Existence and Stability of Magnetic 3*d* Moments in Noble- and Transition-Metal Hosts

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Mainly based on data for local susceptibilities and 3*d* spin rates of dilute Fe ions in many metals, we conclude that the existence and stability of Fe, Co, and Ni moments in Cu, Ag, Au, and certain transition-metal hosts are governed by impurity-3*d* host-*d* electron interactions. As the leading contribution to moment stability we propose ferromagnetic-3*d* host-*d* exchanges which in certain hosts successfully suppress spin fluctuations arising from antiferromagnetic *d*-*sp* exchanges. All host-dependent trends of moment stability of Mn, Fe, Co, and Ni ions in metals are consistent with our proposal.

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Local-magnetic-moment studies have played a major part in the investigation of magnetism of 3*d* ions in dilute alloys, spin-glasses, and concentrated systems.[1,2] The magnetism of 3*d* ions in noble metals has often been regarded as being basically similar to the behavior of 3*d* ions in *sp* metals where the existence of local moments arise from intra-atomic correlations of the 3*d* electrons.[3] On the other hand, it has been recognized that the moment formation of 3*d* ions in transition metals additionally depends on impurity-3*d* host-*d* and possibly on intrahost-*d* band interactions which are most obvious for giant-moment systems, e.g., Fe and Co in Pd.[4] Usually the *d* electron states are regarded as itinerant but group together on the atoms to form local moments.[1] The interplay of intra-atomic, interatomic, and intrahost band interactions is highly complex so that it is usually difficult to relate model predictions to real systems. This is reflected by the poor (essentially missing) answers of theory to the central question of why 3*d* moments exist in certain hosts but not in other hosts.[1-4]

The host dependence of 3*d* moment formation and stability in noble- and transition-metal hosts is the main subject of the present study. At first we present data of the local magnetism and 3*d* spin dynamics of extremely dilute ^{54}Fe ions (<1 ppm) in noble- and *d*-metal hosts measured by perturbed γ-ray distribution techniques following heavy-ion reactions and recoil implantation (time-differential perturbed angular distribution method). Along with data in the literature and with results recently obtained for Fe in *sp* metals,[5] these data yield new insight into the qualitatively different influences of 3*d* host-*d*, and 3*d* host-*sp* hybridization on 3*d* magnetism.

The experiments were performed at the VICKSI accelerator of the Hahn-Meitner-Institut in Berlin. We followed essentially the experimental procedures described previously,[5-7] as the spin-rotation patterns $R(t)$ of ^{54}Fe in Cu, Ag, Au, and in nearly all *d* metal hosts were measured as functions of temperature in an external field of 2 T. The systems were produced by the reaction ^{45}Sc(^{12}C,$p2n$). From the Larmor frequencies $\omega_L(T)=\hbar^{-1}\mu_N g_N B_{\rm ext}\beta(T)$, the local susceptibilities $\beta-1$ are extracted (Fig. 1). Fe in V, Nb, Ta, Mn, Re, Ru, and Os is found to be nonmagnetic, characterized by $\beta(T)\equiv 1$ (Fig. 1), whereas Fe in Cr, Mo, W, Rh, Ir, Pd, Pt, Cu, Ag, and Au exhibit Curie-Weiss-type β's and thus local moments (Fig. 1). For Fe in Sc, Y, Ti, Zr, and Hf we have observed (at least) two frequencies in the $R(t)$ spectra, which correspond to different lattice sites of Fe. In these hosts one response is found to be nonmagnetic with $\beta(T)\equiv 1$ while the other is magnetic with a temperature-dependent $\beta<1$.[8] If available, $\beta(T)$ data from Mössbauer-effect measurements[2,9] agree with our $\beta(T)$ results. As far as we know, reliable data on the magnetism of Fe in Sc, Y, Ti, Zr, Hf, Cr, Mn, and Os have not been published previously.

In addition, we were able to extract nuclear magnetic relaxation times $\tau_N(m)$ (Refs. 6 and 7) from the observed damping of the spin-rotation spectra for Fe in Mo, Rh, Pd, Pt, and Au, which yields information on the spin relaxation rates τ_J^{-1} of the single Fe ion (Figs. 2 and 3). Values for τ_J^{-1} are extracted from $\tau_N(m)$ with the relation[6-8]

$$\tau_J^{-1}=2(\mu_N/\hbar)^2 S_{\rm eff}^{-1}(S_{\rm eff}+1)g_N^2 B^2(0)\tau_N(m)\,.$$

Effective spins $S_{\rm eff}$ and magnetic hyperfine fields $B(0)=-11$, -13, -30, -31, and -20 T for Fe in Mo,

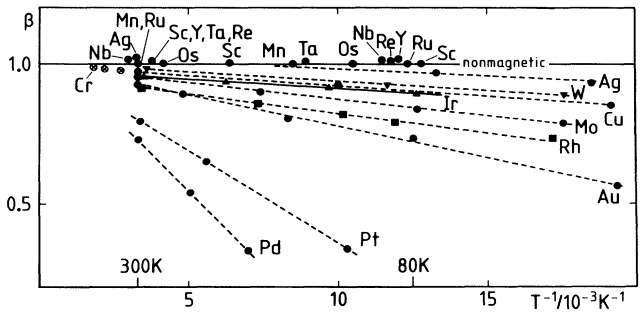

FIG. 1. Local susceptibilities vs $1/T$ for Fe ions in noble and transition metals. The dashed lines serve to guide the eye.

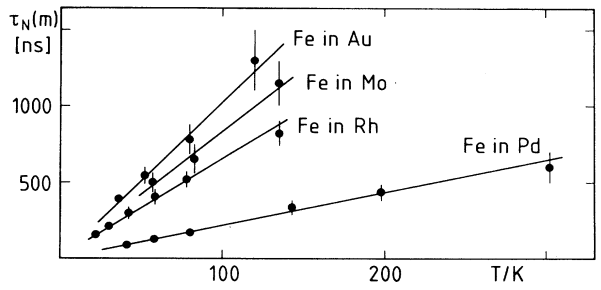

FIG. 2. Nuclear magnetic relaxation times $\tau_N(m)$ and thus the Fe spin rates of very dilute Fe ions in Mo, Rh, Pd, Pt, and Au follow a Korringa law. The data for Fe in Pt fall on the line for Fe in Pd.

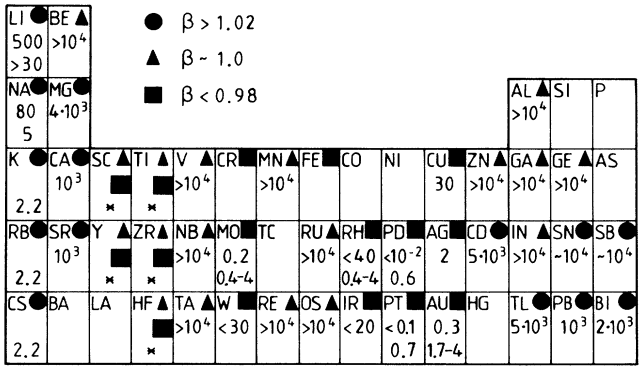

FIG. 3. Characterization of Fe magnetism in metallic elements. Triangles, circles, and squares indicate nonmagnetic, ionic-type (Ref. 5), and S_{eff}-type behavior, respectively. For Fe in Sc, Y, Ti, Zr, and Hf see text and Ref. 8. Numbers directly below the element symbol represent T_K in K as derived from susceptibility data compiled in Refs. 2, 5, and 9 and in Fig. 1. The other number represents Fe spin rates τ_J^{-1} in 10^{12} s^{-1} taken at 100 K by use of data in Fig. 2 and Ref. 5.

Rh, Pd, Pt, and Au, respectively, can be taken from Refs. 2 and 9. Thus the extracted value corresponds to the lower limit for τ_J^{-1} given in Fig. 3. For Fe in Mo, Rh, and Au we have estimated[8] a range of τ_J^{-1} values (Fig. 3) by accounting for possible orbital contributions to $B(0)$ and thus to τ_J^{-1}. As a notable feature, $\tau_N(m)$ and thus τ_J^{-1} nicely follows a Korringa-type behavior $\tau_N(m) \propto \tau_J^{-1}(T) \propto T$ over wide temperature ranges (Fig. 2). The various data for $\beta(T)$ and the spin dynamics of isolated Fe ions in *sp* metals,[5,7] noble metals, and *d* metals (Figs. 1 and 2), obtained by the same method, are a benefit of the study of the host dependence of Fe magnetism.

To work out the basic trends of the host dependence of Fe magnetism in Fig. 3, we characterize the systems by the observed sign of $\beta-1$ (compare Ref. 5) and by the Fe moment instability which can be scaled by spin-fluctuation temperatures T_K (Fig. 3) as deduced from susceptibility data using a Curie-Weiss law $C/(T+T_K)$. The nonmagnetic Fe systems ($\beta=1$) are labeled by $T_K > 10^4$ K. If we are directly sensitive to spin fluctuations, the spin rates provide a second valuable scaling of Fe moment stability. According to the Korringa relation,[5-7] $\tau_J^{-1}=4\pi\hbar^{-1}[N_l(E_F)J_{\text{mix}}]^2 k_B T$, the τ_J^{-1} rates taken at 100 K (Fig. 3) are proportional to the exchange coupling squared. The results exhibit the following essential features:

(a) If magnetic, Fe in *sp* metals reflects ionic (or J_{eff})-type magnetism where the intact *LS* coupling always leads to positive $\beta-1$ values (Ref. 5 and Fig. 3). In contrast, magnetic Fe ions in noble and *d* metals always exhibit negative $\beta-1$ values (Figs. 1 and 3) and thus negative $B(0)$ values along with non-half-integral moments parametrized by S_{eff}.[2,9]

(b) Whereas T_K for Fe in *sp* metals increases rapidly and systematically with reciprocal host volume and thus with lattice pressure,[5] such a correlation does not exist for Fe in noble and *d* metals (Fig. 3).

(c) Instead, Fe moments in noble- and *d*-metal hosts occur in group sequences (Fig. 3, except for Fe in bcc iron).

(d) Because of smaller host volumes, antiferromagnetic *d-sp* exchanges and thus T_K should increase considerably for Fe in Cu, Ag, Au, and in *d* metals compared to Fe in, e.g., Zn, Cd, and Mg. Thus extrapolating the host dependence of β and T_K found for Fe in *sp* metals (Ref. 5, Fig. 3), one expects even larger T_K values and (almost) vanishing $\beta-1$ values and moments for Fe in noble- and *d*-metal hosts due to *d-sp* exchanges alone.

(e) On the contrary, a drastic decrease of T_K by several orders of magnitude is observed in Mo, W, Rh, Ir, Pd, Pt, Cu, Ag, and Au, accompanied by the occurrence of S_{eff}-type magnetism, by Curie-type $\beta-1$, and by Korringa-type Fe spin rates (Figs. 1-3).

(f) τ_J^{-1} and hence exchange couplings in several noble and *d* metals (Fig. 3) are found to be comparable or even smaller than those observed for the fully localized $J=4$, $3d^6$ state of Fe^{2+} in Na, K, Rb, and Cs.[5,7]

We now outline the most important features of a physical picture by which all these results can be explained consistently. Obviously, the magnetism of Fe in noble- and transition-metal hosts exhibits clear-cut and qualitative differences to the behavior of Fe in *sp* metals. The results (a)-(f) directly imply a crucial role for the interatomic $3d$ host-*d* interaction on the magnetism of Fe in hosts with *d* band electrons including Cu, Ag, and Au. The abrupt increase of moment stabilities for Fe in noble- and some *d*-metal hosts as compared to *sp*-metal hosts (see Fig. 3) suggests that moment-stabilizing $3d$, host-*d* interactions are required to decrease the spin-fluctuation rates arising from *d-sp* exchanges alone [see (d)]. As the most probable and consistent explanation

for the existence and stability of Fe moments in Cu, Ag, Au, and certain *d*-metal hosts, we propose ferromagnetic 3*d*, host-*d* interactions which can compete with the always antiferromagnetic *d*-*sp* exchanges and can suppress spin fluctuations by several orders of magnitude. The sign of the *d*-*d* interaction can be obtained from the host-*d* spin polarization. After a brief discussion of result (a), we will concentrate on a more detailed description of the role of *d*-*d* interactions on Fe moment stabilities [results (b)–(f)]. Then we will show that the proposed picture is also supported by the host dependence of moment stabilities for Mn, Co, and Ni ions.

Considering result (a), the change from ionic-type magnetism for Fe in *sp* metals[5] to a S_{eff}-type mechanism for Fe in Cu, Ag, Au, and *d*-metal hosts (Fig. 3) is almost certainly induced by 3*d*, host-*d* hybridization. Usually one can expect a large hybridization due to the large spatial and energetic overlap of Fe (and other magnetic) 3*d* states with host-*d* states in noble and *d* metals. For several 3*d* ions in noble metals and in some *d* metals, a strong *d*-*d* hybridization has been established by, e.g., results from high-energy electron spectroscopies[10] and from various local spin-density calculations.[11–13] The *d*-*d* hybridization increases the tendency towards itinerant and covalent 3*d* behavior which can destroy ionic configurations and can effectively reduce orbital contributions leading to negative $B(0)$ and $\beta - 1$ values (Figs. 1 and 3). The assumption of large crystal fields of about 1 eV for 3*d* ions in metals, by which orbital contributions can be also reduced, should be regarded with reservation, since crystal fields for Fe (Refs. 5 and 7) and other 3*d* and 4*d* ions[6] in *sp* metals have been found to be smaller than the *LS* coupling.

Next we relate the stability and spin fluctuations of Fe moments in *d* metals to the *d*-*d* interaction, in particular to its sign. While spin fluctuations due to *d*-*sp* and *d*-*d* exchanges in real systems are hard to estimate by theory, information about possible *d*-*d* interactions and their sign can be obtained from the host-*d* spin polarization. Usually, *d*-*d* interactions lead to spin-polarized host-*d* electrons near the impurity, induced by exchange interactions of Ruderman-Kittel-Kasuya-Yosida type, mediated by *d* conduction electrons, and also induced by covalent admixtures.[1,11–15] Information on host spin polarizations are available from, e.g., (i) spin-density calculations which yield antiferromagnetic host-*sp* spin polarizations but strongly matrix-dependent host-*d* polarizations.[11–13] (ii) According to coupling rules, discussed by, e.g., Moriya,[1,14] a spin of a more than half-filled 3*d* shell impurity, such as Fe, Co, and Ni, induces a ferromagnetic *d* spin polarization in hosts with a nearly filled or a nearly empty *d* shell. (iii) Stearns[15] has investigated the sign, strength, and range of *d* spin polarizations induced by interactions of Fe 3*d* with *d* electrons of impurities which can also serve as a guide for host spin polarization.

We now discuss the central results (b)–(f) in light of our above proposal. Ferromagnetic-3*d*, host-*d* interactions are widely accepted for the giant moment systems Fe in Pd and Pt (Refs. 1 and 4) exhibiting large host spin polarizations[13] and extremely large suppressions of spin fluctuations (Figs. 2 and 3). A ferromagnetic *d*-*d* interaction for Fe in Rh, Ir, Pd, Pt, Cu, Ag, and Au with a nearly filled *d* band is expected from coupling rules,[1,14] the results of Stearns,[15] and from calculations for, e.g., Fe in Pd (Ref. 13) and in Cu[11,12]. Thus ferromagnetic *d*-*d* interactions seem to be the main reason for the high moment stability of Fe in Rh, Ir, Cu, Ag, and Au, whereas Fe in the neighboring groups Ru, Os, Zn, and Cd is found to be nonmagnetic (Fig. 3). A good test of our proposal stems from the high-Fe moment stabilities observed in Mo and W along with the nonmagnetic behavior in the neighboring group V, Nb, and Ta (Figs. 1–3). The host-*d* spin polarization is calculated to be ferromagnetic for Fe in Mo, but changes sign for Fe in Nb.[12] Within our proposal, a ferromagnetic *d*-*d* interaction is responsible for the existence of Fe moments in Mo (and Cr, W), whereas an antiferromagnetic *d*-*d* exchange for Fe in Nb (and V, Ta) increases T_K in addition to *d*-*sp* exchanges leading to nonmagnetic behavior in agreement with experiment. The calculations predict large Fe moments of $\sim 3\mu_B$ in both Mo and Nb,[12] which agree with experiment for Fe in Mo since T_K is very low, but disagree with experiment for Fe in Nb, most probably because of T_K being too large. It should be noted that spin fluctuations are not included in cluster and spin-density approaches.[11–13] More generally, the abrupt changes from highly stable Fe moments in, e.g., Mo, W, Rh, Ir, Cu, Ag, and Au to nonmagnetic for Fe in V, Nb, Ta, Mn, Re, Ru, Os, Zn, and Cd (Figs. 1 and 3) can be interpreted by the ferromagnetic part of the *d*-*d* interaction as being too weak, or as changing sign (or as being almost absent in Zn and Cd) so that the antiferromagnetic *d*-*sp* exchange is sufficient to destroy the Fe magnetism [see (d)]. The proposed ferromagnetic *d*-*d* interaction is also consistent with the occurrence of Fe moments in group sequences [result (c)] and with the missing correlation with lattice pressure [result (b)]. Albeit the lattice site for the magnetic Fe ions in Sc, Y, Ti, Zr, and Hf (Ref. 8) is unknown at present, one is led to argue that the occurrence of Fe moments in these hosts (Fig. 3) with a nearly empty *d* band is also related to ferromagnetic *d*-*d* interactions.

The moment stability of Co and Ni in metallic elements follows basically the same trends as discussed for Fe systems. Disregarding alkali-metal hosts, Co and Ni are found to be nonmagnetic in the *sp* metals investigated hitherto. Moments have been found for Co in Cu, Au, Mo, W, Rh, Pd, and Pt (Refs. 2 and 16) and for Ni in Pd.[13] Thus the existence of Co moments in just those hosts, where Fe exhibits very stable moments (Fig. 3), also seems to be governed by ferromagnetic *d*-*d* interac-

tions. Presumably because of a smaller intra-atomic exchange splitting, T_K values for Co (Refs. 2 and 16) are systematically larger compared to Fe in the same host.

Mainly because of larger intra-atomic exchange splittings, T_K values for Mn in *sp* metals[2,16] are about 10^4 times smaller compared to Fe in the same host. In noble metals T_K for Mn is about 10^2 times smaller than those for Fe, whereas T_K for Mn and Fe are comparable in Mo, Rh, Pd, and Pt.[2,16] This suggests that the moment-stabilizing *d-d* interaction is weaker for the nearly half-filled-shell Mn impurity in Cu, Ag, and Au and much weaker for Mn in *d*-metal hosts compared to Fe in the same host. This view is consistent with spin-density calculations for 3*d* ions in noble metals,[11,12] Mo,[12] and Pd,[13] which yield the tendency that Fe, Co, and Ni ions induce ferromagnetic host-*d* spins, whereas Cr induces antiferromagnetic host-*d* spins. The host-*d* spins induced by Mn ions reflect a subtle behavior between ferromagnetic and antiferromagnetic polarization.

In summary, all host-dependent trends of existence and stability of Mn, Fe, Co, and Ni moments in noble- and *d*-metal hosts can be consistently explained by moment-stabilizing 3*d*, host-*d* interactions. The data and interpretations of this work provide an important basis for further experimental and theoretical studies of the existence and host dependence of local moments and their spin fluctuations. Ferromagnetic, collective 3*d*, host-*d* interactions should have a crucial influence in spin-glass systems and can be also important for the magnetism of 3*d* ions on surfaces and interfaces, e.g., if one uses Cu, Ag, and Au substrates or overlayers. Moreover, the *d-d* interactions, discussed in the present work, seem to be closely related to short-range order in Fe metal near the ordering temperature[17] and address the physics of local moments and spin correlations in magnetic transition metals and alloys.

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