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Spin fluctuations of isolated Fe impurities in Pd-based dilute alloys: effect of ferromagnetic host spin polarization

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Abstract

The magnetic moment and spin fluctuation temperature T_{SF} of isolated Fe atoms in a number of Pd-based binary alloys, namely $Pd_{0.95}M_{0.05}$ (M = Ni, Rh, Mo, Ag, Cd, In, Sn, Th and U), have been determined from the local susceptibility $\chi_{loc}(T)$ of ^{54}Fe probe nuclei measured by means of the time differential perturbed angular distribution (TDPAD) technique. Depending on the element M added to the Pd matrix, the results derived from Curie–Weiss analysis, $\chi_{loc}(T) = C/(T + T_{SF})$, reveal strong enhancement or suppression of the ferromagnetic host spin polarization S_h associated with the giant moment of Fe. Concurrent with the variation in host spin polarization, we have observed a large change in the spin fluctuation temperature T_{SF}, showing an exponential rise with diminishing value of S_h. The results, analysed on the basis of the Kondo model, indicate that spin fluctuations caused by the antiferromagnetic interaction associated with the negative conduction electron spin polarization are suppressed progressively by an incremental addition of a positive contribution to the effective exchange interaction.

1. Introduction

Local magnetism of dilute 3d impurities in metallic hosts continue to attract considerable interest both on experimental and on theoretical fronts. A key problem of current interest is the study of spin fluctuations arising from the exchange interaction between a local moment and the itinerant conduction electrons of the host. Over the past several years, extensive data have been collected for many dilute as well as concentrated alloys including strongly correlated electron systems such as heavy-fermion compounds [1, 2]. The results are generally discussed within the framework of the Kondo model, whereby the local moment of the impurity atom is considered to induce an antiferromagnetic spin polarization of the host conduction electrons,

which, via Heisenberg-type s–d exchange interaction, causes a dynamic fluctuation of the moment, leading to the loss of magnetism below a characteristic temperature T_K/T_{SF}, known as the Kondo/spin fluctuation temperature. Recent experimental studies have indicated that the sign of induced spin polarization of host conduction band electrons plays a crucial role in determining the spin fluctuation behaviour of 3d and 4d impurities in metallic hosts [3–7]. While an increase in the antiferromagnetic interaction enhances T_{SF}, it has been argued that an introduction of a ferromagnetic host spin polarization can cause drastic suppression of the spin fluctuation [3–6], leading to lower T_{SF}. On the theoretical side, extensive studies have been carried out using many different approaches [1] including modern methods, e.g., local spin density (LSD) calculations [8]. Although the calculations have provided important information concerning the occurrence and magnitude of the impurity local moment, it has been difficult to treat spin fluctuations within the existing theoretical models. Therefore, it is desirable to carry out more experimental studies—on single magnetic impurities in metallic alloys—dedicated to examining the influence of host polarizations on the spin fluctuation behaviour.

In this regard, isolated Fe impurities in Pd-based binary alloys can perhaps offer an ideal condition. Pure Pd metal is known to exhibit exchange-enhanced susceptibility with a Stoner enhancement factor of ∼4.5 [9], which makes it an incipient ferromagnet. As such, small concentrations of magnetic 3d impurities, e.g., Fe, Co, Ni, dissolved into Pd are known to induce strong ferromagnetic spin polarization of host d-band electrons extending over several atomic lengths and thereby giving rise to the occurrence of giant moments with extremely small T_{SF} values [10–13]. On the other hand, impurities like V and Cr have instead been shown to induce an antiferromagnetic spin polarization [14, 15]. Thus, by alloying Pd with small concentrations of suitably selected elements, the strength of the ferromagnetic spin polarization of the Pd 4d-band electrons around an isolated Fe impurity can be made to increase or decrease. Therefore, a microscopic investigation of the magnetic response of an Fe impurity in Pd-based binary alloys is likely to provide important information on the effect of host spin polarization on the spin fluctuation behaviour of the magnetic moment associated with the impurity. In this respect, time differential perturbed angular distribution (TDPAD) spectroscopy, which has been found to be extremely useful for studying magnetism and spin dynamics of extremely dilute impurities in metals and alloys, is particularly suitable [16, 17].

In this paper, we report the giant moment and spin fluctuation behaviour of isolated Fe impurities in a number of Pd-based binary alloys, namely $Pd_{0.95}M_{0.05}$ (M = Ni, Rh, Mo, Ag, Cd, In, Sn, Th and U), via measurements of the local susceptibility of a ^{54}Fe nuclear probe using the TDPAD method. With the addition of a small amount of different solutes, we find a suppression or an enhancement of the ferromagnetic spin polarization of host matrix, with a large concomitant increase or decrease in the T_{SF} value, respectively, depending on the number of valence electrons added to or removed from the Pd 4d band. We show that the spin fluctuations caused by antiferromagnetic Kondo interaction associated with negative conduction electron spin polarization are suppressed progressively by an incremental addition of a positive contribution to the effective exchange interaction.

2. Experimental details

The Pd alloys, namely $Pd_{0.95}M_{0.05}$ (M = Ni, Mo, Rh, Ag, Cd, In, Sn, Th and U), were prepared by arc melting stoichiometric quantities of high-purity (>99.99%) elemental metals in an argon atmosphere. The alloys were rolled to thin foils of 0.5 mm thickness and then annealed at 900 °C for 4–5 days, followed by rapid quenching in ice cold water. The structure, composition and homogeneity of the samples were verified by x-ray diffraction and energy dispersive analysis of x-rays (EDAX) techniques. We did not find indications of the presence of any intermetallic phase or chemical clustering in our samples.

The TDPAD experiments were carried out at the Pelletron heavy-ion accelerator facility, TIFR, Mumbai. The magnetic response of Fe atoms in the hosts of interest was studied via hyperfine interaction of the 10^+ isomeric state of ^{54}Fe nucleus ($T_{1/2} = 360$ ns, $g_N = 0.728$) [18]. The probe nuclear state was produced by the reaction ^{45}Sc (^{12}C, p2n) ^{54}Fe using a 40 MeV pulsed ^{12}C beam. The ^{54}Fe nuclei recoiling out of the thin Sc target foil were implanted deep ($\sim$1–2 μm) inside the Pd alloy hosts at concentrations well below 1 ppm. The measurements were performed within a time window of 10 ns to 2 μs immediately after implantation. These experimental conditions ensure negligible impurity–impurity interaction, and the results reflect the magnetic response of a truly isolated impurity. The observations were made in the temperature range 25–300 K in a transversely applied magnetic field B_{ext} of 2 T. The time spectra for various γ-energies from the 10^+ isomeric state in ^{54}Fe were collected using two high-purity germanium detectors, each having an efficiency of $\sim$30% and a time resolution of $<$4 ns for $E_\gamma = 1.3$ MeV. The detectors were placed at $\pm 135^\circ$ with respect to the beam direction. From the background corrected normalized counts $N1$ and $N2$ for the two detectors, the spin rotation spectra $R(t)$ defined as [16, 17]

$$R(t) = (N1 - N2)/(N1 + N2) \tag{1}$$

were constructed and then fitted with the function [16, 17]

$$R(t) = (3/4)A_2 e^{-t/\tau_N} \sin(2\omega_L t - \phi) \tag{2}$$

to extract the Larmor frequency ω_L and the nuclear relaxation time τ_N. In the presence of an external magnetic field B_{ext}, the observed ω_L corresponds to the effective magnetic field $B_{eff} = B_{ext} + B_{hf}$ seen by the nucleus. Here, B_{hf} is the hyperfine field at the nuclear site. For paramagnetic hosts, B_{hf} is proportional to the applied magnetic field and $\omega_L = g_N \mu_N \beta B_{ext}$, where β is known as the paramagnetic enhancement factor and β-1 gives a measure of the local susceptibility of Fe. Here, $\beta = 1 \pm 0.02$ reflects the nonmagnetic behaviour of Fe, while $\beta < 1$ and $\beta > 1$ indicate the presence of spin and orbital local moment of Fe, respectively [16, 17].

3. Results and discussion

Figure 1 shows typical spin rotation spectra $R(t)$ and their Fourier transforms observed for ^{54}Fe in Pd–M alloys. Each spectrum shows a well defined single frequency with high amplitude, indicating that most of the implanted Fe atoms contributing to $R(t)$ were located at a unique lattice site, which most likely is substitutional. From a comparison of the observed A_2 values with those reported for various metals including liquid Hg [19], the fraction of ^{54}Fe probe atoms contributing to the observed $R(t)$ spectra turns out to be more than 85%. Here, we like to point out that in the random alloys under investigation, the $R(t)$ spectra are expected to show a superposition of multiple frequencies arising from different atomic configurations in the near-neighbour (NN) environment of the Fe probe. Such features have been observed for many systems, including $Au_{1-x}Ag_x$ [20], $Au_{1-x}Cr_x$ [21] studied recently via TDPAD measurements. However, in the case of Pd–M alloys, our data show a single frequency with little indication of any other resolvable component, as reflected by the Fourier spectra shown in figure 1. The observed ω_L, therefore, corresponds to the average value from all possible NN contributions. For host materials with large exchange enhancement as studied here, it seems likely that the different NN configurations give rise to strongly overlapping Larmor frequencies, which could not be resolved in the present measurements.

Figure 2 displays the $\beta(T)$ spectra of ^{54}Fe in $Pd_{0.95}M_{0.05}$ alloys for different solutes. The data could be fitted with a Curie–Weiss-type relation, $\beta(T) - 1 = C/(T + T_{SF})$, where the Curie constant $C = g\mu_B(S_{eff} + 1)\ B(0)/3k_B$ provides a measure of the net magnetic moment

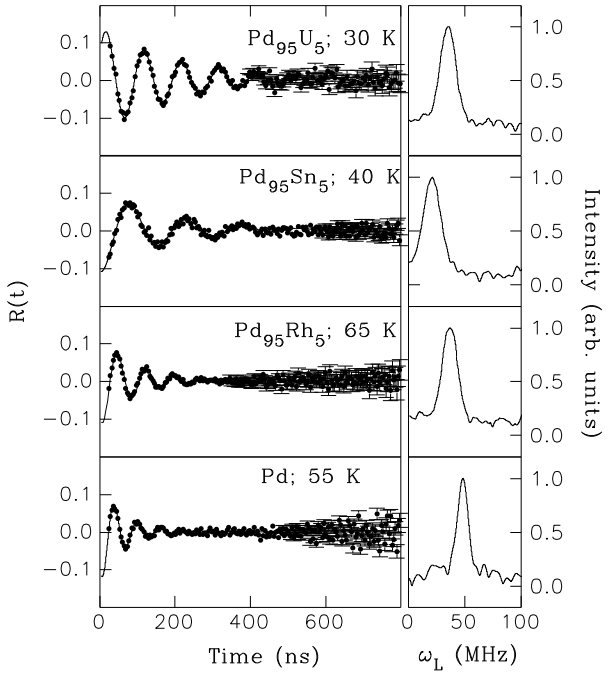

Figure 1. Typical spin rotation spectra $R(t)$ and their Fourier transforms for ^{54}Fe in some $Pd_{0.95}M_{0.05}$ alloys.

$\mu_T = (gS_{\rm eff})$ seen by the Fe probe. Here, $B(0)$ is the Fe magnetic hyperfine field at $T = 0$ K and $S_{\rm eff}$, the effective spin, is the sum of the Fe impurity spin $S_{\rm imp}$ and any possible spin polarization $S_{\rm h}$ of the host conduction electrons. The results derived for different solutes are summarized in table 1. The μ_T and $S_{\rm h}$ values, estimated using $B(0)$ values taken from [22–24] and $S_{\rm imp} \sim 1.75$ corresponding to Fe magnetic moment $\mu_{\rm Fe} \sim 3.5\ \mu_{\rm B}$ [11], are also shown in table 1. For Fe in pure Pd metal, the observed total moment $\mu_T \sim 11.5\ \mu_{\rm B}$ reflects the existence of a giant moment with a large ferromagnetic spin polarization $S_{\rm host} = 3.95$ of Pd 4d-band electrons, consistent with the results reported earlier [10–12]. With the addition of small amounts of different types of solute to the Pd matrix, the host spin polarization associated with the giant moment of Fe changes significantly. While the magnitude of $S_{\rm h}$ increases for M = Ni and Rh, yielding much higher values of μ_T compared to the value in pure Pd host, the data for M = Mo, Ag, Cd, In, Sn, Th and U show substantial reduction of the host spin polarization. Here, we like to emphasize that any uncertainty in $B(0)$, and in the consequent spread in μ_T and $S_{\rm h}$ values estimated, do not alter the observed trend and essential conclusions drawn from it. From the results shown in figure 2 and table 1, it appears that the change of Fe magnetism in Pd–M alloys depends on the electronic structure of the solute element M. With the exception of the data for Pd–Ni, where an additional spin polarization due to the Ni magnetic moment [10–12, 25, 26] also contributes to $S_{\rm h}$, the observed variation in the induced ferromagnetic spin polarization of the host matrix can be explained in terms of solute-dependent changes in the Stoner enhancement factor caused by filling or emptying of the Pd 4d band, which in turn depends on the number of valence electrons added or removed by the solute atom M.

The $\beta(T)$ data also yield information on the Fe moment stability, which can be scaled by the spin fluctuation temperature $T_{\rm SF}$ derived from the Curie–Weiss fit. The results for different

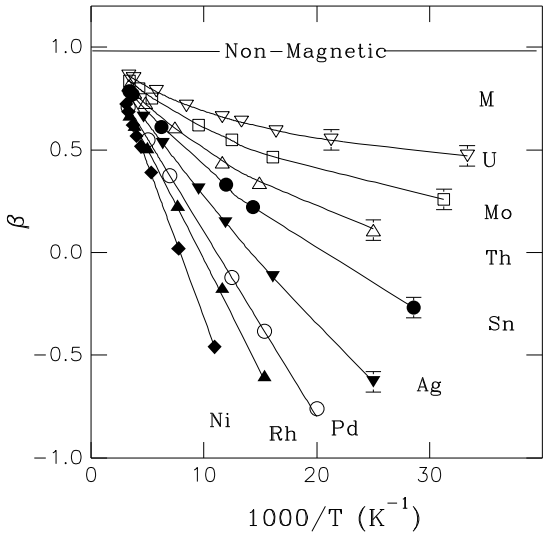

Figure 2. Paramagnetic enhancement factor β of ^{54}Fe in different $Pd_{0.95}M_{0.05}$ alloys plotted as a function of inverse temperature. The solid lines correspond to fits by the Curie–Weiss law: $\beta(T) - 1 = C/(T + T_K)$, where $\beta = 1 \pm 0.02$ represents the non-magnetic behaviour of Fe.

Table 1. Summary of Curie constant C, spin fluctuation temperature T_{SF}, net magnetic moment at the Fe site μ_T, and host spin polarization S_h for Fe in $Pd_{0.95}M_{0.05}$ alloys. Numbers within brackets show the corresponding estimated errors. The second column shows the number of valence electrons n added to (positive values) or removed from (negative values) the Pd 4d band; n = solute concentration× the number of outer electrons of the solute atom.

Solute M	n	C (K)	T_{SF} (K)	μ_T (μ_B)	S_h
Ni	−0.10	−151(2)	0.1(3)	20.5(3)	8.50(15)
Rh	−0.05	−102(2)	0.3(3)	13.3(3)	4.9(15)
Pd	0.00	−91(2)	0.6(3)	11.5(2)	3.95(10)
Ag	0.05	−81(2)	2(1)	10.1(2)	3.40(15)
Cd	0.10	−77(2)	5(2)	9.5(2)	2.99(15)
In	0.15	−71(2)	11(3)	8.6(2)	2.68(20)
Sn	0.20	−70(2)	18(4)	8.4(2)	2.46(18)
Th	0.20	−69(2)	21(5)	8.3(2)	2.41(25)
V	0.25	−66(2)	33(8)	7.8(3)	2.17(20)
Mo	0.30	−58(3)	62(15)	7.0(5)	1.81(30)
U	0.30	−56(4)	80(15)	6.6(5)	1.61(30)

Pd–M alloys are listed in table 1. For Fe in pure Pd, the observation of Curie-like susceptibility reflects a very small value of T_{SF} (<1 K), which is consistent with the results reported in the literature [13]. In the case of Pd–M alloys for M = Ni and Rh, the measured $\beta(T)$ also indicate extremely low T_{SF} values. On the other hand, for M = Mo, Ag, Cd, In, Sn, Th and U, the derived values of T_{SF} turn out to be much higher. Moreover, the value of T_{SF} increases progressively in the sequence Pd < Ag < Cd < In < (Sn, Th) < (Mo, U). The observed trend indicates that like S_h, the T_{SF} of Fe in Pd–M alloys also depends on the electronic structure of the solute, particularly on the number of electrons added to or removed from the d band of Pd. As one notable feature, the results shown in table 1 reveal that an increase in T_{SF} is accompanied by a reduction in the magnitude of S_h.

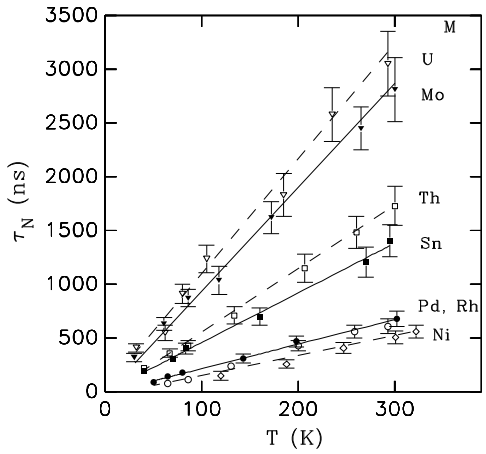

Figure 3. Nuclear relaxation time τ_N of ^{54}Fe probe in different Pd–M alloys plotted as a function of temperature. The solid lines correspond to fits with the Korringa relation (see text). For visual clarity the data for M = Ag, Cd and In have been omitted.

Information about the spin fluctuation temperature of Fe in Pd–M alloys can also be obtained from the nuclear relaxation time τ_N extracted from the damping observed in the $R(t)$ spectra. For an isolated magnetic impurity in a metallic host, the observed damping is related to the spin fluctuation rate τ_J^{-1}, via the relation $\tau_J^{-1} = 2(\mu_N g_N B(0)/\hbar)^2(S+1)S^{-1}\tau_N$ [16, 17], whose temperature dependence follows the Korringa relation $\tau_J^{-1} = \pi/\hbar[(2S+1)J_{ex}\rho]^2 k_B T$. Here, J_{ex} is the exchange interaction between the magnetic moment and the conduction electrons of the host matrix, and ρ is the density of states at Fermi energy. Applying the Kondo model [27] and using the $(J_{ex}\rho)$ value obtained from the $\tau_N(T)$ data, the spin fluctuation temperature T_{SF} can be estimated from the relation $T_{SF} = T_F \exp[-1/(J_{ex}\rho)]$, where T_F is the Fermi temperature for the host. Figure 3 shows the variation of τ_N with temperature for ^{54}Fe in different Pd–M alloys. For Fe in pure Pd, the $\tau_N(T)$ data yield $(J_{ex}\rho) \sim 0.08$ and the corresponding $T_{SF} \sim 0.3$ K shows a good agreement with the result obtained from the $\beta(T)$ data. Compared to pure Pd metal, the τ_N values observed for Pd–M alloys turn out to be smaller for M = Ni and Rh, while they are significantly higher in the cases of M = Ag, Cd, In, Sn, Th, Mo and U. It is important to mention that for Pd–M alloys studied here, the damping in the $R(t)$ spectra would have contributions arising from dynamic fluctuations of the Fe moment as well as from the broadening of ω_L due to the distribution of the local environment. Although it is difficult to rule out the latter, considering that τ_N increases with decreasing magnetic response of Fe, and that it also exhibits linear (Korringa-like) temperature dependence, it is reasonable to assume that the relaxation observed in the spin rotation spectra for the Pd–M alloys arises predominantly because of the dynamic fluctuations of the Fe moment. The T_{SF} estimated from the $\tau_N(T)$ data turned out to be <0.1 K for Ni and ∼11, 19, 53, 82 K for Sn, Th, Mo and U, respectively, which are in good agreement with the values obtained from $\beta(T)$ data (see table 1).

In the following, we mainly discuss our results for the spin fluctuation temperature of Fe in Pd–M alloys and begin by analysing the experimental data within the framework of the Kondo model, where fluctuation of the magnetic moment is considered to arise due to an antiferromagnetic interaction between the impurity spin and the negative spin polarization of the host conduction electrons. The fluctuation rate scaled by the T_{SF} value depends on the magnitude of the effective interaction strength $J_{ex}\rho$ between Fe 3d and host conduction

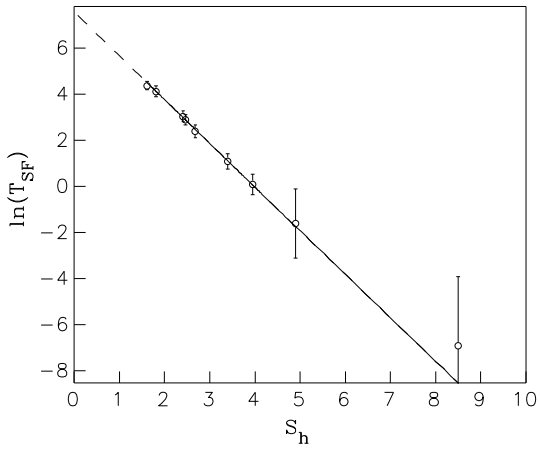

Figure 4. Plot of $\ln(T_{SF})$ versus S_h. The straight line through the data points is a guide to the eyes.

electrons. Here, $J_{ex} \sim -|V|^2/\epsilon_d$ is the exchange constant, which depends on the hybridization strength $|V|$, and ϵ_d is the position of the impurity virtual bound state (VBS) [1] relative to the Fermi energy. For the Fe impurity in Pd–M alloys, the hybridization strengths are expected to be large due to the strong overlap of the Fe 3d states with the host d band. A rough estimation using formulae given in [28–31] yield $|V| \sim 0.5$ eV. Assuming the VBS to be close to the Fermi level ($\epsilon_d < 0.2$ eV), the value of T_{SF} would result in being $>10^4$ K. We would like to emphasize that for the dilute Pd–M alloys studied here, the small variation in $|V|$ or ρ due to changes in interatomic distances and electron concentration, respectively, do not yield such an appreciable reduction in T_{SF} as seen from our experimental data. A reduction in T_{SF} might be possible with tuning of the Fermi level as reported for some U intermetallic alloys [32]. However, in the present case the change in E_F estimated using the free-electron model turns out to be very small (<0.1 eV), which cannot explain the observed trend. As a plausible mechanism, we suggest that a positive spin polarization, giving rise to a ferromagnetic interaction between the Fe 3d and host conduction electrons, can cause such a drastic reduction of T_{SF}.

To examine the effect of host spin polarization on the spin fluctuation temperature, we look into the trends of Fe magnetism in Pd–M alloys. From the results summarized in table 1, it can be easily noticed that the T_{SF} of Fe increases concomitantly with decreasing magnitude of positive host spin polarization S_h. Figure 4 shows the variation of $\ln(T_{SF})$ as a function of S_h for different Pd–M alloys, which reveals a clear exponential dependence of T_{SF} on S_h. The data when extrapolated to $S_h = 0$, where antiferromagnetic Kondo interactions start to take over, yield the value of $T_{SF} \sim 2000$ K. Such a high value of T_{SF} implies that the Fe moment in Pd–M alloys at this point would be highly unstable, rendering it to be non-magnetic, which is consistent with the predictions based on the Kondo model. Starting from this non-magnetic case, the observed sharp reduction in T_{SF} with increasing magnitude of S_h (see figure 4) suggests that the spin fluctuation of Fe is strongly suppressed by the ferromagnetic interaction between the Fe moment and the induced positive spin polarization of the matrix. The features of Fe magnetism in Pd–M alloys thus illustrate that a ferromagnetic spin polarization of the host matrix has a crucial effect on the spin fluctuation temperature, and complement our earlier results reported for the 4d moment of Rh impurity in dilute PdFe alloys [4].

In summary, we have investigated the local magnetism of an isolated Fe impurity implanted into a number of Pd-based binary alloys, namely $Pd_{0.95}M_{0.05}$ (M = Ni, Mo, Rh, Ag, Cd, In, Sn,

Th and U), by using the TDPAD technique. We have observed a reduction or an enhancement of the ferromagnetic spin polarization of the host matrix depending on the type of solute, and therefore on the number of electrons added to or removed from the 4d band of Pd. Concurrent with this, we find a large variation in T_{SF}, showing an exponential increase with decreasing magnitude of S_h. The results, analysed on the basis of the Kondo model, indicate that the spin fluctuations caused by the antiferromagnetic interaction associated with the negative conduction electron spin polarization are suppressed progressively by an incremental addition of a positive contribution to the effective exchange interaction.

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