Local Magnetic Moment Formation of Fe Ions in *sp*-Band Metal Hosts

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Spin and orbital magnetism of Fe ions in *sp* metals are reduced simultaneously from stable ionic Fe^{2+} to nonmagnetic behavior with increasing lattice pressure. The various data and interpretations of the host and temperature-dependent susceptibilities, of $3d$ spin dynamics, and of crystal fields of Fe ions in *sp* metals provide a new critical test of models on moment formation, *d-sp* exchanges, and the Kondo effect of $3d$ ions in *sp* metals. Fe in *sp* metals reflects basic features common to certain $4f$ systems, but with qualitative differences from the magnetism of Fe in noble metals.

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Usually local magnetic moments of $3d$ ions in metals are parametrized by an effective spin S_{eff}, as exhibited for Fe in noble metals and in certain d-band metal hosts. In most approaches, the d electrons are assumed to be itinerant and their orbital contributions are assumed to be quenched by large hybridization and/or crystal fields (CF). Starting with the pioneering work of Friedel and Anderson,[1] the impurity d states in a *sp* metal are often described by virtual bound states overlapping with the *sp* conduction band. In contrast, Hirst[2] suggested an ionic-type approach for magnetic $3d$ ions in noble and *sp* metals which has been thought to be applicable only to $4f$ systems. This approximation starts with ionic ground states, split by the crystal field, and then takes into account hybridization with the host conduction band. The electronic structure and magnetism of $3d$ and $4f$ states in metals are also of central interest for models dealing with spin fluctuations related to the Kondo problem.[3,4]

However, it is not easy to relate model predictions to real systems. On the theoretical side, important quantities of $3d$ moment formation are not sufficiently well understood, e.g., the interactions of the impurity $3d$ with the s, p, and d electrons of the hosts, the atomic spin, and orbital correlations among the $3d$ electrons, and the role of CF effects. Experimental difficulties arise from the fact that Fe, Co, and Ni ions are (almost) nonmagnetic in those *sp* metals in which they can be dissolved. As a consequence, the magnetism of $3d$ ions in noble metals has attracted the special attention of theorists and experimentalists, mainly because these systems are regarded to be simple enough to test model predictions for $3d$ states in *sp* metals. However, the interactions between the impurity $3d$ and host d-band electrons can have a strong influence on the moment formation of Fe in Cu, Ag, and Au.

Essential parts of the experimental difficulties can be overcome by our applying perturbed γ-ray distribution techniques following heavy-ion reactions and recoil implantation (time-differential perturbed angular distribution method) which allow local magnetic-moment studies in alloying as well as in nonalloying systems.[5-7]

Because of the recent observation of a localized ionic $3d^6$ ground state of Fe^{2+} with $L=2$, $S=2$, and $J=4$ in LS coupling in K, Rb, and Cs,[7] we now face the situation that ionic- and S_{eff}-type magnetism occur for the same ion in different host metals. In view of this new phenomenon we have performed a systematic study of Fe moment formation in *sp* metals to investigate the following questions: In which hosts do Fe ions reflect ionic behavior, reduced susceptibilities, S_{eff}-type magnetism, or nonmagnetic behavior? Is it possible to find transitions from ionic- to S_{eff}-type Fe behavior as a function of lattice pressure? What can be learned about the role of hybridization, spin fluctuations, and crystal fields? What are the similarities and differences of the magnetism of Fe in *sp* metals as compared to the magnetism of f ions in metals? We will demonstrate that the observed host and temperature (T) dependences of the Fe magnetism allow a direct test of theoretical models. The resulting picture of Fe magnetism in *sp* metals is simple enough to answer essential parts of the questions formulated above. Moreover, the results yield new insight into Fe moment formation in noble metals.

The systems, most of which are nonalloying, were pro-

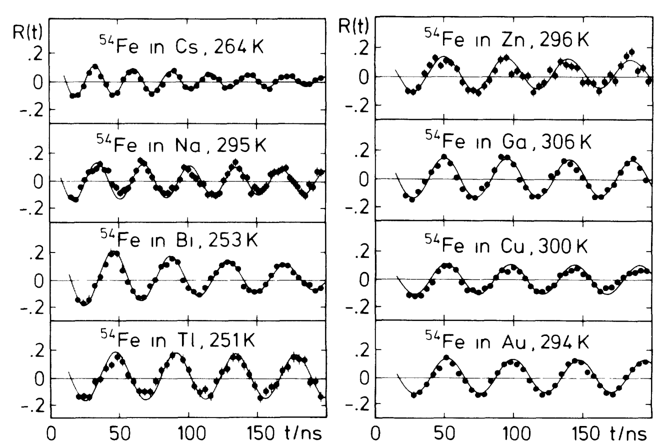

FIG. 1. Host dependence of the spin rotation of ^{54}Fe in several *sp* metals and in Cu and Au observed in an external field of 2 T.

duced by recoil implantation of ^{54}Fe ions out of a thin-Sc foil into metallic elements following the heavy-ion reactions ^{45}Sc (^{12}C, $p2n$) or ^{45}Sc (^{13}C, $p3n$). Pulsed ^{12}C and ^{13}C beams in the energy range 42-53 MeV were provided by the VICKSI accelerator at the Hahn-Meitner-Institut in Berlin. By these reactions, the $I^{\pi}=10^{+}$, $T_{1/2}=360$-ns isomeric state of ^{54}Fe was excited. This technique produces an extremely dilute nuclear probe for the detection of the static and dynamic magnetic Fe response via the observation of spin rotation spectra $R(t)$ in the range 20 to 300 K by the time-differential perturbed angular distribution method.[6,7] Typical examples are shown in Fig. 1.

From the Larmor frequencies $\omega_L(T)=\hbar^{-1}\mu_N g_N B_{ext}\beta(T)$, the local susceptibilities $\beta-1$ can be extracted. The results are displayed in Fig. 2. For the case of stable Fe^{2+} in, e.g., Cs (Fig. 2) $\beta-1$ follows a Curie law $\beta-1=g_J\mu_B(J+1)B(0)/k_BT$, where the magnetic hyperfine field $B(0)$ is given by the sum of a positive, essentially orbital term $B_J=+125$ T and a negative term $B_s=-28$ T, which describes the contribution due to the spin polarized core and conduction electrons.[7] In general the sign of $B(0)$ and thus of $\beta-1$ depends on the dominance of orbital or spin contributions. For reasons which will become clear below, we divide the Fe systems into three classes according to the $\beta(T)$ values observed: Systems with $\beta-1>0.02$ are labeled as ionic (or J_{eff}) type, systems with $\beta-1\equiv1$ within 0.02 as nonmagnetic, and systems with $\beta-1<-0.02$ as S_{eff} type Fe ions in sp metals reflect ionic-type or nonmagnetic behavior (Fig. 2). As is well known from, e.g., Mössbauer effect measurements[8] and the reinvestigation of this work, Fe in Cu, Ag, and Au exhibit S_{eff}-type magnetism with $\beta<1$ dominated by negative B_s values (see Fig. 2 for Fe in Cu and Au).

Now a central test of one electron versus ionic-type models involves the occurrence under increasing hybridization of transitions from systems with $\beta>1$ to systems with $\beta<1$ or alternatively to nonmagnetic systems. If we consider first one-electron approaches based on Anderson-type models, and disregard the too localized systems Fe in Na, K, Rb, and Cs, moderately positive $\beta-1$ values, such as for Fe in Ca,[6] might be expected if the orbital splitting is assumed to be larger than the $3d$ linewidth.[6,9] S_{eff}-type magnetism can be parametrized by a linewidth which is smaller than the spin splitting but larger than the orbital splitting so that orbital moments are quenched, whereas the S_{eff} moments survive. By construction, such models including orbital magnetism and CF effects predict a rather sharp transition with increasing hybridization from systems with $\beta>1$ to systems with $\beta<1$, and thus increasing moment instability as schematically shown in Fig. 3(a). The transition point $\beta_{Tr}=1$ can only be reached in systems where a positive B_J is canceled by a negative B_s. In view of the large B_J and $|B_s|$ values involved such a fortuitous cancellation, and the resulting nonmagnetic situation around B_{Tr} is very unlikely to occur.

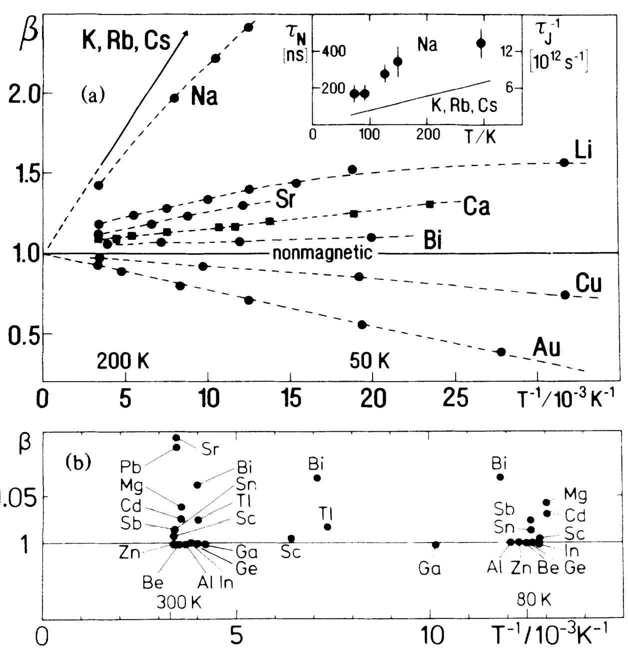

FIG. 2. Local susceptibilities vs $1/T$ for Fe in sp metals, Cu, Au, and Sc. Part of the data for Fe in Ca are taken from Ref. 6. Besides the Curie lines for Fe in K, Rb, Cs, and Au, the dashed lines serve to guide the eye. Inset: The spin dynamics of Fe in Na in comparison with data for Fe in K, Rb, and Cs taken from Ref. 7. Note the expanded β scale in (b).

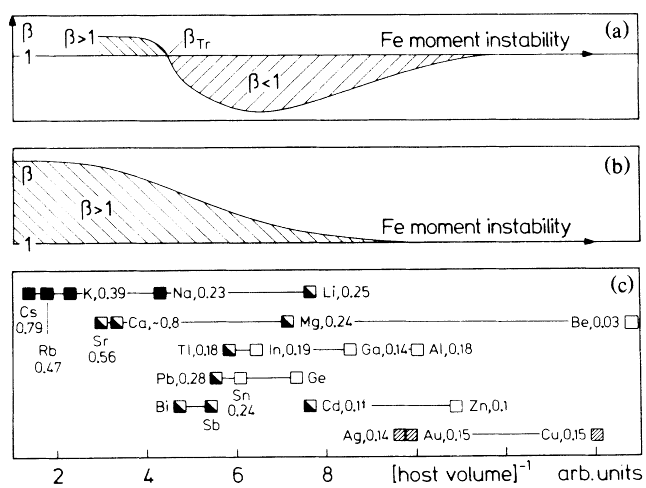

FIG. 3. (a),(b) Schematically the β behavior with increasing Fe moment instability as predicted by different models (see text). (c) Correlation of β of Fe in metals with reciprocal host volume and with $N(E_F)$ of the hosts (numbers next to the elements). The observed Fe behavior (see Fig. 2) is indicated by the symbols: filled squares, nearly stable Fe^{2+}; half-filled squares, moderately positive $\beta-1$; open squares, nonmagnetic; hatched squares, negative $\beta-1$.

On the other hand, giving up the premise that CF splittings are larger than the LS coupling, ionic-type models predict a continuous transition from $\beta > 1$ to $\beta = 1$ with increasing moment instability as schematically shown in Fig. 3(b).

For an experimental test of these ideas, the observed host dependence of Fe moment formation is of key importance. As shown in Fig. 3(c), the magnetism of Fe in *sp* metals strongly correlates with the volume of the host cells which in turn can be used to scale the lattice pressure acting on the Fe ion (compare Ref. 5 for Ce in metals). In particular for Fe in group sequences [see Fig. 3(c)], lattice pressure should be well correlated to hybridization because of the similar character and band structure of host conduction electrons. With increasing lattice pressure and thus with increasing hybridization, we observe a continuous reduction of β of Fe in the sequence K, Na, and Li, and a transition from $\beta > 1$ to the (almost) nonmagnetic $\beta = 1$ for Fe in all other *sp* metal group sequences[10] [see Figs. 2 and 3(c)]. Even at high lattice pressures we never observed any indication of S_{eff}-type magnetism for Fe in *sp* metals; Fe in small volume *sp* metal hosts, e.g., in Be, Zn, Al, and Ga, is found to be nonmagnetic with high accuracy [Figs. 2(b) and 3(c)]. The results provide evidence that the spin and orbital magnetism of Fe in *sp* metals vanish simultaneously, leading to the nonmagnetic situation under increasing lattice pressure. These results rule out the situation in Fig. 3(a); instead, they are nicely consistent with the ionic picture with intact LS coupling shown in Fig. 3(b).

As can be seen by the inspection of Fig. 2, the type of T dependence of β for Fe in *sp* metals is strongly host dependent and correlates with lattice pressure also. With increasing lattice pressure, $\beta(T)$ varies from a Curie-type behavior of the $3d^6$ state of Fe^{2+} in K, Rb, and Cs to an almost T-independent behavior as for Fe in Bi.

All basic features of the host as well as of the T dependence can be qualitatively explained by a picture based on an ionic configuration. In this model the tendency towards magnetic behavior is driven by intact intra-atomic spin and orbital correlations of the LS coupled Fe $3d^6$ shell, and the tendency towards nonmagnetic behavior is essentially driven by spin fluctuations caused by the Fe $3d$-host *sp* electron hybridization. With increasing lattice pressure, the hybridization and thus the effective antiferromagnetic *d-sp* exchange coupling $N_l(E_F)J_{\mathrm{mix}}$ increases, causing in turn a drastic increase of Fe moment instability which can be scaled by Kondo temperatures T_K. $N_l(E_F)$ is the local density of states at the Fe site. For a qualitative discussion of the host-dependent trends of β, one can use the proportionality $|N_l(E_F)J_{\mathrm{mix}}| \propto N_l(E_F)V_{\mathrm{mix}}^2/|U|$.[4,11] As the leading mechanism for the strong reduction of Fe magnetism with lattice pressure, we suggest the increase of the matrix element for *d-sp* hybridization, V_{mix}^2, which approximately scales with the reciprocal host cell volume squared.[12] Increasing V_{mix}^2 can lead to a drastic enhancement of the local *d-sp* density of states at E_F (compare Ref. 13 for the "Kondo resonance" in Ce systems), which can be the reason for the poor correlation of the observed β with $N(E_F)$ of the host [Fig. 3(c)]. Host-dependent changes of U seem to be less decisive.[11] Within this picture, the reduction and T dependence of β for Fe in *sp* metals (Fig. 2) can be roughly parametrized by a Curie-Weiss law $\beta - 1 = C/(T + T_K)$ (where C is the Curie constant of stable Fe^{2+}) with rapidly increasing T_K values in the sequence K, Na, Li, Sr, Ca, Pb, Bi, and Mg. The T_K values for the stable systems Fe in K, Rb, and Cs are much smaller than the experimental T's, whereas $\beta(T)$ for Fe in Bi, Mg, and Cd can be reproduced by $T_K \sim 10^3$ K, To test this interpretation, we were able to measure the magnetic nuclear relaxation time and thus the $3d$ spin rate τ_J^{-1} for Fe in Na which is found to be twice as large as the spin rate for the stable system Fe in K, Rb, and Cs (Ref. 7) in the range of 80 to 300 K, as shown in the inset of Fig. 2(a). Thus the reduction of β for Fe in Na [Fig. 2(a)] is correlated with a substantial increase of the $3d$ spin rate which is proportional to the square of the exchange coupling. For Fe in Li we found that $\tau_J^{-1} > 30 \times 10^{-12}$ s^{-1} in the range 30–300 K. The weakly magnetic systems Fe in, e.g., Tl, Sb, and Sn, and even the nonmagnetic systems can be parametrized by extremely large T_K values and/or by large hydridization which might lead to a breakdown of the intra-atomic correlations and to a partly delocalization of the Fe $3d$ electrons.

The role of possible CF effects on $\beta(T)$ seems to be relatively unimportant. CF splittings are known to be undetectably small for Fe in K, Rb, and Cs, where the total splitting is at most 0.03 eV.[7] For the other Fe systems with $\beta > 1$, possible CF splittings are most probably smaller than the LS coupling. Moreover, the transition from $\beta > 1$ to $\beta = 1$ and the nonmagnetic Fe systems cannot be reproduced by CF effects. One necessarily needs high T_K values and/or strong hybridization for explaining the vanishing $\beta - 1$. It can be that possible CF splittings for Fe in *sp* metals are smaller than the spin linewidths or experimental T's in the systems investigated hitherto. We argue that the role of CF effects on the magnetism of $3d$ ions in metals has to be reinvestigated in general.

These various data and interpretations for the host and T-dependent β values, and $3d$ spin rates, and for crystal fields of Fe ions in *sp* metals provide a new basis for a critical test of model predictions about local moment formation, antiferromagnetic *d-s* and *d-p* exchanges, and the Kondo effect of $3d$ ions in *sp* metal hosts.

Moreover, these results provide a new basis for our comparing the local magnetism of $3d$ with f systems. Ionic-type configurations, predominant orbital contributions to $\beta(T)$, and CF splittings smaller than the LS coupling are widely known for $4f$ ions in metals.[2,5,13,14] The feature that $\beta-1$ of a LS coupled Fe state in sp metals vanishes with increasing lattice pressures bears resemblance to the behavior of the more f electron ions Pr, Nd, Pm,[14] and Np[15] in metallic systems. The spin rates and T_K values for Fe in Na, K, Rb, and Cs are comparable to those observed in nearly stable Ce and Pr systems.[5,13,14] Strong correlations of the reduction and T dependences of the magnetic behavior with lattice pressure have also been reported for Ce, Pr, Nd, and Pm systems[5,13,14] and have been interpreted as being governed by hybridization essentially scaled by T_K values. In summary, the magnetism of Fe in sp metals bears a striking resemblance to the $4f$ systems considered above, but reflects partly qualitative differences from the spin magnetism observed for Fe in hosts with d-band electrons.

Finally, we discuss a consequence of the results of this work on $3d$ moment formation in Cu, Ag, and Au. By extrapolating the Fe moment stability observed in sp metals one expects (almost) vanishing $\beta-1$ values and thus (almost) nondetectable Fe moments in Cu, Ag, Au, and in d metal hosts. Disregarding the Fe $3d$-host d electron interaction, lattice pressure, and the strength of the Fe $3d$-sp hybridization and thus the Fe moment instability should increase considerably for Fe in Cu, Ag, and Au, compared to Fe in Zn, Cd, and other sp metals [see Figs. 2 and 3(c)]. However, Fe in Cu, Ag, and Au exhibit S_{eff}-type moments [Fig. 2(a)] with moment stabilities being several orders of magnitude larger than those of Fe, in e.g., Zn, Cd, Be, Mg, and Ca. T_K values as deduced from the susceptibility are 28, 2, and 0.3 K for Fe in Cu, Ag, and Au, respectively.[8] In a forthcoming paper we will propose that Fe $3d$-host d interactions play a crucial role for the moment formation of Fe in Cu, Ag, Au, and in certain d metal hosts, which can lead to a substantial stabilization of the Fe moments. In the context of the present subject we have to note that data for Fe (and other $3d$ ions) in Cu, Ag, and Au cannot be used for a critical test of models on the moment formation and d-s exchange of $3d$ states in sp metals.

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[10]The β values plotted in Figs. 2 and 3(c) probably can be attributed to Fe at substitutional lattice sites. For some cases, such as for Fe in Mg, Ca, Sr, Pb, and Bi, we have observed an additional frequency with $\beta(T)\equiv 1$, which likely corresponds to a fraction of Fe at interstitial sites where large lattice pressures are acting on the Fe ions. See also: D. Riegel, K. D. Gross, and M. Luszik-Bhadra, Annual Report of Bereich P, Hahn-Meitner-Institut, Berlin 1987 (unpublished), p. 163.

[11]D. Riegel, K. D. Gross, and M. Luszik-Bhadra, Phys. Rev. Lett. **59**, 1244 (1987). Following the same procedure as used for Mo^{1+} we have estimated the atomic correlation energy $|U|$ for Fe^{2+} in Rb and Cs to be ~ 1 eV. Under the premise that the $3d^6$ shell remains localized, the Born-Haber cycle yields even larger $|U|$ values for Fe^{2+} in other sp metals.

[12]Besides lattice pressure, the character of conduction electrons seems to have an influence on V^2_{mix} and Fe moment instability, also. As is probably reflected in Figs. 2 and 3(c), β is more effectively reduced by p-like than by s-like host electrons if compared at the same host volumes.

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