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# Knight Shift Studies of Transition Metals: Rhodium and Rhodium Intermetallic Compounds

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The temperature dependence of the nuclear magnetic resonance (nmr) of $Rh^{103}$ in rhodium metal has been examined. From the linearity of the Knight shift ($K$) versus susceptibility ($\chi$) plot, it is deduced that all of the temperature variation in $\chi$ is of $d$-spin origin; the slope of the $K$-versus-$\chi$ curve yields a core-polarization hyperfine field of $-0.323\times10^6$ Oe spin. An analysis of the separate contributions to the $K$ and $\chi$ based on a two-band model is given, and some considerations offered on the exchange enhancement of $\chi$ in the Rh-Pd alloy system. Nmr has also been observed and the Knight shifts determined in the intermetallic compounds $RhSn_2$, $LaRh_2$, RhSi, $ThRh_3$, and $URh_3$. A value of the $Rh^{103}$ nuclear moment $\mu^{103}=-0.0879\pm0.0001\ \mu_n$ (uncorrected for diamagnetic shielding) is obtained.

## I. INTRODUCTION

An increasing interest in the electronic properties of the transition metals, their alloys and intermetallic compounds has come, in part, from the detailed information afforded by nuclear magnetic resonance (nmr) and Mössbauer effect studies. In particular, Knight shift studies of Pt,[1] Pd,[2] and the superconductors, $V_3Si$ and $V_3Ga$[3] have, in conjunction with measurements of the susceptibility and specific heat, made possible a partitioning of the spin and orbital contributions to the magnetization of these metals.

In this paper we extend these studies to Rh metal and some Rh intermetallic compounds. From the temperature dependence of the Knight shift and the susceptibility of Rh metal, the $d$-spin core polarization hyperfine field is obtained. A partitioning of the spin and orbital contributions to the susceptibility and Knight shift is made which is consistent with the electronic specific heat and susceptibility of the Pd-Rh alloy system.

## II. EXPERIMENTAL DETAILS

With the exception of $RhSn_2$, all of the intermetallic compounds were prepared by arc melting. $RhSn_2$ was made by induction heating in an argon atmosphere using dense alumina crucibles. X-ray analysis was used to confirm the crystallographic structures. $ThRh_3$ and $URh_3$ have the cubic $L1_2$ structure.[4] $LaRh_2$ has the $C15$ structure. RhSi has the $B20$ structure[5] and $RhSn_2$ is tetragonal in the low-temperature phase.[6] Samples were prepared from the intermetallic compounds by crushing and then screening them with a 400-mesh sieve. The rhodium metal was obtained as a finely divided sponge[7] of nominal purity in excess of 99.95%. All measurements on the intermetallic compounds were made at 4.2°K with the sample immersed in a bath of liquid helium. The rhodium metal resonance was also examined in the region 90-300°K. A Varian #4540 temperature-control unit was utilized for this purpose. A crossed coil spectrometer was used for the nmr measurements along with a conventional electromagnet.

## III. EXPERIMENTAL OBSERVATIONS

### A. nmr of $RhSn_2$—Nuclear Moment of $Rh^{103}$

The isotope $Rh^{103}$ ($I=\frac{1}{2}\hbar$) is 100% naturally abundant. The earliest determination[8] of its nuclear moment was obtained from hyperfine structure in the optical spectra of RhI. From transitions between excited $4d^85p$ configurations and the ground state $4d^85s$; ${}^4F_{9/2}$ the hfs splitting for the $5s$ electron was obtained and from the Fermi-Segrè relation, a value of $\mu^{103}=-0.10\mu_n$ was computed.

Until the present work the only observation of $Rh^{103}$ nmr was in metallic rhodium.[9] To derive a value for $\mu^{103}$ the resonance data must be corrected for the Knight shift resulting from the electronic paramagnetism. If one corrects for the $s$ conduction-electron hyperfine field alone, as was originally done, a value of the $s$ Knight shift $K_s=0.36\%$ is obtained[10] and the value $\mu^{103}=-0.08782\ \mu_n$ is deduced. However, it was subsequently realized that the $d$-band electrons contribute to the spin and orbital paramagnetism and thus to the Knight shift of all transition metals.[1] Therefore, we have selected an intermetallic compound for which one might reasonably expect the $d$-like orbitals on the rhodium ions to be fully occupied. Such a filled $d$-band metal would have no $d$ contribution,

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[1] A. M. Clogston, V. Jaccarino, and Y. Yafet, Phys. Rev. **134**, A650 (1964).
[2] J. A. Seitchik, A. C. Gossard, and V. Jaccarino, Phys. Rev. **136**, A1119 (1964).
[3] W. E. Blumberg, J. Eisinger, V. Jaccarino, and B. T. Matthias, Phys. Rev. Letters **5**, 149 (1960); A. M. Clogston and V. Jaccarino, Phys. Rev. **121**, 1357 (1961); A. M. Clogston, A. C. Gossard, V. Jaccarino, and Y. Yafet, Rev. Mod. Phys. **36**, 170 (1964).
[4] A. E. Dwight, J. W. Downey, and R. A. Conner, Jr., Acta Cryst. **14**, 75 (1961).
[5] S. Geller and E. A. Wood, Acta Cryst. **7**, 441 (1954).
[6] E. Hellner, Z. Krist. **107**, 99 (1956).
[7] Englehard Industries Inc., Newark, New Jersey.
[8] H. Kuhn and G. K. Woodgate, Proc. Roy. Soc. (London) **A64**, 1090 (1950).
[9] P. B. Sogo and C. D. Jeffries, Phys. Rev. **98**, 1316 (1955).
[10] In calculating the $s$-electron Knight shifts it has been assumed that there are 0.5 conduction electrons per atom in rhodium metal and 1.0 conduction electrons per rhodium atom in $RhSn_2$. Values of the $s$-electron hyperfine field in the metal are discussed in the section on Interpretation.

spin or orbital, to the paramagnetic susceptibility. $\mathrm{RhSn_2}$ is diamagnetic[11] and the observed Knight shift need only be corrected for $s$-like character to the conduction band.[10] The calculated value $K(\mathrm{RhSn_2})=+0.45\%$ results in a value $\mu^{103}=-0.08786\pm0.0001\mu_N$, where all the error arises from the uncertainty in the estimate of $K$.

### B. Other Rhodium Intermetallic Compounds

Nmr of $\mathrm{Rh^{103}}$ was observed, and the Knight shifts determined in the intermetallic compounds RhSi, $\mathrm{LaRh_2}$, $\mathrm{ThRh_3}$, and $\mathrm{URh_3}$ (see Table I). The "zero" of Knight shifts was established using the results on $\mathrm{RhSn_2}$ and the discussion given above. The variation of the Knight shifts is considered in the section on discussion of results.

### C. Temperature Dependence of the Rhodium Metal nmr

The nmr of $\mathrm{Rh^{103}}$ in rhodium metal was examined as a function of temperature below 300°K. The field $H_0$ for resonance, at a fixed frequency $\nu_0=1.94500$ Mc/sec, as a function of temperature is shown in Fig. 1. The temperature dependence of the susceptibility $\chi^{12}$ in the same region is shown as well. In Fig. 2 both sets of data are combined in a plot of $H_0$ versus $\chi$ with temperature the implicit parameter. Because $H_0$ and $\chi$ are found to be linearily related a separation of some of the contributions to the shift can be made, as we shall show.

TABLE I. Knight shifts of rhodium intermetallic compounds at 4.2°K. The zero of Knight shifts is established by assuming that for $\mathrm{RhSn_2}$ only an $s$ like contribution to the spin density of the conduction electrons is present at the rhodium site; a value of $K=+0.45\%$ is calculated for this compound (see text).

| Compound | $\mathrm{ThRh_3}$ | $\mathrm{URh_3}$ | $\mathrm{LaRh_2}$ | RhSi |
|---|---|---|---|---|
| % Shift | 0.49±0.02 | 0.00±0.02 | 0.78±0.01 | 0.33±0.01 |

The observed peak-to-peak separation for the derivative of the absorption curve is approximately 3 Oe. The calculated nuclear dipolar contribution to the linewidth is only 0.23 Oe. We estimate the demagnetization broadening that results from the finite paramagnetism and the use of randomly shaped particles to be 1 Oe. It was not possible to vary the magnetic field in this investigation so that no conclusions can be drawn concerning the linewidth in the limit of zero applied magnetic field.

## IV. INTERPRETATION

### Susceptibility

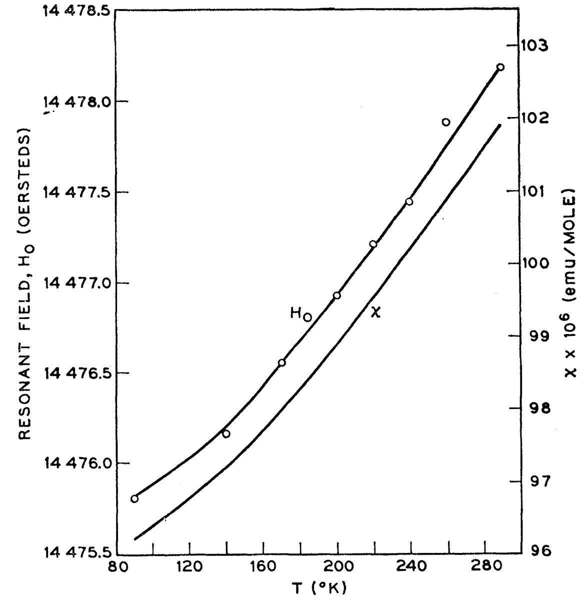

FIG. 1. The experimentally observed field for resonance, at a fixed frequency of 1.94500 Mc/sec, for the $\mathrm{Rh^{103}}$ nmr in rhodium metal as a function of temperature. The measurements of the temperature dependence of the susceptibility by Budworth and collaborators (see Ref. 12) are also shown.

In the analysis of the susceptibility and Knight shift of platinum[1] a two-band ($s$ and $d$) model was adopted. The total susceptibility $\chi(T)$ was expressed as

$$\chi(T)=\tfrac{2}{3}\chi_p^s+\chi_p^d(T)+\chi_{vv}+\chi_{\mathrm{dia}}\,, \tag{1}$$

where $\frac{2}{3}\chi_p^s$ is the free electron like Pauli spin susceptibility of the $s$ band suitably corrected for the Landau diamagnetism and $\chi_{\mathrm{dia}}$ is the ion-core diamagnetic susceptibility. $\chi_p^s$ and $\chi_{\mathrm{dia}}$ were estimated and the $d$-spin and $d$-orbital susceptibilities $\chi_p^d(T)$ and $\chi_{vv}$, respectively, were separately obtained from an

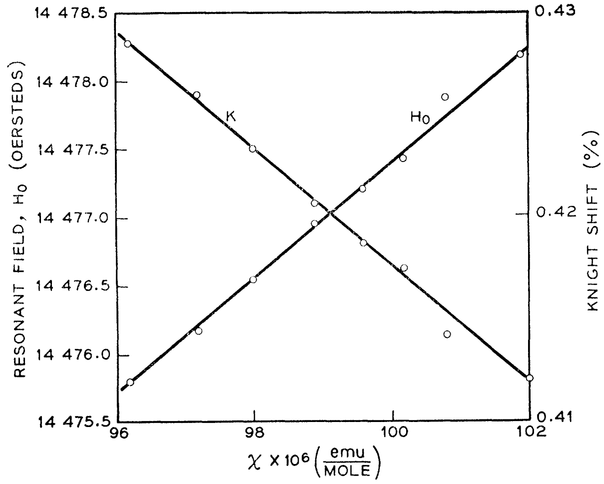

FIG. 2. The experimentally observed field for resonance of the $\mathrm{Rh^{103}}$ nmr in rhodium metal versus the susceptibility, with temperature the implicit variable. The Knight shift versus susceptibility data is also shown. The zero of the Knight shift scale is not precisely known because the nuclear moment of $\mathrm{Rh^{103}}$ has been determined to an accuracy of only ±0.1%.

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[11] The susceptibility of $\mathrm{RhSn_2}$ is $-1.02\times10^{-4}$ emu/mole; R. C. Sherwood and H. J. Williams (private communication).

[12] D. W. Budworth, F. E. Hoare, and J. Preston, Proc. Roy. Soc. (London) **A257**, 250 (1960).

analysis of the Knight shift versus susceptibility diagram. The origins of the separate contributions to $\chi(T)$ and the reasons for choosing only $\chi_p{}^d(T)$ to be temperature-dependent are discussed in Ref. 1.

We cannot strictly follow the above procedure because $\mathrm{Rh}^{103}$ nmr has not been observed in a nonmagnetic, nonmetallic material and some absolute uncertainty exists as to the "zero" of Knight shifts in any rhodium-metal study. However, a partitioning of the susceptibility in Rh can be had from an examination of the susceptibilities and electronic specific heats of the Pd-Rh alloy system.[12,13] Using the values of $\chi_p{}^d(0)$ and $\chi_{vv}$ so obtained and the estimates of the hyperfine fields for the $s$ and $d$ electrons we will then construct a Knight shift diagram for Rh metal and show that it is reasonably consistent with the nuclear moment and "zero" of Knight shifts deduced from the nmr data of $\mathrm{RhSn}_2$.

$\chi_p{}^s$: The changes in the susceptibility of Pd upon alloying with Ag and other filled $d$-shell elements have led to estimates of 0.4—0.6 for the number of $s$ electrons per atom $n_s$, in Pd metal (in the two-band model $n_s=n_d$, the number of $d$ holes per atom). Since the density of states $N(E)$ is much larger in the $d$ band than it is in the $s$ band, and we have assumed $N_s(E)\sim E^{1/2}$, the small change in $E_F$ in going from Pd to Rh will correspondingly involve only a small change in $N_s(E_F)$. We therefore use the value $\chi_p{}^s=6.2\times10^{-6}$ emu/mole deduced for Pd[2], when $n_s=0.5$, as being constant throughout the entire Pd-Rh system.

$\chi_{\mathrm{dia}}$: An estimate of $\chi_{\mathrm{dia}}$ is obtained by subtracting the free-electron spin susceptibility ($n_s=1$) from the measured $\chi$ of Ag metal since in our model Pd-Rh alloys and Ag differ only by the latter having the 4-$d$ band filled. The value computed for $\chi_{\mathrm{dia}}$ is $-25\times10^{-6}$ emu/mole.

$\chi_{vv}$ and $\chi_p{}^d(0)$: The orbital paramagnetism of the $d$ electrons must be considered since they form a partially filled degenerate band. This term we denote by $\chi_{vv}$ since it is the analog in metals of the Van Vleck temperature-independent paramagnetism. In Pd metal, it was estimated that $\chi_{vv}\simeq30\times10^{-6}$ emu/mole and we assume that it is substantially constant for all Pd-Rh alloys. Some justification for this hypothesis will be established below.

The dominant contribution to the susceptibility of these alloys, however, results from the spin paramagnetism of the $d$ electrons which is large because $N_d(E_F)$ is sizable and the fact that intraband $d$-$d$ exchange further enhances $\chi_p{}^d(T)$. The exchange-enhanced susceptibility $\chi_p{}^d$ may be expressed as

$$\chi_p{}^d=\chi_0{}^d/(1-J\chi_0{}^d)\,, \qquad (2)$$

where $\chi_0{}^d$ is the $d$ spin susceptibility in the absence of exchange and $J$ is a parameter proportional to the $d$-$d$ exchange energy: $J>0$. Taking the electronic $g$ factor to be 2, then $\chi_0{}^d(0)=2\beta^2N_d(E_F)$ and $\chi_p{}^s=2\beta^2N_s(E_F)$. Since exchange does not influence the electronic specific heat we may utilize measurements of the latter quantity, which directly determine $N_d(E_F)+N_s(E_F)$, to compute the exchange enhancement of the susceptibility.[1] In Fig. 3 we compare the variation of $\chi(0)$ with that of $\chi_{\mathrm{sp.ht.}}\equiv\chi_0{}^d(0)+\chi_p{}^s$ as a function of Pd concentration in the Pd-Rh alloy system.

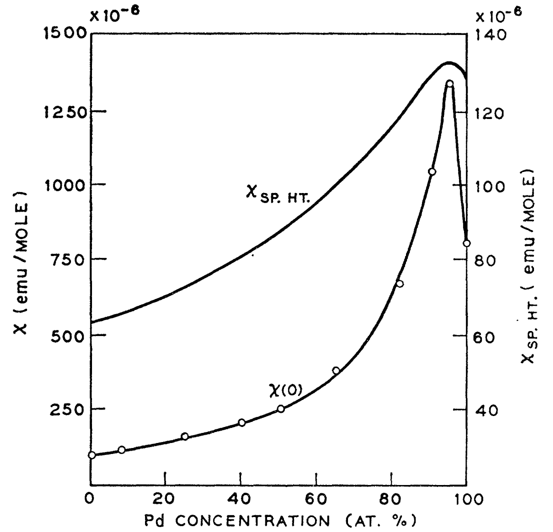

FIG. 3. The measured susceptibility extrapolated to 0°K, $\chi(0)$, is shown as a function of Pd concentration for the Pd-Rh alloy system. For comparison $\chi_{\mathrm{sp.ht.}}$ as calculated from specific-heat measurements is also plotted.

From Eq. (1) and our estimates of $\chi_p{}^s$, $\chi_{\mathrm{dia}}$, and $\chi_{vv}$, we have $\chi_p{}^d(0)=\chi(0)-9\times10^{-6}$ emu/mole. Then using the measured $\chi_{\mathrm{sp.ht.}}$ and Eq. (2) we may compute $J$

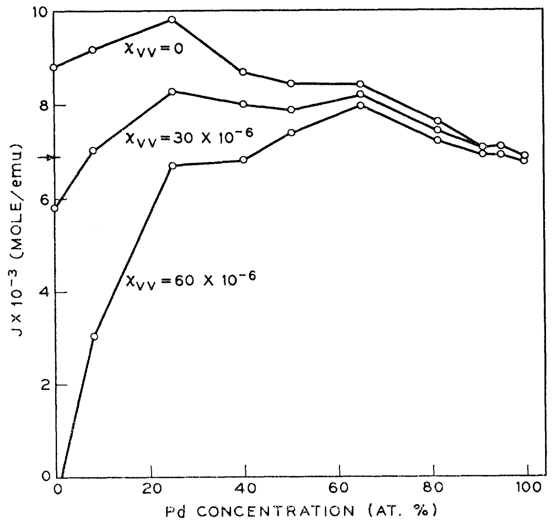

FIG. 4. Computed values of the exchange parameter $J$ for the Pd-Rh alloy system are shown as determined from susceptibility and specific-heat data for $\chi_{vv}=0$, 30, and $60\times10^{-6}$ emu/mole.

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[13] A. Manuel and J. M. P. St. Quinton, Proc. Roy. Soc. (London) A273, 412 (1963).

as a function of Pd concentration. This is shown in Fig. 4. Most satisfying is the fact that $J$ is approximately constant (for the choice $\chi_{vv}=30\times10^{-6}$ emu/mole) as one might expect since the exchange interaction per electron should not vary appreciably for small changes in the Fermi energy. That $J$ is sensitive to the assumed value of $\chi_{vv}$ is shown by the other two curves of Fig. 4, where $\chi_{vv}$ is taken to be 0 and $60\times10^{-6}$ emu/mole.

The values of the various contributions to $\chi(0)$ for Rh metal are summarized in Table II.

## Knight Shift

The Knight shift for a transition-metal ion nucleus at a site of cubic symmetry may be expressed as[1]

$$K(T)=\alpha_s\chi_p{}^s+\alpha_d\chi_p{}^d(T)+\beta\chi_{vv}+\delta K_{\mathrm{dia}}. \qquad (3)$$

The first term is the contribution to the shift arising from the $s$ electrons while the $d$ electron spin and induced orbital hyperfine fields give rise, respectively, to the second and third terms. The chemical shift in the metal relative to the reference material is contained in $\delta K_{\mathrm{dia}}$ and is negligibly small. The quantities $\alpha_s$ and $\alpha_d$ are $0.895\times10^{-4}$ times the hyperfine fields per spin in the metal for the $s$-contact and $d$-core polarization processes, respectively, and $\beta=(2/A)\langle 1/r^3\rangle_{\mathrm{met}}$; $A$ is Avogradro's number and $\langle 1/r^3\rangle$ is expressed in atomic units.

Concerning the sign of the hyperfine fields we known the $s$ contact and orbital hyperfine fields are intrinsically positive (i.e., $\alpha_s$ and $\beta>0$) whereas experimental evidence in other transition metals and their intermetallic compounds indicates that the core-polarization fields $H_{HF}(d)$ are negative (i.e., $\alpha_d<0$). In fact it was experimental and theoretical work on the core-polarization fields of $3d$ ions in nonmetallic crystals in which $H_{HF}(d)<0$ that suggested similar results were to be expected in the transition metals. The relative signs of the hyperfine fields are particularly important in identifying which contribution to the paramagnetism is temperature-dependent and we shall now utilize this to determine $\alpha_d$ in rhodium metal.

$\alpha_d$: It is explicitly assumed in (1) and (3) that all of the temperature dependence of $\chi$ is contained in $\chi_p{}^d(T)$. If this be so, a plot of $K$ versus $\chi$, with temperature the implicit parameter, should be linear with slope $\alpha_d$. The data of Fig. 2 shows that this is the case and, because $[dK(T)/d\chi(T)]<0$, that it is only $\chi_p{}^d$ that is varying with temperature. From the slope of the line we obtain $\alpha_d=-28.9$ (emu/mole)$^{-1}$ corresponding to $H_{HF}(d)=-0.323\times10^6$ Oe. Note that $K_d(T=0)\equiv\alpha_d\chi_p{}^d(T=0)=-0.25\%$.

$\alpha_s$: The quantities $\alpha_s$ and $\beta$ are estimated from optical hfs data and from Hartree-Fock free-ion calculations, respectively. A separation $\Delta\nu=0.023$ cm$^{-1}$ is found between hfs doublets in the optical transitions from the excited $4d^85p$ configurations to the ground state, $4d^85s$: ${}^4F_{9/2}$, of Rh$^{103}$. As the predominant contribution to the observed splitting arises from the $5s$ electron, we obtain a value of 0.041 cm$^{-1}$ for the hfs interaction constant $a_{5s}({}^4F_{9/2})$ from the relation $a_{5s}({}^4F_{9/2})=9/5\Delta\nu$. Using the value of $\mu^{103}$ determined from the RhSn$_2$ nmr experiment and the value of $a_{5s}$ given above we find for the hyperfine field per spin $H_{5s}=9.5\times10^6$ Oe.[14] In general, the $s$ hyperfine field in a metal differs from the free-atom value. Choosing a value of $\xi=0.7$ for the reduction factor, as has been determined experimentally for Ag, we obtain $H_{5s}{}'=6.7\times10^6$ Oe, $\alpha_s=590$ (emu/mole)$^{-1}$ and $K_s\equiv\alpha_s\chi_p{}^s=+0.36\%$.

TABLE II. The values for the Pauli susceptibility of the conduction electrons $\chi_p{}^s$, the diamagnetism of the core electrons $\chi_{\mathrm{dia}}$, and the orbital paramagnetism $\chi_{vv}$ are estimated as described in the text. The $d$-electron spin susceptibility at 0°K, $\chi_p{}^d(0)$, was determined from the measured susceptibility $\chi$ and the relation $\chi=\frac{2}{3}\chi_p{}^s+\chi_p{}^d+\chi_{\mathrm{dia}}+\chi_{vv}$. $J$ was evaluated using Eq. (2).

| $\chi_p{}^s\left(\frac{\text{emu}}{\text{mole}}\right)$ | $\chi_p{}^d(0)\left(\frac{\text{emu}}{\text{mole}}\right)$ | $\chi_{\mathrm{dia}}\left(\frac{\text{emu}}{\text{mole}}\right)$ | $\chi_{vv}\left(\frac{\text{emu}}{\text{mole}}\right)$ | $J\left(\frac{\text{emu}}{\text{mole}}\right)^{-1}$ |
|---|---|---|---|---|
| $6.2\times10^{-6}$ | $86\times10^{-6}$ | $-25\times10^{-6}$ | $30\times10^{-6}$ | $5.8\times10^{3}$ |

$\beta$: No optical hfs data of sufficient accuracy exists to determine the orbital hyperfine field of a Rh $4d$ electron. However, recent Hartree-Fock calculations of $\langle r^n\rangle$ have been made for several $4d$-shell transition ions and from these we deduce a value of $\langle r^{-3}\rangle_{4d}=6.4$ au for the configuration $4d^9$ of the Rh$^{\mathrm{II}}$ ion. [*Note added in proof.* An ESR determination of $\langle r^{-3}\rangle_{4d}=5.8$ a.u. for Rh$^{\mathrm{II}}$ in ZnWO$_4$ has recently been obtained. M. G. Townsend, J. Chem. Phys. **41**, 3149 (1964)]. Again, as was done for V, Pd, and Pt, we assume $\langle r^{-3}\rangle_{\mathrm{met}}=\frac{3}{4}\langle r^{-3}\rangle_{4d}$ which yield values of $\langle r^{-3}\rangle_{\mathrm{met}}=4.8$ au, $\beta=108$ (emu/mole)$^{-1}$ and $K_{vv}\equiv\beta\chi_{vv}=+0.32\%$.

Adding all of the contributions to the Knight shift we find that, at $T=0$°K, $K=0.43\%$. A graphical $K$ versus $\chi$ representation is shown in Fig. 5 and should be compared with those diagrams previously constructed for Pt and Pd to discern the relative importance of spin and orbital contributions to the

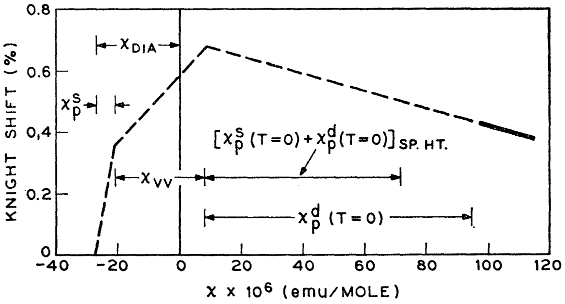

FIG. 5. A complete Knight shift versus susceptibility diagram for rhodium metal. The solid line is the "observed" portion of the diagram. The numerical details for construction of the diagram are given in the text.

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[14] This is comparable to the Ag$^{109}$ hyperfine field $H_{5s}=10.5\times10^6$ Oe but somewhat greater than the estimate quoted by W. D. Knight, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 2, p. 93.

Knight shifts and susceptibilities of these transition metals. The manner in which the total rhodium-metal Knight shift was obtained allows an independent determination of the nuclear moment to be made. We find $\mu^{103} = -0.08778\mu_N$, which differs by only 0.1% from our $RhSn_2$ determination of $\mu^{103}$.

The sensitivity of the value of $\mu^{103}$ determined from the rhodium-metal data to the choice of parameters is exemplified by the following: Had we taken $J = 6.9 \times 10^3$ (emu/mole)$^{-1}$, which is the value for Pd, as the value appropriate to all Rh-Pd alloys then our values of $\chi_{vv}$ and $\chi_p{}^d(0)$ would become $20.6 \times 10^{-6}$ and $95.3 \times 10^{-6}$ emu/mole, respectively. In this case the total Knight shift is reduced to 0.34%, and from this a value of $\mu^{103} = -0.08786\mu_n$ would be obtained which, fortuitously, is in agreement with the $RhSn_2$ value.

### High-Temperature $K$ and $\chi$ Data

The behavior of the susceptibility of rhodium at elevated temperatures[15] is quite remarkable as may be seen from the inset of Fig. 6. As the interpretation of the low-temperature (<300°K) susceptibility and nmr data necessarily attributes all of the temperature dependence of $\chi$ to $\chi_p{}^d$ it appeared worthwhile to see if this remains so at high temperatures as well. Unfortunately neither $\chi(T)$ nor $[d\chi(T)/dT]$ are the same at the one temperature, 20°C, that is common to both the low- and high-temperature measurements. Nevertheless, we have compared our Knight shift results at 373, 465, and 546°K with the $\chi$ results by arbitrarily correcting the less accurate high-temperature data to fit at 20°C; a constant correction of $-4 \times 10^{-6}$ emu/mole was applied to all high-temperature points.

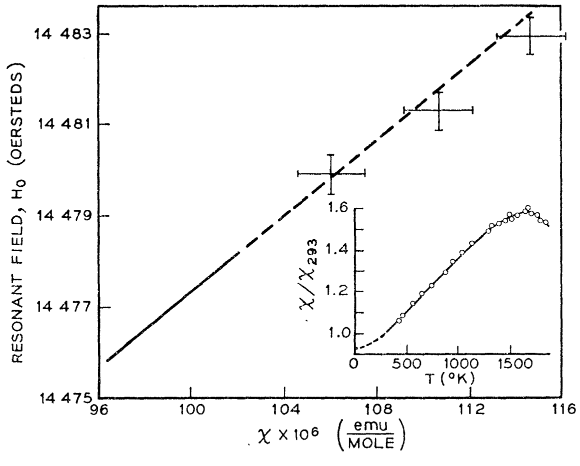

FIG. 6. High-temperature plot of $K$ versus $\chi$ data. The solid line is the low-temperature $K$ versus $\chi$ data reproduced from Fig. 2. The high-temperature susceptibility measurements shown in the inset were made by Kojima and collaborators (see Ref. 15). A constant correction of $-4 \times 10^{-6}$ emu/mole was applied to their data in order to obtain agreement at 290°K with the susceptibility measurements shown in Fig. 1.

The extension of the $K$ versus $\chi$ plot so obtained is shown in Fig. 6. The accuracy in both nmr and susceptibility data is indicated by the error bars. The dotted line is an extension of the low-temperature $K$ versus $\chi$ plot of Fig. 2 and, within the experimental error, fits the observations at elevated temperatures. Thus, we may conclude that essentially all of the variation in $\chi(T)$ below 600°K is of $d$-spin origin.[16]

## V. DISCUSSION

We have utilized the nmr of $Rh^{103}$ in the intermetallic compound $RhSn_2$ to determine the nuclear magnetic moment $\mu^{103}$ and therefore the "zero" of Knight shifts for the following reasons. Solid solutions or intermetallic compounds consisting of almost filled $d$-shell transition metal atoms (Co, Ni, Rh, Pd, Ir, or Pt) that are alloyed with atoms with filled $d$ shells (e.g., Cu, Zn, Al, or Sn) often have small (i.e., free-electron like) paramagnetic susceptibilities. On a crude rigid band model this is to be expected if the number of valence electrons contributed by the filled $d$-shell atoms exceeds the number of $d$ holes of the transition metal atoms, when properly weighted according to the relative proportions of the two types of atoms, since any $d$-like band will be fully occupied in this case. The conduction band will then have only $s$ and/or $p$ character and likewise only an $s$ and/or $p$-like Knight shift. Both $RhSn_2$ and RhSi satisfy this criterion and it is satisfying that their Knight shifts are approximately the same.

On the other hand, $LaRh_2$, $URh_3$, and $ThRh_3$ are quite paramagnetic ($\sim 10^{-4}$ emu/mole) indicating that in these instances the conduction band may have appreciable $d$-like character particularly at the Rh sites. The different Knight shifts observed for each of these intermetallic compounds would then reflect the competition between the negative core polarization and positive orbital contributions to $K$.

Concerning core polarization hyperfine fields, it is interesting to note that in Pd metal and Rh metal the values of $H_{HF}(d)$ differ by a factor of 2. Since little data exists on core polarization fields in metals to date, it is difficult to know whether this result is unusual or not. However, extensive experimental work on the core polarization fields of $3d$-shell paramagnetic ions in nonmetallic crystals generally indicate only a slight variation with atomic number. Perhaps Rh nmr studies of Pd-rich RhPd alloys will determine whether the large difference in $H_{HF}(d)$ in the pure metal is of atomic or band structure origin.

## ACKNOWLEDGMENTS

We wish to thank R. C. Sherwood and H. J. Williams for measuring the susceptibilities of the rhodium intermetallic compounds.

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[15] H. Kojima, R. Tebble, and D. Williams, Proc. Roy. Soc. (London) **A260**, 237 (1961).

[16] M. Shimizu and A. Katsuki, J. Phys. Soc. Japan (to be published). We thank these authors for a preprint of their work.