Nuclear Magnetic Resonance in Exchange-Enhanced Metals: ^{103}Rh Knight Shifts and Relaxation Rates in Palladium-Rhodium and Nickel-Rhodium Alloys*

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(Received 3 August 1970)

Low-temperature ($T \approx 1 - 4$ °K) measurements of the resonance shift K, spin-lattice relaxation time T_1, and inhomogeneous linewidth W of ^{103}Rh in the two alloy systems $Pd_{1-x}Rh_x$ ($0.02 \leq x \leq 1$) and $Ni_{1-x}Rh_x$ ($0.38 \leq x \leq 1$) have been carried out using transient NMR techniques. In $Pd_{1-x}Rh_x$ both $T_1 T$ and K vary monotonically with K decreasing from $+0.43$ to -15%, and $T_1 T$ from 9.2 to 0.7 sec °K. Similar results are found in $Ni_{1-x}Rh_x$, with K decreasing from $+0.43$ to -8.1%, and $T_1 T$ from 9.2 to 1.2 sec °K. The ^{103}Rh NMR in both alloy systems is characterized by severe inhomogeneous broadening, with W approaching K in magnitude in some cases. This result demonstrates that the local susceptibility is very sensitive to statistical variations in the near-neighbor alloy composition. The minimum K value in Pd-Rh agrees with the infinite-dilution value $K = -14.7\%$ obtained by Rao, Matthias, and Shirley using perturbed-angular-correlation techniques, and indicates that K is essentially independent of x for Rh concentrations up to ~ 5 at.%. A comparison of this result with the ^{105}Pd Knight shift in palladium metal shows that the local susceptibility at the rhodium sites is approximately three times greater than the palladium host susceptibility. This deviation from rigid-band behavior develops gradually with decreasing rhodium concentration for $x < 0.4$. In contrast, the Ni-Rh NMR data suggest that the rhodium susceptibility is significantly smaller than the nickel susceptibility at all rhodium concentrations. An analysis of the ^{103}Rh shift and relaxation data for Pd-Rh and Ni-Rh demonstrates that both quantities are dominated by an exchange-enhanced d-spin (core-polarization) hyperfine mechanism for sufficiently low rhodium concentrations. Moreover, the observed relationship between K and $T_1 T$ is shown to be more characteristic of a uniform-enhancement model than a localized spin-fluctuation model even in dilute *Pd*Rh alloys. On the basis of this behavior, it is argued that a local-moment description of dilute rhodium impurities in palladium is inappropriate.

I. INTRODUCTION

During recent years, extensive experimental investigations of the paramagnetic group-VIII transition metals and their alloys have provided considerable insight into the nature of exchange-enhancement effects in nearly ferromagnetic metals. The thermal and magnetic properties of the isoelectronic alloys Pd-Rh[1,2] and Ni-Rh[3] have been of particular importance in this connection. Palladium and nickel, which have one more valence electron than rhodium, produce a rapid increase in the electronic-specific-heat coefficient γ and magnetic susceptibility χ in these alloys with increasing concentration. The Pd-Rh alloys remain paramagnetic over the entire concentration range, with γ and χ reaching maximum values near 5 at.% rhodium.[1,2,4] The Ni-Rh alloys, on the other hand, are ferromagnetic at sufficiently low temperatures for rhodium concentrations below ~ 37 at.%.[3] The marked difference between the two alloy systems can be attributed possibly to the larger Coulomb repulsion between electrons on nickel sites than on palladium sites. In fact, it seems likely that the concentration dependences of the various bulk properties are strongly influenced in these alloys by intra-atomic effects. To date, most discussions of the Pd-Rh and Ni-Rh alloy properties have been based on the rigid-band approximation, although the validity of this approach for strongly paramagnetic alloys has been questioned.[5] A serious breakdown of the rigid-band approximation has recently been observed in extremely dilute *Pd*Rh alloys.[6] Hyperfine-shift measurements of the ^{100}Rh nuclear magnetic resonance (NMR) by means of γ-γ perturbed-angular-correlation (PAC) techniques led to the conclusion that a localized magnetic moment appears on the rhodium solute atoms at sufficiently low concentrations. Moreover, the Curie-Weiss form of the temperature-dependent rhodium susceptibility was taken as evidence for Kondo spin compensation. Deviations from rigid-band behavior in the corresponding $4d$ alloy system *Pt*Ir had previously been inferred from ^{195}Pt Knight-shift measurements.[7] The importance of intra-atomic effects has also been established by NMR studies of the related alloys Cu-Ni,[8] Ag-Pd,[9] Cu-Pd,[10,11] Cu-Pt,[11] and Pt-Pd.[12,13] Since the NMR technique provides a microscopic probe of the local magnetic response of an alloy, it is particularly suited for such investigations.

In this paper we present the result of a ^{103}Rh NMR study of paramagnetic $Pd_{1-x}Rh_x$ and $Ni_{1-x}Rh_x$ alloys in the composition ranges $0.02 \leq x \leq 1$ and $0.38 \leq x \leq 1$, respectively.[14] The present study was motivated in part by the unexpected success of the rigid-band model in accounting for the bulk properties of dilute *Pd*Rh alloys,[4] in striking contrast with the

interpretation of the PAC experiments.[6] The absence of electric quadrupole interactions for ^{103}Rh $(I = \frac{1}{2})$ makes this isotope particularly suitable for studies of magnetic hyperfine interactions. Our experimental techniques are described briefly in Sec. II. Results of low-temperature measurements $(T \approx 1 - 4\,^{\circ}\text{K})$ of the ^{103}Rh resonance shift K, linewidth W, spin-lattice relaxation time T_1, and echo phase-memory time T_2 are given in Sec. III. Our results are related to the bulk properties in Sec. IV. In particular, we estimate the magnitude of the exchange enhancements of K and T_1T in the most paramagnetic alloys. On the basis of these estimates we are able to discuss the applicability of the rigid-band model to these alloys. The principal conclusions obtained from this work are summarized in Sec. V.

II. EXPERIMENTAL TECHNIQUES

Alloys of $\text{Pd}_{1-x}\text{Rh}_x$ and $\text{Ni}_{1-x}\text{Rh}_x$, with $x \geq 0.02$ and $x \geq 0.38$, respectively, were prepared by mixing appropriate quantities of the elemental metals (300 mesh),[15] pressing the mixtures into small (~ 5 g) pellets, and melting them in an argon arc furnace which was equipped with a water-cooled copper hearth and a $\frac{1}{8}$-in.-diam thoriated tungsten electrode. Sample homogeneity was assured by repeated turning and remelting of the alloy ingots. The ^{103}Rh nuclear resonance was studied in 200–300 mesh alloy chips which were mixed with an equal volume of powdered NaCl for electrical isolation. Comminution of the alloys was accomplished with a small programmed milling machine using tungsten carbide cutters. A few initial experiments on selected Pd-Rh and Ni-Rh compositions established that prolonged annealing of the alloy powders at temperatures near the respective melting points had no observable effect on any of the nuclear-resonance properties. For this reason, all subsequent experiments involved samples which had not received any heat treatment after arc melting.

Because of sensitivity considerations, the NMR measurements were restricted to low temperatures $(T \approx 1 - 4\,^{\circ}\text{K})$, which were achieved by immersing the samples in liquid helium. The nuclear resonances were detected with a phase-coherent crossed-coil transient spectrometer. Spin echoes were produced with two equal-width rf pulses using a 15-kW gated amplifier. A Fabri-Tek 952/1062 high-speed multichannel analyzer provided adequate signal-to-noise ratios by allowing standard signal-averaging techniques to be employed.

Measurements of Knight shifts K, spin-relaxation times T_1 and T_2, and resonance line shapes were carried out in external fields near 60 kOe using a Nb-Zr superconducting solenoid. The field-strength calibration was based on the ^{109}Ag NMR in metallic silver whose frequency-to-field ratio at $4\,^{\circ}$K was

taken to be[16]

$$\nu^{(109)}(\text{metal})/H = 0.199\,150 \text{ kHz/Oe} . \qquad (2.1)$$

The ^{103}Rh Knight shifts were computed relative to the reference ratio[17]

$$\nu^{(103)}(\text{ref})/H = 0.133\,80 \text{ kHz/Oe} . \qquad (2.2)$$

Spin-lattice relaxation times were obtained from the experimental recovery rates of the echo amplitude following a comb of saturating rf pulses. Phase-memory times were obtained from the echo decay as a function of time separation between the two rf pulses. The pulse amplitude for both T_1 and T_2 measurements corresponded to rotating fields $H_1 \approx 150$–200 Oe. Line shapes were obtained from the field dependence of the echo intensity using rf pulse widths which were large compared to the reciprocal linewidths.

III. EXPERIMENTAL RESULTS

The properties of the ^{103}Rh NMR in elemental rhodium metal have been described earlier.[18,19] During the course of the present study we obtained at $4\,^{\circ}$K

$$\nu^{(103)}(\text{metal})/H = 0.134\,374\,(3) \text{ kHz/Oe} , \qquad (3.1)$$

where the number in parentheses indicates the estimated uncertainty in the preceding digit. The addition of either palladium or nickel to rhodium results in severe broadening of the ^{103}Rh NMR as well as a shift in the mean position of the resonance toward higher magnetic fields. These effects are illustrated for several Pd-Rh compositions by the spin-echo spectra shown in Fig. 1. The concentration dependences of the linewidth and the position of maximum echo intensity are summarized in Fig. 2 for Pd-Rh and in Fig. 3 for Ni-Rh. No resonances were observed in a $\text{Ni}_{0.65}\text{Rh}_{0.36}$ alloy. This indicates that the onset of ferromagnetic ordering in Ni-Rh occurs at a nickel concentration near 63 at.%, in agreement with earlier observations.[3] The negative resonance shifts can be attributed to d-spin (core-polarization) hyperfine interactions which increase rapidly in magnitude with decreasing rhodium concentration. This result supports the generally accepted view that the bulk susceptibility in these alloys is predominantly of d-spin origin.[18]

With decreasing rhodium concentration the ^{103}Rh phase-memory times increase. For example, $T_2 = 9$, 14, 17, and 27 msec in $\text{Pd}_{1-x}\text{Rh}_x$ for $x = 1.0$, 0.6, 0.4, and 0.2, respectively. The decay curves were nearly Gaussian in every case. Similar results were obtained for Ni-Rh. The extremely long phase-memory times confirm that the observed linewidths result from inhomogeneous broadening. Most likely, the widths reflect a spatial variation in the local susceptibility, suggesting that the local magnetic properties are quite sensitive to the rela-
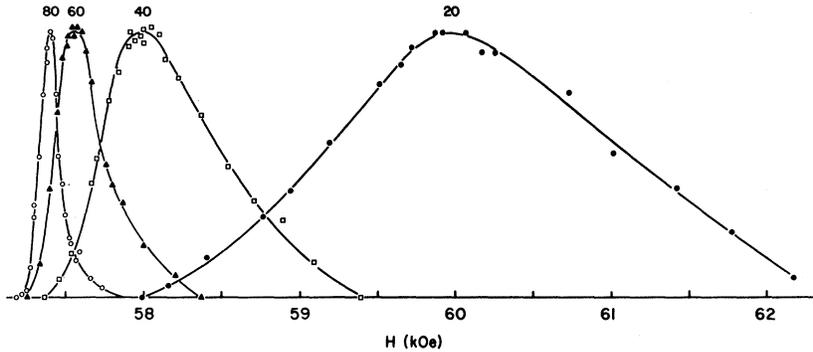
FIG. 1. Experimental spin-echo spectra at 7.70 MHz for ^{103}Rh in $Pd_{1-x}Rh_x$ as a function of x (in at.%).

tive number of palladium or nickel atoms in near-neighbor shells. This behavior is quite similar to the discontinuous magnetization behavior of magnetic impurities in many alloys (e.g., Co in Nb-Mo[20] and Rh-Pd[21]; Fe in Nb-Mo[21,22]). The asymmetry of the ^{103}Rh line shapes observed in the present study, particularly in the rhodium-rich alloys, follows directly from this explanation because of the strongly nonlinear variation of K with alloy composition.

The experimental ^{103}Rh spin-lattice relaxation rates are summarized in Fig. 4 for Pd-Rh and in Fig. 5 for Ni-Rh. (The scatter in the Ni-Rh data near the critical composition can probably be attributed to slightly different thermal histories of the samples, since even small changes in the degree of short-range structural order are expected to have a strong effect on the magnetic properties of alloys in this composition range.) The data were, in all cases, obtained at ~7-8 MHz and field strengths corresponding to the positions of peak echo amplitude. Pulse widths of 15 μsec assured that a significant fraction of the ^{103}Rh spins were sampled even in the most dilute alloys. The general trend of the relaxation data follows that of the resonance shifts. One can conclude from this similarity that the d-spin (core-polarization) interaction provides the dominant relaxation mechanism at sufficiently low rhodium concentrations. In view of the spatial inhomogeneity of the local d-spin susceptibility, as inferred from the NMR line broadening, it was expected that the spin-lattice relaxation rates would increase monotonically with increasing field strengths in passing across the resonance profile. This requires, of course, that the ^{103}Rh spins are sufficiently decoupled by the inhomogeneous broadening that spectral spin diffusion is suppressed. This was established experimentally in a $Pd_{0.60}Rh_{0.40}$ sample by frequency scanning the resonance profile in the presence of a continuous saturating comb of fixed-frequency (7.7 MHz) pulses of width $t_w = 50$ μsec centered on the position of peak resonance intensity. No significant saturation effects were detected outside a central region of frequency width

~$2/t_w$. Having verified the ineffectiveness of spin-diffusion processes, the spin-lattice relaxation rates were then determined at three different positions on the resonance profile using identical 50-μsec rf pulse widths as in the "hole-burning" experiment. The results, which are summarized in Table I, clearly demonstrate the expected trend. Moreover, the data suggest that there exists a rather definite relationship in Pd-Rh between the static rhodium susceptibility (as measured by K) and the low-frequency dynamic rhodium susceptibility (as measured by T_1T) which is independent of alloy composition. This can be seen by referring the -0.2 and -1.6% positions on the $Pd_{0.60}Rh_{0.40}$ resonance profile to compositions whose peak echo amplitudes occur at these shift values (see Fig. 2). The corresponding relaxation times of ~4.0 and 2.0 sec °K, respectively, as estimated from the
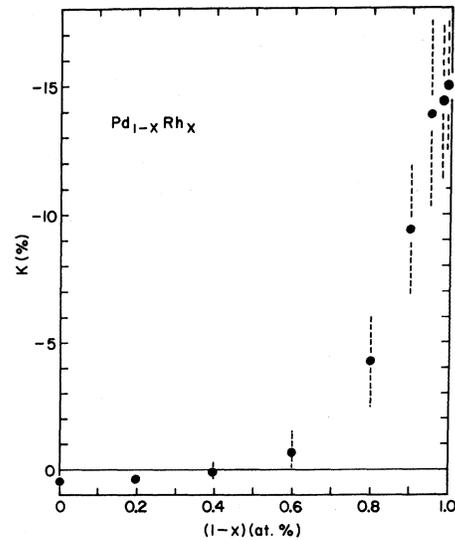

FIG. 2. Composition dependence of ^{103}Rh resonance shifts in Pd-Rh alloys. The points refer to the positions of maximum spin-echo amplitude; the dash verticle lines indicate the inhomogeneous widths (measured between half-amplitude points on the spin-echo spectra).
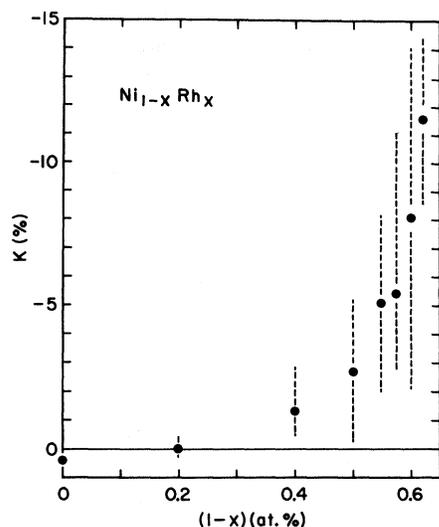
FIG. 3. Composition dependence of ^{103}Rh resonance shifts in Ni-Rh alloys. The notation is the same as Fig. 2.

FIG. 5. Composition dependence of ^{103}Rh spin-lattice relaxation rates in Ni-Rh alloys.

data in Fig. 4, are in good agreement with the $Pd_{0.60}Rh_{0.40}$ data listed in Table I. Since the slope $d(T_1 T)^{-1}/d|K|$ decreases markedly with decreasing rhodium concentration, the sensitivity of $T_1 T$ on position is also expected to decrease. For example, applying the above arguments to the $Pd_{0.80}Rh_{0.20}$ composition leads to predicted relaxation times of ~ 1.6 and 1.1 sec °K for the low- and high-field half-amplitude positions, respectively. Experimentally we observed $1.4(2)$ and $1.2(2)$ sec °K, respectively. Unfortunately, sensitivity problems arising from the rapidly increasing linewidths precluded a more definitive examination of this point in the low-rhodium-concentration regime. The same difficulties made it impossible to obtain useful information about the position dependence of $T_1 T$
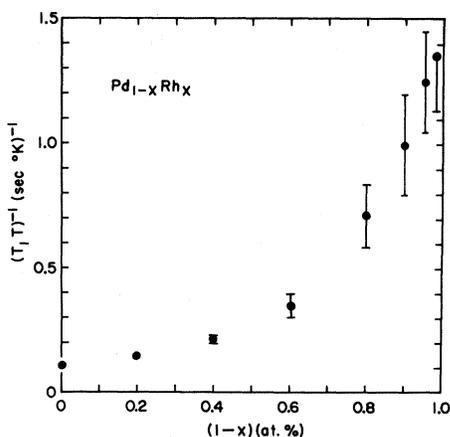
in Ni-Rh.

Because of the rapid variation of the bulk susceptibility with rhodium concentration in dilute PdRh alloys,[1,2,4] the resonance data in the rhodium concentration range $x \approx 0$–10 at.% are of particular interest. Table II summarizes our results for these alloys together with the PAC data of Rao et al.[6] In contrast to the bulk susceptibility, the resonance shifts and relaxation rates are seen to be essentially composition independent for $x \lesssim 5$ at.%. Moreover, the shifts are approximately three times larger than the ^{105}Pd shift ($\sim -4.0\%$) in pure palladium.[23]

IV. DISCUSSION

A. Resonance Shifts

The experimental ^{103}Rh resonance shifts in the Pd-Rh alloy system support the earlier conclusion of Rao et al.[6] that the local susceptibility of dilute rhodium impurities in palladium is significantly larger than the host susceptibility. Moreover, the present results demonstrate that the breakdown of the rigid-band approximation in Pd-Rh is not re-

FIG. 4. Composition dependence of ^{103}Rh spin-lattice relaxation rates in Pd-Rh alloys. The vertical error bars represent estimated experimental uncertainties.
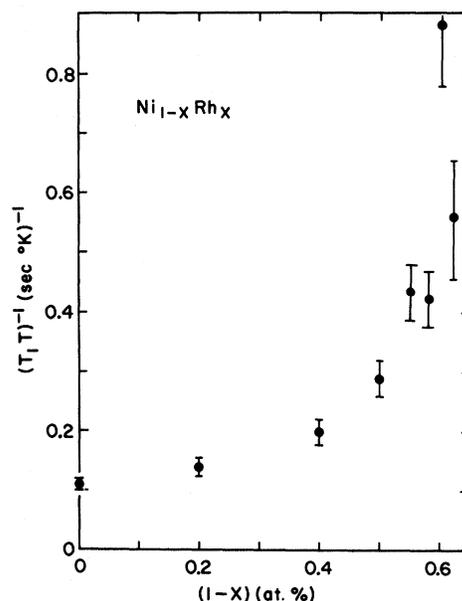
TABLE I. Position dependence of ^{103}Rh spin-lattice relaxation times in $Pd_{0.60}Rh_{0.40}$. The notation (l), (p), and (u) refers to the low-field half-amplitude, peak-intensity, and high-field half-amplitude positions on the resonance profiles, respectively.

Position	$K(\%)$	$T_1 T$ (sec °K)
(l)	-0.2	$3.6(3)$
(p)	-0.8	$2.5(2)$
(u)	-1.6	$2.1(2)$

stricted to extremely low rhodium concentrations. For example, the severe inhomogeneous broadening of the resonance profiles over the entire concentration range provides a clear indication that the local susceptibility is strongly influenced by the near-neighbor environment. Information about the relative magnitudes of the rhodium and palladium susceptibilities is provided by the observed relationship between the *mean* [103]Rh resonance shift and the bulk alloy susceptibility χ as displayed in Fig. 6 for $x \geq 5$ at. %. The gradual increase in $d\,|K|/d\chi$ with increasing susceptibility can be attributed to an increase in the ratio of the average susceptibilities $(\langle\chi_{Rh}\rangle/\langle\chi_{Pd}\rangle)$ of the two atomic constituents. Thus, the data suggest that the excess susceptibility at the rhodium sites relative to that at the palladium sites develops gradually as the rhodium concentration decreases. Because of the relatively small magnitude of the pure rhodium susceptibility and its initially weak dependence on palladium concentration, it is probable that the rigid-band approximation is valid for sufficiently high rhodium concentrations (i.e., $\langle\chi_{Rh}\rangle/\langle\chi_{Rd}\rangle \approx 1$ in the limit of large x). This view is supported by the experimental slope $d\,|K|/d\chi$ in the rhodium-rich alloys which corresponds to an effective hyperfine field

$$H_{hfs} \equiv \mu_B N \frac{dK}{d\chi} = -\frac{340 \pm 30 \text{ kOe}}{\mu_B} \ . \tag{4.1}$$

This field may be identified with the rhodium d-spin (core-polarization) hyperfine field (H^d_{hfs}) since the observed variations in K and χ are most likely dominated by d-spin interactions. The magnitude of the d-spin hyperfine field is in excellent agreement with the rhodium hyperfine field (≈ -350 kOe/μ_B)[6] in dilute PdRh and the palladium hyperfine
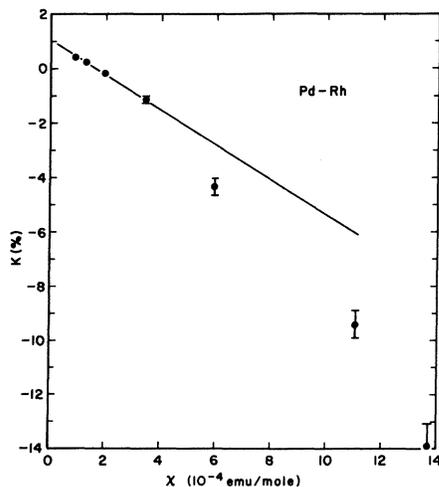

FIG. 6. Variation of mean [103]Rh resonance shifts in $Pd_{1-x}Rh_x$ with bulk-alloy susceptibility. Composition ($x = 5$–100 at. %) is the implicit variable.

TABLE II. Composition dependence of [103]Rh NMR data in dilute PdRh alloys for the temperature range 1–4 °K.

at. % Rh	$K(\%)$	T_1T (sec °K)
10	$-9.4(5)$	1.0(2)
5.0	$-13.9(7)$	0.8(2)
3.0	$-14.4(7)$	
2.0	$-15.1(5)$	0.75(20)
~ 0	$-14.7(3)^a$	

[a]Reference 6.

field $(-345 \pm 10$ kOe/$\mu_B)^{23}$ in the elemental metal, as determined by PAC and NMR techniques, respectively. Both hyperfine fields were inferred from measured values of $dK/d\chi$ with *temperature* as an implicit variable. The PAC determination was based on temperatures above 400 °K where the rhodium-induced host polarization appears to be no longer significant.

In view of the predicted weak dependence of H^d_{hfs} on atomic number within a given transition-element period,[24] the similarity between the rhodium and palladium hyperfine fields discussed above provides some confidence that the assumptions which entered into their respective determinations were basically sound. It should be noted in this connection that an earlier estimate of H^d_{hfs} for elemental rhodium metal,[18] based on the same NMR technique used previously for palladium metal, yielded an anomalously small value (-160 kOe/μ_B). In this case, however, the observed temperature dependence of the Knight shift was exceedingly weak. For this reason, small temperature-induced changes in either the s-contact or d-orbital contributions to the shift might have had a significant influence on $dK/d\chi$. One must, of course, keep the possibility in mind that s-d admixture and exchange-polarization effects can also have a strong influence on H^d_{hfs}. Despite these uncertainties, the close agreement between the PAC and NMR results suggests that rhodium and palladium experience essentially identical effective d-spin (core-polarization) hyperfine fields in Pd-Rh alloys.

A knowledge of the respective hyperfine fields permits the bulk susceptibility of dilute PdRh alloys to be partitioned into rhodium and palladium contributions. Adjusting the measured low-temperature ($T \leq 4$ °K) resonance shifts for an estimated[18] $+0.7\%$ s-contact plus d-orbital contribution yields $K_d \approx -15.5$ and -4.7% for [103]Rh in PdRh and [105]Pd in pure palladium metal, respectively. In this temperature range, the local rhodium d-spin susceptibility therefore exceeds the host susceptibility by the factor 3.3. The measured bulk susceptibility, on the other hand, gives $d\ln\chi/dx \approx 28$. Thus, only $\sim 12\%$ of the impurity susceptibility is localized at the rhodium sites, the other 88% presumably being

distributed over near-neighbor palladium sites. If the host spin polarization is restricted to the 12 nearest neighbors, each would contribute ~ 7% of the observed impurity susceptibility. It also follows that at a rhodium concentration of 5 at.%, the average host susceptibility corresponds to 39% of the local rhodium susceptibility. The PAC experiments of Rao et al.[6] have shown that the rhodium and palladium susceptibilities in PdRh have distinctly different temperature dependences. Anomalously small values of $dK/d\chi$ at temperatures below 400 °K indicate that the impurity susceptibility persists to higher temperatures at the rhodium sites than at the near-neighbor palladium sites.

Although the qualitative features of the ^{103}Rh nuclear resonances in Ni-Rh are very similar to those in Pd-Rh, there exist several essential differences. For example, the inhomogeneous broadening is more severe. Moreover, the composition dependence of $dK/d\chi$, as shown in Fig. 7, is in the opposite direction to that observed in Pd-Rh. We must, therefore, conclude that the local nickel susceptibility is greater than the rhodium susceptibility. That nickel and palladium, despite their isoelectronic structures, behave quite differently as solutes in rhodium metal, is not unexpected. In the case of Pd-Rh, the alloy properties are undoubtedly dominated by band-structure effects since the $4d$ elements palladium and rhodium occupy neighboring positions in the periodic system, and the charge contrast $\Delta Z = 1$, therefore, constitutes the only major perturbation. Nickel, on the other hand, introduces in addition to the same charge contrast, a substantially larger repulsive electron-electron potential which presumably leads to strong local exchange-enhancement effects. (The weaker spin-orbit coupling of nickel may also be of significance in this regard.[25]) There is consequently no reason to expect the rigid-band approximation to be appropriate for Ni-Rh even for small nickel concentrations. This view is confirmed by the initial slope $dK/d\chi$ which yields the anomalously small hyperfine field ~ − 190 kOe/μ_B. Assuming that the rhodium hyperfine field in Ni-Rh has the same magnitude as in Pd-Rh, independent of composition, the ratio of the nickel and rhodium d-spin susceptibilities may be estimated from the expression

$$\frac{dK_{d(Rh)}}{d\chi} = \frac{H_{hfs}^d}{\mu_B N}\left(1 + (\chi_{d(Ni)}/\chi_{d(Rh)} - 1)\Big/\frac{d\ln K_{d(Rh)}}{dc}\right)^{-1},$$
(4.2)

which is valid in the limit of small nickel concentrations c. Substituting the appropriate experimental quantities,[26] we find $\chi_{d(Ni)}/\chi_{d(Rh)} \approx 4.4$. Because of the sensitivity of the result to the assumed rhodium hyperfine field, the magnitude of this ratio has only qualitative significance. The accuracy of the result is sufficient, however, to establish the exis-

tence of local exchange-enhancement effects on nickel sites in dilute RhNi alloys.

B. Spin-Lattice Relaxation Rates

The large magnitude and negative sign of the ^{103}Rh resonance shifts in Pd-Rh and Ni-Rh are indicative of the dominant role of the d-spin (core-polarization) hyperfine mechanism in these alloys for sufficiently low rhodium concentrations. This behavior is a direct consequence of an exchange enhancement of the d-spin susceptibility which can become very important in transition metals (such as palladium) having high-electronic-state densities at the Fermi level. Since it is known that repulsive electron-electron interactions in metals also enhance nuclear spin-lattice relaxation rates,[27-29] it is probable that the measured rates are determined almost entirely by the exchange-enhanced d-spin mechanism. Qualitative support for this contention is provided by the observed composition dependences of $(T_1 T)^{-1}$ which follow the same general trend as do the resonance shifts in both Pd-Rh and Ni-Rh.

The importance of the relaxation data lies in the fact that the magnitude of the product $K^2 T_1 T$ gives some indication of the relative localization of the one-electron impurity potential in cases where only a single (spin-dependent) hyperfine mechanism is important.[30] Specifically, for the d-spin mechanism considered here,

$$K^2 T_1 T = 8 F_d^{-1} K(\alpha)^{-1},$$
(4.3)

where

$$8 \equiv (\gamma_e/\gamma_n)^2(\hbar/4\pi k_B).$$
(4.4)

The inhibition factor F_d is equal to the average-reciprocal-orbital degeneracy at the Fermi level[31] and arises from the fact that the strength of the
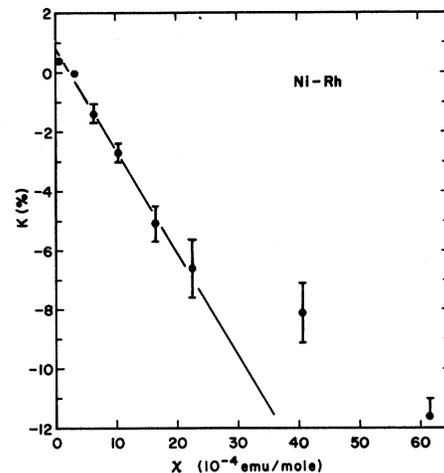

FIG. 7. Variation of mean ^{103}Rh resonance shifts in Ni-Rh with bulk-alloy susceptibility.

d-spin (core-polarization) hyperfine coupling is, in general, independent of the subband index. The nuclear spin therefore senses only the symmetric fluctuation mode in which the spin polarization of the subbands fluctuate in phase.[32] The coupling to the antisymmetric modes vanishes identically. The factor $K(\alpha)$ corrects for differences in the exchange enhancements of K^2 and $(T_1 T)^{-1}$.[28,29] These quantities are related to the *local* wavenumber- and frequency-dependent spin susceptibility

$$\chi(\vec{q}, \omega) = \sum_{\vec{q}'} \chi(\vec{q}, \vec{q}', \omega) . \qquad (4.5)$$

The resonance shift is proportional to the longitudinal static susceptibility $\chi(0, 0)$ whose enhancement relative to a noninteracting electron gas is given by the Stoner factor $(1 - \alpha)^{-1}$, where $0 \le \alpha \le 1$. A pure transition metal may be described by the uniform exchange-enhancement model for which the random-phase approximation (RPA) yields[33]

$$\alpha = [U + (F_d^{-1} - 1)J] N(0)_d F_d , \qquad (4.6)$$

where $N(0)_d$ is the bare density of d states at the Fermi level, while U and J are the intra-atomic Coulomb and (Hund's rule) exchange potentials. (In addition, interatomic electron-electron interactions may also contribute to the exchange enhancement.[34,35]) For the case of the impurity susceptibility in an alloy, local-enhancement effects must be considered and the form of α depends on the details of the applicable model.

In contrast to the resonance shift, the nuclear spin-lattice relaxation rate is proportional to a wavenumber average of the imaginary part of the transverse dynamic susceptibility $\chi(q, \omega_L)$ evaluated at the nuclear Larmor frequency ω_L.[28] In general, the exchange enhancement of $\chi(q, \omega)$ is q dependent. As a consequence, $K(\alpha)$ depends not only on α but also on the detailed q dependence of the susceptibility enhancement. At $q = 0$, the enhancement of $\chi''(q, \omega_L)$ is given by $(1 - \alpha)^{-2}$. However, in most metals the enhancement factor decreases monotonically with increasing wavenumber. This yields $K(\alpha) \to 0$ in the limit $\alpha = 1$. A particularly simple situation occurs, however, in dilute alloys for which

the impurity potential is strongly localized. In that case, the susceptibility enhancement at the impurity site is essentially independent of wavenumber in the range of interest $q \le 2k_F$. Hence, the impurity-site NMR is characterized by $K(\alpha) \approx 1$ even for large values of α.[30,36]

The relative importance of uniform exchange-enhancement effects on K and $(T_1 T)^{-1}$ in strongly paramagnetic metals can be most easily established by an examination of the available data for pure palladium. Estimates of the s-contact, d-spin (core-polarization), and d-orbital contributions to the relaxation rate evaluated in the noninteracting-electron approximation are given in Table III, which also lists the experimental rate for comparison. The s-contact rate was obtained by scaling the ^{109}Ag relaxation rate in metallic silver[9,19] according to the free-electron model by the factor

$$(n_{s(Pd)}/n_{s(Ag)})^{2/3} = 0.50 ,$$

where $n_{s(Pd)} = 0.36$ and $n_{s(Ag)} = 1$ are the respective numbers of "s-like" electrons in palladium[37] and silver. The d-spin and d-orbital rates were calculated using the tight-binding expression[31,38]

$$R_i = 2hk_B[H_{hfs}^i N(0)_d]^2 F_i , \qquad (4.7)$$

where $N(0)_d$ is defined for one direction of the spin. The hyperfine fields were taken to be[23]

$$H_{hfs}^d = -0.35 \times 10^6 \text{ Oe}/\mu_B$$

and

$$H_{hfs}^{orb} = +0.66 \times 10^6 \text{ Oe}/\mu_B .$$

The corresponding orbital-inhibition factors $F_d = \frac{1}{3}$ and $F_{orb} = \frac{2}{9}$ were based on the assumption that the d states near the Fermi level arise principally from the t_{2g} orbitals.[39] The density of states

$$N(0)_d = 6.5 \times 10^{11} \text{ (erg atom)}^{-1}$$

was derived from the recent augmented-plane-wave (APW) band-structure result of Mueller et al.,[40]

$$N(0) = 7.1 \times 10^{11} \text{ (erg atom)}^{-1},$$

by subtracting an estimated "s-electron" contribution

$$N(0)_s = 0.6 \times 10^{11} \text{ (erg atom)}^{-1}$$

corresponding to 0.5 free electrons per atom. The discrepancy between the calculated and observed[41] rates in Table III is clearly outside the combined uncertainties in the estimated parameters. It appears that a 27-fold exchange enhancement of the d-spin (core-polarization) rate is needed to account for the experimental rate. The enhancement of the d-spin shift, on the other hand, is approximately 11 (i.e., $\alpha \approx 0.9$). This value follows from the measured low-temperature susceptibility[4] which gives

TABLE III. Comparison of calculated and observed ^{105}Pd spin-lattice relaxation rates $R \equiv (\gamma_n^2 T_1 T)^{-1}$ (in units of 10^{-6} sec $°K^{-1}$ Oe^2) in palladium metal. The calculated values refer to a noninteracting electron-gas model as discussed in the text.

		Calculated	Observed
R_s	=	0.034	
R_{orb}	=	0.076	
R_d	=	0.031	
R_{total}	=	0.14	0.95(10)[a]

[a]Reference 41.

$$N(0)_\chi = 72 \times 10^{11} \ (\text{erg atom})^{-1} \ .$$

We may infer, therefore, that $K(\alpha) \approx 0.22$ in palladium metal.

Before accepting the above $K(\alpha)$ value it is important to consider the possible importance of other contributions to $(T_1 T)^{-1}$ which are not shown in Table III. The most obvious of these is the d-spin (dipolar) rate. In cubic crystals such as palladium, the static dipolar interaction vanishes because of symmetry; its fluctuation amplitude, however, is nonzero and can, therefore, provide a nuclear relaxation mechanism.[38] In the noninteracting limit and for our choice of orbital occupation numbers, the resulting dipolar rate is related to the core-polarization rate by

$$R_{\text{dip}}/R_d = \tfrac{5}{49}(H_{\text{hfs}}^{\text{orb}}/H_{\text{hfs}}^d)^2 \ . \tag{4.8}$$

Using our hyperfine-field estimates, we obtain $R_{\text{dip}} \approx 0.36 R_d$. Since the dipolar relaxation process is driven by d-spin fluctuations, one might expect that its exchange enhancement is equal in magnitude to that of the core-polarization process. However, this is not the case. In contrast to the core-polarization interaction, the dipolar interaction couples only through the antisymmetric spin-fluctuation modes, the symmetric coupling being zero by symmetry. The exchange enhancement of the antisymmetric fluctuation amplitude, however, is greatly reduced over that of the symmetric response since it is opposed by Hund's-rule exchange.[39] For example, in the static limit the antisymmetric response is enhanced by the factor $[1 - (U - J) \times N(0)_d F_d]^{-1}$ rather than $[1 - \alpha]^{-1}$ as defined earlier for the uniform-enhancement model. Although the ratio J/U is not accurately known, it is certainly of sufficient magnitude to make the exchange-enhanced dipolar relaxation rate unimportant. Another contribution to $(T_1 T)^{-1}$ which has been neglected so far in our discussion is the exchange enhancement of the d-orbital relaxation rate.[42] The appropriate enhancement factor is related to $(U - J)$ as in the case of the dipolar rate and is therefore again smaller than the d-spin (core-polarization) enhancement factor. Thus, our assertion that the d-spin (core-polarization) hyperfine mechanism is the dominant source of both the Knight shift and the spin-lattice relaxation rate appears to be consistent with the available facts. Finally, it should be remarked that we have tacitly assumed an electronic g value equal to 2 in our discussion. Although it is believed[43] that the palladium g value is strongly anisotropic, it appears unlikely that its average value deviates sufficiently from the free-electron value to effect our conclusions.

Having established the importance of exchange-enhanced hyperfine interactions in palladium metal, we turn to a consideration of the relationship be-

tween K and $T_1 T$ for ^{103}Rh in the most paramagnetic Pd-Rh and Ni-Rh alloys. The observed variation of $\mathcal{S}/K^2 T_1 T$ as a function of K^{-1} is shown in Fig. 8. [The choice of K^{-1} as an independent variable is based on the fact that $K^{-1} \propto (1 - \alpha)$ for small changes in $N(0)_d$.] The similarity between the Pd-Rh and Ni-Rh results is immediately apparent. It is also noteworthy that the pure palladium result fits the experimental trend. More importantly, Fig. 8 demonstrates quite clearly that $K(\alpha)$ tends toward zero in both alloys as α approaches unity (i.e., as $K \to \infty$). This behavior follows directly from the uniform exchange-enhancement model and is inconsistent with any localized spin-fluctuation model.[30] More specifically, if the rhodium susceptibility in dilute PdRh alloys were *locally* exchange enhanced, one would expect $K(\alpha)$ to approximate the host value.[44] This is clearly not the case. Since the electronic specific heat of PdRh is nearly composition independent for rhodium concentrations in the range 0–20 at.%, we may define a local α value in these alloys by scaling $(1 - \alpha)^{-1}$ according to the experimental ratio of the rhodium resonance shifts to that of pure palladium. Furthermore, by adjusting the experimental $K^2 T_1 T$ products for an estimated shift of $+0.7\%$ and a relaxation rate of $0.11 \times 10^{-6} \sec {}^\circ \text{K}^{-1} \text{Oe}^2$ (both arising from the combined effects of s-contact and d-orbital interactions), as well as an orbital degeneracy factor $F_d = \tfrac{1}{3}$, it is possible to infer the corresponding $K(\alpha)$ values as was done above for palladium metal. The results of this analysis are plotted for rhodium concentrations of 2, 5, 10, and 20 at.% in Fig. 9 together with the palladium $K(\alpha)$ value. Also shown
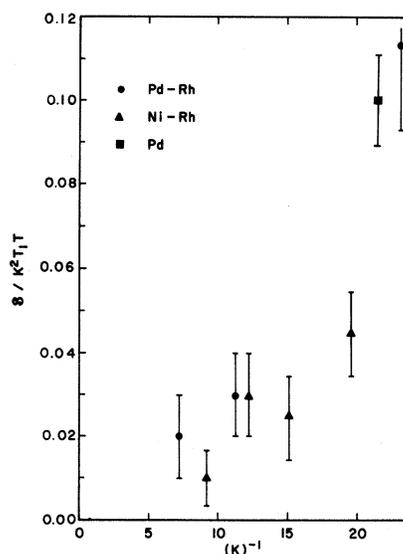

FIG. 8. Experimental dependence of $\mathcal{S}/K^2 T_1 T$ for ^{105}Pd in palladium metal, and ^{103}Rh in strongly exchange-enhanced Pd-Rh and Ni-Rh alloys.
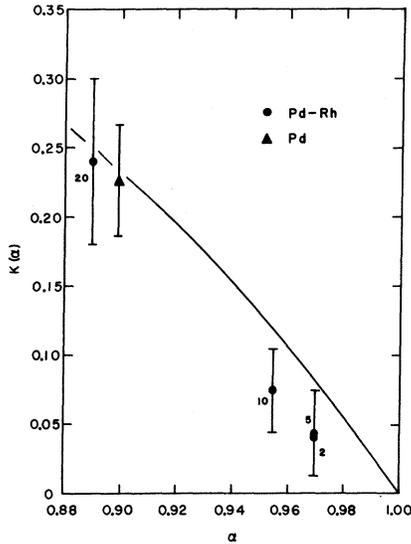
FIG. 9. Plot of $K(\alpha)$ vs α for ^{105}Pd in palladium metal and for ^{103}Rh in Pd$_{1-x}$Rh$_x$ ($x = 2$, 5, 10, and 20 at.%). The solid line is the prediction of the RPA δ-function interaction model.

is the RPA prediction for a free-electron gas subjected to a δ-function (i.e., zero-range) electron-electron interaction potential. The agreement is fortuitously good. Since finite-range electron-electron interactions and the nonspherical "jungle-gym" d-hole Fermi surface of palladium would change the predicted slope $dK(\alpha)/d\alpha$ in opposite directions, it is likely that the effect of these perturbations on the q dependence of the enhancement factor largely cancels.

The present results contrast sharply with the properties of the $3d$ impurities chromium[45] and manganese[45] in aluminum as well as chromium[46] and nickel[47] in platinum, for which $S/F_dK^2T_1T \gtrsim 1$. The small $K(\alpha)$ values observed for ^{103}Rh in PdRh are evidently associated with a weak spatially extended impurity potential. In other words, the q dependence of the impurity-site susceptibility $\chi(q, \omega_L)$ in PdRh in the wavenumber range of interest for nuclear relaxation behaves qualitatively like that of a uniformly exchange-enhanced metal. Such behavior would not be expected if the impurity potential were strongly localized and the host spin polarization were due to a weak spin-dependent potential localized at the impurity sites, as is commonly assumed for "giant-moment" alloys such as

Pd Fe. The observation of different temperature dependences of the rhodium and near-neighbor palladium susceptibilities must therefore be attributed to differences in the respective local density-of-states functions $N(E)$ resulting entirely from potential scattering. Because of the large exchange enhancement even small differences in the structure of $N(E)$ can presumably cause large changes in $\chi(T)$. To ascribe the observed magnetic properties of dilute rhodium impurities in palladium to local-moment behavior would therefore seem to be unnecessary. Finally, we note that the extended nature of the impurity susceptibility in Pd Rh undoubtedly accounts for the qualitative success of the rigid-band model in explaining the bulk properties of these alloys.

V. CONCLUSIONS

The addition of either palladium or nickel to rhodium metal causes large increases in the magnitude of the ^{103}Rh d-spin (core-polarization) resonance shifts and spin-lattice relaxation rates. In general, the results of our NMR experiments in Pd-Rh and Ni-Rh demonstrate that the magnetic properties of both alloy systems deviate markedly from rigid-band behavior. Not only is the local rhodium susceptibility extremely sensitive to statistical variations in the near-neighbor alloy composition, but on the average it exceeds that of the palladium sites in Pd-Rh and is smaller than that of the nickel sites in Ni-Rh.

The exchange enhancement of the ^{103}Rh spin-lattice relaxation rate, although very important, is much smaller than that of the square of the resonance shift. This implies that the exchange enhancement of $\chi(q, \omega_L)$ decreases strongly with increasing wavenumber. Since such behavior is more characteristic of a uniform-enhancement model than any localized spin-fluctuation model, we conclude that a local-moment description is inappropriate for rhodium impurities in palladium. The Curie-Weiss temperature dependence of the rhodium susceptibility must therefore be attributed to structure in the local density-of-states function near the Fermi level rather than to Kondo spin compensation.

*Work supported by the U. S. Atomic Energy Commission.

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