palladium sponge was either mixed with silicone oil (DuPont #703), or used in dry form, in which case rf penetration resulted from surface oxidation which appears to occur rapidly in palladium powders. No signals were observed in palladium-paraffin samples, perhaps because of hydrogen contamination from the hydrocarbon.<sup>8</sup>

The relaxation rates were measured in the temperature range 1–4°K by transient, crossed-coil induction techniques. The rf excitation was provided by an incoherent pulsed oscillator. Experiments on rhodium were performed at frequencies near 7 Mc/sec, while those on palladium and silver were carried out near 9 Mc/sec. The relevant nuclear moment data are summarized in Table II. The magnetic field required for

TABLE I. Principal impurities in palladium specimens as determined by spectrographic analysis. Concentrations are given in ppm.

Impurity	Sample 1	Sample 2
Fe	7	10
Ni	3	6
Cu	49	17
Pb	85	40
Ag	6	38
Co, Mn, Cr	<1	<1

our experiments was produced by a compensated, 0–60 kOe, superconducting solenoid whose field uniformity exceeded 0.01% over a ½-in.-diam sample volume. Temperatures to 1°K were attained by pumping on liquid <sup>4</sup>He which was contained in a separate vacuum-jacketed sample Dewar.

All the relaxation data reported in this paper were derived from observations of spin-echo amplitudes using a receiver which was essentially identical to that utilized in our study of molybdenum.<sup>16</sup> The echoes were produced by two rf pulses of equal width.<sup>17</sup> The short dephasing times ( $T_2^* < T_2$ ) necessary for echo formation resulted from both field and sample inhomogeneities. Typical echo widths ( $2T_2^*$ ) ranged from 30–70 μsec in palladium to ~1 msec in the other two metals.

<sup>12</sup> Engelhard Industries, Inc., 113 Astor Street, Newark, New Jersey.

<sup>13</sup> United Mineral and Chemical Corporation, 16 Hudson Street, New York 13, New York.

<sup>14</sup> Electronic Space Products, Inc., P. O. Box 18795, Los Angeles, California.

<sup>15</sup> A. J. Manuel and J. M. P. St. Quinton, Proc. Roy. Soc. (London) A273, 412 (1963).

<sup>16</sup> A. Narath and D. W. Alderman, Phys. Rev. 143, 328 (1966).

<sup>17</sup> E. L. Hahn, Phys. Rev. 80, 580 (1950).

TABLE II. Summary of nuclear moment data.

	Abundance (%)	<i>I</i>	$\mu^a$
<sup>103</sup> Rh	100	$\frac{1}{2}$	–0.0879 <sup>b</sup>
<sup>105</sup> Pd	22.23	$\frac{5}{2}$	–0.639 <sup>c</sup>
<sup>107</sup> Ag	51.35	$\frac{3}{2}$	–0.1130 <sup>d</sup>
<sup>109</sup> Ag	48.65	$\frac{3}{2}$	–0.1299 <sup>d</sup>

<sup>a</sup> In units of the nuclear magneton, without corrections for diamagnetic shielding.

<sup>b</sup> Reference 7.

<sup>c</sup> Reference 8.

<sup>d</sup> Reference 9.

(The extremely narrow echoes in palladium are presumably due to strain-induced quadrupole interactions.) The width ( $\tau_w$ ) of the rf pulses was always adjusted to satisfy  $\tau_w < 2T_2^*$ .

Spin-spin relaxation times ( $T_2$ ) were determined by measuring the decay of the echo amplitudes as a function of increasing rf pulse separation ( $\tau$ ), and thus represent phase memory times.

Spin-lattice relaxation times ( $T_1$ ) were determined by measuring the recovery of the echo amplitude following saturation of the nuclear spin system by an rf “comb.” Because of the complete saturation which can be achieved with this technique, exponential recovery curves are easily obtained.

### III. EXPERIMENTAL RESULTS

The results of our experimental measurements are summarized in Table III. The spin-spin relaxation times ( $T_2$ ) correspond to the time required for the refocused transverse magnetization to decay to 1/e of its initial magnitude. The values of  $T_2$  listed for rhodium and silver are independent of temperature. The value given for <sup>105</sup>Pd was obtained at 2°K; at 4°K,  $T_2$ (<sup>105</sup>Pd) is about 15% shorter. This decrease is presumably due to contributions from the spin-lattice relaxation process which is very rapid in palladium. The decay of the transverse magnetization has a Gaussian form for rhodium and both silver isotopes. This is shown in Figs. 1 and 2 by the linear relationship between  $\ln[M(2\tau)/M(0)]$  and  $(2\tau)^2$ . The decay curve for palladium, however, is exponential, as shown in Fig. 3. The  $T_1T$  data in Table III apply to the entire range 1–4°K, since no variation of this quantity with temperature was detected.

Our results may be compared with previous observations by noting the following qualitative relationships

TABLE III. Nuclear spin relaxation data for metallic rhodium, palladium, and silver.

Isotope	$T_2$ (msec)	$T_1T$ (sec°K)
<sup>103</sup> Rh	10.5±1.0	10 ±2
<sup>105</sup> Pd	5.6±0.5	0.11±0.02
<sup>107</sup> Ag	10.4±0.2	12 ±1
<sup>109</sup> Ag	9.1±0.2	9 ±1

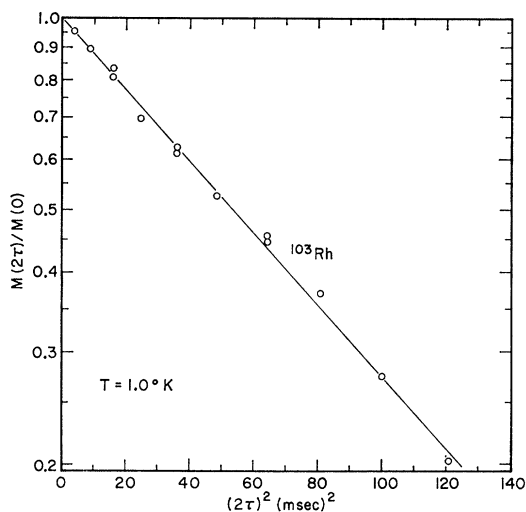


FIG. 1. Plot of the  $^{103}\text{Rh}$  spin-echo amplitude in rhodium metal as a function of  $(2\tau)^2$ , where  $\tau$  is the time separation between the two rf pulses.

(see Sec. IVB) between  $T_2$  and the peak-to-peak separation  $\Delta\nu$  (in frequency units) of the absorption derivative:

$$\text{Gaussian shape: } \Delta\nu = \sqrt{2}(\pi T_2)^{-1}; \quad (3.1)$$

$$\text{Lorentzian shape: } \Delta\nu = (\sqrt{3}\pi T_2)^{-1}. \quad (3.2)$$

#### A. Rhodium

A width of 3 Oe was observed for the  $^{103}\text{Rh}$  NMR by Seitchik *et al.*<sup>7</sup> These authors estimated that demagnetization broadening, due to randomly shaped particles, contributed 1 Oe to the measured linewidth. Our value of  $T_2 = 10.5$  msec corresponds to a width of only 0.32 Oe (43 cps).

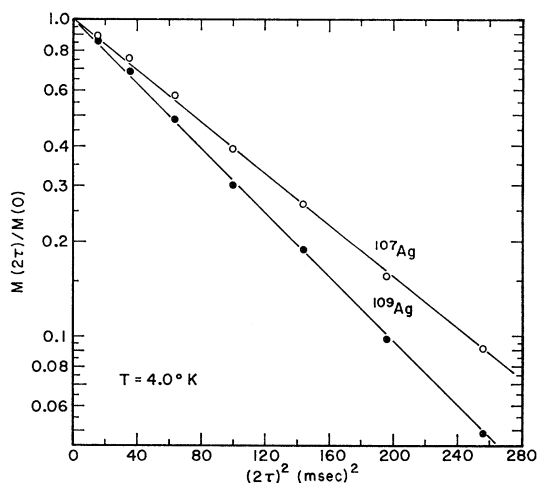


FIG. 2. Plot of the  $^{107}\text{Ag}$  and  $^{109}\text{Ag}$  spin-echo amplitudes in silver metal as a function of  $(2\tau)^2$ , where  $\tau$  is the time separation between the two rf pulses.

#### B. Palladium

A width of  $9 \pm 2$  Oe, independent of temperature in the range 4.2–300°K, has been reported by Seitchik *et al.*<sup>8</sup> Approximately 4 Oe were attributed to demagnetization effects. Our result, on the other hand, predicts a Lorentzian line shape with a width of 0.18 Oe (35 cps) below 4°K. At higher temperatures broadening due to spin-lattice relaxation is expected to become important. We expect that  $T_1 = T_2$  above  $\sim 20^\circ\text{K}$ , giving rise to a Lorentzian line shape with temperature-dependent width. At 300°K the expected linewidth (assuming  $T_1 T_2$  to be temperature independent) is thus 2.7 Oe. In obtaining these estimates we have ignored the strain broadening, which is very severe in our samples as evidenced by the observation of very narrow spin echoes.

The spin-lattice relaxation times in palladium are remarkably short compared to those in rhodium and silver. Seitchik *et al.*<sup>8</sup> reported the observation of absorption mode signals in palladium at very low rf levels at temperatures as low as 4.2°K. The saturation behavior of the absorption signal may be estimated from the saturation parameter

$$S = [1 + (\gamma_N H_1)^2 T_1 T_2]^{-1}, \quad (3.3)$$

where  $\gamma_N$  is the nuclear gyromagnetic ratio and  $H_1$  is the magnitude of the driving field. At 4°K our values for  $T_1$  and  $T_2$  yield  $S = 0.5$  when  $H_1 = 0.08$  Oe. This value of  $H_1$  would appear to be consistent with the observations of Seitchik *et al.*<sup>8</sup>

#### C. Silver

Previous estimates of  $T_2$  in silver were derived from linewidth data. Sogo and Jeffries<sup>10</sup> observed a Gaussian line shape for  $^{109}\text{Ag}$  at room temperature with a separa-

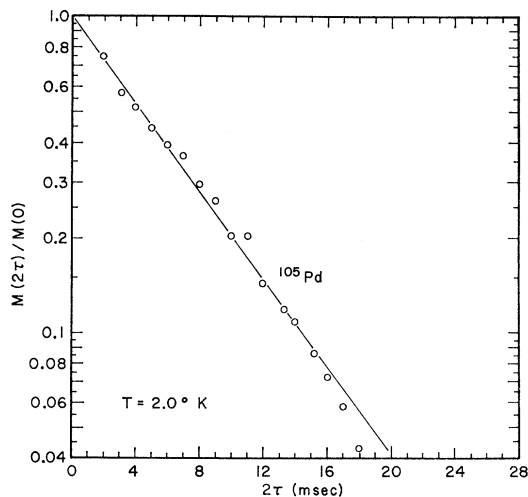


FIG. 3. Plot of the  $^{106}\text{Pd}$  spin-echo amplitude in palladium metal as a function of  $2\tau$ , where  $\tau$  is the time separation between the two rf pulses.

tion between derivative extrema of  $115 \pm 15$  cps. Poitrenaud and Winter<sup>11</sup> reported a linewidth of  $100 \pm 5$  cps for the same resonance. Our transient measurements correspond to linewidths ( $T \leq 4\text{K}^\circ$ ) of 43 and 49 cps for  $^{107}\text{Ag}$  and  $^{109}\text{Ag}$ , respectively, and are thus qualitatively consistent with the cw results.

Our  $T_1$  values for silver are in disagreement with the results of Poitrenaud and Winter.<sup>11</sup> These authors inferred  $T_1 T$  values of  $3.6 \pm 0.3 \text{ sec}^\circ\text{K}$  for  $^{107}\text{Ag}$ , and  $2.7 \pm 0.3 \text{ sec}^\circ\text{K}$  for  $^{109}\text{Ag}$  from room-temperature saturation experiments.

We conclude this section by noting that the transient technique gives significantly longer transverse relaxation times in rhodium and palladium than would be predicted from the reported cw linewidths. This discrepancy suggests that the cw resonances were inhomogeneously broadened. Such broadening is not unexpected in palladium because of the possibility of nuclear quadrupole interactions with random strain-induced electric field gradients. The source of broadening in rhodium ( $I = \frac{1}{2}$ ), however, is not clear. It is possible that it is the result of impurity-induced spatial variations of the Knight shift.

#### IV. DISCUSSION

In this section we examine in some detail the processes which are responsible for the observed spin-lattice and spin-spin relaxation rates in rhodium, palladium, and silver.

##### A. Spin-Lattice Relaxation

Since the experimental values of  $T_1 T$  are independent of temperature, it is reasonable to assume that relaxation arises from interactions of the nuclear spins with the conduction electrons. Magnetic hyperfine interactions give rise to four different relaxation mechanisms. In transition metals with partially filled  $s$  and  $d$  bands these may be described as (a) contact interactions with the  $s$  band,<sup>2</sup> (b) contact interactions due to core polarization of the filled  $s$  shells by the unfilled  $d$  band,<sup>4</sup> (c) interactions with the orbital magnetic moment of the  $d$  band,<sup>3</sup> and (d) spin-dipolar interactions with the  $d$  band.<sup>3</sup> In the tight-binding approximation the respective relaxation rates,  $R_i = (T_1 T)_i^{-1}$ , are given by

$$\begin{aligned} \text{(a)} \quad R_s &= 2hk_B\gamma N^2 [H_{\text{hf}}(s)N_s(\zeta_0)]^2, \\ \text{(b)} \quad R_{\text{cp}} &= 2hk_B\gamma N^2 [H_{\text{hf}}(d)N_d(\zeta_0)]^2 \left[ \frac{1}{3}f^2 + \frac{1}{2}(1-f)^2 \right], \\ \text{(c)} \quad R_{\text{orb}} &= 2hk_B\gamma N^2 [H_{\text{hf}}(\text{orb})N_d(\zeta_0)]^2 \left[ \frac{2}{3}f(2 - (5/3)f) \right], \\ \text{(d)} \quad R_{\text{dip}} &= 2hk_B\gamma N^2 [H_{\text{hf}}(\text{orb})N_d(\zeta_0)]^2 \\ &\quad \times \left[ (1/49)((5/3)f^2 - 2f + 2) \right], \quad (4.1) \end{aligned}$$

where  $h$  is Planck's constant,  $k_B$  is Boltzmann's constant,  $f$  is the average fractional admixture of  $4d(\Gamma_5)$  states at the Fermi level, and an electronic  $g$  value of two has been assumed. The  $5s$  contact and  $4d$  core-polarization hyperfine fields in the metal per electron are denoted by  $H_{\text{hf}}(s)$  and  $H_{\text{hf}}(d)$ , respectively; the orbital hyperfine

field per unit orbital angular momentum is denoted by  $H_{\text{hf}}(\text{orb})$ . The state densities per unit energy interval at the Fermi energy  $\zeta_0$  for the  $s$  and  $d$  bands, for one direction of the spin, are denoted by  $N_s(\zeta_0)$  and  $N_d(\zeta_0)$ , respectively. In the case of silver, only the contact mechanism is important; for rhodium and palladium, however, all four processes have to be considered. In general, the total relaxation rate is given by the sum of the four processes described above.

Reasonably accurate values for the hyperfine fields and state densities which appear in (4.1) have already been derived in connection with analyses of Knight-shift data for rhodium,<sup>7</sup> palladium,<sup>8</sup> and silver.<sup>18</sup> The results are summarized in Table IV. Before comparing our measured spin-lattice relaxation rates with predictions based on the tight-binding expressions (4.1), it is useful to review briefly the assumptions and approximations which underlie the parameters in Table IV. Among the three metals considered here, silver presents the least complicated situation. The Knight shift ( $K$ ) in silver is presumably dominated by the contact interaction, and is therefore given by

$$K_s = H_{\text{hf}}(s)\chi_s\mu_B^{-1}, \quad (4.2)$$

where  $\chi_s$  is the  $s$ -band magnetic susceptibility per atom, and  $\mu_B$  is the Bohr magneton. In the one-electron approximation the low-temperature susceptibility is related to the density of states by

$$\chi_s = 2\mu_B^2 N_s(\zeta_0). \quad (4.3)$$

The density of states is proportional to the electronic specific-heat coefficient  $\gamma$ :

$$N_s(\zeta_0) = \frac{2}{3}\gamma(\pi k_B)^{-2}. \quad (4.4)$$

Thus the measured shift in silver,<sup>9</sup>  $K_s = +0.522\%$ , combined with the experimental value<sup>19</sup>  $\gamma = 0.601 \text{ mJ/mole }^\circ\text{K}^2$  yields directly the contact hyperfine field given in Table IV. A comparison of this value with the free-atom value, obtained by the atomic beam resonance method, showed<sup>18</sup> that  $H_{\text{hf}}(s)$  in the metal is reduced relative to its atomic value by a factor  $\xi = 0.70$ . Subsequent interpretations of the Knight shifts in rhodium<sup>7</sup> and palladium<sup>8</sup> were based on the assumption that the same reduction factor is also appropriate for the contact

TABLE IV. Summary of hyperfine fields (in units of  $10^6$  Oe) and state densities (in units of  $10^{14}$  cgs/atom) in rhodium, palladium, and silver.

Metal	$H_{\text{hf}}(s)$	$H_{\text{hf}}(d)$	$H_{\text{hf}}(\text{orb})$	$N_s(\zeta_0)$	$N_d(\zeta_0)$
Rh <sup>a</sup>	3.35	-0.161	0.60	0.64	5.52
Pd <sup>b</sup>	3.22	-0.345	0.66	0.64	11.7
Ag <sup>c</sup>	3.49	...	...	0.807	...

<sup>a</sup> Reference 7.

<sup>b</sup> Reference 8.

<sup>c</sup> Reference 18.

<sup>18</sup> W. D. Knight, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 2, p. 93.

<sup>19</sup> W. S. Corak, M. P. Garfunkel, C. B. Satterthwaite, and A. Wexler, *Phys. Rev.* **98**, 1699 (1955).

TABLE V. Comparison of calculated and observed spin-lattice relaxation rates in rhodium, palladium, and silver. The units are  $(\text{sec}^\circ\text{K})^{-1}$ . The core-polarization and orbital rates in parentheses correspond to  $f=\frac{3}{4}$  and those without parentheses to  $f=1$ .

	$^{108}\text{Rh}$	$^{106}\text{Pd}$	$^{107}\text{Ag}$	$^{109}\text{Ag}$
$R_s$	0.061	0.12	0.170	0.225
$R_{\text{cp}}$	0.003 (0.002)	0.15 (0.09)	...	...
$R_{\text{orb}}$	0.032 (0.058)	0.37 (0.66)	...	...
$R_{\text{di p}}$	0.005 (0.004)	0.06 (0.05)	...	...
$R$ (predicted)	0.101 (0.125)	0.70 (0.92)	0.170	0.225
$R$ (observed)	0.10	9.1	0.08	0.11

hyperfine fields in these metals. The core-polarization fields in rhodium and palladium were determined by relating the observed temperature dependences of the Knight shifts to corresponding variations of the magnetic susceptibility. This procedure relies on the assumption that only the  $d$ -spin susceptibility contributes significantly to the strong temperature dependence of the susceptibility in these metals. The orbital hyperfine fields  $H_{\text{hi}}(\text{orb})=2\mu_B\langle r^{-3} \rangle$  were derived from Hartree-Fock calculations<sup>20</sup> of  $\langle r^{-3} \rangle$ . The orbital hyperfine field in the metal was assumed to have  $\frac{3}{4}$  of its atomic value. It should be emphasized<sup>4</sup> that the values of  $\langle r^{-3} \rangle$  which enter into the orbital Knight shift and orbital relaxation expressions need not be identical. The reason for this is that the former is given by an appropriate average over all occupied states, whereas the latter only involves an average over states near the Fermi level. We shall assume, however, that these averages are the same. This is equivalent to the assumption that the radial dependence of the wave function is reasonably constant for all occupied states. Finally, the total state densities for palladium and rhodium,  $N(\zeta_0)=N_s(\zeta_0)+N_d(\zeta_0)$ , were obtained from the measured electronic specific heats. The partitioning of the state densities into  $s$  and  $d$  parts was accomplished by taking  $N_s(\zeta_0)$  to be the density corresponding to a free-electron band containing 0.5 electron per atom.

The remaining unknown parameter in (4.1) is the admixture coefficient  $f$ . Fortunately, for reasonable values of  $f$  the total relaxation rate does not depend strongly on this parameter. Using (4.1) together with the constants listed in Table IV we have calculated the relaxation rates for rhodium, palladium, and silver. The results are compared in Table V with our experimental observations. The agreement between theory and experiment is reasonably good for rhodium and silver, but very poor for palladium. In the following we shall discuss possible reasons for these results.

We consider first the situation in silver. The expression for the contact relaxation rate in (4.1) may be combined with (4.2) to give

$$K_s^2 R_s^{-1} = (\pi \hbar^3 k_B \gamma_N^2 \gamma_e^2)^{-1} [\chi_s / N_s(\zeta_0)]^2, \quad (4.5)$$

<sup>20</sup> 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.

where  $\gamma_e = 2\mu_B \hbar^{-1}$ . Our calculated values of  $R_s$  for  $^{107}\text{Ag}$  and  $^{109}\text{Ag}$  were based, in effect, on the Korringa relation,<sup>2</sup> which is obtained from (4.5) by substituting the expression (4.3) for  $\chi_s$ .

$$K_s^2 R_s^{-1} = h(4\pi k_B)^{-1} (\gamma_e / \gamma_N)^2. \quad (4.6)$$

The quantities which appear on the right-hand side of (4.6) are all known. Nevertheless, the Korringa relation overestimates the relaxation rate in silver by a factor of about 2. Similar results have been obtained for other  $s$ -band metals,<sup>21</sup> although the discrepancies are generally not as large as observed here. The failure of (4.6) may be attributed to many-body interactions. In the first place, electron-electron interactions may enhance<sup>22</sup> the spin susceptibility relative to the prediction (4.3) of the independent-electron model. Secondly, the density of states in (4.5) refers to the density of states of the non-interacting electron gas.<sup>23</sup> The value calculated from the specific heat, on the other hand, is believed to be somewhat larger, principally as a result of electron-phonon interactions.<sup>23</sup> Although both of these effects would tend to increase  $T_1$ , their exact magnitude is not known. It is interesting to note, however, that a calculation for silver by Pines<sup>22</sup> yielded a value of  $\chi_s$  which is about 48% larger than that given by (4.3). Such an enhancement would account quantitatively for our measured relaxation rates. Moreover, in view of the close agreement between the observed<sup>19</sup> and free-electron values of  $\gamma$  it appears unlikely that the electron-phonon enhancement of the specific heat is nearly large enough in silver to give the required twofold increase in  $T_1$ . It should be noted that any increase of  $\chi_s$  over the independent-electron value implies a proportional decrease in the contact hyperfine field in metallic silver, as can be seen from (4.2). Thus, the reduction factor  $\xi$  may be as small as 0.47.<sup>22</sup>

The above interpretation must be viewed with some caution. First of all, it was assumed that the contact interaction is the only source of hyperfine coupling in silver. Furthermore, it was assumed that the theoretical expression (4.1) for the contact relaxation rate is valid even in the presence of many-body effects, provided only that the "bare-electron" density of states is used. Recently, however, Moriya has shown<sup>24</sup> that the electron-electron interaction in an  $s$ -band metal enhances not only the static magnetic susceptibility (and thus the Knight shift), but to a lesser extent also enhances the spin-lattice relaxation rate. This calculation was based on the random-phase approximation using a screened Coulomb potential of the  $\delta$ -function type. Moriya's work shows that the modification of the Korringa relation (4.5) due to the repulsive electron-

<sup>21</sup> See, for example, A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, London, 1961), Chap. IX.

<sup>22</sup> D. Pines, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1955), Vol. 1, p. 367.

<sup>23</sup> R. E. Prange and L. P. Kadanoff, *Phys. Rev.* **134**, A566 (1964).

<sup>24</sup> T. Moriya, *J. Phys. Soc. Japan* **18**, 516 (1963).

electron interactions is somewhat smaller than predicted by Pines,<sup>21,22</sup> particularly for large values of the interaction constant. It is not possible, therefore, to attach any quantitative significance to the agreement between the observed  $T_1$  values in silver and those calculated using Pines' collective-electron susceptibility. Nevertheless, it appears that most of the observed deviation from the Korringa relation in silver can be attributed to an exchange enhancement of  $\chi_s$ . This implies that the contact hyperfine field in the metal (averaged over all states at the Fermi level) is at least 50% smaller than that of the neutral silver atom.

The excellent agreement in rhodium between theory and experiment must be somewhat fortuitous, although it provides evidence that the analysis is qualitatively correct in this case. The uncertainty connected with the choice of parameters<sup>7</sup> is sufficiently great, however, that no conclusions can be drawn concerning the magnitude of many-body effects in this metal.

We now turn our attention to palladium, where the observed spin-lattice relaxation rate exceeds the predicted rate by a factor of about 10. We have been unable to establish with certainty the reason for this large discrepancy. However, there appear to be three possible mechanisms which could account for this result.

The most obvious explanation involves relaxation due to long-range interactions with paramagnetic impurities, especially since impurities such as iron and cobalt are known to produce large, localized moments in palladium.<sup>25</sup> Although we cannot eliminate this possibility entirely, we feel that the impurity mechanism is not very important in our samples. This belief is based primarily on the observation of identical rates in two different samples of relatively high purity (Table I). It is also supported by the  $T^{-1}$  temperature dependence of the relaxation times.

A more attractive explanation is provided by the possibility of an exchange enhancement of the relaxation rate. According to Moriya's theory,<sup>24</sup> such an enhancement should be particularly large in palladium because the repulsive interactions between  $d$ -band electrons are particularly strong in this metal. An indication of the magnitude of these interactions is provided by the observation of a 5.6-fold enhancement of the 0°K  $d$ -spin susceptibility.<sup>8</sup> Moriya's model calculation predicts that a fivefold enhancement of  $\chi_s$  should be accompanied by a threefold enhancement of the contact relaxation rate. Unfortunately, no quantitative conclusions can be derived from this result since the model is not directly applicable to the present case. It is probable that the exchange interaction in palladium enhances primarily the core-polarization ( $d$ -spin) relaxation rate. Thus, in view of the relatively small magnitude of  $R_{op}$  (Table V), the exchange enhancement would have to be very large before the total relaxation rate would be increased significantly.

<sup>25</sup> J. Crangle, *Phil. Mag.* **5**, 335 (1960).

A third mechanism becomes important if <sup>105</sup>Pd possesses a sufficiently large electric quadrupole moment. Spin-lattice relaxation due to electric quadrupole interactions between nuclear spins and non- $s$  conduction electrons has been discussed by Mitchell<sup>26</sup> and Obata,<sup>27</sup> and was detected recently in molybdenum metal.<sup>16</sup> Obata's tight-binding expression may be written for  $d$  electrons as

$$R_Q = 2\pi k_B \hbar^{-1} (e^2 Q_{\text{eff}} / I)^2 [3(2I+3)/245(2I-1)] \times [N_d(\zeta_0) \langle r^{-3} \rangle]^2 [(5/3)f^2 - 2f + 2], \quad (4.7)$$

where  $Q_{\text{eff}}$  is the effective nuclear electric quadrupole moment, which may differ somewhat from the true moment  $Q$  because of antishielding effects.<sup>28</sup> The magnitude of  $Q^{105}$  is unfortunately not known. We may, however, use (4.7) to obtain an upper limit estimate of  $Q_{\text{eff}}$  for <sup>105</sup>Pd by comparing this expression with the difference between the calculated and observed rates given in Table V. Using  $\langle r^{-3} \rangle = 5.25$  a.u. and  $N_d(\zeta_0) = 11.7 \times 10^{11}$  cgs/atom as before, we find  $Q_{\text{eff}} = 4.2 \times 10^{-24}$  cm<sup>2</sup> for  $f=1$ , and  $Q_{\text{eff}} = 4.5 \times 10^{-24}$  cm<sup>2</sup> for  $f = \frac{3}{5}$ . These values seem somewhat large. Nevertheless, this calculation shows that the quadrupole relaxation process must be important in palladium if  $Q_{\text{eff}} > 1 \times 10^{-24}$  cm<sup>2</sup>.

## B. Spin-Spin Relaxation

In the absence of inhomogeneous broadening, the most useful technique for studying nuclear spin-spin relaxation processes involves either measurements of the cw NMR line shape or the shape of its Fourier transform, the free-precession decay following a single  $\pi/2$  rf pulse. The moments of the line shape which can be obtained from such measurements provide a convenient basis for comparing theory with experiment. This approach, however, was not applicable in the present study since sample and magnet inhomogeneities provided the dominant sources of line broadening. Hence, the spin-spin relaxation rates were determined by measurements of the spin-echo amplitude following two pulses of equal width but variable time separation. The decay of the echo envelope (i.e., loss of phase memory) gives a measure of the fluctuations of the local field and is unaffected by static variations of the local field across the sample volume. Unfortunately, the spin-spin interactions which determine the true homogeneous line shape generally lead to both static and dynamic effects in solids.<sup>29</sup> As a consequence, the echo envelope usually gives only a partial measure of the actual cw linewidth. Thus, in the case of a Gaussian line resulting from dipolar interactions, the use of (3.1) together with  $T_2$ 's derived from spin-echo measurements only yields a lower limit estimate of the second moment  $\langle \Delta\nu^2 \rangle = \frac{1}{4} (\Delta\nu)^2$ . The exact magnitude of the error

<sup>26</sup> A. H. Mitchell, *J. Chem. Phys.* **26**, 1714 (1957).

<sup>27</sup> Y. Obata, *J. Phys. Soc. Japan* **19**, 2348 (1964).

<sup>28</sup> R. Sternheimer, *Phys. Rev.* **84**, 244 (1951).

<sup>29</sup> B. Herzog and E. L. Hahn, *Phys. Rev.* **103**, 148 (1956).

introduced by (3.1) is not known but is expected to be small from dipolar couplings among *like* spins.

The contribution to the second moment of the resonance from dipolar interactions between nuclear spins is given for a primitive lattice by the standard expression<sup>30</sup>

$$\langle \Delta \nu_i^2 \rangle_{aa} = (\gamma_i/2\pi)^2 [(3f_i/5)(\gamma_i \hbar)^2 I_i(I_i+1) + (4f_j/15)(\gamma_j \hbar)^2 I_j(I_j+1)] \sum r^{-6}, \quad (4.8)$$

which relates the second moment (in cps) for the *i*th isotopic species in a powdered specimen to the relative abundances of like ( $f_i$ ) and unlike ( $f_j$ ) isotopes, and their respective gyromagnetic ratios ( $\gamma_i$  and  $\gamma_j$ ). Using the lattice sum  $\sum r^{-6} = 115.6 a_0^{-6}$  for the fcc lattice calculated by Gutowski and McGarvey,<sup>31</sup> and lattice constants<sup>32</sup>  $a_0 = 3.794 \text{ \AA}$  (Rh),  $3.879 \text{ \AA}$  (Pd), and  $4.077 \text{ \AA}$  (Ag), we find

$$\begin{aligned} {}^{103}\text{Rh} \langle \Delta \nu^2 \rangle_{aa}^{1/2} &= 15.8 \text{ cps}, \\ {}^{105}\text{Pd} \langle \Delta \nu^2 \rangle_{aa}^{1/2} &= 50.3 \text{ cps}, \\ {}^{107}\text{Ag} \langle \Delta \nu^2 \rangle_{aa}^{1/2} &= 18.7 \text{ cps}, \\ {}^{109}\text{Ag} \langle \Delta \nu^2 \rangle_{aa}^{1/2} &= 22.4 \text{ cps}. \end{aligned} \quad (4.9)$$

Dipolar broadening by itself gives rise to a nearly Gaussian line shape, and hence a width of  $2 \langle \Delta \nu^2 \rangle_{aa}^{1/2}$ . Since the echo decays of <sup>103</sup>Rh, <sup>107</sup>Ag, and <sup>109</sup>Ag were found to be Gaussian, it is useful to compare our experimental results for these isotopes directly with (4.9). The observed rates (Table III) and (3.1) yield

$$\begin{aligned} {}^{103}\text{Rh} \langle \Delta \nu^2 \rangle_{\text{obs}}^{1/2} &\geq 21 \pm 2 \text{ cps}, \\ {}^{107}\text{Ag} \langle \Delta \nu^2 \rangle_{\text{obs}}^{1/2} &\geq 21.6 \pm 0.5 \text{ cps}, \\ {}^{109}\text{Ag} \langle \Delta \nu^2 \rangle_{\text{obs}}^{1/2} &\geq 24.7 \pm 0.5 \text{ cps}. \end{aligned} \quad (4.10)$$

It is significant that the experimental second moments *exceed* the calculated dipolar second moments. This shows that indirect nuclear spin-spin interactions contribute to the linewidth. In a metal containing only  $I = \frac{1}{2}$  isotopes with nearly identical magnetic moments, an indirect exchange interaction between nearest-neighbor spin pairs of the form  $A \mathbf{I}_a \cdot \mathbf{I}_b$  leads to a second moment<sup>5</sup>

$$\langle \Delta \nu_i^2 \rangle = \langle \Delta \nu_i^2 \rangle_{aa} + 3f_j(A/\hbar)^2. \quad (4.11)$$

Poitrenaud and Winter<sup>11</sup> have deduced  $A/\hbar = 26.5 \pm 1.5$  cps for silver from cw linewidth studies. This value yields second moments for <sup>107</sup>Ag and <sup>109</sup>Ag which are somewhat larger than the experimental lower-limit estimates in (4.10), as required. Since rhodium contains only a single isotope (i.e.,  $f_j = 0$ ), the scalar interaction would contribute only to the fourth moment in this case and thus tend to narrow the resonance. For a sufficiently

large value of  $A$ , the line shape would become Lorentzian with a width given exactly by (3.2). The apparent broadening suggested by (4.9) and (4.10) must therefore be associated with pseudo-dipolar<sup>6</sup> contributions to the linewidth arising from non-*s* conduction electrons. It is possible that indirect exchange is responsible for the exponential echo decay observed in palladium. However, the uncertainties connected with the magnitude and distribution of strain-induced quadrupole interactions are sufficiently great that no definite conclusions can be drawn from our data concerning the <sup>105</sup>Pd spin-spin relaxation process.

## V. CONCLUSIONS

The present work has been concerned with a study of nuclear spin relaxation processes in metallic rhodium, palladium, and silver.

The experimental spin-lattice relaxation rates for rhodium and silver are in qualitative agreement with predictions based on the independent-electron model and previously published Knight-shift data. In the case of silver a more quantitative comparison between theory and experiment is possible because it is reasonable to assume that only the Fermi contact interaction contributes significantly to the spin-lattice relaxation process in this nearly free-electron metal. On this basis, the calculated rate exceeds the observed rate by a factor of 2. This discrepancy is most easily explained by assuming that the spin susceptibility of silver is exchange-enhanced by about 40% over its independent-electron value. Such an interpretation leads to the important conclusion that the average contact hyperfine field per electron at the Fermi level in silver has a value of only  $\sim 2.5 \times 10^6$  Oe compared to its free-atom value of  $4.98 \times 10^6$  Oe. This corresponds to a reduction factor  $\xi = 0.50$  which compares with the usual estimate of  $\xi = 0.70$ . In principle, it should be possible to extract similar information concerning the magnitude of many-body effects from nuclear relaxation data for transition metals. In practice, however, this is a difficult task because of the large uncertainty which is involved in the separation of the measured rates into *s* and *d* contributions. The achievement of significant progress in that direction may only be possible when reliable estimates of  $N_s(\xi_0)/N_d(\xi_0)$  become available from band-structure calculations.

The observed spin-spin relaxation rates in rhodium and silver provide evidence that indirect spin-spin interactions in these metals are considerably weaker than the direct dipolar interactions. Our results for silver are qualitatively consistent with previous cw estimates of the indirect-exchange constant in this metal. In rhodium, our measurements indicate the presence of a pseudo-dipolar contribution to the cw linewidth.

Our results for palladium are strikingly different from those for rhodium and silver. The measured <sup>105</sup>Pd

<sup>30</sup> See, for example, Ref. 24, Chap. IV.

<sup>31</sup> H. S. Gutowski and B. R. McGarvey, J. Chem. Phys. **20**, 1472 (1952).

<sup>32</sup> The lattice constants were taken from the *Handbook of Chemistry and Physics* (Chemical Rubber Publishing Company, Cleveland, Ohio, 1959).

spin-lattice relaxation rate was found to be ten times faster than predicted. This enhancement might be associated with the strong electron-electron interactions in this metal. This conclusion, however, is quite tentative since electric-quadrupole and paramagnetic-impurity processes may also contribute significantly. The impurity mechanism may be important despite the high purity of our samples, because of the long range of indirect spin couplings in palladium. It is hoped that

nuclear resonance studies in the Rh-Pd and Pd-Ag alloy systems, presently in progress, will make it possible to interpret the spin-lattice relaxation rates in pure palladium with greater certainty.

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### Absorption of Light Due to Interband Transitions in Sodium\*

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The intrinsic absorbing power due to interband transitions in Na is calculated, using orthogonalized plane waves to evaluate the matrix elements appearing in the oscillator strengths, and a realistic band structure, obtained from a pseudopotential interpolation scheme, to perform the sum over  $k$  space. It is found that for a pseudopotential form factor  $V_{110}$  in reasonable agreement with the results of Fermi-surface measurements and band calculations, the calculated absorbing power is an order of magnitude smaller than that indicated by the experimental data of Mayer and co-workers, or by the data of Ives and Briggs.

#### INTRODUCTION

RECENT experiments by Mayer and co-workers<sup>1</sup> on the optical spectra of the alkali metals from the near infrared to the near ultraviolet, performed under conditions of high surface purity and in high vacuum, have demonstrated the existence of resonance behavior in the absorptivity at energies below the band-theoretically predicted onset of interband absorption. In K and Cs this resonance is sufficiently large and broad to mask completely the interband threshold. On the other hand, in Na one can clearly distinguish the Drude absorption in the infrared region, the resonance near 1.7 eV, and the interband absorption region beginning near the value 2.0 eV, predicted by theory. At low temperature,  $-183^\circ\text{C}$ , the resonance disappears, and only the Drude and interband contributions to the absorptivity are present in Na. The origin of the resonance is as yet poorly understood, and for this reason it was felt that any comparison of the band-theoretically calculated absorptivity with experiment was most likely to succeed for a metal where this resonance was weakest. For this reason we will concentrate on Na throughout the remainder of this paper.

Butcher<sup>2</sup> has calculated the absorptivity of the alkali

metals using the one-electron approximation and a nearly free-electron band model. In his calculation he leaves as an adjustable parameter the pseudopotential form factor  $V_{110}$ , [ $V_{110}=V(\mathbf{G})$ ,  $\mathbf{G}=(1, 1, 0)2\pi/a$ , where  $a$  is the lattice constant], which he uses to fit the experimental results of Ives and Briggs.<sup>3</sup> Fitting the Ives-Briggs data for Na he obtained  $V_{110}=0.323$  eV; when Butcher's results are fitted to Mayer's data for Na one obtains  $V_{110}=0.457$  eV. This value for  $V_{110}$  is in marked disagreement with those inferred from the band calculations of Ham and others<sup>4</sup> and from Fermi-surface data.<sup>5</sup>

Examining Butcher's work one comes to the conclusion that within the one-electron approximation there are a number of deficiencies in Butcher's band model which might account for the discrepancy.

Primary among these is Butcher's use of plane waves to calculate the oscillator strengths. While it is known that Na is an excellent "nearly free-electron" metal to the extent that its Fermi surface is nearly spherical, it is by no means true that its one-electron wave functions are plane waves. A serious deficiency in the choice of plane waves is their lack of orthogonalization to the core states. As Herring<sup>6</sup> has shown, the use of orthogo-

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<sup>1</sup> H. Mayer and M. H. El Naby, *Z. Physik* **174**, 289 (1963); B. Hietel, Ph.D. dissertation, Dresden (unpublished). H. Mayer, Conference on Optical Properties of Solids, Paris, 1964 (to be published).

<sup>2</sup> P. N. Butcher, *Proc. Phys. Soc. (London)* **A64**, 50 (1951).

<sup>3</sup> H. E. Ives and H. B. Briggs, *J. Opt. Soc. Am.* **26**, 238 (1936); **27**, 181, 395 (1937).

<sup>4</sup> F. S. Ham, *Phys. Rev.* **128**, 82 (1962); V. Heine and I. Abarenkov, *Phil. Mag.* **9**, 451 (1964).

<sup>5</sup> C. C. Grimes and A. F. Kip, *Phys. Rev.* **132**, 1991 (1963); D. Shoenberg and P. J. Stiles, *Proc. Roy. Soc. (London)* **281**, 62 (1964).

<sup>6</sup> C. Herring, *Phys. Rev.* **57**, 1169 (1940).