Magnetic ordering in exchange-enhanced $(Pd_{1-y}Ag_y)_{100-x}Fe_x$ and $(Pd_{1-y}Rh_y)_{100-x}Fe_x$ alloys

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Magnetization measurements are reported for several $Pd_{1-y}Ag_y$ and $Pd_{1-y}Rh_y$ host alloys doped with $x = 0.5$-, 1.0-, and 2.0-at.% Fe to form $(Pd_{1-y}Ag_y)_{100-x}Fe_x$ (where $0 \leq y \leq 0.50$) and $(Pd_{1-y}Rh_y)_{100-x}Fe_x$ (where $0 \leq y \leq 0.75$). The experiments were carried out with a vibrating-sample magnetometer at temperatures ranging from 3 °K to room temperature and for fields up to 20 kOe. The dependences of the paramagnetic susceptibility, effective magnetic moment, and magnetic-ordering temperature on the Fe concentration and host matrix susceptibility (and, consequently, the electronic structure) were explored and the results provide some support for the existing molecular-field theories that describe the region of ferromagnetic ordering in exchange enhanced alloys. From the observed linear dependence of the ordering temperature on the host-matrix susceptibility and the saturation moment per Fe atom, values were obtained for the molecular-field coefficient (describing the localized moment to Pd $4d$-electron interaction), α, and the exchange-interaction constant, J. For the $(Pd_{1-y}Ag_y)_{100-x}Fe_x$ system, we find $\alpha = 1.1 \times 10^3$ mole/emu and $J = 0.071$ eV, while for $(Pd_{1-y}Rh_y)_{100-x}Fe_x$, $\alpha = 1.3 \times 10^3$ mole/emu and $J = 0.084$ eV.

I. INTRODUCTION

Alloys involving dilute additions of transition-metal elements to metallic hosts have been the subject of considerable research activity for many years.[1] The principal motivation for studying such systems is to understand the detailed nature of magnetic ordering in metals. In this problem, a primary consideration is whether or not a localized moment is sustained on the transition-metal impurity. Friedel[2] has proposed a criterion whereby a localized moment will exist if the Fermi energy of the host is low enough such that the d-states of the transition-metal atoms lie in the vicinity of the Fermi energy. In the picture suggested by Anderson,[3] the criterion for local-magnetic-moment occurrence is based on a Coulomb repulsive energy between electrons in a spin-up and spin-down d-state (Coulomb correlation integral), and the density of states. A good discussion of the Friedel[2] and Anderson[3] models, as well as recent advances in describing the formation of localized moments, is given in Refs. 4 and 5. A second consideration is the degree to which the host is spin polarized by the localized moment. The nature of the host response will depend on whether it is (i) a simple metal, (ii) a transition metal with no significant exchange enhancement, or (iii) a transition metal with significant exchange enhancement. A good discussion of the various host responses is given in Ref. 6. Finally, a third consideration is the existence and nature of possible magnetic ordering involving both the localized moments and the matrix response. The nature of the ordering can range from ferromagnetic to spin-glass (see Ref. 6).

A classical example of a system involving ferromagnetic ordering of localized moments in an exchange-enhanced host is the dilute solutions of Fe in Pd and Pd-rich alloys.[7-9] Originally, the magnetic behavior of such systems was explained as follows. The spin magnetic moment of a central Fe atom polarizes and couples with moments of the *nearest-neighbor* Pd atoms, forming a "giant moment." If these giant moments then interact with each other, ferromagnetism could occur.[10,11] However, there are serious problems with such a picture. For example, the observed paramagnetic susceptibility does not obey the Curie-Weiss law above the ordering temperature. Some phenomenological models have been proposed that involve corrections to the effective magnetic moment per Fe atom that depend on the temperature-dependent susceptibility of the host.[9,12] Such models still fail at high temperature. There is now, however, clear evidence to indicate that the giant moment arises from the polarization of a large number of Pd neighbors (perhaps as many as 100) by a single Fe atom. Neutron scattering measurements confirm the existence of a *long-range* Pd polarization.[13] Even at relatively low Fe concentrations (~0.5 at.%), the average Fe-Fe distance is probably somewhat smaller than or comparable to the range of Pd

matrix polarization. The exhange interaction responsible for the Pd matrix polarization is strongly enhanced and expected to be essentially of one sign (at least for the d-band holes). Thus it should not show large oscillations of the Ruderman-Kittel-Yosida type, such as might be expected in the conduction-electron polarization for simple metals. It was originally argued by Abrikosov and Gor'kov[14] that the polarization of the Pd $4d$-electrons does not localize at the position of the dissolved Fe. Instead, they suggest that a uniform polarization of the Pd $4d$-electrons must be considered in a band or itinerant picture.

Three theoretical models based on a localized magnetic moment for the dissolved atom and a polarization of the host $4d$-band have been developed.[15-17] Of particular interest is the theoretical work by Takahashi and Shimizu[15] in which they assume (i) a simple rigid-band model for the $4d$-electrons, (ii) the direct interaction between the dissolved atoms can be neglected for small concentrations ($\lesssim 1$ at.%), (iii) the magnetic moments of the dissolved atoms are localized on them, (iv) the polarization of the $4d$-band is spatially uniform, and (v) the interactions among the $4d$-electrons as well as between the $4d$-electrons and the localized moment are independent of the concentration of the dissolved atoms and the composition of the host. With regard to (v) above, Takahashi and Shimizu[15] introduce constant values for the molecular-field coefficients to describe (a) the localized moment to $4d$-electron interaction and (b) the $4d$-electron to $4d$-electron interaction (α and γ, respectively, in their paper). They obtain expressions for the paramagnetic susceptibility, effective magnetic moment, and magnetic-ordering temperature in terms of the host electronic structure (density of states), impurity concentration, and molecular-field coefficients. Direct relationships are established with the host-matrix susceptibility. Comparison of their theory with existing magnetization data on Pd containing various concentrations of Fe and Co impurities shows good agreement.[7,8,10,11] Although some magnetization[9,18-20] and Mössbauer[21] data are available on Pd-rich alloys, no extensive study has been undertaken to determine the dependence of the susceptibility, effective moment, and ordering temperature on the host susceptibility and impurity concentration. Since the enhanced susceptibility of Pd can be decreased and eventually suppressed by alloying with Rh and Ag (neighboring elements of Pd in the $4d$ series), such systems provide us with an excellent opportunity to study how the behavior of ferromagnetic ordering in exchange-enhanced hosts depends on the host electronic structure. A recent paper by Nieuwenhuys[22] reviews in a critical fashion a large variety of experimental data on the alloys of Co, Fe, and Mn dissolved in Pd.

In this paper, we explore in detail the dependences of the paramagnetic susceptibility, effective magnetic moment, and magnetic-ordering temperature on the impurity concentration and host-matrix susceptibility (and, consequently, the electronic structure) by studying several $Pd_{1-y}Ag_y$ and $Pd_{1-y}Rh_y$ host alloys doped with 0.5-, 1.0-, and 2.0-at.% Fe form $(Pd_{1-y}Ag_y)_{100-x}Fe_x$ and $(Pd_{1-y}Rh_y)_{100-x}Fe_x$. This represents an extension of some early and preliminary work by Cannella *et al.*[18,19] in which the low-field ac susceptibility of a series of $Pd_{1-y}Ag_y$ alloys containing Fe showed a clear region of ferromagnetic behavior with a transition to a spin-glass-like behavior when the host-matrix susceptibility was appreciably reduced. We are able to make some comparisons favorable to the theory of Takahashi and Shimizu,[15] as well as calculate values for the molecular-field coefficient, spin quantum number, and exchange-interaction constant.

It should be noted that the other two molecular-field treatments[16,17] for ferromagnetic ordering in exchange-enhanced alloys yield results similar to the Takahashi-Shimizu[15] theory. Kim[16] introduces a new repulsive exchange-type interaction between conduction electrons which is mediated by the flipping motion of localized spins. He attributes the ferromagnetism observed in Pd-rich alloys containing Fe impurities to ferromagnetism of the host-metal conduction electrons. Doniach and Wolfarth[17] treat the polarization induced in the Pd d-band due to the local moments by using a linear-response approximation. In this way, they obtain the same results as Takahashi and Shimizu[15] without the need for assuming a spatially uniform host $4d$-band polarization and a rigid-band model.

II. EXPERIMENTAL

A. Sample preparation

Pure Pd (99.995%), Ag (99.999%), Rh (99.995%), and Fe (99.999%) were mixed in the appropriate proportions to make the $(Pd_{1-y}Ag_y)_{100-x}Fe_x$ and $(Pd_{1-y}Rh_y)_{100-x}Fe_x$ alloys. The various compositions studied, along with the magnetic data to be described later, are listed in Tables I–IV. (Since the Fe concentrations are small, ≤ 2 at.%, ingots were initially made with higher Fe content and then diluted.) The constituents were melted together in an argon arc furnace and remelted several times to ensure homogeneity. The ingots were cut and ground into spheres of approximately 0.2 g. The spheres were sealed in quartz tubes under a helium atmosphere and annealed at 1000 °C for

48 h. The tubes were subsequently quenched into room-temperature (RT) water.

B. Magnetic measurements

All measurements of the bulk magnetization σ and magnetic-ordering temperature T_c were carried out on a P.A.R. Model 155 vibrating-sample magnetometer (Foner method[23]). Temperatures ranging continuously from 3 °K to room temperature were obtained with the related cryogenic accessories, while magnetic fields were available up to 20 kOe. The magnetometer was calibrated against the known saturation magnetization for Ni (room-temperature value of 55.01 emu/g). The temperature calibration was based on the ideal Curie-Weiss behavior of the paramagnetic salt $Gd_2(SO_4)_3 \cdot 8H_2O$.

C. Other measurements

X-ray analysis demonstrated that similarly prepared samples were single phase and had lattice parameters consistent with the nominal compositions of the alloys. Portions from some of the original ingots were drawn into wires and annealed as described above. The temperature dependences of the electrical resistivities were measured for the wires, and preliminary results have been published elsewhere.[24]

As indicated in Sec. I, the present work is an extension of some early preliminary work carried out by a low-field (~ 5 Oe) ac mutual inductance technique.[18,19] However, all of the vibrating-sample magnetometer data presented in Sec. III were obtained from samples newly constructed by the procedure described above. For comparison, several of the samples used in the earlier work were reexamined with the vibrating-sample magnetometer.

D. Host susceptibility

In order to make quantitative comparisons between existing theories and our measurements, reliable values for the host-matrix susceptibility χ_0 are required. Such data are available in the literature for pure Pd (Hoare and Matthews[25]) $Pd_{1-y}Ag_y$ alloys (Hoare, Matthews, and Walling[26] and Doclo, Foner, and Narath[27]), and $Pd_{1-y}Rh_y$ alloys (Budworth, Hoare, and Preston[28], Manuel and St. Quinton,[29] and Doclo, Foner, and Narath[27]). Detailed tabulations are given that provide both the composition and temperature dependences. Simple interpolation or extrapolation was used to evaluate the host susceptibility at a temperature T for a particular alloy, $\chi_0(T)$. At the lowest temperature, some of the published $Pd_{1-y}Ag_y$ host susceptibility data exhibit a slight increase which is apparently caused by small amounts of Fe impurity in the starting Pd material.[26] By suitable extrapolation, we were able to make the necessary correction. This difficulty was realized by Manuel and St. Quinton,[29] and their $Pd_{1-y}Rh_y$ data need no such correction.

III. RESULTS AND ANALYSIS

A. $(Pd_{1-y}Ag_y)_{100-x}Fe_x$ alloys

1. Magnetic-ordering temperature

Measurements of the magnetic-ordering temperature for the $(Pd_{1-y}Ag_y)_{100-x}Fe_x$ alloys were made with the vibrating-sample magnetometer by observing the bulk sample magnetic moment as a function of temperature for small magnetic fields (~ 40 and 80 Oe). Samples with a spin-glass type of ordering possessed the characteristic "cusp," while ferromagnetically ordered samples exhibited a sharp "step" at the transition temperature. Figure 1 shows the observed ordering temperature T_c as a function of the host susceptibility evaluated at T_c, $\chi_0(T_c)$, for the $Pd_{1-y}Ag_y$ alloys doped with 0.50-, 1.0-, and 2.0-at.% Fe impurity (triangles, squares, and circles, respectively). The closed symbols indicate a ferromagnetic transition, while the open symbols represent a spin-glass behavior. The straight lines are best fits to the data. The theory of Takahashi and Shimizu[15] relates T_c to $\chi_0(T_c)$ by

$$T_c = [N_i g^2 \mu_B^2 S(S+1)\alpha^2/3k_B]\chi_0(T_c)\,, \qquad (1)$$

where N_i is the impurity concentration, g is the g-factor (assumed to be 2), μ_B is the Bohr magneton, S is the impurity spin quantum number, α

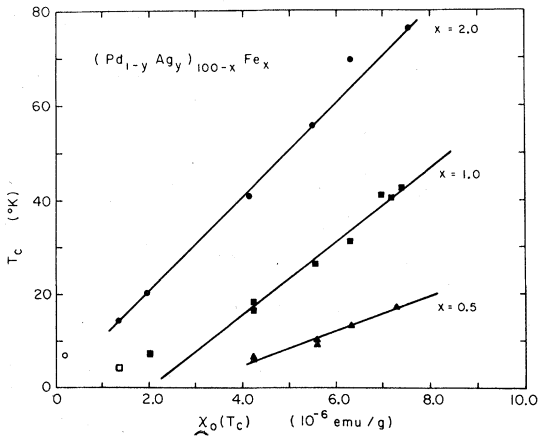

FIG. 1. Magnetic-ordering temperature T_c in °K vs host-matrix susceptibility evaluated at T_c, $\chi_0(T_c)$, in emu/g for the $(Pd_{1-y}Ag_y)_{100-x}Fe_x$ alloys: $x = 0.5$—triangles, $x = 1.0$—squares, and $x = 2.0$—circles. Closed symbols are ferromagnetic; open symbols are spin glass. Straight lines are best fits to data.

is the molecular-field coefficient describing the localized moment to 4*d*-electron interaction, and k_B is the Boltzmann constant. We see that the theory predicts a linear dependence of T_c on $\chi_0(T_c)$ which passes through the origin and has a slope proportional to N_i. Our results do show a linear dependence; however, only the line fitted to the 2.0-at.% Fe system passes close to the origin. This fact was pointed out by Nieuwenhuys[22] in his review of early Mössbauer work by Levy *et al.*[21] We obtain slopes of 3.75×10^6, 7.80×10^6, and 10.0×10^6 °Kg/emu for the 0.50-, 1.0-, and 2.0-at.% Fe lines, respectively. These slopes are in the ratio of 1 : 2.1 :2.7, which indicates that the 0.50- and 1.0-at.% Fe alloys are consistent with each other; however, the slope for the 2.0-at.% Fe alloys is somewhat lower then expected. This might be due to the fact that a 2.0-at.% concentration of Fe is not "dilute" enough, resulting in direct Fe-Fe interactions which were neglected by the theory. From the measured slopes and Eq. (1), we calculate values for $\alpha g[S(S+1)]^{1/2}$ to be 8.00×10^5, 7.96×10^5, and 6.51×10^5 g/emu for 0.50-, 1.0-, and 2.0-at.% Fe, respectively. These values will be used in later discussions.

We note that the T_c values for the $(Pd_{1-y}Ag_y)_{100-x}Fe_x$ alloys reported in this work are in very good agreement with those obtained previously by ac mutual inductance and Mössbauer techniques.[18,21] The only exception is an incorrect value of 25.3 °K previously reported in Ref. 18 for $(Pd_{0.975}Ag_{0.025})_{99.0}Fe_{1.0}$; our new value for this composition is 31.5 °K. Excellent reproducibility was obtained when we remeasured (on the vibrating-sample magnetometer) T_c for several samples used in the original magnetic work. The small discrepancies in T_c that exist between the magnetic and Mössbauer determinations have been discussed previously.[21]

2. *Magnetic moment*

Values of the magnetic moment per Fe atom for the ferromagnetic $(Pd_{1-y}Ag_y)_{100-x}Fe_x$ alloys were obtained from saturation magnetization data, $\sigma_{0\infty}$. The behaviors of the various bulk sample magnetizations were determined as a function of temperature and magnetic field, and extrapolations to 0 °K and infinite field provided the saturation values. Figure 2 shows the saturation magnetic moment (in μ_B) per Fe atom, p_z, as a function of the host susceptibility at 0 °K, $\chi_0(0\ °K)$, for the $Pd_{1-y}Ag_y$ alloys doped with 0.5-, 1.0-, and 2.0-at.% Fe impurity (triangles, squares, and circles, respectively). The theory of Takahashi and Shimizu[15] relates p_z to χ_0 (0 °K) by

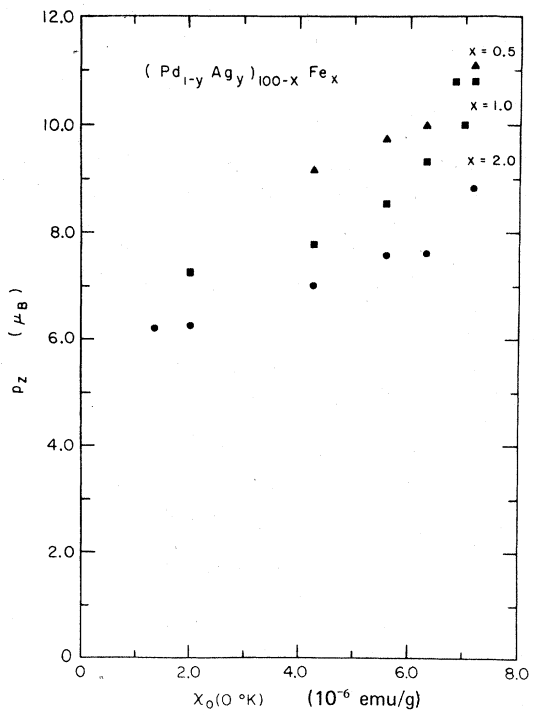

FIG. 2. Effective magnetic moment per Fe atom, p_z, in μ_B vs host-matrix susceptibility evaluated at 0°K, $\chi_0(0°K)$, in emu/g for the $(Pd_{1-y}Ag_y)_{100-x}Fe_x$ alloys: $x=0.5$—triangles, $x=1.0$— squares, and $x=2.0$ circles.

$$p_z = gS\mu_B[1+\alpha\chi_0(0°K)], \tag{2}$$

where all the quantities have been defined above. We see that the theory predicts a linear dependence of p_z on $\chi_0(0\ °K)$ with an intercept of $gS\mu_B$ and a slope of $gS\mu_B\alpha$. Our results do show that as the host susceptibility is decreased with the replacement of Pd by Ag in the alloys, the magnetic moment per Fe atom decreases, but not linearly, for all three Fe concentrations. The deviation from linear behavior might possibly arise from the host susceptibility data, $\chi_0(0\ °K)$. In Sec. II, we noted that some of the published $Pd_{1-y}Ag_y$ host susceptibility data had to be corrected for small amounts of unwanted Fe impurity. As discussed later in Sec. IV, the value for α that is obtained from the slopes of the T_c vs $\chi_0(T_c)$ data does describe the general increase in p_z with $\chi_0(0\ °K)$, even though the dependence is not linear.

For a given host susceptibility, the moment per Fe atom is greatest for the 0.5-at.% Fe alloys, followed by the 1.0-at.% Fe alloys and finally the 2.0-at.% Fe alloys. The p_z vs $\chi_0(0\ °K)$ behavior for the three series of alloys tends to extrapolate to $p_z \gtrsim 6.0\mu_B$ as $\chi_0(0\ °K)$ is suppressed. From the theory of Takahashi and Shimizu,[15] as $\chi_0(0\ °K)\to 0$, $p_z \to gS\mu_B$ and hence our data would indicate gS

$\gtrsim 6.0$, or $S \gtrsim 3.0$ if g is taken to be 2.0. This value for S is larger than the $\frac{3}{2}$ value that is usually associated with moments localized on Fe impurities in Pd.[30] It is also larger than the $\frac{5}{2}$ maximum value allowed by Hund's rules. The observed moments do decrease as χ_0 is decreased, but they do not "collapse" either completely, or to a value that can be reasonably associated with an isolated Fe impurity. A possible explanation could be that the Pd atoms that are nearest neighbors to an Fe atom do couple to form a so-called "giant moment," while the more distant Pd atoms polarize in a manner that can be considered uniform and treated in a band picture.

3. *Paramagnetic susceptibility*

Measurements of the bulk sample magnetization at room temperature were made as a function of magnetic field for the $(Pd_{1-y}Ag_y)_{100-x}Fe_x$ alloys. For all of our samples, the magnetic-ordering temperature is considerably below RT, and plots of the magnetization versus field yielded straight lines that passed through the origin. First of all, this indicates that no observable ferromagnetic phase exists at RT in any of the samples. Such phases might occur if some of the Fe atoms were clustered. Second, values of the total RT susceptibility $\chi(\mathrm{RT})$ can be obtained from the slopes. We calculated the (excess) RT paramagnetic susceptibility associated with the Fe impurity, $\chi_p(\mathrm{RT})$, by subtracting the RT host-matrix susceptibility $\chi_0(\mathrm{RT})$ from $\chi(\mathrm{RT})$, i.e., $\chi_p(\mathrm{RT}) = \chi(\mathrm{RT}) - \chi_0(\mathrm{RT})$. Figure 3 shows $\chi_p(\mathrm{RT})$ vs $\chi_0(\mathrm{RT})$ for the $Pd_{1-y}Ag_y$ host alloys doped with 0.5-, 1.0-, and 2.0-at.% Fe impurity (triangles, squares, and circles, respectively). We note that as $\chi_0(\mathrm{RT})$ is decreased, $\chi_p(\mathrm{RT})$ decreases monotonically, but somewhat slowly, for all Fe concentrations, and extrapolates to finite values for $\chi_0(\mathrm{RT}) = 0$. Also, for any value of $\chi_0(\mathrm{RT})$ the corresponding values of $\chi_p(\mathrm{RT})$ are essentially in direct proportion to the Fe impurity concentration N_i.

Table I summarizes the magnetic data for the

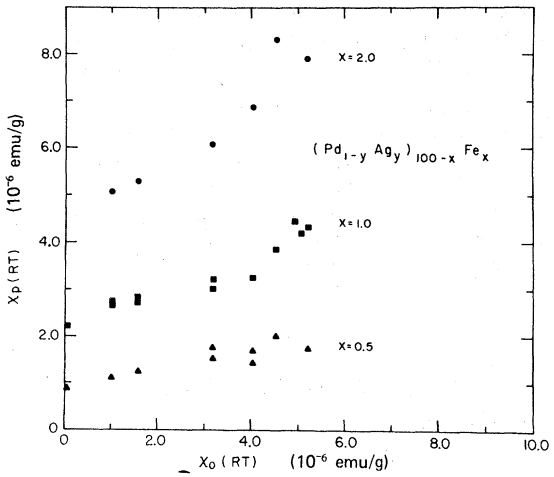

FIG. 3. Excess RT paramagnetic susceptibility associated with the Fe impurity, $\chi_p(\mathrm{RT})$, in emu/g vs host-matrix susceptibility evaluated at RT, $\chi_0(\mathrm{RT})$, in emu/g for the $(Pd_{1-y}Ag_y)_{100-x}Fe_x$ alloys: $x = 0.5$—triangles, $x = 1.0$—squares, and $x = 2.0$—circles.

$(Pd_{1-y}Ag_y)_{99.5}Fe_{0.5}$ alloys: column 1 lists the fraction of Pd atoms that have been replaced by Ag atoms, y; column 2 lists the effective magnetic moment per Fe atom, p_z; column 3 lists the host-matrix susceptibility evaluated at 0 °K, $\chi_0(0\,^\circ\mathrm{K})$; column 4 lists the magnetic-ordering temperature T_c; column 5 lists the host-matrix susceptibility evaluated at T_c, $\chi_0(T_c)$; column 6 lists the RT paramagnetic susceptibility associated with the Fe impurity, $\chi_p(\mathrm{RT})$; and column 7 lists the host-matrix susceptibility evaluated at RT, $\chi_0(\mathrm{RT})$. The 0.5-at.% Fe alloys for $y = 0.25$, 0.33, and 0.50 remained paramagnetic down to the lowest temperature available, 3 °K. The corresponding magnetic data for the $(Pd_{1-y}Ag_y)_{99.0}Fe_{1.0}$ and $(Pd_{1-y}Ag_y)_{98.0}Fe_{2.0}$ alloys are summarized in Tables II and III, respectively. The magnetic-ordering temperature for $(Pd_{0.50}Ag_{0.50})_{99.0}Fe_{1.0}$ was very close to the lowest temperature available, thereby preventing an accurate measurement.

TABLE I. Magnetic moments, ordering temperatures, paramagnetic susceptibilities, and host susceptibilities for the $(Pd_{1-y}Ag_y)_{99.5}Fe_{0.5}$ alloys.

Composition (y)	p_z (μ_B)	$x_0(0\,^\circ\mathrm{K})$ (10^{-6} emu/g)	T_c (°K)	$x_0(T_c)$ (10^{-6} emu/g)	$x_p(\mathrm{RT})$ (10^{-6} emu/g)	$x_0(\mathrm{RT})$ (10^{-6} emu/g)
0.00	11.1	7.17	17.5	7.27	1.70	5.21
0.025	9.99	6.33	13.7	6.32	1.99	4.53
0.05	9.76	5.61	10.5	5.60	1.67	4.03
0.10	9.18	4.27	6.8	4.22	1.74	3.17
0.25	...	...	...	...	1.24	1.56
0.33	...	...	...	...	1.11	1.00
0.50	...	...	...	...	0.87	0.042

TABLE II. Magnetic moments, ordering temperatures, paramagnetic susceptibilities, and host susceptibilities for the $(Pd_{1-y}Ag_y)_{99.0}Fe_{1.0}$ alloys.

Composition (y)	p_z (μ_B)	χ_0(0 °K) (10^{-6} emu/g)	T_c (°K)	$\chi_0(T_c)$ (10^{-6} emu/g)	χ_p(RT) (10^{-6} emu/g)	χ_0(RT) (10^{-6} emu/g)
0.00	10.8	7.17	42.6	7.40	4.30	5.21
0.005	10.0	6.99	40.9	7.17	4.17	5.07
0.01	10.8	6.82	41.6	6.94	4.42	4.93
0.025	9.32	6.33	31.5	6.31	3.84	4.53
0.05	8.56	5.61	26.9	5.56	3.21	4.03
0.10	7.78	4.27	16.4	4.21	2.98	3.17
0.25	7.29	1.99	6.4	1.98	2.75	1.56
0.33	...[a]	...	4.5[a]	1.34	2.65	1.00
0.50	...	...	...	...	2.20	0.042

[a] Spin glass.

B. $(Pd_{1-y}Rh_y)_{99.0}Fe_{1.0}$ alloys

1. Magnetic-ordering temperature

Measurements of the magnetic-ordering temperature for the $(Pd_{1-y}Rh_y)_{99.0}Fe_{1.0}$ alloys were made in the manner described above for the $(Pd_{1-y}Ag_y)_{100-x}Fe_x$ alloys. Figure 4 shows T_c as a function of $\chi_0(T_c)$ for all of the 1.0-at.% Fe alloys. Data points for the $(Pd_{1-y}Rh_y)_{99.0}Fe_{1.0}$ alloys have the fractional Rh composition designated, i.e., $y = 0.00$, 0.01, 0.04, 0.05, 0.07, 0.10, and 0.20. The data points for the $(Pd_{1-y}Ag_y)_{99.0}Fe_{1.0}$ alloys (replotted from Fig. 1) are without the designations. In both cases, the closed symbols represent our measurements and the open symbols are data taken from the work of Clogston *et al.*[9]

Since Rh and Ag are adjacent to Pd in the second row of transition elements, this combined series of 1.0-at.% Fe alloys represents a systematic variation of the electron concentration and, hence the Fermi energy E_F. The electronic density of states versus energy for Pd, $g(E)$, has been determined from low-temperature specific-heat measurements on $Pd_{1-y}Rh_y$ and $Pd_{1-y}Ag_y$ alloys by assuming the rigid-band model.[31] As we proceed to the right in the second row by decreasing the Rh content in $Pd_{1-y}Rh_y$, $g(E_F)$ reaches sharp peak at approximately $y = 0.05$ and then falls off as the Rh content is reduced to zero (pure Pd). $g(E_F)$ continues to decrease as Ag is added to form $Pd_{1-y}Ag_y$. Figure 4 shows that both the ordering temperature and the host-matrix susceptibility have composition dependences similar to $g(E_F)$ (i.e., they reach a maximum near $y = 0.05$). However, the dependence of T_c on $\chi_0(T_c)$ as predicted by the theory of Takahashi and Shimizu[15] [Eq. (1)] would have all the data points lying along a common straight line that passes through the origin. This is not the case as seen in Fig. 4; the T_c vs $\chi_0(T_c)$ curve is "double-valued." We note that the data for the $(Pd_{1-y}Rh_y)_{99.0}Fe_{1.0}$ alloys with $0.05 \leq y \leq 0.20$ do assume a nearly linear behavior, as well as the previously described $(Pd_{1-y}Ag_y)_{99.0}Fe_{1.0}$ alloys with $0 \leq y \leq 0.25$. It is as if the T_c vs $\chi_0(T_c)$ dependence shifts from one straight line to another in the concentration region where $g(E_F)$ passes through a sharp maximum. Neither line, however, passes through the origin.

TABLE III. Magnetic moments, ordering temperatures, paramagnetic susceptibilities, and host susceptibilities for the $(Pd_{1-y}Ag_y)_{98.0}Fe_{2.0}$ alloys.

Composition (y)	p_z (μ_B)	χ_0(0 °K) (10^{-6} emu/g)	T_c (°K)	$\chi_0(T_c)$ (10^{-6} emu/g)	χ_p(RT) (10^{-6} emu/g)	χ_0(RT) (10^{-6} emu/g)
0.00	8.86	7.17	76.4	7.56	7.89	5.21
0.025	7.60	6.33	69.7	6.30	8.27	4.53
0.05	7.58	5.61	56.0	5.49	6.83	4.03
0.10	7.01	4.27	41.0	4.14	6.04	3.17
0.25	6.25	1.99	20.4	1.97	5.28	1.56
0.33	6.19	1.34	14.5	1.33	5.06	1.00
0.50	...[a]	...	7.0[a]	0.18	5.08	0.042

[a] Spin glass.

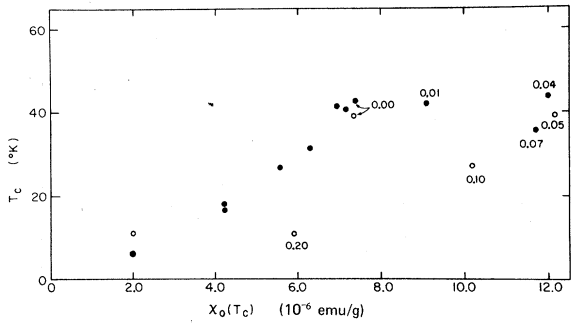

FIG. 4. Magnetic-ordering temperature T_c in °K vs host-matrix susceptibility evaluated at T_c, $\chi_0(T_c)$, in emu/g for both $(Pd_{1-y}Rh_y)_{99.0}Fe_{1.0}$ alloys (with fractional Rh composition y designated) and $(Pd_{1-y}Ag_y)_{99.0}Fe_{1.0}$ alloys (without designations). Closed symbols—present work, open symbols—Clogston *et al.* (Ref. 9).

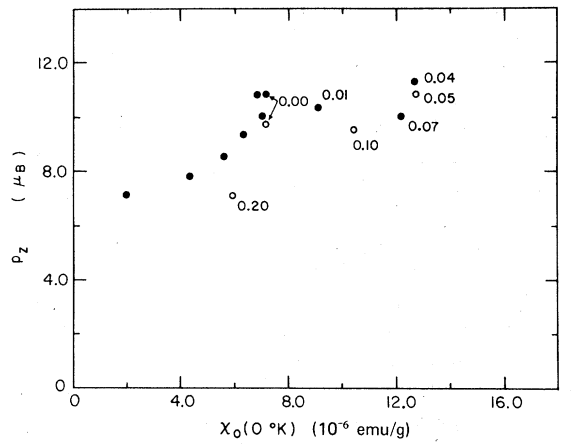

FIG. 6. Effective magnetic moment per Fe atom, p_z, in μ_B vs host-matrix susceptibility evaluated at 0 °K, χ_0(0°K), in emu/g for both $(Pd_{1-y}Rh_y)_{99.0}Fe_{1.0}$ alloys (with fractional Rh composition y designated) and $(Pd_{1-y}Ag_y)_{99.0}Fe_{1.0}$ alloys (without designations). Closed symbols—present work, open symbols—Clogston *et al.* (Ref. 9).

Although the behavior for the $(Pd_{1-y}Rh_y)_{99.0}Fe_{1.0}$ is not ideally linear, we have estimated a slope of 4.2×10^6 °K g/emu which results in $\alpha g[S(S+1)]^{1/2} = 6.0\times10^5$ g/emu.

In Fig. 5, T_c (data points and left-hand ordinate) and $\chi_0(T_c)$ (dashed curve and right-hand ordinate) are plotted as a function of the composition. The solid symbols are our measurements and the open symbols are data from Clogston *et al.*[9] This figure illustrates how the behavior of the ordering temperature parallels that of the host susceptibility.

2. *Magnetic moment*

Values of the magnetic moment per Fe atom for the ferromagnetic $(Pd_{1-y}Rh_y)_{99.0}Fe_{1.0}$ alloys were obtained from saturation magnetization data in the manner described above for the $(Pd_{1-y}Ag_y)_{100-x}Fe_x$ alloys. Figure 6 shows p_z as a function of χ_0(0 °K) for all of the 1.0-at.% Fe alloys. Again, data points for the $(Pd_{1-y}Rh_y)_{99.0}Fe_{1.0}$ alloys have the fractional Rh composition designated, i.e., y = 0.00, 0.01, 0.04, 0.05, 0.07, 0.10, and 0.20. The data points for the $(Pd_{1-y}Ag_y)_{99.0}Fe_{1.0}$ alloys (replotted from Fig. 2) are without the designations. In both cases, the closed symbols represent our measurements, and the open symbols are data taken from the work of Clogston *et al.*[9]

The behavior of p_z vs χ_0(0 °K) illustrated in Fig. 6 is quite similar to that of T_c vs $\chi_0(T_c)$ shown in Fig. 4. The magnetic moment per Fe atom does increase with the host susceptibility, but the dependence is again double-valued, which is not in-

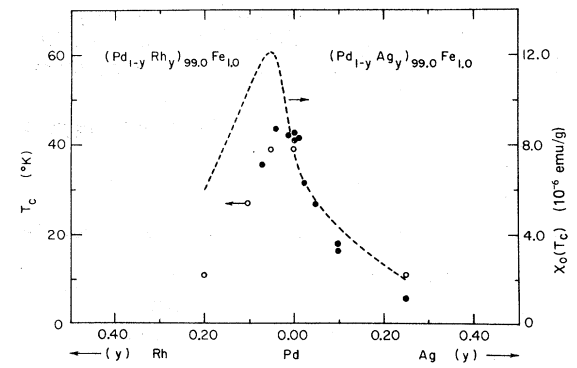

FIG. 5. Magnetic-ordering temperature T_c in °K (data points and left-hand ordinate) and host-matrix susceptibility evaluated at T_c, $\chi_0(T_c)$, in emu/g (dashed curve and right-hand ordinate) vs fractional composition y for both $(Pd_{1-y}Rh_y)_{99.0}Fe_{1.0}$ and $(Pd_{1-y}Ag_y)_{99.0}Fe_{1.0}$ alloys. Closed symbols—present work, open symbols—Clogston *et al.* (Ref. 9).

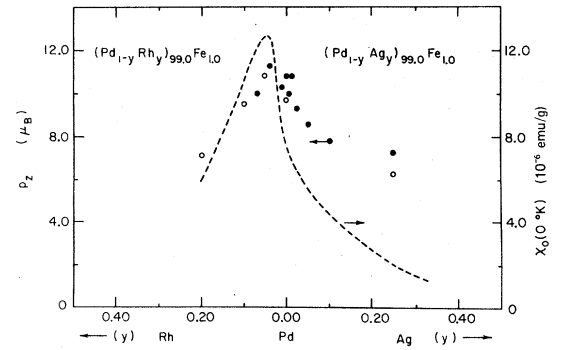

FIG. 7. Effective magnetic moment per Fe atom, p_z, in μ_B (data points and left-hand ordinate) and host-matrix susceptibility evaluated at 0 °K, χ_0(0 °K), in emu/g (dashed curve and right-hand ordinate) vs fractional composition y for both $(Pd_{1-y}Rh_y)_{99.0}Fe_{1.0}$ and $(Pd_{1-y}Ag_y)_{99.0}Fe_{1.0}$ alloys. Closed symbols—present work, open symbols—Clogston *et al.* (Ref. 9).

dicated by the theory. There is a shift in behavior as the composition is varied such that $g(E_F)$ passes through the sharp maximum. We have indicated earlier that p_z extrapolates to $\gtrsim 6.0\mu_B$ as χ_0 is suppressed by the addition of Ag to the alloys. As seen in Fig. 6, when χ_0 is suppressed by the addition of Rh, p_z extrapolates to approximately $3.5\mu_B$. If we take $g=2$, the Rh-rich extrapolation would yield a value of $S \approx 1.8$, which is reasonably close to the $\frac{3}{2}$ value.

In Fig. 7, p_z (data points and left-hand ordinate) and $\chi_0(0\ ^\circ K)$ (dashed curve and right-hand ordinate) are plotted as a function of the composition. The solid symbols are our measurements and the open symbols are data from Clogston *et al.*[9] The figure illustrates how the behavior of p_z parallels that of χ_0.

3. *Paramagnetic susceptibility*

Values of the RT paramagnetic susceptibility associated with the Fe impurity for the $(Pd_{1-y}Rh_y)_{99.0}Fe_{1.0}$ alloys were obtained in the manner described above for the $(Pd_{1-y}Ag_y)_{100-x}Fe_x$ alloys. Figure 8 shows χ_p(RT) as a function of χ_0(RT) for all the 1.0-at.% Fe alloys. As before, data points for the $(Pd_{1-y}Rh_y)_{99.0}Fe_{1.0}$ alloys have the fractional Rh composition designated, i.e., $y=0.00$, 0.01, 0.04, 0.07, 0.50, and 0.75. The data points for the $(Pd_{1-y}Ag_y)_{99.0}Fe_{1.0}$ alloys (replotted from Fig. 3) are without designations. We note that, in contrast to the behavior for the $(Pd_{1-y}Ag_y)_{99.0}Fe_{1.0}$ alloys, when χ_0(RT) is suppressed by the replacement of Pd with Rh in $(Pd_{1-y}Rh_y)_{99.0}Fe_{1.0}$, χ_p(RT) is also suppressed. Table IV summarizes the magnetic data for the $(Pd_{1-y}Rh_y)_{99.0}Fe_{1.0}$ alloys. The alloys with $y=0.50$ and 0.75 remained paramagnetic down to the lowest temperature available, 3 °K.

The results for three of our alloys which have solely Pd as the host matrix can be compared with the existing magnetic data on $Pd_{100-x}Fe_x$. Our values of the magnetic-ordering temperature and effective magnetic moment for $Pd_{99.5}Fe_{0.5}$, $Pd_{99.0}Fe_{1.0}$, and $Pd_{98.0}Fe_{2.0}$ fall on the corresponding T_c vs x and p_z and x curves which have previously been established for the well-known $Pd_{100-x}Fe_x$ system.[7,8]

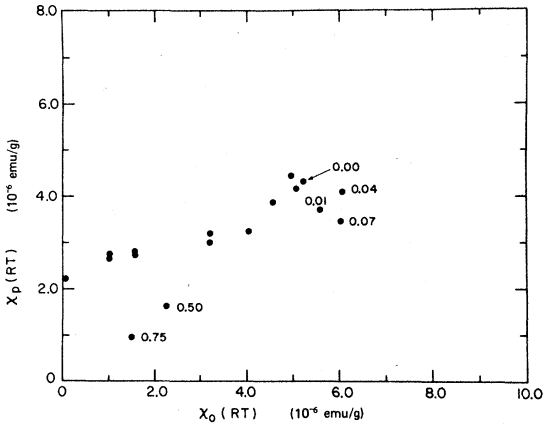

FIG. 8. Excess RT paramagnetic susceptibility associated with the Fe impurity, χ_p (RT), in emu/g vs the host-matrix susceptibility evaluated at RT, χ_0(RT), in emu/g for both $(Pd_{1-y}Rh_y)_{99.0}Fe_{1.0}$ alloys (with fractional Rh composition y designated) and $(Pd_{1-y}Ag_y)_{99.0}Fe_{1.0}$ alloys (without designations.

IV. DISCUSSION AND CONCLUSIONS

The objective of this work was to investigate the dependences of the paramagnetic susceptibility, effective magnetic moment, and magnetic-ordering temperature on the host-matrix susceptibility and impurity concentration for a system involving a dilute transition-metal impurity (Fe) dissolved into a transition-metal host matrix possessing significant exchange enhancement ($Pd_{1-y}Rh_y$ and $Pd_{1-y}Ag_y$). Of particular interest was the comparison of our experimental results to a theory by Takahashi and Shimizu,[15] which is based on a localized magnetic moment for the dissolved atom and a uniformly polarized host d-band.

In summary, our results provide some support

TABLE IV. Magnetic moments, ordering temperatures, paramagnetic susceptibilities, and host susceptibilities for the $(Pd_{1-y}Rh_y)_{99.0}Fe_{1.0}$ alloys.

Composition (y)	p_z (μ_B)	$x_0(0\ ^\circ K)$ (10^{-6} emu/g)	T_c (°K)	$x_0(T_c)$ (10^{-6} emu/g)	x_p(RT) (10^{-6} emu/g)	x_0(RT) (10^{-6} emu/g)
0.00	10.8	7.17	42.6	7.40	4.30	5.21
0.01	10.3	9.11	42.0	9.11	3.67	5.58
0.04	11.3	12.7	43.6	12.0	4.08	6.05
0.07	10.0	12.2	35.6	11.7	3.43	6.02
0.50	...	...	...	...	1.63	2.24
0.75	...	...	...	...	0.96	1.50

for the theory, but discrepancies exist in the detailed behavior. The most serious discrepancies are realized when the dependences of the magnetic-ordering temperature, effective magnetic moment, and paramagnetic susceptibility on the host-matrix susceptibility are considered for $(Pd_{1-y}Rh_y)_{99.0}Fe_{1.0}$ and $(Pd_{1-y}Ag_y)_{99.0}Fe_{1.0}$ together. For all three dependences, Rh substitution with $0.05 \leq y \leq 0.20$ produces a different behavior than Ag substitution with $0.00 \leq y \leq 0.25$. It was pointed out that this change in behavior, which results in double-valued curves, occurs at approximately the same composition as the sharp maximum in $g(E_F)$. However, the simple rigid-band approach is suspect here, since in one case we are replacing Pd atoms with transition-element Rh atoms and in the other case with noble-element Ag atoms. A different local magnetic coupling is indeed anticipated.

For the $(Pd_{1-y}Ag_y)_{100-x}Fe_x$ alloys, the observed dependence of T_c on $\chi_0(T_c)$ was linear as predicted by the theory, although only the slopes (which should be directly proportional to N_i) for the 0.5- and 1.0-at.% Fe alloys had the expected ratio. It was suggested that the low value of the slope for the 2.0-at.% Fe alloys might arise because such a concentration of Fe is not dilute enough, resulting in direct Fe-Fe interactions which were neglected by the theory. In addition, measurements of the high-field susceptibility for $Pd_{100-x}Fe_x$ alloys indicate that there exists a lowering of the host-Pd-matrix susceptibility for Fe concentrations $\gtrsim 1.0$ at.%.[32,33] The fact that only the T_c vs $\chi_0(T_c)$ line for the 2.0-at.% Fe alloys passes through the origin is not explained. From the T_c vs $\chi_0(T_c)$ data for the $(Pd_{1-y}Ag_y)_{100-x}Fe_x$ alloys, we calculate $\alpha g[S(S+1)]^{1/2} = 7.98\times10^5$ g/emu as being a representative value (average of the values for the 0.5-and 1.0-at.% Fe alloys). As in the earlier work by Cannella *et al.*,[18,19] our experimental results indicate a transition from ferromagnetic to spin-glass-like behavior when the host-matrix susceptibility is appreciably reduced.

From the p_z vs $\chi_0(0\ ^\circ K)$ behavior for the $(Pd_{1-y}Ag_y)_{100-x}Fe_x$ alloys, it was seen that the moment per Fe atom decreases slowly as $\chi_0(0\ ^\circ K)$ decreases. For a given host susceptibility, the moment per Fe atom decreases as the Fe concentration, x, increases. Extrapolation of the p_z vs $\chi_0(0\ ^\circ K)$ data for all three Fe concentrations leads to a value of $p_z = gS\mu_B \gtrsim 6.0\mu_B$ (or spin quantum number of $S \gtrsim 3.0$) for vanishing host susceptibility. It was noted that the observed moments do not collapse either completely, or to a value that can be reasonably associated with an isolated Fe impurity. A possible explanation is that the Pd atoms that are nearest neighbors to an Fe atom do couple to form a giant moment, while the more distant Pd atoms polarize in a manner that can be considered uniform, and treated in a band picture. This is not inconsistent with the theory of Takahashi and Shimizu,[15] as the formalism still remains intact. By using the value of $\alpha g[S(S+1)]^{1/2}$ obtained from the ordering temperature data and S from the moment data, we calculate the molecular-field coefficient that describes the interaction between the localized moment on the Fe and the Pd $4d$-electrons, α, to be 1.2×10^5 g/emu (1.1×10^3 mole/emu). Also, a value of 0.071 eV for the exchange-interaction constant J can be obtained from

$$J = \tfrac{1}{2}N_0 g^2 \mu_B^2 \alpha\ , \tag{3}$$

where N_0 is Avogadro's number and the other quantities have been defined above. On the other hand, if we assume $S = \frac{3}{2}$ and still use $\alpha g[S(S+1)]^{1/2} = 7.98\times10^5$ g/emu from our ordering temperature data, we obtain $\alpha = 2.1\times10^5$ g/emu (1.9×10^3 mole/emu) and $J = 0.12$ eV. The latter values for α and J are very close to the values previously published,[21] but they are not consistent with the magnetic-moment data.

From the χ_p(RT) vs χ_0(RT) behavior for the $(Pd_{1-y}Ag_y)_{100-x}Fe_x$ alloys, it was observed that the RT paramagnetic susceptibility associated with the Fe impurity decreases slowly as the host susceptibility decreases and extrapolates to a finite value. Also, for a given host susceptibility, the paramagnetic susceptibility scaled with the Fe impurity concentration.

For the $(Pd_{1-y}Rh_y)_{99.0}Fe_{1.0}$ alloys, T_c vs $\chi_0(T_c)$ tended to be linear for $y \geq 0.05$, although not passing through the origin. From the slope, we estimated a value of $\alpha g[S(S+1)]^{1/2} = 6.0\times10^5$ g/emu. In contrast to the $(Pd_{1-y}Ag_y)_{100-x}Fe_x$ alloys, as the host susceptibility was suppressed, the effective magnetic moment per Fe atom decreased to a value of $p_z \approx 3.5\mu_B$ or $S \approx 1.8$, which is almost the $\frac{3}{2}$ value for a single Fe atom. From the above values, we estimate $\alpha = 1.4\times10^5$ g/emu (1.3×10^3 mole/emu) and $J = 0.084$ eV. Also, in contrast to the $(Pd_{1-y}Ag_y)_{100-x}Fe_x$ alloys, the RT paramagnetic susceptibility associated with the Fe impurity became very small as the host susceptibility was reduced.

Similar studies have been carried out on two other systems involving dilute Fe additions to Pd-rich host alloys. In a very recent work, Domb *et al.*[34] studied $(Pd_{1-y}Au_y)_{100-x}Fe_x$ alloys by magnetization and Mössbauer techniques. For $y \lesssim 0.50$, the alloys are strongly exchange enhanced and the ordering is ferromagnetic. The Takahashi-Shimizu[15] theory appears to consistently describe their data in terms of the local moment to Pd $4d$-electron

coupling [Eq. (2)], but not in terms of the inter-impurity coupling [Eq. (1)]. A possible explanation for the discrepancy is that the Fe concentrations studied (2- and 6-at.%) are too large to be considered dilute, are required by the theory. From the saturation moment data, Domb *et al.*[34] calculate $\alpha = 1.8\times 10^3$ mole/emu and $J = 0.12$ eV. For $y \gtrsim 0.50$, the magnetic ordering is spin-glass, and the results are understandable in terms of existing theories based on fluctuations in exchange couplings of Fe spins.

Geballe *et al.*[35] have measured the saturation moment per Fe atom in some $(Pd_{1-y}Pt_y)_{99.0}Fe_{1.0}$ alloys. Their values are consistent with the p_z vs $\chi_0(0\,^\circ K)$ behavior observed for $(Pd_{1-y}Ag_y)_{99.0}Fe_{1.0}$ in this work.

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