Spin Fluctuation and Local Magnetism of Isolated Rh Ions in Paramagnetic Dilute PdFe Alloys

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(Received 12 August 1991)

Large 4*d* spin magnetic moments with small spin fluctuation rates have been measured for isolated Rh impurities in paramagnetic dilute PdFe alloys using the time-differential perturbed-angular-correlation method. The Curie-Weiss–like local susceptibility reflects enhanced Rh moment stability with the small addition of Fe into the Pd host, indicated by a drastic reduction of the spin fluctuation temperature. We suggest that magnetism and moment stability of Rh in the PdFe system are mainly governed by an interatomic ferromagnetic exchange interaction between the Rh 4*d* and the Pd *d*-band electrons.

PACS numbers: 75.20.Hr, 75.30.Et, 76.80.+y

The formation of a magnetic moment on isolated transition metal impurities dissolved into nonmagnetic metallic hosts continues to be a topic of experimental as well as theoretical interest. A key area of investigation has been the study of spin fluctuations and moment instabilities caused by the exchange interaction between the impurity *d* and the host conduction electrons. Extensive data are now available for the magnetism of 3*d* ions in various metals [1]. Recent experimental studies have revealed that the host *sp*- and *d*-type conduction electrons have different influences on the impurity magnetism and spin fluctuation rates of 3*d* ions [2,3]. In comparison, much less information is available on the magnetic behavior of isolated 4*d* impurities in transition metal hosts. Experimentally, the existence of a 4*d* moment was first reported for dilute Rh impurities in a Pd host [4]. Recently, a quasistable spin magnetic moment characterized by a high spin fluctuation temperature $T_{SF} \sim 280$ K was reported for isolated Ru ions in Pd metal [5]. It was suggested that the host *d*-band electrons have a strong influence on the occurrence and stability of 4*d* spin magnetic moments in Pd. As far as we know, stable 4*d* magnetic moments have not been observed in hosts containing *d*-band electrons. As a result of the lack of experimental data important questions such as how to stabilize 4*d* moments in transition metal hosts and what sort of interaction can suppress spin fluctuations of 4*d* ions in *d*-band metals have remained poorly understood. Experimental measurements dedicated to investigate the influence of *d*-band electrons on the spin fluctuation rate and the stability of 4*d* magnetic moments have therefore become important. In this direction we have made a microscopic investigation of 4*d* magnetism for isolated Rh ions in dilute PdFe alloys using the time-differential perturbed-angular-correlation (TDPAC) method. The addition of Fe in the Pd host is known to produce significant ferromagnetic polarization of host conduction electrons [6] and can thus provide information on the role of the *d*-*d* interaction on spin fluctuation rates and moment stability of 4*d* ions in *d*-band metals.

In this Letter we report on the local magnetic behavior of isolated Rh impurities in paramagnetic PdFe alloys. The Curie-Weiss-type local susceptibility $\beta - 1 = C/(T + T_{SF})$ shows a strongly reduced spin fluctuation temperature T_{SF} with the very small addition of Fe into Pd. The observed trend of Rh magnetism suggests that the high moment stability signified by the low T_{SF} value is caused by an interatomic ferromagnetic interaction between Rh 4*d* and Pd host *d*-band electrons.

PdFe alloys with 0.2, 0.5, 1.0, and 2.0 at.% Fe were prepared by arc-melting stoichiometric quantities of 99.999% pure Pd and Fe in argon atmosphere. The alloys were annealed at 900 °C for 4 days and subsequently quenched in ice cold water. The Fe concentration in the specimens was ascertained independently using the energy dispersive x-ray analysis (EDAX) method.

Microscopic investigation of magnetic moment formation of Rh impurities in the Pd and PdFe systems was carried out by measuring the local susceptibility of ^{100}Rh probe ions produced during the electron conversion decay of ^{100}Pd, employing the TDPAC method. The parent ^{100}Pd activity (half-life, 3.6 days) was produced by the nuclear reaction ^{89}Y(^{16}O,$p4n$) using a 90–95-MeV oxygen beam provided by the heavy-ion accelerator facility at TIFR, Bombay, and were recoil implanted into thin foils (4 mg/cm^2) of Pd and PdFe alloys. The concentration of ^{100}Pd in the hosts turns out to be < 1 ppm. We have used the 74-keV, $I = 2^+$ level in ^{100}Rh ($T_{1/2} = 235$ ns, $g_N = 2.151$) as a nuclear probe for the detection of magnetic interactions. The magnetic response of the Rh ions was measured in the paramagnetic region far above the ferromagnetic Curie temperature of the alloy system, by observing spin rotation patterns in an external magnetic field of 11 kOe [7].

Figure 1 shows examples of spin rotation patterns $R(t)$ from which the Larmor frequency ω_L and the nuclear relaxation time τ_N could be extracted [7]. From $\omega_L = h^{-1}\mu_N g_N B_{ext}\beta(T)$, the local susceptibility $\beta - 1$ was derived, where β is the paramagnetic enhancement factor [8]. The results are shown in Fig. 2 along with the data obtained for Rh in pure Pd metal. Our $\beta(T)$ results for Rh in Pd are consistent with those reported in Ref. [4] which are also shown in Fig. 2. Here $\beta = 1$ characterizes nonmagnetic behavior while $\beta < 1$ and $\beta > 1$ are respec-

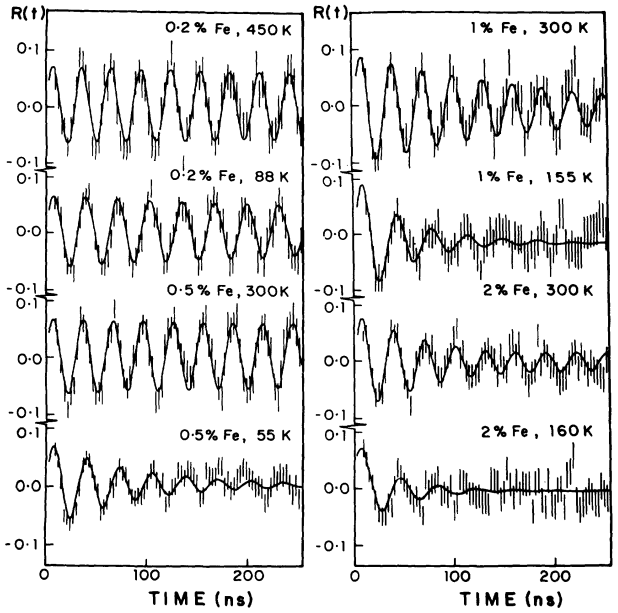

FIG. 1. Spin rotation spectra of ^{100}Rh in PdFe alloys at various temperatures measured in external magnetic field B_{ext} of 11 kOe.

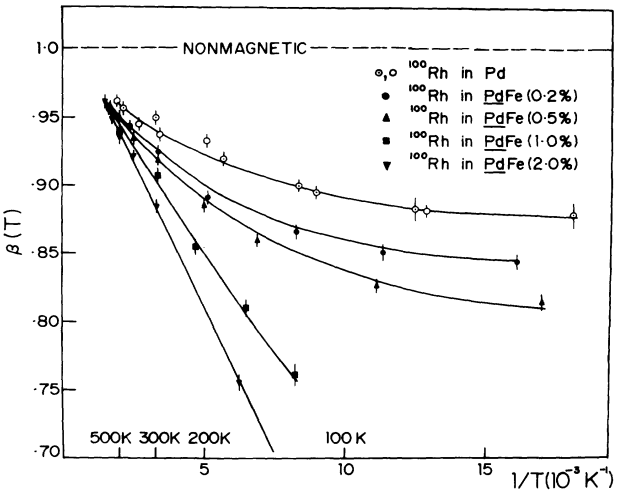

FIG. 2. Local susceptibility $\beta(T)$ of Rh in different PdFe alloys as a function of temperature. The continuous lines correspond to fits for Curie-Weiss behavior $\beta-1=C/(T+T_{SF})$.

tively taken as the signature for the occurrence of spin and orbital magnetic moment on the impurity ion [7].

All spectra show well-defined frequencies with high amplitude, consistent with the assumption that most of the implanted Pd ions probably come to rest at a substitutional site in the Pd host. However, the spectra for alloys with ≥ 1 at.% Fe could be fitted with a superposition of two frequencies. The observed amplitudes for the two frequencies were found to be consistent with estimated probabilities for zero and one Fe atom in the first nearneighbor (1nn) shell in these fcc Pd(Fe) dilute alloys. For the discussion of magnetism at Rh we mainly consider the majority component corresponding to Rh with zero Fe in the 1nn shell. We shall see below that the observation of the second frequency does not alter the essential conclusions drawn in the paper.

The local susceptibilities of Rh in the PdFe alloys were observed to vary strongly with temperature which could be fitted to a Curie-Weiss law $\beta-1=C/(T+T_{SF})$. The results are summarized in Table I. The derived values of the Curie constant C turned out to be quite large and were found comparable to the results obtained for some $3d$ ions in certain transition metal hosts, e.g., Fe in Cu, Rh, Ir [3]. The large negative value of C along with the Curie-Weiss–like behavior for $\beta(T)$ is consistent with the presence of spin magnetic moment for Rh in the systems investigated [4,5,7]. It should be noted that in the alloys with ≥ 1 at.% Fe the minority component corresponding to Rh with one Fe in the 1nn shell has a much stronger magnetic response and a Curie-like temperature dependence ($T_{SF}\sim 0$). The magnetic moment of Rh which scales with the total spin $S=S_{imp}+S_{host}$ can be extracted from the Curie constant $C=g_S\mu_B(S+1)B(0)/3k$ [7]. The $B(0)$ for $4d$ ions is estimated to be -350 kOe/μ_B [9]. For Rh in many metallic systems $B(0)$ has been found to vary from -200 to -350 kOe [10]. We have used $B(0)=-200$ kOe corresponding to $S_{imp}\sim 0.3$ and estimated the magnetic moment for Rh and the host spin polarization (S_{host}) produced at the nearby Pd atoms. The values obtained for different PdFe alloys are also listed in Table I. The Rh magnetic moment is found to increase from $\sim 5\mu_B$ in Pd to $\sim 7\mu_B$ in Pd(2% Fe) along with a substantial increase in S_{host}. Even if we take S_{imp} to be as high as 0.5 and therefore $B(0)=-350$ kOe, the moment for Rh would turn out to be quite large ranging from $\sim 2.0\mu_B$ in Pd to $\sim 4\mu_B$ in Pd(2% Fe). The high magnetic moments estimated for Rh in the PdFe system show close similarity to the behavior of Fe, Co, Ni in the Pd host and suggest the occurrence of giant $4d$ magnetic moment, consistent with the observations made for Ru ions in the Pd host [5].

TABLE I. Summary of the derived values for the Curie constant (C), host polarization (S_{host}), Rh magnetic moment (μ), spin fluctuation temperature (T_{SF}), and Rh $4d$ spin relaxation rate (τ_J^{-1}), in Pd(Fe) alloys. For 1 and 2 at.% Fe in Pd, data marked with asterisks correspond to the minority component (see text).

Host	C (K)	S_{host}	μ (μ_B)	T_{SF} (K)	τ_J^{-1} (s^{-1})
Pd	−30	2.10	4.82	220(10)	3.6×10^{13}
Pd(0.2% Fe)	−31	2.20	5.05	130(15)	2.1×10^{13}
Pd(0.5% Fe)	−33	2.45	5.50	95(15)	1.4×10^{13}
Pd(1.0% Fe)	−35	2.68	5.96	30(10)	6.8×10^{12}
	−45*	3.80*	8.20*	∼0	···
Pd(2.0% Fe)	−40	3.24	7.08	<20	$<1.3\times10^{12}$
	−66*	6.20*	13.0*	∼0	···

The $\beta(T)$ data also yield information on the stability of the Rh magnetic moment which can be scaled by the spin fluctuation temperature (T_{SF}) derived from the Curie-Weiss fit. As a notable feature the data show a drastic reduction of the T_{SF} value when a small amount of Fe is added to the Pd matrix (see Table I). For example, the T_{SF} value decreases from about 220 K for Rh in Pd to less than 30 K for Pd with only 1 at.% Fe. The decreasing trend of T_{SF} in the PdFe alloys indicates strong suppression of Rh $4d$ spin fluctuation rates τ_J^{-1} with increasing Fe concentration. As discussed above, the Curie-like $\beta(T)$ seen for the fraction arising from Rh with one Fe near neighbor reflects even smaller T_{SF} values and thus supports the conclusions drawn below.

An estimation of the $4d$ spin fluctuation rate can also be obtained from the nuclear relaxation time τ_N extracted from the damping in the $R(t)$ spectra using $\tau_N^{-1} = 2(\mu_N/\hbar)^2 g_N^2 (S+1) S^{-1} B(0)^2 \tau_J$ [11]. Figure 3 shows the τ_N results for Rh in Pd and PdFe alloys. The spectra for Rh in the pure Pd host show large τ_N values at all temperatures. Compared to the observation in Pd, the $R(t)$ results in PdFe alloys show strong damping even at very small Fe concentrations. The observed damping would have contributions from the dynamic fluctuation of the Rh moment and from the distribution of Larmor frequencies caused by inhomogeneous local environment. Tentatively assuming that the damping is solely caused by dynamic magnetic interaction, we have estimated the τ_J^{-1} values at 300 K which are listed in Table I. The τ_J^{-1} values so obtained could be converted into spin fluctuation temperatures using the uncertainty principle

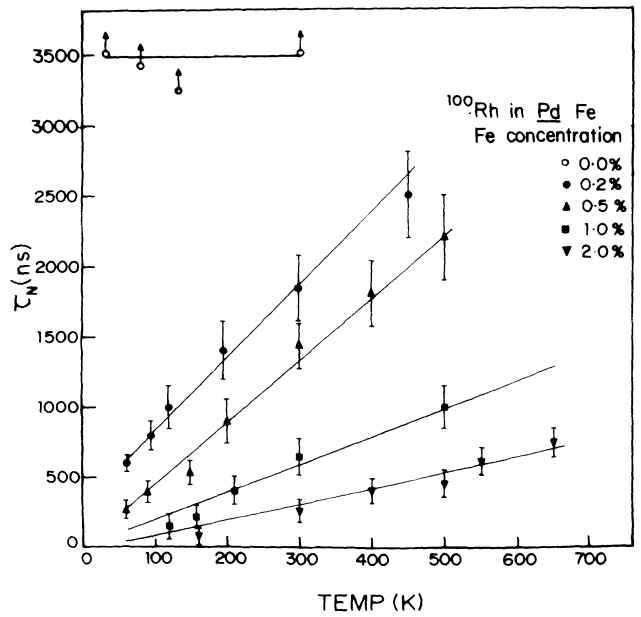

FIG. 3. Nuclear relaxation time τ_N at different temperatures for Rh in Pd and PdFe alloys. Lines through the data points are drawn for visual guidance.

$T_{SF} = (h/k_B)\tau_J^{-1}$. The results are found to be in good agreement with those obtained from the $\beta(T)$ data. Although we cannot rule out a contribution to the damping from the distribution in ω_L, from the above analysis the assumption that dynamic effects are dominant seems reasonable.

Before discussing the magnetism of Rh in PdFe alloys in terms of the interaction between Rh $4d$ and host d-band electrons we have to ensure that the observed $\beta(T)$ is not a manifestation of short-range magnetic ordering in the alloy system. First, our measurements have been made in a temperature range much above the Curie temperatures of the alloys. Besides, the onset of magnetic ordering in the host usually causes a sharp decrease in the initial amplitude of the $R(t)$ spectra [12]. Our data did not show appreciable change in amplitude down to 50 K. The above points along with the temperature dependence of β suggest that the observed magnetic response does not arise from the short-range magnetic ordering in the alloys.

In the following we mainly discuss the trend of the Rh moment spin fluctuation temperature (T_{SF}) in PdFe alloys obtained from the $\beta(T)$ data and show that the spin fluctuation rate, and hence the magnetic moment stability, is strongly related to the strength and sign of the host polarization induced on the nearby Pd atoms and therefore to the interatomic exchange interaction between the Rh $4d$ and the Pd d-band electrons. For dilute magnetic impurities in metallic hosts the degree of moment stability scaled by T_{SF} depends on the spin fluctuation rate which in turn is proportional to the effective exchange coupling $\{N_L(E_F)J_{exc}\}$ of the magnetic d (or f) states with the host conduction electrons, where $N_L(E_F)$ is the local density of states at the Fermi level and J_{exc} is the exchange integral [13]. Recent photoemission studies have revealed that the density of states in Pd does not change when alloyed with Fe [14]. Approximating $N_L(E_F)$ to be equal to $N(E_F)$ in the host, the high moment stability can arise from an enhanced value of J_{exc} which in the present case is mainly between the impurity d and the host d states. The relative strength of the d-d interaction in the alloys can be scaled by the strength of the host polarization S_{host}, i.e., the moment induced on the nearby Pd atoms. The results listed in Table I show an enhancement of S_{host} with Fe concentration. The higher value of host polarization at larger Fe concentration is consistent with the results obtained from neutron diffraction studies in PdFe alloys which show an increase of moment on Pd from zero to $0.5\mu_B$ [15]. The large polarization of the Pd d band at higher Fe concentration is also supported by data from recent photoemission studies [16]. The increase in S_{host} (induced Pd moment) would imply a higher exchange interaction strength between the Rh $4d$ and the Pd d electrons. Examining the trend of Rh magnetism shown in Table I, it becomes clear that the T_{SF} values are strongly reduced with increasing S_{host}. From these results we are inclined to believe that T_{SF} and

thus spin fluctuation rates are greatly suppressed by the interatomic exchange interaction between Rh $4d$ and Pd d-band electrons.

Next we provide arguments for the sign of the exchange interaction just discussed and its implication on the spin fluctuation rate. Under the premise of Kondo-type models, magnetic moment instabilities arise due to an antiferromagnetic exchange interaction between the impurity d and the host conduction electrons [13]. From the systematics of the Kondo temperature observed for $3d$ ions it has been seen that moment instability increases with the value of the antiferromagnetic exchange coupling strength [1–3]. Thus, if we assume the Rh-$4d$-host-d exchange interaction to be antiferromagnetic, its increasing trend observed in the PdFe system would have resulted in higher spin fluctuation rates and therefore larger T_{SF} values. Contrary to this expectation the magnetism of Rh shows a sharp decrease in the T_{SF} value. Therefore, we suggest that the interaction between Rh $4d$ and host d-band electrons is ferromagnetic and thus responsible for the suppression of spin fluctuation temperature and high stability of $4d$ moment on Rh. Support for ferromagnetic d-d interaction is provided by theoretical calculations using the local-spin-density approximation which show positive host polarization for Rh in Pd [5]. The conclusions arrived at in the present work are consistent with the spin fluctuation behavior of $3d$ ions in certain hosts containing d-band electrons, where the high moment stability indicated by the small T_{SF} value has been suggested to be caused by ferromagnetic interaction between $3d$ and host d electrons [2].

In summary, we have made a microscopic investigation on the magnetism of isolated Rh ions in dilute PdFe alloys and shown that $4d$ spin fluctuation rates can be suppressed by inducing strong ferromagnetic polarization in the host d band and thereby increasing the interatomic exchange interaction between Rh $4d$ and host d states. The ferromagnetic d-d interaction seems to be the common mechanism for the high stability of $3d$ and $4d$ moments in hosts containing d-band electrons.

We thank Dr. R. G. Pillay for helpful discussion. We also thank V. V. Krishnamurthy and the Pelletron staff for their help during the experiment.

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[1] For a compilation of experimental data see K. H. Fisher, in *Landolt-Börnstein: Numerical Data and Functional Relationships in Science and Technology*, edited by K. H. Hellwege and J. L. Olsen (Springer-Verlag, Berlin, 1982), Vol. 15, p. 289.

[2] D. Riegel, L. Büermann, K. D. Gross, M. Luszik-Bhadra, and S. N. Mishra, Phys. Rev. Lett. **61**, 2129 (1988).

[3] S. N. Mishra, L. Büermann, K. D. Gross, M. Luszik-Bhadra, and D. Riegel, Phys. Rev. Lett. **63**, 2594 (1989); D. Riegel, L. Büermann, K. D. Gross, M. Luszik-Bhadra, and S. N. Mishra, Phys. Rev. Lett. **62**, 316 (1989).

[4] G. N. Rao, E. Matthias, and D. A. Shirley, Phys. Rev. **184**, 325 (1969).

[5] K. D. Gross, D. Riegel, and R. Zeller, Phys. Rev. Lett. **65**, 3044 (1990).

[6] J. A. Mydosh and G. J. Nieuwenhuys, in *Ferromagnetic Materials*, edited by E. P. Wohlfarth (North-Holland, Amsterdam, 1980), Vol. 1, p. 71; also for a recent theoretical study see A. Oswald, R. Zeller, and P. H. Dederichs, Phys. Rev. Lett. **56**, 1419 (1986).

[7] For a recent review, see H. E. Mahnke, Hyperfine Interact. **49**, 77 (1989).

[8] C. Günther and I. Lindgren, in *Perturbed Angular Correlation*, edited by E. Karlsson, E. Matthias, and K. Siegbahn (North-Holland, Amsterdam, 1964), p. 357.

[9] R. E. Watson and A. J. Freeman, in *Hyperfine Interactions*, edited by A. J. Freeman and R. B. Frankel (Academic, New York, 1967), p. 53.

[10] A. Narath and H. T. Weaver, Phys. Rev. B **3**, 616 (1971).

[11] A. Abragram and R. V. Pound, Phys. Rev. **92**, 943 (1953).

[12] C. Hohenemser, L. Chow, and R. M. Suter, Phys. Rev. B **26**, 5056 (1982).

[13] J. W. Wilkins, in *Valence Instabilities*, edited by P. Wachter and H. Boppart (North-Holland, Amsterdam, 1982), p. 1.

[14] J. F. van Acker *et al.*, Phys. Rev. B **38**, 10463 (1988).

[15] J. W. Cable, E. O. Wollan and W. C. Koehler, Phys. Rev. **138**, A755 (1965).

[16] J. F. van Acker, P. J. W. Weijs, J. C. Fuggle, K. Horn, H. Haak, and K. H. J. Buschow, Phys. Rev. B **43**, 8903 (1991).