Magnetism of Dilute Fe Ions in Solid and Liquid Hg: Is It Governed by the Interaction of Fe 3*d* with Hg 5*d* Band Electrons?

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By applying the perturbed-γ-ray-distribution method following heavy-ion reactions we have observed strong magnetic moments for isolated Fe ions in solid and liquid Hg reflecting a Curie-type local susceptibility along with a small Fe spin-fluctuation rate. The magnetism of Fe ions in Hg exhibits qualitative differences from the behavior of Fe in *sp* band metal hosts but is strikingly similar to the magnetism of Fe in hosts with *d* band electrons, including Cu, Ag, and Au. We propose that the interaction of Fe 3*d* with Hg 5*d* band electrons is crucial for the existence and stability of Fe moments in Hg.

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The formation of local magnetic moments of 3*d* atoms in metallic hosts is a key problem in the area of magnetism. During the past decades extensive experimental investigations have been made using several 3*d* ions dissolved into a variety of host metals with different electronic and lattice structures.[1] The hybridizations of impurity 3*d* states with the *s*, *p*, and *d* conduction electrons of the host metals are crucial parameters for the existence and characteristic features of the magnetism of 3*d* ions in metals. Recent works have revealed that 3*d* ions exhibit qualitatively different types of magnetism in *sp* and *d* band metal hosts.[2,3] While 3*d* moments in *sp* metal hosts are described by an ionic-type model,[2] their magnetic behaviors in *d* metal hosts are governed by interatomic interactions of impurity 3*d* states with host *d* band electrons. The moments of 3*d* ions in *d* metal hosts are usually parametrized by an effective spin S_{eff}. In view of these results, dedicated studies of the different role of the hydridization of impurity 3*d* with *s*, *p*, and *d* band host electrons for the existence and stability of magnetic moments are desirable.

In this Letter we report on the observation of strong magnetism of isolated Fe ions in liquid and solid Hg. By extrapolating the systematic trends of the magnetism observed for Fe ions in *sp* metal hosts we expect nonmagnetic behavior or strongly reduced ionic-type magnetism for Fe in Hg. Surprisingly, Fe ions in Hg exhibit spin magnetism with high moment stabilities similar to Fe in some *d* band metals. Because of these unexpected results we have also performed a detailed investigation of the Fe magnetism in Zn and Cd hosts which allows a comparison of the Fe behavior in these hosts with similar electronic structures. The trends of Fe magnetism in the sequence Zn, Cd, Hg along with the magnetic behavior known for Fe ions in *sp* metals and in certain *d* band hosts, particularly in Cu, Ag, and Au, give new insight about the influence on magnetism of the qualitatively different interactions of Fe 3*d* states with host *sp* or *d* electrons. We propose that the occurrence and the characteristic features of the magnetism of Fe in Hg is governed by a ferromagnetic interaction of Fe 3*d* with Hg 5*d* band electrons.

Neither experimental nor theoretical local-moment studies of isolated Fe ions in Hg have been made so far. Experimental difficulties arise from the low solubility of Fe in mercury. However, such nonalloying systems can be investigated by the time-differential perturbed-γ-ray-distribution method (TDPAD).[4] We used the 360-ns isomer of ^{54}Fe as a nuclear probe for the detection of the magnetic response of the Fe ions. The systems and isomers were produced by recoil implantation following the heavy-ion reaction $^{45}\text{Sc}(^{12}\text{C},p2n)^{54}\text{Fe}$. The experiments were performed at the VICKSI accelerator at the Hahn-Meitner-Institut in Berlin, using a pulsed ^{12}C beam of energy 42 MeV. For a more detailed description of experimental aspects see Refs. 2–4.

Figure 1 shows spin-rotation spectra $R(t)$ of ^{54}Fe in Zn and Hg, recorded at temperatures between 30 and 300 K in an external field B_{ext} close to 2 T. From the observed Larmor frequencies $\omega_L(T)=\hbar^{-1}\mu_N g_N B_{\text{ext}} \times\beta(T)$, the local susceptibilities $\beta(T)-1$ can be deduced. The results are displayed in Fig. 2, where $\beta\equiv 1$ characterizes nonmagnetic behavior as found for Fe in Zn. The large changes found for the $R(t)$ spectra of Fe in Hg as a function of temperature (Fig. 1) indicate the presence of local Fe moments. From the nearly equal amplitudes of $R(t)$ observed for Fe in liquid Hg and the solid systems it follows that nearly all Fe recoils contribute to $R(t)$ in Zn, Cd, and solid Hg (Fig. 1). Whereas the spectra for Fe in liquid Hg reflect one (undamped) frequency, the $R(t)$ spectra for Fe in solid Hg are consistent with the superposition of two frequencies, which are most clearly visible in the spectra observed at $T\leq 82$ K (see Fig. 1). One of these frequencies might correspond to substitutional and the other to interstitial sites for the undersized Fe ions implanted in the Hg lattice.

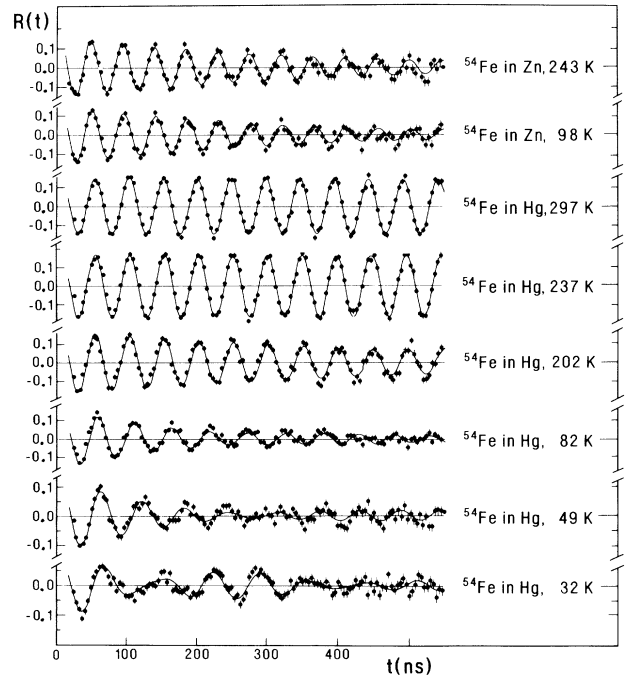

FIG. 1. Spin-rotation patterns $R(t)$ of isolated ^{54}Fe ions in Zn and in liquid and solid Hg as a function of temperature in an external field of 2 T. The temperature-dependent frequencies reflect the existence of strong local Fe moments in Hg.

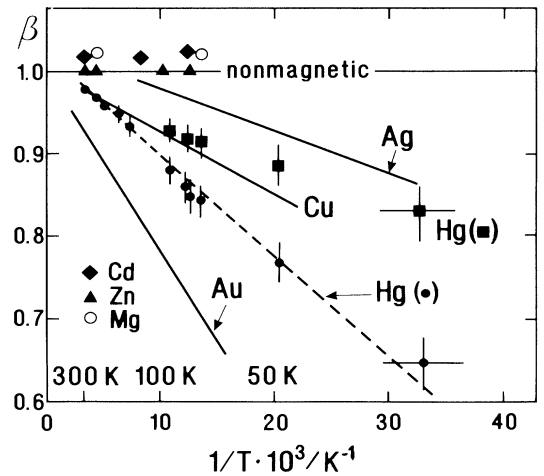

FIG. 2. Local susceptibilities vs $1/T$ for Fe in Mg, Zn, Cd, and Hg. The $\beta(T)$ data for Fe in Cu, Ag, Au, and Mg, taken from Refs. 2 and 3, are included for comparison. The lines for Fe in Au, Ag, Cu, and Hg represent nearly Curie-type behavior.

In both lattice sites Fe shows magnetic behavior. The β values for Fe in liquid Hg and for the major component of Fe in solid Hg can be well fitted by one Curie line (Fig. 2), which seems to favor the assumption that the majority component corresponds to Fe ions in substitutional sites. The essential conclusions of this work do not depend on an unambiguous assignment of the lattice sites to the frequencies. For the discussion of Fe magnetism in Hg we will mainly consider the majority component.

The negative $\beta-1$, observed for both Fe lattice sites in Hg (Fig. 2), implies negative magnetic hyperfine fields, $B(0)$, at the Fe nucleus. This indicates that (negative) spin contributions to $B(0)$, which arise from spin-polarized Fe core electrons and from spin-polarized conduction electrons, are larger than possible positive orbital contributions.[2-4] The $\beta(T)$ values for Fe in Hg are comparable to those known for Fe in Cu, Ag, and Au,[3] which are included in Fig. 2 for comparison.

The data also yield information on the stability of the Fe moment in Hg. The degree of moment instability can be scaled by spin-fluctuation temperatures T_K, which are estimated from the susceptibility data using a Curie-Weiss law $\beta-1=\text{const}\times(T+T_K)^{-1}$. Such a fit to the data of Fe in Hg yields a value of $T_K \leq 20$ K.

Before discussing the magnetism observed for Fe in Hg in terms of the interactions of the Fe $3d$ with the conduction electrons of the Hg host, we like to ensure that we are dealing with the case of isolated Fe ions and not with Fe clusters in Hg. It is possible that Fe clusters in Hg might reflect S_{eff}-type magnetism due to the strong interatomic Fe-$3d$-Fe-$3d$ interaction. In this context we note that a suspension of Fe microcrystals in Hg shows strong paramagnetism which is presumably dominated by Fe-$3d$-Fe-$3d$ interactions.[5] In the present work the concentration of the produced Fe ions is less than 0.1 ppm and there is only a very short time of about 20 ns between the production of the Fe ion in Hg and the starting time of the measurement of $R(t)$ (Fig. 1). These two features, along with the temperature dependence of the $R(t)$ spectra (Figs. 1 and 2), ensure that the observed magnetism stems from isolated Fe ions in Hg.

We now discuss how the characteristic features of the magnetism observed for Fe ions in Hg exhibit basic qualitative differences compared to the magnetism of Fe ions in *sp* band metal hosts. All results of a systematic study of the magnetism of Fe ions in *sp* band metal hosts can be explained by an ionic-configuration-based picture, where the tendency towards magnetic behavior is driven by intra-atomic spin and orbital correlations of the *LS*-coupled Fe $3d^6$ shell and where the tendency toward nonmagnetic behavior is essentially driven by spin fluctuations caused by the hybridization of Fe $3d$ with host *sp* electrons.[2] Magnetic Fe ions in *sp* band metals always exhibit positive $\beta-1$ and $B(0)$ values, in contrast to the results for Fe in Hg. A second severe discrepancy stems from the high stability of the Fe moment in Hg, as reflected by the small T_K deduced above. The instability of the Fe moment in *sp* metal hosts has been found to correlate strongly with the reciprocal of the host cell volume, which largely determines the trends of the *d-sp* hybridization strengths and thus the trends of the *d-sp* exchange coupling and T_K (Ref. 2). In view of these

systematics, it is interesting to compare the behavior of Fe in Hg to the magnetism observed for Fe in *sp* metal hosts with comparable volume and similar electronic structures, in particular, Mg, Zn, and Cd. As collected in Table I and Fig. 2, very small but positive $\beta-1$ values have been observed for Fe in Mg and Cd, and also in the neighboring Tl,[2] which can all be characterized by T_K values around 5×10^3 K. Fe in Zn is found to be nonmagnetic, characterized by $\beta-1\equiv0$ and $T_K>10^4$ K (Fig. 2 and Table I). By extrapolating the magnetic behavior known for Fe in, e.g., Mg, Zn, Cd, and Tl to Fe in Hg one should expect almost nonmagnetic behavior or weak magnetic behavior with small positive $\beta-1$ and large T_K values.

For a rough estimate of the relative trends of the *d-sp* hybridization for Fe in selected hosts, we compare the *s*-electron density $|\Psi_s|^2$ of the neighboring host atom at the Fe ion site, using atomic wave functions[6] (Table I). For the distance between the Fe and host atom, we use the average $d^*=(d_1+d_2)/2$, where d_1 is $2R(12)_{\text{host}}$ and $d_2=R(12)_{\text{host}}+R(12)_{\text{Fe}}$, and where $R(12)_{\text{host}}$ and $R(12)_{\text{Fe}}$ are the metallic radii for ligancy 12 for the host and pure Fe metal, respectively. Thus the chosen d^* approximately corrects for a lattice relaxation around the Fe ion. As collected in Table I, the trends of the estimated $|\Psi_s|^2$ values are consistent with the trends of the magnetic behavior observed for Fe in Mg, Cd, and Zn, but strongly disagree with the high moment stability (small T_K) deduced for Fe in Hg and also for Cu, Ag, and Au.

We note that it is unlikely that an assumption of large crystal fields can explain the observed Fe behavior in Hg. Up to now, intensive studies of the magnetism of 3*d* and 4*d* ions in *sp* band metal hosts have not given any indication of measurable crystal-field effects.[2,4] For several *d* ions in *sp* band metals crystal-field splittings have been measured to be smaller than the *LS* coupling.[2,4,7] Thus the question arises why the crystal field assumed for Fe in Hg should be much larger compared to *d* ions in other *sp* band metal hosts? Furthermore, we emphasize that the assumption of large crystal fields might parametrize the negative $\beta-1$ values, but still cannot account for the drastic changes of T_K observed for Fe in Hg compared to T_K in other *sp* band metal hosts. Third, we mention that the assumption of large crystal fields for Fe in solid Hg leads to the problem of how to explain the smooth transition of $\beta-1$ in going from solid to liquid Hg[8] (Fig. 2).

Clearly, the results of Fe magnetism in Hg presented above show basic qualitative differences from the behavior of Fe in *sp* band metals. Instead, the magnetism of Fe in Hg exhibits all the basic features of the Fe magnetism in *d* metal hosts and in Cu, Ag, and Au. Magnetic Fe ions in *d* metal hosts and in Cu, Ag, and Au always reflect negative $\beta-1$ and negative $B(0)$ values which can be regarded as one characteristic feature of the S_{eff}-type magnetism. It has been suggested that negative $\beta-1$ and $B(0)$ values are a consequence of the hybridization of the Fe 3*d* with the *d* band electrons of the host. This hybridization increases the tendency towards itinerant, and covalent 3*d* behavior, can destroy ionic configuration, and can effective reduce orbital contributions to $\beta-1$ and $B(0)$ (Ref. 3). As a second characteristic feature of the S_{eff}-type magnetism, it has been proposed that the spin-fluctuation temperature, and thus the existence and stability of Fe moments observed in Cu, Ag, Au, and in certain *d* metal hosts, crucially depend on a moment-stabilizing, ferromagnetic interaction of the Fe 3*d* with the *d* band electrons of the host.[3] One is led to argue that the high moment stability observed for Fe ions in Hg and its drastic discrepancy with β and T_K measured for Fe in *sp* band metal hosts can be caused by a ferromagnetic interaction of Fe 3*d* with the host *d* band electrons of Hg.

We now try to relate the relative trends of the observed Fe magnetism to very approximate and simple estimates for the trends of hybridization between the Fe 3*d* and host *d* band electrons. The sign of the possible *d-d* interaction will be discussed below. At first, the strength

TABLE I. Sign of $\beta-1$ (Fig. 2) and T_K values for Fe ions in host metals, taken from Refs. 2 and 3, and this work. E_d-E_F is the energy difference of the upper edge of the *d* band relative to E_F for the pure host, taken from Ref. 9. 2 times the metallic radius R_{12} of the pure host with ligancy 12 can be compared with d^*, which corrects for lattice relaxations around the undersized Fe ions in a host. $|\Psi_s|^2$ and $|\Psi_d|^2$ are the densities of the *s* and *d* electrons of the neighboring host atom at the Fe site (see text).

Host	Sgn($\beta-1$)	T_K (K)	E_d-E_F (eV)	$2R_{12}$ (Å)	d^* (Å)	$\lvert\Psi_s\rvert^2$ ($10^{-4}a_0^3$)	$\lvert\Psi_d\rvert^2$ ($10^{-6}a_0^3$)
Cu	Negative	30	1.7	2.56	2.55	36	8.6
Ag	Negative	2	3.4	2.88	2.79	28	10
Au	Negative	0.3	1.8	2.92	2.82	28	17.8
Zn	···	$>10^4$	9.3	2.76	2.70	22	2.7
Cd	Positive	5×10^3	9.6	3.08	2.94	18	2.8
Hg	Negative	<20	6.9	3.14	2.98	18	5.0
Mg	Positive	5×10^3	···	3.20	3.02	16	···

of the hybridization might decrease with the distance between the Fermi level and the host d band, values of which are collected in Table I, using photoemission data.[9] These energetic considerations suggest as a trend larger d-d hybridizations for Fe in Cu, Ag, Au,[10] and Hg compared to Fe in Zn and Cd. Secondly, we consider the d-electron density $|\Psi_d|^2$ of the neighboring host atom at the Fe site, proceeding analogously as above for the estimate of $|\Psi_s|^2$. The results suggest, in addition to the trends of the energetic overlap, a larger d-d hybridization for Fe in Hg compared to Fe in Zn and Cd (see Table I).

Under the premise of a moment-stabilizing, ferromagnetic interaction of the Fe $3d$ with the host d band electrons, the trends of $|\Psi_d|^2$ and $|\Psi_s|^2$ satisfactorily agree with the trends of the observed magnetism in all hosts under consideration. A ferromagnetic sign of the d-d interaction is supported by the coupling rule that the spin of a more-than-half-filled-$3d$-shell impurity, such as Fe, induces a ferromagnetic host d spin polarization in hosts with nearly filled d bands.[3,11] A ferromagnetic d-d interaction has been suggested to be the main reason for the small T_K values, i.e., high moment stabilities, observed for Fe ions in, e.g., Rh, Ir, Pd, Pt, Cu, Ag, and Au.[3] It is reasonable to assume that interactions between the Fe $3d$ and the nearly filled host d bands in Zn, Cd, and Hg would be ferromagnetic also. As the main reason for the existence and stability of Fe moments in Hg, we suggest a ferromagnetic interaction between Fe $3d$ and Hg $5d$ band electrons, which is large enough to successfully compete with the antiferromagnetic d-sp exchanges and which can suppress spin fluctuations by several orders of magnitude, consistent with the small T_K observed. For Fe in Zn and Cd, a possible moment-stabilizing d-d interaction seems to be too weak; the magnetic behavior for these systems can be interpreted as being governed by the antiferromagnetic d-sp exchanges leading to high T_K values, which are found to be comparable to the T_K's for Fe in Mg (Table I) and in other sp band metal hosts.[2] Similar to Fe in Cu, Ag, Au, and in other d band metal hosts, the drastic decrease of the spin-fluctuation rate observed for Fe in Hg is accompanied by the appearance of S_{eff}-type magnetism with negative $B(0)$ and $\beta - 1$ values.

In summary, Fe ions exhibit spin magnetic moments in solid and liquid Hg, which contrasts with magnetic behavior observed for Fe in sp band metals. All characteristic phenomena observed for Fe in Hg are strikingly similar to those observed for Fe in d band metal hosts including Cu, Ag, and Au. The estimated trends for the energetic and spatial overlap of the Fe $3d$ with host d and s electrons also provide good arguments in favor of a crucial role of a ferromagnetic interaction between Fe $3d$ and Hg $5d$ band electrons. It seems to be a challenge to theory to try to find a better qualitative and quantitative picture for the d-d interactions and their very sensitive influence on the spin fluctuations and magnetism of $3d$ ions in metals.

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