Magnetic-Moment Formation and Spin Dynamics of Isolated 4*d* Ions in Palladium

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By applying the perturbed-γ-ray-distribution method following heavy-ion reactions we have observed nonmagnetic behavior for Mo and Tc ions in Pd, but a high local susceptibility for Ru in Pd consistent with the formation of a giant 4*d* moment. These trends agree with local-spin-density calculations, yielding a magnetic moment for Ru in Pd and a strong ferromagnetic host-*d*-spin polarization if Ru, Rh, and Pd ions in Pd are locally magnetized by a small magnetic field. We suggest that the occurrence of magnetism and the spin-fluctuation temperatures for 4*d* and 3*d* ions in Pd are strongly correlated with the sign and strength of the induced host-*d*-spin polarization.

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Recently, it has been proposed that the magnetism of 3*d* ions in metals strongly depends on the type of conduction electrons in the host.[1,2] 3*d* ions in *sp*-band metals reflect an ionic-type magnetism where the tendency towards magnetic behavior is driven by intra-atomic correlations of a spin-orbit-coupled 3*d* configuration and where the tendency towards nonmagnetic behavior is essentially governed by spin fluctuations caused by the antiferromagnetic exchanges of impurity 3*d* electrons with host *sp*-band electrons. This ionic-type picture can be even generalized to the magnetism of 4*d* ions in alkali-metal hosts exhibiting the phenomena of large orbital contributions, extremely small spin rates, and well-defined ionic 4*d* configurations.[1] A qualitatively different behavior has been observed for 3*d* ions in hosts with *d*-band electrons including Cu, Ag, Au, and even Hg. It has been proposed that the magnetism in these systems is widely governed by interatomic interactions between impurity-3*d* and host-*d*-band electrons. This interatomic *d*-*d* interaction is assumed to produce the more itinerant, spin-dominated magnetism, which usually is parametrized by an effective spin $S_{\rm eff}$, and, moreover, is assumed to govern the existence and stability of magnetic 3*d* moments in hosts with *d*-band electrons.[2]

Perhaps the most illustrative example for the crucial role of interatomic 3*d*–host-*d*-electron interactions on magnetism is 3*d* ions in Pd, which has attracted much interest since the observation of giant moments.[3] For example, for Fe in Pd, the total moment is $10\mu_B$. It is believed that interatomic 3*d*–host-*d*-band interactions induce extremely large host-*d*-spin polarizations around the 3*d* shell in such giant-moment systems. Another interesting feature is the extraordinarily high moment stability found for certain 3*d* ions in Pd, which corresponds to a very small spin-fluctuation rate or Kondo temperature T_K. Despite extensive experimental and theoretical work dedicated to 3*d* ions in Pd (see, e.g., Ref. 4), the origin of the extreme high moment stabilities and their dependence on the 3*d* ion species has not been clarified as yet.

Stimulated by the many interesting aspects of the physics of 3*d* ions in Pd and also by the occurrence of strong magnetism for 4*d* ions in alkali-metal hosts, we have explored the possible occurrence of magnetism for 4*d* ions in Pd. In this Letter, we report on experimental and theoretical studies of the magnetism and electronic structure of 4*d* ions in Pd, with special attention to the role of interatomic *d*-*d* interactions. Some of the questions investigated are as follows: Can one find local 4*d* magnetism in Pd? If so, which 4*d* ions reflect magnetic behavior? What is the influence of interatomic *d*-*d* interactions on the magnetism; in particular, what is the sign and magnitude of the host-*d*-spin polarizations?

Macroscopic studies of 4*d* ions in Pd are hampered by the enhanced susceptibility of the Pd host, so that it is difficult to disentangle impurity and host effects. Such difficulties can be largely avoided by the application of the perturbed-angular-γ-ray-distribution (TDPAD) method, which allows microscopic studies of the magnetism of extremely dilute (<1 ppm) 4*d* ions in Pd. The systems were produced by recoil implantation following heavy-ion reactions. For the detection of the magnetic hyperfine interaction we used the isomeric states in ^{90}Mo (lifetime $\tau=1600$ ns, *g* factor $g_N=-0.174$), ^{94}Tc ($\tau=7$ ns, $g_N=1.0$), and ^{95}Ru ($\tau=15$ ns, $g_N=0.86$) which were produced by the nuclear reactions ^{61}Ni(^{36}Ar, $\alpha 2pn$)^{90}Mo, ^{78}Se(^{19}F,$3n$)^{94}Tc, and ^{63}Cu(^{36}Ar,$3pn$)-^{95}Ru, respectively. Pulsed ^{36}Ar beams with energy 135 MeV and ^{19}F beams with energy 75 MeV were provided by the VICKSI accelerator at the Hahn-Meitner-Institut, Berlin. The target assembly was mounted to a Cu cold finger of a He cryostat which allowed a temperature variation between 20 and 300 K. Spin-rotation patterns $R(t)$ were measured with various γ lines in an

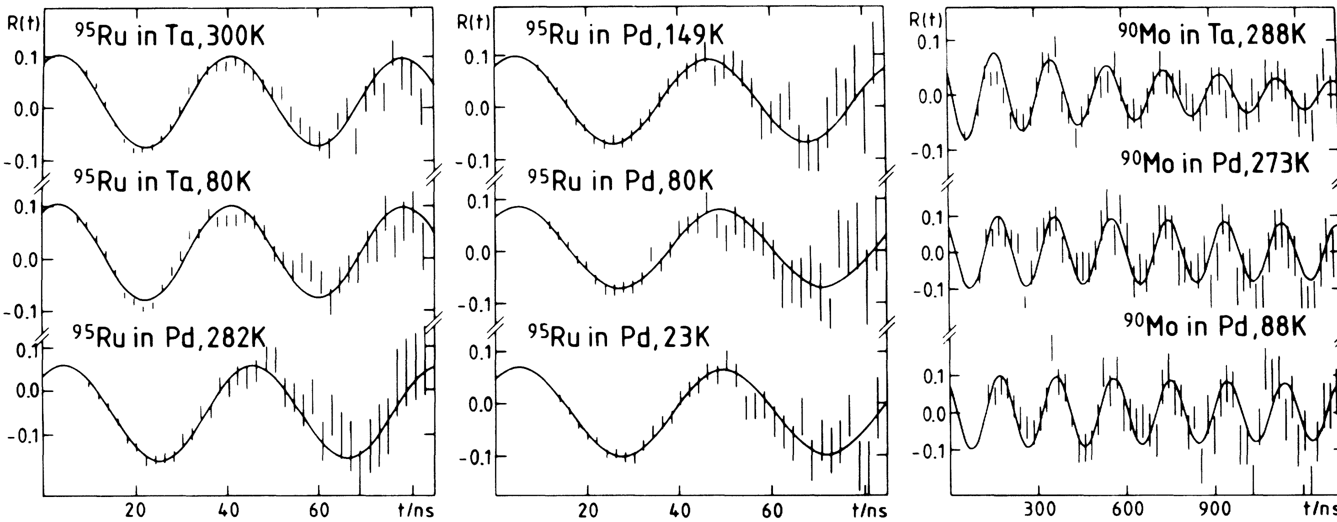

FIG. 1. Spin-rotation patterns $R(t)$ of ^{95}Ru and ^{90}Mo ions in Pd and Ta. The decreased temperature-dependent frequencies reflect the magnetic Ru moment in Pd.

external field B_{ext} of 2 T. A detailed description of local-moment studies by the TDPAD method can be found in Ref. 5.

Examples of $R(t)$ are given in Fig. 1. From $R(t)$ the Larmor frequency ω_L can be deduced, which, using $\omega_L(T)=\hbar^{-1}g_N\mu_N B_{ext}\beta(T)$, yields a measure of the local susceptibility[2,5] $\beta(T)-1$. The observation of only one frequency for Mo, Tc, and Ru in Pd, along with the experience for 3d ions implanted in hosts such as Pd, Ni, Cu, Rh, Ag, Ir, Pt, and Au,[2,5] provides a good argument for the assumption that the implanted 4d ions occupy substitutional lattice sites in Pd. Figure 2 shows the $\beta(T)$ results for Mo and Ru systems and also the data for ^{100}Rh in Pd measured by Rao, Matthias, and Shirley;[6] $\beta(T)\equiv 1$ represents nonmagnetic behavior as, e.g., found for Mo and Ru in Ta and Pt. The results for 4d ions in Pd can be summarized as follows: (i) For Mo, and with less accuracy also for Tc ions from the middle of the 4d row, we have found nonmagnetic behavior in Pd, whereas Ru and Rh in Pd turn out to be strongly magnetic. (ii) The $\beta(T)$ for Ru and Rh ions in Pd are smaller than 1 and strongly temperature dependent. (iii) For both systems the local susceptibility can be well parametrized by a Curie-Weiss-type behavior, $\beta-1\simeq C/(T+T_K)$, which yields the estimates $C\simeq -57$ K, $T_K\simeq 280$ K for Ru in Pd and $C\simeq -30$ K, $T_K\simeq 210$ K for Rh in Pd. The corresponding fits are shown in Fig. 2. For comparison, we have included in Fig. 2 susceptibility data for Pd metal,[7] which also can be parametrized by a Curie-Weiss law with $C=-20$ K and $T_K\simeq 400$ K. The observation of a Curie-Weiss-type behavior for all magnetic 4d systems shown in Fig. 2 disfavors an interpretation in terms of an exchange-enhanced Pauli susceptibility along with uncertain assumptions for its temperature dependence (cf. Ref. 6).

The derived C values compare with the Curie constants deduced for the classical moment systems of 3d ions in noble- and transition-metal hosts. For Ru in Pd, C is even twice as large as for Fe in Au and only 30% smaller than for Fe in Pd.[2] The Curie constant $C=2\mu_B \times(S_t+1)B(0)/3k_B$ scales with the total spin $S_t=S_0+S_h$ of the impurity cell S_0 plus the host-d-spin polarization S_h and with the hyperfine field $B(0)$ at the nucleus of the 4d impurity,[2,5] for which we use the estimate $B(0)/S_0=-70$ T (see Ref. 6). Even if one assumes S_0 to be as large as 0.5 for Ru in Pd, this yields $S_t=2.6$, i.e., a total moment of more than $5\mu_B$. Using smaller S_0 values one finds even higher S_t estimates. From this consideration it appears likely to us that Ru and presumably also Rh form giant 4d moments in Pd.

Parallel to the experimental investigations, we have applied local-spin-density calculations in order to get theoretical information about the magnetism and electronic structure for 4d ions in Pd, in particular, for the

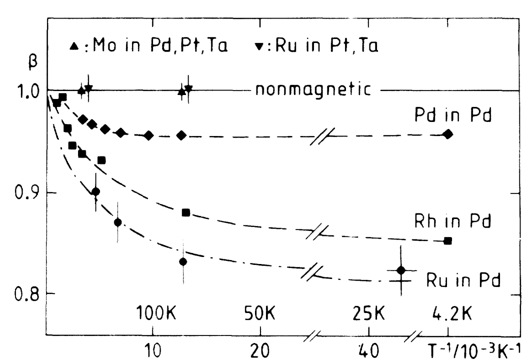

FIG. 2. Local susceptibilities for Mo, Ru, Rh (taken from Ref. 6), and Pd (taken from Ref. 7) ions in Pd metal. The dashed lines represent Curie-Weiss fits to the data.

induced host-d-spin polarization. The calculations are based on the muffin-tin Green's-function method to solve the single-particle Kohn-Sham equations. The details of the method can be found elsewhere,[8] and we restrict ourselves to noting that potential perturbations on the $4d$ atom and 86 nearest Pd neighbors are determined self-consistently. Angular momenta up to $l_{max}=4$ are included and the form of von Barth and Hedin for the exchange and correlation is used, with parameters as chosen by Moruzzi, Janak, and Williams.[9] The correct embedding of the cluster of 87 atoms into the infinite Pd crystal is given by the Green's function of the host. In our calculations we first applied a constant local magnetic field within the atomic cell of the $4d$ ions. The self-consistent results for the induced $4d$ moments M_0^+ and the induced moments M_1^+ on the nearest-neighbor Pd atoms are given in Table I together with the experimental results and older calculations for $3d$ ions.[4] (Note that the $3d$ results were obtained with 43 perturbed atoms, $l_{max}=2$, and without applied field.) The calculated moments M_0^+ for Ru and Rh are rather large and we investigated whether they are stable after the field is switched off. For Rh and also for Tc the self-consistency iterations converged very slowly to the nonmagnetic result ($M_0=0$, $M_t=0$) indicating that these $4d$ ions are almost magnetic. Rather surprisingly, but in agreement with our experiments, we found a stable magnetic moment of $M_0=0.30\mu_B$ for Ru in Pd. It is surrounded by an extended magnetization cloud with a total magnetization of $0.77\mu_B$ within the 87 considered atoms. Since self-consistency iterations easily miss a magnetic solution if it is energetically close to a nonmagnetic one, we tried to obtain a magnetic solution for Rh by increasing the atomic number from $Z=44$ (for Ru) to $Z=45$ (for Rh) in noninteger steps of 0.1. We found the maximal moment for $Z=44.2$ with a value of $0.50\mu_B$ and a corresponding total magnetization of $1.41\mu_B$. For $Z>44.4$ no magnetic solution was found.

TABLE I. Experimentally derived values for the Kondo temperatures T_K, Curie constants C, and moments M_{expt} and theoretical results on the magnetism of d ions in Pd. M_0 and M_t represent the moments at the d ion site and the corresponding total moments as obtained from *ab initio* calculations. M_0^+ and M_1^+ refer to the calculated moments at the $4d$ ion site and at the first neighboring Pd atom with application of an internal field. All moments are given in units of μ_B. NM denotes nonmagnetic.

	Mo	Tc	Ru	Rh	Pd
C (K)	NM	NM	−57	−30	−20
T_K (K)			280	210	400
M_0	0	0	0.30	0	0
M_t	0	0	0.77	0	0
M_0^+	0.028	0.081	0.685	0.111	0.013
M_1^+	−0.001	+0.001	+0.038	+0.010	+0.002
M_1^+/M_0^+	−0.027	+0.008	+0.056	+0.094	+0.126
	Cr	Mn	Fe	Co	Ni
T_K (K)[a]	200	$<10^{-2}$	$<10^{-3}$	0.1	30
M_{expt}[b]		6.5–8	10–12	9–10	4.6
M_0[b]	3.14	4.13	3.47	2.28	0.92
M_t[b]	2.69	5.12	5.53	4.60	2.18
M_1[b]	−0.024	+0.048	+0.102	+0.114	+0.063
M_1/M_0[b]	−0.008	+0.012	+0.029	+0.050	+0.068

[a]References 2 and 10. [b]Reference 4.

Compared to the experiments, the calculated results correctly reproduce the trend of the magnetism of $4d$ ions in Pd. However, the strength of the magnetic effects seems to be underestimated by the calculations. Using the above relations for the Curie constant and $B(0)$, the calculated moments allow us to estimate theoretical C values, which for Ru, Rh, and Pd in Pd turn out to be smaller than the experimental values by a factor of 2–6. Such a difference between experimental and theoretical values for the total magnetization is at least partly explained by the fact that more than the 86 considered Pd atoms contribute. Also, for $3d$ ions in Pd, the calculations yielded only about half of the total moment observed experimentally[4] (Table I). The theoretical result of a very extended ferromagnetic spin-polarization cloud supports our suggestion that Ru and Rh in Pd can be classified as giant-$4d$-moment systems.

In the following we discuss the role of intra-atomic and interatomic spin correlations on the occurrence and stability of $4d$ magnetism in Pd and its dependence on the $4d$ ion species. As a major point we discuss that the existence and stability of $4d$ and $3d$ moments in Pd are strongly correlated with the sign and strength of the induced host-d-spin polarization, i.e., are strongly correlated to interatomic d-d interactions. The correlation between interatomic d-d interactions and moment stability must be considered in a qualitative way since at present spin-fluctuation rates or Kondo temperatures cannot be predicted by theory.

The observed trend of magnetism for $4d$ ions in Pd is strikingly different from the behavior of $3d$ ions in sp metals and also of $4d$ ions in alkali-metal hosts. For these systems magnetic moments and/or the highest moment stabilities have been found for d ions with nearly half-filled d shells, i.e., for Cr,Mn and for Mo,Tc,[1,5,10] which can be explained by the maximum of intra-atomic spin correlations for these ions. In particular, for $4d$ ions in alkali metals the dominant role of intra-atomic correlations has been clearly established by the finding of very stable moments for Mo (and Tc) but strongly unstable behavior for Ru and nearly nonmagnetic behavior for Rh and Pd in Rb and Cs.[1,5,11] A comparison of these results with the behavior of $4d$ ions in Pd indicates that aside from intra-atomic correlations an interatomic d-d interaction must be regarded as an important mechanism for the occurrence and stability of $4d$ moments in Pd.

In fact, by inspection of Table I one finds that whenever moments with high stabilities are observed for $4d$ and

3*d* ions in Pd, this phenomenon is accompanied by a large calculated ferromagnetic host-spin polarization. As a measure of the host-*d*-spin polarization we use the moment M_1 (or M_1^+) induced at the nearest-neighboring Pd site and the ratio M_1/M_0 (or M_1^+/M_0^+), where M_0 (or M_0^+) is the moment of the impurity cell. The highest values for these quantities have been calculated for *d* ions at the end of the *d* rows, i.e., for Ru, Rh, and Pd in Pd and for Fe, Co, and Ni in Pd. In contrast, Mo (with an applied local field) and Cr ions induce an antiferromagnetic host-*d*-spin polarization in Pd. The values calculated for Tc and Mn ions in Pd indicate a small ferromagnetic host-*d*-spin polarization (Table I).

The observed trends for the occurrence and spin-fluctuation temperatures T_K of 4*d* and 3*d* moments in Pd are consistent with the proposal that a ferromagnetic host-*d*-spin polarization not only enhances the total moment but can also lead to a drastic stabilization of the moments by suppressing the spin fluctuations expected from the antiferromagnetic *d*-*sp* exchanges (see also Ref. 2). Within this picture, the observed magnetic effects for Ru, Rh, and Pd in Pd (Fig. 2 and Table I) can be mainly attributed to a sufficiently large suppression of T_K caused by the strong interatomic ferromagnetic *d*-*d* interaction. The nonmagnetic behavior observed for Tc and Mo ions, which can be parametrized by $T_K > 10^4$ K (compare Ref. 2), can be interpreted by assuming the moment-stabilizing *d*-*d* interaction as being too weak for Tc in Pd and absent for Mo in Pd. Further support for a drastic suppression of T_K for the late 4*d* ions in Pd is given by the finding that 4*d* ions are (nearly) nonmagnetic in any other host, disregarding the alkali metals.

Similar trends have been found for T_K of 3*d* ions in Pd. Presumably because of larger intra-atomic correlations, T_K values for 3*d* ions are systematically smaller than for 4*d* ions in Pd (Table I). For Fe, Co, and Ni in Pd, the observed T_K values are by far the smallest compared to T_K of these ions in any other metallic host. Analogously to the magnetic 4*d* ions in Pd, the suppression of T_K observed for Mn, Fe, Co, and Ni in Pd seems to be correlated with the strength of the induced ferromagnetic host-*d*-spin polarization (Table I). Finally, we discuss the results for Cr in Pd. In contrast to Cr in some *sp* and noble metals, a weak moment with a high $T_K \simeq 200$ K has been deduced for Cr in Pd (Table I). To our mind, for this very different behavior found for Cr compared to other 3*d* ions in Pd, no satisfactory interpretation has been given hitherto, but now seems to be possible based on the trends for stability and host-spin polarization found for both 4*d* and 3*d* ions in Pd. Analogously to Mo in Pd, Cr ions induce a negative host-spin polarization in Pd, which reduces the total moment and which we regard as the main reason for the drastic increase of T_K observed for Cr in Pd compared to T_K observed for Mn and Fe in Pd (Table I).

In summary, we have investigated the magnetic behavior of 4*d* ions in Pd. Different from the trends of 3*d* moment formation in metals, there is no magnetism for 4*d* ions with nearly half-filled *d* shells in Pd but large magnetic effects for Ru and Rh ions in Pd. Local-spin-density calculations correctly reproduce the observed trends of 4*d* moment formation as a function of the 4*d* ions and predict a large ferromagnetic host-spin polarization for the magnetic ions Ru and Rh in Pd and also in Pd metal. The systematic trends for the occurrence and spin-fluctuation temperatures of 4*d* as well as of 3*d* moments in Pd are found to be strongly correlated with the sign and strength of the host-*d*-spin polarization. With regard to the high value of $S_{\rm eff} \simeq 2.6$ estimated for Ru in Pd and the large spatial extent of the calculated polarization cloud, it appears very likely to us that Ru and Rh in Pd can be classified as giant-moment systems, analogously to the widely investigated 3*d* systems, such as Mn, Fe, and Co in Pd.

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