^{109}Ag Knight-shift versus magnetic-susceptibility relationship in $Pd_{1-x}Ag_x$

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(Received 21 October 1982)

The strong variation with temperature T and silver mole fraction x of the magnetic susceptibility χ of the $Pd_{1-x}Ag_x$ alloy system is interpreted by means of a semiphenomenological function $\chi_{PdAg}(T,x)$ deduced from spin-fluctuation-model and thermodynamic (especially entropic) considerations. The different contributions to χ_{PdAg} are analyzed by relating them to their counterparts in the ^{109}Ag Knight-shift $^{Ag}K_{PdAg}$ via the linear $^{Ag}K_{PdAg}$ vs χ_{PdAg} interrelation with both T and x (on the paramagnetic, Pd-rich side) and with x (on the diamagnetic, Ag-rich side) as implicit parameters.

I. INTRODUCTION

In standard two- (d- and s-) band—model notation, the total paramagnetic susceptibility of pure solid Pd (Ref. 1) can be formulated as

$$\chi_{Pd}=\chi_d(T)+\chi_{orb}+\chi_{dia}+\tfrac{2}{3}\chi_s \; . \tag{1}$$

There, $\chi_d(T)$ is the Stoner-enhanced strongly temperature- (T-) dependent Pauli d-spin part associated with the nearly filled narrow d band. χ_{orb}, χ_{dia}, and $\frac{2}{3}\chi_s$ are the temperature-independent paramagnetic d-band orbital, ion core diamagnetic, and (Landau-corrected) Pauli s-spin contributions, respectively. The total Knight shift of ^{105}Pd in Pd metal[2] reads

$$^{Pd}K=K_d(T)+K_{orb}+K_{dia}+K_s \; , \tag{2}$$

where $K_d(T)$ is the (negative) d-band—induced core polarization contact, K_{orb} the d-band orbital, K_{dia} the differential ion core diamagnetic, and K_s the s-band direct-contact contribution. In term-by-term correspondence to Eq. (1) the shift ^{Pd}K can be rewritten as

$$^{Pd}K=A_d\chi_d(T)+A_{orb}\chi_{orb}+A_{dia}\chi_{dia}+A_s\chi_s \; . \tag{3}$$

The quantities A_i ($i=d$,orb,dia,s) are appropriate hyperfine coupling constants averaged over the Fermi surface and related to the corresponding effective hyperfine fields $B_{\rm eff}^{(i)}$ by

$$A_i=B_{\rm eff}^{(i)}/L\mu_B \; , \tag{4}$$

μ_B is Bohr's magneton and L Avogadro's number with the contributions to χ being used in units of susceptibility per mole. The relationship $^{Pd}K(T)$ vs $\chi_{Pd}(T)$ with T as implicit parameter is linear and a Jaccarino-plot analysis of Eqs. (1)—(3) shows that both $\chi_d(T)$ and $K_d(T)$ are dominating the orbital, diamagnetic, and s-spin contributions which furthermore tend to cancel.[2] Immediately above $T=0$ both $\chi_d(T)$ and $K_d(T)$ vary as $+T^2$ and reach a maximum at about 85 K.[1,2] Beyond its maximum $\chi_d(T)$ smoothly switches from Pauli-Stoner behavior via Curie-Weiss behavior to asymptotic high-temperature Curie behavior $\propto 1/T$. This anomalous temperature variation of $\chi_d(T)$ of Pd has been formulated analytically by a semiphenomenological function within $0\leq T<T_m$ (melting point) and interpreted from the spin-fluctuation (SF) point of view in two previous papers.[3]

In the completely miscible substitutional alloy system $Pd_{1-x}Ag_x$ one observes[4] a rapid decrease with x (silver mole fraction) of the T-dependent magnetic bulk susceptibility

$$\chi_{PdAg}(T,x)=\chi_d(T,x)+\chi_{orb}(x)+\chi_{dia}(x) +\tfrac{2}{3}\chi_s(x) \; . \tag{5}$$

Alloying Pd with small amounts of Ag leads to a reduction of the d-spin susceptibility maximum[5] in the low-temperature isopleths χ_d ($T,x=$const) within $0<x\lesssim 0.06$. The isothermal bulk susceptibility χ_{PdAg} ($\widetilde{T}=$const,x) shows a rapid monotonous decrease with increasing x on the Pd-rich side of $Pd_{1-x}Ag_x$. This strong variation with x predominantly stems from the d-spin part $\chi_d(T,x)$ in Eq. (5) and is caused by Pd d-band filling when magnetic Pd is mixed with nonmagnetic Ag. In previous papers[6,7] our semiphenomenological ansatz[3] for the pure Pd metal case (1) has been extended to the alloy case (5) by using thermodynamic (especially entropic) arguments.

Owing to polarization of the common s band by the nearly filled Pd d band, the Knight shift ^{Ag}K of the ^{109}Ag nuclei in Pd-rich $Pd_{1-x}Ag_x$ alloys[8,9] closely follows the strong variation of χ_{PdAg} upon

Pd d-band filling with increasing Ag content. As a consequence, the Jaccarino plot ${}^{Ag}K(T,x)$ vs $\chi_{PdAg}(T,x)$ with T and/or x as implicit parameters also turns out to be linear.[9] Therefore, the ^{109}Ag nuclei of nonmagnetic silver selectively probe the variation with T and x of the magnetic susceptibility of the nearby Pd atoms in Pd-rich $Pd_{1-x}Ag_x$.

In this paper, the variation (5) with T and x of χ_{PdAg} will be reanalyzed in the light of the linear ${}^{Ag}K$ vs χ_{PdAg} relationship: In Sec. II our semi-phenomenological susceptibility concept[3,6,7] will be justified by theoretical considerations. In Sec. III the conclusions about the change in electronic structure upon alloying Pd with Ag drawn from this concept will be supported and complemented by means of the interrelation between ${}^{Ag}K$ (selective) and χ_{PdAg} (global).

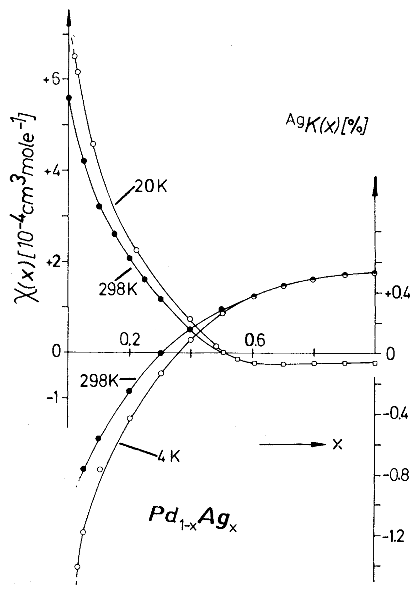

FIG. 1. $Pd_{1-x}Ag_x$ within $0 \leq x \leq 1$. (i) Experimental molar magnetic susceptibility $\chi(x)$ (left-handed scale). Data at 20 K due to Hoare *et al.* (Ref. 4) (open circles) with $\chi(x=0.4)$ being interpolated and due to Abart *et al.* (Ref. 7) (open squares); data at 298 K due to Brill and Voitländer (Ref. 9) (closed circles). (ii) Experimental ^{109}Ag Knight-shift $K(x)$ (right-hand scale). Data at 4 K due to Narath (Ref. 8) (open circles) and data at 298 K due to Brill and Voitländer (Ref. 9) (closed circles).

II. MAGNETIC SUSCEPTIBILITY $\chi(T,x)$ OF $Pd_{1-x}Ag_x$

Adding Ag to Pd rapidly deenhances the total magnetic susceptibility (5) of $Pd_{1-x}Ag_x$. This behavior has been analyzed in Refs. 6 and 7 as follows:

(a) For $x \gtrsim 0.06$ the steep monotonous descent with x of the dominant Pauli-Stoner d-spin susceptibility isotherms χ_d (T=const,x) goes with a monotonous decrease in their spread (T dependence).[6] The isotherms $\chi_d(x)$ intersect[7] at $x=x_0=0.55$, where they reach their lowest T-independent value of $\chi_d(T,x=x_0)=0$.

(b) The paramagnetic d-band orbital part χ_{orb} of Eq. (5) weakly increases with x and then falls off to zero at $x=x^*=0.64$, where the Pd d band is filled.[6]

(c) The ion core diamagnetic part χ_{dia} weakly increases (becomes less negative) with x due to Pd d-band filling up to $x=x^*=0.64$ and then remains independent of x up to $x=1$ (pure silver).[7]

(d) The small paramagnetic Pauli s-spin part χ_s in (5) appears to be constant for $x<x^*=0.64$ (see Refs. 6 and 7 and below) and then weakly increases with x due to common s-band filling[7] up to $x=1$ (pure silver).

(e) Both χ_{dia} and χ_s further show a very weak linear[7] variation with T which can be neglected against the variations (a)—(d) in first approximation. This T dependence is due to a change in the thermal volume expansion with increasing x in Ag-rich $Pd_{1-x}Ag_x$.

A superposition of the two-band—model contributions (a)—(d) mentioned above leads to the total alloy susceptibility[6]

$$\chi_{PdAg}(T,x)=\chi_d(T,x)\Theta(x-x_0)+[\chi_{orb}(x)+\chi_{dia}(x)+\tfrac{2}{3}\chi_s]\Theta(x-x^*)+[\chi_{dia}+\tfrac{2}{3}\chi_s(x)]\Theta(x^*-x) \tag{6}$$

within $0 \leq x \leq 1$. $\Theta(x-y)$ is a step function which equals unity (zero) for x smaller (greater) than y.

By virtue of χ_{dia} (negative) the bulk susceptibility isotherms $\chi_{PdAg}(x)$ cross the x axis at $x \sim 0.5$. Immediately below the x axis they intersect[7] at $x=x_0=0.55$. Beyond x_0 their spread (or variation with T) remains negligibly weak and they bend off to form a shallow minimum χ_{PdAg}^{min} at $x=x^*=0.64$. The pure silver susceptibility at $x=1$ is only slightly less negative than χ_{PdAg}^{min} (cf. Fig. 1).

In the following, starting from the pure Pd case ($x=0$) we will discuss in detail the unusually steep descent with increasing x of the dominant d-spin susceptibility contribution $\chi_d(T,x)$ on the Pd-rich side of $Pd_{1-x}Ag_x$. In particular, further theoretical arguments will be given to justify our semi-phenomenological ansatz[6] for $\chi_d(T,x)$.

A. d-spin susceptibility of pure Pd ($x=0$)

The internal magnetic energy of a model system of N local atomic Pd d-spin moments μ in a configuration with $N/2+m$ spins up and $N/2-m$ spins down (N even, m integer) in a constant magnetic field B is given by

$$U_{\rm mag}(m)=-2m\mu B\ . \tag{7}$$

The number of states with d spin excess $2m$ is

$$g(N,m)=N!/[(N/2)+m]![(N/2)-m]!\ . \tag{8}$$

Expanding the factorials, one obtains for $|m|<N$ the Gaussian distribution[10]

$$g(N,m)\propto \exp(-2m^2/N)\ , \tag{9}$$

and hence the generalized magnetic entropy

$$\begin{aligned} S_{\rm mag}(m)&=k_B \ln g(N,m)\propto -2k_B m^2/N \\ &=-Nk_B(2m\mu)^2/2M_0^2 \end{aligned} \tag{10}$$

(k_B is Boltzmann's constant). There, the square of the fluctuating total paramagnetic Pd d-spin moment $2m\mu$ is scaled to the square of the maximum total moment $M_0=N\mu$.

In our discussion[3] of the anomalous temperature dependence of the enhanced paramagnetic Pd d-spin susceptibility $\chi_d(T)$, we have considered temperature-induced d-spin moment fluctuations (SF) of the Moriya type[11]:

$$\begin{aligned} &M^2(T)=M_\infty^2 f(T)\ , \\ &f(T)=1-(1+S/T_0)\exp(-2ST/T_0)\ . \end{aligned} \tag{11}$$

These SF increase linearly with T as

$$M^2(T)=M_\infty^2(S/T_0)T+\cdots\ , \tag{12}$$

and above the characteristic SF temperature $T_{\rm SF}=T_0/S$ they reach the saturation value of M_∞^2 in the asymptotic high-temperature Curie limit of $T\to\infty$. $S\sim 10$ is the Stoner enhancement factor and $T_0\sim 2900$ K the unrenormalized degeneracy temperature of the Pd d holes.[3] Inserting Eq. (11) into the generalized magnetic entropy function (10) one has

$$S_{\rm mag}(m)\propto -Nk_B(2m\mu)^2/2M_\infty^2 f(T)\ . \tag{13}$$

From the generalized magnetic Helmholtz free energy

$$F_{\rm mag}(m)=U_{\rm mag}(m)-TS_{\rm mag}(m) \tag{14}$$

and the equilbrium (eq) condition $(\partial F/\partial m)_{T,N,B}=0$, one deduces

$$m_{\rm eq}=N\mu f(T)B/2k_BT$$

and (15)

$$F_{\rm mag}(m_{\rm eq})\propto -N\mu^2 f(T)B^2/2k_BT\ ,$$

and hence the isothermal magnetic d-spin susceptibility

$$\begin{aligned} \chi_d(T)&=\left[\frac{-\partial^2 F_{\rm mag}(m_{\rm eq})}{\partial B^2}\right]_{T,N} \\ &=N\mu^2 f(T)/k_BT \\ &=(C/T)[1-(1+S/T_0) \\ &\qquad\times\exp(-2ST/T_0)]\ . \end{aligned} \tag{16}$$

By virtue of $f(T)/T=S/T_0$ at $T=0$, the susceptibility (16) at $T=0$ is enhanced by S,

$$\chi_d(0)=CS/T_0 \tag{17}$$

and remains finite in accordance with the third law. Ansatz (16) interpolates between the low-temperature Pauli-Stoner paramagnon behavior[3,12]

$$\chi_d=\chi_d(0)[1-\tfrac{2}{3}(ST/T_0)^2+\cdots] \tag{18}$$

of itinerant d electrons and asymptotic high-T Curie behavior

$$\chi_d=C/T \tag{19}$$

of localized d spins in pure Pd.[3] In the expression for the Curie constant,

$$\begin{aligned} C&=N\mu^2/k_B=M_\infty^2/Nk_B \\ &=\langle M_\infty^2\rangle/k_B\ . \end{aligned} \tag{20}$$

$\langle M_\infty^2\rangle$ is the mean-square deviation from the fluctuating paramagnetic Pd d-spin net moment $\langle M_\infty\rangle=0$ in the saturation limit $T\to\infty$. From Eq. (16) one recovers the classical dissipation fluctuation theorem[13]

$$N\mu^2 f(T)=\langle M^2(T)\rangle=k_BT\chi_d(T) \tag{21}$$

with the averaged T-dependent fluctuation amplitude $\langle M^2(T)\rangle$ vanishing at $T=0$ for Fermi-liquid behavior and approaching $k_BC=\langle M_\infty^2\rangle$ for local saturation moment behavior at high T.

As has been shown in Ref. 3, the well-known maximum of the low-temperature susceptibility of pure Pd (which is still a matter of debate) can be incorporated separately by adding a phenomenological term $\delta\chi_d(T)$ to the right-hand side (rhs) of Eq. (16) to give

$$\chi_{\rm Pd}(T)=\chi_d(T)+\delta\chi_d(T)\ . \tag{22}$$

$\delta\chi_d(T)$ makes the total d-spin susceptibility $\chi_{\mathrm{Pd}}(T)$ rise as $+T^2$ immediately above $T=0$ and converge to $\chi_d(T)$ after passing through a maximum at ~ 85 K.

In $\mathrm{Pd}_{1-x}\mathrm{Ag}_x$ small amounts ($x \lesssim 0.06$) of silver rapidly suppress[6] $\delta\chi_d(T)$. Therefore, our discussion of the decrease of $\chi_{\mathrm{Pd}}(T)$ with x in $\mathrm{Pd}_{1-x}\mathrm{Ag}_x$ will be confined to that of the term $\chi_d(T)$ in Eq. (22).

B. d-spin susceptibility of $\mathrm{Pd}_{1-x}\mathrm{Ag}_x$

The canonical ensemble partition function for PdAg

$$Q=g(N,N_{\mathrm{Ag}})(f_{\mathrm{Ag}})^{N_{\mathrm{Ag}}}(f_{\mathrm{Pd}})^{N-N_{Ag}} \tag{23}$$

describes the N_{Ag} silver atoms as a lattice gas[14] for which the $N_{\mathrm{Pd}}=N-N_{\mathrm{Ag}}$ palladium atoms provide the sites. The configurational degeneracy factor

$$g(N,N_{\mathrm{Ag}})=N!/N_{\mathrm{Ag}}!(N-N_{\mathrm{Ag}})! \tag{24}$$

denotes the number of ways one can pick up paramagnetic Pd atoms from the crystal containing a total of N atoms (labeled sites) and replace them by N_{Ag} nonmagnetic Ag atoms. The corresponding Gibbs free energy is given by

$$G=-k_BT\ln Q+Nk_BT\ . \tag{25}$$

In Stirling's approximation one has

$$G=Nk_BT[x\ln x+(1-x)\ln(1-x)+x\ln c] + Nk_BT \tag{26}$$

with $x=N_{\mathrm{Ag}}/N$ the silver mole fraction and $c=f_{\mathrm{Pd}}/f_{\mathrm{Ag}}$ the ratio of the intrinsic particle partition function of palladium to that of silver in the alloy. The excess term $x\ln c$ in Eq. (26) describes the deviation from ideal (purely random) mixing ($c=1$). The nonideality parameter $c\neq 1$ can be associated with the change in electronic structure upon alloying Pd with Ag (Refs. 6 and 7) (see below). The ratio

$$r(x)=G/Nk_BT = 1+x\ln x+(1-x)\ln(1-x)+x\ln c \tag{27}$$

gives a measure of the fractional decrease with x in Gibbs free energy per atom in the alloy. The ratio $r(x)$ can be expected to change effectively the degree of randomness in orientation and magnitude of the paramagnetic Pd d-spin moments in PdAg. Therefore, incorporating $r(x)$ into the generalized magnetic entropy (13) and into Eqs. (14) and (15), one has

$$S_{\mathrm{mag}}(m,T,x)\propto -Nk_B(2m\mu)^2/2M_\infty^2 f(T)r(x) \tag{28}$$

and at magnetic equilibrium

$$\begin{aligned} m_{\mathrm{eq}}&=N\mu f(T)r(x)B/2k_BT\ ,\\ F_{\mathrm{mag}}(m_{\mathrm{eq}})&\propto -N\mu^2 f(T)r(x)B^2/2k_BT\ . \end{aligned} \tag{29}$$

Hence, the isothermal magnetic-alloy d-spin susceptibility is

$$\begin{aligned} \chi_d(T,x)&=N\mu^2 f(T)r(x)/k_BT\\ &=\chi_d(T)[1+x\ln x+(1-x)\ln(1-x)+x\ln c] \end{aligned} \tag{30}$$

with $\chi_d(T)$ given by Eq. (16). According to Eq. (30), the T- and x-dependent magnetic d-spin susceptibility $\chi_d(T,x)$ decreases monotonously with x due to randomizing the magnetic Pd d-spin moments by mixing of Pd with nonmagnetic Ag.[6,7]

In Ref. 7 experimental evidence has been given for the susceptibility isotherms χ_d ($T=\mathrm{const},x$) of $\mathrm{Pd}_{1-x}\mathrm{Ag}_x$ to intersect at $x=x_0=0.55$ (cf. Fig. 1), i.e., with Eq. (30) one has

$$1+x_0\ln x_0+(1-x_0)\ln(1-x_0)+x_0\ln c=0\ , \tag{31}$$

which gives $c=0.567$. From Eqs. (29) and (30) one also deduces that magnetochemical equilibrium

$$\left[\frac{\partial F_{\mathrm{mag}}(m_{\mathrm{eq}})}{\partial x}\right]_{T,B}=\ln[cx/(1-x)]=0 \tag{32}$$

is reached at $x=x^*=(1+c)^{-1}=0.64$. There, the bulk susceptibility (6) of $\mathrm{Pd}_{1-x}\mathrm{Ag}_x$ is observed to attain its lowest value[6,7] (cf. Fig. 1).

At detailed equilibrium in $\mathrm{Pd}_{1-x}\mathrm{Ag}_x$ the charge $N_{\mathrm{Ag}}ze$ of N_{Ag} silver atoms (with effective valence z) minus the hole charge $-N_{\mathrm{Pd}}n_he$ of N_{Pd} palladium atoms (with an effective atomic hole number n_h) equals the charge $(N_{\mathrm{Ag}}+N_{\mathrm{Pd}})n_se$ added to the common s band (with an average number n_s per atom of conduction s electrons), i.e.

$$zx+(1-x)n_h=n_s$$

or

$$x(z-n_s)+(1-x)(n_h-n_s)=0 \tag{33}$$

with x the mole fraction of Ag. The lever-rule-like charge neutrality condition (33) reflects the coherent-potential approximation (CPA) of overall zero scattering.[15] Assuming that the valence $z_0=1$ of pure Ag will be altered in PdAg by the intrinsic stability ratio $c=f_{\mathrm{Pd}}/f_{\mathrm{Ag}}$ (see above) to give the effective valence $z=cz_0$, one has with Eq. (33)

$$n_h(x)/n_s=1-cx/(1-x)=n(x;c)\ . \tag{34}$$

Function (34) describes the decrease of the effective number $n_h(x)$ of Pd d-band holes per Pd atom scaled to the effective number

$$n_s = n_h(0) = c z_0 x^* = (1-x^*) z_0 = 0.36 \ . \tag{35}$$

of common s-band electrons per Pd atom[16] with increasing Ag content x in the range $0 < x \leq x^* = 0.64$. At $x = x^*$ one has $n_h(x^*) = 0$ and the d-hole paramagnetism vanishes. Therefore, via Eqs. (33)–(35) the nonideality parameter $c = 0.567$ in the excess entropic term $x \ln c$ of Eq. (30) is related to charge rearrangement and change in electronic band structure of $Pd_{1-x}Ag_x$ within $0 < x \leq x^*$.

As will be shown in the following, the electronic quantities $n(x;c)$ and n_s can further be used to characterize the variation with x of the orbital, core diamagnetic, and s-spin contributions to the alloy susceptibility (6).

C. Orbital, core diamagnetic, and s-spin susceptibility contributions

In pure Pd ($x = 0$) the susceptibility contributions χ_{orb}, χ_{dia}, and $\frac{2}{3}\chi_s$ nearly cancel.[2] Their weak variations with x, which are dominated by the rapid decrease with x of χ_d on the Pd-rich side of $Pd_{1-x}Ag_x$, become vital for $x \gtrsim 0.5$.

(a) In default of more precise knowledge about the x-dependent paramagnetic d-band orbital part $\chi_{\mathrm{orb}}(x)$, we have proposed in Ref. 6 the phenomenological ansatz

$$\begin{aligned}\chi_{\mathrm{orb}}(x) = \chi_{\mathrm{orb}}(0)[(1-x)n(x;c) \\ + (Z/2)x(1-x)n(x;c)] \\ \times \Theta(x - x^*)\end{aligned} \tag{36}$$

with $\chi_{\mathrm{orb}}(0) = +20\times10^{-6}$ cm^3/mole as parameter[2] and $n(x;c)$ given by Eq. (34). The first term on the rhs of Eq. (36) is due to the above-mentioned Pd d-band filling and the second term due to the corresponding change in the effective interaction between Pd atoms and nearest-neighbor Ag atoms ($Z = 12$ for fcc PdAg). According to Eq. (36), $\chi_{\mathrm{orb}}(x)$ weakly increases with x above $\chi_{\mathrm{orb}}(0)$ and then drops to its lowest value zero at $x = x^* = 0.64$.

(b) The weak variation with x of the core diamagnetic susceptibility χ_{dia} in $Pd_{1-x}Ag_x$ has been formulated in Ref. 7 as

$$\begin{aligned}\chi_{\mathrm{dia}}(x) = \{\chi_{\mathrm{dia}}(0)n(x;c) \\ + \chi_{\mathrm{dia}}(1)[1 - n(x;c)]\}\Theta(x - x^*) \\ + \chi_{\mathrm{dia}}(1)\Theta(x^* - x)\end{aligned} \tag{37}$$

with $n(x;c)$ given by Eq. (34) and $\chi_{\mathrm{dia}}(0) = -34\times10^{-6}$ cm^3/mole, $\chi_{\mathrm{dia}}(1) = -27\times10^{-6}$ cm^3/mole as parameters.[17] The term in { } accounts for the change from $\chi_{\mathrm{dia}}(0)$ into $\chi_{\mathrm{dia}}(1)$ due to the fractional decrease $n(x;c) = n_h(x)/n_s \rightarrow 0$ of the effective number of Pd d-band holes within $0 < x \leq x^* = 0.64$ (Pd-d filling upon alloying with Ag with the effective number n_s of common s-band electrons taken to be constant[7,18]).

(c) The weak variation with x of the s-spin susceptibility χ_s in $Pd_{1-x}Ag_x$ has been formulated in Ref. 7 as

$$\begin{aligned}\chi_s(x) = \chi_s(0)\Theta(x - x^*) \\ + \{\chi_s(0)(z_0/n_s)(1-x) \\ + \chi_s(1)[1 - (z_0/n_s)(1-x)]\} \\ \times \Theta(x^* - x)\end{aligned} \tag{38}$$

with n_s given by Eq. (35) and $\chi_s(0) = 8\times10^{-6}$ cm^3/mole, $\chi_s(1) = 12\times10^{-6}$ cm^3/mole as parameters.[19] The term in { } describes the change from $\chi_s(0)$ into $\chi_s(1)$ upon the fractional increase $1 - (z_0/n_s)(1-x) \rightarrow 1$ of the effective number of s band electrons within $x^* < x \leq 1$ (common s-band filling upon alloying with Ag after the Pd d band has been filled[7,18]).

According to this analysis, in $Pd_{1-x}Ag_x$ the variation with x of all susceptibility contributions χ_d, χ_{orb}, χ_{dia}, and χ_s is influenced by changes in electronic structure. These are scaled to n_s, the effective number of common s-band electrons. The basic assumption made about n_s is its constancy (corresponding to no s-band–d-band electron charge transfer) upon Pd d-band filling for $x < x^* = 0.64$.

In the following, our semiphenomenological susceptibility function $\chi_{\mathrm{PdAg}}(T,x)$ shall further be analyzed in conjunction with the ^{109}Ag Knight shift[8,9] $^{\mathrm{Ag}}K(T,x)$ in $Pd_{1-x}Ag_x$ because K probing s-electron charge-transfer effects can serve as a test for the above assumption.

III. $^{\mathrm{Ag}}K(T,x)$ vs $\chi_{\mathrm{PdAg}}(T,x)$ RELATIONSHIP

A. Pd-rich PdAg alloys

The anomalously strong variation with T and x of the total magnetic susceptibility of $Pd_{1-x}Ag_x$ on the paramagnetic Pd-rich side has been discussed above as being mainly due to randomizing of Pd d-spin moments combined with Pd d-band filling. For $x < x^* = 0.64$ the common s band is polarized magnetically by the nearly filled Pd d band.[8,9] Therefore, the ^{109}Ag nuclei of nonmagnetic silver can serve as a selective NMR probe of the neighboring magnetic Pd atoms: The ^{109}Ag Knight shift $^{\mathrm{Ag}}K(T,x)$ can be expected to monitor the T- and x-dependent Pd d-band susceptibility part as well as the common s-band part. The core diamagnetic susceptibility contribution can be omitted because the ^{109}Ag NMR is observed relative to $AgNO_3$ as diamagnetic standard.[8,9]

On the paramagnetic side, a plot of the experimental $^{Ag}K(T,x)$ data at 4 K (Ref. 8) and 298 K (Ref. 9) versus the dominant d-spin part $\chi_d(T,x)$ [see Eq. (30)], up to $x=x_0=0.55$ with both T and x as implicit parameters gives the strongly linear relationship (cf. Fig. 2),

$$^{Ag}K_{\text{expt}}(T,x)=a\chi_d(T,x)+b \tag{39}$$

with $a=-2790$ mole %/cm^3 and $b=+0.35\%$. By extrapolating $T\rightarrow 0$ and $x\rightarrow 0$, one has $\chi_d(0,0)=717\times10^{-6}$ cm^3/mole [see Eq. (17) and Ref. 3] and

$$^{Ag}K_{\text{expt}}(0,0)=-1.65\% \ , \tag{40}$$

as well as the net silver hyperfine field in units of tesla (T),

$$\begin{aligned} B_{\text{net}} &= {}^{Ag}K_{\text{expt}}(0,0)L\mu_B/100\chi_d(0,0) \\ &= -12.9 \text{ T} \end{aligned} \tag{41}$$

for infinite dilution of Ag in Pd. The latter value is comparable with the corresponding values of -12.1 T and -13.9 T in AgPt (Ref. 20) and ferromagnetic AgNi,[21] respectively. With the net hyperfine coupling constant $A_{\text{net}}=B_{\text{net}}/L\mu_B$ of the ^{109}Ag nuclei being almost constant, the different extrapolated values of $^{Ag}K_{\text{expt}}(0,0)$ mainly stem from different Pd, Pt, and Ni host susceptibilities $\chi_d(0,0)$.

The rhs of Eq. (39) is the sum of a negative (T,x)-dependent and a positive constant term. The

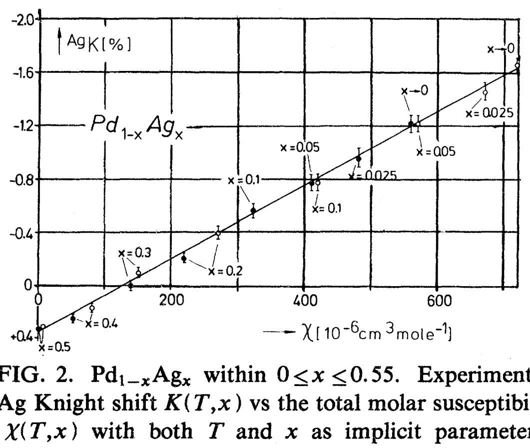

FIG. 2. $Pd_{1-x}Ag_x$ within $0\le x\le 0.55$. Experimental ^{109}Ag Knight shift $K(T,x)$ vs the total molar susceptibility $\chi(T,x)$ with both T and x as implicit parameters. Closed circles: $K(x)$ and $\chi(x)$ data at 298 K due to Brill and Voitländer (Ref. 9). Open circles: $K(x)$ data at 4 K due to Narath (Ref. 8) and $\chi(x)$ data at 4 K interpolated from the work of Hoare *et al.* (Ref. 4). Full line: Theoretical $K(T,x)$ vs a $\chi_d(T,x)+b$ plot (see text) with the dominant d-spin contribution $\chi_d(T,x)$ to $\chi(T,x)$ given by Eq. (30).

former closely follows the strong monotonous variation with x of the Pd host d-spin susceptibility isotherms χ_d $(T=\text{const},x)$ and the decrease in their spread (variation with T) up to their intersection at $x=x_0=0.55$. Within experimental error the T dependence of both magnetic d-spin susceptibility and Ag Knight-shift in $Pd_{1-x}Ag_x$ vanishes[9] at $x=x_0$ (cf. Fig. 1). Therefore, one may attribute $a\chi_d(T,x)$ in Eq. (39) to the Pd d-band–induced[8,9] spin-polarization silver NMR shift $^{Ag}K_d(T,x)$ according to

$$\begin{aligned} a\chi_d(T,x) &= {}^{Ag}K_d(T,x) \\ &= {}^{Ag}K_d(0,0)\chi_d(T,x)/\chi_d(0,0) \\ &= A_d\chi_d(T,x)100(\%) \ . \end{aligned} \tag{42}$$

With the effective d-spin hyperfine coupling constant

$$\begin{aligned} A_d &= a/100 = {}^{Ag}K_d(0,0)/100\chi_d(0,0) \\ &= -27.9 \end{aligned}$$

in units of mole/cm^3 (χ_d in units of cm^3/mole), one deduces the corresponding effective d-spin hyperfine field $B^d_{\text{eff}}=A_dL\mu_B=-15.6$ T and in the limit $T\rightarrow 0$, $x\rightarrow 0$ the silver d shift $^{Ag}K_d(0,0)=-2\%$.

The constant contribution of $b=+0.35\%$ to the total ^{109}Ag NMR shift (39) can readily be related to the s shift, i.e.,

$$b={}^{Ag}K_s=A_s\chi_s(0)100=0.35\% \ . \tag{43}$$

With $\chi_s(0)=8\times10^{-6}$ cm^3/mole (Ref. 19) one has $A_s=438$ mole/cm^3 corresponding to $B^s_{\text{eff}}=245$ T on the paramagnetic Pd-rich side of $Pd_{1-x}Ag_x$. Narath[8] estimated $^{Ag}K_s=0.34\%$ for $x\rightarrow 0$ via the measured low-temperature ^{109}Ag nuclear spin-lattice s contact relaxation rate $(^{Ag}T_{1,s})^{-1}$ and the Korringa relation. According to Eq. (39), $b={}^{Ag}K_s$ remains constant with increasing silver mole fraction x. This indicates that the effective number n_s of common s-band electrons does not change upon the Pd d-band filling up to $x\sim x^*=0.64$. Therefore, our basic assumption $n_s=\text{const}$ within $0<x<x^*$ involved in the electronic function (34) is justified by the ^{109}Ag Knight-shift data which essentially rule out s-band–d-band electron charge transfer in accordance with CPA calculations[18] on $Pd_{1-x}Ag_x$.

Our analysis (cf. Fig. 2) indicates that the change in sign ($-$ to $+$) of the experimental silver NMR shift $^{Ag}K_{\text{expt}}(T)$ at $x=0.36$ $(T\rightarrow 0)$ (Ref. 8) and at $x\rightarrow 0.3$ $(T=298$ K) (Ref. 9) (cf. Fig. 1) is due to the constant positive contribution $^{Ag}K_s=0.35\%$ only. The linear $^{Ag}K_{\text{expt}}$ vs χ_{PdAg} relationship (39) excludes the small weakly x-dependent d-band orbital susceptibility contribution; see Eq. (36). This is in accordance with the previous partitioning of $^{Ag}K_{expt}$ into s- and d-spin contributions and neglecting orbital and differential ion diamagnetic effects.[8,9]

B. Ag-rich PdAg alloys

On the Ag-rich side of $Pd_{1-x}Ag_x$ beyond $x=x_0=0.55$ the silver Knight-shift $^{Ag}K_{expt}$ shows no T-dependence within experimental error.[9] It only increases weakly with x from $x=x^*=0.64$ up to the pure silver value[8] of $^{Ag}K_{expt}(x=1)=+0.52\%$ (cf. Fig. 1). $^{Ag}K_{expt}(x)$ can readily be identified with an x-dependent s shift and related to the s-spin susceptibility part $\chi_s(x)$: On the Ag-rich side of $Pd_{1-x}Ag_x$ the shift $^{Ag}K_{expt}(x)$ monitors the weak increase with x of $\chi_s(x)$ due to common s-band filling; see Eq. (38). The plot of $^{Ag}K_{expt}(x)$ vs $\chi_s(x)$ with x as implicit parameter is linear within $x^* < x \leq 1$ (cf. Fig. 3):

$$^{Ag}K_{expt}(x) = {}^{Ag}K_s(x) = a\chi_s(x) + b\,(\%)\ . \qquad (44)$$

There,

$$\chi_s(x) = [\chi_s(1) - \chi_s(0)](z_0/n_s)x + \text{const} \qquad (45)$$

[see Eq. (38)], and $a = 28\times 10^3$ mole%/cm^3, $b = 0.19\%$. Following the treatment of Froidevaux,[22] from

$$\chi_s(x) = (1-x)\chi_s^{Pd} + x\chi_s^{Ag}$$

and (46)

$$^{Ag}K_s(x) = [{}^{Ag}K_s(1)/\chi_s(1)]\chi_s^{Ag}(x)\ ,$$

one finds with (44) in the dilute limit of $x \to 1$:

$$\chi_s^{Pd}(x\to 1) = \lim_{x\to 1}\{\chi_s(1) + [d\,{}^{Ag}K_s(x)/dx][\chi_s(1)/{}^{Ag}K_s(1)] - [d\chi_s(x)/dx]\}$$
$$= \chi_s(1) + (z_0/n_s)[\chi_s(1) - \chi_s(0)]\{[a\chi_s(1)/{}^{Ag}K_s(1)] - 1\}\ . \qquad (47)$$

Equation (47) yields $\chi_s^{Pd}(x\to 1) = 0.67\chi_s(1) \sim 8\times 10^{-6}$ cm^3/mole which agrees with the value of the s-spin susceptibility $\chi_s(0)$ of pure Pd.[19] The fact that $\chi_s^{Pd}(x\to 1) \sim \chi_s(0)$ also confirms the aforementioned no s-electron charge-transfer concept.

In the limit $x\to 1$ of pure silver one further deduces with $^{Ag}K_{expt}(1) = 0.52\%$ and $\chi_s(1) = 12\times 10^{-6}$ cm^3/mole (Ref. 19) the effective hyperfine field

$$B_{eff} = {}^{Ag}K_{expt}(1)L\mu_B/100\chi_s(1) = 242 \qquad (48)$$

in units of tesla. This value is comparable with the corresponding value of 245 T obtained above from the constant s-band Knight-shift contribution (43) on the Pd-rich side of $Pd_{1-x}Ag_x$.

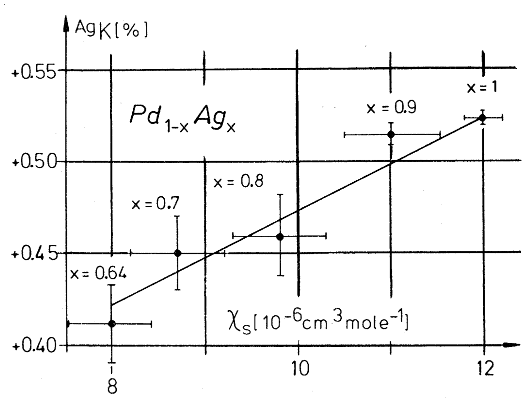

FIG. 3. $Pd_{1-x}Ag_x$ within $0.64 \leq x \leq 1$. Experimental ^{109}Ag Knight shift vs the s-spin contribution $\chi_s(x)$ to the total molar magnetic susceptibility $\chi(x)$ with x as implicit parameter. Closed circles: $K(x)$ data at 4 K due to Narath (Ref. 8) with $K(x=0.64)$ being interpolated. $\chi_s(x)$ data from $\chi_s(x) = \frac{3}{2}[\chi(x) - \chi_{dia}]$ with $\chi_{dia} = \text{const} = -27\times 10^{-6}$ cm^3/mole (see text) and $\chi(x)$ measured at low temperatures by Abart *et al.* (Ref. 7). Full line: Theoretical $K(x)$ vs a $\chi_s(x)+b$ plot (see text) with $\chi_s(x)$ given by Eq. (38).

C. Additional remarks

Our result of unravelling the d- and s-spin contributions to $^{Ag}K(T,x)$ and $\chi_{PdAg}(T,x)$ via linear K vs χ Jaccarino plot analysis qualitatively differs from a previous study of Brill and Voitländer.[9] They found another linear relationship between

$$^{Ag}K_{expt}(T,x) - {}^{Ag}K_s(x) \sim {}^{Ag}K_d(T,x)$$

and (49)

$$\chi_{expt}^{PdAg}(T,x) \sim \chi_d(T,x)\ .$$

There, the T-independent direct-s contact Knight-shift

$$^{Ag}K_s(x) = {}^{Ag}K_s(1)[n_s(x)/n_s(1)]^{1/3} \qquad (50)$$

results from scaling the pure silver shift $^{Ag}K_s(1) = 0.52\%$ with the average number $n_s(x)$ of common parabolic s-band electrons.[9] In Eq. (50) the weak x dependence is taken to be linear, i.e.,

$$n_s(x) = \begin{cases} 0.36 + 0.4x, & 0 \leq x \leq 0.6 \\ x, & 0.6 \leq x \leq 1\ . \end{cases} \qquad (51)$$

Ansatz (51) simply accounts for the model of Dugdale and Guénault.[23] These authors assumed that Pd acts on alloying like having 0.6 d holes due to a linear rigid s-band shift downwards relative to a rigid d band in $Pd_{1-x}Ag_x$ so as to make $n_s(0)=0.36$ d holes for pure Pd (Ref. 16) and 0.6 d holes for $x=0.6$, where the Pd d band is expected to be filled. The ${}^{\mathrm{Ag}}K_s(x)$ analysis [(50 and (51)] of Brill and Voitländer[9] is in contradiction to no–charge-transfer concepts for PdAg (Refs. 18 and 24) which imply a constant number of s electrons at the Ag sites and hence ${}^{\mathrm{Ag}}K_s=\mathrm{const}$ on the Pd-rich side. The K vs χ study presented favors the no–charge-transfer point of view and yields

$$\begin{aligned} &{}^{\mathrm{Ag}}K_s=\mathrm{const}\;, \\ &{}^{\mathrm{Ag}}K_d(T,x)={}^{\mathrm{Ag}}K_d(0,0)\chi_d(T,x)/\chi_d(0,0)\;, \end{aligned} \tag{52}$$

on the Pd-rich side [see Eqs. (42) and (43)]. According to Eq. (52) the d-electron polarization-induced solute shift ${}^{\mathrm{Ag}}K_d(0,0)=-2\%$ is simply scaled with the alloy susceptibility d-spin part $\chi_d(T,x)$ within $0<T\leq 298$ K for $x<x^*=0.64$. On the Ag-rich side we have

$$ {}^{\mathrm{Ag}}K_{\mathrm{expt}}(x)\propto\chi_s(x)/\chi_s(1) \tag{53}$$

due to common s-band filling [see Eq. (44)]. Besides $\chi_d(T,x)$ and $\chi_s(x)$ discussed in Sec. II, no further assumptions like (49)–(51) are needed.

D. Comments on the thus far unobserved ^{105}Pd Knight-shift in $Pd_{1-x}Ag_x$

According to Eq. (39) in $Pd_{1-x}Ag_x$ the variation with x of the silver NMR shift ${}^{\mathrm{Ag}}K(x)$ (selective average) is proportional to that of the magnetic susceptibility $\chi_{\mathrm{PdAg}}(x)$ which is an average over the bulk. Therefore, χ_{PdAg} does not seem to exhibit appreciable local variations, i.e., the selective (partial) susceptibility averages (over Pd atoms and Ag atoms, respectively) essentially do not differ in the case of $Pd_{1-x}Ag_x$. From similar arguments Froidevaux[22] has inferred the absence of local susceptibility variations in the system $Pt_{1-x}Au_x$. The apparently homogeneous bulk susceptibility of $Pd_{1-x}Ag_x$ further implies that the ^{109}Ag NMR shift and the still unobserved ^{105}Pd NMR shift in $Pd_{1-x}Ag_x$ will show qualitatively the same variation with increasing x, i.e., a steep monotonous ascent leading from negative to positive values on the Pd-rich side (cf. Fig. 1). The observation of NMR on ^{105}Pd [nuclear spin $I=\frac{5}{2}$) in PdAg possibly is rendered difficult by nuclear electrical quadrupole moment effects $Q({}^{105}\mathrm{Pd})=0.8$ barns[25]]. As already mentioned (Sec. I), in pure Pd metal the strong variation with T of the positive enhanced d-spin susceptibility $\chi_d(T)$ [see Eq. (16)] is monitored by the negative d-spin–induced core polarization ^{105}Pd Knight shift ${}^{\mathrm{Pd}}K_d(T)$.[2] Therefore, in $Pd_{1-x}Ag_x$ the strong variation with both T and x of the predominant paramagnetic d-spin alloy susceptibility part $\chi_d(T,x)$ [see Eq. (30)] should also be tracked by the ^{105}Pd NMR shift ${}^{\mathrm{Pd}}K_d(T,x)$. In detail, one may assume the dominant core polarization contribution ${}^{\mathrm{Pd}}K_d(0,0)$ to be scaled with $\chi_d(T,x)$ to give

$$ {}^{\mathrm{Pd}}K_d(T,x)={}^{\mathrm{Pd}}K_d(0,0)\chi_d(T,x)/\chi_d(0,0) \tag{54}$$

in analogy to Eq. (52). Krieger and Voitländer[26] have calculated ${}^{\mathrm{Pd}}K_d(0,0)=-3.88\%$ employing the moment perturbation treatment of Das *et al.*[27] and the Korringa-Kohn-Rostoker (KKR) method. In the extrapolation limit $T\rightarrow 0$, $x\rightarrow 0$, from Eq. (54) one deduces

$$\begin{aligned} d\,{}^{\mathrm{Pd}}K_d/d\chi_d&=K_d^{\mathrm{Pd}}(0,0)/\chi_d(0,0) \\ &=(B_{\mathrm{eff}}^{d}/L\mu_B)100 \end{aligned}$$

and hence the effective Pd d-spin hyperfine field $B_{\mathrm{eff}}^{d}=-30T$ consistent with the estimate from Jaccarino-plot analysis on pure Pd with T as implicit parameter.[2] One may further assume that the ^{105}Pd nulcei in $Pd_{1-x}Ag_x$ will also undergo a d-band orbital NMR shift

$$ {}^{\mathrm{Pd}}K_{\mathrm{orb}}(x)={}^{\mathrm{Pd}}K_{\mathrm{orb}}(0)\chi_{\mathrm{orb}}(x)/\chi_{\mathrm{orb}}(0)\;, \tag{55}$$

tracking the weakly x-dependent orbital susceptibility part $\chi_{\mathrm{orb}}(x)$ given by Eq. (36) (cf. Sec. II). The orbital shift ${}^{\mathrm{Pd}}K_{\mathrm{orb}}(0)$ of pure Pd has been estimated[2] to be $+0.36\%$ corresponding to an effective orbital hyperfine field $B_{\mathrm{eff}}^{\mathrm{orb}}=+100T$ with $\chi_{\mathrm{orb}}(0)=+20\times10^{-6}$ cm^3/mole.

Finally, applying the no s-electron charge-transfer concept to the s-band part ${}^{\mathrm{Pd}}K_s$ of the ^{105}Pd NMR shift, one has

$$ {}^{\mathrm{Pd}}K_s=\mathrm{const}\;, \tag{56}$$

i.e., upon Pd d-band filling (on the Pd-rich side) as well as upon common s-band filling (on the Ag-rich side) the direct s contact shift ${}^{\mathrm{Pd}}K_s$ is expected to retain its pure Pd value ${}^{\mathrm{Pd}}K_s=0.18\%$ (as calculated by Krieger and Voitländer[26]).

Measurements of

$$ {}^{\mathrm{Pd}}K(T,x)={}^{\mathrm{Pd}}K_d(T,x)+{}^{\mathrm{Pd}}K_{\mathrm{orb}}(x)+{}^{\mathrm{Pd}}K_s $$

on $Pd_{1-x}Ag_x$ being lacking, magnetic investigations on the system $Pt_{1-x}Ag_x$ with both nulcei ^{109}Ag and ^{195}Pt ($I=\frac{1}{2}$) observable by NMR are useful for the sake of comparison. The low-temperature magnetic bulk susceptibility $\chi_{\mathrm{PtAg}}(x)$ of metastable $Pt_{1-x}Ag_x$ alloys[20] qualitatively shows the same variation with

x as that of $Pd_{1-x}Ag_x$, and both experimental NMR shifts $^{Ag}K_{expt}(x)$ and $^{Pt}K_{expt}(x)$ apparently track $\chi_{PtAg}(x)$. These observations on PtAg may confirm the assumptions (54)–(56) concerning the ^{105}Pd shift still to be observed in $Pd_{1-x}Ag_x$.

ACKNOWLEDGMENT

The authors are indebted to K. H. Bennemann for helpful comments.

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